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Conduction-only transport phenomena in compressible bivelocity fluids: Diffuse interfaces and Korteweg stresses

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"Diffuse interface" theories for single-component fluids—dating back to van der Waals, Korteweg, Cahn-Hilliard, and many others—are currently based upon an *ad hoc* combination of thermodynamic principles (built largely upon Helmholtz's free-energy potential) and so-called "nonclassical" continuum-thermomechanical principles (built largely upon Newtonian mechanics), with the latter originating with the pioneering work of Dunn and Serrin [Arch. Ration. Mech. Anal. **88**, 95 (1985)]. By introducing into the equation governing the transport of energy the notion of an interstitial work-flux contribution, above and beyond the usual Fourier heat-flux contribution, namely, $\mathbf{j}_q = -k\nabla T$, to the energy flux, Dunn and Serrin provided a rational continuum-thermomechanical basis for the presence of Korteweg stresses in the equation governing the transport of linear momentum in compressible fluids. Nevertheless, by their failing to recognize the existence and fundamental need for an independent volume transport equation [Brenner, Physica A **349**, 11 (2005)]—especially for the roles played therein by the diffuse volume flux $\mathbf{j}_v$ and the rate of production of volume π_v at a point of the fluid continuum—we argue that diffuse interface theories for fluids stand today as being both *ad hoc* and incomplete owing to their failure to recognize the need for an independent volume transport equation for the case of compressible fluids. In contrast, we point out that bivelocity hydrodynamics, as it already exists [Brenner, Phys. Rev. E **86**, 016307 (2012)], provides a rational, non-*ad hoc*, and comprehensive theory of diffuse interfaces, not only for single-component fluids, but also for certain classes of crystalline solids [Danielewski and Wierzba, J. Phase Equilib. Diffus. **26**, 573 (2005)]. Furthermore, we provide not only what we believe to be the correct constitutive equation for the Korteweg stress in the class of fluids that are constitutively Newtonian in their rheological response to imposed stresses but, equally importantly, we establish the explicit functional forms of Korteweg's phenomenological thermocapillary coefficients appearing therein.

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I. INTRODUCTION

A. Background

This paper is the natural sequel to a recent bivelocity-based publication by the author [1], bearing the seemingly oxymoronic title "Fluid mechanics in fluids at rest." There, we focused upon steady-state, conduction-only transport processes occurring in compressible single-component bivelocity fluids, with such processes animated solely by the action of an externally imposed, time-independent uniform temperature gradient. Drawing upon both theoretical and experimental data, seemingly unimpeachable arguments of a fairly elementary and transparent nature were outlined in that paper, demonstrating the need in *compressible* fluid mechanics for two independent velocities rather than one. (A single velocity field suffices for incompressible fluids.) The centrality of heat conduction in the demonstration enabled us to use the phenomenon of thermophoresis [2] to make the experimental case [1] for the existence of two different velocity fields. The need for two independent velocities was shown therein to hold true irrespective of whether or not the fluid was flowing or at rest, and of whether the transport process was, or was not, time independent. At the time of its writing, discussion of the broader physical and philosophical ramifications of the paper's findings was largely postponed to a subsequent paper, so as not to distract from the paper's main goal, namely, that of demonstrating the viability of the dual-velocity scheme with respect to its accord with all known pertinent physical principles [3–5].

What follows below is that implicitly promised "subsequent paper." Explicitly, we return here to the same conduction-only transport scenario addressed in that predecessor paper [1], but now focusing on the broader, physical and philosophical consequences of such conduction-only, steady-state transport phenomena. In particular, the present work focuses exclusively on the steady-state, conduction-only diffuse transport of mass, momentum, energy, entropy, and volume (MMEEV) through compressible, single-component, viscous fluid continua bounded externally by mass-impermeable boundaries, when animated solely by gradients $\nabla\rho$ in the fluid's mass density ρ arising from nonuniformities in the distribution of mass and, hence, of corresponding nonuniformities in the statistical, time-averaged, spatial distribution of the fluid's Brownian molecules.

By default, convection and transient phenomena, constituting the only other physically recognized modes of transport, are both now regarded from the outset as being absent, leaving conduction as the sole mechanism enabling transport through the fluid of the particular physical property of interest. In a few instances we will have occasion to depart from the conduction-only scenario and write out the complete version (i.e., including convection and time-dependent transport processes) of the otherwise conduction-only equation. To avoid confusion as to which of the two possible versions is being referred to, we

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[*] Deceased.

will place an asterisk next to the equation number applicable to the complete version of the transport-related equation.

In what follows we discuss both monovelocity and bivelocity fluids. The "mono" prefix refers, implicitly, in the context of our present paper to the class of fluids obeying the Navier-Stokes-Fourier (NSF) equations [6–9]. For such fluids, heat and entropy are the only physical properties capable of undergoing purely conductive transport. Moreover, even if the fluid were to be incompressible, such that $\rho = \text{const}$ (so that $\nabla\rho = \mathbf{0}$) throughout, heat and entropy would still be capable of undergoing this conduction-only mode of transport, not only in the NSF model, but also in the bivelocity model.

Given this prior knowledge-based background, we focus in what follows primarily on those other physical properties, namely, (i) a nondissipative diffuse momentum flux $\mathbf{j}_\mathbf{M}$ represented by the Korteweg stress appearing in the linear momentum transport equation, (ii) a thermomechanical work flux $\mathbf{j}_w$ appearing in the energy transport equation, and (iii) the diffuse volume flux $\mathbf{j}_v$ appearing in the volume transport equation. These three items are absent from the conduction-only NSF model irrespective of circumstances, but present in the conduction-only bivelocity model whenever $\nabla\rho \neq \mathbf{0}$. Common to these three fluxes is the fact that each vanishes identically when $\mathbf{j}_v = \mathbf{0}$, as is the case when the NSF model prevails.

Physical consequences pertinent to conduction-only transport phenomena in bivelocity fluids are cited in our paper. Importantly, included therein is an elementary theoretical demonstration of the reality (existence) of Korteweg stresses [10], divorced from the complex, purely continuum-thermomechanical or mathematical theoretical attempts at proofs of its existence currently found in the literature [11–21].

Among other findings, our work establishes the presence of a close relationship between our conduction-only bivelocity theory and "gradient-energy" and "gradient-stress" theories associated with the notion of diffuse interfaces [22–29]—such commonality notwithstanding the wide gulf in their respective theoretical foundations between thermodynamics and continuum mechanics.

B. Compressible fluids

For the single-component fluids being studied in our paper, mass-density gradients $\nabla\rho$ (hereafter usually referred to simply as "density gradients") can arise only from the existence of temperature and/or pressure gradients, ∇T and ∇p [owing to the fluid's equilibrium equation of state $\rho = \rho(p,T)$], and then only in cases where at least one of the fluid's respective coefficients of thermal expansion and isothermal compressibility [30,31], namely,

$$\beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p \quad \text{and} \quad \kappa = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_p, \tag{1.1*}$$

is nonzero. In the case of gases, β is non-negative for ideal gases. For liquids, β can be positive, zero valued (e.g., in the case liquid water at 4 °C and 1 atm pressure), or negative. On the other hand, κ is necessarily always positive for both gases and liquids, since that attribute assures the fluid's thermodynamic stability [32]. Accordingly, as $\kappa > 0$, all fluids are, strictly speaking, "compressible" to some extent, although nowhere in the subsequent analysis will the need exist for us to take advantage of this nonzero κ value, even in the case of liquids. Thus, in subsequent discussions, where appropriate, we feel free to cling to the hypothetical existence of a so-called "incompressible" fluid, $\rho = \text{const}$, especially when concerned with liquids.

Apart from the momentum transport emphasis placed on our analysis by reference to Korteweg's stress [10], we also elaborate on the energy transport aspect of our work regarding the existence of a bivelocity-based, conduction-only, thermomechanical work flux $\mathbf{j}_w$ lying above and beyond that of the thermodynamically animated heat flux $\mathbf{j}_q$, and contributing thereby to the complete conduction-only energy flux $\mathbf{j}_e = \mathbf{j}_q + \mathbf{j}_w$, whose divergence $\nabla\cdot\mathbf{j}_e$ appears in the energy-transport equation. In the course of doing so we relate this work flux to the prescient prior work on the subject by Dunn and Serrin [14] and Dunn [15], who used their continuum-mechanical gradient-energy and gradient-stress findings to probe the physicality of Korteweg stresses, whose existence at the time was largely hypothetical. However, since esoteric, rational continuum-mechanical principles alone, rather than widely accepted elementary physical principles, were used to affect their efforts, none of their resulting conclusions can be said to demonstrate, *unequivocally*, the existence of either Korteweg stresses or of the thermomechanical work flux. At best, the physical existence of such stresses was merely shown to be a theoretical constitutive possibility. Moreover, Dunn and Serrin failed to explicitly identify the existence of the diffuse volume flux $\mathbf{j}_v$ [3], thereby rendering their work incomplete.

The antecedents of Dunn and Serrin (1985)—beginning originally with van der Waals (1873) [23] and Korteweg (1901) [10], and, later, including prominent contemporary researchers such as Cahn and Hilliard (1951) and their subsequent followers [27]—took a different tack towards addressing the above-cited class of Korteweg-like problems of interest. In particular, these precedent arguments began by invoking thermodynamic principles based upon *ad hoc* extensions of Helmholtz's free-energy potential [32,33] from equilibrium to near-equilibrium transport phenomena, but then only to those transport phenomena that are *nondissipative*. The latter restriction limits such free-energy-based theories to situations in which convection (mass motion) is absent so that $\mathbf{v} = \mathbf{0}$, as, for example, in the case of solids. Accordingly, the Cahn-Hilliard thermodynamic or Lagrange multiplier class of publications [27] bearing on Korteweg stresses and the like is limited in scope to either fluids at rest or to transport phenomena taking place in certain classes of solids. Given our focus on conduction-only phenomena in fluids, discussion of the possible application of Cahn-Hilliard's theory to transport in solids is postponed until later. Suffice it to say here that within its limited realm of applicability, Cahn-Hilliard-like nondissipative theories have been shown to accord well with experimental data on solids, but then only when used in conjunction with experimentally established parameters for the requisite phenomenological coefficients chosen to best fit the data.

It would appear from the above-cited limitations of both the pre- and post-Dunn and Serrin (1985) analyses that there currently exists no complete, first-principle's theory of transport phenomena available for compressible fluids (the latter including both gases and liquids) that is free of *ad hoc* assumptions or other rational flaws. This, however, is not true. Rather, we—together with a few other researchers [4,5,17,18]—believe that the bivelocity model [3] provides a physically acceptable, first-principle's theory, at least in the case of rheologically Newtonian fluids [7].

It is the avowed purpose of our paper to bring to the attention of the reader, in the most transparent manner possible, the fact that a rational physical theory already exists under whose heading a straightforward theory of "diffuse interfaces" already exists—at least for Newtonian fluids—but without the theory itself being focused exclusively on singular regions of the fluid. We do this by focusing exclusively on conduction-only bivelocity transport processes, despite the fact that the results obtained in this manner are already known to apply in the general case. Our conduction-only suppression of terms in the general case—whose presence would surely detract from allowing the reader to easily recognize the critical roles played by our three different bivelocity-based nondissipative momentum, thermomechanical work, and diffuse volume fluxes—will be seen to contribute significantly towards effecting the goal of transparency.

Apart from the goal of merely rendering already existing bivelocity results more transparent to readers, we use this opportunity to expose readers to the likely reasons why recognition of the need for a separate volume transport equation (together with the constitutive equation for the diffuse volume flux appearing therein), independent of the mass transport (i.e., continuity) equation, did not arise until long after that of the other common linear diffuse fluxes. The latter include (i) linear momentum (Navier-Newton's rheological law), (ii) heat (Fourier's law), and (iii) in the case of mixtures, Fick's law. Moreover, we provide a physical interpretation of the steady-state fractional rate of production of volume π_v at a space-fixed point in a completely quiescent fluid.

II. GENERIC PRECONSTITUTIVE TRANSPORT EQUATIONS: VOLUME TRANSPORT

In this section we present universally accepted, generic, preconstitutive transport equations applicable to both monovelocity and bivelocity fluids. These general balance equations governing the transport of the extensive MMEEV physical properties are set forth for both space-fixed (i.e., Eulerian) and so-called material (i.e., Lagrangian) choices of control volume. These broadly general preconstitutive laws are (or should be) regarded by the fluid-mechanics and related scientific communities as being equally applicable [1] to both monovelocity and bivelocity fluids, independently of the fluid's molecular, rheological, or thermal material properties. Explicitly, for a specific extensive physical property, the term preconstitutive "transport" equation or preconstitutive "balance" equation refers to that universally accepted formulation of the transport law that exists prior to inserting therein the explicit constitutive law (e.g., Fourier's law) governing transport of that property within a particular rheological fluid continuum.

