Fluid mechanics in fluids at rest

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Using readily available experimental thermophoretic particle-velocity data it is shown, contrary to current teachings, that for the case of compressible flows independent dye- and particle-tracer velocity measurements of the local fluid velocity at a point in a flowing fluid do not generally result in the same fluid velocity measure. Rather, tracer-velocity equality holds only for incompressible flows. For compressible fluids, each type of tracer is shown to monitor a fundamentally different fluid velocity, with (i) a dye (or any other such molecular-tagging scheme) measuring the fluid's mass velocity v appearing in the continuity equation and (ii) a small, physicochemically and thermally inert, macroscopic (i.e., non-Brownian), solid particle measuring the fluid's volume velocity \mathbf{v}_{v} . The term "compressibility" as used here includes not only pressure effects on density, but also temperature effects thereon. (For example, owing to a liquid's generally nonzero isobaric coefficient of thermal expansion, nonisothermal liquid flows are to be regarded as compressible despite the general perception of liquids as being incompressible.) Recognition of the fact that two independent fluid velocities, mass- and volume-based, are formally required to model continuum fluid behavior impacts on the foundations of contemporary (monovelocity) fluid mechanics. Included therein are the Navier-Stokes-Fourier equations, which are now seen to apply only to incompressible fluids (a fact well-known, empirically, to experimental gas kineticists). The findings of a difference in tracer velocities heralds the introduction into fluid mechanics of a general bipartite theory of fluid mechanics, bivelocity hydrodynamics [Brenner, Int. J. Eng. Sci. 54, 67 (2012)], differing from conventional hydrodynamics in situations entailing compressible flows and reducing to conventional hydrodynamics when the flow is incompressible, while being applicable to both liquids and gases.

DOI: 10.1103/PhysRevE.86.016307

PACS number(s): 47.10.A-

I. INTRODUCTION

A. Background

Eight years ago we published a paper in this journal [1] whose title was posed in the form of a question: "Is the tracer velocity of a fluid continuum equal to its mass velocity?" At the time, lacking the theoretical tools, and in the face of experimental data insufficient to furnish a convincing and unequivocal answer, we gave a tentative response of "no" when the flow is compressible and "yes" for incompressible flows. It has taken since then to make these assertions ironclad by furnishing theoretical proofs thereof, as well as to accumulate additional evidence in support of these answers. Developing a theoretical proof required evolving a bipartite theory of continuum fluid mechanics, "bivelocity hydrodynamics," a new branch of continuum mechanics, whose major findings were recently summarized elsewhere [2]. That publication should be viewed as a companion paper to what is written here, although it does not, itself, touch upon any aspect of the subject of tracers, the principal focus of the current paper. Freed by the companion paper of the need here to substantiate the lengthy physicomathematical arguments underlying our answers, we concentrate in what follows on providing the reader with a straightforward account of the reasoning behind our tracer-related conclusions.

The seemingly oxymoronic, but nevertheless wholly appropriate title of our present paper, "Fluid mechanics in fluids at rest," was deliberately chosen to be provocative in order to advance a second, broader theme, for which the tracer question constitutes but a special case. This refers to the existence of the heretofore unrecognized theoretical limits of applicability of the Navier-Stokes-Fourier (NSF) paradigm to incompressible flows, while advancing arguments in favor of the more generally applicable bivelocity paradigm [2], valid for both compressible and incompressible flows.

Despite the fluid being at rest-referring to the absence of macroscopic mass motion of the fluid-the fundamental mass, momentum, and energy conservation laws [3] underlying single-component hydrodynamics in quiescent fluids will nevertheless be seen to remain as relevant here as they are when the fluid is flowing. We focus on the quiescent case because the analysis is then especially transparent. Despite this focus on fluids at rest, the main conclusions issuing therefrom will be seen to apply irrespective of whether the fluid is flowing or at rest. The greater transparency arising for quiescent fluids stems from the fact that the slower the fluid moves, the greater is the magnitude of the extent by which predictions emanating from the bivelocity paradigm deviate from their traditional NSF counterparts. Furthermore, the smallness of the Reynolds numbers encountered when addressing quiescent fluids furnishes additional simplifications in the subsequent calculations, enabling, for example, transient phenomena to be viewed asymptotically as quasistatic.

B. Compressible flows

The major conclusion of bivelocity theory is that for fluids displaying linear rheological and thermal constitutive behavior the NSF paradigm is applicable only to incompressible flows. For compressible flows (of both gases and liquids) the NSF equations should be replaced by the more comprehensive bivelocity paradigm summarized here. The bivelocity model

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reduces to the NSF model in the incompressible limit. Other, less well-documented conclusions, pertinent, for example, to key aspects of hydrodynamics beyond the linear constitutive range, are briefly cited at the end of the paper.

The basic ideas underlying bivelocity hydrodynamics have existed for almost a decade [1,4-6], albeit being incomplete until now [2]). Its completion was based upon recognizing the need to prescribe the requirement that the constitutive equations entering into the theory satisfy a condition of mechanical equilibrium (see Eq. (6.16) of Ref. [2]), namely $\nabla \cdot \mathbf{P} - \rho \hat{\mathbf{f}} = \mathbf{0}$, where **P** is the pressure tensor, ρ the mass density, and $\hat{\mathbf{f}}$ the specific body force. The basis for this requirement follows the arguments of Prigogine, as set forth in De Groot and Mazur [7, pp. 43-44] in recognizing that mechanical equilibrium in fluids occurs well before that of thermodynamic equilibrium and hence necessarily underlies any theory of transport phenomena [3]. The companion paper shows, unequivocally, that the classical NSF paradigm [8] is intrinsically restricted to incompressible flows. In place of the latter model of fluid-mechanical behavior, bivelocity hydrodynamics poses a new paradigm in its stead, one equally valid for both compressible and incompressible flows. The theory of tracer behavior will be seen as intimately linked to the distinction between these two classes of flows.

Owing to the well-documented disparity of theoretical NSF-based predictions with experiments performed upon compressible gases, gas kineticists [9] have long known, empirically, that the NSF equations were inaccurate when applied to compressible flows of fluid continua. Our analysis goes one step further, showing that this "inaccuracy" stems from the intrinsic inapplicability to compressible flows of the NSF paradigm itself. Reasons offered by gas kineticists for the empirically observed breakdown in the reliability of the paradigm are based upon invoking the Boltzmann equation [10,11], a molecular theory, resulting in more-or-less *ad hoc* explanations of the transition phenomenon owing to their inability to solve this intractable equation. In contrast, our bivelocity explanation of the breakdown is strictly continuum in nature.

At least for the case where only modest departures from local near-equilibrium conditions prevail, and hence for which circumstances the principles of linear irreversible thermodynamics (LIT) [7] can confidently be assumed to apply, bivelocity hydrodynamics will be seen to provide a unifying theme, one that removes the artificial distinction currently existing between compressible and incompressible hydrodynamics. This is accomplished by the introduction into hydrodynamics of a second, independent velocity-the fluid's volume velocity \mathbf{v}_v —above and beyond that of the fluid's mass velocity v appearing in the continuity equation. The difference between the two velocities at a point in the fluid is found to be quantified by and (because of constitutive linearity) proportional to the local mass density gradient $\nabla \rho$, assuring thereby that bivelocity theory merges smoothly into NSF theory in the limiting case where the flow is incompressible, such that $\rho = \text{const.}$

C. The fluid's mass velocity v

In Newtonian mechanics the notion of the velocity of an object at a point in space is a strictly kinematical concept, wholly divorced from any aspect of the object's mass. For example, in focusing on the velocity of a just-launched rocket whose thrusters are releasing combustion gases to their surroundings as it makes its way through the atmosphere, one identifies the velocity of the rocket (relative to, say, Earth), independently of the unburned mass of fuel and oxidant remaining on board.

Standing in marked contrast to the independence of the Newtonian concept of velocity from any linkage to mass is the fact that in theoretical fluid mechanics the notion of the fluid's velocity at a point in space is inseparably linked to the concept of mass. This is so because in fluid mechanics the theoretical concept of velocity at a point in a fluid continuum draws upon use of the law of conservation of mass,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{n}_m = 0, \qquad (1.1)$$

in order to constitutively define the fluid's velocity,

$$\mathbf{v} := \frac{\mathbf{n}_m}{\rho},\tag{1.2}$$

to which we henceforth refer as the fluid's mass velocity. It is this strictly formal, abstract definition of the fluid's velocity, intimately tied to mass-related physical concepts involving the fluid's density ρ and its mass-flux \mathbf{n}_m , that enables (1.1) to be rewritten in its more usual continuity-equation form:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{1.3}$$

It is on this strictly mass-based foundation that the kinematical concept of the fluid's velocity at a point in the continuum emerges.

The mass flux density \mathbf{n}_m appearing in Eq. (1.1) is defined such that with $d\mathbf{S}$ a directed element of surface area situated at a fixed point \mathbf{x} of the fluid, the scalar $d\mathbf{S} \cdot \mathbf{n}_m$ gives the temporal rate at which mass is flowing across that surface. That the vector \mathbf{n}_m is a field variable at point \mathbf{x} , independent of the orientation of the surface element, is proved by the so-called "tetrahedron argument" [8].

The argument here is that in theoretical fluid mechanics the velocity symbol v does not pertain to the movement of an object, since neither the mass flux nor the mass density in Eq. (1.2) is an "object," namely an extensive material entity consisting of a permanent collection of matter, and composed for all time of exactly the same molecules. (For example, with regard to the rocket, the object whose velocity was sought was the rocket casing.) It is only in connection with experimental fluid mechanics, where a tracer is inserted into the fluid in an attempt to monitor the attribute termed the fluid's "velocity" v as defined by Eq. (1.2), that the word velocity is used in the same purely kinematical sense as it is in Newtonian mechanics.

In what follows we deal only with single-component fluids, although key elements of multicomponent bivelocity theory are already available [12].

II. TRACER MEASUREMENTS OF FLUID VELOCITY

Tracers are used in experimental fluid mechanics to measure the velocity \mathbf{v} of a flowing fluid by monitoring the tracer's spatiotemporal movement through space and assuming that the tracer is entrained in the fluid's mass flow. Tracer velocities are interpreted by use of the fundamental kinematical operational definition

$$\mathbf{v}(\mathbf{x},t) = \left(\frac{\partial \mathbf{x}}{\partial t}\right)_{\mathbf{x}_0} \tag{2.1}$$

of the velocity of an object, where **x** denotes the object's (i.e., tracer's) position at time *t* following its initial introduction at time t = 0 into the fluid at some arbitrary point **x**₀. Explicitly, the goal of a tracer is to relate the experimentally defined tracer's velocity as determined by use of (2.1) to the theoretically defined mass-velocity symbol **v** appearing in Eq. (1.2). It is this search that, for us, provides the motivating entry into the subject of bivelocity hydrodynamics.

Two elementary classes of tracers are commonly used to measure the fluid's velocity. These are typified by (i) a colored soluble dye, whose tracer velocity as defined by (2.1)henceforth is denoted as v', and (ii) a small, physicochemically and thermally inert, macroscopic (i.e., non-Brownian) solid particle, whose tracer velocity is denoted by v''. Were the flowing, single-component fluid to be, say, photochromic [13], the actual introduction of a dye into the fluid in connection with item (i) would prove unnecessary, since the tracer (now constituting a collection of the photochromic fluid's molecules) could itself be initially colorized in the neighborhood of some fluid point by use of lasers, which would not introduce the addition to the fluid of a foreign substance in order to introduce the color to be tracked. It is to this general type of "molecular tagging" [14] to which we later refer when speaking of a dye tracer.

During tracer experiments one directly measures the velocity \mathbf{v}' of the dye tracer or the velocity \mathbf{v}'' of the particle tracer. However, one cannot directly measure the fluid's mass velocity \mathbf{v} itself, the latter as defined constitutively by Eq. (1.2). As such, how does one know that either \mathbf{v}' or \mathbf{v}'' , if indeed either, is the physical realization of the abstract symbol \mathbf{v} appearing in the continuity equation (1.3)?

Ever since Euler's [15] founding of theoretical fluid mechanics as a rational scientific discipline in 1755 it has been implicitly assumed by fluid mechanicians that both types of tracer velocity measurements, dye and particle, necessarily yield the same outcome, namely that $\mathbf{v}' = \mathbf{v}''$ irrespective of specific circumstances (i.e., whether, for example, the flow occurs isothermally or nonisothermally, compressibly, or incompressibly, etc.). Furthermore, when interpreting the outcome of those tracer experiments, both tracers are invariably assumed to be the physical realization of the fluid's mass velocity \mathbf{v} , such that

$$\mathbf{v}' = \mathbf{v}'' = \mathbf{v}.\tag{2.2}$$

Our perspective with respect to this relation is to insist that if it is indeed true, then the two independent claims implicit therein, say $\mathbf{v}' = \mathbf{v}''$ and $\mathbf{v}'' = \mathbf{v}$, need to be proved theoretically, rather than being taken for granted. Pursuit of the voracity of this claim using bivelocity hydrodynamics is the dominant theme of this paper. Indeed, these kinematical tracer questions constituted the original motivating force [1,4] leading to the creation of bivelocity theory in the first place.

A. Review of evidence against Eq. (2.2)

Incontrovertible evidence, both theoretical and experimental—the latter as embodied in the phenomenon of thermophoresis [16,17] and the former as embodied in bivelocity theory [2]—is presented in what follows, thereby contradicting the universality of several of the naive beliefs expressed by Eq. (2.2).

