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Proc. R. Soc. Lond. A. **365**, 467–494 (1979)
Printed in Great Britain

New variational-Lagrangian thermodynamics of viscous fluid mixtures with thermomolecular diffusion

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(*Communicated by Sir James Lighthill, F.R.S. – Received* 2 *May* 1978 – *Revised* 6 *November* 1978)

A principle of virtual dissipation generalizing d'Alembert's principle to nonlinear irreversible thermodynamics is applied to viscous fluid mixtures with coupled thermomolecular diffusion. Original dynamical field equations are obtained directly from the variational principle. The use of new fundamental concepts and methods in the thermodynamics of open systems avoids the difficulties inherent in the classical Gibbs approach. The dissipative forces incorporated explicitly in the field equations are expressed by means of a dissipation invariant evaluated in detail in terms of coupled viscous and diffusive properties. Partial pressures and dissipative stresses are given new, unambiguous thermodynamic definitions. Lagrangian type equations with generalized coordinates are also obtained directly from the variational principle. They provide a powerful tool of simplified analysis of complex open systems as well as the foundation of a variety of finite element methods.

1. Introduction

The principle of virtual dissipation of irreversible thermodynamics (Biot 1975, 1976*a*) constitutes the fundamental mathematical tool for the analysis of evolution of open non-equilibrium collective systems. It is essentially a generalization of d'Alembert's principle to thermodynamics. It is obtained by adding to the virtual work of frozen inertia forces the virtual work of frozen dissipative forces which is called virtual dissipation. Traditionally the virtual work of the inertia forces is expressed in terms of material displacements of the particles in a closed system. The procedure has been extended to open systems by expressing this virtual work in terms of mass flow across an open cell (Biot 1977*a*).

The object of this paper is to apply the principle of virtual dissipation to fluid mixtures with thermomolecular diffusion, and to derive directly by a variational procedure the fluid dynamical equations of the continuum as well as the Lagrangian equations in terms of generalized coordinates. The procedures, concepts and results are fundamentally different from those of other schools (Green & Naghdi 1969, 1971). Equations obtained are of simple and general symmetric form which includes explicitly the quantitative terms due to entropy production. They are based on two fundamental invariants, a collective potential and a dissipation function, which completely describe the reversible and irreversible properties of the system.

The new concepts involved in the thermodynamics of open systems as derived more extensively earlier (Biot 1976*b*, 1977*b*) are briefly outlined in § 2. The thermobaric and convective potentials are shown to replace the chemical potential, thus avoiding the difficulties which are inherent in the classical Gibbs treatment. Entropies and internal energies are also defined in a new way as collective concepts which involve supply cells as part of the system.

Entropy flow and production are considered in § 3. The total entropy flow as the sum of a conductive and a convective term leads to a fundamental entropy balance equation which involves new definitions (Biot 1977*a, c*). The entropy produced by viscosity and thermomolecular diffusion is also evaluated. The fundamental invariance under solid translation and rotation is taken into account. This leads to the concept of dissipative stresses as distinct from the pressures. Both are defined thermodynamically in a new way.

The principle of virtual dissipation is presented in § 4 in the context of fluid mixtures, and is used in § 5 to derive variationally the dynamical equations of the mixture. The continuous field variables governed by these equations are new. They are the entropy displacement and the mass displacement vectors of each substance and in addition a scalar which is the entropy produced per unit volume. A general energy flux theorem is derived in § 6 which leads to the concept of energy flux vector.

Application of the variational principle to incompressible mixtures requires a special treatment as shown in § 7. This introduces a Lagrangian multiplier which may be interpreted as the total pressure of the mixture.

Lagrangian equations based on a description of the mixture by generalized coordinates are derived in § 8 directly from the variational principle without using the field equations. They involve the evaluation of the two fundamental invariants as functions of the generalized coordinates. This formulation provides a powerful tool for the approximate analysis of complex systems and in the development of a variety of finite element methods as indicated in § 9.

2. NEW THERMODYNAMICS OF OPEN SYSTEMS

A 'collective potential' was shown (Biot 1954, 1955) to provide the key fundamental concept in the systematic development of non-equilibrium thermodynamics. In this earlier work it was referred to as 'generalized free energy' because it coincides with the Helmholtz free energy in the particular case of isothermal systems. The concept was applied to piezoelectric crystals (Mindlin 1961, 1974). More recently a completely general variational formulation of nonlinear, non-equilibrium thermodynamics has been derived from the concept of collective potential (Biot 1975, 1976*a, b*). A direct physical definition of this concept was introduced (Biot 1976*b*, 1977*b, c*) by considering a 'hypersystem' constituted by primary cells $C_{p\alpha}$, large rigid supply cells C_{sk} and a large rigid isothermal reservoir at the constant temperature T_0 called a thermal well TW. Each supply cell $\mathrm{C}_{\mathrm{s}k}$ contains a pure substance k. The substances are all at the same pressure and temperature p_0, T_0. It was shown (Biot 1976*b*, 1977*b*) that this condition is required in order to avoid Gibbs' paradox. The system of primary cells $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha}$ is non-isothermal, each cell being at its own temperature T_α. The hypersystem $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha} + \Sigma_k \mathrm{C}_{\mathrm{s}k} + \mathrm{TW}$ undergoes *reversible* transformations by which matter and heat are transferred *internally* between cells. This transformation is accomplished solely by mechanical work by the use of forces acting on the system, as well as fluid pumps and heat pumps. According to the first principle this work is represented by the internal energy V of the hypersystem.

It defines the collective potential V. The transformation being reversible, the total change of entropy is zero. Hence

$$S + S_{\mathrm{TW}} = 0, \tag{2.1}$$

where S is the increase of entropy of the collective system $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha} + \Sigma_k \mathrm{C}_{\mathrm{s}k}$, while S_{TW} is the increase of entropy of the thermal well. We may write

$$S_{\mathrm{TW}} = H_0/T_0, \tag{2.2}$$

where H_0 is the thermal energy acquired by the thermal well.

The internal energy V of the hypersystem is

$$V = U + H_0, \tag{2.3}$$

where U is the internal energy of the system $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha} + \Sigma_k \mathrm{C}_{\mathrm{s}k}$. Elimination of H_0 and S_{TW} between equations (2.1) (2.2) and (2.3) yields

$$V = U - T_0 S. \tag{2.4}$$

Consider now a completely general irreversible transformation of the primary system of cells $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha}$ where external work is performed on this system but no matter or heat is provided to the system as a whole. According to the first principle neglecting kinetic energy, we write

$$U = W - G, \tag{2.5}$$

where G is the increase of potential of the system in a potential force field such as gravity while W is the work performed by other forces. From (2.4) and (2.5) we derive

$$V + G - W = -T_0 S. \tag{2.6}$$

We have called

$$\mathscr{P} = V + G \tag{2.7}$$

the *mixed collective potential* (Biot 1975, 1976*a*, *b*, 1977*b*) because it unifies mechanical and thermodynamic properties. Since the primary system receives no matter or heat from the environment, we replace S by S^* to indicate that it represents the entropy *produced* by the primary system. Hence (2.6) is written (Biot 1975, 1976*a*)

$$\mathscr{P} - W = -T_0 S^*. \tag{2.8}$$

While the system $\Sigma_\alpha \mathrm{C}_{\mathrm{p}\alpha}$ itself is closed, subsystems of primary cells and the cells themselves are open, and may exchange heat and matter among themselves or with another subsystem which represents the environment.

The collective potential possesses the important property of additivity. This means that

$$V = \sum_{\alpha} \mathscr{V}_{\alpha}, \tag{2.9}$$

where $\mathscr{V}_{\alpha}$ is the collective potential of each cell $C_{p\alpha}$. Hence we may analyse its fundamental properties for a single rigid primary cell C_p and we shall refer to its collective potential $\mathscr{V}$ as the *cell potential*. The justification for this is derived from the fact that the state of the collective system $C_p + \Sigma_k C_{sk}$ is completely determined by the state variables of the cell C_p alone. This can be seen considering C_p to contain a homogeneous mixture of fluid substances at the temperature T. The state variables of the cell are T and the mass increase M^k of each substance in the cell measured from a certain initial state. These masses are obtained from the supply cells so that the state of $\Sigma_k C_{sk}$ is also determined by M^k. Hence the state variables T, M^k of C_p completely determine the state of the collective system $C_p + \Sigma_k C_{sk}$.

Similarly the collective entropy $\mathscr{S}$ and energy $\mathscr{U}$ of the system $C_p + \Sigma_k C_{sk}$ are completely determined by the variables T, M^k. For this reason we may call $\mathscr{S}$ the *entropy of the primary cell* and $\mathscr{U}$ the *energy*. We may write for the cell

$$\mathscr{V} = \mathscr{U} - T_0 \mathscr{S}. \tag{2.10}$$

Furthermore the variables M^k and $\mathscr{S}$ may be chosen as state variables of the cell.

The cell potential has been expressed in terms of new concepts (Biot 1976*b*, 1977*b*) as follows. By definition we may write

$$\mathrm{d}\mathscr{V} = \sum_{k} \psi_k \mathrm{d}M^k + \theta \mathrm{d}s_T, \tag{2.11}$$

where ψ_k is the *thermobaric potential*. It represents the reversible work required to transfer a unit mass of substance k from the supply cell C_{sk} to the primary cell C_p. The term $\psi_k \mathrm{d}M^k$ represents the work required to transfer a mass $\mathrm{d}M^k$. The process is called a thermobaric transfer. The term $\theta \mathrm{d}s_T$, where

$$\theta = T - T_0, \tag{2.12}$$

represents the work required by a heat pump extracting heat from TW at the temperature T_0 and injecting an amount of heat $T \mathrm{d}s_T$ into C_p at the temperature T. This heat injection increases the entropy of C_p by the amount $\mathrm{d}s_T$.

The value of ψ_k has been shown to be

$$\psi_k = \int_{p_0,\, T_0}^{p_k,\, T} \left(\frac{\mathrm{d}p'_k}{\rho'_k} + \theta' \mathrm{d}\bar{s}_k \right). \tag{2.13}$$

The variable pressure and density of the substance along the path of integration are p'_k and ρ'_k, the variable temperature is T' with $\theta' = T' - T_0$, and $\mathrm{d}\bar{s}_k$ is the entropy differential of the unit mass along the path. The pressure p_k is the pressure of the substance brought to equilibrium with the cell C_p through a semi-permeable membrane. *By definition this pressure p_k is called the partial pressure of the substance k in the mixture* contained in C_p at the temperature T. The first term in (2.13) represents the work of a mechanical pump and includes the work of extraction from C_{sk} and the work of injection into C_p. The second term represents the work of a heat pump required to change the temperature of the substance arbitrarily along the path of integration in infinitesimal steps. The value of the integral (2.13) is independent of the path.

