Unsolved Problems in Fluid Mechanics

Biographical sketch of Howard Brenner

Born and raised in New York City, Howard Brenner received his Bachelor's degree in Chemical Engineering from Pratt Institute in 1950 and D.Eng.Sci. from New York University in 1957. His 48-year career as a chemical engineering faculty member includes New York University (1955-1966), Carnegie-Mellon University (1966-1977), the University of Rochester --- as Departmental Chair (1977-1981) and, since 1981, MIT, where he is currently W.H. Dow Professor. Brenner has co-authored three fluid dynamics and transport phenomena books, namely "Low Reynolds Number Hydrodynamics (1965)," "Interfacial Transport Processes and Rheology (1991), " and "Macrotransport Processes (1993)." Honors include the American Institute of Chemical Engineer's "Lewis," "Walker," and "Alpha Chi Sigma" Awards, the American Society for Engineering Education's "Senior Research Gold Medal Award, " the American Chemical Society's Kendall Award in "Colloid and Interface Science," the "Bingham Medal" of the Society of Rheology, and the American Physical Society's "Fluid Dynamics Prize." Brenner holds membership in the National Academy of Sciences, the National Academy of Engineering, and the American Academy of Arts & Sciences. Lifelong research interests focus on hydodynamics and transport processes in fluid-particle systems --- addressing both fundamentals and applications. He has published about 250 papers in these fields. Most recently, his work has shown that the classical notions of fluid-mechanical transport processes in systems involving mass density gradients, dating back to the founders of the subject, including Euler, Navier, Stokes and Fourier, are patently wrong on principle. Concomitantly, Brenner's discovery and quantification of the notion that volume can be transported diffusively, i.e. molecularly (above and beyond the purely convective transport of volume accompanying the movement of mass) has been used to modify the basic momentum and energy transport equations in fluid continua, thereby correcting the works of the above-cited authors. He is currently working on a transport phenomena/continuum mechanics monograph encompassing these modifications.

Unsolved Problems in Fluid Mechanics:
On the Historical Misconception of Fluid Velocity as Mass Motion, Rather than Volume Motion

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Abstract

Existing experimental data on the thermophoretic velocity of a small, rigid, non-Brownian particle through an otherwise quiescent gaseous continuum, when re-interpreted as representing the motion of a passive tracer entrained in a moving fluid, reveals that macroscopic fluid movement (*motion*) can occur purely diffusively, by the movement of volume, without a concomitant (convective) movement of mass[1,2]. This experimental fact negates Euler's 250-year old generic, mass-based definition[3] of the velocity field in fluid continua, undermining thereby the heretofore seemingly rational foundations[4,5] of fluid mechanics and derivative subjects. This, in turn, requires a fundamental re-formulation of the basic equations of fluid mechanics[6,7] as well as of molecular theories[8,9] of transport processes[10,11] in fluid continua. This detailed re-fashioning, which is effected elsewhere[1], is based upon recognizing that volume can be transported purely diffusively[12], representing, *inter alia*, a previously unrecognized mechanism for momentum and energy transport in fluids.

Let me begin by congratulating the Ohio State Chemical Engineering Department on the occasion of its 100th anniversary. I am flattered to have been asked to participate in the celebratory exercises surrounding this happy occasion. May the Department continue to successfully serve the needs of its students, its faculty, the University, the chemical engineering profession, and the community of scholars at large.

Like several other invitees on this occasion, I was asked to emote on the subject of "Unsolved Problems in Chemical Engineering," specifically in the general area of Fluid Mechanics. However, having succeeded in identifying a problem crying out for solution, how is an indefatigable researcher expected to prevent his mind from attempting to solve the very problem or problems that he/she has identified as being unsolved? And woe to the speaker who actually succeeds in solving these. For this very action will render him incapable of presenting his lecture entitled "Unsolved Problems in Chemical Engineering," leaving him with the unpleasant alternative of identifying and writing about yet another unsolved problem, and so on, *ad infinitum*, *ad nauseum.* This is a logical conundrum, one that I strongly suspect the planners of this lecture series failed to anticipate. Obviously, they failed to reckon with Heisenberg's *uncertainty principle*, whereby the mere act of observing a system alters the state of that system --- the system here being the "unsolved problem" that one was asked to identify and discourse upon.

