

Is the tracer velocity of a fluid continuum equal to its mass velocity?

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Owing to its size independence in the so-called near-continuum vanishingly small Knudsen number regime ($\text{Kn} \ll 1$), thermophoretic particle motion occurring in an otherwise quiescent gas under the influence of a temperature gradient is here interpreted as representing the motion of a tracer, namely, an effectively point-size test particle monitoring the local velocity of the undisturbed, particle-free, compressible gas continuum through space. “Compressibility” refers here not to the usual effect of pressure on the gas’s mass density ρ but rather to the effect thereon of temperature. Our unorthodox continuum interpretation of thermophoresis differs from the usual one, which regards the existence of thermophoretic forces in gases as a strictly *noncontinuum* phenomenon, involving thermal stress-induced Maxwell slip (“thermal creep”) of the gas’s mass velocity \mathbf{v}_m at the surface of the particle, with \mathbf{v}_m denoting the velocity appearing in the continuity equation expressing the law of conservation of mass. Explicitly, instead of regarding the thermally animated particle as moving *through* the gas, we regard the particle (in its hypothesized role as a tracer of the undisturbed, particle-free, fluid motion) as moving *with* the gas, through space; that is, the particle is viewed as simply being entrained in the flowing gas, which, as a result of an externally applied temperature gradient, was already in motion prior to the tracer’s introduction into the fluid—albeit not mass motion (which is, in fact, identically zero) but rather volume motion. This tracer-particle interpretation of experimental thermophoretic particle velocity measurements raises fundamental issues in regard to the universally accepted Newtonian rheological law constitutively specifying the viscous or deviatoric stress \mathbf{T} as being proportional to the (symmetrized, traceless) fluid velocity gradient $\nabla \mathbf{v}$, with \mathbf{v} identified as being the fluid’s mass velocity \mathbf{v}_m . Rather, it is argued in the case of compressible fluids, including liquids, that \mathbf{v} should, instead, be chosen as the fluid’s volume flux density or current density \mathbf{n}_v , the latter being formally equivalent to the fluid’s volume velocity \mathbf{v}_v , which differs from \mathbf{v}_m except in the case of incompressible fluids. Apart from this strictly constitutive issue in regard to \mathbf{T} , it is further argued that the fluid’s tracer or Lagrangian velocity $\mathbf{v}_l := (\partial \mathbf{x} / \partial t)_{\mathbf{x}_0}$ along the fluid’s spatiotemporal trajectory $\mathbf{x} = \mathbf{x}(\mathbf{x}_0, t)$ is equal to \mathbf{v}_v , rather than to \mathbf{v}_m . This too is contrary to the heretofore unquestioned supposition that the conceptually distinct fluid velocities \mathbf{v}_l and \mathbf{v}_m are not only equal but are, in fact, synonymous. To the extent that $\mathbf{v}_l \neq \mathbf{v}_m$ in the nonisothermal fluid case, an optical dye- or photochromic-type experiment (each of the latter two experiments presumably serving to measure \mathbf{v}_m) will record a different velocity than would a comparable tracer particle velocity measurement, one that measures \mathbf{v}_l .

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I. INTRODUCTION

This paper offers, *inter alia*, an unconventional, purely continuum interpretation of existing thermophoretic particle velocity data [1] for gases in the so-called near-continuum small Knudsen number regime [2]. Moreover, during the course of the analysis, basic hydrodynamic relations are developed for more general situations in which temperature gradients exist within a fluid, the latter including liquids. The applicability of these formulas and notions transcends the particular thermophoresis focus of the present paper.

Epstein’s [3] widely accepted explanation of thermophoresis in this regime invokes Maxwell’s [4] ubiquitous thermal creep boundary condition, involving temperature-gradient-induced slip of the mass velocity \mathbf{v}_m along the particle surface, in conjunction with use of the classical Navier-Stokes (creeping flow) equation governing \mathbf{v}_m for the incompressible fluid case, $\nabla \cdot \mathbf{v}_m = 0$. In contrast, our alternative, strictly continuum, explanation of the phenomenon of thermophoresis retains the classical no-slip condition, albeit

imposed upon the volume velocity \mathbf{v}_v [5,6] rather than upon \mathbf{v}_m , while concurrently introducing a corresponding \mathbf{v}_v -based modification of Newton’s original \mathbf{v}_m -based rheological law entering into the formulation of the Navier-Stokes (NS) equation [7]. Moreover, our analysis of thermophoretic motion is believed to be applicable not only to gases but also to liquids, although the limited amount and quality of the liquid-phase data currently available in support of this thesis are considerably less authoritative than in the gaseous case.