A *relative specific entropy* is defined as

$$\bar{s}_k = \int_{p_0,\,T_0}^{p_k,\,T} \mathrm{d}\bar{s}_k. \tag{2.14}$$

The increase of collective entropy of $C_p + \Sigma_k C_{sk}$ owing to a thermobaric transfer is $\bar{s}_k \mathrm{d}M^k$. Hence the entropy differential of C_p is written

$$\mathrm{d}\mathscr{S} = \sum_k \bar{s}_k \mathrm{d}M^k + \mathrm{d}s_T. \tag{2.15}$$

$\bar{s}/k$

Note that this expression is valid only for the reversible process of transfer described above. However it provides a way of evaluating the *cell entropy* $\mathscr{S}$ defined above as a collective concept.

In equations (2.11) and (2.15), $\mathrm{d}M^k$ and $\mathrm{d}\mathscr{S}$ are state variables of the cell while $\mathrm{d}s_T$ is not.

Elimination of $\mathrm{d}s_T$ between these two equations yields

$$\mathrm{d}\mathscr{V} = \sum_k \phi_k \mathrm{d}M^k + \theta \mathrm{d}\mathscr{S}, \tag{2.16}$$

where

$$\phi_k = \psi_k - \theta \bar{s}_k \tag{2.17}$$

is the *convective potential* (Biot 1977*b*, *c*). Using the value (2.13) of ψ_k we derive the property

$$\mathrm{d}\phi_k = \mathrm{d}p_k/\rho_k - \bar{s}_k \mathrm{d}\theta. \tag{2.18}$$

The cell potential (2.10), that is

$$\mathscr{V} = \mathscr{V}(M^k, \mathscr{S}), \tag{2.19}$$

is a function of M^k and $\mathscr{S}$, with

$$\frac{\partial \mathscr{V}}{\partial M^k} = \phi_k, \quad \frac{\partial \mathscr{V}}{\partial \mathscr{S}} = \theta. \tag{2.20}$$

An alternative expression for the convective potential is obtained by substituting the value (2.13) of ψ_k into (2.17). We obtain

$$\phi_k = \bar{\epsilon}_k - T\bar{s}_k, \tag{2.21}$$

where

$$\bar{\epsilon}_k = \int_{p_0,\,T_0}^{p_k,\,T} \left(\frac{\mathrm{d}p'_k}{\rho'_k} + T'\,\mathrm{d}\bar{s}_k\right) = \frac{p_k}{\rho_k} - \frac{p_0}{\rho_{0k}} + \int_{p_0,\,T_0}^{p_k,\,T} \left[-p'_k\,\mathrm{d}\left(\frac{1}{\rho'_k}\right) + T'\,\mathrm{d}\bar{s}_k\right], \tag{2.22}$$

while ρ_{0k} and ρ_k are densities at p_0, T_0 and p_k, T respectively. The quantity $\bar{\epsilon}_k$ defines the *relative specific enthalpy* of the substance in C_p.

Attention is called to an important feature of this new approach. Within a given hypersystem the quantities ϕ_k, $\bar{s}_k$ and $\bar{e}_k$ contain *no undetermined constants*, in contrast with traditional concepts.

Also the quantities V, U, S, $\mathscr{V}$ and $\mathscr{S}$ are completely defined as increases from a given initial state of the collective system for which they are put equal to zero.

The entropy $\mathscr{S}$ of a cell of unit volume may be evaluated as a function of the masses M^k added and the temperature T by integrating (2.15) along an arbitrary path. We denote by $\bar{s}_k(M^k, T)$ the relative specific entropy of any particular substance k. Since the partial pressure p_k is a function of M^k and T, $\bar{s}_k$ is a function of the same variables. We first integrate equation (2.15) at constant temperature T_0, the masses added varying from zero to M_k. We then maintain the masses constant and heat the cell to the temperature T. Integration of (2.15) along this path yields

$$\mathscr{S} = \sum_k \int_0^{M^k} \left[\bar{s}_k(M^k, T_0) + \frac{h_k^{mv}}{T_0}(M^k, T_0)\right] \mathrm{d}M^k + \int_{T_0}^{T} \frac{c(M^k, T')}{T'} \mathrm{d}T'. \tag{2.23}$$

In this expression $h_k^{mv}(M^k, T_0)$ is the heat absorbed by the cell when a unit mass of substance k is added reversibly at constant volume and constant temperature T_0, while $c(M^k, T')$ is the cell heat capacity at constant $M^k(k = 1, 2, \ldots)$, constant volume and variable temperature T'. From expression (2.23) we derive the temperature

$$T = T(M^k, \mathscr{S}) \tag{2.24}$$

as a function of M^k and $\mathscr{S}$.

When the primary system is a continuum Ω the potential of an infinitesimal cell of volume $\mathrm{d}\Omega$ is $\mathscr{V}\,\mathrm{d}\Omega$, where $\mathscr{V}$ is the local potential per unit volume. According to the additive property (2.9) the collective potential of the continuum is the volume integral

$$V = \int_\Omega \mathscr{V}\,\mathrm{d}\Omega. \tag{2.25}$$

3. Fundamental entropy balance equation and entropy production

Consider a domain Ω of the fluid mixture. The rate of entropy increase of this domain is

$$\dot{S} = \int_\Omega \left(\dot{s}^*_{\mathrm{NT}} + \frac{\dot{h}}{T}\right) \mathrm{d}\Omega - \int_A \sum_k \bar{s}_k \dot{M}^k_i n_i \mathrm{d}A. \tag{3.1}$$

The dot designates a time derivative. The rate of heat acquired per unit volume is $\dot{h}$ and $\dot{s}^*_{NT}$ is the rate of entropy produced per unit volume by irreversible processes other that thermal conduction. The second integral is over the boundary A of Ω with a unit normal n_i. The rate of mass flow of substance k per unit area is the vector $\dot{M}^k_i$ and $\bar{s}_k$ is the relative specific entropy (2.14) of substance k in thermodynamic equilibrium with the mixture at the point considered through a semipermeable membrane. The summation sign will be omitted for vector and tensor indices.

We may write

$$\dot{h} = -\partial \dot{H}_i / \partial x_i, \tag{3.2}$$

where $\dot{H}_i$ is the rate of heat flow per unit area, and x_i are the coordinates. By substituting the value (3.2) into (3.1) and transforming the surface integral into a volume integral, we obtain

$$\dot{S} = \int_\Omega \left(\dot{s}^* - \frac{\partial \dot{S}_i}{\partial x_i}\right) \mathrm{d}\Omega, \tag{3.3}$$

where

$$\dot{s}^* = \dot{s}^*_{\mathrm{NT}} - \frac{1}{T}\dot{S}^{\mathrm{t}}_i \frac{\partial T}{\partial x_i}, \quad \dot{S}^{\mathrm{t}}_i = \frac{\dot{H}_i}{T}, \tag{3.4}$$

and

$$\dot{S}_i = \sum_k \bar{s}_k \dot{M}^k_i + \dot{S}^{\mathrm{t}}_i. \tag{3.5}$$

The first terms $\bar{s}_k \dot{M}^k_i$ represent the rate of convected entropy, $\dot{S}^{\mathrm{t}}_i$ is the entropy flux due to thermal conduction, and $\dot{S}_i$ is the total entropy flux. The rate of entropy production due to thermal flux alone is (per unit volume)

$$-\frac{1}{T}\dot{S}^{\mathrm{t}}_i \frac{\partial T}{\partial x_i} = \frac{1}{k}\dot{S}^{\mathrm{t}}_i \dot{S}^{\mathrm{t}}_i, \tag{3.6}$$

where k is the local coefficient of thermal conduction. Hence

$$s^* = s^*_{\mathrm{NT}} + \dot{S}^{\mathrm{t}}_i \dot{S}^{\mathrm{t}}_i / k \tag{3.7}$$

is the rate of entropy produced per unit volume. Since equation (3.3) is valid for an arbitrary domain Ω we may write

$$\dot{\mathscr{S}} = \dot{s}^* - \partial \dot{S}_i / \partial x_i, \tag{3.8}$$

where $\mathscr{S}$ is the entropy per unit volume. Equation (3.8) constitutes the fundamental entropy balance equation already obtained earlier (Biot 1977*a*, *c*). It generalizes Meixner's result (1941) which is restricted to purely thermal flow. Integration with respect to time, with zero initial values, yields

$$\mathscr{S} = s^* + s, \tag{3.9}$$

where

$$s = -\partial S_i / \partial x_i \tag{3.10}$$

represents the entropy supplied by convection and conduction while S_i was called the entropy displacement (Biot 1976*a*, 1977*a*, *c*).

Another equation of the same 'holonomic' type is the mass conservation condition

$$M^k = -\partial M^k_i / \partial x_i, \tag{3.11}$$

where M^k is the mass supplied by convection per unit volume, assuming zero initial values. The total mass of substance k per unit volume is

$$m_k = m_{0k} + M^k, \tag{3.12}$$

where m_{0k} is the initial mass for $M^k = 0$.

We shall now evaluate the rate of dissipation due to thermomolecular diffusion and viscosity. This is expressed as

$$T\dot{s}^* = 2\mathscr{D}_{\mathrm{tm}} + 2\mathscr{D}_{\mathrm{v}} \tag{3.13}$$

where T is the local temperature and $\dot{s}^*$ is the rate of entropy production per unit volume. The terms $2\mathscr{D}_{\mathrm{tm}}$, $2\mathscr{D}_{\mathrm{v}}$ represent the dissipation due respectively to thermomolecular diffusion and the viscosity. They are uncoupled owing to Curie's principle.

As already shown repeatedly (Biot 1977*a*, *c*, *d*) the dissipation due to thermomolecular diffusion is a quadratic form in the rate variables $\dot{M}_i^k, \dot{S}_i$. As such it embodies the validity of Onsager's principle (1930, 1931, 1953; Machlup 1953) as a local property for coupled diffusion phenomena. However the coefficients of this quadratic form vary from point to point and depend on the local state variables. It must also satisfy two fundamental invariant properties. It must be isotropic and must vanish for a solid translation of the mixture. To this effect we introduce the velocities

$$v_i^k = \dot{M}_i^k/m_k \tag{3.14}$$

of the various substances, and hence the dissipation function due to thermomolecular diffusion is a quadratic form in v_i^k and $\dot{S}_i^{\mathrm{t}}$.

