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A two-phase model for compaction and damage
1. General Theory

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Abstract. A theoretical model for the dynamics of a simple two-phase mixture is presented. A classical averaging approach combined with symmetry arguments is used to derive the mass, momentum, and energy equations for the mixture. The theory accounts for surficial energy at the interface and employs a nonequilibrium equation to relate the rate of work done by surface tension to the rates of both pressure work and viscous deformational work. The resulting equations provide a basic model for compaction with and without surface tension. Moreover, use of the full nonequilibrium surface energy relation allows for isotropic damage, i.e., creation of surface energy through void generation and growth (e.g., microcracking), and thus a continuum description of weakening and shear localization. Applications to compaction, damage, and shear localization are investigated in two companion papers.

1. Introduction

The dynamics of two-component, or two-phase (and in general multiphase), media is a complex and well-studied field [see *Drew and Passman*, 1999] with innumerable natural applications to sediment and soil mechanics [*Biot*, 1941; *Hill et al.*, 1980; *Birchwood and Turcotte*, 1994; see *Furbish*, 1997, and references therein], glaciology [*Fowler*, 1984], oil recovery and magma dynamics [*McKenzie*, 1984; *Spiegelman*, 1993a, 1993b, 1993c], crystallization in metal alloys [*Ganesan and Poirier*, 1990], and slurries [*Loper*, 1992]. Analysis of dilatant plasticity [*Mathur et al.*, 1996], rate-and-state friction models of earthquake dynamics [*Segall and Rice*, 1995; *Sleep*, 1995, 1997, 1998], and void-volatile self-lubrication models of the generation of plate tectonics from mantle flow [*Bercovici*, 1998] also employ the concept of two phases by relating porosity to a weakening effect or a state variable.

One of the most complex issues in the mechanics of two-phase media concerns the physics of the interface between the phases [*Groenwald and Bedeaux*, 1995; *Osmolovski*, 1997]. Interface and surface dynamics is also a vital field for the study of rock mechanics and material science [*Jaeger and Cook*, 1979; *Atkinson*, 1987; *Atkinson and Meredith*, 1987]. One of the primary manifestations of an interface is its intrinsic surface energy, partially expressed as surface tension. Surface energy and tension are relevant both for melt dynamics in the process of crystallization [*Tiller*, 1991a, 1991b; *Lasaga*, 1998] and percolation under capillary forces [*Harte et al.*, 1993; *Stevenson*, 1986]. It is also generally recognized that the damage of materials involves the generation of a surface energy on newly developed cracks and voids [*Griffith*, 1921; *Jaeger and Cook*, 1979; *Atkinson*, 1987; *Atkinson and Meredith*, 1987].

The effects of surface tension have been considered for two-phase systems [*Drew*, 1971; *Drew and Segel*, 1971; *Stevenson*, 1986; *Ni and Beckerman*, 1991; *Straub*, 1994; *Groenwald and Bedeaux*, 1995; *Osmolovski*, 1997], although, to our knowledge, they have not been self-consistently incorporated in a closed, fully three-dimensional, two-phase continuum theory. In this paper we derive the simplest possible general equations for a two-phase medium, accounting for the possibility of surface free energy existing on the interface between the two media. Although this surface en-

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ergy is often considered to be in static equilibrium with the net work done by the pressure fields of the two phases [e.g., *Ni and Beckerman*, 1991], we propose a more general relation in which surface energy is generated through nonequilibrium energy sources such as deformational work. Thus the theory provides a simple model not only of compaction with and without surface tension but also of the creation of surface energy through deformation, and hence microcracking and damage. However, the theory is based on viscous fluid mechanics, and thus it is most applicable to viscous and/or long-timescale mantle-lithosphere processes, such as magma dynamics and plate boundary formation through ductile localization mechanisms.

Although some of the equations derived in this model differ little from those derived previously [*Drew*, 1971; *Drew and Segel*, 1971; *Loper and Roberts*, 1978; *Hills et al.*, 1983, 1992; *McKenzie*, 1984; *Fowler*, 1984, 1990a, 1990b; *Richter and McKenzie*, 1984; *Ribe*, 1985, 1987; *Bennon and Incropera*, 1987; *Scott*, 1988; *Scott and Stevenson*, 1989; *Ganesan and Poirier*, 1990; *Poirier et al.*, 1991; *Loper*, 1992; *Turcotte and Phipps Morgan*, 1992; *Spiegelman* 1993a, 1993b, 1993c; *Gidaspow*, 1994; *Schmeling*, 2000; see *Drew and Passman*, 1999], others are signficantly different or are entirely new. Thus it is necessary that the formalism for arriving at the theory be established; admittedly, this formalism is not in itself new, so its presentation will be as brief as possible. In the following subsections we will derive conservation laws, which, in two-phase theory, involve a particular averaging scheme [*Drew*, 1971; *Drew and Segel*, 1971; *Ganesan and Poirier*, 1990; *Ni and Beckerman*, 1991]. Although the averaging method has been discussed elsewhere, we will require it to carry out some of the derivation; thus we describe it by example, i.e., through consideration of the mixture's properties and the conservation of mass law.

To keep our theory as simple as possible, we make the following assumptions:

1. Both media have constant densities and are thus incompressible.

2. Both media behave as highly viscous fluids (such that inertia and acceleration are neglected, i.e., forces are always in balance), and their individual viscosities are constant.

3. The two-phase mixture remains isotropic, i.e., on average (see below for how the average is defined), pores and grains are not collectively elongated in a preferred direction. (Some discussion of anisotropy, however, is included in this development.)

Nevertheless, the two-phase mixture will have nonconstant effective density and viscosity. Other simplifying assumptions will be stated as necessary.

2. Mixture Properties

2.1. Phase Properties and Averaging

We define the two phases as fluid and matrix to be consistent with much of the classic literature on this topic. However, we derive all equations to maintain their symmetry; that is, until we make a symmetry-breaking assumption about an extreme difference between the fluid phase and matrix phase, they are strictly speaking both incompressible, constant-viscosity fluids, and thus how we label them should be irrelevant. Therefore an interchange of labels must result in the same equations. We will refer to this symmetry as "material invariance."

We define the fluid and matrix phases to have densities ρ_f and ρ_m and viscosities μ_f and μ_m, all of which are constant. The two phases have true (or microscopic) velocities, $\tilde{\mathbf{v}}_f$ and $\tilde{\mathbf{v}}_m$ within their respective volumes, and similarly for pressures and stresses. However, in a two-phase or mixture theory, we cannot know the location of every parcel of fluid or matrix; thus we must average all quantities over some volume; the size of this volume determines the validity of the continuum limit for two-phase theory. This limit is analogous to that for single-phase continuum theory in which the volume over which properties are averaged must be large enough to contain sufficient numbers of molecules but must also be small enough to distinguish gradients in properties. In two-phase theory the volume must be large enough to contain sufficient numbers of pores or grains but small enough to resolve gradients. As pore and grain sizes can become macroscopic, the volume size is potentially very constrained, and thus it is much easier to violate the two-phase continuum limit [*Bear*, 1988; *Furbish*, 1997; *Drew and Passman*, 1999].

Once the two materials, the matrix and fluid, are combined, the mixture has additional properties prescribed by a distribution function which locates pores of fluid or grains of matrix (Figure 1); we define this distribution function θ which is 1 inside the fluid pores and 0 in the matrix [*Drew*, 1971; *Drew and Segel*, 1971; *Fowler*, 1984; *Ganesan and Poirier*, 1990; *Ni and Beckerman*, 1991]. The function θ is used to average properties over fluid or matrix volumes. In particular, porosity, i.e., the volume fraction of fluid (assuming the matrix is saturated), is an average quantity defined as

$$\phi = \frac{1}{\delta V} \int_{\delta V} \theta dV, \tag{1}$$

where δV is the total volume of an element of mixture. The masses of fluid and matrix in the volume δV are thus the integrals of ρ_f and ρ_m over the fluid and matrix volumes, respectively

$$M_f = \int_{\delta V} \rho_f \theta dV \ , \quad M_m = \int_{\delta V} \rho_m (1-\theta) dV, \tag{2}$$

which, because the densities are constant, are simply $M_f = \phi \rho_f \delta V$ and $M_m = (1-\phi)\rho_m \delta V$. The fluid velocity averaged over the fluid volume is $\mathbf{v}_f$, defined such that

$$\phi \mathbf{v}_f = \frac{1}{\delta V} \int_{\delta V} \tilde{\mathbf{v}}_f \theta dV, \tag{3}$$

where $\mathbf{v}_f$ is often referred to as the interstitial velocity, while

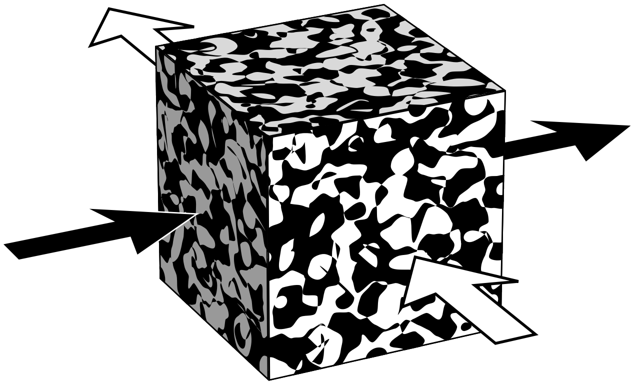

Figure 1. Schematic of a control volume δV with a mixture of fluid (white) and matrix (black). Shading also represents the distribution function θ which is 1 in the fluid and 0 in the matrix. The curve which marks the boundary between black and white as viewed in the figure is the intersection of the interface between the phases and the surface of the control volume, as denoted by C_i in (25). Arrows illustrate the flux of fluid and matrix mass, momentum or energy through exposures of fluid and matrix at the surface of the control volume.

$\phi \mathbf{v}_f$ is the Darcy velocity. The matrix velocity $\mathbf{v}_m$ is similarly defined such that

$$(1-\phi)\mathbf{v}_m = \frac{1}{\delta V}\int_{\delta V} \tilde{\mathbf{v}}_m (1-\theta) dV. \qquad (4)$$

Since the two media are assumed incompressible, their true velocities $\tilde{\mathbf{v}}_f$ and $\tilde{\mathbf{v}}_m$ are solenoidal ($\boldsymbol{\nabla}\cdot\tilde{\mathbf{v}}_f = \boldsymbol{\nabla}\cdot\tilde{\mathbf{v}}_m = 0$); however, the averaged velocities $\mathbf{v}_f$ and $\mathbf{v}_m$ are not solenoidal since they have been averaged over pore or grain volumes that are variable in space and time.

2.2. Interfacial Area Density

An additional property of the mixture concerns the fabric of the mixture which is specified by the location and orientation of the interface between the two phases. The interface location and orientation are given by $\boldsymbol{\nabla}\theta$, which is in essence a Dirac δ function, centered on the interface, times the unit normal to the interface (in fact, pointing from the matrix to the fluid, in the direction of increasing θ). Thus the net interface area within a volume δV is simply

$$\delta A_i = \int_{\delta V} |\boldsymbol{\nabla}\theta| dV. \qquad (5)$$

However, in a mixture formalism we cannot know the location and orientation of the interface between fluid and matrix, and thus we must define an averaged property. In this paper we assume isotropy of the interface (i.e., on average, it has no preferred direction) and that in the control volume δV, there is an average interfacial area per unit volume, $\alpha = \delta A_i/\delta V$ [see also *Ni and Beckerman*, 1991). Since the system is isotropic, we assume that this single quantity is sufficient to characterize the density of the interface. The area density α is necesarily a function of porosity since it must vanish when the medium becomes a single-phase system, i.e., when $\phi = 0$ or 1. As discussed by *Ni and Beckerman* [1991], one simple possibility is that $\alpha \sim \phi(1-\phi)$; however, we generalize this assumption to

$$\alpha = \alpha_o \phi^a (1-\phi)^b \ , \qquad (6)$$

where α_o, a, and b are assumed constants that depend on the material properties of the phases. Although the general theory presented here does not depend on the exact form of the function $\alpha(\phi)$ (and indeed, other forms of the function are possible), we adopt (6) in the following application papers [*Ricard et al.*, this issue; *Bercovici et al.*, this issue]. We next briefly consider the implications of the constant α_o, while the constants a and b are further constrained in section 2.2.3.

2.2.1. Constant $\boldsymbol{\alpha_o}$. The constant α_o is an important property throughout the development and application of this model; it has units of m^{-1} and is inversely related to characteristic pore and grain size. Although we cannot offer an exact demonstration of this relation, it can be understood by a very simple conceptual example [after *Spry*, 1983). We consider a volume where the pores and grains are the same shape and size for all porosities and these grains and pores fit together exactly; for simplicity, we choose a cubical volume with sides L and cubical pores and grains of side $d << L$. The total number of pores and grains together is $N_{\rm tot} = (L/d)^3$, and if we have N pores, then the porosity is $\phi = N/N_{\rm tot}$. For a small number of pores ($N \ll N_{\rm tot}$) the net interfacial surface area is $A_i = N 6 d^2$, while for a large number of pores (or small number of grains) where $N \rightarrow N_{\rm tot}$ we have $A_i = (N_{\rm tot} - N) 6 d^2$ (for example, with $N_{\rm tot} - 1$ pores, there is just one cubic grain of side d). Thus a symmetric formula that gives both limits for A_i would be $A_i = [N(N_{\rm tot} - N)/N_{\rm tot}] 6 d^2$, or since $N = N_{\rm tot}\phi$, $A_i = N_{\rm tot}\phi(1-\phi)6d^2$. The interface area per volume is

$$\alpha = \frac{A_i}{N_{\rm tot} d^3} = \frac{6}{d}\phi(1-\phi), \qquad (7)$$

which, by comparison to (6), implies that $\alpha_o = 6/d$ (and clearly values of a and b different from unity account for noncubic pore and grain shapes). Although this is a highly idealized example, it illustrates that α_o is characteristic of the inverse of pore or grain size d. For silicates, grain and pore sizes range from microns to milimeters [*Spry*, 1983], and thus α_o can be as much as 10^6 m^{-1}.