We propose a fundamental modification of Newton’s viscosity law, wherein the velocity \mathbf{v} appearing in the constitutive expression

$$\mathbf{T} = 2\mu \overline{\nabla \mathbf{v}} + \kappa \mathbf{I} \nabla \cdot \mathbf{v} \quad (1)$$

for the deviatoric stress \mathbf{T} is here assumed to be given by the fluid’s volume velocity [5],

$$\mathbf{v} = \mathbf{v}_v, \quad (2)$$

rather than by its usual mass velocity,

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$$\mathbf{v} = \mathbf{v}_m. \quad (3)$$

The symbol \mathbf{v}_m refers to the velocity appearing in the continuity equation $\partial\rho/\partial t + \nabla \cdot (\rho\mathbf{v}_m) = 0$, or, which is equivalent,

$$-D_m \ln \rho / Dt = \nabla \cdot \mathbf{v}_m, \quad (4)$$

with $D_m/Dt := \partial/\partial t + \mathbf{v}_m \cdot \nabla$ the so-called material derivative. In Eq. (1) μ is the shear viscosity, κ the bulk viscosity, and \mathbf{I} the unit dyadic. The overbar appearing in the expression for \mathbf{T} in Eq. (1) denotes the symmetric and traceless portion of the dyadic which it surmounts; that is, $\bar{\mathbf{D}} := \frac{1}{2}(\mathbf{D} + \mathbf{D}^T) - \frac{1}{3}\mathbf{I}(\mathbf{I}:\mathbf{D})$ for any dyadic \mathbf{D} .

Why should one question the validity of Newton's \mathbf{v}_m -based viscosity law $\mathbf{T} = 2\mu\bar{\nabla}\mathbf{v}_m + \kappa\mathbf{I}\nabla \cdot \mathbf{v}_m$? Objective experimental evidence existing in the literature in support of this constitutive relation is based primarily upon the *incompressible*, isothermal fluid case, where ρ is uniform throughout the fluid (while also supposing the usual \mathbf{v}_m -based no-slip boundary condition to be applicable at solid surfaces). In contrast, the present paper addresses key evidence regarding these issues for the case of "compressible" fluids, where ρ is no longer constant throughout the gas owing to temperature variations therein. Explicitly, in what follows we critically examine single component (essentially isobaric) gas flow data associated with thermophoretic particle motion in nonisothermal gases subjected to externally imposed homogeneous temperature gradients, where the gas density $\rho = \rho(T)$, rather than being uniform throughout the fluid, varies locally with temperature T . At the same time as we question Newton's viscosity law, we also inquire as to why an exception should be made, as has been done by Epstein [3] in his explanation of thermophoresis, to the usual \mathbf{v}_m -based no-slip boundary condition in circumstances where the conventional incompressible *continuum* NS equations are nevertheless used to describe the fluid motion.

The usual assumption of a no-slip tangential velocity boundary condition at a solid surface requires that

$$\mathbf{I}_s \cdot \mathbf{v} = \mathbf{0} \quad \text{on solid surfaces,} \quad (5)$$

where the dyadic $\mathbf{I}_s := \mathbf{I} - \mathbf{nn}$ is the surface projection operator, in which \mathbf{n} is the unit outer normal vector on the solid surface. For the time being we leave upon the question of whether the velocity \mathbf{v} appearing in Eqs. (1) and (5) is given by \mathbf{v}_m or \mathbf{v}_v , with the correct physical choice eventually to be decided on the basis of comparing the respective theoretical calculations based thereon of the particle's thermophoretic velocity \mathbf{U} with experimental data for each of the two cases. Complete specification of the vector velocity boundary condition at a solid surface necessitates further imposing the usual mass velocity requirement that the solid be impenetrable to mass flow:

$$\mathbf{n} \cdot \mathbf{v}_m = 0 \quad \text{on solid surfaces,} \quad (6)$$

wherein no doubt exists as to which velocity is to be used in the latter expression.

