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VARIATIONAL LAGRANGIAN-THERMODYNAMICS OF NONISOTHERMAL FINITE STRAIN MECHANICS OF POROUS SOLIDS AND THERMOMOLECULAR DIFFUSION

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Abstract—The nonisothermal finite strain dynamics of a porous solid containing a viscous fluid is developed on the basis of a new thermodynamics of open systems and irreversible processes. The same theory is applicable to the mechanics of a nonporous solid with thermomolecular diffusion of a substance in solution. New fundamental concepts of "thermobaric" and "convective" potentials are presented in the context of porous solids. Field equations and Lagrangian equations with generalized coordinates are derived directly from a variational principle of "virtual dissipation". Inclusion of nonlinear viscoelasticity and plastic behavior is indicated. Partial saturation of pore fluid is discussed. The theory is applicable to the mechanics of a non porous solid with thermolecular diffusion of several molecular species in solution, and under certain conditions to the analogous case of a porous solid containg a fluid mixture. It is shown how the Lagrangian equations provide the foundation of finite element methods.

1. INTRODUCTION

The isothermal and nondynamical finite strain mechanics of porous media has been developed in a recent paper[1], and applied to the particular case of semi-linearity[2]. The porous solid contains a viscous compressible fluid.

Our purpose here is to extend the finite strain theory to nonisothermal deformations and to include dynamical forces. Thermodynamic coupling is taken into account between the Darcy type flow through the pores and the heat flow through both convection and thermal conductivity. Under certain assumptions the thermodynamic theory is completely isomorphic to the case of *thermomolecular diffusion* of a non porous solid containing molecules in solution. Also the theory is readily extended to the case of a porous solid containing a mixture of fluids with filtering effects and to non porous solids with thermomolecular diffusion of a variety of molecular species in solution. The approach embodies a new thermodynamics which is a natural outgrowth of the authors earlier variational Lagrangian thermodynamics in the linear context[3, 4]. The fundamental step is provided by a generalization of d'Alembert's principle to non linear irreversible thermodynamics and referred to as the "*Principle of virtual dissipation*", which has been applied to nonlinear thermorheology[5–7]. In addition in the case of open systems two new concepts have been introduced, the *thermobaric potential*[7, 8] and another replacing the chemical potential which is referred to below as the *convective potential*. The thermobaric potential is a generalization of the pressure function used earlier in the isothermal case[1, 2]. A non-traditional collective potential[5] is also used which is essentially the same as introduced earlier in the linear theory[3] in 1955.

Following a procedure applied repeatedly by the author, Onsager's principle[9–12] is embodied in a local dissipation function whose coefficients vary from point to point and governs the coupled diffusive fluid and thermal flows including the Knudson effect. However the theory is more general and applies to properties which are not governed by Onsager's principle such as plasticity.

The finite strain is described by either Green's tensor, or other components which often are more convenient. They may be *nontensorial* and were developed in more detail in earlier work[13–15].

Nonlinear viscoelasticity and plasticity are also discussed based on the same unified thermodynamics.

Field and Lagrangian equations are derived directly from the principle of virtual dissipation. The Lagrangian equations govern a complex system described in terms of global generalized coordinates as shown in detail for the particular case of heat transfer[22]. It is indicated how these equations provide the foundation for a variety of finite element methods, using the generalized coordinates to describe the continuous system by means of discrete subelements.

Attention should be called to the fact that the virtual dissipation principle provides the field of Lagrangian equations directly from the physical model in analogy with Hamilton's or d'Alembert's principles in mechanics. This is in contrast with the current emphasis on starting from already known differential field equations in order to derive a variational procedure leading to a new treatment for each particular case.

The present theory is also fundamentally different from the nonlinear mechanics of mixed continua using Eulerian type variables which does not provide an adequate physical description and has led to much confusion and errors. The present material description has been usefully applied by many authors. More recently along these lines, physically realistic discussions and solutions have been provided by Rice and Cleary[16–18], and for the nonlinear mechanics of porous and granular solids by Barzant and Krizek[19, 20].

Note that the thermodynamic approach used here and initiated in 1954 is fundamentally different and more general than that of Coleman[21]. It constitutes a complete departure from current traditional concepts and methods.

2. THERMOBARIC POTENTIAL

A novel approach to the finite strain mechanics of porous fluid containing solids in the context of isothermal deformations, was developed by introducing the key concept of *pressure function*[1]. For nonisothermal deformations we will show that a generalization of this concept may be obtained. We shall refer to it as the *thermobaric potential.*

Let us briefly recall its isothermal definition. We consider a rigidly jacketed sample of the porous solid containing a compressible fluid. It is initially of unit volume and atmospheric pressure p_0. We call it a primary cell C_p and consider it as part of a certain thermodynamic system. The other part of this system is a large rigid reservoir of fluid also at the pressure p_0 which we shall call a supply cell C_s. The temperature T_0 of the whole system is maintained constant. We now assume the fluid in the primary cell to be at the pressure p, and evaluate the work required to transfer a unit mass of fluid reversibly and isothermally from the supply cell to the primary cell. This work is expressed by

$$\psi = \int_{p_0}^{p} \frac{dp}{\rho} \tag{2.1}$$

where ρ is the fluid density

$$\rho = \rho(p) \tag{2.2}$$

expressed as a function of the variable fluid pressure p. For simplicity we use the same notation p for the variable pressure in the integral and the upper limit p. The value (2.1) of the work is easily verified by integration by parts[1]. This yields three terms which represent respectively, the work required to extract a unit mass from the supply cell, the work required to compress the fluid isothermally to the pressure p, and the work required to inject it into the primary cell. Since there is no overall change of volume the work of the atmospheric pressure is zero. Hence ψ represents the total work performed on the system of the two cells. Actually of course instead of a unit mass we must consider the transfer of an infinitesimal mass dm of fluid and the work required in this case is $\psi\, dm$. Thermodynamically this work is equal to the increase of total free energy F_m of the two cells. Hence we may write

$$dF_m = d\mathcal{U}_m - T_0\, d\mathcal{S}_m. \tag{2.3}$$

The two cells C_s and C_p may be considered as a *collective system* where $d\mathcal{U}_m$ and $d\mathcal{S}_m$ represent the increase of collective energy and collective entropy of this system. The present definition of ψ is the same as introduced in earlier work[1, 2] for the isothermal case.

The concept has been generalized for nonisothermal thermodynamic systems[7, 8]. In the particular problem considered here it may be generalized as follows. We adjoin to the collective system of the two cells a third component constituted by a large isothermal reservoir at the temperature T_0 which we call a *thermal well.* We now assume the primary cell C_p to be at the temperature T with a fluid pressure p. In order to transfer reversibly a mass $\mathrm{d}m$ of fluid from C_s to C_p we must now heat the fluid gradually and reversibly to the temperature T, at the same time as we raise its pressure. This can be done if for every increase of pressure $\mathrm{d}p$ during the transfer we inject a certain amount of heat using a *heat pump* with the thermal well serving as a heat source. We assume that the primary cell acquires no other heat energy except that provided convectively by the foregoing transfer. Again we use the same notation T to designate the variable temperature during the transfer as well as the final temperature of the primary cell. The increase of total collective entropy of the two cells C_p and C_s due to this transfer is

$$\mathrm{d}\mathcal{S}_m = \left[\int_{p_0T_0}^{pT} \mathrm{d}\bar{s}\right] \mathrm{d}m = \bar{s}\,\mathrm{d}m \tag{2.4}$$

where $\bar{s}$ is the increase of entropy of a unit mass of fluid when its pressure and temperature increase from p_0T_0 to pT. We shall call $\bar{s}$ the *relative entropy* of the fluid. Similarly the increase of total collective energy of the two cells due to the transfer is

$$\mathrm{d}\mathcal{U}_m = \left[\int_{p_0T_0}^{pT} \left(\frac{\mathrm{d}p}{\rho} + T\,\mathrm{d}\bar{s}\right)\right] \mathrm{d}m. \tag{2.5}$$