2.2.2. A note on anisotropy. Although we assume isotropy, a few words on extensions to anisotropy are warranted since one of the eventual applications of this theory involves cracked media which are distinctly anisotropic. Information about fabric anisotropy is necessarily related to interface orientation, and thus we expect that an averaged tensor property defining this fabric should involve $\boldsymbol{\nabla}\theta$. In general, anisotropic properties, such as various conductivities of laminae (e.g., alternating layers of conducting and insulating material), can be constructed from second-order dyads based on the normals to the laminae. Moreover, fabric anisotropy should also depend on interface area density since a region with zero area density should be isotropic. We therefore define a fabric tensor to involve dyads based on $\boldsymbol{\nabla}\theta$ and to recover, under isotropy, the area density α; one such obvious possibility is

$$\underline{\boldsymbol{\alpha}} = \frac{1}{\delta V}\int_{\delta V}\frac{\boldsymbol{\nabla}\theta\boldsymbol{\nabla}\theta}{|\boldsymbol{\nabla}\theta|}dV. \tag{8}$$

which is symmetric to insure real principal (eigen-) values. Obviously, the trace of this tensor is $Tr(\underline{\boldsymbol{\alpha}}) = \alpha$ and thus if the system is isotropic $\underline{\boldsymbol{\alpha}} = \frac{1}{3}\alpha\underline{\mathbf{I}}$, where $\underline{\mathbf{I}}$ is the identity matrix. (Note that a fabric tensor might also involve other components such as dyads of the interface tangent $\hat{\mathbf{r}}\times\boldsymbol{\nabla}\theta$, where $\hat{\mathbf{r}}$ is a unit vector directed away from an arbitrary coordinate origin.) We postulate that many potentially anisotropic properties of the mixture (e.g., permeability) should be related to $\underline{\boldsymbol{\alpha}}$. However, $\underline{\boldsymbol{\alpha}}$ involves five independent quantities in addition to α (six total), requiring additional closure relations. As even the isotropic theory is complex enough (as shown in this paper, it leads to 10 unknowns requiring as many equations), we will remark on anisotropy and $\underline{\boldsymbol{\alpha}}$ where they are likely to be included if desired but will not attempt to provide a rigorous anisotropic theory (see *Sleep* [1998] for discussion of anisotropy in rate-and-state theories of earthquake dynamics).

2.2.3. Interface curvature. As discussed in later sections, we consider surface tension on the interface, whose resulting force intriniscally involves interface curvature; it is thus useful to relate α (and $\underline{\boldsymbol{\alpha}}$) to the average curvature of the interface. If we assume isotropy and that α is indeed a function of ϕ, then one can show that $d\alpha/d\phi$ is related to the sum of the interface curvatures. This can be understood by a simple conceptual example (although it also arises generally from considerations of thermodynamics on an interface; see Appendix A2). Consider a model of an isotropic two-phase medium as being made up of spherical pores (or grains, although we will refer only to pores for simplicity), and that the distribution of sizes of pores is not extremely broad within a selected volume δV. At the simplest level, consider N spherical pores of one size, i.e., each with radius r; in this case each element of interface has two identical principal curvatures equal to $1/r$ (in contrast to, say, a cylinder of radius r, which also has two principal curvatures, but one is 0, while the other is $1/r$). Moreover, $\phi = N4\pi r^3/(3\delta V)$ and $\alpha = N4\pi r^2/\delta V$; thus $d\alpha/d\phi = (d\alpha/dr)/(d\phi/dr) = 2/r$, which equals the sum of the principal curvatures. (Although α/ϕ has dimensions similar to curvature, it is not the sum of the principal curvatures as can be seen in this example; one can also repeat the example with cylinders to see that $d\alpha/d\phi$ not α/ϕ properly represents the sum of curvatures.) If the volume δV has N spherical pores and the radius of the ith pore is r_i, then the average curvature is $\overline{1/r} = (1/N)\sum_{i=1}^{N} 1/r_i$, the porosity is $\phi = [4\pi/(3\delta V)]\sum_{i=1}^{N} r_i^3 = N4\pi\overline{r^3}/(3\delta V)$, and $\alpha = (4\pi/\delta V)\sum_{i=1}^{N} r_i^2 = N4\pi\overline{r^2}/\delta V$. If the distribution in sizes of pores is sufficiently narrow within the volume (which can more or less be selected arbitrarily), then $\overline{1/r} \approx 1/\overline{r}$, $\overline{r^n} \approx \overline{r}^n$ (where n is 2 or 3), and thus $d\alpha/d\phi$ will still be roughly the sum of the average curvatures. Therefore the sum of interface curvatures is represented by $d\alpha/d\phi$ (again, see also Appendix A2).

Adopting (6), we find that

$$\frac{d\alpha}{d\phi} = \alpha_o a\phi^{a-1}(1-\phi)^{b-1}(1-\frac{\phi}{\phi_c}) \tag{9}$$

where $\phi_c = a/(a+b)$. It is clear that the sign and magnitude of the average interface curvature depend on porosity. When ϕ is very small, the medium contains mostly small dispersed pores of fluid, and thus the average curvature is large and positive (again, curvature is defined here to be positive when the interface is concave to, or encloses, the fluid and negative when it is convex to the fluid or encloses matrix); when ϕ is close to 1, the medium contains small dispersed grains of matrix, and the curvature is thus large and negative. Indeed, in the limits that $\phi \to 0$ and $\phi \to 1$ the average curvature should be infinite in magnitude. This suggests that both a and b are < 1. Moreover, the change in sign of the curvature occurs at $\phi = \phi_c = a/(a+b)$. If the system is purely symmetric, then $a = b$ and the change in sign of curvature is at $\phi = 1/2$. However, for real systems, a and b can be very different. For foams (in which the air is the fluid phase) the curvature remains positive to very large porosities, suggesting that $a \gg b$. For silicate melts, interconnectedness of melt (i.e., dihedral angles $< 60^o$) and even disaggregation at low melt fractions [see *Harte et al.*, 1993] suggest a behavior opposite to foam; that is, the curvature becomes negative at low porosity, or $a \ll b$.

As indicated above, surfaces are generally defined to have two distinct principal curvatures locally (i.e., on an infinitesimal area element) and the sum of these curvatures determines the surface tension force [*Landau and Lifshitz,* 1987]. With isotropy and averaging, these curvatures are either the same or (because of random orientiation of elongate or laminar grains and pores) their volume averages are the same. However, with anisotropy due to coherent alignment of elongate or laminar grains and pores, the distinct curvatures would be manifested as a fabric in the medium, even after averaging. Since the averaging is over a volume containing whole pores and grains, it involves all the possible curvatures on the surface area of a pore (or grain), not just the two local curvatures on an area element. Thus the volume average of the curvature of an interface should have at least three characteristic principal curvatures (e.g., consider ellipsoidal pores) which we assume are extractable from the fabric tensor $\underline{\boldsymbol{\alpha}}$, in particular $d\underline{\boldsymbol{\alpha}}/d\phi$. We assume that the three principal curvatures are the principal values of $d\underline{\boldsymbol{\alpha}}/d\phi$; for example, the sum of these principal curvatures is a tensor invariant equal to $Tr(d\underline{\boldsymbol{\alpha}}/d\phi) = d\alpha/d\phi$, which is consistent with our isotropic formulation for the sum of the principal curvatures.

3. Conservation of Mass

Changes of fluid mass inside the volume δV depend on the loss of fluid through the surface of the volume and, if appropriate, the rate at which matrix is converted to fluid and vice versa (e.g., by melting and solidification). For this paper we are not concerned with transfer of mass between phases, and thus we neglect this conversion rate, which is straightforward to include (see section 6) and has been discussed extensively in previous studies [*Hills et al.*, 1983, 1992; *McKenzie*, 1984; *Spiegelman*, 1993a, 1993b, 1993c]. The rate of change of fluid mass is thus

$$\frac{\partial}{\partial t}\int_{\delta V}\rho_f\theta dV = -\int_{\delta A}\rho_f\tilde{\mathbf{v}}_f\cdot\hat{\mathbf{n}}\theta dA \qquad (10)$$

where the area integral on the right-hand side represents the net rate of expulsion of fluid through pores exposed on or intersecting the volume's surface area δA (Figure 1) and $\hat{\mathbf{n}}$ is the unit normal of the area element dA. Clearly, we wish to express the area integral in terms of the divergence of the average velocity $\mathbf{v}_f$ and the porosity ϕ. However, this is only permissible under certain conditions relating to the size of the volume δV. In particular, consider a cubic volume centered on the point (x, y, z) and extending over the ranges $x-\delta x/2 \le x \le x+\delta x/2$, $y-\delta y/2 \le y \le y+\delta y/2$, $z-\delta z/2 \le z \le z+\delta z/2$, where $\delta V = \delta x\delta y\delta z$. We can examine the area integral over just one face of this volume, say at the face parallel to the $y-z$ plane and located at $x+\delta x/2$. We first require that any integral (at any x) over the area $\delta y\delta z$ includes a sufficient sampling of pores in order to be continuous in x, and thus the area $\delta y\delta z$ cannot be too small. However, we also require that δx is small enough for this integral to vary no more than linearly in x. With these limitations, and applying the integral mean-value theorem to linear functions, we may write

$$\begin{aligned}&\left[\int_{z-\delta z/2}^{z+\delta z/2}\int_{y-\delta y/2}^{y+\delta y/2}\tilde{v}_{f_x}\theta dydz\right]_{x+\delta x/2}\\&=\frac{1}{\delta x}\int_{x}^{x+\delta x}\left[\int_{y-\delta y/2}^{y+\delta y/2}\int_{z-\delta z/2}^{z+\delta z/2}\tilde{v}_{f_x}\theta dydz\right]dx\\&=v_{f_x}(x+\delta x/2,y,z)\phi(x+\delta x/2,y,z)\delta y\delta z. \qquad (11)\end{aligned}$$

This gives a practical example of the size constraints on δx, δy, and δz. For this integral the area $\delta y\delta z$ cannot be too small, but δx cannot be too large; considering the other area integrals, the same constraint exists for all permutations of δx, δy, and δz, and thus the length segments can be neither too big nor too small.

The integrated fluxes through the other five faces of the volume lead to similar results as in (11); the sum of all the resulting area integrals, divided by δV, can be replaced with a divergence, assuming small enough δx, δy, and δz, and thus (10) becomes

$$\frac{\partial\phi}{\partial t}+\boldsymbol{\nabla}\cdot[\phi\mathbf{v}_f]=0. \qquad (12)$$

(However, since δx, δy, and δz are not, in fact, infinitesimal, spatial differential operators in two-phase theory are only approximations of their normal continuum counterparts.) An identical treatment can be made for the mass of matrix material leading to the symmetric equation

$$\frac{\partial(1-\phi)}{\partial t}+\boldsymbol{\nabla}\cdot[(1-\phi)\mathbf{v}_m]=0. \qquad (13)$$

Material invariance between (12) and (13) means that replacement of f by m, and ϕ by $1-\phi$, in (12) gives (13) and vice-versa.

We may also define mixture and difference quantities, given, for any general quantity q, by

$$\bar{q}=\phi q_f+(1-\phi)q_m, \qquad \Delta q = q_m - q_f\ , \qquad (14)$$

respectively; $\bar{q}$ is, of course, materially invariant or symmetric, while Δq is antisymmetric. We can thus combine the mass equations in two ways, i.e., by first adding (12) and (13) to yield

$$\boldsymbol{\nabla}\cdot\bar{\mathbf{v}}=0 \qquad (15)$$

(where $\bar{\mathbf{v}}$ is the mixture or mean velocity) and second by finding $(1-\phi)\times$ (12) $-\phi\times$ (13), to obtain

$$\frac{\partial\phi}{\partial t}+\bar{\mathbf{v}}\cdot\boldsymbol{\nabla}\phi=\boldsymbol{\nabla}\cdot[\phi(1-\phi)\Delta\mathbf{v}] \qquad (16)$$

(where $\Delta\mathbf{v}$ is the velocity difference or phase separation velocity). An interchange of the implicit subscripts f and m leaves these equations unchanged.

The entire development above is, of course, fairly trivial and has been presented innumerable times and in various forms in previous papers and texts [*Drew*, 1971; *Drew and Segel*, 1971; *McKenzie*, 1984; *Ganesan and Poirier*, 1990; *Ni and Beckerman*, 1991]; we have only provided it to demonstrate the formalism, as well as the necessary assumptions, for obtaining further conservation laws, which are gradually more complex and novel.

Before proceeding to the other conservation laws, it is necessary to establish one more relation regarding volume integrals involving products of fluid or matrix velocity and $\boldsymbol{\nabla}\theta$; these, in particular, arise when we consider stress tensors. Since the individual phases are assumed incompressible, their true velocities are solenoidal ($\boldsymbol{\nabla}\cdot\tilde{\mathbf{v}}_f=\boldsymbol{\nabla}\cdot\tilde{\mathbf{v}}_m=0$). Therefore the average of the divergence of the fluid velocity over the fluid volume is zero, leading to

$$\begin{aligned}&\frac{1}{\delta V}\int_{\delta V}(\boldsymbol{\nabla}\cdot\tilde{\mathbf{v}}_f)\theta dV\\&=\frac{1}{\delta V}\int_{\delta V}[\boldsymbol{\nabla}\cdot(\tilde{\mathbf{v}}_f\theta)-\tilde{\mathbf{v}}_f\cdot\boldsymbol{\nabla}\theta]dV=0 \qquad (17)\end{aligned}$$

Given the same constraints and assumptions leading from (10) to (12), this relation yields

$$\frac{1}{\delta V}\int_{\delta V}\tilde{\mathbf{v}}_f\cdot\boldsymbol{\nabla}\theta dV=\boldsymbol{\nabla}\cdot[\phi\mathbf{v}_f] \tag{18}$$

We arrive by similar arguments at the symmetric relation for the matrix velocity field

$$\frac{1}{\delta V}\int_{\delta V}\tilde{\mathbf{v}}_m\cdot\boldsymbol{\nabla}(1-\theta)dV=\boldsymbol{\nabla}\cdot[(1-\phi)\mathbf{v}_m] \tag{19}$$

Both (18) and (19) are obviously related to changes in porosity through (12) and (13).