As a consequence of this unanticipated phenomenon, coupled with my own tenacity and sheer brilliance (not to mention an obvious lack of modesty), I stand before you today as a failure, a man unable to honestly present a talk entitled: "Unsolved Problems in Chemical Engineering." I will, therefore, instead, present a lecture entitled: "A Previously Unsolved Problem in Chemical Engineering," more pretentiously subtitled: "On the Historical Misconception of Fluid Velocity as Mass Motion, Rather than Volume Motion." The formal lecture notes pertaining to this topic follow subsequently, after the overview of the general topic given immediately below.

Overview of the Problem

According to all standard works and research publications on fluid mechanics, the velocity $\mathbf{v}$ at a point of a fluid continuum is governed by the movement of mass through a hypothetical surface fixed in space, as witness the first appearance of the symbol $\mathbf{v}$ for velocity in the well-known continuity equation of fluid mechanics, $\partial\rho/\partial t + \nabla\bullet(\rho\mathbf{v}_m) = 0$. On the other hand, the velocity of a material object is measured experimentally by tracking its temporal movement through space. (Anyone who as ever thrown a ball to a catcher will recognize that this is, indeed, the way to measure velocity.) Adapting this scheme to the measurement of fluid velocity, an object (a "tracer") — which is sufficiently small such as to not disturb the pre-existing fluid motion into which it is introduced — can be visually tracked in time so as to the monitor the undisturbed fluid movement serving to convect the

passive tracer through space; that is, the tracer merely renders visible the otherwise invisible continuum fluid motion existing its absence, without itself affecting that very movement! But where is the experimental and/or theoretical proof that the tracer and mass velocities are indeed the same?

This is (or rather was) the "unsolved problem" with which I began to prepare my talk. Based upon seemingly unequivocal experimental and theoretical grounds, I arrived at the surprising conclusion that these two velocities are, in well-defined circumstances, generally unequal. Indeed, in certain circumstances, namely in the case of phoretic phenomena (e.g. thermophoresis), involving the motion of a small, non-Brownian particle through a bounded, single-component fluid under the influence of a temperature gradient (in the absence of gravity effects), no continuum mass motion whatsoever exists at any point of the fluid, as is easily verified from the Navier-Stokes, continuity, and energy equations, together with the thermal equation of state for the fluid. Nevertheless, a thermophoretic particle, one animated by an externally-imposed fluid temperature gradient, is observed to move through the fluid from high to low temperature. And this particle qualifies as a "tracer," since its velocity is (observed experimentally to be) independent of its size, thereby enabling us to regard it as an effectively point-size object! This constitutes a physically authenticated situation in which the mass and tracer velocities of the fluid differ. The standard explanation for the phenomenon of thermophoretic motion (at least in gases), dating back constitutively to Maxwell in 1879, and consistent with the particle's size-independence, argues that the phenomenon arises from non-continuum fluid-mechanical effects existing near the surface of the particle, and involving a violation of the no-slip velocity condition at the particle surface. This, despite the fact that the Knudsen numbers (mean-free path to particle size) characterizing the fluid motion were vanishingly small during those experiments for which particle-size independence of the thermophoretic velocity was observed.

We offer here an alternative, strictly continuum, non-slip explanation of phoretic phenomena, albeit one based upon a major modification of the Navier-Stokes equations governing the fluid's convective and diffusive momentum transport processes in continua, wherein it is claimed that the mass velocity appearing in the continuity equation is not, in fact, the velocity of the fluid continuum (as measured by a tracer)! The consequences of the proposed general velocity inequality are profound, in that they undermine the basic fluid-mechanical and chemical engineering transport principles that we all learned in school,

James Clerk Maxwell

principles currently assumed to govern all fluid-mechanical transport phenomena.

Has Fundamental Research in Transport Phenomena Been Ossified By Its Own Success

During the roughly 30-year period beginning in the mid-1950's, chemical engineering research moved heavily into the area of engineering science. This effort was largely characterized by an intense focus on transport phenomena, including mass, species, energy, and momentum transport processes. Much of the codification of knowledge in the field at the beginning of that era was embodied in the classic 1960 textbook by Bird, Stewart and Lightfoot, which, after a lapse of 40 years, was brought up to date by the recent publication of a second, thoroughly revised edition[10], co-authored by these same authors, a very singular accomplishment given the time lapse. The seemingly classical status of this the subject would lead one to believe that no outstanding problems of a truly fundamental nature remain to be resolved in this field. Undoubtedly, much is yet to be accomplished in terms of actually solving the pertinent transport equations in the context of specific applications, an activity largely delegated nowadays to computers. Even in the realm of

