

On Equilibrium and Primary Variables in Transport in Porous Media

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Abstract. Thermodynamic equilibrium, which involves mechanical, thermal, and chemical equilibria, in a multiphase porous medium, is defined and discussed, both at the microscopic level, and at the macroscopic one. Conditions are given for equilibrium in the presence of forces between the surface of the solid matrix and the fluid phases. The concept of *approximate thermodynamic equilibrium* is introduced and discussed, employing the definition of a *thermodynamic potential*. This discussion serves as the basis for the methodology of determining the number of degrees of freedom in models of phenomena of transport (of mass, energy, and momentum) in porous media. Equilibrium and nonequilibrium cases are considered. The proposed expressions for the number of degrees of freedom in macroscopic transport models, represent the equivalent of *Gibbs phase rule* in thermodynamics.

Based on balance considerations and thermodynamic relationships, it is shown that the number of degrees of freedom, NF, in a problem of transport in a deformable porous medium, involving NP fluid phases and NC components, under nonisothermal conditions, with equilibrium among all phases and components, is

$$NF = NC + NP + 4.$$

Under nonequilibrium conditions among the phases, the rule takes the form

$$NF = NC \times NP + 2NP + NC + 4.$$

In both cases, when fluid phase velocities are determined by Darcy's law, NF is reduced by NP. When the solid matrix is nondeformable, NF is reduced by 3. The number of degrees of freedom is also determined for conditions of approximate chemical and thermal equilibria, and for conditions of equilibrium that prevail only among some of the phases present in the system. Examples of particular cases are presented to illustrate the proposed methodology.

Key words: thermodynamic degrees of freedom, primary variables, porous medium thermodynamics, thermodynamic equilibrium, multiphase transport, surface forces.

List of Main Symbols

D_{α}^E Coefficient of dispersion of E in an α -phase.

D_{α}^{γ} Coefficient of molecular diffusion of a γ -component in an α -phase.

$D_{\alpha}^{*\gamma}$ Coefficient of molecular diffusion of a γ -component in an α -phase in a porous medium.

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- e Density of an extensive quantity, E .
- e_{α}^{γ} Density of E_{α}^{γ} ($= E$ per unit volume of α -phase).
- E_{α}^{γ} An extensive quantity, E , of a γ -component in an α -phase (e.g., $E = m, m^{\gamma}, H$).
- \mathcal{E} Energy.
- $f_{\alpha \rightarrow \beta}^E$ Rate of transfer of E from an α -phase to a β -one, across their common microscopic interface per unit volume of porous medium.
- f_{α}^{γ} Generalized force acting on γ -component in α -phase.
- g Gravity acceleration.
- G Gibbs free energy.
- H Enthalpy.
- j^H Microscopic conductive heat flux ($= \rho u(\mathbf{V}^H - \mathbf{V})$).
- \tilde{j}^{γ} Microscopic diffusive mass flux of a γ -component relative to the mass weighted velocity ($= \rho^{\gamma}(\mathbf{V}^{\gamma} - \mathbf{V})$).
- \tilde{j}^E Microscopic diffusive flux of E .
- \tilde{j}^{γ} Microscopic diffusive mass flux of a γ -component.
- \mathbf{J}^H Macroscopic conductive heat flux.
- \mathbf{J}^{γ} Macroscopic diffusive flux of a γ -component.
- \mathbf{J}^{*E} Dispersive flux of E .
- k_{α} Effective permeability of an α -phase.
- m Mass.
- m^{γ} Mass of a γ -component.
- m_{α}^{γ} Mass of a γ -component in an α -phase.
- n_{α}^{γ} Mole fraction of a γ -component in an α -phase.
- NC Number of components.
- NE Number of constraints.
- NF Number of degrees of freedom.
- NP Number of phases.
- NV Number of variables.
- p Pressure.
- p_{α} Pressure in an α -phase.
- $R_{\alpha\beta}$ Radius of curvature of an $\alpha - \beta$ -interface.
- S Entropy.
- S^* Entropy function of an element.
- S_{α} Saturation of an α -phase.
- $S_{\alpha\beta}$ Area of surface of contact of α -phase with all other phases (denoted by β) within \mathcal{U}_o .
- t Time.
- T Temperature.

u_α	Specific internal energy of an α -phase.
\mathbf{u}_α	Velocity of a surface (e.g., of $\mathcal{S}_{\alpha\beta}$).
U	Internal energy.
\mathcal{U}	Volume.
\mathcal{U}_o	Volume of domain of REV.
$\mathcal{U}_{o\alpha}$	Volume of α -phase in REV.
v	Specific volume of mass ($= 1/\rho$).
\mathbf{V}	Mass weighted velocity of a fluid phase.
\mathbf{w}	Displacement.
x	Horizontal coordinate.
\mathbf{x}	Position vector.
\mathbf{x}'	Position vector of point at the microscopic level.
\mathbf{x}_o	Position vector of the centroid of an REV.
z	Vertical coordinate (positive upward).

Greek Letters

α	Symbol for an α -phase.
β	Symbol for a β -phase.
ϵ_α^γ	Symbol denoting E_α^γ per unit mass of α -phase.
γ	Symbol denoting a γ -component.
$\gamma_{\alpha\beta}$	Surface tension between α - and β -phases.
$\Gamma^{E_\alpha^\gamma}$	Rate of production of E_α^γ per unit mass of an α -phase.
δ	Unit tensor.
η	Coefficient of thermoelasticity.
θ_α	Volumetric fraction of an α -phase ($\equiv \mathcal{U}_\alpha/\mathcal{U}_o$).
λ_α	Thermal conductivity of an α -phase.
λ_α^*	Coefficient of thermal conductivity of an α -phase in a porous medium.
$\Lambda_\mathcal{E}$	Lagrange multiplier for energy.
$\Lambda_{m\gamma}$	Lagrange multiplier for mass of γ -component.
$\Lambda_\mathcal{U}$	Lagrange multiplier for volume.
μ_α	Dynamic viscosity of an α -phase.
μ'_α	Bulk viscosity of an α -phase.
μ_α^γ	Chemical potential of a γ -component of an α -phase.
ρ_b	Bulk mass density of soil.
ρ_α	Mass density of an α -phase.
ρ_α^γ	Mass density of a γ -component in an α -phase.
σ	Stress tensor.

σ'_s	Effective stress ($\equiv \overline{\sigma'_s}$).
τ	Shear stress. Deviatoric stress.
ϕ	Porosity.
φ	Potential energy function.
Φ	Thermodynamic potential.
ω_α^γ	Mass fraction of a γ -component in an α -phase.

Subscripts

a	Air.
g	Gas.
f	Fluid.
ℓ	Liquid.
s	Solid.
w	Water.
α	α -phase.
β	β -phase.
λ	λ -phase.

Superscripts

H	Heat.
γ	γ -component.

Special Symbols

$(\overline{\cdot})^\alpha$	Intrinsic phase average of (\cdot) ($= \frac{1}{u_{o\alpha}} \int u_o(\cdot) dU$).
$\overset{\circ}{G}$	Deviation of G from its intrinsic phase average, \overline{G}^α , over an REV.
$\frac{D_E(\cdot)}{Dt}$	Material derivative of (\cdot) , as observed by the E -continuum.

1. Objective

A rather large number of variables is required in order to describe the complete macroscopic (= averaged) behavior of a porous medium system comprised of multiple multicomponent fluid phases under nonisothermal conditions (e.g., Bear and Bachmat, 1991; Hassanizadeh and Gray, 1979; Bear and Nitao, 1992; Coats, 1979). However, the actual number of variables for which a solution of partial differential equations is required is much smaller. The number of degrees of freedom is the *smallest* number of variables needed to fully define present and future states of a considered system. We shall refer to these variables as *primary variables*. All other state variables of the system can be obtained from the primary ones through the use of constitutive relationships and definitions. A case that requires special attention is when all phases and components within a system are at *equilibrium*, or when the rate of transformation of the system from one state to another is sufficiently

slow, so that it can be assumed to be continuously close to equilibrium. Under such conditions, the number of primary variables is further reduced.

Gibbs phase rule (see any text on thermodynamics) states that the state of a system composed of NP phases and NC components under conditions of equilibrium is fully defined (at the microscopic level) by NF state variables, with NF determined by the relationship

$$NF = NC - NP + 2. \quad (1)$$

For example, in the case of a single fluid phase composed of a single component, say H₂O, NF = 2. This means that the state of the system at equilibrium is fully defined by two independent variables, say the pressure, p , and the temperature, T . We could, however, select also p and the phase density, ρ , as primary variables, with the constitutive relation $\rho = \rho(p, T)$.

As a second example, consider two fluid phases: a liquid, consisting of a single component, water, and a gas, composed only of water vapor. This means that we have two phases and one component, and by the Gibbs phase rule, we have one degree of freedom. Suppose we select T as the independent variable. Because water and water vapor are in equilibrium, the system can exist at only one value of pressure at any given temperature (see any pressure-temperature diagram for a single substance H₂O). Once we know p and T , we can determine the densities of the two phases.

Here, we are concerned with multiple multicomponent fluid phases *in a porous medium*. Moreover, we are interested in cases in which the phases are *in motion*, the solid matrix may be deformable, and the description of transport (of mass, momentum, and energy) is *at the macroscopic level*. Our objective is to determine the number of degrees of freedom for such a system.

2. Thermodynamic Equilibrium in a Porous Medium

A system under *thermodynamic equilibrium* or *approximate thermodynamic equilibrium* has a much smaller number of degrees of freedom than otherwise. The concept of thermodynamic equilibrium is complicated by its usage at different levels: the microscopic level (which is obtained by averaging over the molecular one), and the macroscopic level (obtained by averaging over the microscopic one). Moreover, the term ‘thermodynamic equilibrium’ is often used when at least one of the phases present in the system is in motion. In the latter case, the term ‘local thermodynamic equilibrium’ is often used. It means that each representative elementary volume (REV) in the porous medium domain is sufficiently close to the state of an identical REV that it behaves as a closed system at thermodynamic equilibrium. These concepts and definition will be discussed in detail below.

Consider an REV in a porous medium domain, containing a solid matrix and a number of multicomponent fluid phases. A discussion on the size of an REV is presented by Bear and Bachmat (1991). As an upper limit to the size of an REV

in the case of heterogeneities resulting from gradients in microscopic variables, we require that the variations within the REV of these state variables be within a specified error level (Bear and Bachmat, 1991, pp. 20–21). The REV consists of a set of microscopic points, where we use the term ‘microscopic point’ to denote a point *within* a phase. A lower limit to the size of the REV arises from the assumption of local thermodynamic equilibrium at each microscopic point in the REV which is discussed below.