In fact, as it turns out, bivelocity theory shows, when the flow is compressible, such that $\nabla \rho \neq 0$ in the neighborhood of the point in the fluid where the fluid's velocity **v** is sought, that

$$\mathbf{v}'' \neq \mathbf{v},\tag{2.3}$$

thus conflicting with one aspect of (2.2). That is, particulate tracers do not always move with the fluid's mass velocity. Rather, they do so only when the flow is incompressible.

In contrast to the inequality (2.3), and as is demonstrated in Appendix A (independently of the validity of bivelocity theory),

$$\mathbf{v}' = \mathbf{v} \tag{2.4}$$

in any and all circumstances, compressible or otherwise. That is, the dye tracer always faithfully monitors the fluid's mass velocity.

It follows jointly from Eqs. (2.3) and (2.4) that for compressible flows

$$\mathbf{v}' \neq \mathbf{v}'',\tag{2.5}$$

with equality holding only for incompressible flows. Physically, the source of the difference (2.5) in the respective dyeand particle-tracer velocities lies in the fact that in contrast with the particle-tracer case the domain occupied by the dye's color does not constitute a deterministic, material object. Rather, the dye's molecules (which are the carriers of the color) undergo diffusion owing to their respective Brownian motions. As a result, the dye's center of color, as opposed to the particle's center of mass, is a statistical rather than deterministic object. Since the fluid's mass velocity v is itself a statistical-molecular attribute of the fluid, it turns out that the equality (2.4) of dye and fluid mass velocities holds true under all conditions.

It is thus the difference between the statistical and deterministic natures of the two physical tracer measurements that renders the dye and particle-tracer velocities generally unequal, with equality holding only when the fluid's molecules are, on average (i.e., macroscopically), uniformly distributed. The latter is the case when the fluid is incompressible. It is only when the molecules are, on average, nonuniformly distributed, for which case $\nabla \rho \neq \mathbf{0}$ (constituting a compressible flow), that the respective statistical and deterministic tracer velocities diverge from one another, whereupon the inequality (2.5) prevails. That inequality, when combined with (2.4), gives rise to the fact the particle tracer does not move with the fluid's mass velocity, as set forth in Eq. (2.3). Rather, the particle tracer is shown to move at the fluid's volume velocity.

In summary, it is only for incompressible flows that the fundamental hypothesis (2.2) underlying the experimental verification of the equations of contemporary fluid mechanics is upheld in all circumstances. Amendments to these relations are thus required when the flow is compressible, namely when temperature or pressure gradients (or both) give rise to density gradients within the flow field. Identifying, formulating, and experimentally confirming the viability of these amendments is the sum and substance of bivelocity hydrodynamics.

From an overall perspective the bivelocity paradigm serves to establish the theoretical counterpart of the particle tracer velocity \mathbf{v}'' , such that this tracer velocity constitutes the physical realization of a theoretical quantity that we have termed the fluid's volume velocity, represented by the symbol \mathbf{v}_v , and subsequently define in Eq. (3.10).

III. PRECONSTITUTIVE MASS, MOMENTUM, AND ENERGY CONSERVATION EQUATIONS

A. Generic conservation laws

Prior to the introduction therein of any constitutive laws, the generic mass, linear momentum, and energy equations currently regarded as embodying the general conservation principles underlying fluid mechanics are [3,7,18,19]

(i) mass conservation,

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{v}) = 0; \qquad (3.1)$$

(ii) momentum conservation,

$$\rho \frac{D\hat{\mathbf{m}}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{f}}; \text{ and}$$
(3.2)

(iii) energy conservation,

$$\rho \frac{D\hat{e}}{Dt} = -\nabla \cdot \mathbf{j}_u - \nabla \cdot \mathbf{j}_w. \tag{3.3}$$

In addition to those symbols defined earlier, the new symbols appearing in the above are the specific momentum (or "momentum velocity") $\hat{\mathbf{m}}$; pressure tensor **P**; specific body force $\hat{\mathbf{f}} = -\nabla \hat{\phi}$ (assumed conservative, with $\hat{\phi}$ a time-independent specific potential energy); specific energy

$$\hat{e} = \hat{u} + \hat{e}_k + \hat{\phi}, \qquad (3.4)$$

consisting of internal-, kinetic-, and potential-energies; the heat flux \mathbf{j}_u ("diffuse internal energy flux"); and what we here term the "work-rate" or "rate-of-working" flux \mathbf{j}_w .

The material derivative appearing in the preceding equations is defined as

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla.$$
(3.5)

Furthermore, the pressure tensor is usually decomposed into the sum

$$\mathbf{P} = \mathbf{I} \ p - \mathbf{T},\tag{3.6}$$

in which **I** is the dyadic idemfactor and **T** the deviatoric stress. The latter is assumed here to be both symmetric and traceless. Choosing **T** to be traceless is tantamount to ignoring bulk viscosity effects. While for simplicity we do so in this paper, bivelocity results for the more general asymmetric case are available elsewhere [2].

B. Constitutive relations

In order to effect closure of the trio of conservation equations (3.1)–(3.3), thereby enabling their use in fluid-mechanical applications, constitutive equations are required for each of the symbols appearing therein [except for v, whose constitutive equation is already given by Eq. (1.2). In particular, the goal is to ultimately express all constitutive relations in terms of the trio of independent variables (v, p, T), with all other symbols (both nonequiulibrium- and equilibrium thermodynamically related) being regarded as dependent variables deriving from this set.

In current modes of pedagogical exposition [3,18,19] the selection of constitutive relations to be inserted into the above conservation equations in order to effect their closure invariably proceeds in two sequential steps: (i) formulating those constitutive equations that are regarded as being universal in scope, that is, are independent of the material properties of the particular fluid to which the resulting set of fluid-mechanical equations are ultimately to be applied; and (ii) formulating those material-specific constitutive laws that are specifically applicable only to a restricted class of fluids, for example, NSF fluids.

1. Universal constitutive relations

In the fluid-mechanics literature [3,7,18,19] the set of universally applicable constitutive relations appearing in the mass, momentum, and energy equations are assumed to be

$$\hat{\mathbf{m}} \stackrel{?}{=} \mathbf{v}, \tag{3.7a}$$

$$\hat{e}_k \stackrel{?}{=} \mathbf{v} \cdot \mathbf{v} / 2, \qquad (3.7b)$$

and

$$\mathbf{j}_w \stackrel{\scriptscriptstyle 2}{=} \mathbf{P} \cdot \mathbf{v}, \tag{3.7c}$$

each of which depends functionally upon the fluid's mass velocity (with the same being true of **P**). Subsequently, we show that Eqs. (3.7a) and (3.7b) are, indeed, universal in scope, whereas Eq. (3.7c) is seen as generally applicable only for the case of incompressible flows.

2. Material-specific constitutive relations

Material- or fluid-specific substances are those whose (\mathbf{v}, p, T) constitutive dependence lacks universality and whose transport behavior is therefore specific to a given fluid or to a particular class of fluids. By way of example, the constitutive equations obeyed by the class of materially specific NSF fluids are [3] (i) Navier-Stokes rheological law,

$$\mathbf{T} = 2\eta \overline{\mathbf{\nabla} \mathbf{v}},\tag{3.8}$$

and (ii) Fourier's heat-conduction law,

$$\mathbf{j}_u = -k\boldsymbol{\nabla}T.\tag{3.9}$$

Appearing in these expressions are the fluid's thermal conductivity k and shear viscosity η , each of which depends on (p,T). The overbar surmounting a dyadic, as in Eq. (3.8), represents the dyadic's symmetric and traceless form.

C. Challenges

Bivelocity hydrodynamics [2] departs from the contemporary hydrodynamics embodied in Eqs. (3.1)–(3.7) by challenging the present belief that each of the three Eqs. (3.7) is indeed universal in scope. In reviewing the origin of these three constitutive relations it becomes clear that each is an intuitively based hypothesis rather than an irrefutable physical law. Each of these intensive relations is obviously based upon an implicit analogy with a comparable extensive Newtonian mechanics counterpart, wherein the purely kinematically defined velocity symbol v appearing therein is replaced by the fluid's mass velocity **v**. For example, the Newtonian formula $\mathbf{M} = m\mathbf{v}$ for the extensive linear momentum M of a point-size rigid body of mass m moving through space with velocity \mathbf{v} becomes, when adapted analogically to a fluid continuum via the fact that $\mathbf{M}/m = \mathbf{v}$, is assumed to furnish the constitutive relation (3.7a) for the fluid's specific momentum density. However, the velocity v appearing in the expression for M is a purely kinematical quantity, divorced from that of the body's mass m, as witnessed by their separate appearances in the constitutive formula for M. In contrast, the fluid-mechanical velocity v is not strictly kinematical in nature, owing to its linkage to that of mass via Eqs. (1.1)-(1.3).

However plausible each of the three analogies underlying (3.7) may seem, they nevertheless need to be formally proven if true. Rationally, proofs of each, in order to be acceptable, need to be based either (i) upon well-established and more all-embracing physical principles or, when no such principle exists, (ii) on the accord with experiments of theoretical predictions emanating from having adopted these analogical hypotheses.

With regard to the above issues it is useful to recall that a fluid continuum is, after all, a mathematical rather than physical (material) entity, one that does not literally exist in nature, as opposed to, say, a rigid body in Newtonian mechanics. As such, it should not prove too surprising to learn that the analogy between a hypothetical fluid continuum and a rigid body may not be as exact as might otherwise appear from long experience. Indeed, in this context Serrin [20, p. 134] makes the explicit observation that the conservation equations of continuum fluid mechanics cannot, themselves, be formally derived from their Newtonian mechanics conservation counterparts. Rather, the fluid-mechanical equations appearing in textbooks are said by him to be merely "plausible." These cautions come to the forefront, especially when considered in conjunction with experimental tracer-velocity data suggesting that, in order to rationalize the tracer data, the existence of a second velocity, the fluid's volume velocity $\mathbf{v}'' \equiv \mathbf{v}_v$, may be required in a more comprehensive hydrodynamic theory.

D. Proofs of the universality of Eqs. (3.7a) and (3.7b)

Authoritative physical principles already exist that are sufficient to establish the universality of both Eqs. (3.7a) and (3.7b), but not that of (3.7c).

In particular, theoretical proof of Eq. (3.7a) for the fluid's specific linear momentum density, based upon recent work by others, is offered in Appendix B. Key to the proof is the (perceived) need for the equations of fluid mechanics to

satisfy the principle of conservation of angular momentum, a universally accepted physical principle.

Theoretical proof of the universality of the constitutive relation (3.7b) for the fluid's specific kinetic energy is offered in Appendix C on the basis of the physically required Galilean invariance of the resulting mass, momentum, and energy laws, with such invariance being recognized by the scientific community as an indisputable universally valid, physical principle.

E. Work-rate flux j_w

The constitutive equation for the work-related flux (3.7c)stands alone among the trio of Eqs. (3.7) by virtue of there currently being no proof of either its universality or its lack thereof. No pertinent physical principle having the broad authority, say, of a conservation law or a Galilean invariance principle appears to exist in the case of (3.7c) that would prove sufficient unto itself to enable a decision in the matter. Nevertheless, as subsequently discussed in Sec. V, in the course of demonstrating the latter's lack of universality, it proved possible to repair the situation by drawing upon a combination of reasonably well-accepted theories (LIT together with Boltzmann's gas-kinetic equation) jointly with experimental thermophoretic tracer-velocity data to reach the important conclusion that Eq. (3.7c) lacks universality. This finding challenges the foundations of contemporary fluid mechanics, which rely, inter alia, implicitly upon the universality of that relation.

In particular, it will be seen that the work-rate flux formula (3.7c) is correct only for incompressible fluids. In its stead, and with \mathbf{v}_v the fluid's volume velocity, as defined explicitly by its presence in the expression

$$\mathbf{j}_w = \mathbf{P} \cdot \mathbf{v}_v, \tag{3.10}$$

we tentatively adopt this nested constitutive relation as a hypothesis for use in Eq. (3.3). "Nesting" refers here to the fact that the constitutive equation for **P** is seen to depend upon that for \mathbf{v}_v . As such, the constitutive equations for both need to be determined concomitantly rather than sequentially, as elaborated upon in Sec. V.

Because of this nesting aspect, the amendments to fluid mechanics posed by these considerations impact not only on the energy equation, where the symbol \mathbf{v}_v appears explicitly, but also on the momentum equation (3.2). This is so because of the interlinking (3.10) of the constitutive equation for \mathbf{P} with that of \mathbf{v}_v , jointly with fact that \mathbf{P} appears in the momentum equation. This makes the momentum equation implicitly dependent on the constitutive equation for \mathbf{v}_v , even though \mathbf{v}_v itself appears explicitly only in the energy equation. As a consequence, Eq. (3.10) plays a role in amending fluid-mechanical calculations even for isothermal flows, where the energy equation itself proves irrelevant.

Owing to the constitutive dependence of \mathbf{v}_v (as well that of **P**) on the physical properties of the fluid bring addressed, Eq. (3.10) is, by definition, a material-specific rather than universal constitutive law (unless, of course, \mathbf{v}_v ultimately proves to be constitutively synonymous with \mathbf{v} , such as is currently believed to be the case in conventional fluid mechanics). Furthermore, much as in the NSF case, theoretical

knowledge of the respective constitutive laws governing **P** and \mathbf{v}_v (and \mathbf{j}_u) proves to be accessible only for those situations where LIT suffices as regards the degree of accuracy required in applications involving the consequent constitutive equations. That is, constitutive data for \mathbf{j}_w is available later on in this paper only for those flows whose departures from a state of uniform pressure and temperature are sufficiently small such that *linear* rheological and thermal constitutive laws, typified by those embodied in Eqs. (3.8) and (3.9), provide sufficient accuracy.