The first term is the mechanical work and the second term is the total heat absorbed. From (2.4) and (2.5) we derive

$$\mathrm{d}\mathcal{U}_m - T_0\,\mathrm{d}\mathcal{S}_m = \psi\,\mathrm{d}m \tag{2.6}$$

where

$$\psi = \int_{p_0T_0}^{pT} \left(\frac{\mathrm{d}p}{\rho} + \theta\,\mathrm{d}\bar{s}\right) \tag{2.7}$$

and

$$\theta = T - T_0. \tag{2.8}$$

The value (2.7) of ψ generalizes expression (2.1) to the nonisothermal case. It was obtained earlier[1, 8] and called the *thermobaric potential.* Note that its value is independent of the path of integration. The foregoing transfer process of the mass $\mathrm{d}m$ from C_s to C_p has been called a *thermobaric transfer*[8]

It is also of interest to note that the second term is eqn (2.7) may be written

$$\int_{p_0T_0}^{pT} \theta\,\mathrm{d}\bar{s} = \int_{p_0T_0}^{pT} \frac{\theta}{T}\,\mathrm{d}h \tag{2.9}$$

where $\mathrm{d}h$ is the amount of heat absorbed by the unit mass of fluid at each step of the transfer. Since θ/T is the Carnot efficiency, the integral (2.9) represents the total work accomplished by the heat pumps in the thermobaric transfer of a unit mass of fluid. Hence ψ is the total work accomplished in this transfer.

We should note that the pore fluid pressure p is *defined thermodynamically* as the pressure of an outside fluid in local contact with the solid and in thermodynamic equilibrium with it.

More generally when the substance transferred is not a fluid ψ represents the energy required[8] to transfer a unit mass of substance reversibly.

3. COLLECTIVE POTENTIAL

In the preceding section the mass $\mathrm{d}m$ of fluid was injected into the primary cell, assuming the jacket to be rigid and impervious to heat. The primary cell, being at the temperature T with pore fluid pressure p, is now deformed adiabatically by certain forces acting on the jacket. The forces are those measured in the laboratory in excess of those due to atmospheric pressure, as explained in the paragraph at the end of this section. If we denote by $d\mathscr{W}$ the work of these forces, the increase of the total collective energy of the system is

$$d\mathscr{U}_w = d\mathscr{W}. \tag{3.1}$$

There is no change in entropy. Finally maintaining the jacket rigid again and using a heat pump we inject reversibly by conduction into the primary cell an amount of heat dh. Since the heat injected is at the temperature T it defines an entropy

$$ds_T = \frac{dh}{T}. \tag{3.2}$$

The collective internal energy of the system and its collective entropy increase by the amounts

$$\begin{aligned} d\mathscr{U}_T &= T\,ds_T \\ d\mathscr{S}_T &= ds_T. \end{aligned} \tag{3.3}$$

When we perform the foregoing transformations simultaneously adding the fluid mass dm, the heat $T\,ds_T$ and performing the work $d\mathscr{W}$, the collective energy and entropy of the two cells $C_p + C_s$ increase respectively by the amounts

$$\begin{aligned} d\mathscr{U} &= d\mathscr{U}_{\mathscr{W}} + d\mathscr{U}_m + d\mathscr{U}_T \\ d\mathscr{S} &= d\mathscr{S}_m + d\mathscr{S}_T. \end{aligned} \tag{3.4}$$

We write the differential expression

$$d\mathscr{U} - T_0\,d\mathscr{S} = d\mathscr{W} + \psi\,dm + \theta\,ds_T. \tag{3.5}$$

This expression is obtained by substituting the values (3.4), (2.4), (3.1) and (3.3). It is an exact differential

$$d\mathscr{V} = d\mathscr{U} - T_0\,d\mathscr{S} \tag{3.6}$$

of a function $\mathscr{V}$ of the state variables of the two cells. It contains an arbitrary constant which may be put equal to zero by choosing values for a given initial state. Hence

$$\mathscr{V} = \mathscr{U} - T\mathscr{S}. \tag{3.7}$$

We shall call $\mathscr{V}$ the potential of the primary cell, or simply the *cell potential*. The justification for this is due to the important fact that the thermodynamic state of the supply cell depends only on m the mass of fluid transferred to the primary cell. However m is also a state variable of the primary cell. Hence in spite of the fact that the collective energy $\mathscr{U}$ and collective entropy $\mathscr{S}$ as well as the cell potential $\mathscr{V}$ refer to the pair of cells $C_p + C_s$ *they are functions only of the state variables of the primary cell* C_p.

According to relations (3.5) and (3.7) we may write

$$d\mathscr{V} = d\mathscr{W} + \psi\,dm + \theta\,ds_T. \tag{3.8}$$

At this point it is important to note that s_T is not a state variable of the system. In order to introduce explicitly the state variable $\mathscr{S}$ instead of s_T we write

$$d\mathscr{S} = d\mathscr{S}_m + ds_T = \bar{s}\,dm + ds_T \tag{3.9}$$

which expresses the collective entropy as the sum of the convected entropy $\bar{s}\,\mathrm{d}m$ and the entropy $\mathrm{d}s_T$ acquired by thermal conduction. Elimination of $\mathrm{d}s_T$ between (3.8) and (3.9) yields

$$\mathrm{d}\mathcal{V} = \mathrm{d}\mathcal{W} + \phi\,\mathrm{d}m + \theta\,\mathrm{d}\mathcal{S} \tag{3.10}$$

where

$$\phi = \psi - \theta\bar{s} \tag{3.11}$$

defines a new potential which we shall call the *convective potential.* It was already introduced earlier[8] in a more general physical chemical context. It replaces the concept of chemical potential and is defined quite differently and more precisely on the basis of purely mechanical and calorimetric concepts.

Finally we must consider the deformation of the primary cell. In order to define the strain we consider the primary cell to be initially a cube of unit size which we shall call a *unit element.* An affine transformation of this unit element is represented by the homogeneous linear transformation

$$\xi_i = c_{ij}x_j \tag{3.12}$$

where x_i and ξ_i are the initial and final coordinates. This transformation contains a rotation and a deformation. The deformation is defined in various ways for example by means of Green's tensor

$$\gamma_{ij} = \frac{1}{2}(c_{ki}c_{kj} - \delta_{ij}) \tag{3.13}$$

which is invariant under a solid rotation.

For differential increments of deformation the work done by forces applied to the jacket is

$$\mathrm{d}\mathcal{W} = T_{ij}\,\mathrm{d}\gamma_{ij}. \tag{3.14}$$

As already pointed this is the work in excess of that due to atmosphere pressure. The coefficients T_{ij} define the conjugate stress components.

Alternative definitions of stresses and strains which may be more convenient in applications are discussed in the next section. The cell potential

$$\mathcal{V} = \mathcal{V}(\gamma_{ij}, m, \mathcal{S}) \tag{3.15}$$

is now a function of eight state variables. They are the six strain components $\gamma_{ij} = \gamma_{ji}$ the mass of fluid m acquired by the unit element in the pores and the collective entropy $\mathcal{S}$ of the unit element and its supply cell.