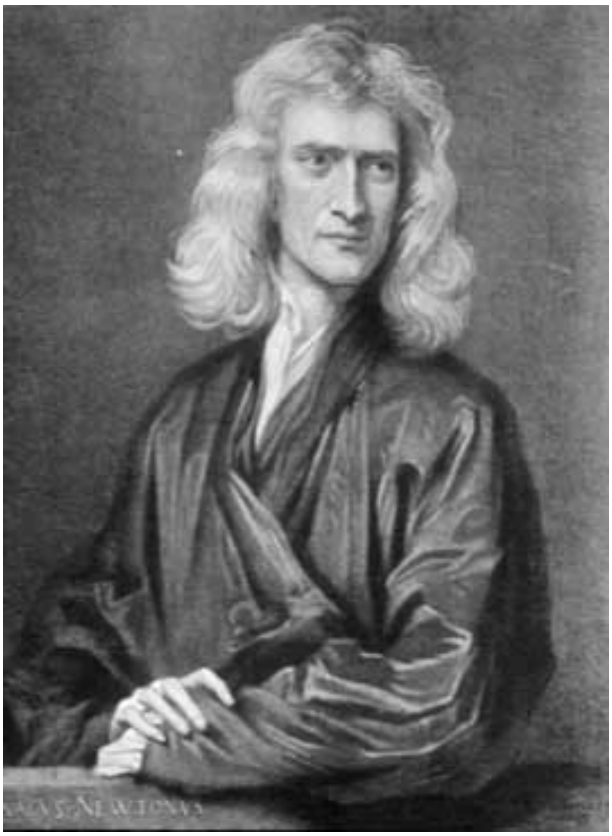
establishing the phenomenological coefficients entering into relevant constitutive equations, the action has largely moved from experiment towards purely statistical-mechanical computation of these parameters. The prevailing view is that, in terms of fundamentals, basic research in transport phenomena, at both the continuum and molecular levels, belongs to the ages. This lecture aims to negate this impression by identifying major problems in the field, as well as providing a prescription for their resolution.

Specifically, a recent publication[1] casts doubt upon the comfortable perspective of a field ossified by its own success. In particular, it appears to me, as well as to several others with whom I have shared my concerns, that a major flaw exists in the fundamental conceptions underlying transport phenomena, traceable back to the physical interpretation to be placed upon the velocity, $\mathbf{v}$, existing at a point of the fluid continuum. Given that this velocity serves to distinguish convective transport from diffusive transport, any problems connected with the proper identification of $\mathbf{v}$ automatically spill over from the continuum into the molecular realm. Even more generally, to the extent that a problem exists in the transport phenomena field, comparable issues necessarily obtain in the related fields of continuum and statistical mechanics, including such subfields as rheology and irreversible thermodynamics. The sole publication[1] claiming to undermine the foundations of transport processes is too new to have been widely studied, much less accepted by the engineering and scientific research communities. Nevertheless, irrespective of its present status, its arguments point up non-trivial questions of a fundamental nature. Explicitly, the currently unresolved issues facing the transport and fluid-mechanical communities are two-fold: (i) Is the proposed new theory correct; and (ii) if so, what are the limitations of its validity, given that it incorporates several idealizations? Irrespective of the answer(s) to these questions, the exercise of attempting to provide rational answers thereto is bound to be informative, certainly to its discussants, and hopefully to a wider audience as well.

On the assumption that the first question is answered in the affirmative, in the sense of recognizing the existence of a basic flaw in our present understanding of the continuum fluid velocity $\mathbf{v}$, these written notes — which are designed to supplement the main verbal lecture, which is more technical in scope — serve to identify what would appear to be the historical source of the misconception. The latter deals essentially with understanding the intellectual background that gave rise to the error in the first place, and which, subsequently, prevented recognition of the logical flaw during the past

Leonhard Euler

250 years following its introduction by Euler in 1755. At the same time, the lecture reinforces the general need for performing critical experiments in the transport phenomena field, or indeed in any field of research, an issue which in today's computer age would surely appear of little import to most young researchers (although obviously still relevant in areas explicitly recognized as a being in a state of flux). In any event, a quick study of the new theory would almost create the impression that such mid-course "corrections" to one's understanding of transport phenomena are important only in specialized circumstances, such as arise, for example, in connection with phoretic phenomena, e.g. thermophoresis or diffusiophoresis, where the pertinent Reynolds number is quite small owing largely to the relatively small sizes of the aerosol and hydrosol particles involved. However, given the current focus on small-scale technological processes, including nanotechnology, microfluidics, and cellular biological transport phenomena, entailing low Reynolds number flows resulting from the small particle and/or conduit sizes encountered, we believe that this newly-altered view of transport processes will ultimately result in novel applications to pertinent physical and biological phenomena. It is with these and related fields in mind that we formally address the following topic.