We write

$$\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}} = \tfrac{1}{2}\sum_{lki} K^{lk} v_i^l v_i^k + \sum_{ki} K^k v_i^k \dot{S}_i^{\mathrm{t}} + (T/2k)\sum_i (\dot{S}_i^{\mathrm{t}})^2. \tag{3.15}$$

It is convenient in this expression to introduce explicitly the summation sign for i instead of the summation convention. For $v_i^k = 0$ the dissipation is reduced to $(T/2k)\,\Sigma_i(\dot{S}_i^{\mathrm{t}})^2$, where $(1/k)\,\Sigma_i(\dot{S}_i^{\mathrm{t}})^2$ is the rate of entropy production (3.6) due to thermal conduction. The dissipation function must be invariant under solid translation. It is shown in appendix I that to satisfy this condition it must be of the form

$$\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}} = \tfrac{1}{2}\sum_{lki} C^{lk}\left(\frac{\dot{M}_i^l}{m_l} - \frac{\dot{M}_i^k}{m_k}\right)^2 + \sum_{ki} K^k \frac{\dot{M}_i^k}{m_k}\dot{S}_i^{\mathrm{t}} + \frac{T}{2k}\sum_i (\dot{S}_i^{\mathrm{t}})^2, \tag{3.16}$$

where the coefficient K^k must satisfy the relation

$$\sum_k K^k = 0. \tag{3.17}$$

The coefficients C^{lk}, K^k and $T/2k$ are functions of the local state variables M^k and $\mathscr{S}$. The dissipation function $\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}$ must be non-negative, hence we must have $C^{lk} \geqslant 0$ while the other coefficients also satisfy suitable conditions. We may substitute into (3.16) the value of $\dot{S}_i^{\mathrm{t}}$ derived from (3.5) as

$$\dot{S}_i^{\mathrm{t}} = \dot{S}_i - \sum_l \bar{s}_l \dot{M}_i^l. \tag{3.18}$$

We obtain

$$\mathscr{D}_{\mathrm{tm}} = \tfrac{1}{2}\sum_{lki} \mathscr{C}^{lk} \dot{M}_i^l \dot{M}_i^k + \sum_{ki} \mathscr{C}^k \dot{M}_i^k \dot{S}_i + (T/2k)\sum_i (\dot{S}_i)^2. \tag{3.19}$$

This value is equal to $\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}$ except that it is now expressed in terms of $\dot{M}_i^k$ and the total entropy flux $\dot{S}_i$ instead of the entropy flux $\dot{S}_i^{\mathrm{t}}$ due to thermal conduction only. In (3.19) the coefficient $\mathscr{C}^k$ includes the coupling between $\dot{M}_i^k$ and the entropy flux $\dot{S}_i$ due to both convection and thermal conduction.

In order to evaluate the dissipation due to the viscosity properties of the mixture we must consider the velocity gradients

$$v_{ij}^k = \partial v_i^k/\partial x_j. \tag{3.20}$$

We assume a Newtonian type viscosity. Again owing to the Onsager principle (1930, 1931) the dissipation function must be a quadratic form in the rate variables v^k_{ij}. Because of isotropy it must be a function of the quadratic invariants which are (retaining the summation rule for tensors)

$$r^l r^k, \quad v^l_{ij} v^k_{ij}, \quad v^l_{ij} v^k_{ji}, \tag{3.21}$$

where

$$r^k = \delta_{ij} v^k_{ij} \tag{3.22}$$

are dilatational strain-rates. The dissipation function due to viscosity is therefore

$$\mathscr{D}_{\mathrm{V}} = \tfrac{1}{2} \sum_{lk} \lambda^{lk} r^l r^k + \tfrac{1}{2} \sum_{lk} \lambda_1^{lk} v^l_{ij} v^k_{ij} + \tfrac{1}{2} \sum_{lk} \lambda_2^{lk} v^l_{ij} v^k_{ji}, \tag{3.23}$$

where λ^{lk}, λ_1^{lk} and λ_2^{lk} are viscosity coefficients, functions of the local state of the mixture hence of M^k and $\mathscr{S}$. If we put

$$r^k_{ij} = \tfrac{1}{2}(v^k_{ij} + v^k_{ji}), \quad \omega^k_{ij} = \tfrac{1}{2}(v^k_{ij} - v^k_{ji}), \tag{3.24}$$

or

$$v^k_{ij} = r^k_{ij} + \omega^k_{ij}, \quad v^k_{ji} = r^k_{ij} - \omega^k_{ij}, \tag{3.25}$$

the dissipation function becomes

$$\mathscr{D}_{\mathrm{V}} = \tfrac{1}{2} \sum_{lk} \lambda^{lk} r^l r^k + \sum_{lk} \eta_1^{lk} r^l_{ij} r^k_{ij} + \sum_{lk} \eta_2^{lk} \omega^l_{ij} \omega^k_{ij}, \tag{3.26}$$

where

$$\eta_1^{lk} = \tfrac{1}{2}(\lambda_1^{lk} + \lambda_2^{lk}), \quad \eta_2^{lk} = \tfrac{1}{2}(\lambda_1^{lk} - \lambda_2^{lk}), \tag{3.27}$$

or

$$\lambda_1^{lk} = \eta_1^{lk} + \eta_2^{lk}, \quad \lambda_2^{lk} = \eta_1^{lk} - \eta_2^{lk}. \tag{3.28}$$

The form (3.26) of the dissipation function brings out explicitly the strain rates r^k_{ij} and the rates of rotation ω^k_{ij}. The dissipation function $\mathscr{D}_{\mathrm{V}}$ must be non-negative. It is shown in appendix II that this implies the necessary and sufficient condition that the matrices $\lambda^{lk} + \frac{2}{3}\eta_1^{lk}$, η_1^{lk}, η_2^{lk} be non-negative, i.e. that for all values of real variables z_k we have

$$\sum_{lk} (\lambda^{lk} + \tfrac{2}{3}\eta_1^{lk}) z_l z_k \geqslant 0, \quad \sum_{lk} \eta_1^{lk} z^l z^k \geqslant 0, \quad \sum_{lk} \eta_2^{lk} z^l z^k \geqslant 0. \tag{3.29}$$

Additional conditions for the coefficients are also obtained if we consider a solid rotation ω_{ij} of the mixture, where $r^k_{ij} = 0$, $\omega^k_{ij} = \omega_{ij}$. In this case the dissipation must disappear. Hence

$$\mathscr{D}_{\mathrm{V}} = \sum_{lk} \eta_2^{lk} \omega_{ij} \omega_{ij}, \tag{3.30}$$

and the coefficients must satisfy the condition

$$\sum_{lk} \eta_2^{lk} = 0. \tag{3.31}$$

Another condition is obtained if we put $\omega^k_{ij} = 0$ and $r^k_{ij} = \delta_{ij} r$. To state that the dissipation vanishes in this case is equivalent to the assumption that bulk viscosity of the mixture is zero. Hence

$$\mathscr{D}_{\mathrm{V}} = \tfrac{9}{2} \sum_{lk} \lambda^{lk} r^2 + 3 \sum_{lk} \eta_1^{lk} r^2 = 0, \tag{3.32}$$

which implies the condition

$$\sum_{lk}(\lambda^{lk}+\tfrac{2}{3}\eta_1^{lk}) = 0. \tag{3.33}$$

However the vanishing of bulk viscosity is not a necessary physical requirement.

4. PRINCIPLE OF VIRTUAL DISSIPATION

A fundamental variational principle of virtual dissipation generalizing d'Alembert's principle to non-equilibrium thermodynamics has been developed (Biot 1954, 1955) and applied to general thermorheology (Biot 1976*a*, 1977*a*, *c*, *d*). It is a natural generalization of the linear Lagrangian thermodynamics initiated earlier (Biot 1954, 1955).

For the reader's convenience we shall present a simplified derivation of the variational principle in the special context of fluid mixtures. Equation (2.8) being valid for arbitrary transformations, we write it in variational form as

$$\delta\mathscr{P}-\delta W+T_0\delta S^* = 0. \tag{4.1}$$

The variations are applied *inside a domain Ω* and the variables to be varied obey the basic conservation constraints (3.10), (3.11). From (2.7) and (2.25) we write

$$\delta\mathscr{P} = \int_\Omega \delta\mathscr{V}\,\mathrm{d}\Omega+\delta G. \tag{4.2}$$

If the body forces are derived from a potential field of scalar potential $\mathscr{G}(x_i)$ per unit mass we may write

$$G = \int_\Omega \rho\mathscr{G}\,\mathrm{d}\Omega, \quad \rho = \sum_k m_k. \tag{4.3}$$

Hence

$$\delta\mathscr{P} = \int_\Omega (\delta\mathscr{V}+\mathscr{G}\delta\rho)\,\mathrm{d}\Omega. \tag{4.4}$$

According to d'Alembert's principle the virtual work of the reversed inertia forces may be included in the work δW of the external forces. In the present case this work is reduced to

$$\delta W = -\sum_i I_i\delta q_i, \tag{4.5}$$

where I_i are generalized inertia forces and q_i the conjugate displacements.

The total virtual entropy variation is

$$\delta S^* = \int_\Omega \delta s^*\,\mathrm{d}\Omega, \tag{4.6}$$

where δs^* is the variation of entropy produced per unit volume. With the values (4.4) (4.5) and (4.6), equation (4.1) becomes

$$\sum_i I_i\delta q_i+\int_\Omega (\delta\mathscr{V}+\mathscr{G}\delta\rho+T_0\delta s^*)\,\mathrm{d}\Omega = 0. \tag{4.7}$$

An important alternative form of this variational principle is obtained by writing, according to (2.16), (2.20);

$$\delta \mathscr{V} = \delta_{\mathrm{r}} \mathscr{V} + \frac{\partial \mathscr{V}}{\partial \mathscr{S}} \delta s^* = \delta_{\mathrm{r}} \mathscr{V} + \theta \delta s^*, \tag{4.8}$$

where

$$\delta_{\mathrm{r}} \mathscr{V} = \sum_k \frac{\partial \mathscr{V}}{\partial M^k} \delta M^k + \frac{\partial \mathscr{V}}{\partial \mathscr{S}} \delta s \tag{4.9}$$

represents a 'restricted variation' of $\mathscr{V}$ obtained by not varying s^*. Substitution of the value (4.8) into (4.7) yields

$$\sum_i I_i \delta q_i + \int_\Omega (\delta_{\mathrm{r}} \mathscr{V} + \mathscr{G} \delta \rho + T \delta s^*) \, \mathrm{d}\Omega = 0. \tag{4.10}$$

This form of the principle of virtual dissipation is directly applicable for our purpose. The term $T\delta s^*$ was called the local virtual dissipation and it was shown (Biot 1975, 1976*a*, 1977*a*) that it is obtained immediately from the rate of dissipation invariant (3.13) as

$$T \delta s^* = \sum_k \frac{\partial \cancel{D}_{\mathrm{v}}}{\partial v_{ij}^k} \delta a_{ij}^k + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}_i^k} \delta M_i^k + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_i} \delta S_i, \tag{4.11}$$

$/\mathscr{D}_{\mathrm{v}}$ ✓

where δM_i^k and δS_i are arbitrary variations of M_i^k and S_i, while δa_{ij}^k is

$$\delta a_{ij}^k = \frac{\partial}{\partial x_j} \delta u_i^k, \tag{4.12}$$

where δu_i^k is the variational displacement of substance k. According to (3.14) it may be expressed as

$$\delta u_i^k = \delta M_i^k / m_k. \tag{4.13}$$

Hence

$$\delta a_{ij}^k = \frac{\partial}{\partial x_j} \left(\frac{\delta M_i^k}{m_k} \right), \tag{4.14}$$

where δM_i^k is the variation of mass displacement.