4. Momentum Equations

For simplicity, we assume (along with many other studies, e.g., *McKenzie* [1984]; *Richter and McKenzie* [1984]; *Spiegelman* [1993a, 1993b, 1993c]) that both fluid and matrix undergo creeping flow; that is, their forces are always in balance and thus acceleration and inertia are neglected. An extension of this to higher Reynolds number systems is tractable [*Loper and Roberts*, 1978; *Hills et al.*, 1983, 1992; *Bennon and Incroprera*, 1987; *Ganesan and Poirier*, 1990; *Ni and Beckerman*, 1991; *Loper*, 1992].

The total force on the fluid phase is the sum of surface and body forces acting on the fluid part of the volume; since these forces are assumed to balance, we arrive at

$$0=\int_{\delta A}\underline{\tilde{\boldsymbol{\sigma}}}_f\cdot(\theta\hat{\mathbf{n}}dA)+\int_{\delta A_i}\underline{\mathbf{H}}_f\cdot\hat{\mathbf{n}}_i dA+\int_{\delta V}\rho_f\mathbf{g}\theta dV, \tag{20}$$

where $\underline{\tilde{\boldsymbol{\sigma}}}_f$ is the true total stress tensor in the fluid, $\mathbf{g}$ is the fluid body force per unit mass, $\underline{\mathbf{H}}_f$ is the effective interfacial stress tensor, and A_i and $\hat{\mathbf{n}}_i$ are the area and unit normal of the fluid-matrix interface (and, obviously, $\hat{\mathbf{n}}_i\equiv-\boldsymbol{\nabla}\theta/|\boldsymbol{\nabla}\theta|$). The first integral on the right-hand side of (20) represents the net surface force acting on the fluid that is exposed at the surface of the volume δV, while the second integral represents the net interfacial force, that is, the force acting on the fluid at the fluid-matrix interface (also referred to as the interaction force [*Drew and Segel*, 1971; *McKenzie*, 1984]). Given that the fluid is an incompressible isoviscous medium, then

$$\underline{\tilde{\boldsymbol{\sigma}}}_f=-\tilde{P}_f\underline{\mathbf{I}}+\underline{\tilde{\boldsymbol{\tau}}}_f, \tag{21}$$

where $\tilde{P}_f$ is the true fluid pressure and

$$\underline{\tilde{\boldsymbol{\tau}}}_f=\mu_f\left(\boldsymbol{\nabla}\tilde{\mathbf{v}}_f+[\boldsymbol{\nabla}\tilde{\mathbf{v}}_f]^t\right) \tag{22}$$

is the true viscous deviatoric stress tensor ($[\ ]^t$ implies tensor transpose). Moreover, we assume for now that the body force per mass is the same for both phases and is entirely gravitational: $\mathbf{g}=-g\hat{\mathbf{z}}$, where g is gravitational acceleration. We can use previous arguments involving area integrals (again, see the discussion surrounding (11)) to rewrite (20) as

$$0=-\boldsymbol{\nabla}[\phi P_f]+\boldsymbol{\nabla}\cdot[\phi\underline{\boldsymbol{\tau}}_f]-\rho_f\phi g\hat{\mathbf{z}}+\mathbf{h}_f, \tag{23}$$

where P_f is the pressure averaged over the fluid volume and $\underline{\boldsymbol{\tau}}_f$ is the viscous stress tensor averaged over the fluid volume. The interaction force $\mathbf{h}_f$ results from forces acting on the fluid across the interface. A similar development for the matrix results in

$$\begin{aligned}0=&-\boldsymbol{\nabla}[(1-\phi)P_m]+\boldsymbol{\nabla}\cdot[(1-\phi)\underline{\boldsymbol{\tau}}_m]\\&-\rho_m(1-\phi)g\hat{\mathbf{z}}+\mathbf{h}_m\end{aligned} \tag{24}$$

where P_m and $\underline{\boldsymbol{\tau}}_m$ are the average pressure and stress in the matrix, while the interaction force $\mathbf{h}_m$ results from forces acting on the matrix across the interface.

Given the complexity of the interface between the phases, precise knowledge of its orientation and location using the continuum (i.e., volume averaging) approach is not possible. Thus the interfacial forces $\mathbf{h}_f$ and $\mathbf{h}_m$ are difficult to quantify and have been the subject of much discussion in the two-phase literature [*Drew and Segel*, 1971; *McKenzie*, 1984; *Ganesan and Poirier*, 1990]. They are generally treated as effective body force vectors, which, in the absence of surface tension, are equal and opposite [*Drew and Segel*, 1971; *McKenzie*, 1984]. However, they are not equal if the interface has an intrinsic surface free energy and tension. The surface tension force acting on a control volume δV is apparent when considering the total force on the whole volume δV of the fluid-matrix mixture, which leads to

$$0=-\boldsymbol{\nabla}\bar{P}+\boldsymbol{\nabla}\cdot\underline{\bar{\boldsymbol{\tau}}}-\bar{\rho}g\hat{\mathbf{z}}+\frac{1}{\delta V}\int_{C_i}\tilde{\sigma}\hat{\mathbf{t}}d\ell \tag{25}$$

(see (14) for the definition of mixture quantities $\bar{P}$, $\underline{\bar{\boldsymbol{\tau}}}$, and $\bar{\rho}$), where $\tilde{\sigma}$ is the true surface tension (with units of N m^{-1}), which differs from surface free energy (denoted by ξ_i in section 5 and Appendix A2), C_i is the curve which traces the intersection between the interface and the surface of the control volume (see Figure 1), $d\ell$ is a line element along C_i, and $\hat{\mathbf{t}}$ is a unit vector that is both normal to the line element $d\ell$ and tangent to the interface (Figure 2)[see also *Drew and Segel*, 1971]. However, we seek the effective surface tension force acting on an element of surface area dA (a small segment of δA); the element dA itself contains the intersection curve c_i, which is a small portion of C_i. As shown in Appendix A1, we can, with isotropy, replace $\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}d\ell$ with $\sigma\alpha\hat{\mathbf{n}}dA$, where σ is a reduced surface tension (the reduction is typically $O(1)$; see Appendix A1). Thus summing over all area elements on δA, the net surface tension force per unit volume becomes $(1/\delta V)\int_{\delta A}\sigma\alpha\hat{\mathbf{n}}dA$, in which case the net force equation assumes the form

$$0=-\boldsymbol{\nabla}\bar{P}+\boldsymbol{\nabla}\cdot\underline{\bar{\boldsymbol{\tau}}}-\bar{\rho}g\hat{\mathbf{z}}+\boldsymbol{\nabla}(\sigma\alpha). \tag{26}$$

The last term in (26) is an effective surface tension body force on the total mixture. (If we were to allow for anisotropy, then $\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}\,d\ell$ would be most likely related to $\sigma\underline{\boldsymbol{\alpha}}\cdot\hat{\mathbf{n}}dA$, in which case, the surface tension force would be replaced by a term proportional to $\boldsymbol{\nabla}\cdot(\sigma\underline{\boldsymbol{\alpha}})$; see also *Drew and Segel* [1971].)

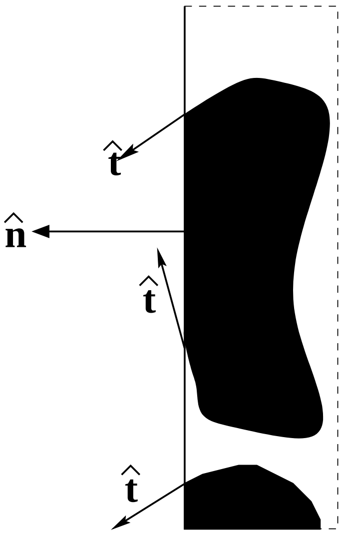

Figure 2. Side view of a cross section of a segment of the mixture adjacent to the surface of a control volume (as shown in Figure 1); the solid line on the left of the rectangular sample shows the surface boundary, while the dashed boundaries indicate that the sample is connected to the rest of the volume. Black and white material is the same as in Figure 1; that is, they represent either fluid or matrix. The unit tangents to the interface (at the intersection with the surface of the control volume) $\hat{\mathbf{t}}$ and unit normal to the surface of the control volume $\hat{\mathbf{n}}$ are illustrated; see text surrounding (25) and (26).

The force equations for each phase, (23) and (24), must sum to equal (26), indicating that

$$\mathbf{h}_f + \mathbf{h}_m = \boldsymbol{\nabla}(\sigma\alpha) \qquad (27)$$

[see also *Drew and Segel* [1971]. Equation (27) might be easily misconstrued as a stress jump condition since it appears similar to the jump condition for the interface between two fluids with surface tension [*Landau and Lifshitz*, 1987; *Leal*, 1992]. Such a jump condition is required at an internal boundary whose shape, location, and orientiation are known and that separates two adjacent but distinct fluid volumes that do not individually fill the entire domain. Given the continuum approach of two-phase theory, however, the specific location and orientation of the interface are unknown; the interface as well as the two phases are treated as continuous quantities that exist at all points in the domain. (Even if anisotropy is allowed, the tensor $\underline{\boldsymbol{\alpha}}$ gives only the average orientation of fabric due to the interface but not the location and orientation of the interface itself.) Thus the two-phase equations do not require an internal boundary condition, and the inappropriate imposition of such a condition would lead to an overdetermined problem. Therefore (27) does not indicate that there is a jump in the interaction forces but rather that the interaction forces themselves each contain some component of the surface tension force. Since surface tension acts through the common interface between fluid and matrix, then the volume-averaged, effective body force $\boldsymbol{\nabla}(\sigma\alpha)$ acts equally on equal-sized particles of fluid or matrix (i.e., it does not act differently on the two phases as does, say, the gravitational body force); we thus assume that at any point (or infinitesimal volume) in the mixture a fraction ϕ of this force acts on the fluid, while a fraction $1-\phi$ acts on the matrix. We therefore write

$$\mathbf{h}_f = \boldsymbol{\eta} + \phi\boldsymbol{\nabla}(\sigma\alpha) \qquad (28)$$

$$\mathbf{h}_m = -\boldsymbol{\eta} + (1-\phi)\boldsymbol{\nabla}(\sigma\alpha) \qquad (29)$$

where $\boldsymbol{\eta}$ is the component of the interaction forces that act equally and oppositely to each other; (28) and (29) automatically satisfy (27).

The force $\boldsymbol{\eta}$ has few constraints. By material invariance, $\boldsymbol{\eta}$ has to be a function of vector variables that are antisymmetric to a switch of the subscripts f and m, such as $\Delta\mathbf{v}$ and $\boldsymbol{\nabla}\phi$. Moreover, $\boldsymbol{\eta}$ must account for (1) the viscous interaction due to relative motion between the fluid and matrix and (2) pressure acting at the interface. The simplest viscous interaction force that preserves Galilean invariance (frame independence) is $c(\mathbf{v}_m - \mathbf{v}_f) = c\Delta\mathbf{v}$, where c is a scalar to be discussed further below [*Drew and Segel*, 1971; *McKenzie*, 1984]. The pressure contribution to the interfacial force must allow for equilibrium (no motion) when pressure is constant everywhere; for example, at least a portion of this force must cancel the part of the pressure force term in (23) that goes as $-P_f\boldsymbol{\nabla}\phi$ (and similarly for (24)). Therefore the most basic form of the interface force is

$$\boldsymbol{\eta} = c\Delta\mathbf{v} + P^*\boldsymbol{\nabla}\phi, \qquad (30)$$

where P^* is some averaged pressure that must be the same in each phase and is invariant to a switch of f and m. In general, we write $P^* = \gamma P_f + (1-\gamma)P_m$, where γ is some unknown weighting that is ≤ 1 and that, like ϕ, switches to $1-\gamma$ if f and m are switched. (Note that in writing P^* as a function of P_f and P_m, we assume that the interfacial average pressures are linearly dependent on the average pressures in each phase; see *Drew and Passman* [1999] for a discussion of interfacial pressure.) Also, if the system were anisotropic, the relation for $\boldsymbol{\eta}$ would need to be adjusted; see the comment at the end of section 4.3.

It is important to recognize that $\boldsymbol{\eta}$ represents the equal and opposite force of one phase against the other, not the force of either phase against surface tension on the interface. In fact, one can see by (26) that all the other forces involving $\boldsymbol{\nabla}\bar{P}$ and $\boldsymbol{\nabla}\cdot\bar{\underline{\tau}}$, etc. work against the surface tension force $\boldsymbol{\nabla}(\sigma\alpha)$. (Indeed, the correct stress jump condition arises from integrating (26) about a vanishingly thin volume centered on the interface, accounting for that the fact that α becomes a Dirac δ function centered on the interface (see (5)), not by integrating (27) about the interface.) Thus the forces $\mathbf{h}_f$ and $\mathbf{h}_m$ include surface tension, while all the other forces potentially balance surface tension.

Therefore, upon substituting

$$\mathbf{h}_f = c\Delta\mathbf{v} + [\gamma P_f + (1-\gamma)P_m]\boldsymbol{\nabla}\phi + \phi\nabla(\sigma\alpha) \qquad (31)$$

$$\mathbf{h}_m = -c\Delta\mathbf{v} - [\gamma P_f + (1-\gamma)P_m]\boldsymbol{\nabla}\phi + (1-\phi)\nabla(\sigma\alpha) \quad (32)$$

into (23) and (24), we obtain (after some rearrangement)

$$\begin{aligned} 0 = &-\phi\left[\boldsymbol{\nabla}P_f + \rho_f g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot\left[\phi\underline{\boldsymbol{\tau}}_f\right] \\ &+ c\Delta\mathbf{v} + (1-\gamma)\Delta P\boldsymbol{\nabla}\phi + \phi\boldsymbol{\nabla}(\sigma\alpha) \end{aligned} \quad (33)$$

$$\begin{aligned} 0 = &-(1-\phi)\left[\boldsymbol{\nabla}P_m + \rho_m g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot\left[(1-\phi)\underline{\boldsymbol{\tau}}_m\right] \\ &- c\Delta\mathbf{v} + \gamma\Delta P\boldsymbol{\nabla}\phi + (1-\phi)\boldsymbol{\nabla}(\sigma\alpha) \end{aligned} \quad (34)$$

We can estimate γ by considering the conditions for no motion; this requires zero velocities, zero nonhydrostatic pressure gradients, zero viscous stresses, and a constant σ (since a gradient in surface tension in a viscous medium can only be balanced by viscous stresses; see *Landau and Lifshitz*, 1987; *Leal*, 1992). In this case, (33) and (34) become

$$(1-\gamma)\Delta P\boldsymbol{\nabla}\phi + \phi\sigma\boldsymbol{\nabla}\alpha = 0 \quad (35)$$

$$\gamma\Delta P\boldsymbol{\nabla}\phi + (1-\phi)\sigma\boldsymbol{\nabla}\alpha = 0, \quad (36)$$

which can only both be true if $\gamma = 1-\phi$.

