

On the definition and derivatives of macroscale energy for the description of multiphase systems

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Abstract

Modeling of flow and transport in environmental systems often involves formulation of conservation equations at spatial scales involving tens to hundreds of pore diameters in porous media or the depth of flow in a channel. Quantities such as density, temperature, internal energy, and velocity may not be uniform over these macroscopic length scales. The external gravitational potential causes gradients in density, pressure, and chemical potential even at equilibrium. Despite these complications, it is important to formulate the thermodynamic analysis of environmental systems at the macroscopic scale. Heretofore, this has been accomplished primarily using the approach of rational thermodynamics whereby the thermodynamic dependence of macroscale internal energy on macroscale variables is hypothesized directly without development of any systematic method for transforming microscale energy dependence from the microscale to the macroscale. However when thermodynamic variables are inhomogeneous at the microscale, the functional dependence of macroscale internal energy on macroscale variables is not a simple extension of the microscale case. In the present work, the relation between the definitions of microscale and macroscale intensive thermodynamic variables is established. Expressions for the material derivatives of macroscale internal energy of phases, interfaces, and common lines are derived from and consistent with their microscopic counterparts by integrating to the macroscale. The forms obtained and the consistency required will be important for use in analyses of systems at scales where microscopic heterogeneities cannot be neglected.

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1. Background

The modeling of flow in environmental systems typically involves solution of differential equations formulated at a scale larger than a minimum fluid continuum scale. The length scale encompasses a representative region of the system of interest. For porous medium flows, the macroscale is much larger than the diameter of a pore and may span tens to thousands of pore diameters such that it ranges from millimeters to meters. The characteristics of the system at a macroscale point are actually characteristics of a representative volume of the system in the region of the point. Additionally, in some cases, averaging is performed over the entire extent of one or more spatial dimensions, such as integration over the thickness of an aquifer, with the result that the scale of the equations in those dimensions is equal to the scale of the physical system. For systems that have no solid phase, integrations may be performed over im-

portant length scales of the physical domain, such as integration over the cross-section of a river or over the depth of an estuary. Thus the averaging is performed over large, inhomogeneous regions such that the energy, velocities, and densities appearing in the governing equations are representative of the averaging region rather than of values at a microscale point. Integration theorems that facilitate the transformation of conservation equations from the microscale to the macroscale or megascale are well known (e.g., [1,2,13,15,27]), but little has been done to transform thermodynamic dependences systematically.

The fact that environmental systems are characterized by quantities such as density, velocity, energy, and temperature reported at length scales on the order of meters raises a number of important questions relating to both measurement and modeling. For example, consider the velocity of the flow of a phase in a typical porous medium. If we examine this system at the microscale, it is possible to identify velocities within each pore and the variation of that velocity across the diameter of the pore. However, because it is not practical to determine the detailed geometry of a porous medium,

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such systems are modeled at a length scale encompassing hundreds, thousands, or many millions of pores. The specification of a “velocity” of one of the phases at this large scale must be done with care. It is important to average the microscale velocities in such a manner that the macroscale velocities are representative of the flow field. If one were able to make measurements of the microscale velocity field within the averaging volume, those measurements should be useful in determining the macroscale velocity. Additionally, the macroscale velocity must be useful in conservation equations of mass, momentum, and energy used to describe the system. A definition of macroscale velocity is without value if it is dependent on the size of the averaging region, is unrelated to microscale behavior, and cannot be employed in equations used to make predictions about the system.

A systematic approach for mathematically transforming variables and conservation equations from the microscale to a larger scale has been described and employed by Hassanizadeh and Gray [17,18]. This approach requires that integration of microscale variables to obtain macroscale analogs be accomplished by assuring that the integrations involved satisfy an additivity property so that extensive properties of a system are conserved regardless of the scale at which they are measured ([17,18,22]). For example, one could define a macroscale velocity representative of an α phase occupying the volume, \mathcal{V}^α , within a macroscale region of interest as

$$\bar{\mathbf{v}}^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \mathbf{v} d\mathcal{V} \quad (1)$$

The problem with this definition is that the integrand does not have physical meaning. The average velocity obtained is merely a spatial average. An alternative definition of average velocity that satisfies the additivity condition is

$$\mathbf{v}^\alpha = \frac{\int_{\mathcal{V}^\alpha} \rho \mathbf{v} d\mathcal{V}}{\int_{\mathcal{V}^\alpha} \rho d\mathcal{V}} \quad (2)$$

In this definition, the integral in the numerator is the total momentum of the α phase within the volume with the quantity $\rho \mathbf{v} d\mathcal{V}$ being the momentum at a microscale point. This integrand is additive. The denominator in this expression is the total mass of α phase within the volume with $\rho d\mathcal{V}$ being the mass at a microscale point. Physically, the average velocity defined in Eq. (2) is the momentum per unit mass. The macroscale velocity defined in this fashion is more easily and properly employed in conservation equations than the spatial average. In cases where the density of the α phase material is constant, the definitions of macroscale velocity provided in Eqs. (1) and (2) are equivalent.

The additivity requirement is useful for developing macroscale measures of mass, velocity, and energy that can be expressed as integrals of microscale properties

and that may be employed in conservation equations. However, to complete the physical description at the macroscale, constitutive forms must be obtained for functions such as the stress tensor and the heat conduction vector. In addition, some additional quantities—such as temperature and chemical potential—must be defined that are characteristic of a macroscale region. When the microscale temperature is constant within the macroscale “point”, the macroscale and microscale temperatures should be equal. However, when the microscale temperature is not constant, the appropriate integration procedure involving temperature that satisfies the additivity principle is not obvious. As another example, when a gravitational field acts on the system and/or flow is occurring, the microscale chemical potential will not be constant within the macroscale averaging volume. The definition of the macroscale chemical potential should relate to its microscale counterpart and should also be useful for modeling of flow and transport at the macroscale.

The principles for systematic change of microscale extensive variables to the macroscale have been elucidated in Hassanizadeh and Gray [17]. However, work to systematically transform the scale of intensive variables—such as pressure, chemical potential, interfacial tension, and temperature—is lacking. Additionally, the microscale internal energy in a homogeneous system has a natural dependence on entropy, masses of the chemical species, and volume (e.g., [3,5,6,9]). When a system is not homogeneous, the microscale energy per volume may still be studied as a function of entropy per volume and the mass densities of the species at the microscale points of interest (e.g., [10]). Kondepudi and Progovine [21] have noted that in inhomogeneous systems, the total internal energy is no longer a function of extensive variables such as entropy, volume, and mass. They state further that one cannot define a single temperature for a macroscale system that has a non-constant microscale temperature field. Therefore, for study of environmental systems where a mathematical “point” corresponds to a physical region consisting of a block of porous medium, the cross-section of a river, or an aerial location on an estuary integrated over the depth, a thermodynamic formalism must be developed with considerable care and with caution.

To be sure, the problem of assuring consistency arises whenever one attempts to apply a formalism developed at one scale to modeling processes at a larger scale. Zubarev et al. [28] have shown that the development of thermodynamic relations from a statistical approach leads to quantities appearing in the equations that are averaged over the grand canonical ensemble. They point out that this is very reasonable since quantities in an ensemble can fluctuate so that the properties observed, corresponding to microscale properties in the present discussion, should be treated as average values.

The problem of formulating a useful thermodynamics is not restricted only to cases where a change in scale occurs. Jou et al. [20] and Maugin [23] have noted that the approaches used at the microscale can be roughly separated into three formalisms: classical irreversible thermodynamics (CIT), rational thermodynamics (RT), and extended irreversible thermodynamics (EIT). CIT is the approach most widely accepted by physicists and physico-chemists [23]. The fundamental hypothesis of this approach is that of local equilibrium. This assumption states that at each instant in time, every point in the system may be considered to be in local equilibrium such that the equilibrium relations among state variables remain valid. CIT is the basis for the range of applications presented by de Groot and Mazur [8]. RT is a formalism whose main objective is to provide a method for deriving constitutive equations [20]. In contrast to CIT, it ignores the relations of thermostatics and hypothesizes thermodynamic functional dependences following a set of axioms. Maugin [23] describes the basic postulates of RT as claiming that those entities that could be defined precisely only at equilibrium in fact exist for any thermodynamic state whatsoever, even largely outside of equilibrium. Therefore, quantities such as temperature and entropy are introduced on a mathematical basis to ensure coherence of the theory and are unrelated to physical quantities. Because of this disconnection, Jou et al. [20] state that it is not possible to check whether or not the temperature measured by a thermocouple corresponds to the temperature used in RT. From a practical point of view, this means that the utility of tables of thermodynamic relations developed from equilibrium considerations or measurements may be limited because the functions that arise in RT are mathematical constructions rather than verifiable expressions concerning the physical state of the system. The origins of this approach, as well as example applications, are found in Coleman and Noll [7] and Truesdell [25]. Despite its limitations, RT has found utility, particularly, in describing the dissipative stresses in solids and fluids. EIT is the latest entry into the attempt to describe the thermomechanical behavior of materials. EIT is an extension of CIT that builds on those relations by including dissipative fluxes as additional independent variables. Thus, at equilibrium the standard CIT functional dependences are recovered. The task in EIT is to find evolution equations for the additional independent variables. EIT is the main focus, for example, of Jou et al. [20].