Isaac Newton

The primitive notion of the (vector) velocity of a material body, namely the directed distance traveled through space divided by the time required to traverse that distance, is one of the most important concepts in our arsenal of theoretical tools required for a quantitative description of physical phenomena. For example, in the case of rigid bodies moving through empty space, the temporal rate of change of this velocity, namely the body's acceleration, plays a fundamental role in determining the forces acting upon the body, and conversely. As such, a clear understanding of how velocity is to be measured experimentally is central to any dynamical description of the behavior of physical systems, rigid or otherwise. In the simplest case, involving the motion of a rigid body moving *in vacuo*, any potential ambiguities regarding the definition of its velocity were removed at the outset by Newton (actually by Euler), who began by initially focusing attention on the motion of a hypothetical mass point, an abstraction. Subsequently, rigid bodies of finite extent were addressed by regarding them as being composed of a finite collection of such idealized point masses, permanently joined together, with its members interacting through centrally-symmetric forces[13]. In such circumstances, and for strictly dynamical reasons arising from the fact that, in the case of point masses, momentum is simply mass times velocity, the velocity of choice for characterizing the motion of a rigid body came to be specified in terms of the movement of its center of mass, a point within the body at which its entire mass is regarded as effectively concentrated.

Thus began the intimate association of velocity with mass, a fraternization subsequently adopted by Euler[3], the "father"[4,5] of continuum fluid mechanics, when, in 1755, he derived the so-called continuity equation[6,7,10,11], a purely *kinematical* field relation, expressing the law of conservation of mass at a point within a fluid continuum in terms of the "velocity," $\mathbf{v}_m$, of the fluid's mass movement. Fluids are, however, deformable rather than rigid. As such, the physical identification of fluid velocity with the movement of mass, so central to rigid-body mechanics, loses its dynamical *raison de etre* in the case of fluids, retaining only a kinematical, purely mass-conservation, rationale for its appearance therein. Failure to appreciate this fundamentally altered role played by mass movement in fluids compared with its role in rigid-body dynamics, along with the failure to recognize that the fluid's Lagrangian or tracer velocity, $\mathbf{v}_l$, may differ from its Eulerian or mass-based velocity, $\mathbf{v}_m$, has led to a *dynamical* and *energetic* misinterpretation of fluid-mechanical phenomena[1]. Demonstration, by experiment, of a difference between $\mathbf{v}_m$ and $\mathbf{v}_l$ constitutes the focus of this lecture, with details provided elsewhere[1] of the impact of this finding upon the correct equations of fluid mechanics and derivative subjects. In the latter scheme, $\mathbf{v}_l$ rather than $\mathbf{v}_m$ is found to constitute the fundamentally correct continuum fluid velocity, not only in terms of the primitive notion of "motion," a purely *kinematical* conception, but also, more importantly, in terms of the fluid's specific momentum density, kinetic energy, and other attributes associated with the literal movement of corporeal bodies through space, representing *dynamical* and *energetic* notions.

In creating the subject of continuum fluid mechanics using rigid-body mechanics as a model, Euler[3,4] introduced the notion of mass *per unit volume*, namely the mass density *field*, $\rho \equiv \rho(\mathbf{x},t)$, at each point $\mathbf{x} \equiv (x,y,z)$ of the fluid continuum and at each instant of time t, an experimentally measurable fluid property. Additionally, he adapted to fluid continua the center-of-mass velocity concept associated with rigid bodies, by defining the fluid velocity field, $\mathbf{v} \equiv \mathbf{v}(\mathbf{x},t)$ (our $\mathbf{v}_m$), such that $\mathbf{v} := \mathbf{n}_m / \rho$, where the mass flux density (or current), $\mathbf{n}_m$, represents the experimentally measured