A. "Incompressible" creeping flow

As is demonstrated *a posteriori*, consistent with Epstein's [3] small Reynolds number analysis of thermophoresis, fluid motion engendered by thermophoretic particle movement at small Knudsen numbers is henceforth assumed to be governed to a satisfactory degree of approximation by the quasistatic creeping flow and "incompressible" continuity equations

$$\mathbf{0} = -\nabla p + \nabla \cdot \mathbf{T} \quad (7)$$

and

$$\nabla \cdot \mathbf{v} = 0, \quad (8)$$

again with the choice, Eq. (2) or Eq. (3), of the velocity \mathbf{v} remaining open [8]. Introduction of Eq. (1) into Eq. (7) followed by use of Eq. (8) yields

$$\nabla p = \mu \nabla^2 \mathbf{v}, \quad (9)$$

in which we have regarded μ as being essentially constant throughout the fluid.

B. Energy equation

In the present single-component gaseous or liquid-phase heat transfer case being analyzed, we suppose that the fluid's equation of state is such that $\hat{v} = \hat{v}(T)$, with $\hat{v} = 1/\rho$ the specific volume of the fluid. By thereby ignoring pressure effects upon fluid density it is thus implicitly assumed in the thermophoretic problem subsequently addressed either that the heat transfer process occurs essentially isobarically, or else that pressure gradient effects upon the density gradient $\nabla\rho$ are small compared with comparable temperature gradient effects. [We do not, however, ignore pressure gradient effects in the creeping flow equation (9).] It is further assumed that the "thermal law of adiabatically additive volumes" [5,9] applies to the fluid in question, corresponding to the approximation that $d\hat{v}/dT = \text{const} = C$, say, independently of T (and, of course, p) or, equivalently, of ρ , at least over small ranges of temperature. The fluid's specific heat capacity \hat{c}_p is also assumed to be a temperature-independent constant.

An internal energy balance leads to the usual transport equation [10] governing the temperature field,

$$\rho\hat{c}_p D_m T / Dt = \nabla \cdot (k \nabla T), \quad (10)$$

in which viscous dissipation (and pressure) effects have been neglected (cf. [10, p. 589]), assumptions which will be justified *a posteriori* in the case of thermophoretic phenomena. Here, k is the fluid's thermal conductivity, which will ultimately be taken to be a constant, independent of T . Use of our assumed additive-volume law, namely, $d\hat{v} = C dT$, leads to the elementary identity $D_m T / Dt = C^{-1} D_m \hat{v} / Dt$. The latter, in conjunction with the fact that $\hat{v} = 1/\rho$, enables Eq. (10) to be rewritten as $-\hat{c}_p C^{-1} D_m \ln \rho / Dt = \nabla \cdot (k \nabla T)$. Comparison of the preceding expression with Eq. (4) thus yields the following "quasi-incompressibility" relation [5,9]:

$$\nabla \cdot \mathbf{v}_v = 0, \quad (11)$$

in which the symbol \mathbf{v}_v is here defined as [11]

$$\mathbf{v}_v := \mathbf{v}_m - (kC/\hat{c}_p) \nabla T. \quad (12)$$

The latter pair of equations effectively accord with those of Pukhnachov [12].

That the right-hand side (RHS) of Eq. (12) does indeed constitutively qualify in present circumstances as being the fluid's volume velocity is shown elsewhere [5]. However, for present purposes the explicit physical interpretation to be assigned to the symbol \mathbf{v}_v , here defined by Eq. (12) and satisfying (11), is functionally irrelevant in terms of what follows [13,14]. The only relevant issue in relation to use of this symbol in the subsequent analysis pertains to the fact that we propose to demonstrate the physical correctness of the choice of Eq. (2) over Eq. (3) by utilizing available experimental thermophoresis data, with the unadorned symbol \mathbf{v} being that appearing in Eqs. (1) and (5). This scheme entails solving the coupled continuity, momentum, and energy equations for the quartet of fields $(\mathbf{v}_m, p, \rho, T)$, using the hypothesis for \mathbf{v} embodied in the union $(2) \oplus (12)$.