F. A brief glimpse of what follows

For the case of single-component fluids, and for modest degrees of departures from equilibrium, the volume velocity at a point in a fluid is seen to be given in terms of the trio (\mathbf{v}, p, T) of independent variables by the constitutive equation [2]

$$\mathbf{v}_v = \mathbf{v} + D_v \nabla \ln \rho, \qquad (3.11)$$

where D_v , whose units are those of a diffusivity, is a phenomenological coefficient termed the fluid's volume diffusion coefficient. This macroscopically defined volume diffusivity, like its conventional diffusion coefficient analogs appearing in transport processes theory [3], is dependent, at most, upon only the pressure and temperature of the fluid, being independent of the fluid's mass velocity. When the fluid is incompressible, such that $\nabla \rho = 0$, Eq. (3.11) shows that the two velocities merge into one, such that $\mathbf{v}_v = \mathbf{v}$, for which case bivelocity hydrodynamics reverts to conventional monovelocity hydrodynamics [3,7,18,19].

The volume diffusivity for the case of dilute gases is found to be given by an expression of the general form [2]

$$D_v = C_v \upsilon, \tag{3.12}$$

where $v = \eta / \rho$ is the kinematic viscosity and C_v is a dimensionless coefficient whose numerical value is very near to unity. Estimates of this coefficient by several authors, each based upon a version of his own bivelocitylike theory, are given later (in Table I).

It often proves convenient to express the difference between the volume and mass velocities in the form of a diffuse volume flux, with the latter defined as

$$\mathbf{j}_{v} := \mathbf{v}_{v} - \mathbf{v}. \tag{3.13}$$

As such, the latter's constitutive formulation for nearequilibrium flows is, from Eq. (3.11),

$$\mathbf{j}_v = D_v \nabla \ln \rho. \tag{3.14}$$

IV. THERMOPHORESIS: PARTICULATE TRACERS

A. Particle image velocimetry

Under the heading of *particle image velocimetry* [21], Wikipedia's current encyclopedic article bearing thereon states that, "Particle image velocimetry (PIV) is an optical method of flow visualization used in education and research. It is used to obtain instantaneous velocity measurements and related properties in fluids. The fluid is seeded with tracer particles which, for sufficiently small particles, are *assumed* [emphasis ours] to faithfully follow the flow dynamics (the degree to which the particles faithfully follow the flow is represented by the Stokes number). The fluid with entrained particles is illuminated so that particles are visible. The motion of the seeding particles is used to calculate speed and direction (the velocity field) of the flow being studied."

The preceding remarks are equivalent to the supposition that the equality sign applies in Eq. (2.3).

B. Thermophoresis

The phenomenon of thermophoresis [16,17] negates this implicit Wikipedia claim, namely that particles of effectively zero size and mass (corresponding to zero Stokes number) are necessarily entrained by the fluid, and hence that their velocities v'' are equal to the velocity v of the fluid, the latter as defined constitutively by Eq. (1.2). With regard to the thermophoretic movement of particles relative to the nonisothermal fluids in which they are immersed, it is already moderately well known [22] to those concerned, for example, with the transport of soot particles during combustion processes that a small, isolated, force- and torque-free solid particle suspended in a nonisothermal fluid does not move with the fluid's mass velocity v. As shown in what follows, this knowledge, when appropriately interpreted and pursued to fruition in the context of bivelocity theory, ultimately provides physical insight, heretofore lacking, into the wellknown failure [8] of the NSF equations to accurately model compressible flow phenomena.

Thermophoresis provides the premier example, indeed the only unequivocal example currently known to the author, showing that the particle-tracer velocity does not always mirror the fluid's mass velocity and confirming thereby the general inequality $\mathbf{v}'' \neq \mathbf{v}$ set forth in Eq. (2.3). In view of the universally valid dye- and mass-velocity equality $\mathbf{v}' = \mathbf{v}$ appearing in Eq. (2.4) it follows that respective dye- and particle-tracer measurements of the fluid's velocity will not generally agree with one another, namely that $\mathbf{v}' \neq \mathbf{v}''$, as set forth in Eq. (2.5).

In the conceptually simplest case, thermophoretic particle motion [16,17] is encountered following the introduction of a solid, macroscopic, particle into an initially quiescent fluid confined between parallel walls maintained steadily at different temperatures. (In the general case the particle need be neither small nor inert to acquire thermophoretic mobility.) Subsequent monitoring of the particle's spatiotemporal movement (occurring from the hotter towards the colder regions of the fluid) establishes that though the original, undisturbed, particle-free fluid was at rest, a force- and torque-free particle nevertheless translates through the fluid despite the absence of any obvious externally imposed animating force. In what follows, we address only situations where the particle is sufficiently small relative to its distance from either wall, so as to rule out the possibility of wall effects impinging upon the particle's motion.

Prior to insertion of the particle, the undisturbed fluid is simply undergoing steady-state heat conduction governed by Fourier's law. Dye introduced into that quiescent fluid in the role of a tracer of the fluid's mass motion will remain at rest (as proved in Appendix A) such that $\mathbf{v}' = \mathbf{0}$,

Author(s) Brenner	Scheme	C_v (Le Pr) ⁻¹	References to researcher's publications	
			Eq. (1.6)	[5]
Öttinger	GENERIC	Pr^{-1}	Eq. (2.82)	[33]
Klimontovich	Modified Boltzmann	Pr^{-1}	Eq. (14.1.2)	[35]
Greenshields-Reese	Experimental interpretation	1	Eq. (4.6)	[36]
Dadzie-Reese et al.	Modified Boltzmann	$(\text{Le Pr})^{-1}$	Eq. (52)	[37]
Eu	Statistical mechanics	$({\rm Le}{\rm Pr})^{-1}$	Eq. (103)	[40]
Koide-Kodama	Stochastic variational	1	Eq. (26)	[41]
Durst <i>et al</i> .	Extended molecular transport	1	Eq. (10a)	[46]
Graur et al.	Quasi-gasdynamics (QGD)	1	Eq. (25)	[47]

TABLE I. C_v values for gases proposed by various authors for use in Eq. (6.3).^{a,b}

^aThe dimensionless Prandtl number is $Pr = \nu / \alpha$. Prandtl numbers for gases are of O(1) [3, Table 9.1.2.].

^bThe dimensionless Lewis number [3] is Le = α / D , where D is the self-diffusivity. Lewis numbers for gases are of O(1); see Table I of [24].

confirming the absence of macroscopic mass motion. This lack of fluid movement appears to rule out entrainment of the thermophoretc particle by fluid motion as the source of its mobility. However, what of the possibility of a second, hidden, fluid "motion" as the entraining flow mechanism—say, the fluid's hypothetical preexisting volume velocity v_v brought on by the Fourier temperature gradient—as a possibility suggested by the independent particle tracer-velocity measurement v''?

1. Inert particles

Whereas a dye tracer remains at rest when introduced into a quiescent nonisothermal fluid, a small (albeit non-Brownian), physicochemically and thermally inert (non-heat-conducting) particle introduced therein in the presumably objective role of a tracer of the fluid's motion, is observed to move thermophoretically through the fluid at a reproducible velocity U_T relative to the walls (and hence relative to the externally imposed temperature gradient). Experimentally, as noted below, U_T , the particle's thermophoretic velocity, is observed to depend upon only the physicochemical properties of the fluid (and the magnitude of the temperature gradient), independently of any and all of the particle's material or geometric properties.

When the fluid is an ideal gas this inert particle velocity is found to be

$$\mathbf{U}_T = -C_s \upsilon \nabla \ln T, \tag{4.1}$$

a formula that has extensive theoretical and experimental support [16,17]. C_s is Maxwell's [23] thermal-creep coefficient, an empirical, experimentally determined, nondimensional constant of O(1), for which the value $C_s \approx 1.15$ (see Table I of Ref. [16]) is frequently cited. In regard to particle geometry, the velocity given by (4.1) is found to be independent of the particle's size and shape, and (when nonspherical [25]) also of the particle's orientation relative to either of the confining walls or, equivalently, relative to the direction of the externally imposed vector temperature gradient. For example, Eq. (4.1) applies equally to both spherical and ellipsoidal particles, in the latter case being independent of the ellipsoid's orientation.

Such solid particle movement through a fluid under the influence of a temperature gradient has been known since at least the time of Tyndall [26]. This type of motion should not be confused with the comparable Marangoni movement

[27] of a liquid droplet though an immiscible, nonisothermal viscous liquid, with motion in that case being animated by the dependence of the droplet's interfacial tension upon the temperature. Marangoni motion reflects the impact of interacting droplet-fluid physicochemical surface forces on particle movement through immiscible fluids, and depends upon droplet size, vanishing in the limit as droplet size shrinks to zero. (Moreover, the droplet speed depends not only on the chemical properties of the fluid continuum, but also on those of the droplet itself, since interfacial tension is a joint property of both the droplet and the surrounding fluid.) In contrast, as seen from Eq. (4.1), the thermophoretic motion of a physicochemically inert solid particle through a gas is size-independent, with the particle's thermophoretic velocity \mathbf{U}_T remaining nonzero even in the extrapolated hypothetical limit of zero size. Moreover, in contrast with the droplet case, the inert particle's velocity is observed to be independent of the particle's chemical constitution.

In addition to the particle's mobility in the absence of any obvious animating force, the size independence and geometric and physicochemical property independence of the particle's thermophoretic velocity as evidenced by Eq. (4.1) are striking phenomena, attributes whose fundamental significance to the subject of fluid kinematics and, ultimately, fluid dynamics and energetics as a whole was not recognized prior to the creation of bivelocity hydrodynamics [1,4]. This importance stems from the fact that whereas the fluid is locally at rest when the particle is absent (i.e., $\mathbf{v}' \equiv \mathbf{v} = \mathbf{0}$, as confirmed by a dye-tracer measurement), the fluid is no longer locally at rest ($\mathbf{v} \neq \mathbf{0}$) in the neighborhood of the particle, even when the particle is effectively only infinitesimal in size and thereby effectively absent from the fluid.

In effect, insufficient attention was paid in the past to the source of the particle's ability to move despite the seeming absence of any animating force. Epstein [28], building on Maxwell's [23] thermal-creep model, explained thermophoretic motion as resulting from temperature gradientinduced slip (thermal creep) of the gas's mass velocity v along the particle surface. Though not incorrect, this explanation fails to reconcile the fundamental physical-scale incompatibility of the notion of slip (a strictly macroscopic phenomenon) with fluid movement occurring along a particle surface of asymptotically zero size.

Given the solidity of the particle, the magnitude of the fluid's velocity \mathbf{v} in proximity to the particle, with the latter pushing the previously quiescent fluid mass out of its way as its moves between walls under the influence of the temperature gradient, must obviously be of the same order of magnitude as the particle's thermophoretic velocity U_T , even in the limit as the particle size shrinks to zero. Apparently, in this limit, an evanescent ghostlike mobile residue of the thermophoretic particle remains present in order to create this finite-size nonzero fluid velocity v despite the gas apparently being at rest. As such, a singularity exists in this limit. While this singularity might seem to be of only mathematical interest, its physical consequences are believed to herald a major advance in the theory of compressible fluid mechanics. Following the pursuit of the physical consequences stemming from this singular behavior, this advance refers, among other things, to the replacement of the NSF paradigm by its bivelocity counterpart.

2. Noninert particles

When the solid particle is heat-conducting rather than being thermally inert (though remaining physicochemically inert) its thermophoretic velocity through a gas is given by Epstein's more general formula [28],

$$\mathbf{U}_T = -\frac{1}{1 + 2(k_S/k)} C_s \upsilon \, \nabla \ln T, \qquad (4.2)$$

valid for the case where the particle is spherical in shape, and only for that shape [25]. When $k_S \ll k$ this formula reduces to (4.1). In contrast, the particle's noninert velocity, (4.2), valid for the case of spherical particles, is thus now dependent upon several of the particle's transport properties, namely k_S , as well as the particle's shape. [The shape effect is evidenced in the work of Mohan and Brenner [25], which derives the generalization of (4.2) for a heat-conducting, slightly deformed sphere, showing that the body's consequent anisotropy renders the particle's velocity \mathbf{U}_T dependent upon the particle's orientation relative to the temperature gradient.] In contrast, in the thermally inert limit $k_s = 0$ the particle's thermophoretic velocity \mathbf{U}_T as given by (4.1) was formally confirmed by these same authors to be independent of the nonspherical particle's orientation relative to the temperature gradient, despite the particle's geometric anisotropy. It is as a result of its particle-dependent attributes that a noninert (i.e., heat-conducting) particle cannot serve as an objective tracer of the fluid's undisturbed motion.