On the assumption that $\gamma = 1-\phi$ for all situations our equations become

$$\begin{aligned} 0 = &-\phi\left[\boldsymbol{\nabla}P_f + \rho_f g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot\left[\phi\underline{\boldsymbol{\tau}}_f\right] \\ &+ c\Delta\mathbf{v} + \phi\left[\Delta P\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}(\sigma\alpha)\right] \end{aligned} \quad (37)$$

$$\begin{aligned} 0 = &-(1-\phi)\left[\boldsymbol{\nabla}P_m + \rho_m g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot\left[(1-\phi)\underline{\boldsymbol{\tau}}_m\right] \\ &- c\Delta\mathbf{v} + (1-\phi)\left[\Delta P\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}(\sigma\alpha)\right]. \end{aligned} \quad (38)$$

The force equations in the form of (37) and (38) are by no means complete since there are various issues that remain to be developed, such as the nature of the surface tension force, the form of the volume-averaged viscous stresses $\underline{\boldsymbol{\tau}}_f$ and $\underline{\boldsymbol{\tau}}_m$, the meaning of c, etc. We will deal with these sequentially.

4.1. Surface Tension Force and Interface Equilibrium

As discussed in section 2.2 the interface area density α is assumed a function of ϕ wherein $d\alpha/d\phi$ is the sum of average interface curvatures. With this assumption the surface tension body force in (26) becomes

$$\boldsymbol{\nabla}(\sigma\alpha) = \sigma\frac{d\alpha}{d\phi}\boldsymbol{\nabla}\phi + \alpha\boldsymbol{\nabla}\sigma. \quad (39)$$

The first term on the right-hand side of (39) represents the surface tension force due to interface curvature, while the second term is a force due to gradients in σ itself which result from temperature fluctuations (or gradients in surfactants; *Landau and Lifshitz*, 1987; *Leal*, 1992). Gradients in σ yield effects such as Marangoni convection wherein temperature anomalies in an exposed, thin fluid layer cause imbalances in surface tension at the layer's free boundary which in turn drive motion (see review by *Berg et al.* [1966]).

In the case of no motion, as in (35) or (36) using $\gamma = 1-\phi$, there can be no gradient in σ (which can only be balanced by viscous stresses in a fluid [*Landau and Lifshitz*, 1987; *Leal*, 1992]), and the force equations yield the equilibrium surface tension (Laplace's) condition (assuming the force balance holds for all $\boldsymbol{\nabla}\phi$)

$$P_f - P_m = \sigma\frac{d\alpha}{d\phi} \quad (40)$$

(see also Appendix A2). However, we must emphasize this condition is only true when the system is static or quasi-static, adiabatic, and in equilibrium; a more general condition will be explored in section 5.

4.2. Average Viscous Stress Tensors

To obtain a closed theory, it is necessary to express the average viscous stress tensors $\underline{\boldsymbol{\tau}}_f$ and $\underline{\boldsymbol{\tau}}_m$ in terms of average velocities $\mathbf{v}_f$ and $\mathbf{v}_m$. While the assumption that these stresses obey the constitutive laws for single-phase media [e.g., *Loper and Roberts*, 1978; *McKenzie*, 1984; *Loper*, 1992] is somewhat ad hoc, we can provide some constraints which partially justify such an approach.

By our definition of volume averaging, the average viscous fluid stress $\underline{\boldsymbol{\tau}}_f$ is given by

$$\phi\underline{\boldsymbol{\tau}}_f = \mu_f\frac{1}{\delta V}\int_{\delta V}\left(\boldsymbol{\nabla}\tilde{\mathbf{v}}_f + [\boldsymbol{\nabla}\tilde{\mathbf{v}}_f]^t\right)\theta dV \quad (41)$$

given that μ_f is assumed constant. Derivation of the relation between $\underline{\boldsymbol{\tau}}_f$ and $\mathbf{v}_f$ requires an evaluation of the integral of the true velocity gradients; by considering one gradient term we can write (again given the same assumptions associated with (11))

$$\begin{aligned} \frac{1}{\delta V}\int_{\delta V}(\boldsymbol{\nabla}\tilde{\mathbf{v}}_f)\theta dV &= \frac{1}{\delta V}\int_{\delta V}\left[\boldsymbol{\nabla}(\theta\tilde{\mathbf{v}}_f) - (\boldsymbol{\nabla}\theta)\tilde{\mathbf{v}}_f\right]dV \\ &= \boldsymbol{\nabla}(\phi\mathbf{v}_f) - \frac{1}{\delta V}\int_{\delta V}(\boldsymbol{\nabla}\theta)\tilde{\mathbf{v}}_f dV. \end{aligned} \quad (42)$$

The other velocity gradient term can be treated identically, leading to

$$\phi\underline{\boldsymbol{\tau}}_f = \mu_f\left\{\boldsymbol{\nabla}(\phi\mathbf{v}_f) + [\boldsymbol{\nabla}(\phi\mathbf{v}_f)]^t - (\underline{\mathbf{U}}_f + \underline{\mathbf{U}}_f^t)\right\}, \quad (43)$$

where

$$\underline{\mathbf{U}}_f = \frac{1}{\delta V}\int_{\delta V}(\boldsymbol{\nabla}\theta)\tilde{\mathbf{v}}_f dV. \quad (44)$$

The tensor $\underline{\mathbf{U}}_f$ contains bulk information about the fluid velocity at the interface; its evaluation is by no means trivial and has been given a variety of treatments [*Ganesan and Poirier*, 1990; *Ni and Beckerman*, 1991]. Although $\underline{\mathbf{U}}_f$ cannot be solved exactly in terms of average velocities, there are several fundamental constraints that can help us estimate its form:

1. $\underline{\mathbf{U}}_f$ must contain a term to insure that the stress tensor $\underline{\boldsymbol{\tau}}_f$ is Galilean invariant. In particular, it must have a part that depends on $(\boldsymbol{\nabla}\phi)\mathbf{u}_f$, where $\mathbf{u}_f$ is some as yet undefined

velocity; in this case, the stress terms dependent on velocity in (43) will appear as $(\boldsymbol{\nabla}\phi)(\mathbf{v}_f - \mathbf{u}_f)$ thereby removing the velocity of the frame of reference.

2. The trace of $\underline{\mathbf{U}}_f$ is given by (18) and thus

$$Tr(\underline{\mathbf{U}}_f) = \phi \boldsymbol{\nabla} \cdot \mathbf{v}_f + \mathbf{v}_f \cdot \boldsymbol{\nabla}\phi. \tag{45}$$

3. The whole stress tensor $\underline{\boldsymbol{\tau}}_f$ itself must have zero trace; that is, it remains the deviatoric stress even after volume averaging. This is required because regardless of how we do any volume averaging, the fluid and matrix are always incompressible, and thus when the mixture is exposed to a uniform isotropic stress, it should not undergo compression and only its pressure should increase.

4. Since $\underline{\mathbf{U}}_f$ is linear in $\tilde{\mathbf{v}}_f$ and θ, it is reasonable to expect that it be linear in $\mathbf{v}_f$ and ϕ (as also suggested by (45)).

5. $\underline{\mathbf{U}}_f$ must contain unique terms; that is, it cannot only be made up of terms that merely cancel all of $\boldsymbol{\nabla}(\phi\mathbf{v}_f)$, thus leading to a null stress tensor $\underline{\boldsymbol{\tau}}_f$. In other words, although $\underline{\mathbf{U}}_f = \boldsymbol{\nabla}(\phi\mathbf{v}_f)$ would satisfy all the previous constraints, it would also lead to $\underline{\boldsymbol{\tau}}_f = 0$, which is unacceptable.

6. Finally, any stress tensor $\underline{\boldsymbol{\tau}}_f$ resulting from the choice of $\underline{\mathbf{U}}_f$ must have a positive definite contribution to the dissipation function, i.e., $\boldsymbol{\nabla}\mathbf{v}_f : \underline{\boldsymbol{\tau}}_f \geq 0$, in order to satisfy the second law of thermodynamics; see section 5 for discussion of dissipation.

The simplest (but by no means unique) form of $\underline{\mathbf{U}}_f$ that satisfies these six basic constraints is

$$\underline{\mathbf{U}}_f = (\boldsymbol{\nabla}\phi)\mathbf{v}_f + \frac{1}{3}\phi\boldsymbol{\nabla}\cdot\mathbf{v}_f\underline{\mathbf{I}}. \tag{46}$$

This leads to a stress tensor given by

$$\phi\underline{\boldsymbol{\tau}}_f = \phi\mu_f\left(\boldsymbol{\nabla}\mathbf{v}_f + [\boldsymbol{\nabla}\mathbf{v}_f]^t - \frac{2}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_f\underline{\mathbf{I}}\right), \tag{47}$$

which is, of course, the simple deviator for nonsolenoidal velocity fields and is thus intuitively appealing. By similar arguments, and by symmetry, we arrive at the relation for the average matrix stress tensor

$$(1-\phi)\underline{\boldsymbol{\tau}}_m = (1-\phi)\mu_m\left(\boldsymbol{\nabla}\mathbf{v}_m + [\boldsymbol{\nabla}\mathbf{v}_m]^t - \frac{2}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_m\underline{\mathbf{I}}\right). \tag{48}$$

Neither (47) nor (48) explicitly contain the bulk viscosity term used by *McKenzie* [1984] since we have precluded compression under a uniform isotropic stress. However, isotropic compaction is allowable if the two phases experience different isotropic stresses; for example, the matrix is isotropically loaded but the fluid is left free to escape (D. McKenzie, personal communication, 2000); as discussed in section 5 (see the explanation surrounding (68)), this process is treated through the pressure difference ΔP instead of through a bulk viscosity effect.

The constitutive laws (47) and (48) are somewhat simpler than those arrived at by various workers [*Ishii*, 1975; *Ni and Beckerman*, 1991] and not very different from what others [*Loper and Roberts*, 1978; *McKenzie*, 1984] have assumed would be the constitutive laws. However, while (47) and (48) are not derived uniquely, they are arrived at more rigorously than usual, and their deduction from the above considerations partially justifies their simple form. Finally, we briefly note that if we were to consider anisotropy it undoubtedly occurs in the tensor $\underline{\mathbf{U}}_f$ (and its matrix counterpart) as it derives from integrals of the quantity $\boldsymbol{\nabla}\theta$; we would thus assume that an anisotropic version of $\underline{\mathbf{U}}_f$ would involve $\underline{\boldsymbol{\alpha}}$, thereby leading to an anisotropic stress tensor.

4.3. Interaction Coefficient c and Darcy's Law

The fluid force equation (37) reduces to something similar to Darcy's law when $\underline{\boldsymbol{\tau}}_f$ (or more precisely μ_f) is negligible and $\Delta P\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}(\sigma\alpha) = 0$ (implying that either the pressure drop balances surface tension or that surface tension and the pressure drop are both zero), i.e.,

$$c(\mathbf{v}_f - \mathbf{v}_m) = -\phi(\boldsymbol{\nabla}P_f + \rho_f g\hat{\mathbf{z}}) \tag{49}$$

[see also *McKenzie*, 1984]. If there is sufficient interconnectedness of pores, (49) suggests that the coefficient c should be related to the permeability of the matrix and the viscosity of the fluid, i.e., $c = \mu_f\phi^2/k$, where the permeability k is a function of porosity ϕ [*McKenzie*, 1984; *Ganesan and Poirier*, 1990]. However, this relation for c cannot be used generally (i.e., for arbitrary viscosities) since it would violate material invariance (i.e., symmetry to a switch of subscripts m and f) of the force equations (37) and (38). We can estimate a more general expression for c by considering the balance of viscous forces at the fluid-matrix interface. We assume that (1) the forces represented by $c\Delta\mathbf{v}$ arise from viscous deformation at the pore and grain scale, i.e., due to deformation of fluid or matrix within the pore or grain; (2) the scales for the viscous force per volume in the two phases have similar forms; and (3) these forces match at the interface. These assumptions lead to a relationship between viscous force scales:

$$\mu_m\frac{\mathbf{v}_m - \mathbf{v}_i}{\delta_m^2} = \mu_f\frac{\mathbf{v}_i - \mathbf{v}_f}{\delta_f^2}, \tag{50}$$

where $\mathbf{v}_i$ is the interface velocity and δ_j is the typical size of an element of phase j (meaning a fluid pore if $j = f$ and a matrix grain if $j = m$). (Equation (50) accounts for the fact that as in simple shear across a boundary, if $\mathbf{v}_m > \mathbf{v}_i$, then $\mathbf{v}_i > \mathbf{v}_f$.) By solving for the interface velocity $\mathbf{v}_i$ in terms of $\mathbf{v}_f$ and $\mathbf{v}_m$, we can estimate the viscous force scale (either side of (50)) and equate it to the interface force on the fluid, leading to

$$c(\mathbf{v}_m - \mathbf{v}_f) = \frac{\mu_m\mu_f(\mathbf{v}_m - \mathbf{v}_f)}{\mu_f\delta_m^2 + \mu_m\delta_f^2}. \tag{51}$$

If we assume that δ_f and δ_m are related to permeability k and (like permeability) are assumed to be functions only of porosity ϕ, then to preserve symmetry of the equations (material invariance), they must be related to the same function of porosity, i.e.,

$$\delta_f = \delta(\phi) \qquad \delta_m = \delta(1-\phi). \tag{52}$$

If we wish to recover Darcy's law, then in the limit $\mu_f \ll \mu_m$ we obtain

$$\lim_{\mu_f/\mu_m \to 0} c = \frac{\mu_f \phi^2}{k(\phi)} = \frac{\mu_f}{\delta^2(\phi)}, \tag{53}$$

which implies we would use $\delta(\phi) = \sqrt{k(\phi)}/\phi$. As expected, permeability is related to pore and/or grain size and thus contains information about the mixture's fabric; therefore k is necessarily also related to the interface density α (see section 2.2). If pore and grain sizes are uniquely represented by permeability, then a general form of c is

$$c = \frac{\mu_m \mu_f \phi^2 (1-\phi)^2}{\mu_f k(1-\phi)\phi^2 + \mu_m k(\phi)(1-\phi)^2}, \tag{54}$$

which has the proper symmetry.