II. THERMOPHORETIC PARTICLE MOTION

The above trio of coupled mass, momentum, and energy transport equations is readily solved [15] so as to eventually obtain the thermophoretic velocity \mathbf{U} through space of a force- and torque-free (non-Brownian) spherical particle in an effectively unbounded fluid under the influence of a steady, externally imposed, temperature gradient, ∇T_0 , say. Explicitly, consider a sphere of radius a immersed in a viscous fluid (gas or liquid) confined between a pair of parallel, impermeable, heat-conducting, hot and cold walls permanently maintained at the respective temperatures T_h and T_c . The hot and cold walls, respectively, situated at $x=0$ and $x=L$, extend to infinity in the y and z directions, so that the externally imposed temperature gradient is $\nabla T_0 := -\hat{\mathbf{x}}(T_h - T_c)/L$, with $\hat{\mathbf{x}}$ a unit vector in the positive x direction. (The minus sign appearing in the latter expression reflects the definition of the gradient operator ∇ , wherein the gradient points in the direction in which the scalar field upon which it operates increases.) Gravity is supposed absent or negligible in what follows. In circumstances where the sphere is situated far from either wall and satisfies the inequality $a/L \ll 1$, we seek to calculate the force (and torque), if any, required to maintain the sphere fixed in place relative to the walls. Such knowledge ultimately permits calculation of the sphere's thermophoretic velocity \mathbf{U} .

A. Boundary conditions

For simplicity, attention is subsequently confined to the case where the sphere is effectively non-heat-conducting compared with the fluid's thermal conductivity. As such, the thermal boundary condition on the sphere surface, say ∂V_s , necessitates that

$$\mathbf{n} \cdot \nabla T = 0 \quad \text{on } \partial V_s. \quad (13)$$

Additionally, it is required that $T=(T_h, T_c)$ at $x=(0, L)$ for $\forall (y, z)$.

The impenetrability of the sphere and walls to mass requires that Eq. (6) be satisfied on these surfaces. Furthermore, the no-slip tangential velocity boundary condition on the sphere and wall surfaces necessitates that Eq. (5) be satisfied thereon. The presence in our modified NS theory of *two* velocities, namely, \mathbf{v}_m and \mathbf{v}_v , rather than a single fluid velocity as in traditional NS problems, raises the question of which of these two velocities is to be selected to satisfy this no-slip condition.

B. Thermophoretic velocity

To calculate the velocity \mathbf{U} of the sphere for each of the two choices of \mathbf{v} , namely, Eqs. (3) and (2), we first solve the above system of steady-state equations and boundary conditions for the fields $(\mathbf{v}_m, \mathbf{v}_v, \rho, T, p)$ for the stationary sphere case $\mathbf{U}=\mathbf{0}$. Knowledge of the fields (\mathbf{v}, p) , with $\mathbf{v}=\mathbf{v}_m$ or \mathbf{v}_v , enables the Cauchy stress tensor $\mathbf{P}=-\mathbf{I}p+\mathbf{T}$ to be calculated for each of these two cases and ultimately, therefrom, the respective forces $\mathbf{F}=\oint_{\partial V_s} dS \mathbf{n} \cdot \mathbf{P}$ [and torques $\mathbf{L}_o=\oint_{\partial V_s} (\mathbf{x} - \mathbf{x}_o) \times dS \mathbf{n} \cdot \mathbf{P}$, about the sphere center "o"], if any, exerted by the fluid on the sphere. In turn, this knowledge of \mathbf{F} and \mathbf{L}_o for the stationary sphere case permits calculation of the quasi-steady velocity \mathbf{U} with which a force- and torque-free sphere will move through space (i.e., relative to the space-fixed walls). This calculation is performed below for each of the two choices of \mathbf{v} .