2.1. EQUILIBRIUM AT THE MICROSCOPIC LEVEL

The assumption of local thermodynamic equilibrium is often cited in textbooks on fluid mechanics in regards to the thermodynamic properties of every (microscopic) point in a phase (= system).

This assumption guarantees that the standard thermodynamic properties, such as temperature, pressure, component density, internal energy, and entropy, can be defined at that point in the fluid continuum. These properties are developed from the theory of statistical mechanics (e.g., Reif, 1965), using averages at the molecular level. Conditions for local thermodynamic equilibrium at the microscopic level are discussed by Kreuzer (1981). Note that in statistical mechanics, the term ‘microscopic’ is used to denote what we would call the molecular level.

The driving force for local thermodynamic equilibrium is molecular collisions. Thus, how fast equilibrium can occur depends on the time, τ_c , required for a sufficient number of molecular collisions to occur. Local equilibrium is violated only under severe nonequilibrium conditions, when changes or phenomena take place over a time span shorter than τ_c , such as in shock waves. By definition, the size of the microscopic REV of a phase is selected such that it includes a sufficiently large number of molecules. This means that this microscopic REV must be much larger than the *mean free path* of the molecules. Equivalently, this size should be such that it enables a sufficiently large number of collisions to ensure that we have meaningful thermodynamic properties at the centroid of the microscopic REV (mentioned above).

We recall that this is the lower limit of the REV size. The microscopic REV must also be much smaller than the domain occupied by the phase. Thus, if we have a sufficiently narrow passage or rarified gas, a microscopic REV may not exist, and the gas may not be treated as a continuum. We then have *Knudsen gas flow* (Bear, 1972, p. 17).

Altogether, we may say that except for extreme cases, e.g., *at the front of a shock wave*, or in a rare gas in a relatively narrow domain, a microscopic REV can always be defined. By averaging the molecular behavior over the microscopic REV, we introduce meaningful thermodynamic variables and constitutive relations.

Once we have determined that an microscopic REV for the considered fluid phase in the considered domain exists, that fluid is always at thermodynamic equilibrium at each microscopic point (= centroid of the microscopic REV), and we

always have meaningful thermodynamical variables and constitutive relations. If we consider multiple components, we have to require that a microscopic REV exists for every component, and that a common REV can be found for all components. Then (except for special cases like those mentioned above), all components *at a microscopic point* are in equilibrium. We say that we have ‘equilibrium at a (microscopic) point,’ or ‘local thermodynamic equilibrium at the point.’

Henceforth, we shall assume that local thermodynamic equilibrium always prevails at every point \mathbf{x}' within every phase present in the void space, and that at every such point, meaningful thermodynamic variables of the phase can be defined.

The temperature, $T(\mathbf{x}')$, pressure, $p(\mathbf{x}')$, and $NC-1$ mass fractions, $\omega^\gamma(\mathbf{x}')$, of the γ -component, uniquely define the thermodynamic state of a fluid at a point \mathbf{x}' within the fluid phase. For a fluid in motion, we also need the velocity, $V(\mathbf{x}')$, at the point. Thus, we have $NC+2$ degrees of freedom for every point at the microscopic level.

For a solid, we also need the displacement, $\mathbf{w}(\mathbf{x}')$, at every point, with respect to the initial position, raising the number of microscopic degrees of freedom to $NC+3$.

2.2. EQUILIBRIUM AT THE MACROSCOPIC LEVEL

We define *local thermodynamic equilibrium* at a point (= centroid of an REV) to mean that the considered point is at approximate thermodynamic equilibrium. Approximate thermodynamic equilibrium is said to prevail at a macroscopic point, if the REV is sufficiently close thermodynamically, to an identical, but sealed, system in complete thermodynamic equilibrium with closed rigid boundaries. By identical, we mean that the configurations of all phases within the two systems are the same, that they both have the same mass of every component and phase, and that both contain the same amount of internal energy. Since the sealed system is at complete equilibrium, all phase velocities in the sealed system are zero. A system in *complete thermodynamic equilibrium* means that all fluxes of mass, energy, and momentum within the system are zero. Unless we specify ‘approximate equilibrium,’ the term equilibrium refers to ‘complete thermodynamic equilibrium.’ This includes also mechanical equilibrium, which is identical to ‘no motion.’ (Note that equilibrium should not be confused with ‘steady state.’ Steady state means that the time rate of change of all thermodynamic variables and fluid velocities is zero. Fluxes may still be nonzero and, hence, large gradients in thermodynamic variables, including pressures, temperatures, and concentrations, may still exist in a system at steady state.)

To define what we mean by an ‘REV in approximate thermodynamic equilibrium’ and by ‘sufficiently close, thermodynamically,’ we need to define *thermodynamic potentials*. We also need to examine the equilibrium of the sealed system.

It is obvious that when an REV at the macroscopic level is in complete thermodynamic equilibrium, all the potentials at the microscopic level are uniform over the REV and have values equal to that of the averaged potential at the macroscopic level.

The microscopic balance equation for an extensive quantity, E , of a phase, can be written as

$$\frac{\partial e}{\partial t} = -\nabla \cdot (e\mathbf{V} - \mathbf{j}^E) + \Gamma^E, \quad (2)$$

where e , \mathbf{j}^E , and Γ^E are the density, the diffusive flux, and the source of E , respectively, and \mathbf{V} is the mass weighted velocity of the phase. For example, E can be the mass of a component.

Following the theory of irreversible thermodynamics (e.g., Groot and Mazur, 1972), we shall express the diffusive flux by a linear law of the form

$$\mathbf{j}^E = -\mathcal{D}^E \nabla \Phi^E, \quad (3)$$

where Φ^E is the *thermodynamic potential* of E . In principle, the diffusive fluxes of the various extensive quantities transported within a system, with each extensive quantity having its own potential, are coupled to each other (e.g., Bear and Bachmat, 1991). For example, in the case of mass transport, coupling occurs among diffusive mass fluxes of the various components, each having its own chemical potential. In this case, the diffusive fluxes vanish only if the gradients of all the potentials vanish. We should, therefore, consider also coupling between the diffusive fluxes of various extensive quantities. However, for the sake of clarity, these coupled fluxes will not be included in our discussion.

Thermodynamic equilibrium with respect to E is given by the requirement

$$\nabla \Phi^E = 0. \quad (4)$$

For E representing the mass of a γ -component, Φ^E is the *chemical potential* of γ , defined by

$$\mu^\gamma = \left. \frac{\partial G}{\partial m^\gamma} \right|_{m^\delta \neq \gamma, T, p}, \quad (5)$$

where m^γ denotes the mass of the γ -component, and

$$G = H - ST$$

is the *Gibbs free energy*, with H , and S denoting the *enthalpy* and the *entropy* of the considered phase, respectively.

For E representing energy, the temperature, T , is the thermodynamic potential. For E representing the momentum within a fluid phase, the thermodynamic potential is the advective velocity, \mathbf{V} .

For a porous medium system in mechanical equilibrium (i.e., equilibrium with respect to momentum), the gradients of the fluid's velocity must vanish for any

fluid phase within the system. Because of the no-slip condition at the solid–fluid boundary, assumed stationary, this implies, that the velocities of all fluids in the system must vanish everywhere. Since this is too restrictive, we define *approximate thermodynamic (mechanical) equilibrium* to mean that velocities are sufficiently small.

Returning to the definition of macroscopic equilibrium, we shall say that an REV is in approximate equilibrium relative to an extensive quantity, E , of an α -phase, if the corresponding thermodynamic potential, Φ_α^E , is sufficiently close to the average of the potential over the α -phase,

$$\frac{\|\Phi_\alpha^E - \overline{\Phi^{E^\alpha}}\|_{\mathcal{U}_{\alpha o}}}{\|\Delta\Phi_\alpha^E\|_{\mathcal{U}_{\alpha o}}} \ll 1, \tag{6}$$

where

$$\|\dots\|_{\mathcal{U}_{\alpha o}} \equiv \left(\frac{1}{\mathcal{U}_{\alpha o}} \int_{\mathcal{U}_{\alpha o}} (\dots)^2 d\mathcal{U} \right)^{1/2} \tag{7}$$

denotes the *root mean-square norm* over the domain (\equiv volume), $\mathcal{U}_{\alpha o}$, of the α -phase within the REV, of volume \mathcal{U}_o , $\overline{\Phi^{E^\alpha}}$ is the average of the potential over the α -phase, and $\Delta\Phi^E = \Phi^E - \Phi_o^E$, where Φ_o^E is some typical value over the porous medium domain, such as the average over the domain.

Nitao and Bear (1994) have presented a condition for this equilibrium condition to hold, based solely on the geometric properties of the α -phase.

Let us supplement the definition of approximate equilibrium for an REV with respect to an α -phase, by introducing a definition of approximate equilibrium between two phases, α and β . We start by requiring that each of the two phases be in equilibrium, i.e., Equation (6) is satisfied for each of them. Furthermore, we require that the values of the phase-averaged potentials be sufficiently close, that is,

$$\frac{|\overline{\Phi^{E^\alpha}} - \overline{\Phi^{E^\beta}}|}{\|\Phi^E\|_{\mathcal{U}_o}} \ll 1. \tag{8}$$

Nitao and Bear (1994) have presented necessary conditions upon the porous media for Equation (8) to hold. They also proved that if all phases in an REV are in approximate equilibrium, so that (6) holds for all phases, then they are also in equilibrium with each other, so that (8) holds.

Condition (8) indicates the important role played by the macroscopic potentials, $\overline{\Phi^{E^\alpha}}$. Consider the energy and mass potentials, $\overline{\Phi^{U^\alpha}}$ and $\overline{\Phi^{M^\alpha}}$. If the deviations in p , T , and ω^γ within an REV (from their respective averages) are sufficiently small within the α - and β -phases, the macroscopic potentials are related to the microscopic ones by

$$\overline{\Phi^{E^\delta}} \approx \Phi_\delta^E \approx \Phi_\delta^E(\overline{p}^\delta, \overline{T}^\delta, \overline{\omega^{\gamma^\delta}}), \tag{9}$$

where $\delta = \alpha, \beta$, Φ_δ^E is the value of the microscopic potential in the δ -phase, and $\Phi_\delta^E(\dots)$ denotes the functional relationship of the microscopic potential for the δ -phase as functions p , T , and ω^γ . (This expression for the energy potential is redundant because it reduces to $\bar{T}^\delta \approx \bar{T}^\delta$.)