We put

$$\sigma_{ij}^k = \partial \mathscr{D}_{\mathrm{v}} / \partial v_{ij}^k. \tag{4.15}$$

By definition we shall call this the partial dissipative stress tensor. This provides a *thermodynamic definition of these partial stresses* based on the dissipation invariant $\mathscr{D}_{\mathrm{v}}$. By using the value (3.23) of $\mathscr{D}_{\mathrm{v}}$ equation (4.15) yields the constitutive equations

$$\sigma_{ij}^k = \delta_{ij} \sum_l \lambda^{lk} r^l + \sum_l \lambda_1^{lk} v_{ij}^l + \sum_l \lambda_2^{lk} v_{ji}^l. \tag{4.16}$$

In case of a single substance

$$\left.\begin{aligned} \lambda^{lk} = \lambda, \quad \lambda_1^{lk} = \lambda_1, \quad \lambda_2^{lk} = \lambda_2, \\ \eta_1^{lk} = \eta, \quad \eta_2^{lk} = \eta_2, \quad r^k = r, \quad r_{ij}^k = r_{ij}. \end{aligned}\right\} \tag{4.17}$$

Equation (3.31) yields $\eta_2 = 0$. Hence from (3.28) $\lambda_1 = \lambda_2 = \eta$, and the constitutive equations (4.16) become

$$\sigma_{ij} = 2\eta r_{ij} + \lambda r \delta_{ij}, \tag{4.18}$$

which is the classical relation for a gas with viscosity coefficients λ, η.

Note that σ^k_{ij} are not the only partial stresses. The other part of the stress is the isotropic partial pressure p_k defined thermodynamically as described above, namely by considering equilibrium of the pure substance k through a semi-permeable membrane with a cell of same concentrations and temperature as the mixture at the point considered. The dissipative stresses are thus defined quite differently from the pressures.

With the definition (4.15) of σ^k_{ij} the virtual dissipation (4.11) is written

$$T\delta s^* = \sum_k \sigma^k_{ij}\delta a^k_{ij} + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}^k_i}\delta M^k_i + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_i}\delta S_i. \tag{4.19}$$

5. VARIATIONAL DERIVATION OF THE FIELD DIFFERENTIAL EQUATIONS OF DYNAMICS OF THE MIXTURE

The state of the mixture is completely defined by the vector fields M^k_i and S_i and the scalar field s^* representing the entropy produced per unit volume. We consider arbitrary variations δM^k_i and δS_i *inside* a domain Ω and apply the principle of virtual dissipation. The virtual work of the inertia forces is

$$\sum_i I_i \delta q_i = \int_\Omega \sum_k m_k a^k_i \delta u^k_i \,\mathrm{d}\Omega = \int_\Omega \sum_k a^k_i \delta M^k_i \,\mathrm{d}\Omega, \tag{5.1}$$

where the virtual displacement δu^k_i is given by (4.13). The acceleration of substance k is

$$a^k_i = \frac{\partial v^k_i}{\partial t} + v^k_j \frac{\partial v^k_i}{\partial x_j}. \tag{5.2}$$

By using relations (2.20) the value (4.9) of $\delta_{\mathrm{r}}\mathscr{V}$ is written

$$\delta_{\mathrm{r}}\mathscr{V} = \sum_k \phi_k \delta M^k + \theta\delta s. \tag{5.3}$$

With these values of $\Sigma_i I_i \delta q_i$ and $\delta_{\mathrm{r}}\mathscr{V}$, and the value (4.19) for $T\delta s^*$, the variational principle (4.10) becomes

$$\int_\Omega \left(\sum_k a^k_i \delta M^k_i + \sum_k \phi_k \delta M^k + \theta\delta s + \mathscr{G}\delta\rho + \sum_k \sigma^k_{ij}\delta a^k_{ij} + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}^k_i}\delta M^k_i \right. \\ \left. + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_i}\delta S_i \right) \mathrm{d}\Omega = 0. \tag{5.4}$$

The variations may be expressed as follows. From (3.10) and (3.11) we obtain

$$\delta M^k = -\partial(\delta M^k_i/\partial x_i), \quad \delta s = -\partial(\delta S_i/\partial x_i). \tag{5.5}$$

Also from (3.11), (3.12), (4.3) and (4.14)

$$\delta\rho = -\partial(\delta M^k_i)/\partial x_i, \quad \delta a^k_{ij} = \partial(\delta M^k_i/m_k)/\partial x_i. \tag{5.6}$$

We integrate by parts the terms containing δM^k, δs, $\delta\rho$ and δa^k_{ij}. Since δM^k_i and δS_i may be chosen arbitrarily inside Ω, while vanishing continuously at the boundary, we equate to zero.the coefficients of these variations. This yields the field differential equations

$$\left.\begin{aligned} a_i^k-\frac{1}{m_k}\frac{\partial\sigma_{ij}^k}{\partial x_j}+\frac{\partial\varphi_k}{\partial x_i}+\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{M}_i^k}&=0,\\ \frac{\partial\theta}{\partial x_i}+\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{S}_i}&=0,\end{aligned}\right\}\tag{5.7}$$

where we have put

$$\varphi_k=\phi_k+\mathscr{G}.\tag{5.8}$$

We need one more equation for the unknown s^*. This is provided by expression (3.13) for the rate of dissipation, namely

$$T\dot{s}^*=2\mathscr{D}_{\mathrm{tm}}+2\mathscr{D}_{\mathrm{v}}=2\mathscr{D}.\tag{5.9}$$

The field equations (5.7) and (5.9) thus obtained by a variational method while extremely general show a remarkable symmetry and simplicity as well as physical significance. This in spite of the great physical complexity of the system. The quantity φ_k has been called 'mixed convective potential' in earlier work (Biot 1977*c*). It includes the work $\mathscr{G}$ accomplished to bring the unit mass to the location x_i in the potential field. We may assume for example that supply cells are located on $\mathscr{G}=0$.

A useful alternative classical expression of the acceleration is

$$a_i^k=\frac{\partial v_i^k}{\partial t}+v_j^k\frac{\partial v_i^k}{\partial x_j}=\frac{\partial v_i^k}{\partial t}+v_j^k\left(\frac{\partial v_i^k}{\partial x_j}-\frac{\partial v_j^k}{\partial x_i}\right)+v_j^k\frac{\partial v_j^k}{\partial x_i}.\tag{5.10}$$

This may be written

$$a_i^k=\frac{\partial v_i^k}{\partial t}+\frac{1}{2}\frac{\partial}{\partial x_i}(v^k)^2+\mathscr{A}_i^k,\tag{5.11}$$

where

$$(v^k)^2=v_i^kv_i^k,\quad \mathscr{A}_i^k=2v_j^k\omega_{ij}^k.\tag{5.12}$$

The vector $\mathscr{A}_i^k$ is proportional to the vector product of the velocity by the vorticity ω_{ij}^k. It satisfies the property.

$$\mathscr{A}_i^k\dot{M}_i^k=2m_kv_i^kv_j^k\omega_{ij}^k=0,\tag{5.13}$$

i.e. the vectors $\mathscr{A}_i^k$ and $\dot{M}_i^k$ are perpendicular.

A physically significant form of the field equations (5.7) is obtained by noting the relations

$$\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{S}_i}=\frac{\partial\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial\dot{S}_i^{\mathrm{t}}},\tag{5.14}$$

$$\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{M}_i^k}=\frac{\partial\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial\dot{M}_i^k}-\bar{s}\frac{\partial\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial\dot{S}_i^{\mathrm{t}}}=\frac{\partial\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial\dot{M}_i^k}-\bar{s}_k\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{S}_i}.\tag{5.15}$$

Using the value

$$\frac{\partial\theta}{\partial x_i}=-\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{S}_i}\tag{5.16}$$

obtained from equations (5.7), we write

$$\frac{\partial\mathscr{D}_{\mathrm{tm}}}{\partial\dot{M}_i^k}=\frac{\partial\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial\dot{M}_i^k}+\bar{s}_k\frac{\partial\theta}{\partial x_i}.\tag{5.17}$$

Also from (5.8) and (2.18) we obtain

$$\frac{\partial \varphi_k}{\partial x_i} = \frac{\partial \phi_k}{\partial x_i} + \frac{\partial \mathscr{G}}{\partial x_i} = \frac{1}{\rho_k}\frac{\partial p_k}{\partial x_i} - \bar{s}_k \frac{\partial \theta}{\partial x_i} + \frac{\partial \mathscr{G}}{\partial x_i}. \tag{5.18}$$

Substitution of the values (5.14), (5.17) and (5.18) into the field equations (5.7) yields

$$a_i^k - \frac{1}{m_k}\frac{\partial \sigma_{ij}^k}{\partial x_j} + \frac{1}{\rho_k}\frac{\partial p_k}{\partial x_i} + \frac{\partial \mathscr{G}}{\partial x_i} + \frac{\partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{M}_i^k} = 0, \tag{5.19}$$

$$\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{S}_i^{\mathrm{t}}} = 0. \tag{5.20}$$

Note that in these equations the dissipative stresses σ_{ij}^k and the partial pressures p_k are defined thermodynamically as explained above.

It is interesting to show that these equations satisfy the total momentum relation for the mixture. We add equations (5.19) after multiplying each by m_k and obtain

$$\sum_k m_k a_i^k - \frac{\partial}{\partial x_j}\sum_k \sigma_{ij}^k + \sum_k \frac{m_k}{\rho_k}\frac{\partial p_k}{\partial x_i} + \frac{\partial \mathscr{G}}{\partial x_i}\sum_k m_k + \sum_k m_k \frac{\partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{M}_i^k} = 0. \tag{5.21}$$

By using expression (3.16) for $\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}$ it is immediately verified that

$$\sum_k m_k \frac{\partial D_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{M}_i^k} = 0. \tag{5.22}$$

Also as shown in appendix III we may write

$$\frac{\partial p}{\partial x_i} = \sum_k \frac{m_k}{\rho_k}\frac{\partial p_k}{\partial x_i}, \tag{5.23}$$

where p is the total pressure of the mixture. Hence equation (5.21) becomes

$$\sum_k m_k a_i^k - \frac{\partial}{\partial x_j}\sum_k \sigma_{ij}^k + \frac{\partial p}{\partial x_i} + \frac{\partial \mathscr{G}}{\partial x_i}\sum_k m_k = 0, \tag{5.24}$$

which is the total momentum equation.

We note that equation (5.23) is self evident for perfect gases since in this case $m_k = \rho_k$ and $p = \sum_k p_k$ (see appendix III).

For the particular case of a single fluid, equations (5.7) coincide with those derived earlier by the same variational procedure (Biot 1977*a*).