In practice it may be convenient to assume that in the initial state the forces acting on the jacket are those which are due only to the atmospheric pressure in the pores and the supply cell is also equal to p_0. In the initial state we put $\mathcal{V} = \mathcal{S} = \gamma_{ij} = m = \theta = 0$. This means that the initial temperature of the unit element is $T = T_0$. Note the m denotes the mass of pore fluid added per unit initial volume. Under these conditions the temperature T of the element may be expressed as a function

$$T = T(\gamma_{ij}, m, \mathcal{S}) \tag{3.16}$$

of the eight variables γ_{ij}, m, $\mathcal{S}$. This point is discussed in more detail in Section 5 below. Note that if the fluid goes through a change of phase from liquid to vapor, the temperature T remains constant through the phase change while $\mathcal{S}$ varies with the proportion of each phase present. Hence the use of $\mathcal{S}$ as a state variable instead of T provides a better description of the state of the system in the present case.

With the value (3.14) the differential (3.10) of the cell potential is

$$d\mathcal{V} = T_{ij}\, d\gamma_{ij} + \phi\, dm + \theta\, d\mathcal{S} \tag{3.17}$$

hence

$$\frac{\partial \mathcal{V}}{\partial \gamma_{ij}} = T_{ij}$$
$$\frac{\partial \mathcal{V}}{\partial m} = \phi$$
$$\frac{\partial \mathcal{V}}{\partial \mathcal{S}} = \theta. \tag{3.18}$$

As already pointed out for the isothermal case[1, 2], by a contact transformation, these results lead to a large number of similar expressions where any group of eight independent variables may be chosen among the sixteen quantities T_{ij} γ_{ij} ϕ m θ $\mathcal{S}$. For example using the function

$$\mathcal{F} = \mathcal{V} - m\phi - \theta\mathcal{S} \tag{3.19}$$

with γ_i, ϕ and θ as independent variables we obtain

$$\frac{\partial \mathcal{F}}{\partial \gamma_{ij}} = T_{ij} \qquad \frac{\partial \mathcal{F}}{\partial \phi} = -m \qquad \frac{\partial \mathcal{F}}{\partial \theta} = -\mathcal{S}. \tag{3.20}$$

We now consider a collection of primary cells, and denote by $\mathcal{V}_\alpha$ the potential of the cell α. The collective potential of this system is defined as

$$V = \sum^{\alpha} \mathcal{V}_\alpha. \tag{3.21}$$

According to (3.7) we may write

$$\mathcal{V}_\alpha = \mathcal{U}_\alpha - T_0\mathcal{S}_\alpha \tag{3.22}$$

where $\mathcal{U}_\alpha$ and $\mathcal{S}_\alpha$ are the collective energy and entropy of the particular primary cell α and the supply cell. Obviously

$$\sum^{\alpha} \mathcal{U}_\alpha = U$$
$$\sum^{\alpha} \mathcal{S}_\alpha = S \tag{3.23}$$

where U and S are the total energy and entropy of the collection of primary cells and the supply cell. From (3.21)–(3.23) we derive

$$V = U - T_0 S. \tag{3.24}$$

This additive property of the total collective potential (3.24) embodied in these results is a key feature of great practical importance which distinguishes it from the traditional thermodynamic potentials.

For a porous solid considered as a continuum with a microstructure the cells are infinitesimal and the summation sign in (3.21) is replaced by a volume integral over the domain Ω occupied by the material in the space of the initial coordinates x_i.

The collective potential is

$$V = \int_\Omega \mathcal{V}\, d\Omega \tag{3.25}$$

where

$$\mathscr{V} = \mathscr{V}(\gamma_{ij}, m, \mathscr{S}, x_k) \tag{3.26}$$

is the local cell potential per unit initial volume, and $d\Omega = dx_1\, dx_2\, dx_3$. If the porous continuum is not homogeneous $\mathscr{V}$ depends on the coordinates x_i.

Remark regarding the implicit inclusion of a constant atmospheric pressure or initial stresses

When the measurements are made in a laboratory where the jacket of the test cell is under constant atmospheric pressure p_0 the work of this pressure need not be formulated explicitly in the work $d\mathscr{W}$ of the external forces. Actually it may be included implicitly in the energy U which is then assumed to contain a term $p_0 v$ where v is the volume of the cell. In this case the stresses T_{ij} in the external work (3.14) on the cell represents the *excess* of the stresses above those due to atmospheric pressure. The stresses due to the atmospheric pressure are

$$T^0_{ij} = p_0 \frac{\partial \Delta}{\partial \gamma_{ij}} \tag{3.27}$$

where Δ is the volume after deformation of a unit initial volume as given by (8.6) below. The total stress is thus $T_{ij} + T^0_{ij}$. We may also consider the case where the jacket is subject to initial stresses T'_{ij} and the pore fluid is at a pressure p_0 different from atmospheric. This situation is frequent in geophysical problems. Again the stresses T_{ij} which appear in expression (3.17) are the stresses in excess over the initial stresses T'_{ij}, the total stresses being $T_{ij} + T'_{ij}$.

Solid with capillary pores. Partial saturation

The pores may be of very small size such that surface tension and adsorption play a major role. In this case the initial state may very well be one of complete dryness of the sample. Note that the fluid pressure p is defined thermodynamically as the pressure of a fluid in contact with the material and in equilibrium with it. One of the outstanding features of such material is the extreme sensitivity of the cell potential to small amounts m of the fluid in the pore. Its value may change rapidly as soon as m differs from zero. Such a behavior is related to the fact that small amounts of moisture in a material may generate enormous stresses if deformation is prevented. In this range of m we may talk of partial saturation and ψ defines a *thermo-capillary potential which generalizes the concept of capillary pressure.*

Chemical potential

The quantity ϕ defined by eqn (3.11) plays a role analogous to what is known as Gibbs' chemical potential μ. In fact in earlier work[7, 8] we have retained the traditional notation μ and the term chemical potential, considering eqn (3.11) as a new definition of this potential in the context of a collective system. However the definitions of ϕ and μ are not exactly the same and the usual evaluation of μ involves an indeterminacy as pointed out by Gibbs himself ([23] page 96) and in standard textbooks ([24] page 278). In addition the definition (3.11) does not involve any chemical property. For these reasons in order to avoid confusion it seems preferable to use the notation ϕ and call it the "convective potential."

4. OTHER TENSORIAL AND NONTENSORIAL DEFINITIONS OF STRESSES AND STRAINS

In physical applications use of Green's strain measure (3.13) and its conjugate stress T_{ij} is not generally convenient. A useful procedure is to define the strain in terms of the coefficients of a local linear transformation relative to locally rotating axes. Such a definition was introduced by the author in 1939 in the context of initially stressed media. An expression valid to the second order for the strain is[13],

$$\epsilon_{ij} = e_{ij} + \frac{1}{2}(e_{ki}\omega_{kj} + e_{kj}\omega_{ki}) + \frac{1}{2}\,\omega_{ik}\omega_{jk}$$

where

$$e_{ij} = \frac{1}{2}(a_{ij} + a_{ji}) \quad \omega_{ij} = \frac{1}{2}(a_{ij} - a_{ji}) \tag{4.1}$$

$$a_{ij} = c_{ij} - \delta_{ij}.$$

The strain in this case is referred to cartesian axes undergoing a local rotation ω_{ij}. However as pointed out before[13] the choice of the rotation is arbitrary and is a matter of convenience. This was discussed in more detail earlier[14]. For example the reference rotating axes may be a material axis plus a material plane containing this axes. In particular in two dimensions we need only a single material direction to define the rotation. The three strain components in this case are[15].

$$\begin{aligned} \epsilon_{11} &= a_{11} + \frac{1}{2} a_{21}^2 \\ \epsilon_{12} &= \frac{1}{2}(a_{12} + a_{21}) + \frac{1}{2} a_{21}(a_{22} - a_{11}). \\ \epsilon_{22} &= a_{22} - \frac{1}{2} a_{21}(2a_{12} + a_{21}) \end{aligned} \tag{4.2}$$

This strain measure is not a tensor. However it is much more convenient than the tensor concept when dealing with anisotropic media. It leads to the very useful concept of "slide modulus"[14] which is also not a tensor component. The whole theory of porous media presented here remains valid replacing γ_{ij} by ϵ_{ij}. Stresses τ_{ij} conjuguate to ϵ_{ij} may not be tensorial and are obtained by the principle of virtual work.