mass of fluid per unit time instantaneously crossing a space-fixed unit area centered at $\mathbf{x}$ at time t. (In fact, it would appear that $\mathbf{n}_m$ cannot actually be measured directly, although the truth of this statement does not impact upon the issues addressed here.) This definition of velocity, which involves experimentally monitoring the movement of mass at a point (and concomitantly measuring the fluid density at that point), appears, superficially, to be similar to, if not identical with, the Newtonian center-of-mass definition of the velocity of a moving body — the "material body"[4,5] in this case being the (differential) element of mass that one is tracking as it crosses the (differential) area centered at $\mathbf{x}$. This experimental protocol differs from the usual scheme for measuring the velocity of a material object, whereby one simply tracks the latter by monitoring its trajectory through space, *without regard to the mass of the object being tracked*. (Optically "tracking" the statistically-averaged movement of, say, a small group of photochromically-labeled or otherwise tagged molecules of the fluid does not qualify as being isomorphic with a tracer velocity measurement. Explicitly, a collection of molecules is not equipollent with a material tracer, the latter being be a single, rigid, corporeal entity.)

It is with Euler's mass-based definition of fluid velocity that we take issue. In particular, a differential mass element (explicitly a so-called differential *material fluid particle*) is neither isomorphic to nor equipollent with a corporeal tracer, in the sense that individual molecules, each possessing its own individual properties (namely mass and velocity), are free to enter and leave the mass element as the latter moves deterministically through space. As such, whereas the *total* amount of mass contained therein remains fixed during the material fluid particle's movement through space, this mass does not consist permanently of the same molecules (i.e., the same "matter"). Accordingly, despite the constancy of its total mass, this differential material "particle" differs fundamentally from the mass point of Newton's rigid-body mechanics. Moreover, in an energetic sense, a material fluid particle constitutes a molecularly "open" (rather than "closed") system as a result of the ability of individual molecules to freely cross its boundaries in either direction. As such, the First and Second laws of thermodynamics are not directly applicable to this system without modification[14].

Despite the fact that the mass-based definition of velocity, $\mathbf{v}_m$, differs from the primitive physical notion of velocity, as embodied in the fluid's tracer velocity, $\mathbf{v}_l$, Euler nevertheless implicitly assumed these two velocities to be one and the same entity (in, say, much the same spirit as Newton earlier hypothesized gravitational and inertial mass to be one and the same entity). To the best of the author's knowledge, this view has gone unchallenged for the past 250 years. Indeed, so pervasive is the universal acceptance of this equality that but a single symbol, typically $\mathbf{v}$, is employed to denote both velocities. Nevertheless, on the basis of both theory and experiment, this assumption was recently shown[1] to be invalid in circumstances where density gradients, $\nabla\rho$, exist within the fluid as a consequence of either composition gradients in multicomponent fluid mixtures undergoing mass transfer or temperature gradients in single-component fluids undergoing heat transfer — that is, in compressible, molecularly inhomogeneous gases and liquids.

Internally consistent, tripartite evidence exists[1] for the general velocity inequality, $\mathbf{v}_m \neq \mathbf{v}_l$, based separately and collectively upon quantitative arguments involving: (i) existing thermophoretic[2] and diffusiophoretic[15] experimental data; (ii) a revised version of the current continuum theory of mass, heat, and momentum transport in fluids[10,11], the revision thereto originating with the recognition that volume can be transported diffusively[12], independently of the movement of mass; and (iii) molecular theory results available in the literature, based upon the well-known Burnett non-continuum additions to the original Chapman-Enskog continuum solutions of the Boltzmann equation[9]. In support of the velocity inequality hypothesis we confine attention in this lecture exclusively to the experimental evidence furnished in connection with item (i).

Thermophoresis is a phenomenon whereby a small, unrestrained, essentially weightless and otherwise force-free particle suspended in a single-component isobaric fluid (usually a gas), within which a steady, essentially homogeneous, temperature gradient exists, is observed to move from regions of high to low temperature[16-19]. Equivalently, a tethered particle experiences a force[20] tending to move it towards the low temperature region. Thermophoretic forces exerted on aerosol particles were first recognized by Tyndall[21] in 1870 when he observed the presence of dust-free regions proximate to hot surfaces in a dust-filled room. A non-continuum "explanation" of the basic physics underlying thermophoretic phenomena, one still invoked today, was provided by Maxwell[22] in 1879 (and, independently, by Reynolds[23] in that same year) when he offered an analysis of the workings of Crookes' radiometer[24], the latter device first exhibited publicly in 1873. Maxwell's molecularly-based explanation invokes the hypothesis of a thin, non-continuum, Knudsen boundary layer (only later so-named) existing in the immediate neighborhood of a solid body bathed by a gas of non-uniform temperature.