The dependence of permeability on porosity has various forms [*Bear*, 1988; *Furbish*, 1997], although these are largely based on empirical estimates in which the matrix is immobile ($\mu_m \gg \mu_f$). For small porosities one often uses the simple model $k(\phi) = k_o \phi^n$ [see *Spiegelman*, 1993c, and references therein]. If there is not sufficient interconnectedness of pores and μ_f is not $\ll \mu_m$, then use of Darcy's law as a constraint is not valid, although a relation of the form given in (51) is probably still general enough to even capture relative motion of isolated bubbles in a matrix [e.g., see *Batchelor*, 1967].

Regardless of whether or not we use permeability and Darcy's law, it is clear that c depends on grain and/or pore size and thus should be related to the interface area density α (see section 2.2). Thus, if the system were anisotropic, we would likely replace c with a tensor $\underline{\mathbf{c}}$ that is related to $\underline{\boldsymbol{\alpha}}$, and the interaction force $c\Delta\mathbf{v}$ would be replaced by $\underline{\mathbf{c}} \cdot \Delta\mathbf{v}$; by the same token, an anisotropic permeability also should be determined by $\underline{\boldsymbol{\alpha}}$. Moreover, the part of the force $\boldsymbol{\eta}$ that represents a pressure acting on the interface (see (30)) would likely be proportional to $\boldsymbol{\nabla} \cdot \underline{\boldsymbol{\alpha}}$ instead of $\boldsymbol{\nabla}\phi$.

5. Energy Conservation, Surface Energy, and Damage

So far, we have derived eight conservation equations: two continuity equations (12) and (13) (or alternatively (15) and (16)) from conservation of mass and six force equations (37) and (38). However, even without anisotropy, this system is still underdetermined since we have nine unknowns, porosity ϕ, six velocities $\mathbf{v}_f$ and $\mathbf{v}_m$ (or alternatively $\bar{\mathbf{v}}$ and $\Delta\mathbf{v}$), and two pressures P_f and P_m (or alternatively $\bar{P}$ and ΔP).

To some extent, the ninth relation that we seek is a constraint on the pressure difference ΔP. For example, a possible ninth equation would be the simple equilibrium surface tension relation (40); while this is a legitimate equation, it is only valid for zero or weak motion and assumes conditions of thermodynamic equilibrium and isentropy (see Appendix A2), which are not general conditions and are inappropriate for problems involving large viscous forces and/or rapidly deforming systems. To incorporate deformation and viscous stress, it is tempting to posit a vector jump condition on total stress such as $\Delta\underline{\boldsymbol{\tau}} \cdot \boldsymbol{\nabla}\phi - \Delta P \boldsymbol{\nabla}\phi = \boldsymbol{\nabla}(\sigma\alpha)$, which would be analogous to an interface condition [*Landau and Lifshitz*, 1987; *Leal*, 1992] in which $\boldsymbol{\nabla}\phi$ serves as crude proxy for the unit normal to the interface. However, as stated earlier, such conditions would be valid only if the interface were well delineated and thus required a boundary condition across it. With the averaging implicit in a mixture theory the interface is not delineated; it is, instead, mathematically treated as a continuous quantity that exists at all points in the domain with a particular concentration (in this case, area per volume α); thus a vector jump condition would be inappropriate and would impose an overdeterminedness on the system.

Perhaps the simplest relation for ΔP, the equilibrium surface tension condition (40), is generally derived from basic thermodynamics (i.e., conservation of energy assuming equilibrium, or minimum energy, and isentropic conditions [*Landau and Lifshitz*, 1987; *Bailyn*, 1994]); see Appendix A2. In this section we attempt to infer a ninth equation to effectively constrain ΔP from a more general thermodynamic approach, i.e., conservation of energy far from equilibrium and with entropy production.

Our basic energy conservation law differs little conceptually from that derived previously [*McKenzie*, 1984; *Poirier et al.*, 1991]; the time rate of change of internal energy within a control volume δV is governed by (1) the rate of loss of this energy through the surface of the volume via both mass transport and diffusion; (2) the rate at which work is done on the volume by the net surface and body forces; and (3) the rate of internal energy or heat production. In our system, however, the internal energy contained within δV exists in not two but three phases, i.e., the fluid and matrix phases and the interface. We will first write down the energy conservation law and then discuss the various assumptions that have gone into it. If ε_f and ε_m are the internal energy per unit mass of the fluid and matrix phases, respectively (averaged over the volumes of their respective phases) and ξ_i is the energy per unit of interface area (averaged over a small volume of the mixture), then the rate of energy change per volume is given by

$$\begin{aligned}\frac{\partial}{\partial t}\Big[\phi\rho_f\varepsilon_f + (1-\phi)\rho_m\varepsilon_m + \xi_i\alpha\Big] &= Q - \boldsymbol{\nabla}\cdot\mathbf{q}\\ &- \boldsymbol{\nabla}\cdot\left(\phi\rho_f\varepsilon_f\mathbf{v}_f + (1-\phi)\rho_m\varepsilon_m\mathbf{v}_m + \xi_i\alpha\bar{\mathbf{v}}\right)\\ &+ \boldsymbol{\nabla}\cdot\left(-\phi\mathbf{v}_f P_f - (1-\phi)\mathbf{v}_m P_m\right.\\ &\left.+ \phi\mathbf{v}_f\cdot\underline{\boldsymbol{\tau}}_f + (1-\phi)\mathbf{v}_m\cdot\underline{\boldsymbol{\tau}}_m + \bar{\mathbf{v}}\sigma\alpha\right)\\ &- \phi\mathbf{v}_f\cdot(\rho_f g\hat{\mathbf{z}}) - (1-\phi)\mathbf{v}_m\cdot(\rho_m g\hat{\mathbf{z}}),\end{aligned} \tag{55}$$

where Q is the inherent rate of energy (heat) production per unit volume, $\mathbf{q}$ is the diffusive energy flux vector (e.g., the heat flow vector). The second term on the right of (55) represents the rate of energy transport across the surface of the volume (Figure 1), the third term represents the rate at which work is done by surface forces on the surface of the volume, and the last two terms represent the rate at which work is done by the body forces on the interior of the volume. As basic as this equation appears, several implicit assumptions necessary for its derivation should be discussed:

1. As appropriate for our creeping flow system, changes in kinetic energy are neglected [see also *McKenzie*, 1984].

2. In (55) the nonlinear products between various dependent quantities (in particular, velocity with energy, pressure, or stress) appear to be represented only with the products of the volume-averaged quantities. This representation is not entirely accurate and therefore warrants some discussion. In particular, say we have two true fluid quantities $\tilde{A}$ and $\tilde{B}$, and their averages A and B are defined in the standard way, e.g., $\phi A = (1/\delta V)\int_{\delta V} \tilde{A}\theta dV$. Then we can also write that $\tilde{A} = A + A'$ and $\tilde{B} = B + B'$, where the averages of the perturbations A' and B' are zero. The volume average of the product $\tilde{A}$ and $\tilde{B}$ differs from the product of A and B, i.e.,

$$\frac{1}{\delta V}\int_{\delta V} \tilde{A}\tilde{B}\theta dV = \phi AB + \frac{1}{\delta V}\int_{\delta V} A'B'\theta dV. \qquad (56)$$

The evaluation of the last term on the right is, of course, a classic problem in turbulence mean field and closure theories. In problems of heat and chemical transport in porous media this term is typically parameterized into a quantity called dispersion, which mathematically looks very much like diffusion [*Bear*, 1988; *Furbish*, 1997]. While this type of dispersive transport might be a reasonable representation of the bulk transport terms, i.e., the nonlinear products between velocities and internal energies, it is possibly less justified for the products between velocities and stresses or pressures. A rigorous estimate of these nonlinear terms invariably requires higher-order closure theories, introducing yet more equations and unknowns. While this problem might prove fruitful in future studies, we presently opt to maintain the maximum level of simplicity. We thus assume that the nonlinear terms in question are zero (meaning essentially a zero correlation between the quantities A' and B', regardless of what these quantities are) or that they can be deemed a form of dispersion and thus absorbed into the quantity $\mathbf{q}$ (thus $\mathbf{q}$ would not necessarily represent only heat flow). Neither assumption is completely satisfactory, yet the alternatives are less so.

3. As discussed in section 4, surface tension, when averaged over an area element on the surface of a control volume, exerts a force per area $\sigma\alpha\hat{\mathbf{n}}$ (where $\hat{\mathbf{n}}$ is the unit normal of the area element). Since this effective averaged force acts equally on particles of matrix and fluid (given that it actually acts through their common interface) we assume that a fraction ϕ of it acts on fluid which moves at velocity $\mathbf{v}_f$, while a fraction $1-\phi$ acts on matrix which moves at velocity $\mathbf{v}_m$. Thus the net rate of work done (per area) on material at the surface by surface tension is assumed to be $(\phi\mathbf{v}_f + (1-\phi)\mathbf{v}_m)\cdot(\sigma\alpha\hat{\mathbf{n}}) = \bar{\mathbf{v}}\cdot\hat{\mathbf{n}}\sigma\alpha$. The integral of this rate of work over the surface of the control volume, taken per unit volume, of course, leads to the term appearing as $\boldsymbol{\nabla}\cdot(\bar{\mathbf{v}}\sigma\alpha)$.

4. The surface energy per volume $\xi_i\alpha$ is an average quantity for the total volume δV and is thus represented as a volumetric energy density. Since the actual surface energy exists on the common interface between phases, the volume-averaged effective energy density $\xi_i\alpha$ is the same for both fluid and matrix. Moreover, this energy is assumed transported by the phases also according to their volumes; that is, while each phase has the same effective energy density, of the total energy in the volume δV the fluid carries a fraction ϕ at a velocity $\mathbf{v}_f$, and the matrix carries a fraction $(1-\phi)$ at $\mathbf{v}_m$. Thus the total bulk transport or flux of $\xi_i\alpha$ is simply $\xi_i\alpha[\phi\mathbf{v}_f + (1-\phi)\mathbf{v}_m] = \xi_i\alpha\bar{\mathbf{v}}$.

The energy equation can be reduced in the standard way by employing continuity equations (12), (13), and/or (15), (16) and momentum (force) equations (37), (38) to arrive at (after some algebra)

$$\begin{aligned} \phi\rho_f\frac{D_f\varepsilon_f}{Dt} + (1-\phi)\rho_m\frac{D_m\varepsilon_m}{Dt} + \frac{\overline{D}\xi_i\alpha}{Dt} \\ = \quad Q - \boldsymbol{\nabla}\cdot\mathbf{q} - \Delta P\frac{\overline{D}\phi}{Dt} + c\Delta v^2 \\ + \ \phi\boldsymbol{\nabla}\mathbf{v}_f : \underline{\tau}_f + (1-\phi)\boldsymbol{\nabla}\mathbf{v}_m : \underline{\tau}_m, \qquad (57) \end{aligned}$$

where $D_j/Dt = \partial/\partial t + \mathbf{v}_j\cdot\boldsymbol{\nabla}$ (in which $j = f$ or m), $\overline{D}/Dt = \partial/\partial t + \bar{\mathbf{v}}\cdot\boldsymbol{\nabla}$, and $\Delta v^2 = \Delta\mathbf{v}\cdot\Delta\mathbf{v}$. However, we have, with our ninth and new equation, introduced three new dependent variables ε_f, ε_m, and ξ_i.

Because both phases are considered incompressible, pressure cannot do work to change the internal energies of either phase. Thus, by basic thermodynamics the internal energies of the phases ε_f and ε_m are influenced only by their respective entropies, which are themselves only functions of temperature; no adiabatic heating can occur in this case [cf. *McKenzie*, 1984]. If we assume that the two phases have different temperatures, we have not reduced the number of unknowns. Thus, for simplicity, we make the common assumption that the phases are in thermal equilibrium with each other [e.g., *McKenzie*, 1984; *Poirier et al.*, 1991] and thus have the same temperature T; the thermal equilibration time between phases is likely to go as $(\kappa\alpha_o^2)^{-1}$, where κ is thermal diffusivity (which is of order 10^{-6} m^2 s^{-1}) and $\alpha_o \sim 10^6$ m^{-1} (see section 2.2.1) and thus thermal equilibration between phases is possibly nearly instantaneous (at least on geologically relevant timescales). Thus, given incompressibility and a single temperature, we write the energy increments (exact differentials) $d\varepsilon_f = c_f dT$ and $d\varepsilon_m = c_m dT$, where c_f and c_m are the heat capacities of the two phases (whether for constant volume or pressure is irrelevant if the phases are incompressible).

For our simple system, both the surface energy per area ξ_i and surface tension σ are functions of T only and can be related according to

$$\xi_i = \sigma - T\frac{d\sigma}{dT} \tag{58}$$

(see Appendix A2). The factor $-d\sigma/dT$ is the entropy per unit area on the interface and is expected to be a positive quantity [*Berg et al.*, 1966; *Tiller*, 1991a; *Bailyn*, 1994](see Appendix A2; cf. *Cardin et al.* [1991]). Thus the surface tension σ is generally found to be a decreasing function of T, e.g., $\sigma = A(1-\beta T)$ [*Bailyn*, 1994]. Such a linear $\sigma(T)$ function only can be true for sufficiently small βT since it is implausible that σ, which represents the electrostatic attraction of interfacial molecules for their own species, would become a repulsion at high enough T; however, σ could conceivably vanish at very high T, meaning the two phases become miscible if hot enough. Thus it may be more appropriate to state that $\sigma = Ae^{-\beta T}$ [see also *Straub*, 1994].