5. EVALUATION OF THE CELL COLLECTIVE ENTROPY AND POTENTIAL

The collective entropy of the cell is obtained by integrating eqn (3.9) along a suitable path from an initial state 1 where $\gamma_{ij} = m = \theta = \psi = \bar{s} = 0$ to a final state 2 defined by the state variable γ_{ij}, m, θ. We write

$$\mathcal{S} = \int_1^2 (\bar{s}\, \mathrm{d}m + \mathrm{d}s_T). \tag{5.1}$$

Note that $\bar{s}(\gamma_{ij}, m, T)$ is the relative entropy of the fluid in contact and thermodynamic equilibrium with the solid in the state defined by γ_{ij}, m and T. We may first deform the material up to a strain γ_{ij} along a path $m = \theta = 0$. The heat absorbed along this path $h_1(\gamma_{ij})$ is a function of γ_{ij}. Then we integrate along the path $\theta = \mathrm{d}\gamma_{ij} = 0$ varying m. The heat absorbed along this path $h_2(\gamma_{ij}, m)$ is a function of γ_{ij} and m. Finally we integrate along the path $\mathrm{d}\gamma_{ij} = \mathrm{d}m = 0$ varying the temperature T. The value of the integral (5.2) thus obtained is

$$\mathcal{S} = \frac{1}{T_0} h_1(\gamma_{ij}) + \frac{1}{T_0} h_2(\gamma_{ij}, m) + \int_0^m \bar{s}(\gamma_{ij}, m)\, \mathrm{d}m + \int_{T_0}^T \frac{1}{T} c(\gamma_{ij}, m, T)\, \mathrm{d}T \tag{5.2}$$

where c is the specific heat of the material per unit initial volume in the state γ_{ij}, m and T for $\mathrm{d}\gamma_{ij} = \mathrm{d}m = 0$. We may solve eqn (5.2) with respect to T and obtain

$$T - T_0 = \theta(\gamma_{ij}, m, \mathcal{S}). \tag{5.3}$$

The value of the cell potential is obtained by integrating (3.17) also along a suitable path. Hence

$$\mathcal{V} = \int_1^2 (T_{ij}\, \mathrm{d}\gamma_{ij} + \phi\, \mathrm{d}m + \theta\, \mathrm{d}\mathcal{S}). \tag{5.4}$$

We may choose the path $\theta = m = 0$ up to a value γ_{ij} of the strain, then $\mathrm{d}\gamma_{ij} = \theta = 0$ up to a value

m, and finally $\mathrm{d}\gamma_{ij} = \mathrm{d}m = 0$ up to a value $\mathcal{S}$. Note that for $\theta = 0$ we may put $\phi = \psi$. We obtain

$$\mathcal{V} = \bar{\mathcal{V}}(\gamma_{ij}) + \int_0^m \psi(\gamma_{ij}, m)\,\mathrm{d}m + \int_0^{\mathcal{S}} \theta(\gamma_{ij}, m, \mathcal{S})\,\mathrm{d}\mathcal{S} \tag{5.5}$$

where $\bar{\mathcal{V}}$ is the elastic strain energy at $\theta = 0$ and $m = 0$.

6. PRINCIPLE OF VIRTUAL DISSIPATION

A variational principle in irreversible thermodynamics developed earlier[3] in a more restricted context has been extended to completely general systems and given the name of "Principle of virtual dissipation"[5]. It constitutes an extension of d'Alembert's principle to irreversible thermodynamics and has been applied to a unified formulation of nonlinear thermorheology[6, 7]. Its derivation for the present case is briefly outlined below.

Consider the porous medium occupying an initial domain Ω, undergoing deformations with internal heat and fluid mass transfer defined by certain field variables. We consider variations of the system such that mass and heat flow variations vanish at the boundary. Conservation constraints are obeyed for internal mass and heat flow. We may write

$$\delta U = \delta W \tag{6.1}$$

where δW is the virtual work of the external forces acting on the system. According to d'Alembert's principle it includes the work of the reversed inertia forces. Also

$$\delta S = \int_\Omega (\delta s + \delta s^*)\,\mathrm{d}\Omega \tag{6.2}$$

where s^* is the entropy produced per unit initial volume and s the entropy supplied by conduction and convection. Since there is no heat or mass flow at the boundary we may write

$$\int_\Omega \mathrm{d}s\,\mathrm{d}\Omega = 0. \tag{6.3}$$

Hence

$$\delta V = \delta U - T_0\delta S = \delta W - T_0 \int_\Omega \delta s^*\,\mathrm{d}\Omega \tag{6.4}$$

or from (3.25)

$$\int_\Omega (\delta\mathcal{V} + T_0\delta s^*)\,\mathrm{d}\Omega - \delta W = 0. \tag{6.5}$$

Using eqns (3.18) we may write

$$\delta\mathcal{V} = \delta_R\mathcal{V} + \frac{\partial\mathcal{V}}{\partial\mathcal{S}}\delta s^* = \delta_R\mathcal{V} + \theta\delta s^* \tag{6.6}$$

where δ_R is a restricted variation obtained by putting $\delta s^* = 0$. Substitution of the value (6.6) of $\delta\mathcal{V}$ into (6.5) and using (3.25) yields

$$\delta_R V - \delta W + \int_\Omega T\delta s^*\,\mathrm{d}\Omega = 0. \tag{6.7}$$

The virtual work δW may be written

$$\delta W = -\sum^{i} I_i\delta q_i + \sum^{i} Q\delta q_i - \delta G \tag{6.8}$$

where δq_i represent any form of coordinates describing material displacements, I_i are inertia forces, Q_i are the applied boundary forces in excess of atmospheric pressure and G is the potential due to gravity or any other similar field.

We derive

$$\delta_R \mathscr{P} + \sum^{i} I_i \delta q_i - \sum^{i} Q_i \delta q_i + \int_\Omega T\delta s^* \, \mathrm{d}\Omega = 0 \tag{6.9}$$

where

$$\mathscr{P} = V + G \tag{6.10}$$

is a "*mixed collective potential*". Equation (6.9) expresses the principle of virtual dissipation obtained earlier[5, 6] in a more general context. The virtual dissipation is $T\delta s^*$ and $T\dot{s}^*$ is the local rate of intrinsic dissipation. It was called intrinsic because the local heat produced is at the temperature T and part of it may still produce useful work in the presence of a thermal well at a lower temperature T_0[5, 6]. (The dot denotes a time derivative.) The virtual dissipation defines dissipative forces X_k by the relation

$$T\delta s^* = \sum^{k} X_k \delta r_k \tag{6.11}$$

where r_k are arbitrary local coordinates. It was shown[3, 5, 6] that Onsager's principle leads to the relation

$$X_k = \frac{\partial \mathscr{D}}{\partial \dot{r}_k} \tag{6.12}$$

where $\mathscr{D}$ is a local dissipation function

$$\mathscr{D} = \frac{1}{2} \sum^{kl} b_{kl} \dot{r}_k \dot{r}_l \tag{6.13}$$

while

$$b_{kl} = b_{lk} = b_{kl}(\gamma_{ij}, m, \mathscr{S}) \tag{6.14}$$

are functions of the local state variables γ_{ij}, m and $\mathscr{S}$. We may also write

$$T\dot{s}^* = \sum^{k} \frac{\partial \mathscr{D}}{\partial \dot{r}_k} \dot{r}_k = 2\mathscr{D} \tag{6.15}$$

where $\dot{s}^*$ is the rate of entropy production per unit initial volume.