(This Knudsen layer is assumed to exist even when the particle size-based Knudsen number is sufficiently small such as to expect purely continuum behavior.) This non-continuum behavior is presumed to result in tangential "slip" of the fluid "velocity" $\mathbf{v}$ (i.e., $\mathbf{v}_m$) along the surface of the non-isothermal body in a direction opposite to that of the surface temperature gradient, giving rise to thermal stresses of hydrodynamic origin exerted on the body, urging the latter towards regions of diminishing bulk fluid temperature.

Maxwell's "thermal stress," cum slip, explanation of the general phenomenon underlies all contemporary theories of thermophoresis in gases[25]. Elsewhere[1,2], however, we argue against this supposed non-continuum, Knudsen slip-layer explanation, suggesting instead an alternative, purely continuum, "no-slip" velocity condition imposed upon $\mathbf{v}_l$, accompanied by appropriate modifications of the basic equations of continuum fluid mechanics, wherein $\mathbf{v}_l$ replaces $\mathbf{v}_m$ in all instances involving the explicit dynamical notion of physical motion through space (as, for example, in the case of the fluid's momentum density or kinetic energy). On the other hand, the mass "velocity," $\mathbf{v}_m$, is retained in those circumstances where the issue is purely kinematical, for example when following the contents of a mass element (i.e., a material fluid particle) as it moves through space.

Irrespective of the correct theoretical explanation of the mechanism underlying thermophoretic motion, the existing correlation[16-18] of empirical experimental data remains viable, and, as such, will be seen to provide an objective test of Euler's $\mathbf{v}_m$ / $\mathbf{v}_l$ velocity equality hypothesis. The main attribute of these data impacting upon the issue of the fluid's velocity (namely the velocity of the undisturbed, particle-free, fluid) lies in the experimentally-observed effect of particle size on thermophoretic velocity in the case where the spherical particle is sufficiently large such as to exhibit no sensible Brownian movement, and yet is sufficiently small such that the temperature varies only imperceptibly over its surface. Experiments[16-18] performed under circumstances where the undisturbed fluid motion in the particle's absence is everywhere identically zero ($\mathbf{v}_m = \mathbf{0}$) reveal that the particle's thermophoretic velocity, $\mathbf{U}$, say, is independent of particle size in the continuum region, where the gas's mean-free path is small compared with the particle's radius (corresponding to an effectively zero Knudsen number, continuum phenomenon).

Explicitly, in the hypothetical (extrapolated) limit of "zero" particle size, a (non-Brownian) spherical thermophoretic particle immersed in the fluid continuum is observed to move with velocity[16-18]

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

where υ and k, are, respectively, the fluid's kinematic viscosity and thermal conductivity, and T is the absolute temperature of the gas; C_s, which is of $O(1)$, is Maxwell's (dimensionless) thermal stress slip coefficient, whose "best fit"[26] experimental value is about 1.2 (slightly larger than Maxwell's original molecular theory-based estimate of 3/4); k_s is the particle's thermal conductivity[27]. In this limit, *such a zero-size particle serves as a "tracer" of the undisturbed, particle-free fluid* movement through space (at least in circumstances where the particle's thermal conductivity is small compared with that of the gas, $k_s/k << 1$, corresponding to an effectively thermally insulated particle, the latter property rendering the tracer "inert"[1] with respect to its physicochemical interaction with the fluid). Explicitly, the tracer velocity, $\mathbf{v}_l$, of the undisturbed non-isothermal fluid is simply equal to $\mathbf{U}$. Inasmuch as $\mathbf{v}_m = \mathbf{0}$ and $\mathbf{v}_l = \mathbf{U} \neq \mathbf{0}$, it follows, *ipso facto*, that $\mathbf{v}_m \neq \mathbf{v}_l$. That the intrinsic source of the fluid "motion" $\mathbf{v}_l$ arises from a temperature gradient is irrelevant to the objective experimental measurement of the fluid's velocity. In fact, it is actually the density gradient rather than the temperature gradient that constitutes the animating force underlying such motion, as confirmed by comparable diffusiophoretic experiments[15], as well as by the general theory of phoretic phenomena[1].