The preceding comments highlight two important, and possibly contradictory, points relating to the thermodynamic description of macroscale systems. First, when the system under consideration is microscopically inhomogeneous, macroscopic energy may not be defined as a function of entropy, volume, and mass. On the other hand, current methods for modeling the thermo-

dynamics of dynamic systems rely on postulation of energy as a function of entropy, volume, and mass (and some dissipative fluxes away from equilibrium) or on independent variables that are not necessarily related to physical quantities. In light of these difficulties, one possible approach for describing macroscale thermodynamics is to transform the microscale relations to the macroscale systematically so that the relation between macroscale energy and macroscale independent variables can be discerned, with the macroscale variables well-defined averages of their microscale counterparts.

Heretofore, the mathematically consistent RT approach has typically been adopted in macroscale continuum mechanics, with macroscale internal energy hypothesized to depend on macroscale variables (e.g., [4,12,19]). However, this process does not require definitions of thermodynamic variables and functional dependences that are consistent with those employed at the microscale and that retain a relation between the macroscale and microscale thermodynamic quantities. Thus no synergy among experiments performed at different scales exists, and the macroscale theories cannot be informed by microscale, or even macroscale, experiments. Ambiguity exists even as to the definition of macroscale temperature. Additionally, in the transformation from the microscale to the macroscale, new independent variables are introduced relating to geometric densities. These variables describe the volume of a phase per total macroscale volume, the interfacial areas between phases per volume, and the length of common line where three phases come together per volume. As with EIT, these new independent variables require evolution equations. For application to real systems, such complex mathematical constructs must have parameters and variables that can be measured and related to the physics of the system of interest.

Despite the difficulties outlined, we are interested in obtaining a thermodynamic description of the state and behavior of a macroscale system, a system for which integration is performed over a representative averaging volume, or some appropriate volume much larger than the microscale, to obtain the definition of variables. The points identified above indicate that, at least for some systems, it is not possible to postulate thermodynamic dependences at the macroscale in a manner that is both mathematically correct and physically meaningful. Therefore, the approach to be adopted here is to make use of microscale thermodynamic relations and transform them to the macroscale. The starting point will be the microscale thermodynamic relations of CIT for phases, interfaces, and common lines. These will be integrated to obtain expressions that relate the derivatives of macroscale energy to the derivatives of other macroscale variables. This is done without having to postulate a functional form at the macroscale. Examination of the macroscale forms reveals when the integrated CIT

forms would be equivalent to forms postulated directly at the macroscale using RT.

Note that, alternatively, one could integrate microscale dependences obtained using RT or EIT to the macroscale. The main idea is to build on reasonable microscale formulations to obtain macroscale thermodynamic formulations that are consistent with and related to those forms. Conservation equations developed at the microscale are transformed to the macroscale using averaging procedures (e.g., [14]). They are not discarded in favor of new macroscale hypotheses. In the same way, the objective of this work is to provide a path for transformation of a microscale formalism to the macroscale as opposed to simply ignoring the useful and consistent results of the microscale formalism.

2. Macroscale relations among thermodynamic quantities for a fluid phase

As has been noted earlier, the formulation of macroscale thermodynamics for a phase is complicated when the system is not at equilibrium or when gradients in any of the microscopic phase properties exist. Specifically, in these instances the total macroscale internal energy for a fluid may not be expressed simply as a function of the macroscale entropy, mass and volume. A functional representation requires inclusion of additional independent variables such that

$$\mathcal{E}_I^\alpha = \mathcal{E}_I^\alpha(\mathcal{S}^\alpha, \mathcal{M}^\alpha, \mathcal{V}^\alpha, \dots) \quad (3)$$

where the superscript α is used to indicate that the quantities are properties of the α phase calculated as integrals over some region of space occupied by α fluid; and the script variable are extensive measures of internal energy (\mathcal{E}_I^α), entropy (\mathcal{S}^α), mass (\mathcal{M}^α), and volume (\mathcal{V}^α). Throughout this analysis, the integration to the macroscale will be performed over phases, interfaces, and common lines within an averaging volume, \mathcal{V} whose size, shape, and orientation are independent of location and time. Therefore, it will be convenient to work with densities defined with respect to that volume. In this case, the equality (3) is expressed:

$$\hat{E}_I^\alpha = \hat{E}_I^\alpha(\hat{\eta}^\alpha, \epsilon^\alpha \rho^\alpha, \epsilon^\alpha, \dots) \quad (4)$$

where the superscript α indicates that the quantities are macroscale properties of the α phase, \hat{E}_I^α is the internal energy of the α phase per averaging volume, $\hat{\eta}^\alpha$ is the entropy of the α phase per averaging volume, $\epsilon^\alpha \rho^\alpha$ is the mass of α phase per averaging volume with ϵ^α being the volume of α phase per averaging volume and ρ^α being the mass density of the α phase. If the independent macroscale variables are obtained by integrating uniform microscale properties, the equality indicated will hold with dependence on only the three variables explicitly indicated. When the microscale precursors of

their macroscale averages are non-uniform, the functional dependence explicitly indicated in Eq. (4) may be incomplete such that additional independent variables are required. Here, the macroscale thermodynamic expressions will be developed based on knowledge of the microscale situation.

Besides obtaining macroscale expressions for the internal energy, the total energy, \hat{E}_T^α , which is the sum of internal, kinetic, and potential energy, can be averaged such that, for the α phase within the averaging volume

$$\begin{aligned} \hat{E}_T^\alpha &= \hat{E}_I^\alpha + \hat{E}_K^\alpha + \frac{1}{2} \epsilon^\alpha \rho^\alpha v^{\alpha 2} + \hat{E}_\psi^\alpha \\ &= \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \left(\hat{E} + \frac{1}{2} \rho v^2 + \rho \psi \right) d\mathcal{V} \end{aligned} \quad (5a)$$

$$\hat{E}_I^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{E} d\mathcal{V} \quad (5b)$$

$$\hat{E}_K^\alpha + \frac{1}{2} \epsilon^\alpha \rho^\alpha v^{\alpha 2} = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \frac{1}{2} \rho v^2 d\mathcal{V} \quad (5c)$$

$$\begin{aligned} \hat{E}_K^\alpha &= \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{E}_K d\mathcal{V} = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \frac{1}{2} \rho \bar{v}^2 d\mathcal{V} \\ &= \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}^\alpha|^2 d\mathcal{V} \end{aligned} \quad (5d)$$

$$\hat{E}_\psi^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \psi d\mathcal{V} \quad (5e)$$

$$\hat{\eta}^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{\eta} d\mathcal{V} \quad (5f)$$

$$\epsilon^\alpha \rho^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho d\mathcal{V} \quad (5g)$$

where \hat{E} is the microscale internal energy density, ρ is the microscale mass density, v is the microscale speed, $\hat{\eta}$ is the microscale entropy density, \mathcal{V}^α is the portion of the averaging volume occupied by the α phase, ψ is an external potential such as gravity, and the four terms on the left side of Eq. (5a) are, respectively, the macroscale expression for the densities of thermodynamic internal energy, a macroscale energy component due to deviations of the microscale velocity from the macroscale value, the macroscale kinetic energy, and the macroscale potential energy. The macroscale quantities on the left sides of Eqs. (5a)–(5e), (5f) and (5g) have units, respectively, of energy per volume, entropy per volume, and mass per volume. Although the relationships between macroscale and microscale quantities in Eqs. (5a)–(5g) are explicit, the relationships between macroscale variables is not known at this point. When the system is at rest, the kinetic energy and the deviation kinetic energy, \hat{E}_K^α , will be zero. For porous media, where the velocities are small, \hat{E}_K^α and the kinetic energy may also be negligible. However, in general, these components must be included when analyzing systems from a macroscale perspective, particularly when turbulence effects or spatial velocity variations are significant. The following

analysis will be geared to finding the relation between the macroscale energy and other thermodynamic quantities when all are defined as appropriate integrals of microscale quantities.