1. The case $\mathbf{v}=\mathbf{v}_m$

This choice leads straightforwardly to the trivial conclusion that $\mathbf{v}_m=\mathbf{0}$ ($\forall \mathbf{x}$) and, furthermore, that $p=\text{const}=p_0$, say (whence $\mathbf{P}=-\mathbf{I}p_0=\text{const}$). As such, the basic trio of transport equations degenerates to the problem of steady-state heat conduction throughout the static fluid domain external to the sphere. From Eq. (10) the temperature field for this case satisfies Laplace's equation $\nabla^2 T=0$ (with k assumed constant throughout the fluid). It is obviously unnecessary to solve explicitly for either the temperature field $T(\mathbf{x})$ [with $\mathbf{x}=(x, y, z)$] or for the concomitant density field $\rho(\mathbf{x})$ in order to arrive at the conclusion that no force or torque acts on the sphere, and hence that $\mathbf{U}=\mathbf{0}$ for this case. Accordingly, the conventional $(\mathbf{v}=\mathbf{v}_m)$ -based incompressible continuity and creeping flow equations, Eqs. (8) and (9), satisfying the usual no-slip mass velocity boundary condition $\mathbf{I}_s \cdot \mathbf{v}_m=\mathbf{0}$ on the sphere surface ∂V_s , fails to predict the existence of thermophoretic particle movement—a result which clearly holds irrespective of the shape of the particle (or even of its thermal conductivity, say k_s , were one to consider the conducting particle case). It was this failure of the traditional $(\mathbf{v}=\mathbf{v}_m)$ -based equation set to predict the experimentally observed thermophoretic movement of particles suspended in gases that led Epstein [3], later followed by others (see the detailed review in Ref. [15]) [16–18], to seek a noncontinuum Maxwell \mathbf{v}_m -slip-based explanation of thermophoresis.

We note here for later reference that whereas $\mathbf{v}_m=\mathbf{0}$ throughout the fluid in present circumstances, there does, nevertheless, exist a nonzero volume velocity field $\mathbf{v}_v(\mathbf{x})$

TABLE I. C'_s values for various monatomic, diatomic, and polyatomic gases at 0 °C and 1 atm pressure.

Monatomic and diatomic gases									
Gas	Ne	Ar	H ₂	N ₂	O ₂	Air	CO	NO	Cl ₂
C'_s	1.50	1.50	1.43	1.37	1.35	1.37	1.32	1.30	1.32
Polyatomic gases									
Gas	H ₂ O		CO ₂	SO ₂	NH ₃	C ₂ H ₄	C ₂ H ₆	CHCl ₃	CCl ₄
	100 °C	400 °C							
C'_s	1.06	1.11	1.28	1.16	1.18	1.25	1.30	1.28	1.23

$\neq \mathbf{0}$ for this $\mathbf{v}=\mathbf{v}_m$ case. This volume velocity may be derived from Eq. (12) in conjunction with the detailed temperature field $T(\mathbf{x})$. Obviously, far from the sphere, \mathbf{v}_v is given by the expression

$$\mathbf{v}_v^{(0)} = - (kC/\hat{c}_p) \nabla T_0 = \text{const} \quad (|\mathbf{x}|/a \rightarrow \infty). \quad (14)$$

This far-field solution also represents the \mathbf{v}_m -based volume velocity field existing throughout the undisturbed, sphere-free fluid confined between the hot and cold walls.

2. The case $\mathbf{v}=\mathbf{v}_v$

With this alternative choice of \mathbf{v} , the transport equations and boundary conditions governing \mathbf{v} , outlined earlier, will be seen to lead to nontrivial physical results, wherein $\mathbf{U} \neq \mathbf{0}$. Among other things, in contrast with the findings for the preceding $\mathbf{v}=\mathbf{v}_m$ case, the no-slip condition $\mathbf{I}_s \cdot \mathbf{v}_v = \mathbf{0}$ on ∂V_s imposed upon the volume velocity \mathbf{v}_v in the present case leads to a situation where, as a consequence of Eq. (12), there is now a slip $\mathbf{I}_s \cdot \mathbf{v}_m = (kC/\hat{c}_p) \nabla_s T$ of the fluid's mass velocity \mathbf{v}_m along the sphere surface ∂V_s . As such, a no-slip condition imposed upon \mathbf{v}_v translates into a slip condition imposed upon \mathbf{v}_m . (Here, $\nabla_s \equiv \mathbf{I}_s \cdot \nabla$ is the surface gradient operator.) In turn, this surface mass motion induces a bulk mass flow $\mathbf{v}_m \neq \mathbf{0}$ throughout the entire fluid [although far from the sphere this mass motion will be sensibly zero, whence the distant volume velocity field for the present $\mathbf{v}=\mathbf{v}_v$ case continues to be given by Eq. (14), in both the presence and absence of the sphere].