Because the transport of volume is key to the subject of bivelocity hydrodynamics in relation to NSF hydrodynamics, we take advantage of this generically based section of our paper to emphasize the phenomenon of volume transport in its full generality, rather than limiting ourselves to the conduction-only transport mode as in the case of the remaining MMEE properties.

A. Generic transport processes

Let the symbol Ψ generically denote one of the extensive MMEEV properties. Let this same symbol also denote the *amount* of the property contained at a given instant of time t within a small fluid domain V bounded by a closed surface ∂V. By definition,

$$\Psi(t) = \int_V \psi(\mathbf{x},t)dV. \tag{2.1*}$$

Here, $\mathbf{x}$ denotes the position vector of a fixed point in the continuum, and $dV \equiv d^3\mathbf{x}$ denotes the volume element. At a given position $\mathbf{x}$ and instant of time t in a fluid continuum, we denote by the position- and time-dependent fields $\hat{\psi}(\mathbf{x},t)$ and $\psi(\mathbf{x},t)$ the respective specific (i.e., per unit mass) and volumetric (i.e., per unit volume) densities of the extensive generic physical property Ψ. These two densities are related by the expression

$$\psi = \rho\hat{\psi}. \tag{2.2*}$$

When the domain V is fixed in space (Eulerian view), the temporal rate of change in the amount of the property contained within the fluid domain V is given by

$$\left.\frac{d\Psi}{dt}\right|_V = \int_V \frac{\partial\psi}{\partial t}dV. \tag{2.3*}$$

On the other hand, when the domain $V \equiv V_{\text{MFP}}(t)$ refers to that of a "material fluid particle" or MFP (Lagrangian view), we have that [34–37]

$$\left.\frac{d\Psi}{dt}\right|_{V_{\text{MFP}}} = \int_{V_{\text{MFP}}} \rho\frac{D\hat{\psi}}{Dt}dV, \tag{2.4*}$$

in which

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla \tag{2.5*}$$

denotes the material derivative. Here, $\mathbf{v}$ is the fluid's mass velocity, namely, the velocity appearing in the continuity equation,

$$\begin{aligned}&\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0, \quad \text{or,} \quad \text{equivalently,}\\ &\qquad\frac{D\rho}{Dt} = -\rho\nabla\cdot\mathbf{v}, \quad \text{or} \quad \rho\frac{D\hat{v}}{Dt} = \nabla\cdot\mathbf{v},\end{aligned} \tag{2.6*}$$

in which $\hat{v} = 1/\rho$ is the specific volume.

B. Production of volume

It is especially important to distinguish between Eqs. (2.3) and (2.4) when focusing on the property of volume, namely, wherein $(\Psi,\psi,\hat{\psi}) \equiv (V,1,\hat{v})$.

1. *Space-fixed domain V*

Unsurprisingly, for the space-fixed domain V, we find from Eq. (2.3) that

$$\left.\frac{dV}{dt}\right|_V = 0. \tag{2.7*}$$

This follows from the fact that, geometrically, the Eulerian domain V is fixed in size, shape, and location for all time.

On the other hand, during transient flows, the amount of mass $(\Psi,\psi,\hat{\psi}) \equiv (M,\rho,1)$ instantaneously present in the volume V, namely, $M(t) = \int_V \rho(\mathbf{x},t)dV$, will generally vary with time in accordance with Eq. (2.3) applied to mass. Explicitly, $dM/dt = \int_V (\partial\rho/\partial t)dV$.

2. *Material domain V_{MFP}*

On the other hand, for the MFP, we have from Eq. (2.4) that

$$\left.\frac{dV}{dt}\right|_{V_{\mathrm{MFP}}} = \int_{V_{\mathrm{MFP}}} \rho\frac{D\hat{v}}{Dt}dV = \int_{V_{\mathrm{MPF}}} \nabla\cdot\mathbf{v}dV = \oint_{\partial V_{\mathrm{MFP}}} d\mathbf{S}\cdot\mathbf{v}. \tag{2.8*}$$

Whereas the volume of the MFP will thus generally change with time for the case of compressible fluids, the amount of mass M contained therein will remain constant for all time, as follows as a consequence of the generic formula (2.4) applied to mass: $dM/dt|_{V_{\mathrm{MFP}}} = 0$. Accordingly, as is well known, the mass of a MFP remains constant in time. However, whereas the total mass of the fluid contained therein remains constant in time, that mass does not generally consist of the *same* set of individual molecules for all time, but rather only the same *number* of molecules. Due to Brownian motion, molecules constantly enter and exit the MFP through its permeable fluid boundaries. Because of this fact, the MFP's contents cannot be viewed as constituting a *closed* system, to which one can—with impunity—apply extensive physical laws applicable to fixed-mass systems, such as those of extensive equilibrium thermodynamics. Indeed, failure to recognize volume as an independently transportable entity, and as a result to derive the (presumably physically incorrect) compressible NSF transport equations found in standard textbooks [6–9,34–37] solely on the basis of balancing input, output, and accumulation contributions for the case of a MFP (rather than for a space-fixed body), almost certainly accounts for the inability of many researchers to have recognized the independent role played by volume transport in fluid mechanics.

C. Generic balance equations

A generic balance law pertaining to transport of the extensive property Ψ, when performed on some arbitrary control volume V, say, bounded by a closed surface ∂V, leads to two equivalent but distinct balance-equation formulations, as discussed below.

1. *Space-fixed (Eulerian) control volume (V)*

When the control volume is fixed in space the generic balance law takes the form [38]

$$\frac{\partial\psi}{\partial t} + \nabla\cdot\mathbf{n}_\psi = \pi_\psi. \tag{2.9*}$$

The property's flux density $\mathbf{n}_\psi$ (hereafter, for brevity, usually referred to simply as the property's "flux") is defined such that with the vector $d\mathbf{S}$ denoting a directed element of surface area at a fixed point $\mathbf{x}$ of the fluid, the quantity $d\mathbf{S}\cdot\mathbf{n}_\psi$ gives the net rate at which the property is crossing that surface per unit time in a direction opposite to that into which the vector $d\mathbf{S}$ is directed. Furthermore, π_ψ represents the temporal rate per unit volume at which the property is being produced at a point of the fluid. For conserved properties Ψ we would thus have that $\pi_\psi = 0$. Physically, the balance equation (2.9) serves to define the notion of production (or creation) as follows: The temporal rate of increase $\int_V \pi_\psi dV$ in the amount $\Psi = \int_V \psi dV$ of the property contained within a space-fixed volumetric domain V bounded by a closed surface ∂V equals the difference between the rate $\int_V (\partial\psi/\partial t)dV$ at which the property is being accumulated within V and the net rate (inflow−outflow), $\oint_{\partial V} d\mathbf{S}\cdot\mathbf{n}_\psi$ at which the property is entering the domain V through its bounding surface ∂V.

2. *Material (Lagrangian) control volume (MFP)*

By definition, a material control volume [6–9,38] consists of a fluid domain V_{MFP}, say, whose bounding surface $\partial V_{\mathrm{MFP}}$ moves through space such that each point $\mathbf{x}$ lying on its surface moves with the instantaneous mass velocity $\mathbf{v}(\mathbf{x},t)$ of the fluid appropriate to that point. The velocity $\mathbf{v}$ refers to the fluid's mass velocity appearing in the continuity equation (2.6), wherein

$$\mathbf{v} := \mathbf{n}_m/\rho. \tag{2.10*}$$

The continuity equation expresses the law of conservation of mass $\partial\rho/\partial t + \nabla\cdot\mathbf{n}_m = \pi_m$. The latter derives from the generic equation (2.9) by choosing $\Psi \equiv M$ in which, in terms of symbols, $\psi \equiv \rho$ and $\mathbf{n}_\psi \equiv \mathbf{n}_m$. Moreover, $\pi_m = 0$, owing to mass conservation.

The generic transport equation for a material control volume can be obtained, purely mathematically, from its predecessor, Eq. (2.9), simply by defining the material derivative operator (2.5). Thus, beginning with Eq. (2.9), the generic balance law for a material domain takes the alternative, but physically equivalent form

$$\rho\frac{D\hat{\psi}}{Dt} + \nabla\cdot\mathbf{j}_\psi = \pi_\psi. \tag{2.11*}$$

The generic quantity $\mathbf{j}_\psi$ appearing in Eq. (2.11) is the diffusive (conductive) flux of the extensive property Ψ, defined generically by the relation

$$\mathbf{n}_\psi := \mathbf{n}_m\hat{\psi} + \mathbf{j}_\psi, \quad \text{or,} \quad \text{equivalently,} \quad \mathbf{n}_\psi := \mathbf{v}\psi + \mathbf{j}_\psi. \tag{2.12*}$$

That is, the diffuse flux $\mathbf{j}_\psi$ of the property Ψ refers to that portion of the property's total flux $\mathbf{n}_\psi$ that is not conveyed piggyback style through space as a result of being entrained within the fluid's local mass movement. In particular, this diffusive flux is solely a statistical consequence of the fluid molecules' Brownian movements acting in concert with inhomogeneities (gradients), $\nabla\psi$ or $\nabla\hat{\psi}$, in the property's density.

A key feature to note with regard to the preceding physical content of this section lies in the fact that the rate of production of the physical property Ψ, represented by the symbol π_ψ in both of the balance equations (2.9) and (2.11), is exactly the same physical quantity, irrespective of whether one adopts the space-fixed or material viewpoint. This is evident from the fact that the latter generic transport equation follows, trivially, from the former generic transport equation merely as a consequence of having performed formal mathematical operations upon the balance equation (2.9). That is, no new physics was introduced during the course of deriving (2.11) from (2.9). This observation proves to be especially important in the case of volume transport (see Sec. VI), where it might otherwise appear that two independent choices of volume production rate π_ψ exist, depending upon which of the two possible choices of control volume was selected when performing the property balance.

From an overall perspective, a principal goal of theoretical fluid mechanics is that of formulating and ultimately solving the set of single-component, postconstitutive transport equations governing MMEEV transport in mobile fluid continua, jointly with that fluid's equilibrium equation of state $p = p(\rho,T)$, and subject to appropriate boundary and/or initial conditions, so as to establish the pressure field $p(\mathbf{x},t)$ [or density field $\rho(\mathbf{x},t)$], temperature field $T(\mathbf{x},t)$, and mass-velocity field $\mathbf{v}(\mathbf{x},t)$ throughout the fluid and for all times. Prediction of the local values of these three fields at each point $\mathbf{x}$ of the fluid domain at time t depends upon the particular fluid-mechanical model adopted, whether monovelocity or bivelocity, and, of course, upon the constitutive equations embodying the property-specific or material characteristics of the fluid quantifying its response to changes [39] in state.

Relatively recently, in an attempt to improve the accuracy of NSF-based compressible continuum predictions—at least in circumstances involving the simplest class of materials, namely, those manifesting *linear* constitutive responses to change—the above-cited program was expanded so as to now include, in addition to the fluid's usual mass velocity $\mathbf{v}$, a second velocity, the fluid's so-called volume velocity $\mathbf{v}_v$ [38,40]. Thus, after a number of false starts, there came into being the subject of bivelocity hydrodynamics [1,3,41,42] for rheologically Newtonian fluids, above and beyond conventional monovelocity NSF hydrodynamics. Independent macroscopic and molecular modeling concepts entered into the foundations of both models, with the former based upon the principles of linear irreversible thermodynamics (LIT) [34–37,43], and the latter upon variants [5] of Boltzmann's gas-kinetic equation [44–48].

D. The fluid's volume velocity $\mathbf{v}_v$

Bivelocity fluid mechanics recognizes the existence of two conceptually distinct velocities, these being, respectively, the fluid's mass velocity $\mathbf{v}$ and its volume velocity $\mathbf{v}_v$. By definition, the fluid's volume flux density $\mathbf{n}_v$ corresponds, dimensionally, to a volume flow per unit area per unit time. With $L \equiv$ length, a volume V has the units of L^3 whereas an area A has the units of L^2. Consequently, the vector field $\mathbf{n}_v$ possesses the units of length per unit time, namely, those of a vector velocity field. Thus, physically, we define the fluid's "volume velocity" $\mathbf{v}_v$ such as to be synonymous with its volume flux density $\mathbf{n}_v$:

$$\mathbf{v}_v := \mathbf{n}_v. \tag{2.13*}$$

In that case we find from the second equality in Eq. (2.12) that

$$\mathbf{v}_v = \mathbf{v} + \mathbf{j}_v, \quad \text{or,} \quad \text{equivalently,} \quad \mathbf{j}_v = \mathbf{v}_v - \mathbf{v}. \tag{2.14*}$$

Thus, the diffuse volume flux $\mathbf{j}_v$ represents the flux of volume $\mathbf{n}_v$ measured relative to the fluid's mass velocity.