Written in a more objective, observer-invariant form, the experimental tracer velocity, and hence the undisturbed fluid velocity, in the case of gases is thus found from eq. (1) to be

$$\mathbf{v}_l - \mathbf{v}_m = -C_s\upsilon\nabla\ln T\,, \qquad (2)$$

with $\mathbf{v}_l$ and $\mathbf{v}_m$ each measured relative to the same reference frame. By way of comparison with the experimental result (2), our theoretical expression[1,2] for this velocity disparity, valid for both gases and liquids, is

$$\mathbf{v}_l - \mathbf{v}_m = -\alpha\beta\nabla T\,, \qquad (3)$$

where $\alpha = k/\rho\hat{c}_p$ and $\beta = \hat{v}^{-1}(\partial\hat{v}/\partial T)_p$ are, respectively, the fluid's thermometric diffusivity and isobaric thermal expansivity, with $\hat{c}_p$ the specific-heat capacity at constant pressure and $\hat{v} = 1/\rho$ the specific

volume. In the case of ideal gases[8,10], $\beta = 1/T$ and $\alpha = (1/4)(9 - 5\gamma^{-1})\upsilon$, where $\gamma = \hat{c}_p / \hat{c}_v$ is the specific heat ratio (possessing the value 5/3 for monatomic gases and 7/5 for diatomic gases). Upon introducing these values into (3), the resulting expression is seen to agree, both constitutively and phenomenologically, with the experimentally-observed undisturbed fluid velocity result cited in (2). In addition to this accord for the gaseous case, the theoretical formula (3) also agrees satisfactorily[1,2] with the limited experimental thermophoretic particle data available for *liquids*[28].

Whereas traditional continuum transport equations[10] governing steady-state heat transfer indicate the particle-free fluid to be at rest, in the sense of the absence of mass motion ($\mathbf{v}_m = \mathbf{0}$), the fact remains that the undisturbed fluid is in motion ($\mathbf{v}_l \neq \mathbf{0}$), as physically evidenced by the movement of a passive tracer inserted into the fluid to monitor the latter's motion through space! How can it be that the fluid is both at rest and yet physically moving? The answer to the paradox lies in the fact while there is no mass motion of the fluid, there nevertheless exists a volumetric fluid motion driven by the fluid's thermal expansivity β acting in concert with the mass density gradient (engendered by the temperature gradient). However, since $\mathbf{v}_m = \mathbf{0}$, this volumetric motion is entirely non-convective, being purely diffusive in nature. Moreover, in the general case, without restriction to purely phoretic-type undisturbed fluid motions, the fluid's Lagrangian velocity, $\mathbf{v}_l$, is identical[1] to its volume velocity, $\mathbf{v}_v$, the latter representing the flux density of volume (volume per unit time per unit area crossing a space-fixed surface), with the diffusive flux density of volume, $\mathbf{j}_v$, defined generically by the expression[1] $\mathbf{j}_v = \mathbf{v}_v - \mathbf{v}_m$. In the single-component heat transfer case, the constitutive equation for this volume current is[1,12] $\mathbf{j}_v = \alpha \nabla \ln \rho$. In the case of steady-state heat transfer through a confined single-component fluid the preceding expression leads eventually[1,2] to the velocity disparity quantified by eq. (3). With an appropriate transposition of symbols, a comparable theoretical result also applies to the case of binary convective-diffusive mass transfer phenomena occurring in isothermal, isobaric fluid mixtures (the latter obeying the "law" of additive volumes), the resulting expression being in accord with experimental diffusiophoretic particle data[15].

The initial strangeness of the notion of a purely diffusive, non-convective mechanism for volume transport represents a failure of one's intuition, arising from a psychological predisposition to associate volume with mass through the intermediary of the fluid's density ρ, especially in the case of liquids. However, like energy, momentum, or entropy, volume is not a material property that can, itself, be directly visualized. Rather, volume is abstract rather than corporeal, and therein lies the difficulty of conceptualizing its movement through space.

From a transport point of view, individual molecules carry with them such extensive properties as mass, momentum, and (kinetic) energy, as they move about through space. But they do not themselves, as individual entities, convey more abstract extensive properties, such as volume (and, say, entropy), since such extensive properties are *collective* in nature, rather than being associated with individual molecules. Addressing this distinction, by extending existing molecular theories[8,9] so as to explicitly recognize and hence take account of the diffusive transport of volume, is clearly prerequisite to any comprehensive continuum theory of transport processes that purports to derive rationally from subcontinuum models of the phenomenon.