If the equilibrium condition between the α and β phases is satisfied, we have

$$\Phi_\alpha^E(\bar{p}^\alpha, \bar{T}^\alpha, \overline{\omega^{\gamma\alpha}}) \approx \Phi_\beta^E(\bar{p}^\beta, \bar{T}^\beta, \overline{\omega^{\gamma\beta}}). \quad (10)$$

This expression constitutes a constitutive relationship. Later, we shall see how this relationship reduces the total number of degrees of freedom for an REV.

The definition of approximate equilibrium with regards to the momentum potential, which is velocity, requires that velocity be approximately uniform over the phase. For a porous medium with a fluid phase satisfying the no-slip condition at solid surfaces, this requires that the fluid velocity be sufficiently small with respect to the coordinate frame fixed to the porous medium REV. A fluid phase that is not connected to a solid phase could, theoretically have non-zero velocities and still be in approximate equilibrium. The corresponding relationship for (10) in the case of the momentum potential requires that the fluid velocities between the two phases be approximate equal. When all phases are in equilibrium with each other, the fluid velocities must be all small, since one of the fluid phases is connected to the solid phase.

A question may arise with regards to whether the fluid velocity is the appropriate potential for momentum because the momentum balance contains the gradient of pressure in addition to gradients of velocity that is part of the deviatoric stress tensor (we assume a Newtonian fluid). We shall later show (see Equation (33)) that the sum of the pressure gradient plus body forces that are present in the momentum balance equation is equal to the sum of the potentials for energy and mass and, therefore, it would be redundant to carry the pressure as part of the momentum potential.

3. Macroscopic Constitutive Relationships

Approximate local equilibrium is often assumed because it leads to constitutive relationships between macroscopic thermodynamic variables. For example, given a relationship between the microscopic variables a and b in the form

$$a = f(b),$$

valid at all points within an α -phase, the usual assumption is that by averaging over the α -phase within an REV, we obtain the corresponding relationship between the macroscopic variables \bar{a}^α and \bar{b}^α ,

$$\bar{a}^\alpha = f(\bar{b}^\alpha). \quad (11)$$

Note that this conclusion is not necessarily correct if a constitutive relationship involves derivatives.

Denoting the deviation of b from its mean by $\overset{\circ}{b} \equiv b - \bar{b}^\alpha$, we have

$$f(b) \approx f(\bar{b}^\alpha) + \overset{\circ}{b} \left. \frac{df}{db} \right|_{\bar{b}^\alpha} + (\overset{\circ}{b})^2 \left. \frac{d^2f}{db^2} \right|_{\bar{b}^\alpha}. \quad (12)$$

Since, by definition, $\overline{\overset{\circ}{b}^\alpha} = 0$, it is seen that

$$\overline{a^\alpha} = \overline{f(b)^\alpha} \approx f(\bar{b}^\alpha) + \overline{(\overset{\circ}{b})^{2\alpha}} \left. \frac{d^2f}{db^2} \right|_{\bar{b}^\alpha}. \quad (13)$$

Thus, if the mean-square deviation, $\overline{(\overset{\circ}{b})^{2\alpha}}$, is sufficiently small within the REV, then the relationship in (11) holds. This condition is satisfied when the constitutive relationship is close to being a linear function. For example, fluid density is almost a linear function of pressure over a large range of pressures. However, for highly nonlinear constitutive relationships, it is necessary to verify that the deviations of the arguments are not too large. Approximate thermodynamic equilibrium is important because thermodynamic variables tend to be distributed approximately uniformly in keeping with our definition of approximate equilibrium, and, thus, under this condition the deviation from the mean will be sufficiently small.

4. Degrees of Freedom for a Porous Medium Under Complete Equilibrium

4.1. WITHOUT SURFACE EFFECTS

We shall start by neglecting the effect of forces emanating from solid surfaces. We also assume that capillary forces are so strong that the gravitational force may also be neglected. Thus, each phase is assumed to be microscopically homogeneous in that the relationships between thermodynamic variables, such as energy as a function of pressure and temperature, do not depend on position within the phase. We shall assume that each phase occupies a *simply connected* domain within the REV.

We wish to investigate the number of degrees of freedom of a system in complete (microscopic) equilibrium, because we have defined macroscopic equilibrium by requiring that the REV be *approximately in complete thermodynamic equilibrium*.

We say that a multiphase system within an REV is in *complete microscopic equilibrium*, when there is no net flux of mass, momentum, and energy within that system. This means that at *all* points within the system (in all phases, including the solid), the velocity is zero, and the diffusive fluxes of the mass of component and of energy (heat conduction) also vanish. In the appendix, we show that such a system is constrained by the following conditions:

- The temperatures are equal at any two points (x' , x'') within the system, viz.,

$$T(\mathbf{x}') = T(\mathbf{x}''), \quad \mathbf{x}', \mathbf{x}'' \in \mathcal{U}_{\alpha o}. \quad (14)$$

This means that the temperature is uniform over the system.

- The chemical potentials of any γ -component is uniform within the system, viz.,

$$\mu^\gamma(\mathbf{x}') = \mu^\gamma(\mathbf{x}''), \quad \mathbf{x}', \mathbf{x}'' \in \mathcal{U}_{\alpha o}. \quad (15)$$

- For a homogeneous phase, the pressure must be uniform at all points within the phase. Thus, within the α -phase subdomain,

$$p(\mathbf{x}') = p(\mathbf{x}''), \quad \mathbf{x}', \mathbf{x}'' \in \mathcal{U}_{\alpha o}. \quad (16)$$

For two phase bodies, say α and β , with a common interface, neglecting the effect of gravity, we have

$$p_\alpha(\mathbf{x}') - p_\beta(\mathbf{x}'') = \frac{2\gamma_{\alpha\beta}}{R_{\alpha\beta}}, \quad \mathbf{x}' \in \mathcal{U}_{\alpha o}, \quad \mathbf{x}'' \in \mathcal{U}_{\beta o}, \quad (17)$$

where $\gamma_{\alpha\beta}$ is the surface tension between the α and β phases, and $R_{\alpha\beta}$ is the (constant) radius of curvature of the interface between them. We recall that actually, $1/R_{\alpha\beta} = 1/R_1 + 1/R_2$, where R_1, R_2 are the principal radii of curvature. Because the pressure is uniform over each phase, $R_{\alpha\beta}$ must be a constant over the interface. A deviation from the constant curvature can come only from the effects of surface forces at the solid surface in contact with the $\alpha\beta$ -interface.

Note that by averaging over the the REV, we obtain

$$p_\alpha - p_\beta \equiv \bar{p}^\alpha - \bar{p}^\beta = \frac{2\gamma_{\alpha\beta}}{R_{\alpha\beta}}, \quad (18)$$

where $R_{\alpha\beta}$ is a function of the volumetric phase fractions θ_α , or, equivalently, of the saturations S_α .

Cases exist in which each phase may occupy a number of disjoint subdomains within the REV. The pressure, p'_α , may then be different in the various α' -subdomains. The pressure within each such subdomain is uniform. We'll still have a pressure difference across the interfaces between adjacent phase bodies, and a radius of curvature of the common interface. It should then be possible to define the difference between the volume averaged phase pressures, and relate it to some averaged radius of curvature for the REV, which, in turn, will be a function of the phase saturations.

Our next task is to consider the number of degrees of freedom for a porous medium domain. We recall that the original form of *Gibbs phase rule* is stated for a 'nonporous medium' case. It cannot account for capillarity and surface forces since interphase boundaries are assumed to be flat.

Let us denote the uniform temperature, chemical potential, and pressure over each phase by T_α , μ_α^γ , and p_α , respectively. Since $\mu_\alpha^\gamma = \mu_\alpha^\gamma(\omega^\kappa, T_\alpha, p_\alpha)$, the mass fraction, ω_α^κ , must also be uniform over each α -phase. Since the temperature is uniform over the entire system, we have $T_\alpha = T$.

The thermodynamic state of each phase is, therefore, completely specified by T , p_α , and ω_α^γ . Together, we have $\text{NP} \times \text{NC} + \text{NP} + 1$ variables, where NP is the number of phases and NC denotes the number of components. Also, values of the $\text{NP}-1$ radii of curvature, $R_{\alpha\beta}$, are required in order to determine the equilibrium conditions for the interfaces. Together, these make up $\text{NV} = \text{NP} \times \text{NC} + 2\text{NP}$ variables.

The number of degrees of freedom is defined as a subset of the NV variables that are independent of each other.

The radii of curvature, $R_{\alpha\beta}$, can be replaced by the volumetric fractions θ_α . From the fact that $\sum_{(\alpha)} \theta_\alpha = \phi$, it follows that there are $\text{NP}-1$ of the θ_α that are independent of each other, and the number of variables remains unchanged.

Altogether, we have the $(\text{NP} - 1) \times \text{NC}$ constraints of the form

$$\mu_\alpha^\gamma(p_\alpha, T, \omega_\alpha^\kappa) = \mu_\beta^\gamma(p_\beta, T, \omega_\beta^\kappa), \quad (19)$$

NP constraints of the form

$$\sum_{(\gamma)} \omega_\alpha^\gamma = 1, \quad (20)$$

and $\text{NP}-1$ constraints of the form

$$p_\alpha - p_\beta = \frac{2\gamma_{\alpha\beta}}{R_{\alpha\beta}}. \quad (21)$$

Together, we have $\text{NE} = \text{NP} \times \text{NC} - \text{NC} + 2 \times \text{NP} - 1$ constraints.

We conclude that the number of degrees of freedom is, therefore,

$$\text{NF} = \text{NV} - \text{NE} = \text{NC} + 1. \quad (22)$$

This is the rule determining the number of degrees of freedom in a porous medium domain under thermodynamic equilibrium with no fluid motion and when the solid is nondeformable.

Note that the number of variables in the original Gibbs phase rule is $\text{NC} - \text{NP} + 2$, which is $\text{NP}-1$ less than the number of degrees of freedom we have found for a porous medium. Unlike the original Gibbs phase rule, the number of primary variables in a porous medium does not depend on the number of phases. A porous medium has NP distinct phase pressures as compared to the single pressure in a nonporous medium. This results in $\text{NP}-1$ additional variables.