C. Summary: Thermophoretic particles

To summarize, when the small, non-Brownian, solid particle is physicochemically and thermally inert, it is our thesis that the particle's thermophoretic movement relative to the fixed walls may be viewed as a purely fluid-mechanical phenomenon, attributable exclusively to an as-yet-unexplained (that is, "unexplained" prior to bivelocity considerations) preexisting condition within the undisturbed fluid itself, independently of any attribute of the tracer particle, whose sole role is to render visible this hidden fluid motion. This allows the possibility that a particle with these properties can play a passive role as the tracer of the quiescent fluid's unexplained motion, namely its volume velocity \mathbf{v}_v . Explicitly, according to this proposed interpretation,

$$\mathbf{v}'' = \mathbf{U}_T = \mathbf{v}_v. \tag{4.3}$$

In other words, it is our contention that the particle's thermophoretic motion is simply the manifestation of a physicochemically, dynamically, and energetically neutral particle being entrained by the undisturbed fluid's preexisting volume flow engendered by the temperature gradient. Equation (4.3) is formally proved in Sec. VII, wherein the volume velocity symbol appearing in the preceding relation is that defined in Eq. (3.10).

As noted in connection with our discussion of Marangoni phenomena, the necessity that the particle be physicochemically inert in order to possibly play the role of an objective tracer of the undisturbed fluid's unexplained motion \mathbf{v}_v stems from the need for such surface phenomena to be absent, allowing only purely hydrodynamic fluid-particle surface effects to prevail. Since the thermophoretic data upon which Eq. (4.1) is based are for motion through ideal gases it is not unreasonable to suppose that physicochemical surface forces were indeed absent. More generally, say for the case of liquids or dense gases (to which bivelocity theory also applies [2]), such inertness can only be testified to by performing repetitive experiments using a variety of phyicochemically different (and differently shaped) particles, wherein measurements of the particle's tracer velocity v'' prove to be replicated for each class of particle used that, concomitantly, also yielded identical tracer velocities U_T . In those circumstances one performs experiments with ever smaller-sized particles of a given class fulfilling the above criteria, subsequently plotting particle speed U_T vs particle size, and eventually graphically extrapolating that data to zero particle size (while bearing in mind that, experimentally, the particle cannot be so small as to undergo any sensible Brownian motion). This extrapolation scheme then furnishes the particle-tracer velocity v".

In summary, our fundamental hypothesis is that a passive particle may, in the context of any and all circumstances (nonisothermal or isothermal, compressible or incompressible, etc.), be viewed as an objective tracer of the undisturbed fluid's hidden volume velocity \mathbf{v}_v if a number of repetitive particle experiments performed using different classes of inert particles all furnish the same extrapolated particle velocity measurement v'', as was found to be the case in connection with Eq. (4.1), but not (4.2). After all, this independence suffices to assure that the velocity being measured is a property solely of the undisturbed fluid, rather than of any physical attribute of the particle. In the present context we are simply stating the seemingly obvious fact, presumably accepted by all fluid mechanicians, that issues of the fluid's nonisothermalicity cannot be relevant to the objective interpretation of tracer velocity experiments. The tracer simply measures some preexisting kinematical attribute of the fluid prior to the tracer's introduction therein, whether that attribute be the fluid's mass or volume velocity or something else.

Bivelocity theory [2] eventually explains that the attending thermophoretic particle motion is attributable to the fact that the particle is simply passively entrained in the nonisothermal fluid's preexisting volume velocity \mathbf{v}_v driven by the difference in wall temperatures. More specifically, thermophoretic motion will be shown to be a consequence of the dependence of the fluid's density upon temperature, as quantified by the fluid's coefficient of thermal compressibility, $\beta = -(\partial \ln \rho / \partial T)_p$. Were the latter to be zero, thermophoretic motion would be absent despite the existence of a temperature gradient. This latter phenomenon, namely immobility in the presence of a temperature gradient, has already been demonstrated experimentally [29], albeit implicitly rather than explicitly, for the case for liquid water near 4 °C, at which temperature water has its maximum density, and hence for which $\beta = 0$. For example, were the respective wall temperatures confining the water to be, say, 1 °C and 7 °C, the thermophoiretic particle would ultimately come to rest roughly midway between the walls, irrespective of whether the particle was initially released into the water nearer to the colder or hotter wall.

Experimental data of other than a thermophoretic nature exist in support of the bivelocity paradigm. These pertain to the flow of gases in microchannels, as summarized in Ref. [2], to which group of transport phenomena should be added the recent work of Dadzie and Brenner [30]. Owing to their remoteness from fundamentals, these confirming data lack the authority and clarity of the present tracerbased kinematical confirmation of bivelocity hydrodynamics. Accordingly, these supporting data are not further discussed here.

V. LINEAR IRREVERSIBLE THERMODYNAMIC MODEL

A. Bivelocity mass, momentum, and energy conservation equations

Introduction of the constitutive equalities (3.7a), (3.7b), and (3.10) into the generic pre-constitutive equation set (3.1)–(3.3) furnishes the following bivelocity mass, momentum, and energy equations:

(i) continuity equation,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0; \qquad (5.1)$$

(ii) momentum equation,

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{f}}; \qquad (5.2)$$

(iii) energy equation,

$$\rho \frac{D}{Dt} \left(\hat{u} + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \hat{\phi} \right) = -\nabla \cdot \mathbf{j}_{u} - \nabla \cdot (\mathbf{P} \cdot \mathbf{v}_{v}).$$
(5.3)

The material derivative appearing in these expressions is defined as in Eq. (3.5).

B. Constitutive equations based on linear irreversible thermodynamics

The totality of nonequilibrium flux symbols appearing in the set of bivelocity transport equations (5.1)–(5.3) requiring constitutive formulation in order to effect complete closure is three in number, explicitly (**T**, $\mathbf{j}_u, \mathbf{v}_v$). [Those equilibrium thermodynamic symbols also requiring constitutive expression in order to effect closure are represented by $(\rho, \hat{u}, \hat{\phi})$.] On the other hand, for the NSF case, only two nonequilibrium flux symbols are required, namely (**T**, \mathbf{j}_u). Despite this difference in numbers, the broad general principles governing LIT—being independent of the number of symbols appearing in the set of transport equations to which LIT is to be applied —are exactly the same in the two cases, whether NSF or bivelocity [7,12].

In the conventional two-symbol NSF case, the use of LIT leads to the following expression for the entropy production rate π_s [7]:

$$T\pi_s = \mathbf{T}: \overline{\mathbf{\nabla}\mathbf{v}} - \mathbf{j}_u \cdot \mathbf{\nabla} \ln T.$$

The two constitutive expressions (3.8) and (3.9) emerge from the above as a consequence of the LIT-based linearity requirement imposed on the resulting flux (**T**, \mathbf{j}_u)-conjugate driving force ($\nabla \mathbf{v}, \nabla \ln T$) constitutive pairs. Moreover, the non-negativity requirements imposed upon the phenomenological viscosity and thermal conductivity coefficients η and k appearing therein arise as a consequence of the required non-negativity of π_s .

In the present three-symbol bivelocity case, the use of LIT [7] leads, analogously, to the following expression for the entropy production rate π_s [2]:

$$T\pi_s = \mathbf{T} : \nabla \mathbf{v}_v - \mathbf{q} \cdot \nabla \ln T + \mathbf{j}_v \cdot (\nabla p - \rho \hat{\mathbf{f}}),$$

involving the trio of fluxes $(\mathbf{T}, \mathbf{q}, \mathbf{j}_v) \equiv (\mathbf{T}, \mathbf{j}_u, \mathbf{v}_v)$ (where $\mathbf{j}_u = \mathbf{q} - p\mathbf{j}_v$ and $\mathbf{v}_v = \mathbf{v} + \mathbf{j}_v$) and their conjugate driving forces $(\nabla \mathbf{v}_v, \nabla \ln T, \nabla p - \rho \mathbf{\hat{f}})$. In turn, the LIT-imposed flux-force linearity requirement furnishes the following three constitutive expressions for the respective diffuse fluxes of momentum, entropic heat, and volume [2]:

$$\mathbf{T} = L_{33} \overline{\mathbf{\nabla} \mathbf{v}_v},\tag{5.4}$$

$$\mathbf{q} = -L_{11} \nabla \ln T + L_{12} (\nabla p - \rho \hat{\mathbf{f}})$$
(5.5)

and

$$\mathbf{j}_{v} = -L_{21} \nabla \ln T + L_{22} (\nabla p - \rho \mathbf{\hat{f}}), \qquad (5.6)$$

in which **q** denotes the "entropic (or Second-law) heat flux" [2]. It is defined in terms of the "energetic (or First-law)] heat flux" j_{μ} appearing in the energy equation (5.3) by the expression [2]

$$\mathbf{j}_u = \mathbf{q} - p \mathbf{j}_v. \tag{5.7}$$

The non-negativity of the entropy production rate jointly with the Onsager reciprocity requirement [7] imposes constraints upon allowable values for the five phenomenological coefficients appearing in Eqs. (5.4)–(5.6).

The above-cited constitutive equations are valid for both gases and liquids.

Were the phenomenological coefficients appearing in the preceding constitutive equation set to be known, it would then follow that introduction of this set of constitutive equations into the transport equations (5.1)–(5.3) would bring closure to the now amended set of fluid-mechanical equations. This closed set constitutes the bivelocity hydrodynamic paradigm. As seen below, it is only the presence of a nonzero value for \mathbf{j}_v that distinguishes bivelocity theory from NSF theory.

1. Phenomenological coefficients

The principles governing LIT [7] require that the phenomenological coefficients $L_{\alpha\beta}$ appearing in the preceding constitutive relations be functions, at most, of only pressure

and temperature, thus being independent of the fluid's mass velocity v. The additional requirements of LIT [7] impose further restrictions on these coefficients, namely that (i) Onsager's reciprocal theorem in the form $L_{21} = L_{12}$ be satisfied and (ii) the temporal rate of entropy production calculated on the basis of the above set of transport equations be non-negative. For ideal gases both of these conditions are shown [2] to be satisfied by the set of phenomenological coefficients subsequently set forth below in Eqs. (5.9a), (5.9b), (6.8a), and (6.8b).

In view of the fact that

$$\mathbf{v}_v = \mathbf{v} + \mathbf{j}_v, \tag{5.8}$$

it follows that $\mathbf{v}_v = \mathbf{v}$ in the limiting case where $\mathbf{j}_v = \mathbf{0}$. That, in turn, from (5.6), requires that $L_{21} = L_{22} = 0$, and hence from the Onsager reciprocity requirement that $L_{12} = 0$ too. Thus, when $\mathbf{j}_v = \mathbf{0}$, Eqs. (5.4) and (5.5), respectively, reduce to the pair of NSF constitutive equations (3.8) and (3.9). Since the $L_{\alpha\beta}$ are functions only of pressure and temperature, this leads to the fact that

$$L_{33} = 2\eta, \tag{5.9a}$$

and

$$L_{11} = kT.$$
 (5.9b)

It follows from the above set of bivelocity equations that knowledge of \mathbf{j}_{v} alone (together with knowledge of the fluid's shear viscosity η and thermal conductivity k) suffices to fully establish the set of bivelocity equations required in applications. The point here is that knowledge of \mathbf{j}_v is, from Eq. (5.6), equivalent to knowledge of the pair of phenomenological coefficients L_{21} and L_{22} . Furthermore, owing to the Onsager relation, knowledge of L_{21} implies comparable knowledge of L_{12} . The latter, in turn, completes knowledge of the constitutive equation for \mathbf{q} , with that result, in turn, furnishing knowledge of the energetic heat flux in Eq. (5.7). It can be seen from this interwoven bivelocity structure that knowledge of the constitutive equation for the diffuse volume flux \mathbf{j}_v alone suffices to establish all necessary amendments that need to be made to the NSF equations in order to render the bivelocity model applicable to compressible fluids.

C. Comments

Despite the somewhat greater complexity of the preceding bivelocity scheme relative to the comparable NSF paradigm, it is worth noting that in relation to current views of fluid mechanics, creation of this structure has required nothing more than acceptance, without change, of the standard principles of LIT [7]. Thus, while there exist a number of so-called *extended* versions of LIT [31,32], designed at least in part to overcome the inapplicability of the NSF equations to compressible flows, ours is not numbered among them. No extension of the fundamental principles underlying LIT has been required here, beyond maintaining an open mind on the assumed constitutive equalities (3.7).

The next section reviews the current availability of theoretical and experimental data pertaining to the phenomenological coefficient values $L_{\alpha\beta}$ required for use in the bivelocity equation set (5.1)–(5.7).

VI. PHENOMENOLOGICAL COEFFICIENT VALUES: CONSTITUTIVE EQUATION FOR j_v

For simplicity in what follows we address only those circumstances for which body forces are absent or negligible, so that in place of Eqs. (5.5)-(5.6) we now have that

$$\mathbf{q} = -k\nabla T + L_{12}\nabla p \tag{6.1}$$

and

$$\mathbf{j}_v = -L_{21} \nabla \ln T + L_{22} \nabla p. \tag{6.2}$$

LIT does not, itself, furnish values for the phenomenological coefficients required to establish the constitutive equations for the diffuse fluxes of momentum, heat, and volume. Rather, the coefficients must be obtained independently of LIT from other sources. These sources include (i) Klimontovich [34] and [35]; (ii) experiment [36]; (iii) molecular theories, such as Burnett's [10] or Grad's [10] solutions of the Boltzmann equation, including extensions of the Boltzmann equation by Dadzie-Reese *et al.* [37,38]; (iii) statistical-mechanical theories [39–43]; (iv) macroscopic theories, either rational, such as the equidiffuse model [44], or *ad hoc* [45–48]; (v) simulation, etc.