Note that in writing (58) we assume that ξ_i is related to the effective or geometrically reduced surface tension σ (see Appendix A1) and thus must be the reduced surface energy itself. This is done for consistency with the assumption that the surface tension work done on the mixture is enacted by σ (as per the force equation (26)). As noted in Appendix A1, the reduction in surface tension with the averaging approach is not large, i.e., of $O(1)$. Moreover, the underestimation of ξ_i can also be thought to partially compensate for the neglect of nonlinear fluctuation energy sources and fluxes (see assumption 2, following (55), and the closing discussion in Appendix A1).

With the above assumptions regarding ε_f, ε_m, and ξ_i the energy equation can be recast (with minor algebra) as

$$\overline{\rho c}\frac{\overline{\overline{D}}T}{Dt} - T\frac{\overline{D}}{Dt}\left(\frac{d\sigma}{dT}\alpha\right) = Q - \boldsymbol{\nabla}\cdot\mathbf{q}$$
$$+\ \Psi - \Delta P\frac{\overline{D}\phi}{Dt} - \sigma\frac{\overline{D}\alpha}{Dt}, \tag{59}$$

where

$$\Psi = c\Delta v^2 + \phi\boldsymbol{\nabla}\mathbf{v}_f : \underline{\tau}_f + (1-\phi)\boldsymbol{\nabla}\mathbf{v}_m : \underline{\tau}_m, \tag{60}$$

$$\overline{\rho c} = \phi\rho_f c_f + (1-\phi)\rho_m c_m, \tag{61}$$

$$\frac{\overline{\overline{D}}}{Dt} = \frac{1}{\overline{\rho c}}\left(\phi\rho_f c_f\frac{D_f}{Dt} + (1-\phi)\rho_m c_m\frac{D_m}{Dt}\right). \tag{62}$$

We have arranged (59) to describe the relation between entropy growth (which would be the left-hand side of the equation, less a factor of T) and possible entropy sources (the right-hand side). The second term on the left-hand side of (59) accounts for interfacial entropy growth.

The last term on the right-hand side of (59) $\sigma\overline{D}\alpha/Dt$ accounts for the growth in reversible surface energy (per unit volume) due to surface tension work (see Appendix A2, equation (A19)). We know from interface stress jump conditions [*Landau and Lifshitz*, 1987; *Leal*, 1992] that the rate of change of this energy is driven by mechanical work from the pressure and viscous stress fields, which are represented by the third and fourth terms on the right-hand side of (59), i.e., Ψ and $-\Delta P\overline{D}\phi/Dt$; however, only portions of these work terms, the reversible portions, affect reversible surface energy, while the irreversible portions contribute only to entropy production.

Even from simple surface tension equilibrium we know that the pressure difference ΔP affects surface energy. However, in nonequilibrium, when dilation or compaction is occurring, a portion of the work done by ΔP arises from viscous resistance to dilation/compaction (see Appendix B) and is thus necessariliy irreversible. We must therefore assume that part of ΔP involves irreversible (viscous) deformation, and we will refer to this part as ΔP_{ir}. The pressure work acting on the interface to change reversible surface energy is thus $-(\Delta P - \Delta P_{ir})\overline{D}\phi/Dt$, while the portion contributing to entropy production is $-\Delta P_{ir}\overline{D}\phi/Dt$. However, by the second law of thermodynamics, this source of entropy production must be positive definite and thus

$$\Delta P_{ir} = -B\frac{\overline{D}\phi}{Dt}, \tag{63}$$

where B is a positive coefficient with units of viscosity. From micromechanical models (see Appendix B) one can infer a simple materially invariant form of this coefficient given by

$$B = K_o\frac{(\mu_f + \mu_m)}{\phi(1-\phi)}, \tag{64}$$

where K_o is a dimensionless constant of $O(1)$.

As stated above, in addition to pressure work on the interface we must also allow for work done on the interface by deviatoric stresses. The deformational work from all deviatoric stresses is represented by the function Ψ. In a single-phase viscous medium, Ψ is readily identified with the dissipation function because the deformation is entirely irrecoverable and thus Ψ is a source of irreversible entropy production or heating; this would also be true in a two-phase medium if the interface had no intrinsic energy. However, in a two-phase medium with interfacial energy the deformational work can act against surface tension to increase the interface area and thus deposit energy into interfacial surface energy. We therefore assume that a fraction of the deformational work associated with Ψ goes to deforming the interface (i.e., works against surface tension) and is stored as surface energy rather than dissipated; we consider this fraction conservative or reversible (although we use the term "reversible" with some qualifications; see below). If we knew the exact location and orientation of the interface, we could estimate the portion of Ψ working to deform the interface (using the stress jump condition [*Landau and Lifshitz*, 1987; *Leal*, 1992]); however, in an isotropic mixture theory the interface, like the phases it separates, mathematically exists at all points in the medium, and its presence is only measured by the area density α. Thus we cannot know specifically what part of Ψ acts on the interface and stores energy as surface energy; we can only assume that a fraction

f of Ψ is stored, i.e., is conservative, or involves reversible work. The remaining part $(1-f)\Psi$ is the dissipative contribution. The quantity f is thus the partitioning fraction (where $0 \leq f \leq 1$), and we refer to the partitioning of a portion of Ψ toward work on the interface and thus to production of surface energy as "damage", although this definition may differ from other definitions of damage [e.g., *Ashby and Sammis*, 1990; *Hansen and Schreyer*, 1992; *Lemaitre*, 1992; *Lyakhovsky et al.*, 1997]. The partitioning of deformational work between a dissipative and a stored component has been noted, in fact, since at least the 1920s [*Farren and Taylor*, 1925; *Taylor and Quinney*, 1934; *Chrysochoos and Martin*, 1989, and references therein] and has been considered in experimental [*Chrysochoos and Martin*, 1989; *Chrysochoos et al.*, 1989, 1996] and theoretical [*Lemonds and Needleman*, 1986; *Povirk et al.*, 1994] studies of ductile void growth, dilatant plasticity, and metal composites.

In total, the reversible portions of the energy growth terms isolated on the right-hand side of (59) must balance or cancel since processes involving only reversible energy and work cannot contribute to internal entropy production. (By analogy, in compressible single-phase fluid mechanics, mechanical pressure work is generally assumed to contribute only to reversible thermodynamic energy; that is, mechanical and thermodynamic pressures are assumed equivalent.) We therefore obtain two energy relations

$$\overline{\rho c}\frac{\overline{\overline{D}}T}{Dt} - T\frac{\overline{D}}{Dt}\left(\frac{d\sigma}{dT}\alpha\right) = Q - \boldsymbol{\nabla}\cdot\mathbf{q} + (1-f)\Psi + K_o\frac{(\mu_f+\mu_m)}{\phi(1-\phi)}\left(\frac{\overline{D}\phi}{Dt}\right)^2 \tag{65}$$

$$\sigma\frac{\overline{D}\alpha}{Dt} = -\Delta P\frac{\overline{D}\phi}{Dt} - K_o\frac{(\mu_f+\mu_m)}{\phi(1-\phi)}\left(\frac{\overline{D}\phi}{Dt}\right)^2 + f\Psi, \tag{66}$$

which are both materially invariant.

Equation (66) describes a basic thermodynamic work statement. That is, the work necessary to create new interfacial area against surface tension is provided by the net work of the two pressure fields (acting against each other on the interface) as well as by viscous deformational work. However, (66) also acts as a nonequilibrium proxy for the interface stress jump (surface tension) condition in an isotropic medium for which the interface location and orientation are unknown and thus represented by averaged quantities. In many ways it bears the same form as a stress-jump condition, however it involves rates of work for all points in the effective medium and is a scalar relation that provides one equation for ΔP.

In the limit that there is zero or negligible motion and deformational work on the interface (i.e., both $f\Psi$ and $B\left(\overline{D}\phi/Dt\right)^2 \approx 0$), (66) becomes

$$\left(\Delta P + \sigma\frac{d\alpha}{d\phi}\right)\frac{\overline{D}\phi}{Dt} = 0, \tag{67}$$

which recovers (40), the equilibrium surface tension condition, assuming (67) holds for any $\overline{D}\phi/Dt$.

If surface tension and damage are negligible ($\sigma = f\Psi = 0$), we obtain a relation for simple isotropic compaction

$$\Delta P = -K_o\frac{(\mu_f+\mu_m)}{\phi(1-\phi)}\frac{\overline{D}\phi}{Dt}, \tag{68}$$

which occurs if each phase is exposed to a different isotropic stress, and the imbalance in stresses or pressures causes one phase to squeeze and expel the other from the mixture (D. McKenzie, personal communication, 2000). Equation (68) predicts compaction of the matrix if $P_m > P_f$. The process of isotropic compaction is discussed by *McKenzie* [1984] with a thought experiment involving spherically-symmetric flow [see *McKenzie*, 1984, Appendix C; see also *Ricard et al.*, this issue). However, in that theory the fluid and matrix pressures are assumed equivalent, and thus resistance to isotropic compaction is provided by a bulk viscosity effect in the matrix. Since the bulk viscosity effect is assumed to reside entirely in the matrix, it can only apply to a system that is explicitly not materially invariant; for example, only the matrix can provide resistance to isotropic compaction. In the theory presented in this paper, resistance to isotropic compaction is instead provided by the pressure difference ΔP, the expression for which, illustrated in (68), is materially invariant, depending on properties of both phases and the interface topology.

It is important to note another possible difference between this theory and some other previous models [e.g., *McKenzie*, 1984; *Spiegelman*, 1993a, 1993b, 1993c]. In the limit $\sigma = 0$, $\mu_f \ll \mu_m$ and thus $\underline{\tau}_f \approx 0$, but where the matrix is deforming at a nonnegligible rate such that (68) applies, the fluid force equation (37) does not recover a simple modified Darcy's law but instead

$$\mathbf{v}_f - \mathbf{v}_m = -\frac{\phi}{c}\left[\boldsymbol{\nabla}P_f + \rho_f g\hat{\mathbf{z}}\right] - \frac{K_o\mu_m}{c(1-\phi)}\frac{\overline{D}\phi}{Dt}\boldsymbol{\nabla}\phi, \tag{69}$$

which suggests that the fluid pressure gradients work not only to move the fluid relative to matrix but also resist the force associated with collapse or dilation of a nonuniform matrix (i.e., with nonconstant porosity). If the matrix is not collapsing/dilating, or gradients in porosity are negligible, then the modified Darcy's law is recovered as expected (i.e., Darcy's law is an empirical relationship strictly relevant only for stationary matrix material).

Equation (66) suggests that work done by deviatoric stresses to change energy on the interface is always positive, which may seem counterintuitive. As a conceptual example, consider a bubble stretched in shear or in an extensional flow such that the interface area and thus surface energy increases; however, if one reverses the shear or extension, the bubble is theoretically unstretched (assuming it has not undergone a capillary instability and broken up) and its surface area and energy decreases. However, (66) suggests that the deformational work acts to make surface area and energy increase regardless of the direction of motion. This result is a manifestation of the imposed isotropy of the system. Pores are assumed never to develop a preferred sense of direction, even under shear or extension. Thus, in a sense, stretching of a bubble results in more smaller bubbles, not a long bubble. Reversing the shear or extension will not by itself recombine the bubbles but instead will break them up even further when it either acts to stretch them (e.g., in shear) or flatten them (in uniaxial compression), creating even more surface area and energy. Thus, while the deformational work can be stored in a nondissipative fashion on the surfaces, the creation of new surface area and surface energy in this formulation cannot be reversed by imposed deformational work. Thus the viscous deformational work on the interface, or damage, would have the appearance of being irreversible, although it is not irreversible in the traditional sense since it is, in fact, storing energy on the interface; indeed, this energy can be recovered as mechanical work if the bubbles recoalesce (which is allowed in this formulation [see *Ricard et al.*, this issue; *Bercovici et al.*, this issue). Such apparent irreversibility is perhaps in keeping with cataclastic processes wherein deformation always causes damage regardless of whether the original application of deformation is reversed.

Constraints on the partitioning fraction f are unfortunately scarce. Empirical calorimetric studies on deformation in metals [*Chrysochoos and Martin*, 1989; *Chrysochoos et al.*, 1989, 1996] have shown that of the order of 15-20% of the applied work goes into surface energy associated with structural defects, e.g., voids, microcracks, and interfaces (i.e., the temperature of the medium increases less than would be expected if all the viscous deformational work went into dissipative heating), although for the initial phases of deformation this fraction is possibly as high as 60% [*Chrysochoos and Martin*, 1989; *Chrysochoos et al.*, 1989, 1996]. However, the f presented here does not necessarily represent this measured partitioning fraction. Given that $d\sigma/dT < 0$, the growth in interfacial entropy (the second term on the left-hand side of (65)) represents an apparent sink of energy while the interfacial area is growing (while $\overline{D}\alpha/Dt = (d\alpha/d\phi)\overline{D}\phi/Dt > 0$) and thus this effect by itself, even with $f = 0$, would give the result that not all of the input energy goes into increasing the temperature of the medium. It would be difficult, in an experiment, to separate this effect from direct partitioning of deformational work into surface energy.

The partitioning fraction f is unlikely to be constant and clearly must depend on the properties of the medium. For example, the extent to which the viscous stresses can act on the interface must depend on the interface area density, and thus we should expect f to depend on α and thus, implicitly, on ϕ. Moreover, since we assume that an amount of deformational work $f\Psi$ is stored as surface energy on the interface, we must also assume that no such work can be stored if the interfacial surface energy is zero, i.e., if $\sigma = 0$; therefore f should be a function of σ. The variability of f is discussed further by *Bercovici et al.* [this issue] who study applications to shear localization and damage.