Remarks on the physical significance of equations (5.7)

The stresses σ_{ij}^k are the dissipative forces across a unit area exerted on the molecules of substance k by all other molecules. Hence it is physically understandable that $\partial \sigma_{ij}^k / \partial x_j$ is equivalent to a body force producing an effect on diffusion. It should be emphasized that equations (5.7) contain only first order dissipative rate effects. In particular the velocity may be written $v_i^k = v_i + v_i^{1k}$ with $\Sigma_k m_k v_i^{1k} = 0$. Hence $v_i = \Sigma_k m_k v_i^k / \rho$ is the barycentric velocity (velocity of the centre of gravity), while

v_i^{1k} represents small rate effects and expression (5.10), for the acceleration a_i^k, may be linearized with respect to v_i^{1k} or even simplified by putting $v_i^{1k} = 0$. To the same approximation the kinetic energy is $\frac{1}{2}\Sigma_k m_k (v^k)^2 = \frac{1}{2}\rho v_i v_i$ and there are no coupling terms between the variables of $\mathscr{D}_{\text{tm}}$ and those of $\mathscr{D}_{\text{v}}$ in the dissipation function (5.9). The latter is a consequence of the requirement of invariance (Curie's law).

6. ENERGY FLUX THEOREM

We add the field equations (5.7) after multiplying each of the first group by $\dot{M}_i^k$ and each of the second group by $\dot{S}_i$. Substituting $\partial\theta/\partial x_i = \partial T/\partial x_i$ and $v_i^k = \dot{M}_i^k/m_k$, and using Euler's theorem

$$2\mathscr{D}_{\text{tm}} = \sum_k \dot{M}_i^k \frac{\partial \mathscr{D}_{\text{tm}}}{\partial \dot{M}_i^k} + \dot{S}_i \frac{\partial \mathscr{D}_{\text{tm}}}{\partial \dot{S}_i}, \tag{6.1}$$

we obtain

$$\sum_k \dot{M}_i^k a_i^k - \sum_k v_i^k \frac{\partial \sigma_{ij}^k}{\partial x_j} + \sum_k \dot{M}_i^k \frac{\partial \varphi_k}{\partial x_i} + \dot{S}_i \frac{\partial T}{\partial x_i} + 2\mathscr{D}_{\text{tm}} = 0. \tag{6.2}$$

We may write

$$\sum_k v_i^k \frac{\partial \sigma_{ij}^k}{\partial x_j} = \sum_k \frac{\partial}{\partial x_j}(v_i^k \sigma_{ij}^k) - \sum_k v_{ij}^k \sigma_{ij}^k. \tag{6.3}$$

Again using Euler's theorem and equation (4.15) for σ_{ij}, we write

$$\sum_k v_{ij}^k \sigma_{ij}^k = 2\mathscr{D}_{\text{v}}. \tag{6.4}$$

Hence

$$\sum_k v_i^k \frac{\partial \sigma_{ij}^k}{\partial x_j} = \frac{\partial}{\partial x_i}\Big(\sum_k v_j^k \sigma_{ji}^k\Big) - 2\cancel{\mathscr{D}}_{\text{v}}. \tag{6.5}$$

$\mathscr{D}_v$

We have interchanged the dummy indices i, j on the right side. Substitution of this value into (6.2) taking into account expression (5.9) for $T\dot{s}^*$ yields

$$\sum_k \dot{M}_i^k a_i^k - \frac{\partial}{\partial x_i}\Big(\sum_k v_j^k \sigma_{ji}^k\Big) + \sum_k \dot{M}_i^k \frac{\partial \varphi_k}{\partial x_i} + \dot{S}_i \frac{\partial T}{\partial x_i} + T\dot{s}^* = 0. \tag{6.6}$$

Consider the terms

$$\sum_k \dot{M}_i^k \frac{\partial \varphi_k}{\partial x_i} + \dot{S}_i \frac{\partial T}{\partial x_i} + T\dot{s}^* = \frac{\partial}{\partial x_i}\Big(\sum_k \dot{M}_i^k \varphi_k + T\dot{S}_i\Big) - \sum_k \varphi_k \frac{\partial \dot{M}_i^k}{\partial x_i} + T\left(\dot{s}^* - \frac{\partial \dot{S}_i}{\partial x_i}\right), \tag{6.7}$$

Taking into account relations (3.8), (3.11) and (5.8), we write

$$-\sum_k \varphi_k \frac{\partial \dot{M}_i^k}{\partial x_i} + T\left(\dot{s}^* - \frac{\partial \dot{S}_i}{\partial x_i}\right) = \sum_k \varphi_k \dot{M}^k + T\dot{\mathscr{S}} = \sum_k \phi_k \dot{M}^k + \theta\dot{\mathscr{S}} + \sum_k \dot{M}^k \mathscr{G} + T_0 \dot{\mathscr{S}}. \tag{6.8}$$

From equations (2.20) we also derive

$$\sum_k \phi_k \dot{M}^k + \theta\dot{\mathscr{S}} = \sum_k \frac{\partial \mathscr{V}}{\partial M^k}\dot{M}^k + \frac{\partial \mathscr{V}}{\partial \mathscr{S}}\dot{\mathscr{S}} = \dot{\mathscr{V}}. \tag{6.9}$$

On the other hand according to (2.10)

$$\mathscr{V} = \mathscr{U} - T_0 \mathscr{S}, \tag{6.10}$$

where $\mathscr{U}$ is the energy per unit volume. From these results we obtain for the terms (6.7) the value

$$\sum_k \dot{M}_i^k \frac{\partial \varphi_k}{\partial x_i} + \dot{S}_i \frac{\partial T}{\partial x_i} + T\dot{s}^* = \frac{\partial}{\partial x_i}(\sum_k \dot{M}_i^k \varphi_k + T\dot{S}_i) + \dot{\mathscr{U}}_i + \mathscr{G} \sum_k \dot{m}_k. \tag{6.11}$$

Note that according to (3.12), $\dot{M}^k = \dot{m}_k$. Substitution of this expression into equation (6.6) yields

$$\sum_k \dot{M}_i^k a_i^k + \frac{\partial}{\partial x_i}(-\sum_k v_j^k \sigma_{ji}^k + \sum_k \dot{M}_i^k \varphi_k + T\dot{S}_i) + \dot{\mathscr{U}} + \mathscr{G}\sum_k \dot{m}_k = 0. \tag{6.12}$$

Consider now the terms containing the accelerations. According to relations (5.11) and (5.13) we obtain

$$\dot{M}_i^k a_i^k = \dot{M}_i^k \frac{\partial v_i^k}{\partial t} + \tfrac{1}{2} \dot{M}_i^k \frac{\partial}{\partial x_i}(v^k)^2. \tag{6.13}$$

Since

$$\dot{M}_i^k = m_k v_i^k, \tag{6.14}$$

relation (6.13) may be written

$$\dot{M}_i^k a_i^k = \frac{1}{2}\frac{\partial}{\partial t}[m_k (v^k)^2] + \frac{1}{2}\frac{\partial}{\partial x_i}[\dot{M}_i^k (v^k)^2] - \frac{1}{2}\left(\dot{m}_k + \frac{\partial \dot{M}_i^k}{\partial x_i}\right)(v^k)^2. \tag{6.15}$$

From mass conservation we have

$$\dot{m}_k + \partial \dot{M}_i^k / \partial x_i = 0. \tag{6.16}$$

Hence

$$\dot{M}_i^k a_i^k = \frac{1}{2}\frac{\partial}{\partial t}[m_k (v^k)^2] + \frac{1}{2}\frac{\partial}{\partial x_i}[\dot{M}_i^k (v^k)^2]. \tag{6.17}$$

With this value equation (6.12) becomes

$$\frac{\partial F_i}{\partial x_i} + \tfrac{1}{2}\sum_k \frac{\partial}{\partial t}[m_k (v^k)^2] + \dot{\mathscr{U}} + \mathscr{G}\sum_k \dot{m}_k = 0, \tag{6.18}$$

where

$$F_i = \tfrac{1}{2}\sum_k \dot{M}_i^k (v^k)^2 - \sum_k v_j^k \sigma_{ji}^k + \sum_k \dot{M}_i^k \varphi_k + T\dot{S}_i. \tag{6.19}$$

The remaining terms in equation (6.18) represent the rate of increase of energy of the mixture per unit volume. Hence F_i is the energy flux per unit area and equation (6.18) constitutes an *energy flux theorem.*

The energy flux vector F_i may be written in a physically more significant form by using relations (2.21), (3.4), (3.5) and (5.8). We write

$$\begin{aligned} \varphi_k &= \phi_k + \mathscr{G} = \bar{\epsilon}_k - T\bar{s}_k + \mathscr{G}, \\ \dot{S}_i &= \sum_k \bar{s}_k \dot{M}_i^k + \dot{S}_i^{\mathrm{t}} = \sum_k \bar{s}_k \dot{M}_i^k + \dot{H}_i/T. \end{aligned} \tag{6.20}$$

With these values we obtain

$$F_i = \tfrac{1}{2}\sum_k \dot{M}_i^k (v^k)^2 - \sum_k v_j^k \sigma_{ji}^k + \sum_k \dot{M}_i^k (\bar{\epsilon}_k + \mathscr{G}) + \dot{H}_i, \tag{6.21}$$

where $\bar{\epsilon}_k$ is the relative specific enthalpy of each substance as defined above and $\dot{H}_i$ is the total heat flux. The first term represents the kinetic energy flux and the second term is the power transmitted by the dissipative forces σ^k_{ji}.

7. Mixture of incompressible fluids

The foregoing results are of course applicable to incompressible fluids as a limiting case. However for the purpose of practical applications a special treatment is in order.

Instead of a rigid cell of unit volume with variable composition and temperature we consider a cell which is also of variable volume v. As shown earlier (Biot 1976*b*, 1977*b*) the differential of the cell potential in this case is

$$\mathrm{d}\mathscr{V} = -p\,\mathrm{d}v + \sum_k \phi_k \mathrm{d}M^k + \theta\,\mathrm{d}\mathscr{S}, \tag{7.1}$$

where p is the total pressure of the mixture. Because of incompressibility we may write

$$\mathrm{d}v = \sum_k \mathrm{d}M^k/\rho_k. \tag{7.2}$$

Substitution of this value in (7.1) yields

$$\mathrm{d}\mathscr{V} = \sum_k \phi'_k \mathrm{d}M^k + \theta\,\mathrm{d}\mathscr{S}, \tag{7.3}$$

where

$$\phi'_k = -\frac{p}{\rho_k} + \phi_k = \frac{1}{\rho_k}(p_k - p - p_0) - \int_{T_0}^{T} \bar{s}_k \mathrm{d}T. \tag{7.4}$$

We note that for incompressible fluids $\bar{s}_k$ is a function only of the temperature. The potential $\mathscr{V}$ of the cell of variable volume is a function, of M^k and $\mathscr{S}$. The pressure difference $p - p_k$ is also a function of the same variables. Because of incompressibility we may increase p and p_k by the same amount without changing the potential $\mathscr{V}$. Hence the variables M^k and $\mathscr{S}$ determine only the difference $p - p_k$.