The models cited in the preceding paragraph, while generally differing significantly from one another in detail, all point independently to the same general constitutive formulation for the diffuse volume flux in single-component gases. (Details behind the present author's own LIT-based arguments can be found in Ref. [2].) Explicitly, in the absence of body forces the general agreement among all of the above-cited sources is that the following general constitutive expression applies to all dilute gases:

$$\mathbf{j}_v = C_v \upsilon \nabla \ln \rho, \, (\mathbf{\hat{f}} = \mathbf{0}), \tag{6.3}$$

wherein the choice of the non-negative, dimensionless, O(1) coefficient C_v varies slightly from one author to the other. This coefficient has either the same value for all gases or is, at most, weakly dependent upon the properties of the particular gas of interest (see Table I for the respective coefficient values). In what follows, we present evidence in support of Eq. (6.3), including evidence posed, not surprisingly, by thermophoretic experiments.

A. Phenomenological coefficients for gases and liquids

The functional relation $\rho = \rho(p,T)$ for the dependence of density upon pressure and temperature is such that

$$d\ln\rho = -\beta dT + \kappa dp, \qquad (6.4)$$

in which

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \tag{6.5}$$

and

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \tag{6.6}$$

are, respectively, the coefficients of thermal expansion and compressibility. From (6.3) it thus follows that

$$\mathbf{j}_{v} = -C_{v}\upsilon\beta T\nabla\ln T + C_{v}\upsilon\kappa\nabla p.$$
(6.7)

Comparison of the latter with (6.2) together with use of Onsager reciprocity gives

$$L_{21} = L_{12} = C_v \upsilon \beta T, \tag{6.8a}$$

and

$$L_{22} = C_v \upsilon \kappa. \tag{6.8b}$$

1. Ideal gases

For ideal gases, where $\beta = 1/T$ and $\kappa = 1/p$, Eq. (6.7) becomes

$$\mathbf{j}_v = -C_v \upsilon \nabla \ln T + C_v \upsilon \nabla \ln p. \tag{6.9}$$

Table I presents a tabulation of C_v values for gases proposed by various authors based upon their own versions of what we have characterized as constituting (at least approximately) a proper "bivelocity" theory. By this bivelocity characterization is meant that irrespective of the choice made by each researcher for the respective constitutive equations governing $(\hat{\mathbf{m}}, \mathbf{v}_k, \mathbf{T}, \mathbf{j}_u)$, all arrive at the same constitutive formula (6.3) for the diffuse volume flux, but with C_v values specific to each author's particular model. The overall scheme by means of which each author arrived at his below-tabulated value is noted in the table.

According to the tabulations in Table I a variety of different bivelocitylike theoretical schemes all arrive, independently, at the common constitutive expression (6.3) for the diffuse volume flux. As emphasized in Sec. V, in our LIT-based scheme [2] it is the nonzero value of this flux alone that distinguishes the bivelocity model from that of the NSF model. (Some of these other bivelocity like schemes may, however, differ from NSF in ways other than solely with respect to the \mathbf{j}_v value.) The large number of entries in Table I, each embodying a very different physical argument for amending the NSF equations in the case of compressible fluids, speaks of a growing consensus among widely varying classes of fluid mechanicians that bivelocity theory is meritorious. It is not our intention here to contrast and compare the relative strengths and weaknesses of each of the varied approaches to the subject, nor to suggest which is the more correct C_v value in Table I. Rather, our goal is simply to exploit the commonality of these findings with regard to the existence of a diffuse volume flux in order to answer the question posed 8 years ago, namely, "Is the tracer velocity of a fluid continuum equal to its mass velocity?"

VII. BIVELOCITY PROOF OF THE PARTICLE-TRACER/VOLUME VELOCITY EQUALITY, $v'' = v_v$ WHERE v_v IS DEFINED IN EQ. (3.10)

A. Introduction

For the previously discussed case of an otherwise quiescent gas confined between two walls while undergoing steadystate heat conduction, our goal in this section is to use the bivelocity equations of the preceding section to calculate the velocity \mathbf{U} of a small, inert, force- and torque-free particle immersed in that gas and to subsequently compare that theoretical result with the experimentally observed velocity $\mathbf{v}'' (\equiv \mathbf{U}_T)$ of a thermophoretic tracer particle, under these same circumstances, for which \mathbf{U}_T is given by Eq. (4.1). The purpose of this exercise is to confirm, by example, that the proposed bivelocity model summarized in Secs. V and VI furnishes theoretical results that accord with experiment. In effect, this exercise creates a formal connection joining bivelocity theory (embodying the two theoretical fluid-mechanical velocities \mathbf{v} and \mathbf{v}_v) to experiment (embodying the two experimental tracer velocities \mathbf{v}' and \mathbf{v}'').

B. Bivelocity fields in the absence of the tracer particle

We begin by first solving the steady-state bivelocity equations governing the state of affairs existing in the undisturbed, particle-free gas prior to the particle's introduction therein. With x a Cartesian coordinate perpendicular to the walls, and with the confining walls situated at x = 0 and x = L, the boundary conditions imposed upon the fluid's temperature field require that

$$T = T_0$$
 at $x = 0$, (7.1a)

and

$$T = T_L \quad \text{at} \quad x = L, \tag{7.1b}$$

with T_0 and T_L the respective wall temperatures. For definiteness we suppose that $\Delta T = T_L - T_0 \ge 0$. By symmetry, the problem is strictly one-dimensional, such that the boundary conditions specifying the impermeability of the confining walls to mass flow require that

$$\mathbf{i}_x \cdot \mathbf{v}^{(0)} = 0 \quad \text{at} \quad x = 0 \tag{7.2a}$$

and at

$$x = L, \tag{7.2b}$$

where \mathbf{i}_x is a unit vector in the *x* direction, and where the superscript (0) refers to conditions existing in the quiescent, undisturbed gas undergoing heat conduction. The unique solution of the bivelocity equations satisfying these boundary conditions is readily found to be

$$\mathbf{v}^{(0)} = \mathbf{0},\tag{7.3}$$

$$p^{(0)} = \operatorname{const} = p_o, \text{ say}, \tag{7.4}$$

$$T^{(0)} = T_0 + \frac{\Delta T}{L}x,$$
 (7.5)

and

$$\mathbf{v}_{v}^{(0)} = \mathbf{j}_{v}^{(0)} = -C_{v}\upsilon\,\nabla\ln T \equiv -\frac{C_{v}\eta\,\nabla T}{\rho T},\qquad(7.6a)$$

or, more explicitly,

$$v_v^{(0)} = j_v^{(0)} = C_v \frac{R}{M_w} \frac{\eta}{p_o} \frac{\Delta T}{L} = \text{const},$$
 (7.6b)

where, in the latter, $\mathbf{v}_v^{(0)} = \mathbf{i}_x v_v^{(0)}$ and $\mathbf{j}_v^{(0)} = \mathbf{i}_x j_v^{(0)}$. In the denominator of (7.6a) we have noted from the ideal gas law that $\rho T = M_w p_o / R = \text{const.}$ That is, while ρ and T both vary with x, their product is independent of x.

In connection with (7.6b), by declaring the volume velocity's speed to be constant throughout the gas, we have regarded the viscosity η as being a constant, independent of temperature. Similarly, we have implicitly assumed the thermal conductivity entering into the calculations leading to (7.5) to be temperature independent. Inclusion of such dependence would have given rise to nonlinear contributions. These will be systematically ignored throughout the subsequent development as being negligible compared with the dominant linear contributions.

C. Bivelocity fields in the presence of the tracer particle

Solution of the bivelocity field equations when the particle is present in the gas requires recognizing the fact that as the particle moves through the gas under the influence of the imposed temperature gradient the particle changes it position relative to the walls, thereby encountering ever-changing local temperatures $T^{(0)}$. As such, the velocity, pressure, and temperature fields (\mathbf{v}, p, T) when the particle is present are necessarily time-dependent, although under the asymptotic circumstances for which we solve these equations those fields may be regarded as quasistatic.

In the course of solving the bivelocity equations one needs also to address the boundary conditions to be imposed upon the bivelocity fields. From the point of view of an observer fixed in the walls, the temperature boundary condition at the surface S of the nonconducting particle requires that

$$\mathbf{n} \cdot k \nabla T = 0 \quad \text{on } S, \tag{7.7}$$

since the heat flux is Galilean invariant. From this same vantage point fixed in the walls, the impenetrability of the particle to the transit of mass through its interior requires that

$$\mathbf{n} \cdot (\mathbf{v} - \mathbf{U}) = 0 \quad \text{on } S, \tag{7.8}$$

with **n** the unit normal vector at a point on S. Furthermore, the tangential velocity boundary condition at the particle surface requires that there be no slip of the fluid's volume velocity [49]:

$$(\mathbf{I} - \mathbf{nn}) \cdot (\mathbf{v}_v - \mathbf{U}) = 0 \quad \text{on } S.$$
(7.9)

In the above expressions $\mathbf{U} = \mathbf{U}_o + \mathbf{\Omega} \times (\mathbf{x} - \mathbf{x}_o)$ is the velocity at a point on the surface of the solid particle measured relative to the fixed walls, while \mathbf{U}_o denotes the particle's velocity at an arbitrary point \mathbf{x}_o fixed in the particle. In addition, $\mathbf{\Omega}$ is the particle's angular velocity relative to the fixed walls. Ultimately, the condition that the particle be force and torque free serves to determine both \mathbf{U}_o and $\mathbf{\Omega}$ in terms of the prescribed parameters of the problem, for example, the difference ΔT in wall temperatures. As it subsequently turns out, the particle, irrespective of its shape, does not rotate. In that case, all points in the particle translate with the same velocity, such that $\mathbf{U} = \mathbf{U}_o$. In anticipation of this fact we suppose, subject to *a posteriori* verification, that $\mathbf{\Omega} = \mathbf{0}$, whence we regard U simply as the velocity of the particle as a whole relative to the walls.

In addition to the boundary conditions at the particle surface there are also boundary conditions to be satisfied on the walls of the apparatus, specifically the temperature boundary condition (7.1a) and (7.1b) and the impenetrability boundary condition (7.2a) and (7.2b). Furthermore, analogous to the usual noslip volume velocity boundary condition imposed at the solid particle surface S, as in Eq. (7.9), we impose a similar no volume-velocity slip condition along the walls:

$$(\mathbf{I} - \mathbf{i}_x \mathbf{i}_x) \cdot \mathbf{v}_v = \mathbf{0}$$
 at $x = 0$ (7.10a)

and

$$x = L.$$
 (7.10b)

D. Asymptotic solution scheme

We do not seek an exact solution of the unsteady-state boundary-value problem outlined above. Rather, with a a characteristic linear particle dimension (e.g., the radius of a sphere was the particle to be spherical) we seek only an asymptotic solution, valid for the case where

$$\varepsilon = \frac{a}{L} \ll 1. \tag{7.11}$$

As discussed by Brenner and Bielenberg [50] in a virtually identical context, this limiting calculation can be effected by using a matched asymptotic expansion scheme based upon use of the small perturbation parameter ε .

Thus, using a matched asymptotic (singular perturbation) scheme, one forms an outer expansion based upon use of the wall separation distance *L* to scale the various length and gradient operator terms appearing in the bivelocity equations and boundary conditions. Not surprisingly, the leading-order outer perturbation fields prove to be closely related to the fields (7.3)–(7.6) existing in the absence of the particle. This is so because at this leading-order level of description of the outer fields, no particle is present in the gas in the limit where $\varepsilon \ll 1$. As such, no outer boundary conditions, other than subsequent matching conditions with the inner fields, are to be specified at the particle surface.

Similarly, one forms an inner expansion based upon use of the characteristic particle linear dimension "a" to scale the various length and gradient operator terms appearing in the bivelocity equations and boundary conditions. At this level of description, and from the point of view of the leadingorder inner perturbation fields, no walls are present in the limit where $\varepsilon \ll 1$. As such, no inner boundary conditions, other than matching conditions with the outer expansion fields, are to be specified in proximity to the walls.

The respective inner and outer expansions, neither of which has yet been uniquely determined, are then asymptotically matched in the usual way, and the condition of no net force and torque on the particle applied to uniquely establish the dominant, leading-order terms in both the inner and the outer fields in the limit where ε is small. The lengthy details governing the respective inner and outer fields, their perturbation expansions, and their ultimate matching in proximity to both the walls and the particle surface are virtually identical to those set forth by Brenner and Bielenberg [50]. As such, they need not be elaborated upon here. The net result of the analysis is that an inert, force- and torque-free particle translates (without rotation) relative to the walls of the apparatus with a velocity given by the size- and shape-independent expression [2]

$$\mathbf{U} = -C_v \upsilon \nabla \ln T. \tag{7.12}$$

The latter represents a purely theoretical result, derived by having solved the bivelocity equations subject to appropriate boundary conditions. It constitutes an asymptotic result, valid for the case where (7.11) applies, and holds independently of any and all properties of the particle. Comparison of (7.12) with (7.6a) shows that

$$\mathbf{U} = \mathbf{v}_{v}^{(0)}.\tag{7.13}$$

That is, the particle is simply carried along (entrained) with the volume velocity of the undisturbed fluid in the neighborhood of the space occupied by the tracer particle.