E. Production of volume

Application of the generic relation (2.9) to the transport of volume furnishes the expression

$$\pi_v = \nabla \cdot \mathbf{n}_v, \quad \text{or,} \quad \text{equivalently,} \quad \pi_v = \nabla \cdot \mathbf{v}_v. \tag{2.15*}$$

Consider a MFP wending its way through space. Suppose that, at some instant of time t, the MFP momentarily wholly occupies a given space-fixed Eulerian domain V, whose center of volume is instantaneously situated at the space-fixed point $\mathbf{x}_0$. At that particular moment, the respective Eulerian and Lagrangian domains of the MFP coincide, such that $V_{\mathrm{MFP}} \equiv V$. By definition, the quantity

$$\overset{\bullet}{V}(\mathbf{x}_0,t) := \int_V \pi_v(\mathbf{x}-\mathbf{x}_0,t)dV, \quad \text{or,} \quad \text{equivalently,}$$
$$\overset{\bullet}{V} := \oint_{\partial V} d\mathbf{S}\cdot\mathbf{n}_v, \tag{2.16*}$$

represents the instantaneous temporal rate at which volume is issuing into the fluid from those points contained in its interior. This rate generally differs from the rate $dV/dt|_{V_{\mathrm{MFP}}}$ [see Eq. (2.8)] at which the particular MFP momentarily occupying the specified Eulerian domain V is increasing its volume. Upon subtracting the last term of Eq. (2.8) from the last term of Eq. (2.16), we obtain

$$\left.\frac{dV}{dt}\right|_{V_{\mathrm{MFP}}} - \overset{\bullet}{V} = \oint_{\partial V_{\mathrm{MFP}}} d\mathbf{S}\cdot\mathbf{j}_V, \tag{2.17*}$$

in which we have used Eqs. (2.13) and (2.14) in the form $\mathbf{j}_v = \mathbf{n}_v - \mathbf{v}$.

F. Interpretation of diffuse volume flux $\mathbf{j}_v$

Equation (2.17) provides the physical interpretation of the diffuse volume flux $\mathbf{j}_v$ as constituting a flow of volume into the MFP through its surface *without accompaniment by a corresponding flow of mass*. This is a consequence of the fact that the MFP consists for all time of the same amount of mass, whereas the volume entering the MFP from all of the points lying in its interior does not bring any mass along with it owing to the law of conservation of mass; that is, despite the quantity called "volume" being created at points within the MFP, no mass is simultaneously being created at these points. Accordingly, the increase in the MFP's volume is attributed to the massless (i.e., "diffuse") flow of volume through the MFP's surface $\partial V_{\mathrm{MFP}}$ into its interior.

The notion of fluid volume being transported through space independently of that of mass is obviously a difficult concept to assimilate. The conceptual difficulty can be traced to the fact that whereas mass is a conserved physical property, volume—likewise viewed as a physical property—is not generally conserved. Basically, the relation between an object's volume V and the object's mass M, namely,

$$V = \frac{M}{\rho}\ \text{(when } \rho = \text{const, or, equivalently, when } \nabla\rho = \mathbf{0}\text{)}, \tag{2.18*}$$

holds in all circumstances where the fluid's density ρ is constant throughout the body. Recall that whereas V and M are extensive physical properties, the density ρ is an intensive *continuum* property. The equilibrium relation (2.18) has always been believed to imply the credibility of the corresponding nonequilibrium *continuum* flux relation

$$\mathbf{n}_v(\mathbf{x},t) = \frac{\mathbf{n}_m(\mathbf{x},t)}{\rho(\mathbf{x},t)}, \tag{2.19*}$$

under any and all circumstances, even when ρ varies with position or time, that is, even when $\nabla\rho \neq \mathbf{0}$ and/or $\partial\rho/\partial t \neq 0$. Remarkably, the continuum relation (2.19) appears not to have been subjected to a critical experimental test. It is this fundamental issue that bivelocity theory has brought into question, and shown in prior work [3] that it is not, in fact, true in any and all circumstances.

Rather, more generally, when applied to volume transport, the first equality in Eq. (2.12) yields, for the case of compressible fluids [3],

$$\mathbf{n}_v = \frac{\mathbf{n}_m}{\rho} + \mathbf{j}_v, \tag{2.20*}$$

with the latter now appearing in place of (2.19). Accordingly, the credibility of (2.19) under all circumstances hinges upon whether or not

$$\mathbf{j}_v = \mathbf{0} \tag{2.21*}$$

under any and all circumstances. Indeed, the NSF equations are implicitly based upon the validity of Eq. (2.21). This issue has been implicitly overlooked ever since the founding of rational fluid mechanics by Euler in 1755 [49], almost 275 years ago. Recall in this context that fluid mechanicians of that era would have been primarily familiar with experiments performed on liquids, but hardly with any at all on gases. And since liquids are largely incompressible, rendering $\rho(\mathbf{x},t) \approx$ const, Eq. (2.19) would surely have constituted a natural working hypothesis, applicable to all single-component fluids. Nevertheless, Euler's pioneering paper constituted the first time that the continuity equation was formulated in its general compressible form $\partial\rho/\partial t + \nabla\cdot(\rho\mathbf{v}) = \mathbf{0}$. As such, Euler's work was clearly intended to apply to *compressible* fluids (perhaps the flow of gases in the atmosphere, since vertical pressure gradients arising from gravity were already known to exist in the atmosphere since the times of Pascal and Toricelli). However, the interpretation of both experiments and theory during the past decade, leading, among other things, to the creation of bivelocity hydrodynamics, has shown us that $\mathbf{j}_v \neq \mathbf{0}$ in general.

In particular, it has been argued, at least in the linear approximation, that the constitutive equation governing this diffuse volume flux in the absence of body forces such as gravity is, for both gases and liquids,

$$\mathbf{j}_v = \alpha\nabla\ln\rho \quad (\hat{\mathbf{f}} = \mathbf{0}), \tag{2.22}$$

where α is the thermometric diffusivity [see Eq. (4.11)], and $\hat{\mathbf{f}}$ is the specific body force. Further discussions pertaining to the existence of a nonzero diffuse volume flux are interspersed throughout the remainder of this paper, especially in Sec. VI, where the difficulties associated with intuitive attempts to understand the physics underlying the phenomenon of *massless* volume transport are noted to be comparable to those encountered in the comparable case of entropy transport. However, before proceeding, we briefly discuss why—despite volume being a regularly encountered extensive physical property Ψ on a par with the other common MMEE properties—there is no NSF volume transport equation.

G. Why is volume transport not included along with mass, momentum, energy, and entropy transport phenomena?

In the case of volume transport [38] we write, as a consequence of the generic transport equation (2.11), that

$$\rho\frac{D\hat{v}}{Dt} = -\nabla\cdot\mathbf{j}_v + \pi_v. \tag{2.23*}$$

The absence of this volume transport equation from the transport literature stems from confusion over the constitutive equation for the production term π_v. In the current literature it is universally believed that, under any and all monovelocity circumstances,

$$\pi_v \overset{?}{=} \nabla\cdot\mathbf{v}, \tag{2.24}$$

whereas, in fact, the correct expression is [see Eq. (2.16)]

$$\pi_v(\mathbf{x}_0,t) = \lim_{V\to 0}\frac{1}{V}\overset{\bullet}{V}. \tag{2.25}$$

The supposed "proof(s)" of Eq. (2.24) offered in the literature, which we briefly review below, can be found in virtually any standard fluid-mechanics textbook [6–9,34–36]. These, as well as our above proof of Eq. (2.25), begin with the observation that, at any given moment t, every space-fixed Eulerian fluid domain V comprising the fluid continuum embodies a material fluid particle, the latter represented by the Lagrangian domain V_{MFP}. That is, proceeding to its ultimate destination, the moving Lagrangian domain V_{MFP} momentarily occupies the stationary Eulerian domain V. However, whereas the volume of the stationary domain V maintains its same value for all time [see Eq. (2.7)], the volume V_{MFP} of the particular MFP instantaneously occupying this domain V is changing with time in accordance with Eq. (2.8), namely,

$$\frac{1}{V_{\text{MFP}}}\frac{dV_{\text{MFP}}}{dt} = \lim_{V_{\text{MFP}}\to 0}\frac{1}{V_{\text{MFP}}}\int_{V_{\text{MFP}}}\nabla\cdot\mathbf{v}\,dV. \tag{2.26*}$$

As the volume production rate $\pi_v(\mathbf{x}_0)$ is operationally defined by virtue of its presence in the space-fixed Eulerian balance equation (2.11)—rather than through its presence in the Lagrangian MFP relation—we see that

$$\pi_v \neq \lim_{V_{\text{MFP}}\to 0}\frac{1}{V_{\text{MFP}}}\frac{dV_{\text{MFP}}}{dt}, \quad \text{when} \quad \pi_v \neq \nabla\cdot\mathbf{v}. \tag{2.27*}$$

Specifically, the correct definition of the volume production rate is that already noted in Eq. (2.25). Indeed, we see that

$$\left.\frac{1}{V}\frac{dV}{dt}\right|_{V_{\text{MFP}}} - \frac{1}{V}\overset{\bullet}{V} = \lim_{V\to 0}\frac{1}{V}\oint_{\partial V_{\text{MFP}}} d\mathbf{S}\cdot\mathbf{j}_V. \tag{2.28}$$

If Eq. (2.24) were to be correct, it would follow from Eq. (2.23) together with the third equality in continuity equation (2.6) that $\nabla \cdot \mathbf{j}_v = \mathbf{0}$ and, hence, in general, that $\mathbf{j}_\mathbf{v} = \mathbf{0}$. In other words, the volume transport equation (2.23) would simply become synonymous with the continuity equation (2.6) governing the transport law for mass. As a consequence, the transport law for volume would cease to furnish a transport law that was independent of the already existing MMEE transport laws. Rather, such a law would be redundant. It is for this mistaken reason that an independent law governing the transport of volume has not existed until recently. And, as an important consequence thereof, the existence of the diffuse volume flux $\mathbf{j}_\mathbf{v}$, and its fundamental role in fluid mechanics, has remained hidden for almost 250 years, ever since Euler's [49] rational formulation in 1755–1757 of the subject of single-component, compressible fluid mechanics.

III. CONDUCTION-ONLY TRANSPORT PROCESSES

This section specializes the generic preconstitutive transport equations set forth in Sec. II to the case where steady-state, conduction-only transport is the only mode of transport available to any member Ψ of the MMEEV class.

In the case of such purely conductive transport processes, for which by definition $\mathbf{n}_m = \mathbf{0}$ (and hence $\mathbf{v} = \mathbf{0}$), it follows from (2.10) and (2.12) that $\mathbf{n}_\psi = \mathbf{j}_\psi$. Furthermore, since transient phenomena are also assumed to be absent, one has that $\partial\psi/\partial t = 0$. As a consequence of Eq. (2.2), together use of the first equality in continuity equation (2.6), we have that $\partial\psi/\partial t = \rho\partial\hat{\psi}/\partial t + \hat{\psi}\partial\rho/\partial t = \rho\partial\hat{\psi}/\partial t - \hat{\psi}\nabla\cdot(\rho\mathbf{v})$. In conjunction with the fact that $\mathbf{v} = \mathbf{0}$, this shows that $\partial\hat{\psi}\,/\,\partial t = 0$ for the present class of steady-state conduction problems.

Consequently, both of the control volume balance equations (2.9) and (2.11) merge into a single conduction-only, steady-state transport equation:

$$\nabla\cdot\mathbf{j}_\psi = \pi_\psi. \tag{3.1}$$

Accordingly, if the property undergoing conduction were to be a conserved property, such that $\pi_\psi = 0$, Eq. (3.1) would then simply become $\nabla\cdot\mathbf{j}_\psi = \mathbf{0}$.

Equation (3.1) represents the fundamental generic preconstitutive equation governing steady-state, conduction-only transport phenomena. In what follows we apply this relation, individually, to the respective transport of MMEEV. Furthermore, to avoid needless repetition, it will henceforth be implicitly understood from this point on that the phrase "conduction-only" disallows *transient* conduction; that is, only *steady-state* conduction phenomena are being considered.