Additionally, we know from microscale thermodynamics that

$$\hat{E} = \hat{E}(\hat{\eta}, \rho) = \theta \hat{\eta} + \mu \rho - p \tag{6a}$$

where θ is the microscale temperature with

$$\frac{\partial \hat{E}}{\partial \hat{\eta}} = \theta \tag{6b}$$

μ is the chemical potential with

$$\frac{\partial \hat{E}}{\partial \rho} = \mu \tag{6c}$$

and p is the microscale pressure. The macroscale internal energy, as defined in Eq. (5b), may then be expressed after substitution of Eq. (6a) as:

$$\hat{E}_I^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} [\theta \hat{\eta} + \mu \rho - p] d\mathcal{V} \tag{7}$$

Introduce as yet undefined macroscale measures of temperature, θ^α , chemical potential, μ^α , and pressure, p^α that are considered constant within \mathcal{V}^α such that:

$$\begin{aligned} \hat{E}_I^\alpha = & \theta^\alpha \hat{\eta}^\alpha + \mu^\alpha \epsilon^\alpha \rho^\alpha - p^\alpha \epsilon^\alpha + \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} [(\theta - \theta^\alpha) \hat{\eta} \\ & + (\mu - \mu^\alpha) \rho - (p - p^\alpha)] d\mathcal{V} \end{aligned} \tag{8}$$

where the definitions of $\hat{\eta}^\alpha$ and ρ^α as given in Eqs. (5f) and (5g) have been employed.

If macroscale thermodynamics are postulated in the same manner as microscale thermodynamics using RT, $\hat{E}_I^\alpha(\hat{\eta}^\alpha, \epsilon^\alpha \rho^\alpha, \epsilon^\alpha)$, the integral terms in Eq. (8) will not be present. Although the macroscale thermodynamic variables such as temperature and chemical potential cannot be related to their microscale counterparts using the RT hypotheses, the macroscale and microscale cases would take on completely analogous forms. However, there is no reason at all that the integrals will generally be zero, particularly in the case where an external potential is influencing the system. The macroscale thermodynamic expression derived from integrating the microscale CIT formulation as Eq. (8) is thus, in general, different from a thermodynamic expression postulated at the macroscale using RT. No postulation of the dependence of macroscale energy on a specific set of independent macroscale variables has been made. The microscale CIT-based relation given in Eq. (8) may be used in the development of the constrained entropy inequality provided expressions can be derived for the introduced, and still arbitrary, macroscale variables θ^α , μ^α , and p^α in terms of integrals of microscale variables. Note that the definitions are not unique. However, the following forms have appeal because they indicate equality of

microscale and macroscale forms when the microscale quantity is constant within the averaging volume

$$\int_{\mathcal{V}^\alpha} \hat{\eta}(\theta - \theta^\alpha) d\mathcal{V} = 0 \tag{9a}$$

$$\int_{\mathcal{V}^\alpha} \rho(\mu - \mu^\alpha) d\mathcal{V} = 0 \tag{9b}$$

$$\int_{\mathcal{V}^\alpha} (p - p^\alpha) d\mathcal{V} = 0 \tag{9c}$$

Simple rearrangement of these equations provides

$$\theta^\alpha = \frac{\int_{\mathcal{V}^\alpha} \hat{\eta} \theta d\mathcal{V}}{\int_{\mathcal{V}^\alpha} \hat{\eta} d\mathcal{V}} = \frac{1}{\hat{\eta}^\alpha \mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{\eta} \theta d\mathcal{V} \tag{10a}$$

$$\mu^\alpha = \frac{\int_{\mathcal{V}^\alpha} \rho \mu d\mathcal{V}}{\int_{\mathcal{V}^\alpha} \rho d\mathcal{V}} = \frac{1}{\epsilon^\alpha \rho^\alpha \mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \mu d\mathcal{V} \tag{10b}$$

$$p^\alpha = \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} p d\mathcal{V} \tag{10c}$$

Thus, in the same way that the macroscale velocity is a weighted integral average of the microscale velocity, the macroscale temperature is an entropy-weighted average of the microscale temperature while the macroscale chemical potential is a mass-weighted average of the microscale chemical potential.

In light of definitions (10a)–(10c), the definition of macroscale internal energy given as Eq. (8) simplifies to

$$\hat{E}_I^\alpha = \theta^\alpha \hat{\eta}^\alpha + \mu^\alpha \epsilon^\alpha \rho^\alpha - p^\alpha \epsilon^\alpha \tag{11}$$

First note that Eq. (11), which expresses macroscale internal energy as a function of macroscale independent variables, is a derived, rather than postulated, macroscopic function. Although it is of the same structure as the microscale equation for internal energy, this equation does not imply a corresponding functional dependence of macroscale energy on macroscale variables of the form $\hat{E}_I^\alpha(\hat{\eta}^\alpha, \epsilon^\alpha \rho^\alpha, \epsilon^\alpha)$. It does show directly that macroscale energy depends on an expanded set of macroscale variables such that $\hat{E}_I^\alpha(\hat{\eta}^\alpha, \epsilon^\alpha \rho^\alpha, \epsilon^\alpha, \theta^\alpha, \mu^\alpha, p^\alpha)$. The actual dependence on any of the last three variables in this expression may be dropped only if microscale temperature, chemical potential, and pressure are homogeneous within the averaging volume. Even though the form of Eq. (11) is the same as obtained from a hypothesis based on RT, the meanings of all the macroscale variables are well defined in terms of microscale variables. This difference can be highlighted by expressing the differential of the macroscale internal energy of Eq. (11) according to

$$\begin{aligned} d\hat{E}_I^\alpha = & \theta^\alpha d\hat{\eta}^\alpha + \mu^\alpha d(\epsilon^\alpha \rho^\alpha) - p^\alpha d\epsilon^\alpha + \hat{\eta}^\alpha d\theta^\alpha \\ & + \epsilon^\alpha \rho^\alpha d\mu^\alpha - \epsilon^\alpha dp^\alpha \end{aligned} \tag{12}$$

Note that the differential of ϵ^α appears in this expression as a surrogate for the differential of volume because the internal energy (and entropy) have been defined per unit averaging volume, not per volume of phase α . The

differential of the microscale internal energy behaves according to [6]

$$d\hat{E} = \theta d\hat{\eta} + \mu d\rho \quad (13a)$$

subject to the Gibbs–Duhem equation:

$$0 = \hat{\eta} d\theta + \rho d\mu - dp \quad (13b)$$

In general, Eq. (12) may not be broken into two parts corresponding to the microscale situation as in Eqs. (13a) and (13b). However, since all the terms in Eq. (12) are macroscale quantities, this equation may be written

$$d\hat{E}_1^\alpha = \theta^\alpha d\hat{\eta}^\alpha + \mu^\alpha d(\epsilon^\alpha \rho^\alpha) - p^\alpha d\epsilon^\alpha + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \hat{\eta} d\theta^\alpha d\mathcal{V} \\ + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \rho d\mu^\alpha d\mathcal{V} - \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} dp^\alpha d\mathcal{V} \quad (14)$$

Then integration of the Gibbs–Duhem equation over the averaging volume and subtraction of the result from Eq. (14) yields:

$$d\hat{E}_1^\alpha = \theta^\alpha d\hat{\eta}^\alpha + \mu^\alpha d(\epsilon^\alpha \rho^\alpha) - p^\alpha d\epsilon^\alpha \\ + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \hat{\eta} d(\theta^\alpha - \theta) d\mathcal{V} + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \rho d(\mu^\alpha - \mu) d\mathcal{V} \\ - \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} d(p^\alpha - p) d\mathcal{V} \quad (15)$$

This equation confirms the fact that, in general, Eq. (4) is a complete expression for the functional dependence of macroscale internal energy only when the sum of the three integrals in Eq. (15) is zero. Therefore postulation of the functional dependence of macroscale thermodynamics is different from integrating the functional dependences postulated at the microscale. The last three integral terms in Eq. (15) account for differences between the form of microscale and macroscale internal energy due to microscale inhomogeneities. Indeed, if the pressure, chemical potential, and temperature within the averaging volume are constant, then these integrals would be zero and Eq. (4) would apply. In other words, the three integrals that survive in Eq. (15) do not arise in the RT approach. They confirm macroscale RT equations and integrally derived macroscale thermodynamic forms are equivalent only when the microscale variables are uniform within the averaging volume. For the case of porous medium flows where the dynamics are slow, neglect of the integrals in Eq. (15) may introduce a negligible error such that the macroscale quantities introduced in the RT approach would be essentially equal to the quantities explicitly defined as integrals of microscale quantities. Furthermore, it is important to recognize that gravitational potential does not appear explicitly in the definition of macroscale internal energy given by Eq. (11). The macroscale gravitational potential, as defined in Eq. (5e) may be included in the analysis as a separate function.