The mathematical details underlying the calculation of \mathbf{U} in the present circumstances are set forth in the Appendix, where it is shown that the sphere's thermophoretic velocity can be calculated trivially via the judicious use of Faxen's laws [19], without the need to literally solve the requisite coupled-equation boundary-value problem. This calculation leads easily to the following expression for the thermophoretic velocity of the nonconducting sphere:

$$\mathbf{U} = -\alpha\beta \nabla T_0, \quad (15)$$

in which $\alpha = k/\rho\hat{c}_p$ and $\beta = (\partial \ln \hat{v} / \partial T)_p \equiv -\rho^{-1}(\partial \rho / \partial T)_p$ are, respectively, the fluid's thermometric diffusivity and thermal expansivity. We note that the product $\alpha\beta \equiv kC/\hat{c}_p$ appearing in Eq. (15) is a temperature-independent constant, since each

of the three thermal transport and equilibrium properties appearing on the right-hand side of this product have, individually, been supposed constant. According to its derivation, Eq. (15) is equally applicable to both gases and liquids. Since $\beta > 0$ for virtually all fluids over the entire range of temperatures encountered in practice, the particle will generally move in a direction opposite to that of the temperature gradient, namely, in the positive x direction, from hot to cold. Among other things, it is interesting to note that the velocity \mathbf{U} given by Eq. (15) is independent of the sphere's size. As such, all other things being equal, and to the extent that our theory proves to be correct, a boulder-sized body will move at exactly the same velocity as would an effectively point-sized (albeit non-Brownian) body.

III. COMPARISON OF EQ. (15) WITH EXPERIMENTAL DATA

A. Gases

By definition, $\alpha = \text{Pr}^{-1} \nu$ where $\text{Pr} = \hat{c}_p \mu / k$ is the fluid's Prandtl number [10] and $\nu = \mu / \rho$ is its kinematic viscosity. Inasmuch as $\beta = 1/T$ for ideal gases, one can write Eq. (15) for such gases in the form

$$\mathbf{U} = -C'_s \nu \nabla \ln T, \quad (16)$$

where the numerical constant $C'_s = 1/\text{Pr}$ is an $O(1)$ dimensionless phenomenological coefficient, dependent only upon the physicochemical properties of the gas. The temperature T appearing in Eq. (16) is to be interpreted as that existing in the particle-free fluid in the neighborhood of the region currently occupied by the (center of) the sphere.

According to Eucken's approximation [10] of the Prandtl number (generally valid for nonpolar gases), one has that $\text{Pr} = 4/(9 - 5\gamma^{-1})$, in which $\gamma = \hat{c}_p/\hat{c}_v$ is the gas's specific heat ratio. As γ values for monatomic and diatomic ideal gases are, respectively, $\gamma \approx 5/3$ and $7/5$, it follows, at least approximately, that $C'_s = 1.5$ for monatomic gases and 1.36 for diatomic gases. More accurately, actual experimental Prandtl number data [10, p. 277] furnish the results shown in Table I for various monatomic, diatomic, and polyatomic gases.

Experimentally [16–18], in the case of gases, the thermophoretic velocity \mathbf{U} of nonconducting non-Brownian spheri-

cal particles is given for small Knudsen numbers $\text{Kn}=\lambda/a \ll 1$ (λ is the mean free path), corresponding to the so-called near-continuum, $O(\text{Kn})$, Hilbert-Chapman-Enskog [2] regime, by the following expression:

$$\mathbf{U} = -C_s v \nabla \ln T. \quad (17)$$

This relation was originally derived theoretically by Epstein [3] (with $C_s=3/4$ in the case of monatomic Maxwell molecules [2,20]). Its constitutive form was subsequently confirmed experimentally by numerous researchers [16–18], albeit with the phenomenological coefficient C_s appearing therein regarded from an experimental perspective as being an adjustable parameter. Equation (17) is obviously identical in constitutive format to our purely theoretical equation (16) for gases in which, however, in place of our constant $O(1)$ coefficient C'_s , there now appears the so-called Maxwell thermal-creep slip coefficient C_s [4].