Interpretation of U(≡v_v) as the particle tracer's experimentally observed thermophoretic velocity U_T (≡v")

Comparison of (7.12) with Epstein's experimentally and theoretically supported thermophoretic-velocity expression U_T given in Eq. (4.1) shows that our theoretical bivelocity result for the particle's force- and torque-free velocity will coincide with the inert particle's thermophoretic velocity when

$$\mathbf{U} = \mathbf{U}_T, \tag{7.14}$$

thus requiring that

$$C_v = C_s. \tag{7.15}$$

Recall that the coefficient C_v arises theoretically from bivelocity theory in connection with the constitutive equation (6.3) for the diffuse volume flux. Expected C_v values for the case of gases were noted in Table I. Whereas C_v is seen to have a rational theoretical basis, the thermal creep coefficient C_S is a more-or-less empirical parameter entering into Maxwell's [23] theory of slip at solid surfaces along which the temperature varies. Though Maxwell presented a theoretical momentum transport-based derivation of his slip boundary condition based upon mid-19th-century gas-kinetic theory, he pointed out that his molecularly based C_S coefficient nevertheless possesses a purely empirical macroscopic aspect owing to the fact that its value depends on whether gas molecules rebounding from the particle's surface are reflected diffusively or specularly. This, of course, cannot be established by molecular arguments alone since the surface is part of a macroscopic body.

The magnitudes of C_v (Table I) and Maxwell's slip coefficient C_s both lie very near to unity, as well as near to one another. Given the respective theoretical uncertainties in their precise numerical values, especially when considered in the light of their common thermophoretic physical status, it is quite reasonable to suppose that Eq. (7.15) constitutes an exact relation. Granting this premise then leads, in turn, to the fact that Eq. (7.14) too is an exact relation. Finally, use of (7.14) together with Eqs. (7.13) and (2.3) shows that

$$\mathbf{v}^{\prime\prime} = \mathbf{v}_v^{(0)}.\tag{7.16}$$

2. Interpretation of the particle-tracer velocity v"

Equation (7.16) provides a physical interpretation of the second type of fluid velocity \mathbf{v}'' observed during the particle-tracer experiment described at the beginning of this paper. In this context, recall from Eq. (7.6) that $\mathbf{v}_v^{(0)}$ is the volume velocity of the quiescent undisturbed fluid. Thus, Eq. (7.13) shows that a small tracer particle is entrained by the undisturbed fluid's pre-existing volume motion, rather than by the fluid's undisturbed mass velocity $\mathbf{v}^{(0)} (\equiv \mathbf{v}')$, as is commonly assumed to be the case. It is only in the case of incompressible flows, for which $\rho = \text{const}$ throughout the flow field, that these two velocities coincide.

Though the volume-based entrainment equation (7.13) has only been shown to hold for the case of quiescent fluids, where mass flow is absent, it is easily shown [2] to also hold for flowing fluids. This is simply a consequence of the fact that the velocity boundary condition satisfied on the surface of the inert particle is one of no-slip of the undisturbed fluid's volume velocity rather than that of no-slip of the fluid's mass velocity. In the limit where $a/L \ll 1$, in which L is the characteristic length on which the undisturbed flow varies, this volume velocity is that of the undisturbed flow.

VIII. VOLUME TRANSPORT

A. Introduction

Though the notion of volume flow has been invoked repeatedly through this paper, we have, thus far, not actually established a direct connection between the contents of this paper and the physical notion of volume. This is evidenced by the fact that the definition of what we have termed the volume velocity (and used the symbol \mathbf{v}_v to denote throughout this paper) is that given by Eq. (3.10). That definition bears only a remote relation to the physical notion of volume through its analogy with the work term pdV appearing in equilibrium thermodynamics. In this section we seek to make the association of the velocity symbol \mathbf{v}_v with the notion of volume more than just a mere analogy.

B. Volume transport and production

The generic Eulerian transport equation [2] governing the transport of any extensive property Ψ through space is

$$\frac{\partial}{\partial t}(\rho\hat{\psi}) + \nabla \cdot \mathbf{n}_{\psi} = \pi_{\psi}, \qquad (8.1)$$

where $\hat{\psi}$ is the specific density, \mathbf{n}_{ψ} the flux, and π_{ψ} the temporal rate of production per unit volume of the property undergoing transport. By using the definition of the material derivative (3.5) together with the decomposition formulation (D3) of the flux \mathbf{n}_{ψ} into convective and diffusive portions, jointly with the continuity equation (1.1), Eq. (8.1) can be transformed into the alternative, but physically equivalent, generic form [2]:

$$\rho \frac{D\hat{\psi}}{Dt} + \nabla \cdot \mathbf{j}_{\psi} = \pi_{\psi}. \tag{8.2}$$

When the extensive property undergoing transport is that of volume ($\Psi \equiv V$), the specific property density is the fluid's specific volume, such that $\hat{\psi} = \hat{v}$. Equation (8.1) thus adopts the form

$$\boldsymbol{\nabla} \cdot \mathbf{n}_v = \boldsymbol{\pi}_v. \tag{8.3}$$

Alternatively, in view of (D6),

$$\nabla \cdot \mathbf{v}_v = \pi_v. \tag{8.4}$$

Furthermore, (8.2) becomes

$$\rho \frac{D\hat{v}}{Dt} + \nabla \cdot \mathbf{j}_v = \pi_v. \tag{8.5}$$

Either one of last two physically equivalent expressions constitutes the volume transport equation.

1. Volume conservation accompanying incompressible flows

When the density of the fluid remains constant during its transport one has by definition that $\hat{v} = \text{const}$ throughout the flow field and hence from (6.3) that $\mathbf{j}_v = \mathbf{0}$. Accordingly, it follows from Eq. (8.5) that

$$\pi_v = 0, \tag{8.6}$$

showing that volume is conserved for incompressible flows. This is, of course, exactly what one would have anticipated for the incompressible case. In that event, Eq. (8.3) becomes

$$\boldsymbol{\nabla} \cdot \mathbf{n}_v = 0 \tag{8.7a}$$

or, equivalently,

$$\boldsymbol{\nabla} \cdot \mathbf{v}_v = \mathbf{0}. \tag{8.7b}$$

Since $\mathbf{v}_v = \mathbf{v}$ for incompressible flows the preceding equation becomes

$$\nabla \cdot \mathbf{v} = 0, \tag{8.8}$$

which is the standard equation used by fluid mechanicians for so-called incompressible flows [18].

Equation (8.5) shows that volume is not generally conserved during compressible flows. It is pertinent to note, philosophically, that the notion of volume production has no counterpart in Newtonian mechanics since the point-size particles of matter comprising a mathematical continuum possess no volume. At best, volume can only be (statistically) attributed to a collection of particles rather to an individual particle. This renders volume fundamentally different from the properties of mass, momentum, and energy, since those properties are possessed by the individual point masses themselves.

The astute reader will have noted that we have not proved that the symbol \mathbf{j}_v defined by its appearance in Eq. (D3), and hence appearing in Eq. (8.5), is the same \mathbf{j}_v as that defined in Eq. (3.13). On the other hand, if we assume them to be synonymous then we arrive via (8.6) at the conclusion that volume is conserved during incompressible flows. Given the reasonableness of that conclusion it seems appropriate to regard the two diffuse volume fluxes as one and the same and to believe that we have justified the use of the word "volume" in connection with our analysis. In any event, the validity of the bivelocity paradigm does not depend in any way upon this equality, or even upon the use of the word volume in connection with the symbol \mathbf{v}_{v} . It appears likely that *molecular* arguments of the type used by Dadzie and Reese [37,38] could be used in an attempt to formulate a more authoritative demonstration of the relation of the symbol \mathbf{v}_v or \mathbf{j}_v to that of volume.

Appendix D provides further arguments buttressing belief in the claim that it is appropriate to assign the name volume to those attributes bearing the subscript "v" and deriving from the symbol \mathbf{v}_v defined by its initial appearance in Eqs. (3.10) and (5.8).

IX. HYDROSTATICS

The material in this section provides two examples illustrating the role played by the principles of "fluid mechanics in fluids at rest," the title of our paper.

A. Introduction

According to standard textbooks [18], mechanical equilibrium in isotropic fluids is governed by the hydrostatic equation

$$\nabla p = \rho \hat{\mathbf{f}}.\tag{9.1}$$

Although the issue of the explicit physical conditions under which mechanical equilibrium is assumed to prevail is usually not mentioned in the course of promoting Eq. (9.1), it is in most cases implicitly understood to refer to a fluid at rest in a bodyforce field, typically gravity. By "a state of rest" is invariably meant the condition wherein the fluid's mass velocity is zero at all points of the fluid. Moreover, the pedagogical level at which the subject of hydrostatic equilibrium is introduced to neophytes normally does not state whether the fluid to which Eq. (9.1) is to be applied is isothermal or nonisothermal. After all, stable steady-state nonequilibrium Fourier heat conduction can occur in nonisothermal fluids at rest when the temperature gradient is antiparallel to gravity.

B. Hydrostatics in nonisothermal fluids at rest

The existence of a temperature gradient in a quiescent fluid, namely one for which $\mathbf{v} = \mathbf{0}$, implies that the fluid, though in a state of mechanical equilibrium, is not at the same time in a state of thermodynamic equilibrium. In that context, thermodynamicists [51] carefully distinguish between mechanical and thermodynamic equilibria. Whereas mechanically oriented derivations [18] of (9.1) define pressure in terms of force per unit area, such that p = dF/dA, thermodynamically oriented derivations regard pressure as a fundamental physical quantity in its own right, independently of that of force, defining pressure as a physical attribute of a fluid defined by an equation of state, $p = p(\rho, T)$. Thus, for example, Kirkwood and Oppenheim [51], and Guggenheim [52] addressing the subject of thermodynamics in a gravitational field of force, provide careful thermodynamic derivations of (9.1). The net effect of this is that thermodynamicists produce exactly the same hydrostatic equation as do the fluid mechanicians, albeit subject to the caveat that the user exercise caution in applications involving nonisothermal fluids, owing to such fluids not being in a state of thermodynamic equilibrium.

C. Bivelocity hydrostatic equation

Without assuming either mechanical or thermodynamic equilibrium, and upon setting $\mathbf{v} = \mathbf{0}$ in Eq. (5.2) we obtain

$$\boldsymbol{\nabla} \cdot \mathbf{P} - \rho \hat{\mathbf{f}} = \mathbf{0},\tag{9.2}$$

in place of the hydrostatic equation (9.1). Use of (3.6) enables this to be rewritten as

$$\nabla \cdot \mathbf{T} - \nabla p + \rho \hat{\mathbf{f}} = \mathbf{0}. \tag{9.3}$$

For the case where $\mathbf{v} = \mathbf{0}$, Eqs. (5.4), (5.9a), and (5.8) combine to yield

$$\mathbf{T} = 2\eta \overline{\mathbf{\nabla} \mathbf{j}_{v}},\tag{9.4}$$

a result valid for both gases and liquids.

Following use of Eq. (6.7) in Eqs. (9.4) and (9.3) furnishes the following form for the bivelocity-based hydrostatic equation:

$$-2C_{v}\nabla\cdot\langle\eta\nabla\{\upsilon[\beta\nabla T+\kappa(\nabla p-\rho\hat{\mathbf{f}})]\}\rangle-\nabla p+\rho\hat{\mathbf{f}}=\mathbf{0}.$$
(9.5)

It is evident from this expression that it is only in the case of isothermal fluids, where $\nabla T = 0$, that the conventional form (9.1) of the hydrostatic equation is upheld. Estimates of the relative magnitude of the deviation of (9.5) from (9.1) occurring in nonisothermal fluids remain to be calculated for both gases and liquids. However, that will not be done here.

In order that the condition $\mathbf{v} = \mathbf{0}$ can actually be achieved in a nonisothermal fluid subject to a body force, the temperature gradient must be antiparallel to both the body force and hence the pressure gradient. In such circumstances the preceding expression becomes a one-dimensional problem, whose structure, however, will not be further explored here.

D. Heat conduction in a gravity field

From Eqs. (5.5), (5.9b), and (6.8a), the entropic heat flux is found to be

$$\mathbf{q} = -k\nabla T + C_v \upsilon \beta T (\nabla p - \rho \hat{\mathbf{f}}). \tag{9.6}$$

From (9.5) it is seen that the last term in the above expression does not vanish for the case of a nonisothermal fluid at rest. That being so, Eq. (9.6) shows, for a specified temperature gradient, that the rate of heat flow through a quiescent fluid is affected by the gravity field. Issues of the magnitude of the effect are deferred to a later date.

X. DISCUSSION

A. An explanation for the presence of v_v in place of v in the work-rate terms in Eqs. (3.7c) and (3.10)

As noted in the preceding section, those fluid mechanicians whose dominant training lies in mechanics choose to define pressure in terms of force per unit area, whereas fluid-mechanicians trained in thermodynamics regard pressure as a fundamental physical quantity in its own right, given by an equation of state. This point has already surfaced in connection with the hydrostatic analysis of Sec. IX. Indeed, it appears that the concept of force enters into the lexicon of thermodynamicists only when they need to derive the fundamental constitutive equation dW = pdV for the work performed during a change in the volume of a system accompanying a reversible change in its state. It is presumably at this point that they draw upon the strictly mechanical

notion of work as force times linear displacement, such that dW = Fdx. Upon multiplying and dividing the latter by area A, and using the mechanical definition, p = F / A, of pressure, together with the kinematical definition dV = Adx of volume change, thermodynamicists thus arrive at the desired relation: dW = pdV.

In the course of deriving the latter constitutive equation for the work performed it is obvious that thermodynamicists implicitly assume, inconsistently, that the mechanical pressure and their thermodynamic pressure are, physically, one and the same. Awareness of their implicit assumption might have led them to contemplate the possibility of the notion of *thermodynamic work rate* as force $d\mathbf{S} \cdot \mathbf{P}$ times volume flux \mathbf{n}_v , a concept distinct from that of the classical notion of *mechanical work rate*, namely force $d\mathbf{S} \cdot \mathbf{P}$ times rate of linear displacement of mass \mathbf{v} .