Terms involving temporal and spatial derivatives of the macroscopic energy variables appear in the macroscale energy transport equations for properties of phases, interfaces, and common lines [14]. By using the time and space averaging theorems, one can convert between derivatives of integrated variables and the integration of derivatives of microscale variables. Such an exchange allows one to develop relations between changes in macroscale energy in terms of changes in macroscale entropy, mass, and volume. For averaging of porous medium flows when a representative averaging volume, \mathcal{V} , that is independent of time and space is used, a transport theorem that allows for the exchange of order of differentiation and integration is a simple extension of that found, for example, in Whitaker et al. [26] and Gray et al. [15]

$$\frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} d\mathbf{f} d\mathcal{V} = d \left[\frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} f d\mathcal{V} \right] \\ + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} f (\mathbf{d}\mathbf{r} - \mathbf{w} dt) \cdot \mathbf{n}^\alpha dS \quad (16)$$

where $S_{\alpha\beta}$ is the interface between the α phase and all other phases within the averaging volume, S_α is the external surface of the averaging volume that is in the α phase, ξ is a microscale coordinate with respect to the centroid of the averaging volume, \mathbf{r} is a position vector, \mathbf{w} is the velocity of the interface, t is time, and \mathbf{n}^α is the unit normal vector at a surface of the α phase and oriented outward from the α phase in the averaging volume. In this expression, ‘ d ’ is a differential at the macroscale. If the function $f = p^\alpha - p$, then Eq. (16) provides the following expression for the pressure:

$$\frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} d(p^\alpha - p) d\mathcal{V} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (p^\alpha - p) (\mathbf{d}\mathbf{r} - \mathbf{w} dt) \cdot \mathbf{n}^\alpha dS \quad (17)$$

Substitution of this expression into Eq. (15) yields:

$$d\hat{E}_1^\alpha = \theta^\alpha d\hat{\eta}^\alpha + \mu^\alpha d(\epsilon^\alpha \rho^\alpha) - p^\alpha d\epsilon^\alpha \\ + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \hat{\eta} d(\theta^\alpha - \theta) d\mathcal{V} \\ + \frac{1}{\mathcal{V}} \int_{\mathcal{V}^\alpha} \rho d(\mu^\alpha - \mu) d\mathcal{V} \\ - \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (p^\alpha - p) (\mathbf{d}\mathbf{r} - \mathbf{w} dt) \cdot \mathbf{n}^\alpha dS \quad (18)$$

Introduce a particular macroscale material derivative by setting $d = D^\alpha/Dt$ where

$$\frac{D^\alpha}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \nabla \quad (19)$$

Substitution of this expression into Eq. (18) provides the equation for the material derivative of the internal energy as:

$$\begin{aligned} \frac{D^\alpha \hat{E}_I^\alpha}{Dt} &= \theta^\alpha \frac{D^\alpha \hat{\eta}^\alpha}{Dt} + \mu^\alpha \frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} - p^\alpha \frac{D^\alpha \epsilon^\alpha}{Dt} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{\eta} \frac{D^\alpha (\theta - \theta^\alpha)}{Dt} d\mathcal{V} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \frac{D^\alpha (\mu - \mu^\alpha)}{Dt} d\mathcal{V} \\ &\quad + \frac{1}{\mathcal{V}^\alpha} \int_{S_{\alpha\beta}} (p - p^\alpha)(\mathbf{v}^\alpha - \mathbf{w}) \cdot \mathbf{n}^\alpha dS \end{aligned} \quad (20)$$

The material derivatives of energy, mass, and entropy are particularly important as it is these derivatives that arise in the conservation equations. This relation among the derivatives of energy, entropy, and mass is needed in other analyses when constraining the entropy inequality with conservation equations of mass, momentum, and energy (e.g. [16]), but with the added advantage of not relying on a macroscale RT postulation of energy dependence.

In some conventions, the total macroscale internal energy is taken to be the sum of the thermodynamic internal energy, \hat{E}_I^α , and the kinetic energy deviation, \hat{E}_K^α , so that:

$$\hat{E}^\alpha = \hat{E}_I^\alpha + \hat{E}_K^\alpha \quad (21)$$

Therefore it is also important to provide expressions for the material derivative of the deviation kinetic energy defined in Eq. (5d) which accounts for the kinetic energy of the system that is due to microscale velocity deviations from the macroscale average value. Define the macroscale deviation kinetic energy per unit mass as:

$$\begin{aligned} K_E^\alpha &= \frac{\int_{\mathcal{V}^\alpha} \left[\rho \left(\frac{1}{2} \bar{v}^2 \right) \right] d\mathcal{V}}{\int_{\mathcal{V}^\alpha} \rho d\mathcal{V}} \\ &= \frac{1}{\epsilon^\alpha \rho^\alpha \mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \left[\rho \left(\frac{1}{2} |\mathbf{v} - \mathbf{v}^\alpha|^2 \right) \right] d\mathcal{V} = \frac{\hat{E}_K^\alpha}{\epsilon^\alpha \rho^\alpha} \end{aligned} \quad (22)$$

Then the material derivative of the macroscale deviation kinetic energy per volume is obtained following the same approach as above as

$$\frac{D^\alpha \hat{E}_K^\alpha}{Dt} = K_E^\alpha \frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} + \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \frac{D^\alpha K_E^\alpha}{Dt} d\mathcal{V} \quad (23)$$

A total macroscale chemical potential is defined that accounts for subscale velocity fluctuations according to

$$\mu_T^\alpha = \mu^\alpha + K_E^\alpha \quad (24)$$

The deviation kinetic energy, K_E^α , in this definition accounts for the deviation of a macroscopically observed chemical potential from the simple volume average of microscale chemical potential in much the same way that Reynolds stresses contribute to the observed stress after time averaging of a turbulent flow. For cases where the flow is very slow, such as in porous media, the deviation kinetic energy will be negligible. However, if one is averaging over systems with faster dynamics, this term

may have to be considered explicitly. Addition of Eqs. (20) and (23) yields:

$$\begin{aligned} \frac{D^\alpha (\hat{E}_I^\alpha + \hat{E}_K^\alpha)}{Dt} &= \theta^\alpha \frac{D^\alpha \hat{\eta}^\alpha}{Dt} + \mu_T^\alpha \frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} - p^\alpha \frac{D^\alpha \epsilon^\alpha}{Dt} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{\eta} \frac{D^\alpha (\theta - \theta^\alpha)}{Dt} d\mathcal{V} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \frac{D^\alpha (\mu - \mu_T^\alpha)}{Dt} d\mathcal{V} \\ &\quad + \frac{1}{\mathcal{V}^\alpha} \int_{S_{\alpha\beta}} (p - p^\alpha)(\mathbf{v}^\alpha - \mathbf{w}) \cdot \mathbf{n}^\alpha dS \end{aligned} \quad (25)$$

or, alternatively, as

$$\begin{aligned} \frac{D^\alpha (\hat{E}_I^\alpha + \hat{E}_K^\alpha)}{Dt} &= \theta^\alpha \frac{D^\alpha \hat{\eta}^\alpha}{Dt} + \mu_T^\alpha \frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \hat{\eta} \frac{D^\alpha (\theta - \theta^\alpha)}{Dt} d\mathcal{V} \\ &\quad - \frac{1}{\mathcal{V}^\alpha} \int_{\mathcal{V}^\alpha} \rho \frac{D^\alpha (\mu - \mu_T^\alpha)}{Dt} d\mathcal{V} \\ &\quad + \frac{1}{\mathcal{V}^\alpha} \int_{S_{\alpha\beta}} p(\mathbf{v}^\alpha - \mathbf{w}) \cdot \mathbf{n}^\alpha dS \end{aligned} \quad (26)$$

When the deviation kinetic energy is small, as in most porous media systems, the difference between Eqs. (20) and (25) is negligible.

In contrast to the RT procedure of postulating macroscale thermodynamics without consideration of microscale relations, all the quantities that appear in Eq. (26) are explicitly defined in terms of their microscale counterparts. This has important implications in that the macroscale quantities may be measured and determined from the microscale distributions. Furthermore, the RT approach postulates $\hat{E}^\alpha = \hat{E}_I^\alpha + \hat{E}_K^\alpha$ as the macroscale internal energy density that is a function of standard thermodynamic variables. That approach is unable to identify how the subscale velocity deviations influence the macroscale functions.

3. Macroscale relations among thermodynamic quantities for an interface

When modeling multiphase flow in porous media, it is necessary to account for the energy associated with interfaces between phases. This energy is evidenced in capillary effects. The transformation from the microscale energy expression to the macroscale expression involves integration over the interface contained within the averaging volume. Furthermore, the boundary or edge of the interface is a common line where three phases come together. The development of the expressions for the macroscale interfacial energy and its derivatives follows along the same lines as that for the phase energy. The actual derivation is somewhat lengthier than for a volume phase because of the terms in the

averaging theorems that account for the curvature of the interface. For convenience, the derivation will only be outlined here.