A. Mass, momentum, energy, entropy, and volume (MMEEV) transport

This section provides explicit preconstitutive equations for the conduction fluxes $\mathbf{j}_\psi$ and production rates π_ψ governing the conduction-only transport of the respective extensive properties of mass ($\Psi \equiv M$), momentum ($\Psi \equiv \mathbf{M}$), energy ($\Psi \equiv E$), entropy ($\Psi \equiv S$), and volume ($\Psi \equiv V$). The diffuse fluxes and production rates in each case are related through the generic relation (3.1). These preconstitutive, conduction-only expressions apply to all fluids, irrespective of whether their transport through space is governed by the monovelocity NSF or bivelocity equations.

1. *Mass transport:* $(\Psi,\hat{\psi},\psi) \equiv (M,1,\rho)$

From (3.1) the transport of mass is seen to be governed by the preconstitutive equation

$$\nabla\cdot\mathbf{j}_m = \pi_m. \tag{3.2}$$

As mass constitutes a conserved physical property, one has that, constitutively, $\pi_m = 0$. This requires that $\nabla\cdot\mathbf{j}_m = \mathbf{0}$. Furthermore, from the first equality in Eq. (2.12), one sees in the case of mass, since $\mathbf{n}_\psi = \mathbf{n}_m$ and $\hat{\psi} = 1$, that $\mathbf{j}_m = \mathbf{0}$. Consequently, in the case of mass we see that Eq. (3.2) is automatically satisfied. In particular, and unsurprisingly, mass cannot be transported by conduction alone, irrespective of whether the fluid in question is monovelocity or bivelocity in nature.

2. *Momentum transport:* $(\Psi,\hat{\psi}\psi) \equiv (\mathbf{M},\hat{\mathbf{M}} = \mathbf{v},\rho\mathbf{v})$

With $\hat{\mathbf{M}} = \mathbf{v} = \mathbf{0}$ the conduction-only specific-momentum density, the generic equation (3.1) adopts the form

$$\nabla\cdot\mathbf{j}_\mathbf{M} = \pi_\mathbf{M}, \tag{3.3}$$

wherein [see Eqs. (A8) and (A2)]

$$\mathbf{j}_\mathbf{M} := -[\bar{\mathbf{T}} + \mathbf{I}(p - \bar{p})] \tag{3.4a}$$

and

$$\pi_\mathbf{M} = -(\nabla p - \rho\hat{\mathbf{f}}). \tag{3.4b}$$

Here, $\bar{\mathbf{T}}$ is the symmetric and traceless nondissipative deviatoric Korteweg stress, $\bar{p}$ is the mean stress, and $\hat{\mathbf{f}}$ is the specific body force. Each of these is operationally defined in context in Appendix A.

3. *Energy transport:* $(\Psi,\hat{\psi}\psi) \equiv (E,\hat{e},\rho\hat{e})$

With the energy of a body consisting generally of its internal, kinetic, and potential energies, it is shown in Appendix B that the conduction-only energy flux satisfies the solenoidal relation

$$\nabla\cdot\mathbf{j}_e = \mathbf{0}. \tag{3.5}$$

As a consequence of the generic relation (3.1) applied to energy transport, it is thus required that

$$\pi_e = 0, \tag{3.6}^*$$

with the latter representing the fact that energy is conserved in accordance with the first law of thermodynamics. In connection with that law, the preconstitutive conduction-only energy flux consists of the sum

$$\mathbf{j}_e = \mathbf{j}_q + \mathbf{j}_w \tag{3.7}$$

of a heat flux $\mathbf{j}_q$ and a thermomechanical work flux $\mathbf{j}_w$. The notion that mechanical work is capable of being transported solely by conduction is implicit in the structure of bivelocity hydrodynamics, as it is too in the prescient work of Dunn and Serrin [14,15]. The contributions of these authors are discussed in Sec. VII.

4. Entropy transport: $(\boldsymbol{\Psi},\hat{\boldsymbol{\psi}}\boldsymbol{\psi}) \equiv (S,\hat{s},\rho\hat{s})$

The conduction-only transport of entropy through monovelocity and bivelocity fluids is, from the perspective of the generic balance equation (3.1), governed by the balance equation

$$\nabla \cdot \mathbf{j}_s = \pi_s, \tag{3.8}$$

wherein $\mathbf{j}_s$ is the diffuse entropy flux and π_s the fractional volumetric rate of entropy production. On physical grounds the entropy production rate is necessarily non-negative, requiring satisfaction of the inequality

$$\pi_s \geqslant 0. \tag*{(3.9)*}$$

5. Volume transport: $(\boldsymbol{\Psi},\hat{\boldsymbol{\psi}},\boldsymbol{\psi}) \equiv (V,\hat{\boldsymbol{v}},\mathbf{1})$

For the case of volume it follows from Eq. (3.1) that the preconstitutive conduction-only transport equation governing volume transport through space obeys the relation

$$\pi_v = \nabla \cdot \mathbf{j}_v, \tag{3.10}$$

with $\mathbf{j}_v$ the diffuse volume flux, and π_v the rate of production of volume per unit volume at a space-fixed point of the fluid. From the generally applicable case, where Eq. (2.14) applies, the diffuse flux of volume in the conduction-only case becomes

$$\mathbf{j}_v = \mathbf{v}_v \equiv \mathbf{n}_v. \tag{3.11}$$

IV. CONSTITUTIVE EQUATIONS FOR THE BIVELOCITY CONDUCTION FLUXES $\mathbf{j}_\psi$ AND PRODUCTION RATES π_ψ

In the context of anticipating specific physical applications of our preconstitutive conduction-only relations set forth in Sec. III, constitutive equations are required for the various conduction fluxes. The conduction fluxes of interest in our present single-component bivelocity and NSF cases are $\mathbf{j}_\mathbf{M}$ [or, alternatively, $\overline{\mathbf{T}}$ and $\bar{p} - p$ as in Eq. (3.4a)], $\mathbf{j}_q$, $\mathbf{j}_w$, $\mathbf{j}_s$, and $\mathbf{j}_v$. When these constitutive equations are in hand, their respective insertions into the appropriate preconstitutive transport equations of Sec. III, which govern conduction-only transport phenomena, bring about closure of the respective sets of bivelocity and NSF differential equations, thus furnishing the appropriate "postconstitutive" conduction-only balance equations for use in applications. These constitutive expressions are given below only for the bivelocity case. The corresponding constitutive equations for NSF fluids may be obtained from these by simply setting $\mathbf{j}_v = \mathbf{0}$ in the expressions given below for the bivelocity case, as we later do explicitly in Sec. V.

A. Conduction-only constitutive equations for bivelocity fluids

The respective conduction-only bivelocity constitutive equations governing the pertinent diffuse fluxes take the following forms.

1. Momentum transport

Here

$$\overline{\mathbf{T}} = 2\mu\overline{\nabla\mathbf{j}_v}, \quad p - \bar{p} = \zeta\nabla \cdot \mathbf{j}_v, \quad \text{and} \quad \pi_\mathbf{M} = -(\nabla p - \rho\hat{\mathbf{f}}) \tag{4.1}$$

[see also Eq. (3.4a)]. In these expressions μ and ζ are, respectively, the fluid's shear and dilatational viscosities for Newtonian fluids. Note from Eqs. (3.3) and (3.4) in conjunction with (4.1) that in the present conduction-only case, were one to set $\mathbf{j}_v = \mathbf{0}$, it would follow that $\nabla p - \rho\hat{\mathbf{f}} = \mathbf{0}$, and hence from (4.1) that $\pi_\mathbf{M} = \mathbf{0}$, as would be expected in that conventional NSF case. On the other hand, in the bivelocity case, where $\mathbf{j}_v \neq \mathbf{0}$, one has from Eq. (4.13) that $\pi_\mathbf{M} \neq \mathbf{0}$. This is an indicator of the fact that, based upon bivelocity theory, the hydrostatic equation does not strictly hold true in quiescent fluids when mass-density gradients $\nabla\rho \neq \mathbf{0}$ are present, as already pointed out explicitly in Sec. IX of Ref. [1]. [This can also be clearly seen from the union of Eqs. (4.2) and (4.10).]

It follows from use of Eqs. (3.3) and (3.4), in conjunction with the above-cited constitutive stress-related and production rate expressions (4.1), that the differential equation governing conduction-only momentum transport in bivelocity fluids is

$$2\nabla \cdot (\mu\overline{\nabla\mathbf{j}_v}) + \nabla(\zeta\nabla \cdot \mathbf{j}_v) = \nabla p - \rho\hat{\mathbf{f}}. \tag{4.2}$$

2. Energy transport

Here

$$\mathbf{j}_q = -k\nabla T, \tag*{(4.3a)*}$$

$$\mathbf{j}_w = \mathbf{P} \cdot \mathbf{j}_v, \tag{4.3b}$$

and

$$\pi_e = 0. \tag*{(4.4)*}$$

The relation $\mathbf{P} = \mathbf{I}\bar{p} - \overline{\mathbf{T}}$ given in Eq. (A2) for the pressure tensor, when considered in conjunction with Eqs. (4.11) and (4.12), shows, as a consequence of Eq. (4.3b), that the work flux density is

$$\mathbf{j}_w = p\mathbf{j}_v - \zeta(\nabla \cdot \mathbf{j}_v)\mathbf{j}_v - 2\mu\mathbf{j}_v \cdot \overline{\nabla\mathbf{j}_v}.$$

As was noted in Eq. (2.22), and as will be set forth later in this section, the constitutive equation for the diffuse volume flux in the absence of body forces such as gravity is $\mathbf{j}_v = \alpha\nabla\ln\rho$. Consequently, apart from nonlinear constitutive contributions embodied in the last two terms on the right-hand side of the equation displayed above, each of those terms also involve three consecutive gradient operations. Given the foundational principles of *linear* irreversible thermodynamics (LIT)—as were originally used in establishing the hypothesized range of applicability of the NSF constitutive relations resulting therefrom [34–37]—the two last terms appearing on the right-hand side of the above are negligible compared with the linear, leading-order term on the right. Accordingly, consistency with LIT requires that the constitutive equation for the work flux be given by the expression

$$\mathbf{j}_w = p\mathbf{j}_v. \tag{4.5}$$

Introduction of the latter into (3.7) yields

$$\mathbf{j}_e = \mathbf{j}_q + p\mathbf{j}_v, \tag{4.6}$$

in which the constitutive equation for the heat flux is given by Fourier's law [50,51], Eq. (4.3a). We note from (3.5) that $\nabla \cdot \mathbf{j}_e = \mathbf{0}$ in the present conduction-only case. As such, the conduction-only energy transport equation satisfies the following differential equation:

$$\nabla \cdot (\mathbf{j}_q + p\mathbf{j}_v) = \mathbf{0}. \tag{4.7}$$

3. Entropy transport

The bivelocity constitutive equation for the diffuse entropy flux is [3]

$$\mathbf{j}_s = \frac{\mathbf{j}_q + p\mathbf{j}_v}{T}. \tag*{(4.8)*}$$

Consequently, from Eqs. (3.8) and (4.7) we find in the conduction-only case that

$$\pi_s = (\mathbf{j}_q + p\mathbf{j}_v) \cdot \nabla \frac{1}{T}. \tag{4.9}$$

4. Volume transport

Based upon the principles of LIT, the constitutive equation governing the diffusive, conduction-only flux of volume is found to be [3]

$$\mathbf{j}_v = \alpha[\beta \nabla T + \kappa(\nabla p - \rho \hat{\mathbf{f}})], \tag*{(4.10)*}$$

where

$$\alpha = \frac{k}{\rho \hat{c}_p} \tag*{(4.11)*}$$

is the thermometric diffusivity. Appearing in Eq. (4.11) are $\hat{c}_p$, the isobaric specific heat, and k, the thermal conductivity coefficient appearing in Fourier's law. The compressibility coefficients β and κ are defined in Eq. (1.1).