Epstein's [3] theoretical derivation of Eq. (17) is based upon Maxwell's [4] gas-kinetic theory analysis of noncontinuum thermal stresses existing in proximity to a solid body along whose surface the proximate gas temperature varies. In turn, these thermal stresses were viewed by Maxwell as causing slip of the gas's mass velocity along that surface, as embodied in his widely cited formula

$$\mathbf{I}_s \cdot \mathbf{v}_m = C_s v \nabla_s \ln T \quad (18)$$

for the relative tangential-slip mass velocity \mathbf{v}_m between the gas and the surface of the particle. In contemporary terms, Maxwell's thermal stresses are regarded as deriving from the noncontinuum, $O(\text{Kn}^2)$, so-called Burnett terms appearing in the Chapman-Enskog [2] small Knudsen number perturbation expansion of the Boltzmann equation for monatomic ideal gases. In gas-kinetic theory [2] deriving from the Boltzmann equation, the NS and Fourier equations are, respectively, regarded as quantifying "near-continuum," $O(\text{Kn})$, linear momentum and internal energy transport phenomena, with the $O(\text{Kn}^0) \equiv O(1)$ "continuum" terms appearing in the perturbation expansion identified with the Euler equations characterizing the mechanics of ideal fluids [21].

Following Maxwell's introduction [4] of his thermal-creep formula Eq. (18) (albeit originally in a different physical context involving the phenomenon of thermal transpiration [22]), and its subsequent adoption by Epstein [3] in rationalizing thermophoresis (strictly, rationalizing the workings of Crookes' radiometer [23]), the nature and magnitude of the slip coefficient C_s has attracted the attention of a number of theoreticians and experimentalists. Theoretical values of C_s have ranged from Maxwell's [4] original, molecularly derived, value of $3/4$ for monatomic Maxwellian molecules to Derjaguin *et al.*'s [18] irreversible thermodynamically derived value of $C_s=3/2$. These compare with Talbot *et al.*'s [17] "best-fit" average experimental value of 1.17 for a variety of different gases. [The fact that Talbot *et al.* [17] and other experimentalists recommend but a *single* C_s coefficient (approx. 1.17) for *all* gases is at odds with our theoretical predictions, according to which this coefficient should vary to some extent with the degree of polyatomicity of the par-

ticular gas (as evidenced by the data in Table I as well as by the Eucken approximation thereof).]

Our theoretical formula (16) (in conjunction with the data for C'_s in Table I) for gaseous continua obviously accords extremely well, both constitutively and phenomenologically, with its "best-fit" experimental data correlation counterpart Eq. (17), the latter valid for the near-continuum, $\text{Kn} \ll 1$ regime. However, our formula Eq. (16) is based upon strictly *continuum* equations and no-slip arguments, albeit nontraditionally supposing the velocity \mathbf{v} appearing in Eqs. (1) and (5) to be given by $\mathbf{v}=\mathbf{v}_v$, whereas Epstein's alternative theoretical formula Eq. (17) derives from *noncontinuum* \mathbf{v}_m -based Maxwell slip arguments [4].

B. Liquids

Reference [15], which extends Eq. (15) to the case of heat-conducting particles, compares the resulting velocity \mathbf{U} with the experimental liquid-phase thermophoretic data of McNab and Meisen [24]. Without repeating what is stated in greater detail in Ref. [15], suffice it to say here that Eq. (15) accords satisfactorily with McNab and Meisen's data. Clearly, liquids are incapable of displaying noncontinuum behavior with respect to rationalizing the thermophoretic movement of macroscopic (non-Brownian) particles. As such, there does not appear to be any rational basis for supposing slip of the velocity \mathbf{v} to occur at a liquid-solid interface, certainly not as a result thereof of the presence of a surface temperature gradient. In any event, in contrast with our Eq. (15), Epstein's formula (17), being applicable on the basis of its derivation only for gases, fails to offer any theoretical explanation for the thermophoretic particle motion observed by McNab and Meisen [24] in liquids, much less furnishing a quantitative *continuum* theory thereof [15].

Semenov and Schimpf [25] offer an alternative \mathbf{v}_m -based theory of thermophoresis in liquids, different from that embodied in Eq. (15). Nevertheless, as in our Eq. (15), the particle's thermophoretic velocity \mathbf{U} is predicted to be proportional to $\beta \nabla T_0$, in addition to being independent of particle size. However, unlike our Eq. (15), which depends only upon the physicochemical properties of the fluid, but not those of the solid particle, Semenov and Schimpf's expression for \mathbf{U} does depend upon the particle's properties, explicitly as embodied in the particle's Hamaker constant. A quantitative comparison of the two theories is offered elsewhere [26] in the context of establishing the extent of their respective accord with experiment. In effect, each furnishes thermophoretic particle velocities \mathbf{U} for liquids that agree reasonably well, at least as regards order of magnitude, with the limited experimental data available, although these data are themselves subject to some interpretative ambiguity.