6. Summary: Final Governing Equations

For convenience, we summarize the final governing equations below:

1. Conservation of mass yields two alternative sets of equations, either a set involving transport of the separate phases

$$\frac{\partial\phi}{\partial t} + \boldsymbol{\nabla}\cdot[\phi\mathbf{v}_f] = 0 \tag{70}$$

$$\frac{\partial(1-\phi)}{\partial t} + \boldsymbol{\nabla}\cdot[(1-\phi)\mathbf{v}_m] = 0 \tag{71}$$

or a mixture/difference set that prescribe transport of porosity and continuity of average velocity

$$\frac{\partial\phi}{\partial t} + \bar{\mathbf{v}}\cdot\boldsymbol{\nabla}\phi = \boldsymbol{\nabla}\cdot[\phi(1-\phi)\Delta\mathbf{v}] \tag{72}$$

$$\boldsymbol{\nabla}\cdot\bar{\mathbf{v}} = 0 \tag{73}$$

and where the average and difference of any quantity q are defined as $\bar{q} = \phi q_f + (1-\phi)q_m$ and $\Delta q = q_m - q_f$, respectively. Mass conversion rates due to a phase change are easily incorporated into the theory by including $\Delta\Gamma/\rho_f$ and $-\Delta\Gamma/\rho_m$ on the right-hand side of (70) and (71), respectively; $\Delta\Gamma = \Gamma_m - \Gamma_f$, where Γ_m is the rate of conversion of matrix mass (per unit volume of total mixture) into fluid and Γ_f is the rate of conversion of fluid into matrix [see also *McKenzie*, 1984; *Spiegelman*, 1993a, 1993b, 1993c). In using these conversion rates one must take care to include them in the derivation of any subsequent relations that use the mass conservation equations.

2. The momentum or force balance equations also yield two alternate sets of equations; one describing the dynamics of the two phases

$$\begin{aligned} 0 = &- \phi\left[\boldsymbol{\nabla}P_f + \rho_f g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot[\phi\underline{\boldsymbol{\tau}}_f] \\ &+\ c\Delta\mathbf{v} + \phi\left[\Delta P\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}(\sigma\alpha)\right] \end{aligned} \tag{74}$$

$$\begin{aligned} 0 = &- (1-\phi)\left[\boldsymbol{\nabla}P_m + \rho_m g\hat{\mathbf{z}}\right] + \boldsymbol{\nabla}\cdot[(1-\phi)\underline{\boldsymbol{\tau}}_m] \\ &-\ c\Delta\mathbf{v} + (1-\phi)\left[\Delta P\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}(\sigma\alpha)\right] \end{aligned} \tag{75}$$

where

$$\underline{\boldsymbol{\tau}}_f = \mu_f\left(\boldsymbol{\nabla}\mathbf{v}_f + [\boldsymbol{\nabla}\mathbf{v}_f]^t - \frac{2}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_f\underline{\mathbf{I}}\right) \tag{76}$$

$$\underline{\boldsymbol{\tau}}_m = \mu_m\left(\boldsymbol{\nabla}\mathbf{v}_m + [\boldsymbol{\nabla}\mathbf{v}_m]^t - \frac{2}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_m\underline{\mathbf{I}}\right). \tag{77}$$

We can also add (74) and (75) to obtain the total or mixture force equation

$$0 = -\boldsymbol{\nabla}\bar{P} + \boldsymbol{\nabla}\cdot\bar{\underline{\boldsymbol{\tau}}} - \bar{\rho}g\hat{\mathbf{z}} + \boldsymbol{\nabla}(\sigma\alpha) \tag{78}$$

and find $\phi\times(75)-(1-\phi)\times(74)$ to obtain a force-difference or "action-reaction" equation

$$\begin{aligned} 0 = &- \phi(1-\phi)\left[\boldsymbol{\nabla}\Delta P + \Delta\rho g\hat{\mathbf{z}}\right] \\ &+\ \boldsymbol{\nabla}\cdot[\phi(1-\phi)\Delta\underline{\boldsymbol{\tau}}] - \bar{\underline{\boldsymbol{\tau}}}\cdot\boldsymbol{\nabla}\phi - c\Delta\mathbf{v}. \end{aligned} \tag{79}$$

3. The energy equation is separated into two coupled equations representing the evolution of thermal energy and rate of work done on the interface:

$$\overline{\rho c}\frac{\overline{\overline{D}}T}{Dt} - T\frac{\overline{D}}{Dt}\left(\frac{d\sigma}{dT}\alpha\right) = Q - \boldsymbol{\nabla}\cdot\mathbf{q} + (1-f)\Psi + B\left(\frac{\overline{D}\phi}{Dt}\right)^2 \tag{80}$$

$$\Delta P\frac{\overline{D}\phi}{Dt} = -\sigma\frac{\overline{D}\alpha}{Dt} + f\Psi - B\left(\frac{\overline{D}\phi}{Dt}\right)^2, \tag{81}$$

where we have rewritten (66) to emphasize that it is invariably a relation for ΔP; again, we can assume for simplicity that $B = K_o(\mu_f + \mu_m)/[\phi(1-\phi)]$ with $K_o \sim O(1)$.

7. Discussion and Conclusion

7.1. Surface Energy Scales for Geophysical Applications

The scale of the surface energy density, or equivalently the surface tension force per area, goes as $\sigma\alpha_o$. As discussed in section 2.2.1, $\alpha_o \sim 10^6\ \mathrm{m}^{-1}$ for a mixture with micron-sized pores and grains. For silicates in contact with melt or water, σ is typically between 0.1 and 1 J m^{-2} [*Spry*, 1983; *Lasaga*, 1998], while surface energies related to fractures can be much higher, i.e., from 10 J m^{-2} to effective values of nearly 1000 J m^{-2} [*Jaeger and Cook*, 1979; *Atkinson*, 1987; *Atkinson and Meredith*, 1987]. To estimate the importance of surface tension, one needs to compare $\sigma\alpha_o$ to other relevant forces. The dimensionless number $\sigma\alpha_o/(\Delta\rho g R)$ indicates the importance of surface tension with respect to the relative buoyancy of the two phases in a system with length scale R. The number $\sigma\alpha_o R/(\mu_m U)$ indicates the importance of surface tension relative to a viscous stress of a system with $\mu_m \gg \mu_f$, a velocity scale U, and changes in velocity over a length scale R. Thus for silicate melts ($\Delta\rho$ of the order of a few hundred kilograms per cubic meter), surface tension is potentially important over length scales of a few hundred meters to a few kilometers [see *Ricard et al.*, this issue). For stresses and microcracking in the lithosphere (assuming $\mu_m > 10^{23}$ Pa s, $U \sim 5$ cm yr^{-1}), surface tension forces are always relatively small, as is to be expected (i.e., surface-tension-driven segregation of rock and fluid in cracked media is negligible, except for possible effects of Ostwald ripening [*Sleep*, 1994]); however, the influence of surface energy on shear localization and cracking is not so much as a driving force but as an intermediary for damage and weakening of the material [*Bercovici et al.*, this issue).

7.2. Future Applications

Apart from a somewhat different treatment of the pressure drop ΔP, surface tension, stress tensors, and other features, our mass and momentum equations do not differ greatly from those of previous workers [e.g., *McKenzie* 1984; *Richter and McKenzie*, 1984; *Spiegelman*, 1993a, 1993b, 1993c]. However, our proposed energy equations provide significantly new physics and describe a variety of effects. *Ricard et al.* [this issue] and *Bercovici et al.* [this issue] examine some of the simplest and most fundamental applications of this theory. For example, when there is little or no deformational work done on the interface ($f\Psi \approx 0$) and surface tension σ is temperature-independent (i.e., $\beta = 0$), the temperature field has no effect on the dynamics (except through thermal buoyancy, which we have neglected, keeping our phases strictly incompressible), and we can ignore the thermal energy equation (80). In this case, we have a simple relation between surface tension and the pressure difference ΔP, and we can thus examine compaction in the presence of interfacial surface tension which has many applications to magma dynamics, oil migration and other problems of percolation through a deformable matrix. This and other compaction problems are examined in *Ricard et al.* [this issue]. When we assume significant viscous deformational work on the interface ($f\Psi > 0$) and a temperature-independent σ (i.e., $\beta = 0$), we again have a decoupled set of equations in which the temperature equation has no bearing on the dynamics, but the occurrence of damage and shear localization is potentially dramatic. These applications to damage and shear localization are addressed by *Bercovici et al.* [this issue].

Appendix A: Surface Tension and Energy Considerations

A1. Effective Surface Tension Force

As shown in (25), the surface tension force acting on the surface area δA of a volume δV is $\int_{C_i}\tilde{\sigma}\hat{\mathbf{t}}d\ell$, where $\tilde{\sigma}$ is the true surface tension, C_i is the intersection between the interface and δA, $d\ell$ is a line element along C_i, and $\hat{\mathbf{t}}$ is a unit tangent to the interface at the intersection. On the area element dA (a small segment of δA) is a portion of the intersection curve c_i, and the surface tension force acting on this element is $\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}d\ell$. With isotropy, we assume that the net surface tension force on dA is only normal to this area element, i.e., in the $\hat{\mathbf{n}}$ direction (since with isotropy the components of $\tilde{\sigma}\hat{\mathbf{t}}$ parallel to dA cancel when summed over this small area); in other words,

$$\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}d\ell = \hat{\mathbf{n}}\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{n}}d\ell. \tag{A1}$$

As with other variables we wish to define an average surface tension. Ideally, we would average $\tilde{\sigma}$ over the domain on which it exists, i.e., the interface between phases. The area of interface contained within the small volume $dAdx_n$ (where dx_n is a line element in the $\hat{\mathbf{n}}$ direction) is $\int_{c_i}(\hat{\mathbf{t}}\cdot\hat{\mathbf{n}})^{-1}d\ell dx_n$, assuming dx_n is small enough that the interface element extends across the length dx_n before leaving the volume. By definition this interface area is also $\alpha dAdx_n$, and thus

$$\alpha dA = \int_{c_i}(\hat{\mathbf{t}}\cdot\hat{\mathbf{n}})^{-1}d\ell. \tag{A2}$$

Moreover, if we define the factor

$$\lambda = \frac{\int_{c_i} \hat{\mathbf{t}} \cdot \hat{\mathbf{n}} d\ell}{\int_{c_i} (\hat{\mathbf{t}} \cdot \hat{\mathbf{n}})^{-1} d\ell}, \tag{A3}$$

then

$$\int_{c_i} \hat{\mathbf{t}} \cdot \hat{\mathbf{n}} d\ell = \lambda \alpha dA, \tag{A4}$$

where typically $\lambda < 1$, although it is of $O(1)$; for spherical fluid pores or matrix grains, as shown below, $\lambda = 2/3$. We can then average the surface tension over the interface area, but with a weighting factor that facilitates estimation of the effective surface tension force; i.e.,

$$\langle \tilde{\sigma} \rangle = \frac{\int_{c_i} \tilde{\sigma} \hat{\mathbf{t}} \cdot \hat{\mathbf{n}} d\ell dx_n}{\int_{c_i} \hat{\mathbf{t}} \cdot \hat{\mathbf{n}} d\ell dx_n}, \tag{A5}$$

which, cancelling the dx_n and using (A1) and (A4), leads to

$$\lambda \langle \tilde{\sigma} \rangle \alpha \hat{\mathbf{n}} dA = \hat{\mathbf{n}} \int_{c_i} \tilde{\sigma} \hat{\mathbf{t}} \cdot \hat{\mathbf{n}} d\ell = \int_{c_i} \tilde{\sigma} \hat{\mathbf{t}} d\ell. \tag{A6}$$

We define the reduced surface tension

$$\sigma = \lambda \langle \tilde{\sigma} \rangle, \tag{A7}$$

and summing over all the area elements in δA, we arrive at the net surface tension force on the control volume

$$\int_{C_i} \tilde{\sigma} \hat{\mathbf{t}} d\ell = \int_{\delta A} \sigma \alpha \hat{\mathbf{n}} dA, \tag{A8}$$

which then leads to (26).

To illustrate the above formalism, we consider a simple example involving a random distribution of spherical fluid pores (or spherical matrix grains, either of which represent isotropic fabric of the mixture). We also assume the true surface tension $\tilde{\sigma}$ is constant.

Any given pore has radius r, and its center is a distance h normal to the area element dA (where dA is assumed much larger than πr^2 so that it samples a sufficient cross section of pores; see Figure A1). We assume $h > 0$ if it is on the side of dA in the $+\hat{\mathbf{n}}$ direction and $h < 0$ if it is on the side in the $-\hat{\mathbf{n}}$ direction (Figure A1). If $|h| < r$, then the pore's surface is cut by the area element dA and the resulting intersection of these surfaces has a circumference $2\pi r \sqrt{1 - h^2/r^2}$. The unit tangent to the interface at this intersection is

$$\hat{\mathbf{t}} = (\sqrt{1 - h^2/r^2}) \hat{\mathbf{n}} + (h/r) \hat{\mathbf{s}}, \tag{A9}$$

where $\hat{\mathbf{s}}$ points radially outward from the center of the intersection circle but in the plane of dA (Figure A1). Thus the total surface tension force pulling on this intersection is $2\pi r(1 - h^2/r^2)\tilde{\sigma}\hat{\mathbf{n}}$ (since the component in the $\hat{\mathbf{s}}$ direction vanishes when integrated around the circumference of the interesection). We assume that any spherical pore that intersects dA has equal probability of being centered anywhere within a distance r on either side of dA, i.e., with $-r < h < +r$. Thus, if N (where $N >> 1$) is the number of randomly distributed pores of radius r centered within a distance r of the area element dA, then the total surface tension force on dA is

$$\frac{N}{2r} \int_{-r}^{+r} 2\pi r \tilde{\sigma} (1 - h^2/r^2) \hat{\mathbf{n}} dh = \frac{4}{3} N \pi r \tilde{\sigma} \hat{\mathbf{n}}. \tag{A10}$$