The macroscale energy, entropy, and mass for an interface between the α and β phases can be obtained by integrating the respective microscale densities, expressed per unit area, over the interface within the volume of interest such that

$$\hat{E}_I^{\alpha\beta} + \hat{E}_K^{\alpha\beta} + \frac{1}{2} a^{\alpha\beta} \rho^{\alpha\beta} v^{\alpha\beta 2} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \left(\hat{E} + \frac{1}{2} \rho v^2 \right) dS \tag{27a}$$

$$\hat{E}_I^{\alpha\beta} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{E} dS \tag{27b}$$

$$\hat{E}_K^{\alpha\beta} + \frac{1}{2} a^{\alpha\beta} \rho^{\alpha\beta} v^{\alpha\beta 2} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \frac{1}{2} \rho v^2 dS \tag{27c}$$

$$\begin{aligned} \hat{E}_K^{\alpha\beta} &= \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{E}_K dS = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \frac{1}{2} \rho \tilde{v}^2 dS \\ &= \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}^{\alpha\beta}|^2 dS \end{aligned} \tag{27d}$$

$$\hat{\eta}^{\alpha\beta} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} dS \tag{27e}$$

$$a^{\alpha\beta} \rho^{\alpha\beta} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho dS \tag{27f}$$

$$\mathbf{v}^{\alpha\beta} = \frac{1}{a^{\alpha\beta} \rho^{\alpha\beta} \mathcal{V}} \int_{S_{\alpha\beta}} \rho \mathbf{v} dS \tag{27g}$$

and

$$a^{\alpha\beta} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} dS \tag{27h}$$

Note that in these equations, ρ is the microscale mass density per area or the excess mass density and $a^{\alpha\beta} \rho^{\alpha\beta}$ is the mass associated with the $\alpha\beta$ interface per averaging volume. The macroscale densities are defined per unit volume, with the exception of $\rho^{\alpha\beta}$ which is mass per area. The interfacial energy is best expressed per unit volume rather than per unit area because it may be directly added to the phase energy per volume to obtain a measure of the total energy per volume of the system. Additionally, the interfacial energy is not expressed per unit mass because such a quantity would create difficulties when the interface is massless.

The microscale internal energy per unit area is given by the thermodynamic relation

$$\hat{E} = \hat{E}(\hat{\eta}, \rho) = \theta \hat{\eta} + \mu \rho + \gamma \tag{28}$$

where γ is the surface tension. The macroscale internal energy per volume, as defined in Eq. (27b), may then be expressed after substitution of Eq. (28) as

$$\hat{E}_I^{\alpha\beta} = \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} [\theta \hat{\eta} + \mu \rho + \gamma] dS \tag{29}$$

Then by analogy with the relations employed for phases:

$$\hat{E}_I^{\alpha\beta} = \theta^{\alpha\beta} \hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} + \gamma^{\alpha\beta} a^{\alpha\beta} \tag{30}$$

where

$$\theta^{\alpha\beta} = \frac{\int_{S_{\alpha\beta}} \hat{\eta} \theta dS}{\int_{S_{\alpha\beta}} \hat{\eta} dS} = \frac{1}{\hat{\eta}^{\alpha\beta} \mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} \theta dS \tag{31a}$$

$$\mu^{\alpha\beta} = \frac{\int_{S_{\alpha\beta}} \rho \mu dS}{\int_{S_{\alpha\beta}} \rho dS} = \frac{1}{a^{\alpha\beta} \rho^{\alpha\beta} \mathcal{V}} \int_{S_{\alpha\beta}} \rho \mu dS \tag{31b}$$

and

$$\gamma^{\alpha\beta} = \frac{1}{a^{\alpha\beta} \mathcal{V}} \int_{S_{\alpha\beta}} \gamma dS \tag{31c}$$

The differential of the macroscale surface internal energy is obtained from Eq. (30) as

$$\begin{aligned} d\hat{E}_I^{\alpha\beta} &= \theta^{\alpha\beta} d\hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} d(a^{\alpha\beta} \rho^{\alpha\beta}) + \gamma^{\alpha\beta} da^{\alpha\beta} \\ &\quad + \hat{\eta}^{\alpha\beta} d\theta^{\alpha\beta} + a^{\alpha\beta} \rho^{\alpha\beta} d\mu^{\alpha\beta} + a^{\alpha\beta} d\gamma^{\alpha\beta} \end{aligned} \tag{32}$$

The differential expression of the microscale surface energy is taken on the surface and obeys the relation

$$d^s \hat{E} = \theta d^s \hat{\eta} + \mu d^s \rho \tag{33a}$$

with the Gibbs–Duhem equation

$$0 = \hat{\eta} d^s \theta + \rho d^s \mu + d^s \gamma \tag{33b}$$

Eq. (32) may be expressed, alternatively, as

$$\begin{aligned} d\hat{E}_I^{\alpha\beta} &= \theta^{\alpha\beta} d\hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} d(a^{\alpha\beta} \rho^{\alpha\beta}) + \gamma^{\alpha\beta} da^{\alpha\beta} \\ &\quad + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} d\theta^{\alpha\beta} dS + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho d\mu^{\alpha\beta} dS \\ &\quad + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} d\gamma^{\alpha\beta} dS \end{aligned} \tag{34}$$

The differential within the integral may be re-expressed in terms of a surface differential, d^s , plus the normal differential making use of the identity

$$d = d^s + (d\mathbf{r} - \mathbf{v} dt) \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot \nabla \tag{35}$$

where \mathbf{v} is the velocity of the interface material. This notation allows for general expressions to be developed without specifying which particular derivative function is being considered. Thus, for example, if the differential of interest is the macroscale del operator with $d = \nabla$, Eq. (35) becomes

$$\nabla = \nabla^s + (\nabla \mathbf{r} - \mathbf{v} \nabla t) \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot \nabla \tag{36}$$

However, $\nabla \mathbf{r}$ is the unit tensor and $\nabla t = 0$ so this equation expresses the spatial del operator with components in a surface of interest and normal to that surface as

$$\nabla = \nabla^s + \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot \nabla \tag{37}$$

Similarly, one can obtain a partial time derivative in space in terms of a partial time derivative on a surface by use of Eq. (35) as:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial t} \Big|_s - \mathbf{v} \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot \nabla \quad (38)$$

In general, one may employ Eq. (35) to obtain

$$\begin{aligned} \mathbf{d}\hat{E}_1^{\alpha\beta} &= \theta^{\alpha\beta} \mathbf{d}\hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} \mathbf{d}(a^{\alpha\beta} \rho^{\alpha\beta}) + \gamma^{\alpha\beta} \mathbf{d}a^{\alpha\beta} \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} \mathbf{d}^s \theta^{\alpha\beta} \, dS + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho \mathbf{d}^s \mu^{\alpha\beta} \, dS \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{d}^s \gamma^{\alpha\beta} \, dS + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \\ &\cdot (\hat{\eta} \nabla \theta^{\alpha\beta} + \rho \nabla \mu^{\alpha\beta} + \nabla \gamma^{\alpha\beta}) \, dS \end{aligned} \quad (39)$$

Integration of Gibbs–Duhem relation (33b) over the interface and subtraction from Eq. (39) yields

$$\begin{aligned} \mathbf{d}\hat{E}_1^{\alpha\beta} &= \theta^{\alpha\beta} \mathbf{d}\hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} \mathbf{d}(a^{\alpha\beta} \rho^{\alpha\beta}) + \gamma^{\alpha\beta} \mathbf{d}a^{\alpha\beta} \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} \mathbf{d}^s (\theta^{\alpha\beta} - \theta) \, dS + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho \mathbf{d}^s (\mu^{\alpha\beta} \\ &- \mu) \, dS + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{d}^s (\gamma^{\alpha\beta} - \gamma) \, dS \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\hat{\eta} \nabla \theta^{\alpha\beta} + \rho \nabla \mu^{\alpha\beta} \\ &+ \nabla \gamma^{\alpha\beta}) \, dS \end{aligned} \quad (40)$$

The transport and gradient theorems for a surface within a porous medium [13,15] may be employed to obtain

$$\begin{aligned} \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{d}^s f \, dS &= \mathbf{d} \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} f \, dS \right] \\ &- \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) f \, dS \right] \\ &+ \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} f (\nabla^s \cdot \mathbf{n}^\alpha) \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \, dS \right] \\ &+ \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} f (\mathbf{d}\mathbf{r} - \mathbf{w} \mathbf{d}t) \cdot \mathbf{v}^{\alpha\beta} \, dC \right] \end{aligned} \quad (41)$$

where $S_{\alpha\beta}$ is the interface between the α and β phases within the averaging volume, \mathbf{w} is the velocity of the common line, $C_{\alpha\beta\sigma}$, that forms the boundary of $S_{\alpha\beta}$, \mathbf{n}^α is the unit normal vector on the $S_{\alpha\beta}$ interface oriented outward from the α phase, ∇^s is the surface del operator, and $\mathbf{v}^{\alpha\beta}$ is a unit vector normal to the boundary curve of $S_{\alpha\beta}$ that is also tangent to the surface. With $f = \gamma^{\alpha\beta} - \gamma$ Eq. (41) can be applied to Eq. (40). Additionally, the macroscale gradients of macroscale thermodynamic properties may be moved outside the integrals such that Eq. (40) becomes

$$\begin{aligned} \mathbf{d}\hat{E}_1^{\alpha\beta} &= \theta^{\alpha\beta} \mathbf{d}\hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} \mathbf{d}(a^{\alpha\beta} \rho^{\alpha\beta}) + \gamma^{\alpha\beta} \mathbf{d}a^{\alpha\beta} \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} \mathbf{d}^s (\theta^{\alpha\beta} - \theta) \, dS \\ &+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho \mathbf{d}^s (\mu^{\alpha\beta} - \mu) \, dS \\ &- \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) (\gamma^{\alpha\beta} - \gamma) \, dS \right] \\ &+ \nabla \theta^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \hat{\eta} \, dS \right] \\ &+ \nabla \mu^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \rho \, dS \right] \\ &+ \nabla \gamma^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \, dS \right] \\ &+ \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (\gamma^{\alpha\beta} - \gamma) (\nabla^s \cdot \mathbf{n}^\alpha) \mathbf{n}^\alpha \cdot (\mathbf{d}\mathbf{r} - \mathbf{v} \mathbf{d}t) \, dS \right] \\ &+ \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\gamma^{\alpha\beta} - \gamma) (\mathbf{d}\mathbf{r} - \mathbf{w} \mathbf{d}t) \cdot \mathbf{v}^{\alpha\beta} \, dC \right] \end{aligned} \quad (42)$$