Introducing the dissipation function the variational principle (6.9) is written

$$\delta_R \mathscr{P} + \sum^{i} I_i \delta q_i - \sum^{i} Q_i \delta q_i + \int_\Omega \sum^{k} \frac{\partial \mathscr{D}}{\partial \dot{r}_k} \delta r_k \, \mathrm{d}\Omega = 0. \tag{6.16}$$

7. DISSIPATION FUNCTION AND ENTROPY PRODUCTION

The deformation of the porous solid is defined by the vector field

$$\xi_i = \xi_i(x_j, t) \tag{7.1}$$

where ξ_i are the coordinates of a material point at time t and x_i are the initial coordinates at $t = 0$. The differential relation

$$\mathrm{d}\xi_i = \frac{\partial \xi_i}{\partial x_j} \mathrm{d}x_j \tag{7.2}$$

defines a local affine transformation analogous to (3.12) where

$$c_{ij} = \frac{\partial \xi_i}{\partial x_j}. \tag{7.3}$$

With this value of c_{ij} the local deformation is defined by Green's tensor (3.13) or the strains defined in Section 4.

The fluid flow and the heat flow are defined by two fields already introduced previously[1, 7, 14, 22]. Consider a unit material area initially perpendicular to the x_i axis. We denote by M_i the total mass of pore fluid which has flowed through this area during its deformation. It satisfies the following *holonomic* mass conservation constraint

$$m = -\frac{\partial M_i}{\partial x_i}. \tag{7.4}$$

Similarly we denote by $\dot{H}_i$ the rate of conduction heat flow through the same area and define a local rate of entropy flow through conduction

$$\dot{S}_i^T = \frac{\dot{H}_i}{T}. \tag{7.5}$$

Again through the same area the local rate of entropy flow through convection is

$$\dot{S}_i^c = \bar{s}\dot{M}_i. \tag{7.6}$$

Integration with respect to time defines a total *entropy displacement* vector

$$S_i = S_i^T + S_i^c. \tag{7.7}$$

The total entropy per unit initial volume is

$$\mathscr{S} = s + s^* \tag{7.8}$$

where s^* is the entropy produced and

$$s = -\frac{\partial S_i}{\partial x_i} \tag{7.9}$$

is the entropy supplied by convection and conduction.

The deformation and thermodynamic state are completely defined by the ten variables ξ_i, M_i, S_i and s^*.

We shall consider the case where the rate of entropy produced per unit initial volume depends only on the rate variables $\dot{M}_i$ and $\dot{S}_i^T$, i.e. on the thermal diffusion, and the fluid flow relative to the solid. The dissipation function is a quadratic form in $\dot{M}_i$ and $\dot{S}_i^T$

$$\mathscr{D}^T = \frac{1}{2} C_{ij}^T \dot{M}_i \dot{M}_j + C_{ij}^{TM} \dot{M}_i \dot{S}_j^T + \frac{T}{2} \lambda_{ij} \dot{S}_i^T \dot{S}_j^T. \tag{7.10}$$

The coefficients C_{ij}^M, C_{ij}^{TM} and λ_{ij} are functions of the local state variables γ_{ij}, m and $\mathscr{S}$. From (7.6) and (7.7) we write

$$\dot{S}^T = \dot{S}_i - \bar{s}\dot{M}_i. \tag{7.11}$$

Substitution of this value into expression (7.10) yields

$$\mathscr{D} = \frac{1}{2} C_{ij} \dot{M}_i \dot{M}_j + C_{ij}^M \dot{M}_i \dot{S}_j + \frac{T}{2} \lambda_{ij} \dot{S}_i \dot{S}_j. \tag{7.12}$$

The coefficients are also function of the local state variables. The last term represents the dissipation when $\dot{M}_i = 0$ hence for pure heat conduction. The thermal resistivity tensor λ_{ij} is the inverse of the thermal conductivity of the deformed mixture of fluid and solid. Its nature has been extensively discussed in[14] for the nonporous thermoelastic solid.

The coefficient C_{ij}^{TM} represents the coupling between mass flow and thermal flow exemplified by the *Knudsen effect* for a rarefied gas in capillary-size pores.

The foregoing results may be further verified as follows. Conservation of entropy is expressed by

$$\int_\Omega \dot{\mathcal{S}}\,\mathrm{d}\Omega = \int_\Omega \dot{s}^*\,\mathrm{d}\Omega - \int_A \left(\bar{s}\dot{M}_i + \frac{\dot{H}_i}{T}\right) n_i\,\mathrm{d}A \tag{7.13}$$

where Ω is the initial domain occupied by the porous solid and A is its boundary. The rate of entropy produced per unit initial volume is $\dot{s}^*$. The rate of entropy flow by convection across a unit initial boundary area is $\bar{s}\dot{M}_i n_i$ and $(\dot{H}_i n_i/T)$ is the rate of entropy flow by conduction across the same unit initial area. The significance of the convective term is obvious if we note that $-\bar{s}\,\mathrm{d}M_i n_i\,\mathrm{d}A$ represents the entropy acquired by the domain Ω when a mass $-\mathrm{d}M_i n_i\,\mathrm{d}A$ is injected reversibly and adiabatically through the surface element $\mathrm{d}A$. Equation (7.13) may be written

$$\int_\Omega \dot{\mathcal{S}}\,\mathrm{d}\Omega = \int_\Omega \left[\dot{s}^* - \frac{\partial}{\partial x_i}\left(\bar{s}\dot{M}_i + \frac{\dot{H}_i}{T}\right)\right] \mathrm{d}\Omega. \tag{7.14}$$

Since Ω is arbitrary we derive

$$\dot{\mathcal{S}} = \dot{s}^* - \frac{\partial}{\partial x_i}\left(\bar{s}\dot{M}_i + \frac{\dot{H}_i}{T}\right) \tag{7.15}$$

which leads to eqn (7.8).

8. VARIATIONAL DERIVATION OF THE FIELD EQUATIONS

The unknown deformation and thermodynamic state is described by the ten field variables ξ_i, M_i, S_i and s^*. We apply the principle of virtual dissipation (6.16) by varying ξ_i, M_i and S_i inside the domain Ω. Since there are no variations $\delta\xi_i$ at the boundary we put $Q_i = 0$. The potential G is

$$G = \int_\Omega (m_0 + m)\mathcal{G}\,\mathrm{d}\Omega \tag{8.1}$$

where $\mathcal{G}$ is the potential of the body force per unit mass and m_0 the initial total mass per unit volume. $\mathcal{G}$ is a function of ξ_i. Hence

$$\delta G = \int_\Omega \mathcal{G}\delta m\,\mathrm{d}\Omega + \int_\Omega (m_0 + m)\frac{\partial \mathcal{G}}{\partial \xi_i}\delta\xi_i\,\mathrm{d}\Omega. \tag{8.2}$$

Also

$$\delta_R\mathcal{P} = \delta_R\mathcal{V} + \delta G = \int_\Omega \delta_R \mathcal{V}\,\mathrm{d}\Omega + \delta G \tag{8.3}$$

where

$$\delta_R\mathcal{V} = \frac{\partial \mathcal{V}}{\partial c_{ij}}\delta c_{ij} + \frac{\partial \mathcal{V}}{\partial m}\delta m + \frac{\partial \mathcal{V}}{\partial \mathcal{S}}\delta s. \tag{8.4}$$

We remember that δ_R implies a variation excluding δs^*.