The pragmatic consequences of our remarks will likely be of interest only to practicing fluid mechanicians and molecular theorists. However, since fluid mechanics often constitutes the first example[6,7] of a non-trivial field theory[4,5] (i.e., a *continuum* theory) to which applied scientists and engineers are exposed as neophytes, the issues raised herein provide a classic textbook example of the more generic philosophical need for such novitiates to appreciate the intimate relation existing between theory and experiment. Explicitly, how is a given physical entity (appearing in a mathematical description of the phenomenon to which the student is being exposed) to be measured experimentally. This lesson is especially needed in the computer age, where, for example, molecular dynamic simulations are often regarded as being isomorphic with the performance of actual physical experiments. That view notwithstanding, in order for the consequences of such theoretical computations to be physically interpreted, the statistical predictions emanating therefrom need to be expressed in terms of their macroscale experimental counterparts. And if such equivalences are subject to possible ambiguities, such as those resulting from an incomplete appreciation of the experimental protocol underlying their definitions, fundamental physical misconceptions can result. Such a misinterpretation has arisen (at least in our view), for example, during attempts to understand the role of literal, molecular-level "boundary conditions" prevailing at solid surfaces, in whose neighborhood the macroscale continuum physics — described by the very equations to which such boundary conditions are meant to apply — is not itself applicable owing to obvious inadequacies in such macrosocale models of the

phenomenon at molecular distances from the surface[29]. Apart from its fluid-mechanical implications, this lecture aims to emphasize, to a broader audience, the general importance of experiments in the theoretical sciences.

In this context of the preceding remarks, it is informative to recite an anecdotal story related by the late, pioneering rheologist, Karl Weissenberg (1893-1976) to a continuum-mechanical audience assembled at Carnegie-Mellon University in the early 1970's, which lecture I had the good fortune to attend. Prefacing his remarks (on Osborne Reynolds theory of dilatation in sand-water mixtures, during which he demonstrated a wonderfully simple illustrative experiment), Weissenberg noted that just prior to World War I he had served as a young applied mathematician at the Kaiser Wilhelm Institute of Physics in Germany, which Einstein visited periodically as part of the his "administrative" responsibilities as Director. On one of these visits, Weissenberg collared Einstein, telling him how much he admired his work, and seeking the latter's advice and counsel regarding an appropriate course of self-study that would permit his metamorphosis from applied mathematician to theoretical physicist. Without a moment's hesitation, Einstein suggested that his questioner learn how to design scientific instruments. Not understanding this response, Weissenberg posited that perhaps Einstein had misunderstood his original query, since his wish was to become a *theoretical* physicist, not an *experimental* one. Einstein assured him that he had not misunderstood the original question, and went on to elaborate that the only mechanism by which one could truly and deeply understand the fundamental meaning of a physical entity appearing in the guise of a mathematical symbol in a theoretical equation was by going through the mental exercise of systematically and methodically identifying the sequence of steps prerequisite to an unambiguous experimental determination of that entity. (Presumably underlying Einstein's response was the decisive role played in his 1905 special theory of relativity by his *gedanken* experiment involving the measurement of time, as well as by his then current efforts to understand the theoretical implications of the seemingly empirical equality of inertial and gravitational mass, an unequivocal experimental fact established earlier by Eötvös[30] in 1889.)

In any event, the fact that the relationship between the experimental measurement of fluid velocity and the symbol **v** appearing in fluid-mechanical equations, posited by Euler some two-and-a-half centuries ago, has, until now, never been properly subjected to rational inquiry and subsequent critical experimental test (most simply, in *compressible* fluids at rest), points up the sagacity of Einstein's advice. This object lesson is particularly striking when viewed in the context of the large number of students and professionals, scientists and engineers, prominent and otherwise (including, of course, myself at an earlier, more naive stage of life), who, despite their often extensive exposure to fluid mechanics, failed to question Euler's implicit assumption positing equality of the fluid's Eulerian and Lagrangian velocities.

In summary, the work briefly reported upon here, if, independently substantiated by others, negates the foundations of 250 years of fluid mechanics, as well as derivative subjects, including continuum mechanics, transport processes, molecular theories of gases and liquids, irreversible thermodynamics, and rheology.

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