We now consider the incompressible continuum. The collective potential of the domain Ω is

$$\dot{V} = \int_\Omega \mathscr{V}\,\mathrm{d}\Omega, \tag{7.5}$$

where $\mathscr{V}$ is the potential per unit volume. Hence $\mathscr{V}$ is now the potential of a rigid cell of unit volume and variable composition, however because of incompressibility the variables M^k are not independent and must satisfy the constraint,

$$\sum_k M^k/\rho_k = 0. \tag{7.6}$$

When applying the principle of virtual dissipation we must take into account the fact that the variations M^k_i of mass displacement are not independent. Due to relation (7.6) they must obey the constraint

$$\sum_k \frac{\delta M^k}{\rho_k} = -\sum_k \frac{1}{\rho_k}\frac{\partial}{\partial x_i}\delta M^k_i = 0. \tag{7.7}$$

Following a classical procedure for this case we write the variational principle (4.10) as

$$\sum_i I_i \delta q_i + \int_\Omega \left(\delta_{\mathrm{r}} \mathscr{V} - \Lambda \sum_k \frac{1}{\rho_k} \frac{\partial}{\partial x_i} \delta M_i^k + \mathscr{G} \delta \rho + T \delta s^*\right) \mathrm{d}\Omega = 0, \tag{7.8}$$

where Λ is a Lagrangian multiplier. In this relation the variations are now arbitrary and we may proceed as we have done for the compressible case. This yields the field equations

$$a_i^k - \frac{1}{m_k} \frac{\partial \sigma_{ij}^k}{\partial x_j} + \frac{\partial}{\partial x_i}(\phi_k' + \mathscr{G} + \Lambda) + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}_i^k} = 0, \tag{7.9}$$

$$\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_i} = 0. \tag{7.10}$$

To these equations we must add equation (5.9) for entropy production. They contain the same field unknowns M_i^k, S_i, s^* as the similar equations (5.7) and (5.9) for the compressible case and an additional one Λ. The additional equation required is the incompressibility condition (7.6) for M^k.

The field equations (7.9), (1.10) may be transformed into a form similar to (5.19), (5.20) by the same procedure as for the compressible case. We obtain

$$a_i^k - \frac{1}{m_k} \frac{\partial \sigma_{ij}^k}{\partial x_j} + \frac{1}{\rho_k} \frac{\partial}{\partial x_i}(p_k - p + \Lambda) + \frac{\partial \mathscr{G}}{\partial x_i} + \frac{\partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{M}_i^k} = 0, \tag{7.11}$$

$$\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}}{\partial \dot{S}_i^{\mathrm{t}}} = 0. \tag{7.12}$$

In these equation $p_k - p$ is a function of the variables M^k and $\mathscr{S}$, with M^k satisfying (7.6).

In order to bring out the significance of Λ we add equations (7.11) after multiplying each by m_k. We obtain

$$\sum_k m_k a_i^k - \sum_k \frac{\partial \sigma_{ij}^k}{\partial x_j} + \frac{\partial \Lambda}{\partial x_i} + \rho \frac{\partial \mathscr{G}}{\partial x_i} = 0. \tag{7.13}$$

In deriving this result we have taken into account the following relations:

$$\sum_k m_k / \rho_k = 1, \tag{7.14}$$

which is derived from incompressibility and unit volume of the primary cell,

$$\frac{\partial p}{\partial x_i} = \sum_k \frac{m_k}{\rho_k} \frac{\partial p_k}{\partial x_i}, \tag{7.15}$$

which is derived in appendix III, and

$$\sum_k m_k \, \partial \mathscr{D}_{\mathrm{tm}}^{\mathrm{t}} / \partial \dot{M}_i^k = 0, \tag{7.16}$$

which is equation (5.22).

Equation (7.13) is the total momentum equation, hence Λ represents the total pressure p of the mixture. Note however that in the field equation (7.11) we may not put $\Lambda - p = 0$ since it is $p_k - p$ which is known as a function of M^k and $\mathscr{S}$ and not p_k.

Expression (2.23) for the entropy is simplified for incompressible fluids since in this case $\bar{s}_k(M^k, T_0) = 0$. Hence

$$\mathscr{S} = \sum_k \int_0^{M^k} \frac{h_k^{mv}(M^k, T_0)}{T_0}\,\mathrm{d}M^k + \int_{T_0}^{T} \frac{c(M^k, T')}{T'}\,\mathrm{d}T'. \tag{7.17}$$

8. GENERALIZED COORDINATES AND LAGRANGIAN EQUATIONS

We represent the unknown vector fields by

$$\left.\begin{aligned} M_j^k &= M_j^k(q_i, x_l, t), \\ S_j &= S_j(q_i, x_l, t), \end{aligned}\right\} \tag{8.1}$$

which are now determined by a finite number of unknown generalized coordinates q_i. We shall assume that the entropy produced does not contribute significantly to the state variables describing the system. This assumption may be introduced as an approximation in a large number of problems. We shall indicate below how the method may be generalized to include s^* in the state variables if needed. The field unknowns are thus replaced by a finite number of variables q_i which are assumed to define with sufficient accuracy the state of the fluid mixture.

In this formulation the variations are

$$\delta M_j^k = \frac{\partial M_j^k}{\partial q_i}\,\delta q_i, \quad \delta S_j = \frac{\partial S_j}{\partial q_i}\,\delta q_i. \tag{8.2}$$

The summation sign with respect to i is omitted. We shall apply the principle of virtual dissipation (4.10) in the domain Ω and write it in the form

$$\int_\Omega \left(\sum_k a_j^k \delta M_j^k + \sum_k \varphi_k \delta M^k + \theta\,\delta s + T\,\delta s^*\right) \mathrm{d}\Omega = 0, \tag{8.3}$$

where φ_k is expressed by (5.8) and according to (4.11) and (4.19) we have

$$\begin{aligned} T\,\delta s^* &= \sum_k \sigma_{jl}^k \delta a_{jl}^k + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}_j^k}\,\delta M_j^k + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_j}\,\delta S_j \\ &= \sum_k \frac{\partial \mathscr{D}_{\mathrm{v}}}{\partial v_{jl}^k}\,\delta a_{jl}^k + \sum_k \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{M}_j^k}\,\delta M_j^k + \frac{\partial \mathscr{D}_{\mathrm{tm}}}{\partial \dot{S}_j}\,\delta S_j. \end{aligned} \tag{8.4}$$

We remember that in the variational principle (4.19) the variations δM_i^k and δS_i are assumed to vanish at the boundary A of the domain Ω. However the variations expressed by (8.2) do not. This does not lead to any difficulty with the terms containing δM_j^k and δS_j since they may be assumed to vanish discontinuously at the boundary A. On the other hand according to equations (5.5) and (5.6) the variations $\delta\rho$, δM^k, δs and δa_{jl}^k contain the gradients of δM^k and δS_j. Hence they become infinite when δM^k and δS_j are discontinuous at the boundary, and therefore contribute an additional finite boundary value to the integral. This contribution is easily derived by integration by parts and the variational principle now becomes (see Appendix IV)

$$\int_\Omega \Big(\sum_k a_j^k \delta M_j^k + \sum_k \varphi_k \delta M^k + \theta \delta s + T\delta s^*\Big)\,\mathrm{d}\Omega = \int_A \left[\sum_k \left(\sigma_{jl}^k \frac{n_l}{m_k} - \varphi_k n_j\right)\delta M_j^k - \theta n_j \delta S_j\right]\mathrm{d}A, \tag{8.5}$$

where n_j is the unit normal to A. This variational equation may be expressed in terms of the variations δq_i as follows.

Since s^* is neglected in the value of the entropy $\mathscr{S}$ we put $\delta\mathscr{S} = \delta s$, and we obtain

$$\delta\mathscr{V} = \sum_k \frac{\partial\mathscr{V}}{\partial M^k}\delta M^k + \frac{\partial\mathscr{V}}{\partial\mathscr{S}}\delta\mathscr{S} = \sum_k \phi_k \delta M^k + \theta\delta s. \tag{8.6}$$

Hence
$$\int_\Omega \Big(\sum_k \varphi_k \delta M^k + \theta\delta s\Big)\,\mathrm{d}\Omega = \int_\Omega (\delta\mathscr{V} + \mathscr{G}\delta\rho)\,\mathrm{d}\Omega = \delta\mathscr{P} = \frac{\partial\mathscr{P}}{\partial q_i}\delta q_i, \tag{8.7}$$

where
$$\mathscr{P} = \int_\Omega (\mathscr{V} + \rho\mathscr{G})\,\mathrm{d}\Omega \tag{8.8}$$

is the mixed collective potential of the system.

The virtual dissipation

$$\int_\Omega T\delta s^*\,\mathrm{d}\Omega = \int_\Omega \left[\sum_k \left(\frac{\partial\mathscr{D}_\mathrm{v}}{\partial v_{jl}^k}\delta a_{jl}^k + \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{M}_j^k}\delta M_j^k\right) + \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{S}_j}\delta S_j\right]\mathrm{d}\Omega \tag{8.9}$$

may be written
$$\int_\Omega T\delta s^*\,\mathrm{d}\Omega = \frac{\partial D}{\partial \dot{q}_i}\delta q_i, \tag{8.10}$$

where
$$D(q_i, \dot{q}, t) = \int_\Omega (\mathscr{D}_\mathrm{v} + \mathscr{D}_\mathrm{tm})\,\mathrm{d}\Omega \tag{8.11}$$

is the total dissipation function. This result is easily verified by considering for example

$$\dot{M}_i^k = \frac{\partial M_j^k}{\partial q_i}\dot{q}_i + \frac{\partial M_j^k}{\partial t}. \tag{8.12}$$

Hence

$$\frac{\partial M_j^k}{\partial q_i} = \frac{\partial \dot{M}_j^k}{\partial \dot{q}_i}. \tag{8.13}$$

We derive (for $\delta S_j = 0$)

$$\sum_k \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{M}_j^k}\delta M_j^k = \sum_k \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{M}_j}\frac{\partial M_j^k}{\partial q_i}\delta q_i = \sum_k \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{M}_j^k}\frac{\partial \dot{M}_j^k}{\partial \dot{q}_i}\delta q_i = \frac{\partial\mathscr{D}_\mathrm{tm}}{\partial \dot{q}_i}\delta q_i. \tag{8.14}$$

We substitute the values (8.7) and (8.10) as well as the variations (8.2) in the variational principle (8.5). Since the variations are arbitrary this yields

$$I_i + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial\mathscr{P}}{\partial q_i} = Q_i, \tag{8.15}$$

where
$$I_i = \int_\Omega \sum_k a_j^k \frac{\partial M_j^k}{\partial q_i}\,\mathrm{d}\Omega \tag{8.16}$$
are generalized inertia forces, and
$$Q_i = \int_A \left[\sum_k \left(\sigma_{jl}^k \frac{n_l}{m_k} - \varphi_k n_j\right)\frac{\partial M_j^k}{\partial q_i} - \theta n_j \frac{\partial S_j}{\partial q_i}\right]\mathrm{d}A \tag{8.17}$$
are generalized boundary driving forces.

These driving forces are of mixed mechanical and thermodynamic nature and represent the effect of the *environment* on the system. They are of the same type as encountered earlier in many different problems (Biot 1970, 1975, 1976*a*, 1977*c*, *d*).