Equation (4.10) can be rewritten as

$$\mathbf{j}_v = \alpha \nabla \ln \rho - \alpha \kappa \rho \hat{\mathbf{f}}. \tag*{(4.12)*}$$

Moreover, as in Eq. (3.10), we have in the conduction-only case that

$$\pi_v = \nabla \cdot \mathbf{j}_v. \tag{4.13}$$

Given our limited experience to date in dealing with volume transport problems in which body forces are present, we urge caution when using Eq. (4.12) in cases where $\hat{\mathbf{f}} \neq \mathbf{0}$. In the absence of such forces one has that

$$\mathbf{j}_v = \alpha \nabla \ln \rho \quad (\hat{\mathbf{f}} = \mathbf{0}). \tag*{(4.14)*}$$

An additional need for caution stems from the fact that were we to consider the case of an incompressible fluid, where $\rho = \text{const}$ throughout, one would have simply that $\mathbf{j}_v = -\alpha\kappa\rho\hat{\mathbf{f}}$. And it is difficult to understand how a body force alone would give rise to the production of volume, as required by (4.13). On the other hand, were the fluid to be truly incompressible, one would have that $\kappa = 0$, in which case the body-force contribution would vanish, and the issue would cease to be relevant. However, as discussed in connection with the first equality in Eq. (1.1), the stability of fluids requires satisfaction of the inequality $\kappa > 0$ [32,33], in which case the possibility of addressing situations where $\rho = \text{const}$ becomes moot.

In connection with the issue of (conservative) body forces it should also be noted in the present conduction-only transport case that such forces, if present, do not appear capable of performing work, in the sense of contributing to the work flux $\mathbf{j}_w$ in Eq. (4.5). This represents yet another need for caution.

B. Comments on the thermomechanical work-flux contribution to the energy flux

The equation of state for ideal gases is such that

$$p = nk_BT, \tag*{(4.15)*}$$

in which n is the volumetric number density of molecules (molecules per unit volume) and k_B is Boltzmann's constant. As k_BT represents the thermal energy per molecule [44–48], it follows that the pressure p could be regarded as serving a dual role, not only as a stress (i.e., force per unit area) but also as constituting the fluid's thermal energy per unit volume at a point of the fluid continuum. Given that latter interpretation, together with the fact that $d\mathbf{S} \cdot \mathbf{j}_v$ represents the volume crossing the surface $d\mathbf{S}$ per unit time, the scalar $d\mathbf{S} \cdot p\mathbf{j}_v \equiv nk_BT(d\mathbf{S} \cdot \mathbf{j}_v)$ then represents the temporal rate at which thermal energy is being conducted across the areal surface element.

While the preceding thermally oriented view might suggest that $p\mathbf{j}_v$, as $\mathbf{j}_q$, is a heat flux rather than a work flux, that alternative view is inconsistent with the origin of the work flux; for in the general case, where both convection and unsteady-state transport processes (in addition, of course, to conduction) are allowed, the work term $\mathbf{j}_w$ originates with the presence of the predecessor of Eq. (4.3b) in the energy equation—explicitly, $\mathbf{j}_w = \mathbf{P} \cdot \mathbf{v}_v$ in the bivelocity case and $\mathbf{j}_w = \mathbf{P} \cdot \mathbf{v}$ in the NSF case. The vector $d\mathbf{S} \cdot \mathbf{P}$ constitutes a force $d\mathbf{F}$, say, whereas $\mathbf{v} = d\mathbf{x}/dt$, in which $d\mathbf{x}$ denotes a *spatial* displacement, namely, a "distance" traversed during a time interval dt. It is obvious that the term $d\mathbf{F} \cdot d\mathbf{x}$ constitutes a force × distance mechanical work term, the latter then appearing in the expression $d\mathbf{S} \cdot \mathbf{j}_w \equiv (d\mathbf{F} \cdot d\mathbf{x})/dt$ for the rate of working per unit time.

V. MONOVELOCITY, NSF CONDUCTION-ONLY CONSTITUTIVE EQUATIONS

In the case of incompressible fluids, where $\rho = \text{const}$ throughout, one has from Eq. (4.14) that $\mathbf{j}_v = \mathbf{0}$, certainly in the case where body forces are absent. In that case it is seen upon comparison of the latter equation with the results of Sec. IV that bivelocity and NSF fluid mechanics merge into a single theory.

Explicitly, in the bivelocity conduction-only constitutive equations set forth in Sec. IV, the only nonzero flux contributions that remain upon setting $\mathbf{j}_v = \mathbf{0}$ therein are

$$\mathbf{j}_e = \mathbf{j}_q = -k\nabla T \tag{5.1}$$

and

$$\mathbf{j}_s = \frac{\mathbf{j}_q}{T}. \tag{5.2}$$

It follows from Eqs. (3.5) and (5.1) that $\nabla \cdot \mathbf{j}_q = \mathbf{0}$, when the usual NSF heat conduction equation $\nabla \cdot (k\nabla T) = \mathbf{0}$ is satisfied. Furthermore, in view of the preceding relations in conjunction with (3.8), it follows that $\pi_s = k(\nabla \ln T)^2$. Hence, since $k \geqslant 0$, this confirms that the entropy production-rate inequality (3.9) is properly satisfied, at least for NSF fluids.

The two fluxes, (5.1) and (5.2), constitute the only nonzero conduction-only contributions to transport in the case of

NSF fluids. Comparison with their bivelocity counterparts in Sec. IV shows the significant extent to which the notion of volume transport has enriched even as trivial a subject as steady-state heat conduction, much less that of other transport phenomena. It will be seen in Sec. VII that some of these bivelocity features with respect to conduction-only momentum and energy transport processes are explicit in the earlier works of others, although not necessarily constitutively formulated in a manner wherein unequivocal agreement exists between those results and ours. These earlier momentum and energy conduction-only additions to transport especially include (i) the 1901 work of Korteweg [10] in relation to Eq. (4.11), who built upon prior diffuse interface contributions by Rayleigh [22] and van der Waals [23], (ii) the gradient-stress and gradient-energy contributions by Cahn and Hilliard and others [27–29], also to diffuse interfaces [24], and (iii) the 1985 work of Dunn and Serrin [14] in the context of their proposal to add a thermomechanical work-flux contribution $\mathbf{j}_w$—not necessarily identical, constitutively, to our Eq. (4.5)—to the heat flux $\mathbf{j}_q$, as in our Eq. (3.7), in order to reconcile Korteweg's theory with the broad general principles of continuum thermomechanics [15].

The NSF-based equality (5.1) between the respective energy and heat fluxes depends implicitly upon belief in the currently accepted NSF view that, because the fluid is quiescent and the temperature field is time independent, the fluid cannot undergo a volume change. And if the volume cannot change, it is implicitly concluded by these NSF researchers that the production of mechanical work (possibly accompanying the flow of heat $\mathbf{j}_q$) is impossible.

Consequently, according to established thermodynamic principles [32], in the strictly NSF conduction-only case, wherein Korteweg stresses and work fluxes are absent, the energy flux and the heat flux are regarded as being synonymous. It is in this context that our belief in the superior accuracy of bivelocity theory over that of NSF brings about a fundamental change in the presently established [7–9,34–37] transport phenomena scenario.

VI. INTUITIVE INTERPRETATION OF $\mathbf{j}_v$ AND π_v

In this section we discuss the physical significance of both the (massless) diffuse volume flux $\mathbf{j}_v$ and the production rate π_v of volume at a fixed point in space. Neither concept is easy to assimilate intuitively owing to one's inevitable tendency to associate volume with mass, as in Eq. (2.18), both of which are extensive properties [52]. As a consequence of this virtually inescapable associative tendency, the notion of a *massless* volume flux, as well as the apparent ability to create volume independently of that of mass, would appear to be oxymoronic.

The underlying difficulty in assimilating volume-based concepts can be traced, at least in part, to the fact that volume, as entropy, is not generally a conserved property. This lack of conservation contrasts with that of the more familiar extensive properties undergoing transport, namely, those of mass, momentum, and energy (MME), all of which are conserved [7–9]. Moreover, unlike its sister quality mass, volume is neither a material substance nor is it a physical attribute that exists in its own right, again in contrast with MME. Nor, again in contrast therewith, does volume or specific volume come to mind when attempting to rationally intuit continuum-mechanical principles from Newton's discrete-body mechanical principles. Rather, volume, as entropy, is an ethereal extensive attribute, not assignable to a point. How, then, is one to understand, even if only intuitively, the notions of a massless volume flux or the rate of production of volume at a fixed point in space without a comparable production of mass?

Nevertheless, just as one is able to deal *operationally*—albeit without much intuitive physical insight—with well-established, but abstract, physical concepts such as the diffuse flux of entropy $\mathbf{j}_s$, or the temporal rate π_s of entropy production at a fixed point of a quiescent fluid, so too can one eventually learn to accept the operational existence of the comparable attributes for volume. Despite such reassuring statements regarding volume's operational acceptance as a transportable extensive physical property, independently of that of mass, volume's integration into the foundations of fluid mechanics is unlikely to come free of controversy [53].

A. Characteristic length scale L

In regard to fluid continua, the association of mass with volume at a point (strictly in the *neighborhood* of that point) arises in connection with the notion of the fluid's density ρ as mass per unit volume or, in terms of its reciprocal, the fluid's specific volume $\hat{v} = 1/\rho$. The issue comes to attention when one contemplates *compressible* fluid continua, wherein density gradients $\nabla\rho$ exist. The ratio $(|\nabla\rho|/\rho)^{-1} \equiv |\nabla \ln \rho|^{-1}$, whose dimensions are those of length, obviously provides a quantitative measure of the possible importance of density gradients in applications. In this context it often proves convenient to define the intrinsic length scale

$$L := \min(|\nabla \ln \rho|^{-1}), \tag{6.1}$$

an assignation accompanying a given physical application.

The importance of the length parameter L arises in the context of its relation to the other length scales characterizing the particular physical problem of interest, be they, for example, (i) the mean-free-path length δ in dealing with Knudsen number (Kn) effects, or (ii) the radius a of a sphere in the course of, say, deriving the correction to Stokes law for the case where the sphere moves through a nonisothermal, strongly thermally stratified compressible fluid, or (iii) the radius R_o, say, of a circular cylindrical microfluidic tube through which a gas is flowing isothermally under the influence of an externally imposed pressure gradient [54–57]. Thus, when scaling the gradient operator ∇ in order to produce a suitable dimensionless gradient operator ∇^*, say, for use in a particular application, one may encounter a multiplicity of length-scale choices during the course of rendering the fluid-mechanical equations dimensionless prior to solving them subject to appropriate boundary conditions. For the examples cited, the possible nondimensional scalings of the gradient operator include $\nabla^* = (a,\delta,R_o,L)\,\nabla$.

How is one to choose the correct scalings of the pertinent dimensional parameters? Clearly, the choice in the examples cited above lies in the magnitudes of the dimensionless size ratios, such as a/L and δ/L (as well, of course, on the Knudsen number $\delta/a = \mathrm{Kn}_a$). It is in circumstances where one (or both) of these size ratios become of $O(1)$, or larger, that the magnitude of L enters the fluid-mechanical analysis. Explicitly, given the constitutive relation (4.14), the obvious universal choice for rendering the diffuse volume flux dimensionless in all cases is

$$\mathbf{j}_v^* = (L/\alpha)\mathbf{j}_v. \tag{6.2}$$

Thus, say, if a compressible fluid were to be flowing through a circular tube of radius R_o, wherein the radial distance of a point from the tube axis was the circular cylindrical coordinate R, it would be natural to attempt, at least initially, to effect the scalings $\nabla^* = R_o\nabla$ and/or $R^* = R/R_o$. Consequently, were the ratio R_o/L to be of $O(1)$ or larger in the particular compressible tube-flow problem of interest (see the examples cited in Refs. [54,55]), it would be necessary to retain diffuse volume effects.

Indeed, experimental data already exist [54–57] to support this view, showing the superiority of the bivelocity equations over those of NSF for compressible fluids, especially in cases of low density (i.e., rarefied) gases. While there exist monovelocity fluid-mechanical transport equations other than those of NSF that also agree with experiment [58,59], they are invariably based upon empirical hypothetical concepts, such as *ad hoc* slip velocities at the system's boundaries, embodying fitting parameters such as experimental data-based accommodation coefficients [58,59]. In contrast, bivelocity theory involves no empirical parameters, either in the transport equations themselves or in the boundary conditions to be imposed upon these equations in the course of effecting their solutions. Rather, the boundary condition prevailing at solid surfaces bounding the flow is one of no slip of the fluid's volume velocity $\mathbf{v}_v$ [54,56,57], as defined in Eqs. (2.13) or (2.14).