The centers of these N spheres are contained within the volume $2rdA$, which is itself centered on the element dA. Statistically, however, this volume intersects $2N$ pores, only N of which cross the center plane with area dA (i.e., there are N pores intersecting each of the volume's two outer surfaces with area dA, assuming that since $dA \gg \pi r^2$, the other surfaces are negligible). Any one of these $2N$ pores whose center is h away from the volume's center plane (where now $-2r < h < 2r$) has a segment of its surface in the volume $2rdA$ with area $2\pi r^2(2 - |h|/r)$. Thus the average pore surface area partially contained in $2rdA$ (assuming randomly distributed pores) is $(1/4r)\int_{-2r}^{2r} 2\pi r^2(2 - |h|/r)dh = 2\pi r^2$. The total surface area of pores in the volume $2rdA$ is therefore $(2N)2\pi r^2 = 4N\pi r^2$, which by definition is also $\alpha 2rdA$. Therefore

$$2\pi N r = \alpha dA, \tag{A11}$$

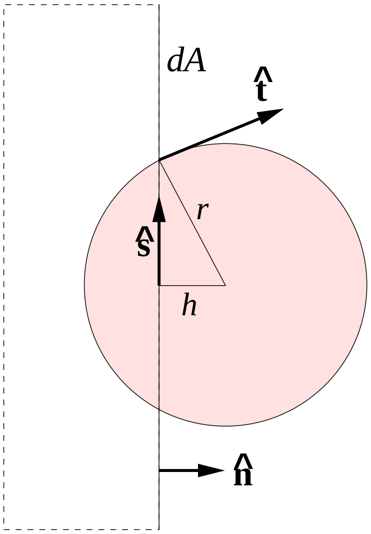

Figure A1. Side view of a cross section of an idealized spherical pore as discussed in Appendix A1. The pore is of radius r centered a distance h from an area element dA (only a small part of which is marked by the solid vertical line) on the surface of the control volume (a portion of the control volume is delineated by dashed lines). Also shown are the relevant unit vectors, i.e., $\hat{\mathbf{n}}$ the unit normal to dA, $\hat{\mathbf{t}}$ the unit tangent to the spherical surface at its intersection with dA, and $\hat{\mathbf{s}}$ the unit vector pointing radially outward from the center of the intersection circle in the plane of dA. If the pore intersects the control volume's surface, then h must be within r of dA, i.e., $-r < h < r$; as shown, with the pore centered to the right of dA, $h > 0$.

and from (A10) the surface tension force on the element dA is $(2/3)\tilde{\sigma}\alpha\hat{\mathbf{n}}dA$; the net surface tension on the surface δA is thus

$$\int_{C_i} \tilde{\sigma}\hat{\mathbf{t}}d\ell = \int_{\delta A} \sigma\alpha\hat{\mathbf{n}}dA, \qquad \text{(A12)}$$

where for this illustrative example the reduced surface tension is

$$\sigma = \frac{2}{3}\tilde{\sigma} \qquad \text{(A13)}$$

(and since $\tilde{\sigma}$ is constant, it is equal to $\langle\tilde{\sigma}\rangle$). To confirm that this result is the same as the general relation (A8), one need only determine the factor λ to see if the reduction in surface tension is predicted correctly. Given N randomly distributed spherical pores centered within a distance h away from dA, (A3) yields

$$\lambda = \frac{\frac{N}{2r}\int_{-r}^{r} 2\pi r(1-h^2/r^2)dh}{\frac{N}{2r}\int_{-r}^{r} 2\pi r dh} = 2/3 \qquad \text{(A14)}$$

which shows that (A7) is consistent with (A13) (and likewise (A8) is consistent with (A12)).

As discussed in section 5, the energy transport laws involve the interfacial surface energy per area ξ_i, which is related to the reduced surface tension σ and not the true surface tension $\tilde{\sigma}$; this means that the surface energy is effectively underestimated. The didactic model with spherical pores presented above can illustrate the need for underestimating this energy in order to be self-consistent. If we move the area element dA in Figure A1 a distance dh in the $\hat{\mathbf{n}}$ direction, then the intersection curve c_i, which must move tangent to the sphere's surface, undergoes a displacement $d\mathbf{x} = (dh/\sqrt{1-h^2/r^2})\hat{\mathbf{t}}$. The energy variation (i.e., the increase in surface energy within the control volume) associated with this motion is (using (A9))

$$d\tilde{E}_i = dh\int_{c_i} \tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{n}}d\ell + \frac{h}{\sqrt{r^2-h^2}}dh\int_{c_i} \tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{s}}d\ell \qquad \text{(A15)}$$

where the first integral accounts for the work of the components of the surface tension perpendicular to the surface dA and the second integral accounts for the work of the components of the surface tension parallel to this surface. The vector $\hat{\mathbf{n}}$ is constant and therefore can commute with the integral sign, in contrast to the radial vector $\hat{\mathbf{s}}$, which depends on the position along c_i. Therefore, using (A6) and (A7), we can write

$$d\tilde{E}_i = \sigma\alpha dh dA + \frac{h}{\sqrt{r^2-h^2}}dh\int_{c_i} \tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{s}}d\ell. \qquad \text{(A16)}$$

Clearly, $\alpha dh dA = dA_i$, which is the change in interface area associated with the volume change $dhdA$. Moreover, as $\tilde{\sigma}$ is assumed constant, the true surface energy per area $d\tilde{E}_i/dA_i = \tilde{\xi}_i = \tilde{\sigma}$ is also constant (see Appendix A2), and thus $d\tilde{E}_i = \tilde{\xi}_i dA_i$. We can further define the reduced energy $\xi_i = \sigma$, and thus the energy change from (A16) is

$$\tilde{\xi}_i dA_i = \xi_i dA_i + \frac{h}{\sqrt{r^2-h^2}}dh\int_{c_i} \tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{s}}\, d\ell \qquad \text{(A17)}$$

or, using $dA_i = \alpha dh dA$,

$$\tilde{\xi}_i = \xi_i + \frac{h}{\alpha dA\sqrt{r^2-h^2}}\int_{c_i} \tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{s}}\, d\ell. \qquad \text{(A18)}$$

The second term in (A18) cannot be treated by an average mixture theory given the lack of general information regarding h, $\hat{\mathbf{t}}$, and $\hat{\mathbf{s}}$; either one must adopt a specific ad hoc model of pore geometry (such as our spherical pore model above) and thus sacrifice generality and material symmetry, or one must include another state variable corresponding to $\int_{c_i}\tilde{\sigma}\hat{\mathbf{t}}\cdot\hat{\mathbf{s}}\,d\ell$ and thus be faced with further closure problems. This is an example of an energy source associated with nonlinear fluctuations, leading to effects such as dispersion as discussed in section 5 (see assumption 2, following (55)). For the spherical pore model, $\xi_i = (2/3)\tilde{\sigma}$, and the reader can readily verify that the integral term in (A18) accounts for the remaining $(1/3)\tilde{\sigma}$ contribution to $\tilde{\xi}_i$. However, since the work of the averaged forces must correspond to a proportional change in the averaged energy, we must, for self-consistency, use ξ_i instead of $\tilde{\xi}_i$.

A2. Surface and Interface Thermodynamics

The surface energy relations used in section 5 arise from the basic thermodynamics of surfaces. For completeness, we derive the more important concepts regarding surface energy and tension, although these can be found in most complete texts on thermodynamics [*Bailyn*, 1994; see also *Safran*, 1994].

To begin with, we note that in this appendix, for simplicity, we make no distinction between true, averaged, or reduced quantities, assuming the same thermodynamic relations apply to all. Thus extra notations such as tilde are not used.

Within a two-phase mixture the interface between the phases is treated as a third phase with its own energy E_i and entropy S_i. Given that the interface is two-dimensional, its spatial presence is measured by an interfacial area A_i (instead of volume), which is worked on by the surface tension σ (instead of by pressure; however, as defined, surface tension acts to reduce surface area while pressure within a volume acts to expand the volume; thus in fact, σ replaces $-P$).

For simplicity, we assume that the interface has no mass and thus no particles of its own (see discussion by *Bailyn* [1994, chapter 7]). We also assume that the interface and the two phases have the same temperature (i.e., they are in thermal equilibrium with each other) and that over the considered volumes the temperature is predominantly uniform [*Bailyn*, 1994].

The interface has the standard thermodynamic relation (i.e., the combined first and second laws of thermodynamics)

$$dE_i = TdS_i + \sigma dA_i \qquad \text{(A19)}$$

and (by an expansion of the scale of the system [see *Bailyn*, 1994]) an Euler equation

$$E_i = TS_i + \sigma A_i, \tag{A20}$$

which together yield the Gibbs-Duhem relation

$$S_i dT + A_i d\sigma = 0. \tag{A21}$$

From (A21) we see that the entropy per area is

$$s_i = S_i/A_i = -\frac{\partial \sigma}{\partial T}, \tag{A22}$$

and thus the energy per area is

$$\xi_i = E_i/A_i = \sigma - T\frac{\partial \sigma}{\partial T}, \tag{A23}$$

which we employ in section 5. Moreover, substitution of $s_i A_i$ and $\xi_i A_i$ into (A19) leads to $d\sigma = (\partial\sigma/\partial T)dT$, which shows that σ is only a function of T.

From these basic thermodynamic relations we can also see where the surface tension equilibrium equation comes from, along with its limitations. The sum of (A19) with the analogous relations for the two phases (whose individual compositions are fixed)

$$dE_j = TdS_j - P_j dV_j \tag{A24}$$

(where, as with the rest of this paper, we use $j = f$ or m to represent the two phases) gives the variation in total energy as

$$dE_{\text{tot}} = TdS_{\text{tot}} + \sigma dA_i - P_f dV_f - P_m dV_m, \tag{A25}$$

where $E_{\text{tot}} = E_f + E_m + E_i$ and similarly for S_{tot}. Equilibrium occurs when total energy is minimized and thus $dE_{\text{tot}} = 0$. The surface tension relation also derives from the assumption that equilibrium is reached isentropically, and thus $dS_{\text{tot}} = 0$ as well. To simplify matters, we consider that the variations in the volumes of each phase are not due to changes in density but due to changes in mixture ratios and that the total volume of the system remains fixed at V_{tot} (imagine a rigid container being fed by two different fluids from separate inlet pipes each at their own pressure). The mixture ratio is represented by the volume fractions of phase f (the fluid) ϕ and of phase m (the matrix) $1-\phi$, which are variable; the phases' volumes are thus $V_f = \phi V_{\text{tot}}$ and $V_m = (1-\phi)V_{\text{tot}}$. In this case, the equilibrium condition leads to

$$\sigma dA_i + (P_m - P_f)V_{\text{tot}} d\phi = 0. \tag{A26}$$

Keeping σ and the pressures fixed over incremental changes in ϕ and A_i, we thus seek the mixture ratio which yields equilibrium; that is, the ϕ at which any work by the pressures (against each other) to change ϕ further would be balanced by the work done by the surface tension to resist change in the interfacial area. Assuming that we can express the interface area A_i in terms of an area density α, we write $A_i = \alpha V_{\text{tot}}$; in this case the equilibrium condition leads to

$$\sigma\frac{\partial \alpha}{\partial \phi} + (P_m - P_f) = 0, \tag{A27}$$

which is analogous to our equilibrum surface tension equation (40) assuming that α is only a function of ϕ.

Appendix B: Interphase Pressure Difference and a Simple Micromechanical Model of Pore Collapse

We consider a simple model of viscous collapse of dispersed pores (or grains) in order to estimate the relation between the interphase pressure difference ΔP and viscous flow. Surface tension effects are neglected; the simple pore or grain geometry is assumed to be conserved during collapse, and thus we ignore large-scale shear stresses as well (i.e., the matrix is only compacting or dilating uniformly under an isotropic stress). We assume that pores are dispersed enough so that we can consider a single pore unaffected by the collapse of other pores; thus we assume porosity $\phi \ll 1$. As pores are squeezed and drained, we must allow for interconnectedness of fluid pathways thereby excluding isolated spherical pores. Thus, for simplicity, we consider a cylindrical pore of radius R that is much smaller than its length so that it can be treated as an infinitely long cylinder. (This approach is similar to that considered by *Fowler* [1984] based on an analysis of boreholes in glaciers by *Nye* [1953].) The cylindrical pore is filled with incompressible fluid of viscosity μ_f and surrounded by incompressible matrix of viscosity μ_m. We further assume constant pressure fields P_f and P_m for the fluid and matrix, respectively, and that the cylinder's radius remains constant along its axis. In this case, the equations of motion for creeping flow allow a fluid velocity in the axial direction of $w_f = Wz$ (where z is the along-axis distance) and in the radial direction of $u_f = -Wr/2$ (r is radial distance), where W is an as yet unspecified constant. We assume matrix motion is primarily radial as it squeezes the pore and by mass conservation has motion $u_m = -WR^2/(2r)$. (This velocity is only approximate since it does not match the axial fluid velocity at the interface, although it does match the fluid shear stress at the interface.) Continuity of normal stress at the interface prescribes that

$$\Delta P = P_m - P_f = (\mu_f + \mu_m)W. \tag{B1}$$

If we define the porosity as $\phi = \Delta Z \pi R^2/\Delta V$ (where ΔZ is the along-axis length of a segment of the pore and ΔV is a volume containing only this pore segment) and note that the radial velocity at the interface is $u_f(R) = u_m(R) = dR/dt$, then $W = -\phi^{-1} d\phi/dt$ leading to

$$\Delta P = -\frac{(\mu_f + \mu_m)}{\phi}\frac{d\phi}{dt}. \tag{B2}$$

We can apply the symmetric development to dispersed cylindrical matrix grains (where $1 - \phi \ll 1$) to arrive at

$$\Delta P = -\frac{(\mu_f + \mu_m)}{1-\phi}\frac{d\phi}{dt}. \tag{B3}$$

A materially invariant relation that accounts for both limits of $\phi \to 0$ and $\phi \to 1$ is

$$\Delta P = -\frac{(\mu_f + \mu_m)}{\phi(1-\phi)}\frac{d\phi}{dt}. \tag{B4}$$

Similar developments can be made for pores of other simple geometries, In general, we can adopt the relation

$$\Delta P = -K_o \frac{(\mu_f + \mu_m)}{\phi(1-\phi)} \frac{d\phi}{dt}, \tag{B5}$$

where K_o is a dimensionless constant of $O(1)$ accounting for unknown pore geometry and interface topology. In our continuum theory we must replace $d\phi/dt$ with a materially invariant material derivative, and as shown by thermodynamic considerations in section 5, this would be $\overline{D}\phi/Dt$.

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