The constraints in (19) and (20) constitute $\text{NP} \times \text{NC} - \text{NC} + \text{NP}$ equations that can be used to solve for some of the variables in terms of the other ones, as long as the resulting nonlinear system of equations is mathematically nonsingular. A set of $(\text{NP} - 1) \times \text{NC} + \text{NP}$ mass fractions can be solved in terms of a remaining set of $\text{NC}-\text{NP}$ mass fractions in some particular phase α_o , p_α , and T . This leaves NP

phase pressures, the temperature, and NC–NP mass fractions within some phase, say $\alpha = 1$, as the NC + 1 degrees of freedom:

$$p_\alpha, \quad (\alpha = 1, \dots, \text{NP}), \quad T, \quad \omega_1^\gamma, \quad (\gamma = 1, \dots, \text{NC} - \text{NP}). \quad (23)$$

Instead of using the NP phase pressures, we can use NP–1 volumetric fractions and the pressure in only one of the phases:

$$p_1, \theta_\alpha (\alpha = 1, \dots, \text{NP}), \quad T, \quad \omega_1^\gamma, \quad (\gamma = 1, \dots, \text{NC} - \text{NP}). \quad (24)$$

Numerically, this choice has advantages when two or more of the phase pressures are close to each other.

4.2. WITH SURFACE EFFECTS

Most textbooks consider thermodynamic equilibria of homogeneous phases. However, a fluid within the void space of a porous medium can experience surface forces arising from charge imbalances at the solid surfaces. Such forces contribute to what is called the ‘matric potential.’ They are important either at low saturations or for fine-grained material, such as clays. Nitao and Bear (1993) discuss this point.

Gravitational forces also act on the fluid. As a result, each fluid phase is microscopically inhomogeneous. This inhomogeneity implies that the basic thermodynamic equations of state become explicit functions of position, in addition to their dependence on pressure, temperature, and concentration. For example, energy will depend on distance from surfaces and elevation. Also note that surface forces can act differently depending on the component. They also depend on distances from the solid surfaces. Therefore, in general, concentrations will also be nonuniform.

For the chemical potential, we have

$$\mu_\alpha^\gamma = \mu_\alpha^\gamma(p_\alpha, T, \omega_\alpha^k, \mathbf{x}'). \quad (25)$$

A particular case arises when the chemical potential can be decomposed in the form,

$$\mu_\alpha^\gamma = \hat{\mu}_\alpha^\gamma(p_\alpha, T, \omega_\alpha^k, \mathbf{x}') + \varphi_\alpha^\gamma(\mathbf{x}'), \quad (26)$$

where $\varphi_\alpha^\gamma(\mathbf{x}')$ is a potential energy function assumed to be purely a function of position and $\hat{\mu}_\alpha^\gamma$ is the function for the fluid under the same conditions, but in the absence of surface and gravitational forces. This decomposition is valid only when the forces are conservative (i.e., have an associated potential energy function) and if there is no intercoupling between forces and intermolecular interactions. In general,

these conditions may not be true. However, we can always define a generalized potential field given by

$$\varphi_\alpha^\gamma(p_\alpha, T, \omega^\kappa, \mathbf{x}') \equiv \mu_\alpha^\gamma(p_\alpha, T, \omega^\kappa, \mathbf{x}') - \hat{\mu}_\alpha^\gamma(p_\alpha, T, \omega^\kappa), \quad (27)$$

and a generalized force field, \mathbf{f} , defined by

$$\begin{aligned} \mathbf{f}_\alpha^\gamma(p_\alpha, T, \omega^\kappa, \mathbf{x}') &\equiv -\nabla \mu_\alpha^\gamma(p_\alpha, T, \omega^\kappa, \mathbf{x}')|_{\omega^\kappa, T, p} \\ &= -\nabla \varphi_\alpha^\gamma(p_\alpha, T, \omega^\kappa, \mathbf{x}')|_{\omega^\kappa, T, p}, \end{aligned} \quad (28)$$

where partial derivatives are taken with the variables ω^κ , T , p fixed. Note that φ_α^γ includes a contribution from gravity equal to $g(z - z_{\text{ref}})$, where z_{ref} is a reference elevation.

We show in the appendix that conditions for equilibrium are given by (14), (15), and (17). However, the condition in (16), which implies a uniform pressure throughout the phase, is, in general, not valid. Note that

$$G_\alpha = \sum_{(\gamma)} \omega_\alpha^\gamma \mu_\alpha^\gamma. \quad (29)$$

Thus,

$$dG_\alpha = \sum_{(\gamma)} \omega_\alpha^\gamma d\mu_\alpha^\gamma + \sum_{(\gamma)} \mu_\alpha^\gamma d\omega_\alpha^\gamma. \quad (30)$$

We also have

$$dG_\alpha = v_\alpha dp_\alpha - s_\alpha dT + \sum_{(\gamma)} \mu_\alpha^\gamma d\omega_\alpha^\gamma + \sum_{(\gamma)} \mathbf{f}_\alpha^\gamma \cdot d\mathbf{x}', \quad (31)$$

in which v_α denotes the specific volume of the α -phase. Equating the two expressions, we have

$$\sum_{(\gamma)} \omega_\alpha^\gamma d\mu_\alpha^\gamma = v_\alpha dp_\alpha - s_\alpha dT + \sum_{(\gamma)} \omega_\alpha^\gamma \mathbf{f}_\alpha^\gamma \cdot d\mathbf{x}'. \quad (32)$$

Therefore,

$$\sum_{(\gamma)} \omega_\alpha^\gamma \nabla \mu_\alpha^\gamma = v_\alpha \nabla p_\alpha - s_\alpha \nabla T + \sum_{(\gamma)} \omega_\alpha^\gamma \mathbf{f}_\alpha^\gamma. \quad (33)$$

From (15) and (14), we have

$$\nabla \mu_\alpha^\gamma = 0, \quad \nabla T = 0 \quad (34)$$

within the α -phase. Thus, from (33), it follows that

$$v_\alpha \nabla p_\alpha + \sum_{(\gamma)} \omega_\alpha^\gamma f_\alpha^\gamma = 0, \quad (35)$$

which shows that p_α is not uniform, but its gradient depends on the generalized forces.

Let us now consider the degrees of freedom of our inhomogeneous system. The chemical potentials and temperature are uniform over the REV. We denote their values by $\mu^{\gamma o}$ and T^o , respectively. We now show that the pressure, temperature, and concentrations at each point \mathbf{x}' can be expressed in terms of these values. Clearly, the temperature is known from

$$T(\mathbf{x}') = T^o. \quad (36)$$

The remaining NC + 1 variables, $p(\mathbf{x}')$ and $\omega^\gamma(\mathbf{x}')$, can be obtained by solving the NC + 1 equations

$$\mu_\alpha^\gamma(p(\mathbf{x}'), T^o, \omega^\kappa(\mathbf{x}'), \mathbf{x}') = \mu^{\gamma o}, \quad (37)$$

and

$$\sum_{(\gamma)} \omega^\gamma(\mathbf{x}') = 1. \quad (38)$$

Therefore, the following functional relationships hold,

$$p_\alpha = p_\alpha(\mu_\alpha^{\gamma o}, T^o, \mathbf{x}') \quad (39)$$

and

$$\omega_\alpha^\gamma = \omega_\alpha^\gamma(\mu_\alpha^{\gamma o}, T^o, \mathbf{x}'). \quad (40)$$

Hence, the thermodynamic state at each point depends only on the NC + 1 variables, $\mu^{\gamma o}$ and T^o .

Next, we show that not all of these variables are independent. For a given set of volumetric fractions, θ_δ , we have from (17) the NP – 1 relationships

$$p_\alpha(\mu_\alpha^{\gamma o}, T^o, \mathbf{x}'^-) - p_\beta(\mu_\beta^{\gamma o}, T^o, \mathbf{x}'^+) = \frac{2\gamma_{\alpha\beta}(\mathbf{x}')}{R_{\alpha\beta}(\mathbf{x}')}, \quad (41)$$

for each interface $S_{\alpha\beta}$, where \mathbf{x}'^- and \mathbf{x}'^+ denote points on the respective sides of the interface. Note that since the pressure is no longer uniform within a phase, the mean radii of curvature are no longer constant.

We assume, as is usually done, that the mean radius of curvature, $R_{\alpha\beta}(\mathbf{x}')$, depends on the volumetric fraction, θ_δ , of all of the phases (actually, it depends also on the past history of the saturations because of hysteresis).

The $\mu^{\gamma o}$'s are not independent, but are related to the NP saturations through the above NP – 1 capillary relationships. We can eliminate NP – 1 of the $\mu^{\gamma o}$'s so that they become functions of the NP – 1 independent saturations and the NC – NP + 1 remaining independent $\mu^{\gamma o}$'s, i.e.,

$$\mu^{\lambda o} = \mu^{\lambda o}(\mu^{\gamma o}, T^o, \theta_\delta), \quad (42)$$

where the indices range over $\lambda = \text{NC} - \text{NP} + 2, \dots, \text{NC}$ and $\gamma = 1, \dots, \text{NC} - \text{NP} + 1$. The degrees of freedom are, therefore, given by

$$\begin{aligned} T^o \\ \mu^{\gamma o} \quad \gamma = 1, \dots, \text{NC} - \text{NP} + 1, \\ \theta_\delta \quad \delta = 1, \dots, \text{NP} - 1. \end{aligned}$$

The total number of degrees of freedom is, therefore, NC + 1. This is the same number as in the case without surface effects or gravitational effects. The difference is that mass fractions and pressures are not primary variables, because they are not uniform over each phase.

A familiar example is a two-phase system ($\alpha = \ell, g$) with two components, water (w) and air (a). The degrees of freedom are T^o , $\mu^{a o}$, and θ_ℓ . From (42), we need the constitutive relationship for the chemical potential of water component as,

$$\mu^{w o} = \mu^{w o}(\mu^{a o}, T^o, \theta_\ell). \quad (43)$$

This relationship is, essentially, what has been called the matric potential relationship, or moisture retention function. If we assume, further, that there is at least a film of water around all solid surfaces and that surface forces are not important for the gas phase, the pressure, p_g , in the gas is uniform under equilibrium conditions. It is then possible to replace $\mu^{a o}$ as a degree of freedom by the gas phase pressure, p_g^o . The system is completely described by the degrees of freedom T^o , p_g^o and θ_ℓ and the relation in (43). This example gives a thermodynamic basis for the degrees of freedom assumed by the soil physics literature.

5. Degrees of Freedom for Phases in Motion

Next, we consider the case in which the phases are in motion, and the system may undergo changes in time. In a porous medium, such a system can never be in *complete* thermodynamic equilibrium. Conditions of mechanical nonequilibrium prevail as a consequence of the transfer of momentum from the moving fluid to the solid by viscous forces. This gives rise to pressure gradients at the microscopic

level within the REV. Temperature gradients may also occur because of viscous dissipation. If these pressure and temperature gradients are large, the system will be far from chemical and thermal equilibrium. Perhaps, more importantly, flow can transport components into the REV, resulting in nonequilibrium concentrations. For a multiphase REV, flow can cause some phases to be under nonequilibrium conditions, and some of the phases may be in nonequilibrium with each other.