The integral terms in this equation account for subscale variations in the thermodynamic properties that cause the macroscale internal energy to deviate from the functional dependence $\hat{E}_1^{\alpha\beta} = \hat{E}_1^{\alpha\beta}(\hat{\eta}^{\alpha\beta}, a^{\alpha\beta} \rho^{\alpha\beta}, a^{\alpha\beta})$ that would be analogous to the microscale situation.

When considering dynamic systems, it is useful to have available an expression that relates the material derivative of the internal energy to the material derivatives of other thermodynamic quantities. Define a macroscale material derivative according to

$$\frac{D^{\alpha\beta}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\alpha\beta} \cdot \nabla \quad (43)$$

This represents a time derivative calculated moving with the average macroscale velocity of the $\alpha\beta$ interface. A time derivative of a property associated with an interface is calculated according to

$$\frac{D^{*\alpha\beta}}{Dt} = \frac{\partial}{\partial t} \Big|_s + \mathbf{v}^{\alpha\beta} \cdot \nabla^s \quad (44)$$

In this expression, the partial time derivative is calculated with surface coordinates fixed and ∇^s is the surface gradient operator. Also, define the macroscale rate of strain tensor as

$$\mathbf{d}^{\alpha\beta} = \frac{1}{2} [\nabla \mathbf{v}^{\alpha\beta} + (\nabla \mathbf{v}^{\alpha\beta})^T] \quad (45)$$

Then Eq. (42) may be expressed in terms of a macroscale material derivative such that

$$\begin{aligned}
\frac{D^{\alpha\beta} \hat{E}_1^{\alpha\beta}}{Dt} &= \theta^{\alpha\beta} \frac{D^{\alpha\beta} \hat{\eta}^{\alpha\beta}}{Dt} + \mu^{\alpha\beta} \frac{D^{\alpha\beta} (a^{\alpha\beta} \rho^{\alpha\beta})}{Dt} \\
&+ \gamma^{\alpha\beta} \frac{D^{\alpha\beta} a^{\alpha\beta}}{Dt} + \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \hat{\eta} \frac{D^{*\alpha\beta} (\theta^{\alpha\beta} - \theta)}{Dt} dS \\
&+ \frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \rho \frac{D^{*\alpha\beta} (\mu^{\alpha\beta} - \mu)}{Dt} dS \\
&- \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{v}^{\alpha\beta} - \mathbf{v}) (\gamma^{\alpha\beta} - \gamma) dS \right] \\
&+ \mathbf{d}^{\alpha\beta} : \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha (\gamma^{\alpha\beta} - \gamma) dS \right] \\
&+ \nabla \theta^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{v}^{\alpha\beta} - \mathbf{v}) \hat{\eta} dS \right] \\
&+ \nabla \mu^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{v}^{\alpha\beta} - \mathbf{v}) \rho dS \right] \\
&+ \nabla \gamma^{\alpha\beta} \cdot \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} \mathbf{n}^\alpha \mathbf{n}^\alpha \cdot (\mathbf{v}^{\alpha\beta} - \mathbf{v}) dS \right] \\
&+ \left[\frac{1}{\mathcal{V}} \int_{S_{\alpha\beta}} (\gamma^{\alpha\beta} - \gamma) (\nabla^s \cdot \mathbf{n}^\alpha) \mathbf{n}^\alpha \cdot (\mathbf{v}^{\alpha\beta} - \mathbf{v}) dS \right] \\
&+ \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\gamma^{\alpha\beta} - \gamma) (\mathbf{v}^{\alpha\beta} - \mathbf{w}) \cdot \mathbf{v}^{\alpha\beta} dC \right] \quad (46)
\end{aligned}$$

The subscale kinetic energy is defined using the notation

$$\begin{aligned}
K_E^{\alpha\beta} &= \frac{\int_{S_{\alpha\beta}} \left[\rho \left(\frac{1}{2} \bar{v}^2 \right) \right] dS}{\int_{S_{\alpha\beta}} \rho dS} \\
&= \frac{1}{a^{\alpha\beta} \rho^{\alpha\beta} \mathcal{V}} \int_{S_{\alpha\beta}} \left[\rho \left(\frac{1}{2} |\mathbf{v} - \mathbf{v}^{\alpha\beta}|^2 \right) \right] dS \\
&= \frac{\hat{E}_K^{\alpha\beta}}{a^{\alpha\beta} \rho^{\alpha\beta}} \quad (47)
\end{aligned}$$

An analogue to Eq. (24) may be used to define a total chemical potential according to

$$\mu_T^{\alpha\beta} = \mu^{\alpha\beta} + K_E^{\alpha\beta} \quad (48)$$

Therefore, the material derivative of the sum of the internal and subscale kinetic energy is obtained from Eq. (46) by replacing $\hat{E}_1^{\alpha\beta}$ with $\hat{E}_1^{\alpha\beta} + \hat{E}_K^{\alpha\beta}$ and by replacing $\mu^{\alpha\beta}$ with $\mu_T^{\alpha\beta}$. When the velocities are small, as with porous media, these additional terms will be negligible.

Eq. (46), or more precisely its counterpart written to include the deviation kinetic energy, can be compared with its counterpart for a phase, Eq. (25), respectively. The surface energy equation contains additional terms that account for the orientation of the surfaces at the microscale, which cannot be discerned directly from a macroscale perspective, and changes in curvature of the surfaces. None of the integral terms would arise if the surface internal energy were simply postulated as having

the same functional dependence on mass, entropy, and area as the microscale counterpart. In fact, all the integral terms that appear in Eq. (46) are zero for the case when the microscale temperature, interfacial tension, velocity, and chemical potential are constant within the averaging volume. In this case, only the first three terms on the right side of Eq. (46) would be non-zero and the functional dependence of macroscale internal energy on macroscale mass, entropy, and area would be identical to the microscale dependence.

4. Macroscale relations among thermodynamic quantities for a common line

Although common lines may seem to be of limited significance in comparison to the phases and interfaces, the forces exerted on a common line by interfaces and the movement of the common line as a fluid phase invades a region may be important. The common line tension is also an essential factor in understanding the contact angle between a wetting phase and a solid. The transformation from the microscale representation to the macroscale form involves integration over the common line and evaluation of functions at the end points of the common line contained within an averaging volume. The derivation is completely analogous to those presented previously. Therefore, only the important definitions and the results are presented.

The macroscale energy, entropy, and mass for a common line where the α , β , and σ phases come together are defined in terms of their microscale counterparts as

$$\begin{aligned}
\hat{E}_1^{\alpha\beta\sigma} + \hat{E}_K^{\alpha\beta\sigma} + \frac{1}{2} l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} v^{\alpha\beta\sigma^2} \\
= \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \left(\hat{E} + \frac{1}{2} \rho v^2 \right) dC \quad (49a)
\end{aligned}$$

$$\hat{E}_1^{\alpha\beta\sigma} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{E} dC \quad (49b)$$

$$\hat{E}_K^{\alpha\beta\sigma} + \frac{1}{2} l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} v^{\alpha\beta\sigma^2} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \frac{1}{2} \rho v^2 dC \quad (49c)$$

$$\begin{aligned}
\hat{E}_K^{\alpha\beta\sigma} &= \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{E}_K dC = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \frac{1}{2} \rho \bar{v}^2 dC \\
&= \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}^{\alpha\beta\sigma}|^2 dC \quad (49d)
\end{aligned}$$

$$\hat{\eta}^{\alpha\beta\sigma} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} dC \quad (49e)$$

$$l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho dC \quad (49f)$$

$$\mathbf{v}^{\alpha\beta\sigma} = \frac{1}{l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} \mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho \mathbf{v} dC \quad (49g)$$

and

$$l^{\alpha\beta\sigma} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} dC \quad (49h)$$

In these equations, the microscale densities on the right side are defined per unit length while the macroscale densities are per unit volume, with the exception of $\rho^{\alpha\beta\sigma}$ which is the macroscale mass per length.