Similar issues with respect to the magnitude of a/L would arise when attempting, for example, to establish the correction to Stokes law for the case of a sphere moving through a strongly stratified isothermal gas. For example, in the case of a colloidal-sized sphere or large polymer molecule of effective radius a sedimenting through an isothermal gas in an ultracentrifuge of radius R_o rotating with angular velocity Ω, one has (since the pressure distribution is given approximately by the formula $\nabla p = \rho\Omega^2 R$) that the characteristic length is [60–63]

$$L := \min \frac{(1 - \hat{c}_v/\hat{c}_p)\hat{c}_p T}{\Omega^2 R_o}. \tag{6.3}$$

Were this length proven to be small, the ratio a/L could conceivably be non-negligible when establishing the sphere's Stokes-law settling velocity. In contrast, "wall effects" on the sphere's motion—as embodied in either of the dimensionless parameters a/R_o or L/R_o—would likely prove to be negligible.

1. *Diffuse interfaces*

Comparable lessons also exist (see Sec. VII) in the case of so-called diffuse interfaces [24], where a continuous transition in density $\rho(x)$ $(-\infty < x < \infty)$ between, say, a liquid and its vapor in single-component fluids [28,29], is characterized by steep density gradients $\nabla\rho$ in the neighborhood of the interfacial region near $x = 0$. In circumstances where the magnitude of the length scale (6.1) is small compared with the respective linear extents of the bulk liquid and vapor regions bounding the interfacial region $x = 0$, a perturbation scheme, involving passage to the mathematical limit of zero interfacial "thickness" in the near-singular region proximate to $x = 0$, then furnishes a discontinuous surface, the "interface," a separate phase, endowed with unique physical properties different from those of the surmounting bulk phases, including surface tension and surface free energy (at least in equilibrium circumstances).

Given the central role played by the existence of density gradients $\nabla\rho$ in the continuum-mechanical analysis of diffuse interfaces, the success of this diffuse interface scheme is seen to involve exactly the same fundamental bivelocity principles as we have been discussing in the preceding length-scale contexts cited. Whereas, by deliberate omission, our diffuse interface comments focused on systems in a state of thermodynamic equilibrium [32,33], it is obvious that similar ideas can be applied in a more general, near-equilibrium, transport process context in order to develop, say, a comprehensive LIT-based theory of interfacial transport processes [9,64,65].

Finally, we note that shock waves [66], especially when they occur in rarefied gases, provide yet another example wherein recognition of the importance of the diffuse volume flux $\mathbf{j}_v$ in the context of the intrinsic length scale L is likely to prove relevant.

2. *Homogeneous versus inhomogeneous molecular distributions*

Our analysis clarifies the importance of distinguishing between Brownian motion occurring in statistically *homogeneous* fluids, where ρ is uniform throughout the fluid, and Brownian motion occurring in statistically *inhomogeneous* fluids, where, as a result of the existence of density gradients $\nabla\rho$, the density ρ—and hence the spatial distribution of molecules—is no longer statistically uniform throughout the fluid. Moreover, the fundamental difference between the homogeneous and inhomogeneous cases explains why heat can, as a result of stochastic Brownian motion, be transported purely conductively (i.e., $\mathbf{j}_q \neq \mathbf{0}$), irrespective of whether the fluid is compressible as in the inhomogeneous distribution case ($\nabla\rho \neq \mathbf{0}$), or incompressible as in the homogeneous distribution case ($\rho = \text{const}$). There, it is the Brownian motion alone, irrespective of the local molecular distribution in space, that proves pertinent. On the other hand, fundamental differences exist between the compressible and incompressible cases as regards the role played by the Brownian motion in regard to, say, the existence or nonexistence of the thermomechanical work flux $p\mathbf{j}_v$. After all, if no expansion or contraction of volume was possible during the conduction-only process, such that $\overset{\bullet}{V} = dV/dt$, as in Eq. (2.16) [see also Eq. (2.25)], there could then be no nonequilibrium work-flux analog $p\,dV/dt$, say, of the equilibrium thermodynamic work $p\,dV$. In that conduction-only case, energy transport would be synonymous with heat flow.

VII. DIFFUSE INTERFACES: RELATIONSHIP OF BIVELOCITY THEORY TO GRADIENT-STRESS AND GRADIENT-ENERGY THEORIES

A. Diffuse interfaces

This section focuses on nonlocal, bivelocity-based, conduction-only contributions to both the stress tensor appearing in the linear momentum equation and the energy flux appearing in the energy equation for the case of inhomogeneous, single-component, fluid continua. Each contribution arises as a consequence of mass-density gradients $\nabla\rho$ present in these fluids. These gradient stress and energy additions are in addition to the usual (Cauchy) stress and energy contributions already present in the NSF equations [6–9]. These contributions arise in the context of the present section whenever the characteristic length scale L defined by Eq. (6.1) is comparable in magnitude to the so-called thickness of the diffuse interfacial region. That near-singular region serves to separate two, more or less, homogeneous bulk fluid phases in mutual contact along a common interface. The two bulk fluids can either be immiscible or miscible. If miscible, the existence of an interface will be transient [67] rather than permanent.

Currently, continuum-thermomechanical analyses of diffuse interfaces are being modeled based, primarily, upon the work of Dunn and Serrin [14], and focused on understanding the origin and properties of Korteweg stresses and related transport phenomena, including the notion of an interstitial thermomechanical work flux. In what follows, we show that bivelocity theory provides a simple entree into their scheme, in addition to filling in missing aspects of their work pertaining to the transport of volume.

B. Gradient-stress and gradient-energy contributions

As already suggested following Eq. (6.3), a close physical and constitutive relationship exists between single-component bivelocity theory for inhomogeneous compressible fluids and comparable gradient-stress and gradient-energy theories, although the latter embodies nonuniform density distributions only in selected regions of the fluid (i.e., in the so-called “diffuse interface” region [24]), rather than possibly throughout the entire fluid, as in the bivelocity case. In general, the thickness of these diffuse, near-singular regions is assumed to be small compared with the physical extent of the bulk fluid regions. As such, in the (mathematically) singular limit, where the thickness of the diffuse interfacial region is small compared with that of the two bulk regions bounding it on either side, the diffuse region becomes asymptotically singular at a macroscopic level of description. That mathematically singular surface, the “interface,” is then regarded as a distinct (two-dimensional) phase in its own right. The singular stress and singular energy additions to be discussed then serve, ultimately, to impose interfacial stress-related and interfacial energy-related boundary conditions [9,36,64,65] upon the bulk-fluid momentum and energy equations at their common, now zero-thickness, interfacial phase boundary.

Gradient-stress contributions to momentum transport arise as a consequence of steep density gradients $\nabla\rho$ normal to the diffuse interfacial region. These are manifested in the form of Korteweg stresses [10] and, at least in conduction-only circumstances, constitute a nondissipative momentum transport mechanism. Gradient-energy contributions to energy transport have a similar origin, and are manifested in the form of a thermomechanical work-related flux [14], analogous to our bivelocity work-related flux $\mathbf{j}_w$, with the latter to be added to the heat flux $\mathbf{j}_q$ in order to obtain the complete conduction-only energy flux $\mathbf{j}_e$, as in Eq. (3.7).

The backgrounds behind diffuse interface theories are reviewed in some detail by Anderson *et al.* [24], as well as more extensively in recent books by Mauri [26] and Hemmerich [25], to which the reader is referred for greater theoretical and experimental background. On a more definitive note, the potential existence of a relationship between bivelocity theory and diffuse interface gradient theories was recently recognized explicitly by a number of authors, including Feireisl and Vasseur [4] and Kotschote [17,18] among others, at least in those cases where the stresses arose directly from Korteweg’s momentum-stress mechanical model.

Following the conduction-only theme permeating our paper, and in the present spirit of simply advocating the potential utility of bivelocity theory in the context of developing a more comprehensive diffuse interface theory than currently exists, we limit our discussion exclusively to such elementary, single-component, single-phase conduction situations where convection and transient phenomena are absent.

C. Background to diffuse-interface or gradient-stress and gradient-energy contributions

Following Rayleigh [22], van der Waals [23] was the first thermodynamicist, subsequently followed by many others—beginning with Korteweg [10], Cahn and Hilliard, and many others [27]—to focus on the special properties engendered in the class of fluids (as well as in elastic solids) within which strong nonuniformities existed in the *local* distribution of matter, especially in asymptotically near-singular regions present in otherwise near-homogeneous bulk fluids, i.e., diffuse interfaces [24]. These early, intuitively argued investigations were founded upon the hypothesis that in near-equilibrium single-component fluids, the Helmholtz free energy per unit volume at a point of the fluid depends functionally not only upon the density ρ and temperature T at that point, but also upon the *nonlocal* mass density gradients $\nabla\rho$ existing in proximate portions of the fluid.

Owing to the somewhat *ad hoc*, non-fluid-mechanical nature of the preceding Helmholtz thermodynamic hypothesis, diffuse interface theory appears to us to lack a proper foundational basis for rigorously studying gradient-stress and gradient-energy contributions in the context of a conceptually well-established, near-equilibrium, fluid-mechanical foundation. Nevertheless, despite this lack, research in the Helmholtz-based, diffuse interface field has continued unabated, with significant progress based on the Cahn-Hilliard model [27] having been recorded [25,26,68] in addressing a variety of closely related applications, primarily in the case of transport phenomena occurring in crystalline solid phases. We point out in what follows that bivelocity theory [3] provides a firmer, simpler, and more applications-friendly theoretical foundation than that provided by the Helmholtz free-energy approach to the subject of transport phenomena occurring proximate to diffuse interfaces.

D. Gradient-stress and gradient-energy contributions in relation to bivelocity theory

We argue below (i) that the conduction-only, deviatoric stress tensor $\mathbf{T}^{+}$, say, arising as a consequence of the existence of the diffuse volume flux $\mathbf{j}_v$ [cf. Eqs. (3.3) and (4.1)], namely,

$$\mathbf{T}^{+} = 2\mu\overline{\nabla\mathbf{j}_v} + \mathbf{I}\zeta\nabla\cdot\mathbf{j}_v, \tag{7.1}$$

is the bivelocity counterpart of the gradient-stress contribution to the above-cited theories, as given by Korteweg's stress tensor [69,70], and (ii) that the conduction-only contribution $\mathbf{j}_e^{+}$, say, to the fluid's energy flux $\mathbf{j}_e$, arising from the existence of the diffuse volume flux $\mathbf{j}_v$, is given by the expression [see Eq. (4.6)]

$$\mathbf{j}_e^{+} = p\mathbf{j}_v. \tag{7.2}$$

In Eq. (7.1), the overbar above a dyadic denotes the dyadic's symmetric and traceless version [see Eq. (A6)]. The rate-of-working flux given by Eq. (7.2) will be seen in what follows to constitute the bivelocity counterpart of the gradient-energy contribution appearing in the above-cited diffuse interface theory.

Together with the constitutive equation $\mathbf{j}_v = (k/\rho\hat{c}_p)\nabla\ln\rho$, as given in Eq. (4.14) for the body-force-free diffuse volume flux, jointly with the further assumption that k and $\hat{c}_p$ are constants, independent of position throughout the fluid, Eq. (7.1) becomes

$$\begin{aligned}\mathbf{T}^{+} = {}& \mathbf{I}\alpha\left(\frac{2}{3}\mu - \zeta\right)\left[2\frac{(\nabla\rho)^2}{\rho^2} - \frac{\nabla^2\rho}{\rho}\right]\\ & - 2\mu\alpha\left[\frac{2(\nabla\rho)(\nabla\rho)}{\rho^2} - \frac{\nabla\nabla\rho}{\rho}\right].\end{aligned} \tag{7.3}$$

1. *Gradient stress in inhomogeneous fluids*

As earlier noted, our bivelocity analysis appears especially closely related to the diffuse interface work of Dunn and Serrin [14,15] as well as to that of others, including, for example, Kotschote [17,18]. Dunn and Serrin (hereafter frequently cited as DS for conciseness), in their prescient paper, "On the thermomechanics of interstitial working," point out that in 1901, Korteweg [10]—interested in modeling fluid capillarity as well as elastic contributions to the Cauchy stress tensor—formulated a nondissipative constitutive equation to be added to the usual Cauchy dissipative deviatoric stress appearing in the linear momentum equation [6,7], so as to include nonlocal effects arising from density gradients $\nabla\rho$.

E. Korteweg stresses

Specifically, Korteweg proposed the following compressible fluid model for such gradient stresses, in which the "equilibrium" (i.e., velocity-independent) portion of the Cauchy deviatoric stress tensor $\mathbf{T}$ appearing in the linear momentum equation is given by the constitutive equation

$$\mathbf{T}^{+} = \mathbf{I}[\alpha\nabla^2\rho + \beta(\nabla\rho)^2] + \delta\nabla\nabla\rho + \gamma(\nabla\rho)(\nabla\rho), \tag{7.4}$$

where the phenomenological coefficients $\alpha,\beta,\gamma,\delta$ are material functions, dependent only upon ρ and T. They are generally referred to as capillary coefficients. Various values have been proposed for these coefficients [14,24] without common agreement among the many researchers on the subject of their functional forms.