We always assumed that conditions hold for each phase to be in equilibrium. We first consider the case where the phases are not necessarily in equilibrium with each other.

The degrees of freedom will be defined as the minimal number of variables that are needed in order to completely describe the system. All other variables are functions of the degrees of freedom or derivatives of the degrees of freedom. Thus, the number of degrees of freedom, NF, is equal to the number of variables, NV, minus the constitutive relationships and constraints, NE, viz.

$$NF = NV - NE. \quad (44)$$

The degrees of freedom will also be called *primary variables*. The primary variables, by definition, cannot solely be algebraically expressed in terms of each other, so they must satisfy partial differential equations, in particular, balance equations.

5.1. BALANCE EQUATIONS

Consider a deformable porous medium domain containing a number of multi-component fluid phases under nonisothermal conditions. Let NP and NC denote the number of fluid phases and of components, respectively. Some or all of the components may be adsorbed on solid. In our conceptual model, we shall regard the adsorbed components as constituting a separate adsorbed phase. We shall denote it by the subscript 'ad'. The solid itself is regarded as an additional (single-component) phase. Storage of energy and mass on interphase boundaries is assumed to be negligible.

Let θ_α denote the volumetric fraction of an α -phase. The macroscopic balance equation of an extensive quantity, E^γ , of the α -phase, having a density e_α^γ ($= E^\gamma$ per unit volume of the α -phase) obtained by averaging the corresponding microscopic equation (Bear and Bachmat, 1991) is

$$\frac{\partial \theta_\alpha e_\alpha^\gamma}{\partial t} = -\nabla \cdot \theta_\alpha (e_\alpha^\gamma \mathbf{V}_\alpha + \mathbf{J}_{h\alpha}^{E^\gamma}) - f_{\alpha \rightarrow \beta}^{E^\gamma} + \theta_\alpha \rho_\alpha \Gamma_\alpha^E, \quad (45)$$

where $\mathbf{J}_{h\alpha}^{E^\gamma}$ denotes the flux due to hydrodynamic dispersion of E_γ in α , and

$$f_{\alpha \rightarrow \beta}^{E^\gamma} = \int_{S_{\alpha\beta}} [e_\alpha (V_\alpha - \mathbf{u}) + \mathbf{j}_\alpha^{E^\gamma} + \epsilon_\alpha^\gamma \mathbf{j}_\alpha^\gamma] \cdot \nu_\alpha \, dS \quad (46)$$

denotes the rate at which E^γ moves from the α -phase to all β -phases across their common interface, $S_{\alpha\beta}$, with ϵ_α^γ denoting E_α^γ per unit mass of α , and $\mathbf{j}_\alpha^{E^\gamma}$ denoting the diffusive flux of E^γ , and \mathbf{u} denoting the velocity of $S_{\alpha\beta}$. Note that all terms in (45) are at the macroscopic level, while those in the integrand of (46) are at the microscopic one (although the same symbols are used).

The balance equation for the mass of a γ -component is obtained by setting $e_\alpha^\gamma = \rho_\alpha \omega_\alpha^\gamma$, where ρ_α is the mass density of the α -phase. The energy balance for the α -phase is obtained by inserting $e_\alpha^{E^\gamma} \equiv e_\alpha^\epsilon = \rho_\alpha u_\alpha$, where u_α is the internal energy (per unit mass) of the α -phase. The momentum balance equation for the α -phase is obtained by setting $e_\alpha^{E^\gamma} \equiv e_\alpha^M = \rho_\alpha \mathbf{V}_\alpha$.

The various dispersive and diffusive fluxes are related to appropriate intensive quantities by *dynamic constitutive* relations.

Mass of a component. The diffusive flux of a γ -component in an α -phase within a porous medium is expressed as an averaged form of Fick's law which takes the form

$$\mathbf{J}_\alpha^\gamma = -\rho_\alpha \omega_\alpha^\gamma \mathcal{D}_\alpha^{*\gamma} \cdot \nabla \mu_\alpha^\gamma, \quad (47)$$

where $\mathcal{D}_\alpha^{*\gamma}$ denotes the coefficient of molecular diffusion in the α -phase that occupies part of the void space in a porous medium domain. It takes into account the *tortuosity* of the phase within the void space. For simplicity, we have regarded the α -phase as a binary system. Actually, there is coupling among components.

The dispersive mass flux of the γ -component, $\mathbf{J}_\alpha^{*\gamma}$, is expressed by a Fickian type law, i.e., the flux is proportional to the gradient of the mass density of the considered component,

$$\mathbf{J}_\alpha^{*\gamma} = -\rho_\alpha \mathbf{D}_\alpha \cdot \nabla \omega_\alpha^\gamma, \quad (48)$$

where \mathbf{D} is the coefficient of dispersion of the α -phase.

The mass balance for the solid phase takes the form

$$\frac{\partial}{\partial t} \theta_s \rho_s = -\nabla \cdot \theta_s \rho_s \mathbf{V}_s. \quad (49)$$

We neglect deformation of the adsorbed phase and diffusion of mass.

The mass balance for the γ -component is given by

$$\frac{\partial}{\partial t} \rho_{ad}^\gamma = -f_{ad \rightarrow \beta}^{m^\gamma}. \quad (50)$$

Here, ρ_{ad}^γ is the REV-averaged mass density of the adsorbed γ -component given by

$$\rho_{ad}^\gamma \equiv \frac{1}{U_o} \int_{U_{ado}} \rho \, dU. \quad (51)$$

where $\rho_{ad}^\gamma = \theta_{ad}\rho_{ad}\omega_{ad}^\gamma$. However, since the volume of the adsorbed phase is usually very small, i.e., $\theta_{ad} \ll \theta_s$, $\theta_{ad} \ll \theta_\alpha$, it is more convenient to use ρ_{ad}^γ as a variable instead of θ_{ad} and ω_{ad}^γ .

Thus, we have NP \times NC mass balance equations for the NC γ -components in the NP fluid phases, NC balance equations for the NC γ components in the adsorbed phase, and one balance equation for the solid matrix. We, therefore, have a total of (NP + 1) \times NC + 1 mass balance equations.

Heat of a phase. The heat flux of a phase at the microscopic level is expressed by Fourier's law. By averaging this law over an REV, we obtain its macroscopic equivalent (e.g., Bear and Bachmat, 1991),

$$\mathbf{J}_\alpha^H = -\lambda_\alpha^* \cdot \nabla T_\alpha, \quad (52)$$

where λ_α^* denotes the coefficient of heat conduction in the α -phase that occupies part of the void space.

We assume that the adsorbed phase, because of its small heat capacity, is in thermal equilibrium with the solid phase ($T_{ad} = T_s$). Therefore, the energy balance equation for the adsorbed phase is not needed. This leaves NP energy balance equations for the phases and one equation for the solid matrix, resulting in a total of NP + 1 energy balance equations.

Momentum of a phase. The diffusive flux of momentum of a phase is expressed by minus the stress tensor in that phase, σ_α . For a fluid phase, the stress tensor can be decomposed into the sum of the shear stress, τ and pressure, p , in the form $\sigma_\alpha = \tau_\alpha - p_\alpha \delta$, where δ denotes the unit tensor.

For a Newtonian fluid phase, the shear stress, τ_α , is expressed in terms of the gradient of the fluid's velocity by the constitutive relationship

$$\tau_\alpha = \mu_\alpha [\nabla \mathbf{V}_\alpha + (\nabla \mathbf{V}_\alpha)^T] + \mu'_\alpha \nabla \cdot \mathbf{V}_\alpha \delta, \quad (53)$$

where μ is the dynamic viscosity, and μ' is the bulk viscosity. Actually, Equation (53) expresses the constitutive equation for a fluid phase. Here, we *assume, as an approximation*, that the same form of expression is valid also at the macroscopic level. The coefficients have to be determined experimentally for any given porous medium.

For the solid matrix, the intrinsic averaged stress in the solid, σ_s , is not the strain producing stress, as we have to take into account the fact that each solid grain (say, in a granular porous medium) is almost completely surrounded by fluid(s), say, water and air. The pressure in the fluids produces an additional stress in the solid (because we refer to stress as positive for tension and to pressure as positive for compression, the pressure in the fluids actually reduces the stress in the solid).

Terzaghi (1925) introduced the concept of *effective stress*, σ'_s , defined for a single α -phase fluid (f) that occupies the entire void space, as

$$\sigma'_s = (1 - \phi)(\sigma_s - \sigma_f), \quad (54)$$

or

$$\sigma_s = \frac{1}{\theta_s} \sigma'_s + \sigma_f, \quad (55)$$

(e.g., Bear and Bachmat, 1991) where $\phi \equiv \theta_s$ is the porosity. Note that here the effective stress is a *phase average* (i.e., per unit area of porous medium), while the solid and fluid stresses are intrinsic phase averages. For a multiphase system, we use an average stress in the fluids occupying the void space, e.g.,

$$\sigma_f = \sum_{(\alpha)} S_\alpha \sigma_\alpha. \quad (56)$$

Usually, we neglect the shear stress in the fluids, so that (55) reduces to

$$\sigma'_s = (1 - \phi)(\sigma_s + p_v \delta), \quad (57)$$

where p_v denotes the average pressure in the fluids that occupy the void space. For example, we may use $p_v = \sum_{(\alpha)} S_\alpha p_\alpha$ where S_α is the α -phase saturation.

For a thermoelastic solid skeleton, we may now relate the deformation to the effective stress by the constitutive relation

$$\sigma'_s = \mu'_s [\nabla \mathbf{w}_s + (\nabla \mathbf{w}_s)^T] + [\mu''_s \nabla \cdot \mathbf{w}_s - \eta(T_\alpha - T_0)] \delta, \quad (58)$$

where \mathbf{w}_s denotes the displacement in the solid matrix, and $\eta = (3\lambda''_s + 2\mu''_s)\alpha_T$. Again, constitutive relation is valid at the microscopic level, i.e., for a thermoelastic solid. Here we have assumed that the same form, but with different coefficients, is also applicable at the macroscopic level.

In order to solve for the displacement, an additional relationship is required—one that relates the solid's velocity to the displacement, viz.,

$$\frac{D\mathbf{v}_s \mathbf{w}_s}{Dt} = \mathbf{V}_s, \quad \text{or approximately} \quad \frac{\partial \mathbf{w}_s}{\partial t} = \mathbf{V}_s, \quad (59)$$

where

$$\frac{D\mathbf{v}_s(\cdot)}{Dt} \equiv \frac{\partial \mathbf{w}_s}{\partial t} + \mathbf{V}_s \cdot \nabla(\cdot) \quad (60)$$

is the material derivative of (\cdot) .