The generalized inertia forces may be expressed in an interesting alternative form in terms of the kinetic energy.
$$\mathscr{T} = \frac{1}{2}\int_\Omega \sum_k m_k (v^k)^2\,\mathrm{d}\Omega = \frac{1}{2}\int_\Omega \sum_k \frac{\dot{M}_j^k \dot{M}_j^k}{m_k}\,\mathrm{d}\Omega. \tag{8.18}$$
Consider the variation of the time integral
$$\delta \int_t \mathscr{T}\,\mathrm{d}t = \int_{t,\Omega} \sum_k \left(\frac{\dot{M}_j^k}{m_k}\frac{\partial}{\partial t}\delta M_j^k - \frac{1}{2}\frac{\dot{M}_j^k \dot{M}_j^k}{m_k^2}\delta m_k\right)\mathrm{d}t\,\mathrm{d}\Omega. \tag{8.19}$$
This may be written
$$\delta \int_t \mathscr{T}\,\mathrm{d}t = \int_{t,\Omega} \sum_k \left[v_j^k \frac{\partial}{\partial t}\delta M_j^k + \tfrac{1}{2}(v^k)^2 \frac{\partial}{\partial x_j}\,\delta M_j^k\right]\mathrm{d}t\,\mathrm{d}\Omega. \tag{8.20}$$
Integration by parts, assuming zero variations for initial and final t, yields
$$\delta \int_t \mathscr{T}\,\mathrm{d}t = -\int_{t,\Omega} \sum_k \left[\frac{\partial v_j^k}{\partial t} + \frac{1}{2}\frac{\partial}{\partial x_j}(v^k)^2\right]\delta M_j^k\,\mathrm{d}t\,\mathrm{d}\Omega + \frac{1}{2}\int_{tA} \sum_k (v^k)^2 n_j \delta M_j^k\,\mathrm{d}t\,\mathrm{d}A. \tag{8.21}$$
By introducing the value (5.11) of the acceleration a_j^k and expressions (8.2) for δM_j^k this becomes
$$\delta \int_t \mathscr{T}\,\mathrm{d}t = -\int_t I_i \delta q_i\,\mathrm{d}t + \int_{t,\Omega} \sum_k \mathscr{A}_j^k \frac{\partial M_j^k}{\partial q_i}\,\delta q_i\,\mathrm{d}t\,\mathrm{d}\Omega + \frac{1}{2}\int_{tA} \sum_k (v^k)^2 n_j \frac{\partial M_j^k}{\partial q_i}\,\delta q_i\,\mathrm{d}t\,\mathrm{d}A. \tag{8.22}$$
On the other hand $\mathscr{T}(q_i, \dot{q}_i, t)$ is a function of q_i, $\dot{q}_i$, and t. With δq_i as arbitrary functions of time vanishing at the limits of time integration, we obtain the classical relation:
$$\delta \int_t \mathscr{T}\,\mathrm{d}t = \int_t \left[\frac{\partial \mathscr{T}}{\partial q_i} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{T}}{\partial \dot{q}_i}\right)\right]\delta q_i\,\mathrm{d}t. \tag{8.23}$$
Equating expressions (8.22) and (8.23) taking into account that δq_i are arbitrary functions of time implies
$$I_i = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{T}}{\partial q_i} + \frac{1}{2}\int_A \sum_k (v^k)^2 n_j \frac{\partial M_{\cancel{j}}^k}{\partial q_i}\,\mathrm{d}A + \int_\Omega \sum_k \mathscr{A}_j^k \frac{\partial M_j^k}{\partial q_i}\,\mathrm{d}\Omega. \tag{8.24}$$

This expression of the generalized inertia forces contains terms involving the kinetic energy $\mathscr{T}$ in the domain Ω. These terms are the same as the classical Lagrangian expressions in terms of generalized coordinates. However in the present case there is an additional boundary integral and a volume integral which involves the vorticity ω_{ij}. This is due to the fact that the generalized coordinates describe the mass displacement at a fixed point instead of the variable coordinates of the moving particles. In other words the generalized coordinates describe *an open system.*

If we put

$$\left.\begin{aligned} Q_i' &= Q_i - \frac{1}{2}\int_A \sum_k (v^k)^2 n_j \frac{\partial M_j^k}{\partial q_i} \mathrm{d}A, \\ \mathscr{M}_i &= \int_\Omega \sum_k \mathscr{A}_j^k \frac{\partial M_j^k}{\partial q_i} \mathrm{d}A, \end{aligned}\right\} \tag{8.25}$$

and introduce the value (8.24) of I_i the Lagrangian equations (8.15) become

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{T}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{T}}{\partial q_i} + \mathscr{M}_i + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathscr{P}}{\partial q_i} = Q_i'. \tag{8.26}$$

It is of interest to note that $\mathscr{M}_i$ is analogous to a generalized Coriolis force and embodies a 'Magnus effect'. In the actual field as well as in the space of generalized coordinates it is perpendicular to the velocity. This can be seen by taking into account relation (5.13) and writing

$$\mathscr{M}_i \dot{q}_i = \int_\Omega \sum_k \mathscr{A}_j^k \frac{\partial M_j^k}{\partial q_i} \dot{q}_i \mathrm{d}\Omega = \int_\Omega \sum_k \mathscr{A}_j^k \dot{M}_j^k \mathrm{d}\Omega = 0. \tag{8.27}$$

This property of perpendicularity is thus invariant. Its existence is a direct consequence of the Eulerian formulation of dynamics which considers the system as a *collection of open cells.*

The force $\mathscr{M}_i$ vanishes whenever the vorticity is zero. Such is the case in potential flow and flow which is either one dimensional, axially symmetric, or spherically symmetric.

In the foregoing Lagrangian formulation we have assumed that the entropy produced s^* does not contribute significantly to the value of the total entropy $\mathscr{S}$ as a state variable. When this is not the case one way to introduce the correction is by first solving the problem by putting $s^* = 0$ as a first approximation and evaluate s^* from the entropy production equation (5.9), i.e.

$$T\dot{s}^* = 2\mathscr{D}, \tag{8.28}$$

where $\mathscr{D}$ is now expressed as a known function of time by the first approximation.

Another procedure is to use the actual value of the entropy

$$\mathscr{S} = s + s^*, \tag{8.29}$$

and to consider s^* as an additional unknown. Again we may use additional generalized coordinates q_i' by writing

$$s^* = s^*(q_i', x_l, t), \tag{8.30}$$

and derive the required number of equations for the additional unknowns. For example if there are n' generalized coordinates q_i' we write equation (8.30) at n' suitably chosen points. Another procedure is to derive the additional equations by applying to (8.30) the method of the variational scalar product (Biot 1970).

The Lagrangian technique of generalized coordinates has been given extensive treatment in the domain of heat transfer (Biot 1970) where its power and accuracy has been abundantly illustrated. It actually leads to new systems analysis methods and a new science of heat transfer which does not involve the use of traditional concepts.

9. FINITE ELEMENT METHODS BY GENERALIZED COORDINATES

The Lagrangian equations provide immediately a large variety of finite element methods by using the values of the field components at discrete points as generalized coordinates. For example in two dimensions we may divide the domain in triangular cells and choose the values of the unknown field variables M_j^k, S_j and s^* at the vertices as generalized coordinates q_i, q_i'. Values of the field inside the triangles are obtained by linear interpolation. The linear interpolation for any variable ζ whose values $\zeta_1\,\zeta_2\,\zeta_3$ are given at three points (x_1, y_1), (x_2, y_2), (x_3, y_3) is obtained from the equation

$$\begin{vmatrix} x & y & \zeta & 1 \\ x_1 & y_1 & \zeta_1 & 1 \\ x_2 & y_2 & \zeta_2 & 1 \\ x_3 & y_3 & \zeta_3 & 1 \end{vmatrix} = 0. \tag{9.1}$$

The Lagrangian equations (8.15) are equal in number to the unknowns M_j^k and S_j at the vertices. The additional equations for s^* are obtained by writing equation (8.28) at each vertex using for m_k and s the average of their constant values in the triangles with this common vertex.

In three dimensions the same method applies with tetrahedral cells.

Many variants and refinements may be imagined based on this approach using other types of interpolation. For example one may use a *local polynomial interpolation* involving values of the field at vertices of a group of neighbouring cells. The superior accuracy of such methods is exemplified by Simpson's rule in the case of quadratures.

APPENDIX I

The dissipation function (3.15), i.e.

$$\mathscr{D}^{\mathrm{t}}_{\mathrm{tm}} = \tfrac{1}{2}\sum_{lki} K^{lk} v_i^l v_i^k + \sum_{ki} K^k v_i^k \dot{S}_i^{\mathrm{t}} + (T/2k)\sum_i (\dot{S}_i^{\mathrm{t}})^2, \tag{I 1}$$

must be invariant under translation hence it must remain unchanged if we replace v_i^k by $v_i^k + v_i$, where v_i is a constant velocity of translation. With this substitution the value of $\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}}$ becomes

$$\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}} = \tfrac{1}{2}\sum_{lki} K^{lk} v_i^l\, v_i^k + \sum_{ki} K^k v_i^k S_i^{\mathrm{t}} + (T/2k)\sum_i (\dot{S}_i^{\mathrm{t}})^2$$
$$+ \sum_i v_i \sum_l \Big(\sum_k K^{lk} v_i^l\Big) + \tfrac{1}{2}\sum_{lki} K^{lk} v_i v_i + \sum_{ki} K^k v_i \dot{S}_i^{\mathrm{t}}. \quad \text{(I 2)}$$

This expression must be independent of v_i for arbitrary values of v_i^k. The necessary and sufficient conditions to be satisfied by the coefficients are

$$\left.\begin{aligned} &\sum_k K^{lk} = 0 \quad \text{for all values of } l, \\ \text{and} \qquad &\sum_k K^k = 0. \end{aligned}\right\} \quad \text{(I 3)}$$

We put

$$\left.\begin{aligned} K^{ll} &= 2C_1^{ll}, \\ K^{lk} &= -2C^{lk} \quad \text{for} \quad l \neq k \quad (C^{ll} = 0). \end{aligned}\right\} \quad \text{(I 4)}$$

The first of conditions (I 3) becomes

$$C_1^{ll} = \sum_k C^{lk}. \quad \text{(I 5)}$$

From those relations we derive

$$\begin{aligned} \sum_{lki} K^{lk} v_i^l\, v_i^k &= 2\sum_{li} C_1^{ll} v_i^l v_i^l - 2\sum_{lki} C^{lk} v_i^l v_i^k \\ &= 2\sum_{li}\Big(\sum_k C^{lk} v_i^l v_i^l\Big) - 2\sum_{lki} C^{lk} v_i^l v_i^k \\ &= \sum_{lki} C^{lk}(v_i^l v_i^l + v_i^k v_i^k - 2v_i^l v_i^k) \\ &= \sum_{lki} C^{lk}(v_i^l - v_i^k)^2. \end{aligned} \quad \text{(I 6)}$$

Hence the dissipation function (I 1) becomes

$$\mathscr{D}_{\mathrm{tm}}^{\mathrm{t}} = \tfrac{1}{2}\sum_{lki} C^{lk}(v_i^l - v_i^k)^2 + \sum_{ki} K^k v_i^k \dot{S}_i^{\mathrm{t}} + (T/2k)\sum_i (\dot{S}_i^{\mathrm{t}})^2. \quad \text{(I 7)}$$