Given that possibility, could such a difference between the respective mechanical and (hypothetical) thermodynamic work rates be reflected in the respective energy equations (3.3), (3.7c), and (5.3), as the source of the additional work-related term $\mathbf{P} \cdot \mathbf{j}_v$ arising in bivelocity theory? After all, the difference in the irreversible thermodynamic and mechanical rates of working in those respective energy equations is $\mathbf{P} \cdot \mathbf{v}_v - \mathbf{P} \cdot$ $\mathbf{v} = \mathbf{P} \cdot (\mathbf{v}_v - \mathbf{v}) \equiv \mathbf{P} \cdot \mathbf{j}_v$. If so, it would be appropriate to refer to the scalar quantity $d\mathbf{S} \cdot (\mathbf{P} \cdot \mathbf{j}_v) \equiv (d\mathbf{S} \cdot \mathbf{P}) \cdot \mathbf{j}_v = d\mathbf{F} \cdot \mathbf{j}_v$ (the latter relation involving the product of a force times a velocity) as the "diffuse rate of working." The proposed name uses the word "diffuse" appropriately, since the extra work contribution arises from molecular rather than macroscopic action, namely as a consequence of Brownian motion (albeit only in inhomogeneous fluids, wherein a density gradient exists).

In effect, in attempting to rationalize the success achieved by the bivelocity work-rate (3.10), we are proposing adoption of the notion of irreversible thermodynamic work $\nabla \cdot (\mathbf{P} \cdot \mathbf{v}_v) \equiv \nabla \cdot (\mathbf{P} \cdot \mathbf{n}_v)$ as a new physical concept, distinct from that of mechanical work, $\nabla \cdot (\mathbf{P} \cdot \mathbf{v})$. Given the status of \mathbf{n}_v as a volume flow in Appendix D, the term $\mathbf{P} \cdot \mathbf{n}_v$ is clearly the analog of the equilibrium thermodynamic work term pdVwhen the latter is adapted so as to include temporal changes, wherein dV appearing therein is replaced by dV/dt, the rate of increase of volume.

B. Magnitude of the bivelocity effect

Define the dimensionless velocity-deficit ratio

$$R_v := \frac{|\mathbf{v} - \mathbf{v}_v|}{|\mathbf{v}|}.$$
(10.1)

 R_v , being null when bivelocity hydrodynamics merges into NSF hydrodynamics, thus provides a measure of the relative importance of the proposed bivelocity amendments to conventional NSF theory. As regards the order-of-magnitude of R_v it follows from Eq. (6.3) that

$$R_v = O\left(C_v \frac{\Delta \rho}{\rho} \frac{1}{\text{Re}}\right),\tag{10.2}$$

in which $C_v = O(1)$, $\Delta \rho$ is a characteristic density difference,

$$\operatorname{Re} = \frac{L|\mathbf{v}|\rho}{\eta} \tag{10.3}$$

is a characteristic Reynolds number, and *L* is a characteristic length over which sensible changes $\Delta \rho$ in density occur (i.e., such that $\Delta \rho / L = O(|\nabla \rho|)$. Equation (10.2) shows that bivelocity amendments are likely to be largest at small Reynolds numbers.

C. Illustration of the flow of volume independently of that of mass

Whereas v quantifies the flow of fluid mass, v_v (or, equivalently, \mathbf{n}_v) quantifies the flow of fluid volume, whatever physical interpretation the reader may wish to assign to such a nonmaterial flow. That is, the reader may have some reluctance in accepting the notion of the "flow" of a nonmaterial substance. To resolve the dilemma, it is useful to recognize the currently unqualified acceptance by fluid mechanicians of heat as "flowing," despite the fact that heat, like volume, is a nonmaterial substance.

Pursuing that analogy, the ability of volume to flow independently of mass belongs in the same category of nonmateriality as the ability of heat to flow independently of mass (such as occurs during Fourier heat conduction). Indeed, in the special case of quiescent (i.e., $\mathbf{v} = \mathbf{0}$) nonisothermal processes occurring in fluids, the notions of heat flow and volume flow prove to be effectively synonymous, sans a dimensional factor dependent upon the fluid's properties. Explicitly, in that case, for both liquids and gases, one finds that [53]

$$\mathbf{n}_v = \frac{\beta}{\hat{c}_p} \mathbf{j}_u, \tag{10.4}$$

in which the heat flux is given by Fourier's law. The physical significance of this relation is displayed pictorially in Ref. [53], where volume, like heat, is seen to be able to pass unimpeded through solid walls.

D. Boltzmann's equation in relation to bivelocity hydrodynamics

The Boltzmann equation [11,54] for gases, which is widely regarded as an authoritative molecular precursor to macroscopic fluid mechanics, would appear to be in direct conflict with the possible existence of two different fluid velocities. After all, Boltzmann's equation appears to give rise, statistically, to but a single macroscopic velocity, namely the fluid's the mass velocity. However, that view is superficial. For, as shown in detail in Ref. [2], our macroscopically derived bivelocity constitutive equations for the stress tensor, heat flux, and volume velocity are identical to their molecularly derived Burnett constitutive counterparts, obtained from Burnett's perturbation solution [55] of the Boltzmann equation for small Knudsen numbers. Accordingly, given this one-to-one correspondence [2] of our two-velocity, diffuse flux, constitutive expressions for the diffuse fluxes $(\mathbf{T}, \mathbf{j}_u, \mathbf{j}_v)$ (with Burnett/Boltzmann's one-velocity constitutive results for this same trio of fluxes with their \mathbf{j}_v given implicitly rather than explicitly [2]), it is clear that currently hidden within some, as yet undefined, Boltzmann-equation statistical

velocity measure there must surely exist a second fundamental velocity, one remaining to be discovered and identified with our volume velocity.

E. Liquids

Our analysis has focused on gases owing to the availability of a large body of experimental and theoretical data pertinent to the motion of tracers in gases. Yet bivelocity hydrodynamics per se is equally applicable to liquids. The only unequivocal data of which we are aware that bears on the present tracervelocity issue for liquids is that of Schermer *et al.* [56]. Those authors compare their experimental thermophoretic velocity data with a large number of proposed models for liquids, including our equidiffuse model [44,50], where, in place of Eq. (4.2) for noninert particles in gases, there now appears the comparable formula for noninert particles in liquids:

$$\mathbf{U}_T = -\frac{1}{1+2(k_S/k)} \frac{1}{\Pr} \upsilon \beta T \, \nabla \ln T. \tag{10.5}$$

The Scherer data agreed closely with the above formula, certainly when compared with all of the other thermophoretic models examined by them. Those models, other than our own, which proved appropriate for comparison over the range of data covered by the conditions of the Schermer *et al.* experiments, differed from the above by orders of magnitude.

F. Nonlinear, non-Newtonian, and other flows not within the province of LIT

Owing to our self-imposed restriction to fluids whose constitutive behavior falls within the purview of LIT, our paper has emphasized amendments only to NSF fluid mechanics, since both classes of fluids, bivelocity and NSF, belong to that linear constitutive category. However, going beyond LIT and its requirement of linear behavior, the more general philosophical consequences of bivelocity hydrodynamics are believed to apply to all fluids, including fluids whose rheological and thermal constitutive responses are nonlinear, such as in the case of non-Newtonian fluids [3]. By this is simply meant that we believe that the general trio (5.1)–(5.3) of preconstitutive bivelocity conservation equations applies to all fluids under all circumstances. The main feature of that belief is that one starts out with the symbol \mathbf{v}_v appearing in place of \mathbf{v} in the work term of the energy equation, with the idea of seeking to ascertain the material-specific constitutive equation for that symbol (along with those for the heat flux \mathbf{j}_u and the viscous stress tensor T). While we were able to use LIT to achieve those goals in the present linear case, where \mathbf{v}_v was found to be given by the constitutive equation (5.8), and \mathbf{j}_v by (6.3), we know of no comparable LIT-like recipe scheme applicable in other, more general, circumstances that could be adapted to address nonlinear constitutive fluid behavior.

XI. SUMMARY AND COMMENTS

A. Summary

Using readily available thermophoretic particle velocity data it was shown, experimentally, contrary to current teachings, that in compressible flows the molecular-tagging velocimetry (MTV, dye-tracer) velocity measurement v' of a flowing fluid's velocity is not the same as the comparable particle-image velocimetry (PIV, particle-tracer) velocity measurement \mathbf{v}'' , with equality holding only for incompressible flows, namely for those flows wherein the density gradient $\nabla \rho$ is zero. Moreover, it was shown theoretically in all circumstances, compressible and incompressible, that (i) $\mathbf{v}' =$ \mathbf{v} , where \mathbf{v} is the fluid's mass velocity appearing in the continuity equation $\partial \rho / \partial t + \nabla \cdot (\rho \mathbf{v}) = 0$; and (ii) $\mathbf{v}'' = \mathbf{n}_v$, where \mathbf{n}_v is the volume flux appearing in the volume transport equation $\nabla \cdot \mathbf{n}_v = \pi_v$, with π_v the temporal rate of production of volume per unit volume at a point of the fluid, the latter vanishing for incompressible fluids. (As \mathbf{n}_v has the units of a velocity, for simplicity this flux is termed the fluid's volume velocity in our paper and represented by the symbol \mathbf{v}_v .)

Recognition of the fact that two independent fluid velocities, mass- and volume-based, are formally required to model continuum fluid behavior was noted to have the effect of overthrowing the foundations of contemporary (monovelocity) fluid mechanics, including the NSF equations, which were shown to apply only to incompressible, a fact well-known, albeit empirically, to experimental gas kineticists. These findings were shown to lead to the development of a new general theory of fluid mechanics, bivelocity hydrodynamics, differing from conventional hydrodynamics in situations entailing compressible flows, and reducing to conventional NSF hydrodynamics when the flow is incompressible. The closely related, but ad hoc independent bivelocitylike theories of other researchers were shown to fully support the need for both mass- and volume-based velocities in the case of compressible fluids. (The use of *ad hoc* is meant to imply that those theories are actually in the nature of hypotheses, rather than rational theories based upon well-established physical principles, such as LIT and Burnett's solution of the Boltzmann equation.)

Distinguishing between respective states of mechanical and thermodynamic equilibrium, our analysis showed that the widely accepted hydrostatic equation $\nabla p = \rho \hat{\mathbf{f}}$ governing the pressure distribution in fluids at rest was valid only for isothermal fluids, and that gravity could affect Fourier's law of heat conduction in quiescent compressible fluids.

B. Comments

The mere existence of thermophoretic particle motion was noted to contradict the commonly held belief that a sufficiently small (albeit non-Brownian) solid macroscopic particle would simply be entrained in the flowing fluid's mass velocity v, irrespective of the physical process giving rise to that tracer velocity. It was the attempt to explain that phenomenon theoretically that led to the creation of bivelocity theory [2]. Because of the overwhelming and elaborate explanatory background that was required in the context of proving that $\mathbf{v}'' = \mathbf{v}_v$ (and to a lesser extent that $\mathbf{v}' = \mathbf{v}$), it may fail to be clearly recognized by the reader that but a single data point was available to provide unequivocal experimental kinematical support for bivelocity theory. We refer to the experimental data implicit in Eqs. (4.1) and (4.3), bearing on the fluid's second velocity, whose existence was identified by its thermophoretic footprint. The issue of unequivocality is compounded by the fact that the condition of no-slip of the volume velocity at the surface of the particle, used in our reconciliation of theory

and experiment, is an empirical relation, divorced from the question of the validity of the bivelocity equations themselves (although we have attempted to prove that this boundary condition has theoretical justification [49]). Obviously, if the entire theory is to stand up to closer scrutiny, much further work is required.

Perhaps the timetable with respect to firmer and independent confirmation of bivelocity theory by others is not as distant as it may seem. As is implicit in the tabulation appearing in Table I, the closely related bivelocitylike theories of others, though differing from ours in key details, is encouraging in that they arrive at very similar results that prove to agree well with a limited amount of experimental data. Moreover, moving beyond our use in this paper of bivelocity theory to address only kinematical issues, we believe that the success of our dynamic bivelocity application to flow in microchannels [30] offers further support in favor of the paradigm.

APPENDIX A: PROOF THAT THE DYE-TRACKING EXPERIMENT FURNISHES THE MASS VELOCITY v' = vAPPEARING IN THE CONTINUITY EQUATION

1. Molecular tagging velocimetry v'

When interpreting a photochromic dye-tracking velocity measurement the domain embodying the bulk of the dye's color is simply regarded as if it were an object to be monitored. With \mathbf{x}' the position of the dye's center of color at time t, and following the dye's initial introduction at time t = 0 into the fluid at point \mathbf{x}'_0 , the fluid's dye-velocity measure $\mathbf{v}'(\mathbf{x}', t)$, as defined by the above dye-tracking protocol is, as in Eq. (2.1),

$$\mathbf{v}' = \left(\frac{\partial \mathbf{x}'}{\partial t}\right)_{\mathbf{x}'_0}.\tag{A1}$$

With $d\mathbf{S}$ a directed element of surface area centered about a point \mathbf{x} fixed in space, and with \mathbf{v}' the statistical-kinematical measure at point \mathbf{x} of the velocity at which the color (and hence mass) moves through space in a small time interval δt , the volume $\delta V'$ of space swept through by the color as it moves through $d\mathbf{S}$ is then given by the expression $\delta V' := d\mathbf{S} \cdot \mathbf{v}' \delta t$. This follows from the fact that $\mathbf{v}' \delta t \equiv \delta \mathbf{x}'$ is the geometric projective displacement of the patch of color occurring during that time and that $d\mathbf{S} \cdot \delta \mathbf{x}'$ is the consequent amount of volume displaced.