Also, with the value (7.12) for the dissipation function $\mathscr{D}$ we write

$$\sum^{k} \frac{\partial \mathscr{D}}{\partial \dot{r}_k} = \frac{\partial \mathscr{D}}{\partial \dot{M}_i} \delta M_i + \frac{\partial \mathscr{D}}{\partial \dot{S}_i} \tag{8.5}$$

In order to evaluate the virtual work of the inertia forces we consider an element of unit initial volume. After deformation this volume becomes

$$\Delta = \det \left| \frac{\partial \xi_i}{\partial x_j} \right| \tag{8.6}$$

where Δ is the Jacobian of the transformation. The momentum of this element in the x_i direction is

$$\mathscr{M}_i = (m_0 + m)\dot{\xi}_i + M'_i\Delta. \tag{8.7}$$

The second term is due to the pore fluid motion relative to the solid and M'_i is the rate of mass flow in the relative motion per unit area of the space ξ_i after deformation. This quantity may be expressed in terms of $\dot{M}_i$ defined above by expressing the rate of mass flow F through an arbitrary material surface in two different ways. We write

$$F = \int_A \dot{M}_i n_i \, \mathrm{d}A = \int_{A'} R'_{ji} \dot{M}_j n'_i \, \mathrm{d}A'. \tag{8.8}$$

The first integral is through a surface A of normal n_i in the space x_i and the second through the *same material surface* A' of normal n'_i in the space ξ_i. The quantity R'_{ij} is the cofactor of $\partial x_i/\partial \xi_i$ in the Jacobian

$$\Delta' = \frac{1}{\Delta} = \det \left| \frac{\partial x_i}{\partial \xi_j} \right| . \tag{8.9}$$

Relation (8.8) shows that

$$\dot{M}'_i = R'_{ji} \dot{M}_j. \tag{8.10}$$

The cofactor R'_{ji} may be expressed in simpler form by considering the linear transformation of $\mathrm{d}\xi_i$ indo $\mathrm{d}x_i$ and solving for $\mathrm{d}\xi_i$. This yields

$$\frac{\partial \xi_i}{\partial x_i} = \frac{R'_{ji}}{\Delta'} = \Delta R'_{ji}. \tag{8.11}$$

With the values (8.10) and (8.11) the momentum (8.7) becomes

$$\mathscr{M}_i = (m_0 + m)\dot{\xi}_i + \dot{M}_j \frac{\partial \xi_i}{\partial x_j}. \tag{8.12}$$

It is a well known theorem of mechanics that the resultant inertia force of a system of variable mass is composed of two terms.

In the present case it is composed of $\partial \mathscr{M}_i/\partial t$ and an additional term due to the rate of flow of momentum of the pore fluid out of the volume Δ. If we neglect the square of the fluid velocity relative to the solid this additional term becomes very simple and the total inertia force per unit initial volume is

$$\frac{\partial \mathscr{M}_i}{\partial t} + \frac{\partial}{\partial x_j}(\dot{\xi}_i \dot{M}_j). \tag{8.13}$$

The virtual work of the inertia forces depends on the virtual displacement $\delta\xi_i$ and a virtual displacement δu_i of the fluid due to δM_i. Per unit initial volume this virtual work is

$$\left[\frac{\partial \mathcal{M}_i}{\partial t}+\frac{\partial}{\partial x_j}(\dot{\xi}_i\dot{M}_j)\right]\delta\xi_i+\int_\Delta \rho(\ddot{\xi}+a_i)\delta u_i \,\mathrm{d}\xi_1\,\mathrm{d}\xi_2\,\mathrm{d}\xi_3. \tag{8.14}$$

The second integral is over the volume Δ of the unit element after deformation, a_i is the acceleration of a fluid particle relative to the solid and ρ is the fluid density. We shall neglect the term $a_i\delta u_i$. This amounts to neglecting the effect of the relative inertia force on the relative fluid motion and is consistent with the assumption that the relative microvelocity field distribution is dominated by viscosity forces and determined entirely by $\dot{M}_i$.

We may write

$$\int_\Delta \rho\delta u_i \,\mathrm{d}\xi_1\,\mathrm{d}\xi_2\,\mathrm{d}\xi_3=\Delta\delta M'_i. \tag{8.15}$$

On the other hand according to (8.10)

$$\delta M'_i=R'_{ji}\delta M_j. \tag{8.16}$$

Hence

$$\Delta\delta M'_i=\frac{\partial\xi_i}{\partial x_j}\delta M_j. \tag{8.17}$$

With these values the virtual work of the inertia forces (8.14) integrated over the volume Ω is written

$$I_i\delta q_i=\int_\Omega\left\{\left[\frac{\partial \mathcal{M}_i}{\partial t}+\frac{\partial}{\partial x_j}(\dot{\xi}_i\dot{M}_j)\right]\delta\xi_i+\ddot{\xi}_i\frac{\partial\xi_i}{\partial x_j}\delta M_j\right\}\mathrm{d}\Omega. \tag{8.18}$$

By introducing the values (8.2), (8.3), (8.5) and (8.18) in the variational eqn (6.16) we derive

$$\begin{aligned}\int_\Omega\Bigg[&\frac{\partial\mathcal{V}}{\partial c_{ij}}\delta c_{ij}+\frac{\partial\mathcal{V}}{\partial m}\delta m+\frac{\partial\mathcal{V}}{\partial\mathcal{S}}\delta s+\mathcal{G}\delta m+(m_0+m)\frac{\partial\mathcal{G}}{\partial\xi_i}\delta\xi_i\\&+\frac{\partial\mathcal{M}_i}{\partial t}\delta\xi_i+\frac{\partial}{\partial x_j}(\dot{\xi}_i\dot{M}_j)\delta\xi_i+\ddot{\xi}_j\frac{\partial\xi_j}{\partial x_i}\delta M_i+\frac{\partial\mathcal{D}}{\partial\dot{M}_i}\delta M_i+\frac{\partial\mathcal{D}}{\partial\dot{S}_i}\delta S_i\Bigg]\mathrm{d}\Omega=0.\end{aligned} \tag{8.19}$$

Using the values (7.3), (7.4) and (7.9) for c_{ij}, m and s, we integrate by parts and cancel the coefficients of $\delta\xi_i$, δM_i and δS_i in the integral. This yields the differential equations

$$\frac{\partial}{\partial x_j}\left(\frac{\partial\mathcal{V}}{\partial c_{ij}}\right)-(m_0+m)\frac{\partial\mathcal{G}}{\partial\xi_i}=\frac{\partial\mathcal{M}_i}{\partial t}+\frac{\partial}{\partial x_j}(\dot{\xi}_i\dot{M}_j) \tag{8.20}$$

$$\frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{V}}{\partial m}+\mathcal{G}\right)+\frac{\partial\mathcal{D}}{\partial\dot{M}}=-\ddot{\xi}_j\frac{\partial\xi_j}{\partial x_i} \tag{8.21}$$

$$\frac{\partial}{\partial x_i}\left(\frac{\partial\mathcal{V}}{\partial\mathcal{S}}\right)+\frac{\partial\mathcal{D}}{\partial\dot{S}_i}=0. \tag{8.22}$$

These nine field equations along with eqn (6.15) for $\dot{s}^*$ namely

$$Ts^*=2\mathcal{D} \tag{8.23}$$

determine the ten unknown field variables.