The microscale thermodynamic relation for the internal energy per unit length of common line is

$$\hat{E} = \hat{E}(\hat{\eta}, \rho) = \theta \hat{\eta} + \mu \rho - \gamma_c \quad (50a)$$

with Gibbs–Duhem equation

$$0 = \hat{\eta} d\theta + \rho d\mu - d\gamma_c \quad (50b)$$

where γ_c is the line tension. The macroscale temperature, chemical potential, line tension, and subscale kinetic energy are defined analogously to those for the phases and interfaces except that the integration region is the common line length rather than the phase volume or interfacial area. Substitution of Eq. (50a) into Eq. (49b) provides the definition for the macroscale common line internal energy per unit volume

$$\hat{E}_1^{\alpha\beta\sigma} = \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} [\theta \hat{\eta} + \mu \rho - \gamma_c] dC \quad (51)$$

Then, analogously to the definitions of phase and interface macroscale properties

$$\hat{E}_1^{\alpha\beta\sigma} = \theta^{\alpha\beta\sigma} \hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} - \gamma^{\alpha\beta\sigma} l^{\alpha\beta\sigma} \quad (52)$$

where

$$\theta^{\alpha\beta\sigma} = \frac{\int_{C_{\alpha\beta\sigma}} \hat{\eta} \theta dC}{\int_{C_{\alpha\beta\sigma}} \hat{\eta} dC} = \frac{1}{\hat{\eta}^{\alpha\beta\sigma} \mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} \theta dC \quad (53a)$$

$$\mu^{\alpha\beta\sigma} = \frac{\int_{C_{\alpha\beta\sigma}} \rho \mu dC}{\int_{C_{\alpha\beta\sigma}} \rho dC} = \frac{1}{l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} \mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho \mu dC \quad (53b)$$

and

$$\gamma^{\alpha\beta\sigma} = \frac{1}{l^{\alpha\beta\sigma} \mathcal{V}} \int_{C_{\alpha\beta\sigma}} \gamma_c dC \quad (53c)$$

The differential of the macroscale internal energy may be expressed as

$$\begin{aligned} d\hat{E}_1^{\alpha\beta\sigma} &= \theta^{\alpha\beta\sigma} d\hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} d(l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma}) - \gamma^{\alpha\beta\sigma} dl^{\alpha\beta\sigma} \\ &+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} d\theta^{\alpha\beta\sigma} dC + \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho d\mu^{\alpha\beta\sigma} dC \\ &- \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} d\gamma^{\alpha\beta\sigma} dC \end{aligned} \quad (54)$$

The general differentials within the integral may be expressed in terms of a component in the one-dimensional common line space, \mathbf{d}^c , and a component normal to the common line. With the unit vector tangent to the com-

mon line indicated as $\boldsymbol{\lambda}$ and the unit tensor denoted as \mathbf{I} , this relation is

$$\mathbf{d} = \mathbf{d}^c + (\mathbf{d}\mathbf{r} - \mathbf{v}d\mathbf{t}) \cdot (\mathbf{I} - \boldsymbol{\lambda}\boldsymbol{\lambda}) \cdot \nabla \quad (55)$$

where \mathbf{v} is the velocity of the material in the common line. This expression bears some similarities to Eq. (35) employed for a surface. Thus Eq. (54) expands to

$$\begin{aligned} d\hat{E}_1^{\alpha\beta\sigma} &= \theta^{\alpha\beta\sigma} d\hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} d(l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma}) - \gamma^{\alpha\beta\sigma} dl^{\alpha\beta\sigma} \\ &+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} d^c \theta^{\alpha\beta\sigma} dC + \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho d^c \mu^{\alpha\beta\sigma} dC \\ &- \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} d^c \gamma^{\alpha\beta\sigma} dC + \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{d}\mathbf{r} - \mathbf{v}d\mathbf{t}) \\ &\cdot (\mathbf{I} - \boldsymbol{\lambda}\boldsymbol{\lambda}) \cdot (\hat{\eta} \nabla \theta^{\alpha\beta\sigma} + \rho \nabla \mu^{\alpha\beta\sigma} - \nabla \gamma^{\alpha\beta\sigma}) dC \end{aligned} \quad (56)$$

Subtraction of the Gibbs–Duhem equation (50b) integrated over the common line from this expression yields

$$\begin{aligned} d\hat{E}_1^{\alpha\beta\sigma} &= \theta^{\alpha\beta\sigma} d\hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} d(l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma}) - \gamma^{\alpha\beta\sigma} dl^{\alpha\beta\sigma} \\ &+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} d^c (\theta^{\alpha\beta\sigma} - \theta) dC \\ &+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho d^c (\mu^{\alpha\beta\sigma} - \mu) dC \\ &- \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} d^c (\gamma^{\alpha\beta\sigma} - \gamma_c) dC \\ &+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{d}\mathbf{r} - \mathbf{v}d\mathbf{t}) \cdot (\mathbf{I} - \boldsymbol{\lambda}\boldsymbol{\lambda}) \\ &\cdot (\hat{\eta} \nabla \theta^{\alpha\beta\sigma} + \rho \nabla \mu^{\alpha\beta\sigma} - \nabla \gamma^{\alpha\beta\sigma}) dC \end{aligned} \quad (57)$$

The transport and divergence theorems for a common line within a porous medium [15] may be expressed in terms of differentials as

$$\begin{aligned} \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \mathbf{d}^c f dC &= \mathbf{d} \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} f dC \right] \\ &- \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{I} - \boldsymbol{\lambda}\boldsymbol{\lambda}) \cdot (\mathbf{d}\mathbf{r} - \mathbf{v}d\mathbf{t}) f dC \right] \\ &- \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \boldsymbol{\lambda} \cdot \nabla^c \boldsymbol{\lambda} \cdot (\mathbf{d}\mathbf{r} - \mathbf{v}d\mathbf{t}) f dC \\ &+ \frac{1}{\mathcal{V}} \sum_{\text{pts}} \mathbf{e} \cdot (\mathbf{d}\mathbf{r} - \mathbf{w}d\mathbf{t}) f \end{aligned} \quad (58)$$

where “pts” refers to the end points of the common line within \mathcal{V} , \mathbf{e} is a unit vector tangent to the common line at the end points and oriented outward from the common line, ∇^c is the del operator along the curve, and \mathbf{w} is the velocity of the end points of the common line. Eq. (58) may be applied to Eq. (57) with $f = \gamma^{\alpha\beta\sigma} - \gamma_c$. Then removal of the macroscale gradients of macroscale quantities from the integrals yields

$$\begin{aligned}
\mathbf{d}\hat{E}_1^{\alpha\beta\sigma} &= \theta^{\alpha\beta\sigma} \mathbf{d}\hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} \mathbf{d}(l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma}) - \gamma^{\alpha\beta\sigma} \mathbf{d}l^{\alpha\beta\sigma} \\
&+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} \mathbf{d}^c (\theta^{\alpha\beta\sigma} - \theta) \, dC \\
&+ \frac{1}{\mathcal{V}} \rho \mathbf{d}^c (\mu^{\alpha\beta\sigma} - \mu) \, dC \\
&+ \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{I} - \lambda\lambda) \cdot (\mathbf{d}\mathbf{r} - \mathbf{v}\mathbf{d}t) (\gamma^{\alpha\beta\sigma} - \gamma_c) \, dC \right] \\
&+ \nabla \theta^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{d}\mathbf{r} - \mathbf{v}\mathbf{d}t) \cdot (\mathbf{I} - \lambda\lambda) \hat{\eta} \, dC \right] \\
&+ \nabla \mu^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{d}\mathbf{r} - \mathbf{v}\mathbf{d}t) \cdot (\mathbf{I} - \lambda\lambda) \rho \, dC \right] \\
&- \nabla \gamma^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{d}\mathbf{r} - \mathbf{v}\mathbf{d}t) \cdot (\mathbf{I} - \lambda\lambda) \, dC \right] \\
&+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \lambda \cdot \nabla^c \lambda \cdot (\mathbf{d}\mathbf{r} - \mathbf{v}\mathbf{d}t) (\gamma^{\alpha\beta\sigma} - \gamma_c) \, dC \\
&- \frac{1}{\mathcal{V}} \sum_{\text{pts}} \mathbf{e} \cdot (\mathbf{d}\mathbf{r} - \mathbf{w}\mathbf{d}t) (\gamma^{\alpha\beta\sigma} - \gamma_c) \quad (59)
\end{aligned}$$

Define a material derivative according to

$$\frac{D^{\alpha\beta\sigma}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\alpha\beta\sigma} \cdot \nabla \quad (60)$$