Appendix II

We shall establish necessary and sufficient conditions for the coefficients λ^{lk}, η_1^{lk} and η_2^{lk} in order that the dissipation function (3.26), namely

$$\mathscr{D}_{\mathrm{v}} = \tfrac{1}{2}\sum_{lk} \lambda^{lk} r^l r^k + \sum_{lk} \eta_1^{lk} r_{ij}^l r_{ij}^k + \sum_{lk} \eta_2^{lk} \omega_{ij}^l \omega_{ij}^k, \quad \text{(II 1)}$$

be non-negative. The indices i, j are summation indices. We shall express these summations explicitly by writing

$$r^k = r_{11}^k + r_{22}^k + r_{33}^k, \quad \text{(II 2)}$$

and putting
$$\mathscr{D}_{\mathrm{V}} = \mathscr{F}_1 + \mathscr{F}_2 + \mathscr{F}_3, \tag{II 3}$$

where
$$\left.\begin{aligned} \mathscr{F}_1 &= \tfrac{1}{2}\sum_{lk} \lambda^{lk} r^l r^k + \sum_{lk} \eta_1^{lk} (r_{11}^l r_{11}^k + r_{22}^l r_{22}^k + r_{33}^l r_{33}^k), \\ \mathscr{F}_2 &= 2\sum_{lk} \eta_1^{lk} (r_{12}^l r_{12}^k + r_{23}^l r_{23}^k + r_{31}^l r_{31}^k), \\ \mathscr{F}_3 &= 2\sum_{lk} \eta_2^{lk} (\omega_{12}^l \omega_{12}^k + \omega_{23}^l \omega_{23}^k + \omega_{31}^l \omega_{31}^k). \end{aligned}\right\} \tag{II 4}$$

Consider first the case where $r_{ij} = \omega_{23} = \omega_{31} = 0$. The dissipation function becomes

$$\mathscr{D}_{\mathrm{V}} = 2\sum_{lk} \eta_2^{lk} \omega_{12}^l \omega_{12}^k. \tag{II 5}$$

Since ω_{12}^l and ω_{12}^k are arbitrary a necessary condition for $\mathscr{D}_{\mathrm{V}}$ to be non-negative is that

$$\sum_{lk} \eta_2^{lk} z_l z_k \geqslant 0 \tag{II 6}$$

for arbitrary variables $z_l z_k$.

Next consider the case $r_{11}^k = r_{22}^k = r_{33}^k = r_{23}^k = r_{31}^k = \omega_{ij}^k = 0$. The dissipation function in this case is

$$\mathscr{D}_{\mathrm{V}} = 2\sum_{lk} \eta_1^{lk} r_{12}^l r_{12}^k. \tag{II 7}$$

Again a necessary condition to be satisfied is

$$\sum_{lk} \eta_1^{lk} z_l z_k \geqslant 0. \tag{II 8}$$

Finally we consider the case $r_{12}^k = r_{23}^k = r_{31}^k = \omega_{ij}^k = 0$. The dissipation function is now

$$\mathscr{D}_{\mathrm{V}} = \mathscr{F}_1. \tag{II 9}$$

We write $\mathscr{F}_1$ in the algebraically equivalent form

$$\begin{aligned} \mathscr{F}_1 = {} & \sum_{lk} (\tfrac{1}{2}\lambda^{lk} + \tfrac{1}{3}\eta_1^{lk})\, r^l r^k \\ & + \tfrac{1}{3}\sum_{lk} \eta_1^{lk} [(r_{11}^l - r_{22}^l)(r_{11}^k - r_{22}^k) + (r_{22}^l - r_{33}^l)(r_{22}^k - r_{33}^k) + (r_{33}^l - r_{11}^l)(r_{33}^k - r_{11}^k)]. \end{aligned} \tag{II 10}$$

If $r_{11}^k = r_{22}^k = r_{33}^k$ the expression reduces to

$$\mathscr{F}_1 = \sum_{lk} (\tfrac{1}{2}\lambda^{lk} + \tfrac{1}{3}\eta_1^{lk})\, r^l r^k. \tag{II 11}$$

Hence we must satisfy the condition

$$\sum_{lk} (\lambda^{lk} + \tfrac{2}{3}\eta_1^{lk})\, z_l z_k \geqslant 0. \tag{II 12}$$

Therefore a necessary condition is that the matrices $\lambda^{lk} + \frac{2}{3}\eta_1^{lk}$, η_1^{lk} and η_2^{lk} be non-negative. It is immediately verified from the values (II 4) and (II 10) of $\mathscr{F}_1$, $\mathscr{F}_2$, $\mathscr{F}_3$, that the condition is also sufficient.

APPENDIX III

The derivation of relation (5.23) is obtained by considering a cell of variable volume v instead of a unit volume. The differential of the cell potential in this case is obtained (Biot 1976*b*, 1977*b*) by adding the term $-p\,\mathrm{d}v$ to expression (2.16) where p is the total pressure acting on the fluid mixture in the cell. Thus

$$\mathrm{d}\mathscr{V} = -p\,\mathrm{d}v + \sum_k \phi_k \mathrm{d}M^k + \theta\,\mathrm{d}\mathscr{S}. \tag{III 1}$$

The variation of the collective potential of the domain Ω is now

$$\delta V = \int_\Omega [-p\delta v + \sum_k \phi_k \delta M^k + \theta\delta\mathscr{S}]\,\mathrm{d}\Omega. \tag{III 2}$$

Variations are applied only in the domain Ω and δv is the variation of volume per unit volume. We shall consider two types of variations which are equivalent, hence yield the same value δV.

In the first type only the volume δv of the fluid cells is varied, assuming no mass flow or heat flow across the boundary of the cells. This corresponds to a displacement δu_i of the mixture with no relative flow of the constituents. Hence

$$\delta v = \frac{\partial}{\partial x_i}\delta u_i, \quad \delta M^k = \delta\mathscr{S} = 0, \tag{III 3}$$

and

$$\delta V = -\int_\Omega p\frac{\partial}{\partial x_i}\delta u_i\,\mathrm{d}\Omega = \int_\Omega \frac{\partial p}{\partial x_i}\delta u_i\,\mathrm{d}\Omega. \tag{III 4}$$

In the second equivalent type of variation the cells are assumed of constant volume ($\delta v = 0$) while masses

$$\delta M^k = -\partial(m_k\delta u_i)/\partial x_i \tag{III 5}$$

are injected adiabatically. From (3.5), for the adiabatic case ($\delta S_i^{\mathrm{t}} = 0$), we derive

$$\delta S_i = \sum_k \bar{s}_k \delta M_i^k = \sum_k \bar{s}_k m_k \delta u_i. \tag{III 6}$$

Hence

$$\delta\mathscr{S} = -\frac{\partial}{\partial x_i}\delta S_i = -\sum_k \frac{\partial}{\partial x_i}(\bar{s}_k m_k \delta u_i). \tag{III 7}$$

Substitution of (III 5) and (III 7) into (III 2) yields

$$\delta V = -\int_\Omega \sum_k \left[\phi_k\frac{\partial}{\partial x_i}(m_k\delta u_i) + \theta\frac{\partial}{\partial x_i}(\bar{s}_k m_k \delta u_i)\right]\mathrm{d}\Omega, \tag{III 8}$$

or

$$\delta V = \int_\Omega \sum_k \left(\frac{\partial\phi_k}{\partial x_i} + \bar{s}_k\frac{\partial\theta}{\partial x_i}\right) m_k\delta u_i\,\mathrm{d}\Omega. \tag{III 9}$$

From (2.18) we derive

$$\frac{\partial\phi_k}{\partial x_i} = \frac{1}{\rho_k}\frac{\partial p_k}{\partial x_i} - \bar{s}_k\frac{\partial\theta}{\partial x_i}. \tag{III 10}$$

Hence

$$\delta V = \int_\Omega \sum_k \frac{m_k}{\rho_k}\frac{\partial p_k}{\partial x_i}\delta u_i\,\mathrm{d}\Omega. \tag{III 11}$$

The two expressions (III 4) and (III 11) for δV must be equal for arbitrary variations δu_i, hence

$$\frac{\partial p}{\partial x_i} = \sum_k \frac{m_k}{\rho_k}\frac{\partial p_k}{\partial x_i}, \tag{III 12}$$

which is relation (5.23).

In this derivation we have assumed compressibility. The result obviously remains valid for incompressible fluids as a limiting case. However a particular derivation for this case is also easily obtained.

We must recall the significance of ρ_k. It is the density of the pure substance at the partial pressure p_k of the substance in the mixture. This pressure was defined as the equilibrium pressure of the pure substance with the mixture through a semi-permeable membrane at a given composition and temperature. Hence in general $\rho_k \neq m_k$. However for a perfect gas $m_k = \rho_k$ and $p = \sum_k p_k$.

APPENDIX IV

The right side of equation (8.5) is obtained as follows. Consider for example the term

$$\int_\Omega \theta \delta s \,\mathrm{d}\Omega \tag{IV 1}$$

in equation (8.3), where

$$\delta s = -\frac{\partial}{\partial x_j}\delta S_j. \tag{IV 2}$$

Equation (8.3) assumes that the normal component $n_j \delta S_j$ of δS_j vanishes at the boundary A of Ω. Therefore we write δS_j in the form

$$\delta S_j = \delta S_j^{(1)} + \delta S_j^{(2)}, \tag{IV 3}$$

where $S_j^{(1)}$ is defined in terms of the generalized coordinates by the expression (8.1), i.e.

$$S_j^{(1)} = S_j(q_i, x_l, t). \tag{IV 4}$$

We then choose $\delta S_j^{(2)}$ so that it is different from zero in a thin layer Ω' near the boundary A of Ω, and such that $n_j \delta S_j$ vanishes at the boundary. Hence at this boundary

$$n_j \delta S_j^{(2)} = -n_j \delta S_j^{(1)} = -n_j \sum_i \frac{\partial S_j^{(1)}}{\partial q_i}\delta q_i. \tag{IV5}$$

The integral (IV 1) becomes

$$\int_\Omega \theta \delta s \,\mathrm{d}\Omega = \int_\Omega \theta \delta s^{(1)} \mathrm{d}\Omega - \int_{\Omega'} \theta \frac{\partial}{\partial x_j}\delta S_j^{(2)} \mathrm{d}\Omega', \tag{IV 6}$$

where $\delta s^{(1)} = -\partial(\delta S_j^{(1)})/\partial x_j$. Since Ω' may be an infinitely thin layer, if we integrate by parts and take into account relation (IV 5) we obtain

$$\int_\Omega \theta \delta s \,\mathrm{d}\Omega = \int_\Omega \theta \delta s^{(1)} \mathrm{d}\Omega + \int_A \theta n_j \delta S^{(1)} \mathrm{d}A. \tag{IV 7}$$

The second term corresponds to the one appearing on the right side of equation (8.5).

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