If the inertial terms are neglected and certain simplifying assumptions are made, the averaged momentum balance equation for a fluid α -phase reduces to the well known Darcy's law,

$$\mathbf{V}_\alpha - \mathbf{V}_s = -\frac{k_\alpha}{\theta_\alpha \mu_\alpha} (\nabla p_\alpha + \rho_\alpha g \nabla z), \quad (61)$$

in which k_α is the effective permeability of the α -phase, and μ_α is its dynamic viscosity.

5.2. DEGREES OF FREEDOM UNDER NONEQUILIBRIUM CONDITIONS

The balance equations assume approximate equilibrium *within* each phase present in the REV, but not *between* phases. The balance equations provide information on the following state variables:

Kind	Number of equations
$\omega_\alpha^\gamma, \rho_{ad}^\gamma$	$NC \times (NP + 1)$
θ_α, θ_s	$NP + 1$
T_α, T_s	$NP + 1$
p_α	NP
V_α, V_s	$NP + 1$
w_s	1

where $\alpha = 1, \dots, NP$. The total number of variables is

$$NV = NC \times NP + NC + 4NP + 4. \tag{62}$$

We have not listed the phase internal energies, u_α , and the densities, ρ_α , as they can be related to the other variables through appropriate constitutive relations, assuming macroscopic thermodynamic equilibrium within each phase. For example,

$$\overline{\rho_\alpha^\alpha} = \tilde{\rho}_\alpha(\overline{p_\alpha^\alpha}, \overline{T_\alpha^\alpha}, \overline{\omega_\alpha^\alpha}), \tag{63}$$

where $\tilde{\rho}_\alpha$ is the same constitutive function as for the microscopic value of density.

The actual number of independent variables is much smaller due to various constraints. There are $NP + 1$ constraints on these variables due to the following relations:

$$\sum_{\alpha=1}^{NP} \theta_\alpha + \theta_s = 1, \tag{64}$$

and

$$\sum_{(\gamma)} \omega_\alpha^\gamma = 1. \tag{65}$$

In addition, we have to take into account the $NP - 1$ capillary pressure relationships,

$$p_1 = p_\alpha - p_{c1\alpha}(\theta_\delta, T_\beta, \omega_\beta^\gamma), \quad \alpha = 2, \dots, NP. \tag{66}$$

The total number of constraints is

$$NE = 2NP. \tag{67}$$

The number of degrees of freedom is equal to

$$NF = NV - NE = NC \times NP + NC + 2NP + 4. \tag{68}$$

To solve for these primary variables, we have the following $NB = NV - NE = NC \times NP + NC + 2NP + 4 = NF$ number of partial differential equations:

Kind	Number of equations
Mass balances	$NC \times NP + NC + 1$
Energy balances	$NP + 1$
Momentum balances	$NP + 1$
Definition of w_s	1

The set of primary variables is, in general, not unique. An example of a set of NF primary variables is:

Kind	Range	Number
ω_α^γ	$\gamma = 1, \dots, NC - 1$ $\alpha = 1, \dots, NP$	$(NC - 1) \times NP$
ρ_{ad}^γ	$\gamma = 1, \dots, NC$	NC
$\theta_s (\equiv 1 - \phi)$		1
p_α	$\alpha = 1, \dots, NP$	NP
T_α	$\alpha = 1, \dots, NP$	NP
T_s		1
V_α	$\alpha = 1, \dots, NP$	NP
V_s		1
w_s		1

Let us show how the other variables can be solved in terms of these primary variables. For example:

- We first solve for the θ_α ($\alpha = 2, \dots, NP$) in terms of the p_α , using the capillary relationships in (66).
- We then solve for θ_1 in terms of the other θ_α and θ_s , using (64).
- Finally, we solve for ω_{NP}^γ , using (65).

At low volumetric fractions, the volumetric fractions may not be a unique function of pressure, and we may need to use volumetric fractions instead of pressure (see Nitao and Bear, 1993). Thus, another possible set of primary variables

TABLE I. degrees of freedom and primary variables for nonequilibrium case

Deformable solid	Darcy's law	Isothermal	NF	Primary variables ($\gamma' = 1, \dots, NC - 1$; $\gamma = 1, \dots, NC$; $\alpha = 1, \dots, NP$)
Yes	No	No	$NC \times NP + NC + 2NP + 4$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_\alpha, V_s, w_s, \theta_s, T_\alpha, T_s$
Yes	Yes	No	$NC \times NP + NC + NP + 4$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_s, w_s, \theta_s, T_\alpha, T_s$
No	Yes	No	$NC \times NP + NC + NP + 1$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, T_s, T_\alpha$
No	No	No	$NC \times NP + NC + 2NP + 1$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_\alpha, T_s, T_\alpha$
Yes	No	Yes	$NC \times NP + NC + NP + 1$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_\alpha, V_s, w_s, \theta_s$
Yes	Yes	Yes	$NC \times NP + NC + 3$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_s, w_s, \theta_s$
No	Yes	Yes	$NC \times NP + NC$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma$
No	No	Yes	$NC \times NP + NC + NP$	$p_\alpha, \omega_\alpha^{\gamma'}, \rho_{ad}^\gamma, V_\alpha$

is obtained by replacing the p_α 's by the set, p_1, θ_α ($\alpha = 2, \dots, NP$). In this case, the p_α , ($\alpha = 2, \dots, NP$) are obtained as functions of the θ_α and p_1 using (66).

Note that within an REV, the number of phases may change as phases may disappear or appear. Thus, the actual number and type of primary variables may change with time.

The primary variables will also depend on the type of problem that is being modeled and the simplifications involved, e.g., whether or not the solid is assumed to be deformable. In the latter case, the variables V_s, w_s , and θ_s are not needed, and NF is reduced by three. Other cases are when the problem is isothermal, so that $T_s = T_\alpha =$ initial temperature. In this case, the temperatures are not needed as primary variables, and NF is reduced by $NP + 1$. If there is approximate thermal equilibrium between phases, $T_s = T_\alpha$, and only the temperature, say T_s , is needed, then NF is reduced by NP . When Darcy's law is valid, the phase velocities V_α can be expressed in terms of the other primary variables so they should not be counted as primary variables. These special cases are summarized in Table I.

If the phases are in thermal equilibrium with each other, the $T_\alpha = T_s$ and the T_α 's can be removed from the set of primary variables and NF is reduced in all of the above cases by the amount NP . If the components on the absorbed solid are in chemical equilibrium with the fluid phases, then the ρ_{ad}^γ are no longer needed as primary variables and NF is reduced by NC .

5.3. DEGREES OF FREEDOM UNDER APPROXIMATE CHEMICAL AND THERMAL EQUILIBRIUM

Suppose that at every point within the domain, and at every instant of time, the system is assumed to be in *approximate thermodynamic equilibrium*, i.e., the system is in chemical and thermal equilibrium with (15) and (14) holding approximately. Here, 'point' means 'macroscopic point,' i.e., the centroid of an REV, and the equilibrium is between the averaged (over the REV) behavior of the phases and the components at that point.

Under equilibrium, we assume that adsorption isotherms take the form,

$$\rho_{ad}^\gamma / \rho_b = f_\alpha(\omega_\alpha^\gamma \rho_\alpha), \quad (69)$$

where ρ_b is the bulk density of the solid matrix (assumed constant), with

$$\rho_b \equiv \frac{1}{U_o} \int_{U_{so}} \rho_s dU. \quad (70)$$

We start with the same $NV = NC \times NP + NC + 4NP + 4$ variables as above. We have the following constraints:

$$\begin{array}{ll} \theta_s + \Sigma_{(\alpha)} \theta_\alpha = 1 & 1 \\ \Sigma_{(\gamma)} \omega_\alpha^\gamma = 1 & NP \\ T_s = T_\alpha & NP \\ \mu_\alpha^\gamma = \mu_\beta^\gamma & (NP - 1) \times NC \\ \rho_{ad}^\gamma / \rho_b = f_\alpha(\omega_\alpha^\gamma \rho_\alpha) & NC \\ \text{capillary pressure} & NP - 1 \end{array}$$

The number of constraints is $NE = NP \times NC + 3NP$. The number of degrees of freedom is

$$NF = NV - NE = NC + NP + 4. \quad (71)$$

The mass balance equations for all components may be summed over all the phases to give NC component balance equations. The exchange fluxes cancel since $f_{\alpha \rightarrow \beta}^\gamma = -f_{\beta \rightarrow \alpha}^\gamma$. This leaves NC mass balance equations for the γ component and one mass balance equation for the solid matrix. Similarly, the exchange fluxes cancel when the phase energy balance equations are summed over all the phases within an REV, resulting in a single energy balance equation.

We now count the number of balance equations.

Mass balance	$NC + 1$
Energy balance	1
Momentum balance	NP
Definition of w_s	1

TABLE II. Degrees of freedom and primary variables for equilibrium case

Deformable solid	Darcy's law	Isothermal	NF	Primary variables ($\gamma = 1, \dots, NC - NP$; $\alpha = 1, \dots, NP$)
Yes	No	No	$NC + NP + 4$	$p_\alpha, \omega_1^\gamma, V_\alpha, V_s, w_s, \theta_s, T_s$
Yes	Yes	No	$NC + 4$	$p_\alpha, \omega_1^\gamma, V_s, w_s, \theta_s, T_s$
No	Yes	No	$NC + 1$	$p_\alpha, \omega_1^\gamma, T_s$
No	No	No	$NC + NP + 1$	$p_\alpha, \omega_1^\gamma, V_\alpha, T_s$
Yes	No	Yes	$NC + NP + 1$	$p_\alpha, \omega_1^\gamma, V_\alpha, V_s, w_s, \theta_s$
Yes	Yes	Yes	$NC + 3$	$p_\alpha, \omega_1^\gamma, V_s, w_s, \theta_s$
No	Yes	Yes	NC	$p_\alpha, \omega_1^\gamma$
No	No	Yes	$NC + NP$	$p_\alpha, \omega_1^\gamma, V_\alpha$

The total number of equations is

$$NB = NC + NP + 4. \tag{72}$$

This is also equal to the number of degrees of freedom, NF.