This represents a time derivative calculated moving with the average macroscale velocity of the $\alpha\beta\sigma$ common line. A time derivative of a property associated with a common line is calculated according to

$$\frac{D^{*\alpha\beta\sigma}}{Dt} = \frac{\partial}{\partial t} \Big|_c + \mathbf{v}^{\alpha\beta\sigma} \cdot \nabla^c \quad (61)$$

In this expression, the partial time derivative is calculated with the linear coordinate along the line fixed and ∇^c is the gradient operator along the common line. Also, define the macroscale rate of strain tensor as

$$\mathbf{d}^{\alpha\beta\sigma} = \frac{1}{2} [\nabla \mathbf{v}^{\alpha\beta\sigma} + (\nabla \mathbf{v}^{\alpha\beta\sigma})^T] \quad (62)$$

Eq. (59) may be expressed in the particular form when the differential is a material derivative as

$$\begin{aligned}
&\frac{D^{\alpha\beta\sigma} \hat{E}_1^{\alpha\beta\sigma}}{Dt} \\
&= \theta^{\alpha\beta\sigma} \frac{D^{\alpha\beta\sigma} \hat{\eta}^{\alpha\beta\sigma}}{Dt} + \mu^{\alpha\beta\sigma} \frac{D^{\alpha\beta\sigma} (l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma})}{Dt} \\
&- \gamma^{\alpha\beta\sigma} \frac{D^{\alpha\beta\sigma} l^{\alpha\beta\sigma}}{Dt} + \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \hat{\eta} \frac{D^{*\alpha\beta\sigma} (\theta^{\alpha\beta\sigma} - \theta)}{Dt} \, dC \\
&+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \rho \frac{D^{*\alpha\beta\sigma} (\mu^{\alpha\beta\sigma} - \mu)}{Dt} \, dC
\end{aligned}$$

$$\begin{aligned}
&+ \nabla \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{I} - \lambda\lambda) \cdot (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{v}) (\gamma^{\alpha\beta\sigma} - \gamma_c) \, dC \right] \\
&- \mathbf{d}^{\alpha\beta\sigma} : \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{I} - \lambda\lambda) (\gamma^{\alpha\beta\sigma} - \gamma_c) \, dC \right] \\
&+ \nabla \theta^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{v}) \cdot (\mathbf{I} - \lambda\lambda) \hat{\eta} \, dC \right] \\
&+ \nabla \mu^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{v}) \cdot (\mathbf{I} - \lambda\lambda) \rho \, dC \right] \\
&- \nabla \gamma^{\alpha\beta\sigma} \cdot \left[\frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{v}) \cdot (\mathbf{I} - \lambda\lambda) \, dC \right] \\
&+ \frac{1}{\mathcal{V}} \int_{C_{\alpha\beta\sigma}} \lambda \cdot \nabla^c \lambda \cdot (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{v}) - (\gamma^{\alpha\beta\sigma} - \gamma_c) \, dC \\
&- \frac{1}{\mathcal{V}} \sum_{\text{pts}} \mathbf{e} \cdot (\mathbf{v}^{\alpha\beta\sigma} - \mathbf{w}) (\gamma^{\alpha\beta\sigma} - \gamma_c) \quad (63)
\end{aligned}$$

Eq. (63) provides information concerning the relation between changes in macroscale internal energy and the macroscale entropy, mass, and volume of a common line. It can be extended to include the deviation kinetic energy by replacing $\hat{E}_1^{\alpha\beta\sigma}$ with $\hat{E}_1^{\alpha\beta\sigma} + \hat{E}_K^{\alpha\beta\sigma}$ and $\mu^{\alpha\beta\sigma}$ with $\mu_T^{\alpha\beta\sigma}$ where $\mu_T^{\alpha\beta\sigma}$ is defined analogously to its counterpart for a surface in Eq. (48). The integral terms that appear in these equations account for orientation and curvature of the common line within the averaging volume and for any non-constancy of the microscale chemical potential, temperature, velocity, and common line tension within the volume.

5. Conclusion

The derivations presented here provide information concerning the thermodynamic relations between macroscale internal energy and other macroscale quantities. The conceptual approach as well as the results of these derivations will have utility in improving the modeling and formulation of multiphase porous medium flows as well as modeling of any flows that are modeled at macroscopic length scales. The derivations illuminate a number of important features. First, explicit relations for macroscale thermodynamic properties as weighted integrals of microscale thermodynamic properties are employed. In an earlier consideration of the derivation of macroscale variables, Narasimhan [24] suggested that pressure be multiplied by a storage parameter before averaging while temperature of a phase be multiplied by a volumetric heat capacity before averaging. Although Gray [11] responded in favor of a definition of macroscale pressure and temperature to satisfy an RT framework, the RT approach does introduce uncertainty about the relationship between microscale and macro-

scale quantities. In the present paper, it has been shown that if pressures and tensions are considered to be energies per region (i.e., volumes, areas, or curves), direct averaging of those quantities over the corresponding region leads to the appropriate macroscale definitions. The appropriate factor to employ in averaging temperature is shown to be the entropy per region. Use of this factor allows a relationship between microscale and macroscale temperature to be established so that the macroscale definition of temperature is consistent with microscale thermodynamics. The macroscale chemical potential is obtained as a mass weighted average of the microscale chemical potential. With these definitions, the macroscale internal energy per averaging volume for phases, interfaces, and common lines per volume are derived, respectively, as

$$\hat{E}_I^\alpha = \theta^\alpha \hat{\eta}^\alpha + \mu^\alpha \epsilon^\alpha \rho^\alpha - p^\alpha \epsilon^\alpha \quad (64a)$$

$$\hat{E}_I^{\alpha\beta} = \theta^{\alpha\beta} \hat{\eta}^{\alpha\beta} + \mu^{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} + \gamma^{\alpha\beta} a^{\alpha\beta} \quad (64b)$$

and

$$\hat{E}_I^{\alpha\beta\sigma} = \theta^{\alpha\beta\sigma} \hat{\eta}^{\alpha\beta\sigma} + \mu^{\alpha\beta\sigma} l^{\alpha\beta\sigma} \rho^{\alpha\beta\sigma} - \gamma^{\alpha\beta\sigma} l^{\alpha\beta\sigma} \quad (64c)$$

These forms are consistent in appearance with their microscale based counterparts and provide the functional form of the macroscale internal energy. A material derivative, for example of Eq. (64a), has the general form:

$$\begin{aligned} \frac{D^\alpha \hat{E}_I^\alpha}{Dt} &= \theta^\alpha \frac{D^\alpha \hat{\eta}^\alpha}{Dt} + \mu^\alpha \frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} - p^\alpha \frac{D^\alpha \epsilon^\alpha}{Dt} \\ &+ \left[\hat{\eta}^\alpha \frac{D^\alpha \theta^\alpha}{Dt} + \epsilon^\alpha \rho^\alpha \frac{D^\alpha \mu^\alpha}{Dt} - \epsilon^\alpha \frac{D^\alpha p^\alpha}{Dt} \right] \end{aligned} \quad (65)$$

By analogy with the microscale case or from the RT perspective, the last group of terms would be zero by the Gibbs–Duhem equation. However, when the microscale thermodynamic properties are not homogeneous within an averaging region, time and/or space derivatives of the macroscale energy are relatively complex in comparison to the same derivatives of the microscale internal energy density. The last terms do not necessarily sum to zero, but they may be expressed in other forms using the averaging theorems (e.g., making use of Eq. (20) in conjunction with Eq. (65)).

For purposes of employing the entropy inequality to develop equations for flow in porous media, it is important to be able to relate the material derivatives of internal energy density to the material derivatives of entropy, mass, and region densities (e.g., [4,11,16]). For cases where the microscale inhomogeneities within an averaging volume are negligible, the macroscale and microscale formulations of the material derivatives of internal energy will be identical in form. However, it has been demonstrated here that, in general, extra terms, which are left as integrals, supplement the material derivatives. These terms account for inhomogeneities of

microscale thermodynamic properties as well as the subscale orientations and curvatures of surfaces and common lines. It is useful to note that these expressions are derived directly from their microscale counterparts rather than by postulating functional forms of internal energy at the macroscale as is done using an RT approach. Averaging of microscopic thermodynamic forms adds consistency to the development of macroscale forms in that just as conservation equations for phases, interfaces, and common lines are derived from their microscale forms by averaging [14], so too are the thermodynamic dependences transformed to the macroscale using the same mathematical tools. Besides being mathematically appealing, this approach also facilitates the practical calculation of macroscale thermodynamic properties by integration of microscale measurements within a system. The approach employed and the thermodynamic expressions developed will have utility in developing macroscale equations for description of water resources problems in which microscale heterogeneities are important. For example, when the averaging region is large enough that gravitational effects cause the pressure within an averaging volume to be non-constant, the formulation of the thermodynamics of the problem as proposed here is important. For problems of flow in porous media using large averaging volumes, sediment transport in rivers, vertically averaged flow in shallow waters, and cross-sectionally averaged flow in rivers, the expanded forms of the thermodynamic dependences will be important.

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