We note that due to the relation $\dot{m} = -\partial \dot{M}_i / \partial x_i$ the inertia term may be written

$$\frac{\partial \mathcal{M}_i}{\partial t} + \frac{\partial}{\partial x_j}(\dot{\xi}_i \dot{M}_j) = (m_0 + m)\ddot{\xi} + \ddot{M}_j \frac{\partial \xi_i}{\partial x_j} + 2\dot{M}_j \frac{\partial \dot{\xi}_i}{\partial x_j}. \tag{8.24}$$

Since

$$\frac{\partial \dot{\xi}_i}{\partial x_j} = \frac{1}{2}\left(\frac{\partial \dot{\xi}_i}{\partial x_j} + \frac{\partial \dot{\xi}_j}{\partial x_i}\right) + \frac{1}{2}\left(\frac{\partial \dot{\xi}_i}{\partial x_j} - \frac{\partial \dot{\xi}_j}{\partial x_i}\right) \tag{8.25}$$

substitution in (8.24) yields a last term analogous to a Coriolis force.

9. COUPLED THERMAL-DARCY FLOW AND THERMOMOLECULAR DIFFUSION

According to eqns (3.18) we may write

$$\frac{\partial \mathcal{V}}{\partial m} + \mathcal{G} = \phi + \mathcal{G} = \varphi$$

$$\frac{\partial \mathcal{V}}{\partial \mathcal{S}} = \theta. \tag{9.1}$$

Hence eqns (8.21) and (8.22) omitting the inertia terms for simplicity, may be written

$$\frac{\partial \varphi}{\partial x_i} + \frac{\partial \mathcal{D}}{\partial \dot{M}_i} = 0$$

$$\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathcal{D}}{\partial \dot{S}_i} = 0. \tag{9.2}$$

They consitiute a thermodynamic generalization for coupled thermal-Darcy flow in a deformed medium. We may refer to φ as a "*mixed convective potential*" since it includes the work against the potential $\mathcal{G}$ required to transfer a unit mass into the primary cell. We assume that the supply cell is located at a point where $\mathcal{G} = 0$. It is of interest to put eqns (9.2) in another form which brings out more explicitly its physical meaning. From (9.1), (2.7) and (3.11) we derive

$$\frac{\partial \varphi}{\partial x_i} = \frac{\partial \phi}{\partial x_i} + \frac{\partial \mathcal{G}}{\partial x_i} = \frac{1}{\rho}\frac{\partial p}{\partial x_i} - \bar{s}\frac{\partial \theta}{\partial x_i} + \frac{\partial \mathcal{G}}{\partial x_i}. \tag{9.3}$$

On the other hand we have

$$\frac{\partial \mathcal{D}}{\partial \dot{S}_i} = \frac{\partial \mathcal{D}^T}{\partial \dot{S}_i^T} \tag{9.4}$$

and from (7.10), (7.11) and (9.4) we derive

$$\frac{\partial \mathcal{D}}{\partial \dot{M}_i} = \frac{\partial \mathcal{D}^T}{\partial \dot{M}_i} + \frac{\partial \mathcal{D}^T}{\partial \dot{S}_i^T}\frac{\partial \dot{S}_i^T}{\partial \dot{M}_i} = \frac{\partial \mathcal{D}^T}{\partial \dot{M}_i} - \bar{s}\frac{\partial \mathcal{D}}{\partial \dot{S}_i}. \tag{9.5}$$

Using the second set of eqns (9.2) this becomes

$$\frac{\partial \mathcal{D}}{\partial \dot{M}_i} = \frac{\partial \mathcal{D}^T}{\partial \dot{M}_i} + \bar{s}\frac{\partial \theta}{\partial x_i}. \tag{9.6}$$

Substitution of the values (9.3), (9.4) and (9.6) in eqns (9.2) yields

$$
\begin{gathered}
\frac{1}{\rho}\frac{\partial p}{\partial x_i}+\frac{\partial \mathcal{G}}{\partial x_i}+\frac{\partial \mathcal{D}^T}{\partial \dot{M}_i}=0 \\
\frac{\partial \theta}{\partial x_i}+\frac{\partial \mathcal{D}^T}{\partial \dot{S}^T}=0.
\end{gathered}
\tag{9.7}
$$

Note that the pore fluid pressure p in those equations is the pressure defined *thermodynamically*. In other words it is the pressure of the fluid in contact with an element of the porous medium and in thermodynamic equilibrium with it.

Equations (9.7) are linear in $\dot{M}_i$ and $\dot{S}_i^T$ with a symmetric coefficient matrix. These properties embody the Onsager relations.

10. NONPOROUS SOLID WITH THERMOMOLECULAR DIFFUSION OF A SUBSTANCE IN SOLUTION

This refers to finite nonisothermal dynamics of a solid which contains a certain molecular species in solution. Under the action of deformations, changes in the temperature and conecntrations generate coupled thermal and molecular diffusion. This introduces a general irreversibility in the systems.

It is quite obvious that this case is completely isomorphic to the foregoing problem of the porous solid. No new theory is required, and the field eqns (8.20)–(8.23) are completely applicable. We exclude of course the additional dissipative term due to solid strain rate which is discussed in Section 11. We have assumed local thermodynamic equilibrium in both cases, and as a result they are governed by the same unifying thermodynamic theory. If the substance in solution is a fluid we consider a state of thermodynamic equilibrium when it is in contact with an element of the solid. Under these conditions the pressure p of the fluid defines the partial pressure of the material in solution and the corresponding thermobaric potential. If the substance cannot be identified with a fluid under conditions of equilibrium with the solid, the general thermodynamic theory remains valid.

11. POROUS SOLID WITH A FLUID MIXTURE, FILTERING PROCESSES, AND NON POROUS SOLID WITH MULTIPLE THERMOMOLECULAR DIFFUSION

The foregoing results may be immediately generalized to porous solids with a mixture of fluids provided molecular diffusion within the pores occurs at a faster rate than convective diffusion so that local equilibrium is assumed. This covers certain *filtering processes* and differential diffusion of adsorbed layers of the various molecular species. Also the theory is the same for a non porous solid with multiple thermomolecular diffusion of several substances in solution.

Each molecular species is denoted by the index k. For each species we write equations similar to (7.4) and (7.11)

$$
m_k=-\frac{\partial M_i^k}{\partial x_i} \qquad \dot{S}_i^T=\dot{S}_i-\sum^k \bar{s}_k \dot{M}_i^k. \tag{11.1}
$$

The cell potential and the dissipation function are

$$
\begin{gathered}
\mathcal{V}=\mathcal{V}(\gamma_{ij}, m_k, \mathcal{S}, x_l) \\
\mathcal{D}=\mathcal{D}(\gamma_{ij}, m_k, \mathcal{S}, x_l, \dot{M}_i^k, \dot{S}_i^T).
\end{gathered}
\tag{11.2}
$$

The latter is a quadratic function of $\dot{M}_i^k$ and $\dot{S}_i^T$. The field equations of Section 8 become

$$
\begin{gathered}
\frac{\partial}{\partial x_j}\left(\frac{\partial \mathcal{V}}{\partial c_{ij}}\right)-(m_0+m)\frac{\partial \mathcal{G}}{\partial t}=\frac{\partial \mathcal{M}_i}{\partial t}+\frac{\partial}{\partial x_j}\left(\sum^k \dot{\xi}_i \dot{M}_j^k\right) \\
\frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{V}}{\partial m_k}+\mathcal{G}\right)+\frac{\partial \mathcal{D}}{\partial \dot{M}_i^k}=-\ddot{\xi}_j\frac{\mathrm{d}\xi_j}{\partial x_i} \\
\frac{\partial}{\partial x_i}\left(\frac{\partial \mathcal{V}}{\partial \mathcal{S}}\right)+\frac{\partial \mathcal{D}}{\partial \dot{S}_i}=0 \quad T\dot{s}^*=2\mathcal{D}.
\end{gathered}
\tag{11.3}
$$

where

$$m = \sum^{k} m_k \qquad \mathcal{M}_i = (m_0 + m)\dot{\xi}_i + \sum^{k} \dot{M}_j^k \frac{\partial \xi_i}{\partial x_j}. \tag{11.4}$$

Also the convective potential becomes

$$\frac{\partial \mathcal{V}}{\partial m_k} = \phi_k = \psi_k - \bar{s}_k \theta. \tag{11.5}$$

The relative entropy $\bar{s}_k$ of each substance in the case of fluids is defined by its state of equilibrium with the solid through a semipermeable membrane[8].