Next, recall that the definition of the mass flux is such that with $d\mathbf{S}$ a directed element of surface area fixed in the space while being centered about some fixed point \mathbf{x} , the temporal rate at which the mass crosses that surface is $d\mathbf{S} \cdot \mathbf{n}_m$. With $\hat{v} = 1/\rho$ denoting the fluid's specific volume, the corresponding amount of fluid volume accompanying that mass, and hence crossing that surface in the small time interval δt , is thus $\delta V := d\mathbf{S} \cdot \mathbf{n}_m \hat{v} \, \delta t \equiv d\mathbf{S} \cdot \mathbf{n}_m / \rho \, \delta t = d\mathbf{S} \cdot \mathbf{v} \, \delta t$. The photochromically developed color that is being tracked is obviously being carried by the fluid's molecules, since it is they that are emitting the color. However, each colored molecule crossing the surface is at the same time also carrying that particular molecule's mass along with it. Consequently, the movement of the color is synonymous with the movement of the fluid's mass.

Upon now, identifying δV with the volume $\delta V'$ defined previously, we find upon equating corresponding terms and

noting that the areal element dS and time interval δt are both arbitrary that

$$\mathbf{v}' = \mathbf{v}.\tag{A2}$$

Thus, dye tracking does, indeed, provide a statistical measure of the fluid's mass velocity, a fact that was already intuited in connection with Eq. (2.2).

APPENDIX B: PROOF OF EULER'S HYPOTHESIS, $\hat{m} = v$

Landau and Lifshitz [19, p. 196] were apparently the first to recognize the need to prove Euler's implicit hypothesis, namely that $\hat{\mathbf{m}} = \mathbf{v}$, rather than to simply accept it as an established fact based on an analogy with the principles of Newtonian mechanics. However, their brief attempt at a proof was incomplete, as noted by Kostdädt and Liu [57], who offered a more authoritative proof of Euler's hypothesis. Liu, later [58] invoking both mechanical and thermodynamic arguments, elaborated further upon his proof, which was endorsed by Öttinger [59], leading them, together with Struchtrup, to ultimately to write a joint paper [60] on the subject, arguing that the failure of Euler's hypothesis to apply would result, *inter alia*, in a violation of the angular momentum equation. An independent proof of this same fact is contained in the Appendix to Ref. [30].

APPENDIX C: PROOF OF THE KINETIC ENERGY CONSTITUTIVE EQUATION, $\hat{e}_k = \mathbf{v} \cdot \mathbf{v}/2$

With \hat{e}_k the specific kinetic energy defined by its appearance in the energy equations (3.3) and (3.4), define the kineticenergy velocity \mathbf{v}_k in terms of the already-defined \hat{e}_k by the relation

$$\hat{e}_k = (1/2)\mathbf{v}_k \cdot \mathbf{v}_k. \tag{C1}$$

We begin by first proving that $\mathbf{v}_k = \mathbf{v}$. Were that to be true it would then follow from the above equation that Eq. (3.7b) was indeed correct.

From the generic energy equation (3.3) together with (3.4) and the definition (3.10) of \mathbf{v}_v we have that

$$\rho \frac{D\hat{u}}{Dt} + \rho \frac{D\hat{e}_k}{Dt} - \rho \mathbf{v} \cdot \hat{\mathbf{f}} = -\nabla \cdot \mathbf{j}_u - \nabla \cdot (\mathbf{P} \cdot \mathbf{v}_v), \qquad (C2)$$

where, with the material derivative given by (3.5), it has been noted that $\rho D\hat{\phi} / Dt = -\rho \mathbf{v} \cdot \hat{\mathbf{f}}$. In addition, from Eqs. (3.2) and (3.7a) the momentum equation is

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{f}}.$$
 (C3)

Consider two possible frames of reference, both pertaining to the same inertial coordinate system: the *O* frame and the *O'* frame, respectively labeling events according to the spatiotemporal coordinates (\mathbf{x}, t) and (\mathbf{x}', t') . The primed frame moves relative to the unprimed frame at a steady, time- and position-independent velocity, say **V**; that is, **V** is independent of the choices of (\mathbf{x}, t) and (\mathbf{x}', t') . Let the origins of these two frames coincide at t = t' = 0, The Galilean transformations connecting these two frames are t = t' and $\mathbf{x} = \mathbf{x}' + \mathbf{V}t'$. With $\nabla = \partial/\partial \mathbf{x}_t$ and $\nabla' = \partial/\partial \mathbf{x}'_{t'}$ the respective gradient operators in the two systems, the material derivative in the *O* frame is given by Eq. (3.5), whereas the corresponding derivative in the O' frame is $D/Dt' = \partial/\partial t'_{\mathbf{x}'} + \mathbf{v}' \cdot \nabla'$, where

$$\mathbf{v} = \mathbf{v}' + \mathbf{V}.\tag{C4}$$

It follows as a consequence of the preceding relations that

$$\nabla' = \nabla \tag{C5a}$$

and

$$D/Dt' = D/Dt.$$
(C5b)

Since the notion of velocity is purely kinematical, independently of whether it is being used in a mass, momentum, or energy context, it follows that

$$\mathbf{v}_k = \mathbf{v}'_k + \mathbf{V} \tag{C6a}$$

and

$$\mathbf{v}_v = \mathbf{v}'_v + \mathbf{V}.\tag{C6b}$$

By identity, $\nabla \cdot (\mathbf{P} \cdot \mathbf{v}_v) = (\nabla \cdot \mathbf{P}) \cdot \mathbf{v}_v + \mathbf{P} : \nabla \mathbf{v}_v$ in Eq. (C2). Use this identity to replace the last term appearing in Eq. (C2). Elimination of the common symbol $\nabla \cdot \mathbf{P}$ between the newly rewritten energy equation Eq. (C2) and the momentum equation (C3) then yields the following relation upon rearrangement using (C1):

$$\rho \frac{D\hat{u}}{Dt} = -\nabla \cdot \mathbf{j}_{u} - \mathbf{P} : \nabla \mathbf{v}_{v} - \rho \mathbf{v}_{k} \cdot \frac{D\mathbf{v}_{k}}{Dt} + \rho \mathbf{v}_{v} \cdot \frac{D\mathbf{v}}{Dt} - (\mathbf{v}_{v} - \mathbf{v}) \cdot \rho \mathbf{\hat{f}}.$$
(C7)

The preceding expression describes the transport of internal energy as seen by the O-frame observer in an inertial reference system. The corresponding equation as seen by the O'-frame observer in this same inertial system is

$$\rho \frac{D\hat{u}}{Dt'} = -\nabla' \cdot \mathbf{j}_{u} - \mathbf{P} : \nabla' \mathbf{v}_{v}' - \rho \mathbf{v}_{k}' \cdot \frac{D\mathbf{v}_{k}'}{Dt} + \rho \mathbf{v}_{v}' \cdot \frac{D\mathbf{v}'}{Dt} - (\mathbf{v}_{v}' - \mathbf{v}') \cdot \rho \hat{\mathbf{f}}, \qquad (C8)$$

in which we have noted that the constitutive expressions for the specific densities ρ , \hat{u} , \hat{f} and the fluxes \mathbf{j}_u and \mathbf{P} , being Galilean invariant, necessarily possess the same values in both the unprimed and primed reference frames. Upon subtracting (C8) from (C7) and subsequently making use of Eqs. (C4)–(C6a) and (C6b) we eventually find that $\mathbf{V} \cdot (D/Dt)(\mathbf{v}_k - \mathbf{v}) = 0$. Since \mathbf{V} is position- and time-independent, this is equivalent to

$$\frac{D}{Dt} \left[\mathbf{V} \cdot (\mathbf{v}_k - \mathbf{v}) \right] = 0.$$
(C9)

The time and position independence of Vthus requires that

$$\mathbf{v}_k = \mathbf{v},\tag{C10}$$

showing that the specific kinetic energy (C1) is indeed given by Eq. (3.7b), namely $\hat{e}_k = \mathbf{v} \cdot \mathbf{v}/2$.

APPENDIX D: ON THE CHOICE OF THE NAME "VOLUME" ASCRIBED TO THE NONMATERIAL FLUID VELOCITY v_n

With $\hat{v} = 1/\rho$ the specific volume, Eq. (3.14) can be rewritten as

$$\mathbf{j}_v = -\rho D_v \nabla \hat{v}. \tag{D1}$$

We emphasize this alternative form with the aim of rationalizing our association of the affixed volume with the symbol \mathbf{v}_v .

In addressing transport processes [3], and as a consequence of the fluid's Brownian motion, several physically different types of diffuse fluxes arise from molecular sources. In this context consider the transport through space of some generic extensive physical property Ψ , for example, mass, momentum, chemical species, entropy, volume, etc. With use of the circumflex symbol $\hat{\psi}$ to denote the specific density of that property (i.e., the amount Ψ per unit mass of the property) at a point in the fluid, all of the elementary diffusion fluxes of that property appearing thus far are, as noted by Woods [61], special cases of the following generic linear constitutive formulation:

$$\mathbf{j}_{\psi} = -\rho D_{\psi} \nabla \hat{\psi}, \qquad (D2)$$

in which D_{ψ} denotes the diffusivity appropriate to that property. Examples of this constitutive group include the following.

(i) Fourier's heat conduction law for the diffuse flux $\mathbf{j}_h = -\rho D_h \nabla \hat{h}$ of enthalpy (or for the isobaric "heat" flux), with \hat{h} the specific enthalpy and H the extensive amount of enthalpy. That the preceding constitutive expression for \mathbf{j}_h is correct follows from the fact, from equilibrium thermodynamics, that $d\hat{h} = \hat{c}_p dT$ for the isobaric case, so that one has that $\mathbf{j}_h = -\rho \hat{c}_p D_h \nabla T$. With $\alpha = k / \rho \hat{c}_p$ the fluid's thermometric diffusivity, the preceding expression can be rewritten as $\mathbf{j}_h = -k\nabla T$ by choosing $D_h \equiv \alpha$. As regards notation, $\mathbf{j}_h \equiv \mathbf{j}_u$ for the present isobaric case in which \mathbf{j}_u is the heat flux appearing in the energy equation (3.3).

(ii) Fick's law for the diffuse flux $\mathbf{j}_{\gamma} = -\rho D \nabla \hat{w}_{\gamma}$ ($\gamma = 1,2$) of chemical species γ in a binary solution, with \hat{w}_{γ} the specific mass or mass fraction of the species (i.e., mass W_{γ} per unit mass of the mixture composed of masses $W_1 + W_2$) and $D_{\gamma} = D$ the binary diffusion coefficient.

(iii) Allowing for poetic license, Navier's diffuse momentum transport law (a dyadic) for the diffuse flux of momentum, $\mathbf{j}_{\hat{\mathbf{m}}} = -\rho \upsilon \overline{\mathbf{V}} \mathbf{\hat{\mathbf{m}}}$, with $\mathbf{\hat{\mathbf{m}}} (\equiv \mathbf{v})$ the specific momentum and $D_{\mathbf{m}} = \upsilon$ the kinematic viscosity.

From the perspective of these existing diffuse transport laws, representing special cases of Woods' generic scheme, one sees that the constitutive equation (D2) for the diffuse volume flux fits perfectly into that scheme, wherein \hat{v} is the specific volume, with volume V being the extensive property undergoing transport. As such, this provides support for the belief that the symbol \mathbf{v}_v pertains to the notion of volume.

There is another equally compelling reason for attaching the name volume to the symbol \mathbf{v}_v . This stems from the fact that, generically, by definition, the (total) flux, say \mathbf{n}_{ψ} , of any extensive property Ψ is, by definition, the sum

$$\mathbf{n}_{\psi} = \mathbf{n}_m \hat{\psi} + \mathbf{j}_{\psi} \tag{D3}$$

of the respective convective and diffusive fluxes of that property (referring to the convective portion as representing the amount of the property carried by the flowing mass). When applied to the transport of volume, this yields

$$\mathbf{n}_v = \mathbf{n}_m \hat{v} + \mathbf{j}_v \tag{D4}$$

for the volume flux \mathbf{n}_v . Since $\hat{v} = 1/\rho$ and in view of (1.2) we thus obtain

$$\mathbf{n}_v = \mathbf{v} + \mathbf{j}_v. \tag{D5}$$

Comparison with (3.13) shows that

$$\mathbf{n}_v = \mathbf{v}_v. \tag{D6}$$

As such, \mathbf{v}_v is, physically, really a flux or current rather than a kinematically defined velocity. This is consistent with the fact, with the symbols l and τ , respectively representing length and time, that the dimensions of the volume flux \mathbf{n}_v are volume (l^3) per unit area (l^2) per unit time (τ), which is equivalent, dimensionally, to l/τ , namely to a velocity.

By analogy with its Fourier heat flux analog \mathbf{j}_u (wherein heat is said to be "flowing"), the view of \mathbf{v}_v or \mathbf{n}_v as a flux that also is flowing, rather than as a velocity that expresses linear movement, renders more palatable the use of the word "flow" when affixed to volume.

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