A possible set of primary variables is $p_\alpha (\alpha = 1, \dots, NP), \omega_1^\gamma (\gamma = 1, \dots, NC - NP), T_s, V_\alpha (\alpha = 1, \dots, NP), V_s, w_s, \theta_s$. Solution of the θ_α in terms of the primary variables is described above for the nonequilibrium case. It is obvious that the T_α 's are obtained through $T_\alpha = T_s$. The values of $\omega_\alpha^\gamma (\alpha = 2, \dots, NP; \gamma = 1, \dots, NC - NP)$ are found through solving the equations

$$\mu_\alpha^\gamma(\omega_\alpha^\kappa, p_\alpha, T_\alpha) = \mu_1^\gamma(\omega_1^\kappa, p_1, T_1). \tag{73}$$

The remaining $\omega_\alpha^\gamma (\alpha = 1, \dots, NP; \gamma = NC - NP + 1, \dots, NC)$ are found by solving

$$\sum_{\gamma=NC-NP+1}^{NC} \omega_\alpha^\gamma = 1 - \sum_{\gamma=1}^{NP-NC} \omega_\alpha^\gamma, \tag{74}$$

where the right-hand side is known and the left-hand side contains the variables to be solved for. The ρ_{ad}^γ 's are obtained from (69). A number of particular cases are considered in Table II.

It is obvious that for isothermal problems, T_s is no longer a primary variable and that NF is reduced by one. For a nondeformable, isothermal system with Darcy's law, we have $NF = NC$.

5.4. PARTIAL PHASE EQUILIBRIUM

It is possible that the exchange of certain extensive quantities between NPE phases ($1 < NPE < NP$) occurs sufficiently fast, so as to establish equilibrium between

them, with respect to the considered quantities. The other NP – NPE phases are not in equilibrium with respect of the same quantities. This means that the potentials associated with the considered quantities are approximately constant over the NPE phases. It is then clear that the number of degrees of freedom is smaller than in the case where all phases are not in equilibrium with each other. In particular, consider the case where NPE phases are in equilibrium with each other with respect to the mass and energy of the NC components. Then, we have the $(\text{NPE} - 1) \times \text{NC}$ constraints from the equality of chemical potentials between the NPE phases, and $\text{NPE} - 1$ constraints for the equality of temperatures, for a total of $\text{NPE} \times \text{NC} - \text{NC} + \text{NPE} - 1$ additional constraints. Adding these to the NE ($= 2\text{NP}$) constraints that correspond to the case of complete nonequilibrium, we obtain

$$\text{NE} = 2\text{NP} + \text{NPE} \times \text{NC} - \text{NC} + \text{NPE} - 1$$

constraints. Since the number of variables is $\text{NV} = \text{NC} \times \text{NP} + \text{NC} + 4\text{NP} + 4$, the number of degrees of freedom is

$$\text{NF} = \text{NV} - \text{NE} = \text{NC} \times (\text{NP} - \text{NPE}) - \text{NPE} + 2\text{NC} + 2\text{NP} + 5.$$

A possible set of primary variable is $\omega_{\alpha_o}^\delta$ ($\delta = 1, \dots, \text{NC} - \text{NPE}$), $\omega_{\alpha'}^\gamma$ ($\gamma = 1, \dots, \text{NC} - 1$), ρ_{ad}^γ ($\gamma = 1, \dots, \text{NC}$), θ_s , p_α , $T_{\alpha'}$, T_s , V_α , w_s , where $\alpha = 1, \dots, \text{NP}$, $\alpha' = 1, \dots, \text{NP} - \text{NPE}$ denotes all the phases that are not in equilibrium, and α_o is one of the NPE phases.

5.5. EXAMPLES

CASE A

Phases: Liquid (ℓ), deformable solid (s).

Components: Water (w).

Degrees of freedom: $\text{NF} = 4$.

Example of primary variables: p_ℓ , T , V_ℓ , V_s .

Balance equations to be solved:

Mass balance for w -component.

Momentum balance for ℓ -phase (or use Darcy's law).

Energy balance for the porous medium.

Momentum balance for porous medium (e.g., equilibrium equation).

CASE B

Phases: Liquid (ℓ), gas (g), deformable solid (s).

Components: Water (w), air (a).

Degrees of freedom: $\text{NF}=6$.

Example of primary variables: p_ℓ , p_g , T , V_ℓ , V_g , V_s .

Balance equations to be solved:

Mass balances for w -component.

- Mass balances for a -component.
- Momentum balance for the ℓ -phase.
- Momentum balance for the g -phase.
- Momentum balance for the porous medium.
- Energy balance for the porous medium.

It may be of interest to note the relations among the various molar fractions of the components in this example.

$$\begin{aligned} \rho_\ell^a + \rho_\ell^w &= \rho_\ell, & \rho_g^a + \rho_g^w &= \rho_g. \\ n_\ell^a + n_\ell^w &= 1, & n_g^a + n_g^w &= 1. \\ \frac{n_g^w}{n_\ell^w} &= \mathcal{K}_{g,\ell}^w(p_\ell, p_g, T), & \frac{n_g^a}{n_\ell^a} &= \mathcal{K}_{g,\ell}^a(p_\ell, p_g, T). \end{aligned}$$

Hence, assuming the \mathcal{K} 's to be independent of the n 's, we have

$$n_g^a = \frac{\mathcal{K}_{g,\ell}^w - 1}{\mathcal{K}_{g,\ell}^a - \mathcal{K}_{g,\ell}^w}, \quad n_\ell^w = \frac{\mathcal{K}_{g,\ell}^a - 1}{\mathcal{K}_{g,\ell}^a - \mathcal{K}_{g,\ell}^w}.$$

CASE C

- Phases: Liquid (ℓ), gas (g), nondeformable solid.
- Components: Water (w), air a , dissolved/volatile component, (γ).
- Degrees of freedom: NF = 6.
- Example of primary variables: $p_\ell, p_g, T, V_\ell, V_g, \omega_\ell^\gamma$.
- Balance equations to be solved:

- Mass balance for γ -components.
- Mass balance for w -component.
- Mass balance for a -component.
- Momentum balance for the ℓ -phase.
- Momentum balance for the g -phase.
- Energy balance for porous medium.

6. Conclusions

We have developed expressions for the number of degrees of freedom, or primary variables, for a variety of cases of flow of multiple multicomponents phases in a deformable porous medium under nonisothermal conditions. Our results require that the phases and the components be in thermodynamic equilibrium. We have, therefore, analyzed the meaning of chemical, thermal, and mechanical equilibria among phases and components, both at the microscopic level and the macroscopic one. We have presented a number of examples to demonstrate the usefulness of the results. The proposed expressions for the number of degrees of freedom represent

the equivalent of Gibbs Phase rule for the case of a porous medium in which phenomena of transport are modeled at the macroscopic level.

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Appendix A. Conditions for Thermodynamic Equilibrium in a Porous Medium

A.1. CONDITIONS WITHIN A PHASE

We derive conditions for equilibrium within a fluid α -phase that occupies the subdomain \mathcal{U}_{α} within the void space of a porous medium domain. Surface forces are included among the forces fields that act on the fluid.

If the considered subdomain is in thermodynamic equilibrium, we may replace its boundary by a rigid closed boundary without changing the thermodynamic state of the system. The second law of thermodynamics applies to a closed system. It states that the total entropy of a closed system is maximized with respect to variations in the thermodynamic state of the system.

In order to apply this law, we first subdivide the phase domain into volume elements \mathcal{U}_k such that the size of each element is sufficiently small to ensure that thermodynamic properties are essentially uniform within it. Let \mathbf{x}'_k denote the center of the k th element, of volume $\mathcal{U}(\mathbf{x}'_k)$, $m^\gamma(\mathbf{x}'_k)$ denote the mass of the γ -component in the element, and $\mathcal{E}(\mathbf{x}'_k)$ denote the internal energy in the element.

The total entropy of the k th element is a function of the mass of component, internal energy, and volume. Because of surface forces and other force fields, it also depends on the location of the center of the element. Denoting this function by the symbol S^* , the entropy of the k th element is

$$S(\mathbf{x}'_k) = S^*(m^\gamma(\mathbf{x}'_k), \mathcal{E}(\mathbf{x}'_k), \mathcal{U}(\mathbf{x}'_k), \mathbf{x}'_k). \quad (75)$$

The total entropy of the phase domain is given by the sum

$$S_\alpha = \sum_{(k)} S^*(m^\gamma(\mathbf{x}'_k), \mathcal{E}(\mathbf{x}'_k), \mathcal{U}(\mathbf{x}'_k), \mathbf{x}'_k). \quad (76)$$

This entropy is maximized with respect to variations in the internal energy distribution, $\mathcal{E}(\mathbf{x}'_k)$, while keeping $m^\gamma(\mathbf{x}'_k)$ and $\mathcal{U}(\mathbf{x}'_k)$ fixed. Because \mathcal{U}_{α} is a closed system, variations in internal energy are subject to the constraint that the total energy is a constant, \mathcal{E}_α . That is,

$$\sum_{(k)} \mathcal{E}(\mathbf{x}'_k) = \mathcal{E}_\alpha. \quad (77)$$

The method of Lagrange multipliers is used to eliminate this constraint by introducing an auxiliary variable, or multiplier, which we call $\Lambda_{\mathcal{E}}$. Instead of maximizing the entropy, the new functional,

$$F = S_{\alpha} + \Lambda_{\mathcal{E}} \left(\sum_{(k)} \mathcal{E}(\mathbf{x}'_k) - \mathcal{E}_{\alpha} \right), \quad (78)$$

is maximized subject to variations in $\mathcal{E}(\mathbf{x}')$ not constrained by (77).

The first-order variation, δF , of F must vanish at the maximum. We find that

$$\begin{aligned} \delta F &= \sum_{(k)} \left. \frac{\partial S}{\partial \mathcal{E}} \right|_{m^{\gamma}, \mathcal{U}} (\mathbf{x}'_k) \delta \mathcal{E}(\mathbf{x}'_k) + \Lambda_{\mathcal{E}} \sum_{(k)} \delta \mathcal{E}(\mathbf{x}'_k) + \delta \Lambda_{\mathcal{E}} \left(\sum_{(k)} \mathcal{E}(\mathbf{x}'_k) - \mathcal{E}_{\alpha} \right) \\ &= \sum_{(k)} \left(\frac{1}{T(\mathbf{x}'_k)} - \Lambda_{\mathcal{E}} \right) \delta \mathcal{E}(\mathbf{x}'_k) + \delta \Lambda_{\mathcal{E}} \left(\sum_{(k)} \mathcal{E}(\mathbf{x}'_k) - \mathcal{E}_{\alpha} \right), \end{aligned} \quad (79)$$

where we used the well-known result,

$$\frac{1}{T} = \left. \frac{\partial S}{\partial \mathcal{E}} \right|_{m^{\gamma}, \mathcal{U}, \mathbf{x}'}. \quad (80)$$

In order for the first-order variation to vanish, we must have

$$\frac{1}{T(\mathbf{x}'_k)} - \Lambda_{\mathcal{E}} = 0. \quad (81)$$

Therefore, T must be constant over \mathcal{U}_{α} .