Korteweg's stress equation (7.4) is an example of a constitutive equation for a material of "grade N" (wherein $N = 2$). In order to be able to model complex spatial interaction effects in materials, the constitutive quantities of interest in that context (at this point, the interest is in stress) are permitted to depend not only on the first gradient of the property of interest, but also on all gradients thereof less than or equal to the integer N. As such, Korteweg's equation gives the stress in a material of grade 2 (often, also referred to by some authors as being of grade 3 [71]). However, as pointed out by DS, all such higher-grade theories are incompatible with the usual continuum theory of thermodynamics (namely, those existing at the time of DS's 1985 writings) used to derive the Korteweg stress. Indeed, unless all of the phenomenological coefficients appearing in Eq. (4.9) vanished identically, Korteweg's model was shown by DS to be incompatible with conventional thermodynamics!

It was argued by DS that a new, broader thermodynamic structure was required in order to achieve compatibility, one that admits not only nontrivial grade 2 Korteweg-type materials but, more generally, materials of arbitrary grade. While noting that several such thermodynamic schemes were potentially available, DS confined attention in their paper to one posited by them as representing a particularly simple and attractive case—further noting that this choice did a "minimum of damage" to the classic conceptual structure embodied in the accompanying auxiliary mass, momentum, and energy conservation equations. By the latter they refer to preservation, in their respective standard original forms, of the purely mechanical principles of linear and angular momentum conservation, together with the purely thermal Clausius-Duhem inequality.

F. Modifications of the energy equation: Thermomechanical work flux

In this spirit, DS focus initially upon modifying the standard energy transport equation. In that context they follow a line of thought useful for energetic-type calculations. Specifically, DS posit the existence of a rate of supply of mechanical energy, namely, their "interstitial work-flux vector" $\mathbf{u}(\mathbf{x},t)$ (which they prove to be a continuum-mechanically objective field), such that the standard energy conservation equation [7] is augmented by adding their thermomechanical work flux $\mathbf{u}$ (modulo an algebraic sign) to the Fourier heat flux $\mathbf{j}_q$ in order to obtain the energy flux. Upon removing the unsteady-state and convective contributions from their proposed general energy transport equation—enabling us thereby to eventually compare the latter with our own conduction-only energy- and stress-related contributions—DS propose that the diffuse energy flux be given by the constitutive formulation

$$\mathbf{j}_e = \mathbf{j}_q - \mathbf{u}, \tag{7.5}$$

in place of its traditional NSF counterpart, $\mathbf{j}_e = \mathbf{j}_q (\equiv -k\nabla T)$. As such, our own energy-based proposal, as embodied in Eqs. (3.7) and (4.5), leading to Eq. (4.6), is, in that sense, comparable to their proposition.

Thus, in addition to the flow of heat, D&S propose, and we quote, "*. . . allowing spatial interactions of longer range to engender a rate of supply* $\mathbf{u}$ *of mechanical energy across every material surface*." DS (see also Ref. [12]) go on to discuss the constitutive implications for the diffuse entropy flux engendered by such work-flux considerations, emphasizing that when venturing beyond the traditional energy-related boundaries of contemporary fluid mechanics that the identification of what they term "the real heat flux" is a rather subtle affair [72]. Indeed, Dunn [15], in a separate publication based upon his Ph.D. research performed under Serrin's supervision, referred to their theory as constituting a new branch of "nonclassical continuum thermodynamics."

1. *Constitutive equation for the thermomechanical work flux*

Although DS discuss broad classes of constitutive relations that are, in their view, continuum-mechanically compatible with their interstitial work flux $\mathbf{u}$, the mathematically formal nature of their arguments, in conjunction with the breadth of its scope, make it difficult to assess the utility of any one of their specific constitutive formulations. At a minimum, they argue that $\mathbf{u}$ consists of respective dynamic and static contributions,

$$\mathbf{u} = -K(D\rho/Dt)\nabla\rho + \bar{\mathbf{w}}, \tag{7.6}$$

wherein the phenomenological capillary coefficient K is regarded as a parameter deriving from Helmholtz's free energy.

As their dynamic contribution vanishes for the case of steady-state, conduction-only situations, for which $D\rho/Dt = \mathbf{0}$, we focus on the static contribution to $\mathbf{u}$, represented by the symbol $\bar{\mathbf{w}}$, for purposes of relating DS's work to our own in the present conduction-only context. Even here, for this purely static contribution, DS do not offer an explicit constitutive proposal—specifically one complete with knowledge not only of its general functional form, but also of the dependence upon density and temperature of the phenomenological coefficient(s) appearing therein for different fluids.

They do, however, make the important observation that $\bar{\mathbf{w}}$ will vanish in situations where $\nabla\rho = \mathbf{0}$ and, moreover, that $\bar{\mathbf{w}}$ must, and we quote, "*. . . always depend on the local strain distortion* $\nabla\rho$ *in a rather simple and explicit way, in fact vanishing at any point where the local measure of distortion,* $\nabla\rho$*, vanishes*." That statement is consistent with the possibility that their static interstitial work flux is closely related to our own rate-of-working flux, $\mathbf{j}_w = p\mathbf{j}_v \equiv p\alpha\nabla \ln\rho$.

Anderson *et al.* [24] and Kotschote [18], as well as others, have sought to clarify, simplify, and otherwise extend the pioneering Dunn-Serrin analysis to other situations. Indeed, Kotschote [18] refers to his resulting set of postconstitutive transport equations as the "Navier-Stokes-Korteweg" (NSK) equations rather than the "Navier-Stokes-Fourier" (NSF) equation set.

2. *Constitutive equations proposed for the Korteweg stress*

Both Anderson *et al.* and Kotschote, among others, arrive at results similar to those of DS, except that, in contrast, each proposes an explicit constitutive form for the so-called "static" contribution $\bar{\mathbf{w}}$ to $\mathbf{u}$. Thus, by way of comparison with results set forth above for the Korteweg stress derived from their respective versions of the work term $\mathbf{u}$, Anderson *et al.* [24] arrive at the expression

$$\mathbf{T}^{+} = \mathbf{I}[K\rho\nabla^2\rho + (1/2)K(\nabla\rho)^2] - K(\nabla\rho)(\nabla\rho), \tag{7.7}$$

whereas Kotschote [17,18] concludes that

$$\mathbf{T}^{+} = \mathbf{I}\rho\nabla\cdot(\kappa\nabla\rho) - \kappa(\nabla\rho)(\nabla\rho), \tag{7.8}$$

in which the coefficient κ is functionally dependent upon the $(\nabla\rho)^2$ contributions to Helmholtz's free energy [27]. Comparable constitutive expressions appropriate to single-component, two-phase, vapor-liquid equilibrium (in proximity to the fluid's critical point) are proposed by Fixman [28] and Felderhoff [29].

In comparing the above expressions with our Eq. (7.3) for the Korteweg stress, it needs to be borne in mind that those expressions are not limited to the conduction-only case. Rather, they apply in completely general circumstances, where both convection and transient behaviors are allowed. However, neither is our Eq. (7.3) limited to the conduction-only case, despite our having presented it in that possibly misleading context.

G. Energy flux

In addition to dealing with $\nabla\rho$-generated gradient stresses, the above-cited respective authors of Eqs. (7.7) and (7.8) also dealt with comparable gradient-energy issues related to DS's thermomechanical work-flux term $\mathbf{u}$ appearing in the energy transport equation. In this context, Anderson *et al.* [24] arrive at the conclusion that the "internal energy flux" $\mathbf{q}_E$ appearing in their energy transport equation is, in their notation,

$$\mathbf{q}_E = -k\nabla T - K_E(D\rho/Dt)\nabla\rho \tag{7.9}^*$$

(with their $\mathbf{q}_E$ apparently identical with our $\mathbf{j}_e$). If so, it would mean in DS's notation that Anderson *et al.*'s interstitial work flux $\mathbf{u} = K_E(D\rho/Dt)\nabla\rho$. But this purely dynamic term lacks DS's static contribution $\bar{\mathbf{w}}$ to $\mathbf{u}$. However, the issue of the explicit form they propose for $\mathbf{u}$ is further beclouded by the fact that their energy equation (which includes both convective and transient effects) includes, in addition to our specific energy density formula $\hat{e} = \hat{u} + (1/2)v^2$, the term $(1/2)K_E(\nabla\rho)^2/\rho$, the latter presumably representing a Helmholtz free-energy contribution to the energy density.

The same constitutive formula (7.9) is also proposed by Kotschote [17,18] for inclusion in his energy transport equation. Specifically, a term essentially identical with the last term of (7.9) also appears in Kotschote's energy transport equation. In contrast, no such term appears in our analysis. However, it needs to be recalled that our bivelocity analysis is based upon *linear* irreversible thermodynamic principles [34]. It is possible that terms currently missing from that *linear* analysis, thereby constituting *nonlinear* irreversible thermodynamic phenomena, might appear at higher order, and thus possibly resolve the disparity. Unfortunately, no such nonlinear theory currently exists, certainly none possessing wide acceptance.

Apart from disparities in the values of the Korteweg phenomenological coefficients, evidenced by the differences between our Eq. (7.3) and those of others, as in Eqs. (7.7) and (7.8), the real source of the disparity between our respective theories lies in the fact that these other authors add a square-gradient term to the constitutive relation for the generic specific density $\hat{\psi}$ appearing in the equation governing transport of the extensive generic property Ψ. For example, the universal preconstitutive equation governing energy transport is

$$\rho\frac{D\hat{e}}{Dt} = -\nabla\cdot\mathbf{j}_e. \qquad (7.10)^*$$

In the absence of body forces, one would normally suppose that the constitutive equation for the specific energy is $\hat{e} = \hat{u} + (1/2)|\mathbf{v}|^2$, wherein, for differentially small changes in the state of the body, $d\hat{u} = \hat{c}_v dT + [(\beta/\kappa)T - p]d\hat{v}$. However, the latter constitutive relation holds only for the reversible or equilibrium case where, in single-component fluids, ρ is uniform through the fluid body. On the other hand, in nonuniform (and hence nonequilibrium) circumstances, where density gradients $\nabla\rho$ exist within the body, one might, at lowest order, be tempted to add a square-density gradient term proportional to $|\nabla\rho|^2$ to the constitutive expression for the specific energy $\hat{e}$, such that

$$\hat{e} = \hat{u} + (1/2)|\mathbf{v}|^2 + (1/2)K_E\rho^{-1}(\nabla\rho)^2. \qquad (7.11)^*$$

Energy-related contributions comparable to the last term in Eq. (7.11) type appear in the diffuse interface works of many others, including Fixman [28] and Felderhoff [29], concerned with single-component, two-phase, vapor-liquid equilibrium. Their presence presumably accounts for the absence of equilibrium, as evidenced by the nonuniformity of ρ. Thus, when one forms the material derivative D/Dt of the last term in Eq. (7.11) for use in Eq. (7.10), the latter term can be manipulated using the continuity equation such as to decompose the contribution

$$\begin{aligned}&\rho(D/Dt)(1/2)K_E\rho^{-1}(\nabla\rho)^2\\ &\quad\equiv(1/2)K_E(D/Dt)(\nabla\rho)^2 = K_E[D(\nabla\rho)/Dt]\nabla\rho\end{aligned}$$

into two portions, such that—certainly in the conduction-only case—one has that $D/Dt = 0$, irrespective of the operand upon which the material derivative operates. It is this nonclassical, nonlinear issue that possibly contributes to the difference between our bivelocity results and those of other diffuse interface researchers.

H. Diffuse entropy flux $\mathbf{j}_s$

As also regards possible additions to the present monovelocity. NSF-based entropy flux $\mathbf{j}_s = \mathbf{j}_q/T$ [see Eq. (5.2)], Cimmelli *et al.*, [11–13]—in their papers on gradient-energy and gradient-stress contributions in the context of Korteweg's model—postulate, as DS, the existence of an interstitial work flux $\mathbf{u}$ to be added to the heat flux $\mathbf{j}_q$ as in our Eq. (4.6) [jointly with Eq. (4.5)]. They then show that its presence contributes, nonlocally, not only to the Korteweg stress and energy fluxes but, equally importantly, to the entropy flux $\mathbf{j}_s$ as well, yielding, *inter alia*, the same entropy flux formula as in our Eq. (4.8). On the other hand, Anderson *et al.* [24] argue that $\mathbf{j}_s = -(k\nabla T)/T$, as in the classical NSF case, although here again the issue is beclouded by the fact that their expression for the specific entropy $\hat{s}$ appearing in their $\rho T D\hat{s}/Dt$ general entropy transport equation includes a square-gradient contribution (see also Ref. [17]) analogous to that appearing in the comparable general $\rho D\hat{e}/Dt$ energy term.