12. SOLID STRAIN RATE, INTERNAL COORDINATES, VISCOELASTICITY AND PLASTICITY

In the foregoing analysis the dissipation was assumed entirely due to thermal conduction and the relative motion of the fluid in the pores. In many cases a realistic analysis requires that much more complex physical behavior be taken into account. First the dissipation in the viscous fluid may depend on the overall strain rate of the solid matrix. In addition local internal coordinates q_k may be used to describe local fluid migration due to squeezing effects between grains and microcracks or uneven pore sizes. Other physical chemical effects may be taken into account. Plasticity may be included by introducing internal coordinates q_s which represent the motion of plastic slip centers. The potential per unit initial volume is then a function

$$\mathcal{V} = \mathcal{V}(\gamma_{iy}, m, \mathcal{S}, q_k, q_s) \tag{12.1}$$

and the total rate of dissipation is

$$\mathcal{D}_t = \mathcal{D} + \mathcal{D}_v + \sum^{s} R_s \dot{q}_s \tag{12.2}$$

where $\mathcal{D}_v$ is the function

$$\mathcal{D}_v = \mathcal{D}(c_{ij}, m, \mathcal{S}, \dot{c}_{ij}, \dot{m}, q_k, q_s, \dot{q}_k, \dot{q}_s). \tag{12.3}$$

It represents the dissipation not due to plasticity and we may assume that it obeys Onsager's principle locally. Hence $\mathcal{D}_v$ is a quadratic form in $\dot{c}_{ij}, \dot{m}, \dot{q}_k, \dot{q}_s$. The dissipation function $\mathcal{D}_v$ embodies along with $\mathcal{V}$ the *non-linear thermoviscoelastic* behavior as discussed in[6] for the non porous solid. It was also discussed in[1] for the isothermal porous solid. Developement of the present combination of both cases follows the same lines.

The last terms $\overset{s}{\Sigma} R_s \dot{q}_s$ in $\mathcal{D}_t$ represent the rate of dissipation due to *plasticity* and R_s is a function or functional of q_s and $\dot{q}_s$. As inciated in[6], the principle of virtual dissipation yields the additional field equations for q_s. *Strain hardening* is represented by freezing the values of q_s for an increasing number of slip centers. On the other hand *internal brittle failure* such as the gradual generation of microcracks is represented by having an increasing number of values of R_s drop to zero as q_s increases. The plasticity treatment may be further generalized by assuming that the relation between R_s and q_s may be temperature dependent. Note that the plastic coordinates q_s may be *coupled* through the expressions (12.1) and (12.3) of $\mathcal{V}$ and $\mathcal{D}_v$. Physically this means that they exert mutual forces on each other through the continuous medium. A viscoelastic interaction of this type is discussed in a more detailed analysis[6]. It may be due physically to elasticity of the surrounding medium and the motion of a continuous field of interacting dislocations distinct from the plastic slip centers.

13. LAGRANGIAN EQUATIONS

In order to simplify the presentation we shall restrict ourselves to the case where there is only a single molecular species in the pores or in solution and that the dissipation is only due to the thermal and material diffusion transport. However the Lagrangian procedure is completely general. We consider the fields ξ_i, M_i, S_i to be expressed in terms of n generalized coordinates q_i as

$$\begin{aligned} \xi_i &= \xi_i(q_k, x_l, t) \\ M_i &= M_i(q_k, x_l, t) \\ S_i &= S_i(q_k, x_l, t). \end{aligned} \tag{13.1}$$

In addition the field s^* of entropy produced is expressed by n' additional coordinate q'_i as

$$s^* = s^*(q'_i, x_l, t). \tag{13.2}$$

The values of q_i and q'_i are unknown functions to be determined. Lagrangian equations for the unknowns q_i are immediately obtained from the variational principle (6.16) without going through the field equations by applying variations δq_i. This implies variations of M_i and S_i at the boundary. In order to make these variations "internal" as required by the variational principle (6.16) we assume that the boundary is in contact with a continuous distribution of fluid cells each with a value θ and φ. They are considered as part of the domain Ω. Following a procedure developed repeatedly in previous work[1, 5, 6, 14] we derive the Lagrangian equations

$$I_i + \frac{\partial \mathcal{D}}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \tag{13.3}$$

where

$$Q_i = \int_A \left(f_i \frac{\partial \xi_j}{\partial q_i} - \varphi n_j \frac{\partial M_j}{\partial q_i} - \theta n_j \frac{\partial S_j}{\partial q_i} \right) \mathrm{d}A. \tag{13.4}$$

This integral over the initial boundary A is a mixed mechanical thermodynamic boundary driving force. The mechanical force per unit initial area at the boundary is f_i in excess of that due to atmospheric pressure, and the first term represents the corresponding generalized forces which are represented as Q_i in the variational principle. The additional terms in Q_i are due to the driving cells at the boundary. Note that $\mathcal{P}$ is a function of q_i, q'_i and t. As shown in[5] the dissipation function of the system is

$$D = \int_\Omega \mathcal{D}\, \mathrm{d}\Omega = D(q_i, q'_i, \dot{q}_i, t). \tag{13.5}$$

If t does not appear explicitly in eqns (12.1) D is a quadratic form in $\dot{q}_i$, with coefficients depending on q_i and q'_i. The generalized inertia force is obtained from (8.18). We write

$$I_i = \int_\Omega \left[\frac{\partial \mathcal{M}_i}{\partial t} \frac{\partial \xi_j}{\partial q_i} + \frac{\partial}{\partial x_k} (\dot{\xi}_j \dot{M}_k) \frac{\partial \xi_j}{\partial q_i} + \ddot{\xi}_k \frac{\partial \xi_k}{\partial x_j} \frac{\partial M_j}{\partial q_i} \right] \mathrm{d}\Omega. \tag{3.16}$$

In addition to the n Lagrangian eqns (13.3) we need n' additional equations for q'_i. These may be obtained by writing the relation

$$T\dot{s}^* = 2\mathcal{D} \tag{13.7}$$

at n' suitably chosen points x_i.

In many practical problems the contribution of s^* to the state variables may be neglected and we may simplify the equations by putting $q'_i = 0$.

The Lagrangian equations open the way to powerful new techniques of analysis of porous media defined as global systems by means of generalized coordinates which bypass the need of any field equations. Such techniques were developed in detail for problems of heat transfer[22] and their extension to mass diffusion problems was discussed.

14. FINITE ELEMENT METHODS

The Lagrangian formulation provides also the foundation of a large variety of finite element methods. For example we may divide the space Ω into a large number of tetrahedral cells. The field values of ξ_i, M_i and S_i at the vertices are chosen as generalized coordinates q_i, while the values of s^* at the same vertices are chosen as q'_i. Values of these fields inside the cell may be represented by linear interpolation of the values at the vertices. The unknowns q_i and q'_i are then determined by the Lagrangian eqns (13.3) and the eqn (13.7) for s^* at each vertex point. Note that the values of γ_{ij}, m and s which appear in the coefficients of eqn (12.7) at each vertex may be chosen as the average of their constant values in the tetrahedra with this common vertex.

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