A similar argument holds by varying the mass of γ -component, $m^{\gamma}(\mathbf{x}'_k)$. The functional to be maximized is

$$F = S_{\alpha} + \Lambda_{m^{\gamma}} \left(\sum_{(k)} m^{\gamma}(\mathbf{x}'_k) - m_{\alpha} \right). \quad (82)$$

The variation is

$$\delta F = \sum_{(k)} \left(\frac{\mu^{\gamma}(\mathbf{x}'_k)}{T} - \Lambda_{m^{\gamma}} \right) \delta m^{\gamma}(\mathbf{x}'_k) + \delta \Lambda_{m^{\gamma}} \left(\sum_{(k)} m^{\gamma}(\mathbf{x}'_k) - m_{\alpha} \right), \quad (83)$$

where the chemical potential μ^{γ} is defined as

$$\mu^{\gamma} \equiv -T \left. \frac{\partial S}{\partial m^{\gamma}} \right|_{\mathcal{E}, \mathcal{U}, m^{\kappa \neq \gamma}, \mathbf{x}'}. \quad (84)$$

An equivalent definition in terms of the *Gibbs free energy*, G_α , is

$$\mu^\gamma = \left. \frac{\partial G}{\partial m_\lambda} \right|_{E, U, m^{\kappa \neq \gamma}, \mathbf{x}'} \quad (85)$$

Hence, for the first-order variation in F to vanish, we must have

$$\frac{\mu^\gamma(\mathbf{x}'_k)}{T} - \Lambda_{m^\gamma} = 0. \quad (86)$$

Therefore, μ^γ must be constant throughout the phase domain, $U_{o\alpha}$.

The volume, $\mathcal{U}(\mathbf{x}'_k)$, of each element can also be varied. However, this cannot be done without moving the centers, \mathbf{x}'_k , of the elements. This, in turn, will affect the entropy function, S^* , since it depends explicitly on \mathbf{x}' due to force fields. The argument that we have just used does not apply. However, when no force fields exist, we may proceed as before and maximize the entropy. The constraint is

$$\sum_{(k)} \mathcal{U}(\mathbf{x}'_k) = U_{o\alpha}, \quad (87)$$

where $U_{o\alpha}$ denotes also the total volume of $U_{o\alpha}$, which is a constant since the outer boundary was replaced by a rigid one. The functional to be maximized is

$$F = S_\alpha + \Lambda_{\mathcal{U}} \left(\sum_{(k)} \mathcal{U}(\mathbf{x}'_k) - U_{o\alpha} \right). \quad (88)$$

Using the relationship

$$\frac{p}{T} = \left. \frac{\partial S}{\partial \mathcal{E}} \right|_{m^\gamma, \mathcal{U}, \mathbf{x}'}, \quad (89)$$

the variation in F is

$$\delta F = \sum_{(k)} \left(\frac{p(\mathbf{x}'_k)}{T} - \Lambda_{\mathcal{U}} \right) \delta \mathcal{U}(\mathbf{x}'_k) + \delta \Lambda_{\mathcal{U}} \left(\sum_{(k)} \mathcal{U}(\mathbf{x}'_k) - U_{o\alpha} \right), \quad (90)$$

which implies that

$$\frac{p(\mathbf{x}'_k)}{T} = \Lambda_{\mathcal{U}}. \quad (91)$$

Therefore, in the absence of force fields, the pressure must be uniform over the phase domain.

The above arguments may be extended to the entire REV domain and not just to a given phase domain. The above steps still hold when the fluid domain

within the REV, including the space within interphase boundaries (\equiv interface), is subdivided into subelements. The explicit dependence of the entropy function upon the microscopic point x'_k accounts not only for inhomogeneity in the force fields, but also for changes in the form of the function for different phases. We conclude that chemical potentials and the temperature must be uniform within the entire fluid portion of the REV, inclusive of interfaces. Pressures, however, are uniform only within phases and, then, only when there are no force fields.

A.2. CONDITIONS ACROSS INTERPHASE BOUNDARIES

From the above discussion, it follows that the chemical potential and temperature are uniform across interphase boundaries. Let us now derive the conditions for pressure across such boundaries.

Consider a volume element, Γ , within an REV, which contains an α -phase, a β -one, and the interface between them. Since, at equilibrium with its surroundings, there exist no fluxes across the boundaries of Γ , we replace the element by an identical element that is thermodynamically isolated, and derive conditions for the isolated element.

The size of the element is made sufficiently small so that any variations in thermodynamic properties over the element, including those due to external force fields, are negligible. At the same time, the element must contain the interface. The size of the element must be much larger than the thickness of the interface in order for the interface to be treated as an infinitely thin surface. Any force field emanating from the interface must have a limited range, one that is much smaller than the element size so that those portions of the α and β phases are affected are so small that they can be neglected and considered as part of the interface.

The entropy of each λ -phase ($\lambda = \alpha, \beta$) can then be expressed as a function of the mass m_λ^γ , of the γ -component, the internal energy, \mathcal{E}_λ , and the volume \mathcal{U}_λ by

$$S_\lambda = S_\lambda(m_\lambda^\gamma, \mathcal{E}_\lambda, \mathcal{U}_\lambda). \quad (92)$$

All the outer boundaries of the element are rigid, so that changes in the phase volume can result only from displacement of the interface. Also note that pressure, temperature, and concentrations are uniform over each respective phase within the element.

We now find the first-order variation in the total entropy, S , of the element, as a result of displacing the interface while fixing the internal energy and the number of component mass, $\delta\mathcal{E} = \delta m^\gamma = 0$. Because the entropy is a local maximum at equilibrium, the equilibrium conditions can be obtained from finding its first-order variation and setting it equal to zero.

The total variation in entropy is a sum of entropy variations of the constitutive parts. Hence,

$$\delta S = \delta S_\alpha + \delta S_\beta + \delta S_{\alpha\beta}, \quad (93)$$

where $\delta S_{\alpha\beta}$ is the entropy variation of the interface. From the first and second law of thermodynamics, it is well known that

$$\delta S_\lambda = \frac{\delta W_\lambda}{T_\lambda}, \quad \lambda = \alpha, \beta. \quad (94)$$

In the above expression, the term δW_λ is the work done by the λ -phase as the interface is displaced.

Let $\delta \mathbf{r}$ denote the displacement vector defined on the interface. The work done by the λ -phase is

$$\delta W_\lambda = \int_{S_{\alpha\beta} \cap \Gamma} \delta \mathbf{r} \cdot (\boldsymbol{\sigma}_\lambda \cdot \boldsymbol{\nu}_\lambda) dS, \quad (95)$$

where $\boldsymbol{\nu}_\lambda$ is a unit vector normal to the interface that is outward to the λ -phase, and $\boldsymbol{\sigma}_\lambda$ is the stress tensor in the λ -phase.

Therefore, the total change in entropy of the λ -phase is

$$\delta S_\lambda = \frac{1}{T} \int_{S_{\alpha\beta} \cap \Gamma} \delta \mathbf{r} \cdot (\boldsymbol{\sigma}_\lambda \cdot \boldsymbol{\nu}_\lambda) dS. \quad (96)$$

The change in entropy of the interface is given by the change in interfacial energy associated with the surface tension, $\gamma_{\alpha\beta}$, between the α and β -phases, so that

$$\delta S_{\alpha\beta} = \frac{\gamma_{\alpha\beta} \delta A_{\alpha\beta}}{T}. \quad (97)$$

The change in surface area can be expressed in terms of displacement (Landau and Lifshitz, 1959) by the expression

$$\delta A_{\alpha\beta} = \int_{S_{\alpha\beta} \cap \Gamma} \frac{\delta \mathbf{r} \cdot \boldsymbol{\nu}_{\alpha\beta}}{R_{\alpha\beta}} dS, \quad (98)$$

where $R_{\alpha\beta}$ is the mean radius of curvature of the $S_{\alpha\beta}$ -surface. It can be expressed in terms of the principal radii of curvature, $R_{\alpha\beta}^{(1)}$ and $R_{\alpha\beta}^{(2)}$, in the form

$$\frac{2}{R_{\alpha\beta}} = \frac{1}{R_{\alpha\beta}^{(1)}} + \frac{1}{R_{\alpha\beta}^{(2)}}. \quad (99)$$

It follows that

$$\delta S_{\alpha\beta} = \frac{1}{T} \gamma_{\alpha\beta} \int_{S_{\alpha\beta} \cap \Gamma} \frac{\delta \mathbf{r} \cdot \boldsymbol{\nu}_{\alpha\beta}}{R_{\alpha\beta}} dS. \quad (100)$$

The entropy variation is, therefore,

$$\delta S = \frac{1}{T} \int_{S_{\alpha\beta}} \delta \mathbf{r} \cdot \left\{ \boldsymbol{\sigma}_\alpha - \boldsymbol{\sigma}_\beta + \frac{\gamma_{\alpha\beta}}{R_{\alpha\beta}} \mathbf{I} \right\} \cdot \boldsymbol{\nu}_{\alpha\beta} dS, \quad (101)$$

where $\boldsymbol{\sigma}_\alpha$ and $\boldsymbol{\sigma}_\beta$ are the limit values of the stress tensors as the interface is approached. In order for the variation to vanish, we must have at every point on the interface

$$\boldsymbol{\sigma}_\alpha \cdot \boldsymbol{\nu}_{\alpha\beta} + \gamma_{\alpha\beta}/R_{\alpha\beta} = \boldsymbol{\sigma}_\beta \cdot \boldsymbol{\nu}_{\alpha\beta}. \quad (102)$$

If we now neglect shear stresses in the fluids, we obtain $\boldsymbol{\sigma}_\alpha = -p_\alpha \boldsymbol{\delta}$, and

$$p_\alpha - p_\beta = \gamma_{\alpha\beta}/R_{\alpha\beta}. \quad (103)$$

The above arguments can be extended to give conditions also across the interface between a fluid phase α and a solid phase s ,

$$\boldsymbol{\sigma}_\alpha \cdot \boldsymbol{\nu} = \boldsymbol{\sigma}_s \cdot \boldsymbol{\nu}. \quad (104)$$

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