I. Summary

In summary, the results of the present section encourage pursuit of a foundational diffuse interface theory based not upon Helmholtz's free-energy thermodynamic model thereof, but rather upon the principles underlying bivelocity theory. This appears warranted in future research goals by virtue of Dunn and Serrin's [14,15] identification of (i) the need for the addition of a thermomechanical work-flux contribution to the traditional heat flux $\mathbf{j}_q$ appearing in the energy transport equation, including independent verification of that need by other researchers, and (ii) the role of this work-flux contribution in continuum-mechanically-based efforts aimed, among other things, at formulating a physically satisfactory theory of Korteweg stresses. Accordingly, it seems likely that general continuum-mechanical and continuum-thermodynamic analyses will need to be modified to account for volume transport, especially for the presence therein of the diffuse volume flux $\mathbf{j}_v$.

VIII. DISCUSSION

A. Pressure distribution in static heat conduction problems

Density gradients invariably coexist along with temperature gradients during conduction-only heat transfer processes. As a consequence thereof, the solution of even the most elementary, one-dimensional, steady-state, heat conduction problem cannot, in principle, be affected without concurrently addressing the solution of the conduction-only Cauchy linear momentum equation, owing to the presence therein of the nondissipative Korteweg stresses. This, in turn, points out, for example, contrary to current wisdom, that the pressure in the fluid undergoing heat conduction cannot generally be spatially uniform during steady-state heat conduction processes owing to the fact that the pressure distribution must be concurrently obtained from the respective joint solutions of the momentum and energy equations. Given the vast amount of experimental data reassuring the viability of the *current* interpretation of heat conduction data (sans our Korteweg stress momentum considerations), it is obvious that momental effects upon the temperature field must be extremely small, as indeed they are in conventional engineering circumstances. But not all circumstances are "conventional." Consider, for example, the much larger magnitude of the density gradients arising in ultracentrifuges [60], cosmological hydrodynamics [73], pollution spreading and avalanches [74], geomechanics [75], and shock waves [66,76]

B. Bivelocity theory for multicomponent fluids

In an attempt to achieve intuitive transparency of our arguments in favor of bivelocity theory over NSF theory for compressible fluids, at least to the extent possible, our paper deliberately restricts attention to the case of single-component fluid continua. However, the general unrestricted bivelocity model (including convection and transient phenomena) already exists for multicomponent *fluid* mixtures [3,77]. Volume transport in multicomponent fluids is vastly more complex than in single-component fluids, as witness, for example, attempts to determine volume production rates in mixtures [78,79], especially where the partial molar or partial specific volumes of the individual chemical species are generally unequal, and hence where unsteady-state convection necessarily arises as a consequence of the diffusion process itself. This is especially true when the species are chemically dissimilar, and therefore gives rise to thermodynamically nonideal solutions upon mixing (in the sense of the Lewis and Randall rule [80] for ideal solutions not being obeyed).

C. Bivelocity theory for crystalline solids

In the multiple species domain we draw the reader's attention to the large body of literature pioneered by Danielewski, Wierzba, and their collaborators [80–84], wherein the bivelocity scheme, focused on the diffusion of volume in crystalline *solids*, has been successfully applied to interpret atomic and vacancy diffusion phenomena occurring in multicomponent crystal lattices—with "success" recognized by the agreement of the bivelocity theory's predictions with experiment.

It is commonly accepted in materials science that two velocities are always necessary to quantify the so-called Kirkendall shift [85] in solid crystalline solutions. The method is based on the postulate that each component's velocity must be divided into two parts: (i) the unique diffusion velocity, which depends on the diffusion potential gradient (the latter being independent of the choice of reference frame), and (ii) the drift velocity, which is common to all species, and depends on the choice of the external reference frame. These concepts arise, for example, in the context of the diffusion of vacancies and atoms within a crystalline lattice. The drift velocity requires specifying an additional relation (beyond the mass conservation law). In reference to the latter, Spalding [86], in 1974, was apparently the first to introduce what Danielewski and Wierzba [87] later referred to as a "volume continuity equation" (or "law of conservation of the molar volume density") for multicomponent crystalline solids.

Among other things, Danielewski and Wierzba [81] used the general philosophy underlying the bivelocity model to rationalize the Kirkendall effect [85] in solids. In the course of doing so, they point out that their work substantiates Darken's [88] well-known explanation of that effect based upon Helmoltz's free-energy principles.

D. Cahn-Hilliard equations: Order parameters

Gurtin [89] proposes yet another, and more general, scheme focused on the preceding gradient-energy and gradient-stress issues in solids, based upon the hypothesized existence of what he terms "microforces." In this context, Gurtin, dealing with what is generally termed an "order parameter" in the literature [90,91] and represented by him as the generic symbol ρ (which includes identifying our own mass density symbol ρ as an order parameter), notes that "*If the sole macroscopic manifestation of atomistic kinematics is the order parameter ρ, then it seems reasonable that interatomic forces may be characterized macroscopically by fields that perform work when ρ undergoes changes*," arguing that the need for a separate microforce balance seems a necessary consequence of the disparate length scales involved. Gurtin further observes in this context that whereas standard forces in continua are associated with macroscopic length scales, microforces describe forces associated with microscopic configurations of atoms [corresponding to our length scale L given in Eq. (6.1) of Sec. VI].

Note added. Recently, I became aware of the pertinent work by Falk [92]. His paper, jointly with our present paper, when generalized to address a broader class of problems than diffuse interfaces, appears to lay the foundation for a comprehensive theory of *nonlocal* linear irreversible thermodynamics (NLIT), of which what we have termed bivelocity theory constitutes but a special case.

Moreover, while experimental support for bivelocity theory for single-component fluids undergoing heat conduction has been cited only for the case of gases, support also exists for its applicability to compressible liquids as well [93].

APPENDIX A: PERTINENT MOMENTUM TRANSPORT RELATIONS ($\boldsymbol{\Psi} \equiv \mathbf{M}$)

In circumstances where, in addition to conductive transport, both convective and transient transport are now temporarily retained, the linear momentum balance equation takes the traditional form [7–9] originally set forth by Cauchy,

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{f}}, \tag{A1*}$$

in which

$$\mathbf{P} = \mathbf{I}\bar{p} - \bar{\mathbf{T}} \tag{A2*}$$

is the pressure tensor (assumed to be symmetric), $\mathbf{I}$ is the idemfactor, $\bar{p}$ is the mean stress

$$\bar{p} = \tfrac{1}{3}\mathbf{I} : \mathbf{P}, \tag{A3*}$$

and $\bar{\mathbf{T}}$ is the symmetric and traceless viscous stress. Appearing in the above is the specific body force $\hat{\mathbf{f}}$, assumed conservative, and thus derived from a time-independent, position-dependent, specific potential-energy function,

$$\hat{\mathbf{f}} = -\nabla \hat{\phi}(\mathbf{x}), \tag{A4*}$$

with $\mathbf{x}$ the position vector.

Double-dot multiplication of (A2) by the idemfactor, followed by use of (A3), yields

$$\mathbf{I} : \bar{\mathbf{T}} = 0, \tag{A5*}$$

showing the deviatoric stress to be traceless. Furthermore, as a result of the symmetry of $\mathbf{P}$ and of the idemfactor, it follows that $\bar{\mathbf{T}}$ too is symmetric. Consequently, $\bar{\mathbf{T}}$ is both symmetric and traceless. The presence of the overbar serves to signify the fact that the dyadic it surmounts is both symmetric and traceless, such that for any dyadic $\mathbf{D}$, say, one has that the relation

$$\overline{\mathbf{D}} = \tfrac{1}{2}(\mathbf{D} + \mathbf{D}^{\mathrm{tr}}) - \tfrac{1}{3}\mathbf{I}\nabla \cdot \mathbf{D} \tag{A6*}$$

constitutes the dyadic's symmetric-traceless formulation.

An alternative, but physically identical, formulation of Cauchy's linear momentum equation (A1), having the form of the generic transport equation (2.11) in which $\hat{\psi} \equiv \hat{\mathbf{M}} = \mathbf{v}$, is given by the expression

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{j}_{\mathbf{M}} + \pi_{\mathbf{M}}, \tag{A7}^*$$

wherein $\pi_{\mathbf{M}}$ is defined in Eq. (3.4b), and

$$\mathbf{j}_{\mathbf{M}} = \mathbf{P} - \mathbf{I}p. \tag{A8}^*$$

Here, p is the thermodynamic pressure, governed by an equilibrium equation of state of the functional form $p = p(T,\rho)$ appropriate to the fluid under discussion, with T being the temperature. Equations (A1) and (A7) are, functionally, fully equivalent, in the sense that they embody exactly the same physics. Equation (3.4a) then follows from these considerations.

1. Conductive transport of momentum

In circumstances where the fluid is quiescent, such that the specific momentum density $\hat{\mathbf{M}}$ (which, constitutively, is identical to the fluid's mass velocity $\mathbf{v}$) is null, so that $\mathbf{v} = \mathbf{0}$, one has from Eq. (A7) that, in the static, conduction-only momentum equation we find that Eq. (3.3) holds true. This is, of course, consistent with the generic form (3.1). From Eqs. (3.4a) and (3.4b) we find that

$$\nabla \cdot \bar{\mathbf{T}} + \nabla(p - \bar{p}) = \nabla p - \rho\hat{\mathbf{f}}. \tag{A9}$$

This same expression derives for the conduction-only case from Cauchy's form of the momentum equation, (A1) and (A2). Equations (A8) and (A9) are applicable to all conduction-only fluids, irrespective of whether the fluid is monovelocity or bivelocity in nature.

APPENDIX B: PERTINENT ENERGY TRANSPORT RELATIONS ($\Psi \equiv E$)

Prior to devoting attention exclusively to the conduction-only case, the general energy equation takes the form [see also Eq. (7.10)]

$$\rho \frac{D\hat{e}}{Dt} = \nabla \cdot \mathbf{j}_e, \tag{B1}^*$$

in which

$$\hat{e} = \hat{u} + \tfrac{1}{2}v^2 + \nabla\hat{\phi} \tag{B2}^*$$

is the specific energy, consisting respectively of internal, kinetic, and potential energies.

In the present conduction-only case, the above becomes

$$\nabla \cdot \mathbf{j}_e = \mathbf{0}, \tag{B3}$$

with $\mathbf{j}_e$ the diffuse energy flux. It thus follows from the general relation (3.1) that energy is conserved, such that

$$\pi_e = 0. \tag{B4}^*$$

APPENDIX C: TRANSPORT OF WORK

In the general case, where convection and transient phenomena, in addition to conduction, are simultaneously present, the mechanical work flux is [3]

$$\mathbf{j}_w = \mathbf{P} \cdot \mathbf{n}_v, \tag{C1}$$

in which, from the second equality in the generic equation (2.12), $\mathbf{n}_v$ is the total volume flux, as given by the expression

$$\mathbf{n}_v = \mathbf{v} + \mathbf{j}_v. \tag{C2}$$

The nonequilibrium equation (C1) may be regarded as the natural generalization of the equilibrium thermodynamic work relation $dW = pdV$. The vector field $\mathbf{n}_v$ has the units of (volume)/(area)(time). But since (volume)/(area) has the units of (length)/(time), namely, the units of a velocity, $\mathbf{n}_v$ effectively has the units of a velocity. This fact is often explicitly represented in previous bivelocity publications by defining the fluid's "volume velocity" $\mathbf{v}_v$, wherein $\mathbf{n}_v \equiv \mathbf{v}_v$, so that

$$\mathbf{v}_v = \mathbf{v} + \mathbf{j}_v. \tag{C3}$$

It follows from the above that in the conduction-only case, for which $\mathbf{v} = \mathbf{0}$, that the work term in Eq. (C1) is given by the expression

$$\mathbf{j}_w = \mathbf{P} \cdot \mathbf{j}_v. \tag{C4}$$

Accordingly, upon use of the universally valid expression (A2), we find that

$$\mathbf{j}_w = -\bar{\mathbf{T}} \cdot \mathbf{j}_v - (p - \bar{p})\mathbf{j}_v + p\mathbf{j}_v. \tag{C5}$$

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