IV. DISCUSSION

A. Justification of the key simplifying assumptions underlying Eq. (15)

Rationalization of use of the creeping flow approximation Eq. (9) to the full NS continuity equations rests upon the smallness of the sphere's Reynolds number $\text{Re}=aU/v$, in

which $U=|\mathbf{U}|$. Use of Eq. (15) together with the facts that $\beta=O(1/T)$ in which $(T_h>T>T_c)$, and $|\nabla T_0|=(T_h-T_c)/L$ thus yields the estimate $\text{Re}=\text{Pr}^{-1}(a/L)$. Inasmuch as we have supposed that $a/L\ll 1$, and since $\text{Pr}=O(1)$ for gases [10], the Reynolds number will always prove to be very small in the case of gases. Moreover, the time- and possibly position-dependent motion of the sphere automatically proves to be quasisteady owing to the smallness of the particle Reynolds number, as well as of the respective magnitudes of the several time scales involved in the unsteady-state transport equations owing to the relatively large distance of the sphere from either wall. The situation is even more favorable in the case of liquids, since their Prandtl numbers are invariably greater, often much greater, than unity [10]. Only in the case of particle motion in liquid metals, for which $\text{Pr}=10^{-3}$ to 10^{-2} [10], would there possibly be any concern about neglecting both unsteady and convective inertial effects.

The pressure and viscous dissipative terms that would, in general circumstances, ordinarily appear in the energy equation (10), but which have been neglected here, are, respectively, $\beta T(D_{mp}/Dt)$ and $2\mu\nabla\mathbf{v}:\nabla\mathbf{v}$ [10, p. 589]. Upon defining $\varepsilon=\beta_o(T_h-T_c)$, in which the subscript “o” represents a characteristic value of the pertinent parameter to which it is affixed, the scaling of the various fields entering into estimates of the relative orders of magnitude of the various terms appearing in the complete energy equation are as follows: $\beta_o=O(1/T_o)$, $\mathbf{v}=O(\varepsilon\alpha_o/L)$, $p=p_o+O(\varepsilon\rho_o\alpha_o^2/L^2)$, $T=T_o+O(T_h-T_c)$, $\rho=\rho_o+O(\varepsilon\rho_o)$, and $\nabla=O(1/L)$. It readily follows from these estimates that the neglected terms in the energy equation are indeed small compared with those retained. This conclusion is especially transparent if attention is limited to the case of relatively small temperature differences $(T_h-T_c)/T_o$ between the walls, with ε then regarded as playing the role of a small perturbation parameter, $\varepsilon\ll 1$. In any event, the general conclusion regarding negligibility remains true even in circumstances where $\varepsilon=O(1)$.

Justification for our having ignored pressure gradient effects in the analysis leading up to Eq. (15) resides in the fact that $\nabla^2\mathbf{v}_v^{(0)}=\mathbf{0}$ according to Eq. (14). Accordingly, the \mathbf{v}_v -based creeping flow equation (9) yields $\nabla p^{(0)}=\mathbf{0}$, thus contributing to the general notion that during thermophoresis pressure gradient effects do not sensibly affect density gradients compared with temperature gradient effects upon the latter. Although this argument applies strictly only to the undisturbed, particle-free flow Eq. (14), the force-free nature of the “disturbed” flow arising when the point-size particle is present ultimately leads to a similar conclusion, surely an obvious one in the case of liquids.

B. Maxwell’s slip condition as a continuum-level phenomenon

As shown earlier, the conventional ($\mathbf{v}=\mathbf{v}_m$)-based continuum creeping flow and incompressible continuity equations (9) and (8), together with the similarly based, no-slip boundary condition (5), fail to predict the existence of thermophoretic forces and, hence, the phenomenon of thermophoresis. Accordingly, the excellent agreement, both constitutively and phenomenologically, of our unconventional \mathbf{v}

$=\mathbf{v}_v$ fluid-mechanical model with gas-phase experiments must be construed as furnishing pertinent evidence in support of Eq. (2) over Eq. (3), the latter of course in the absence of Maxwell slip arising from noncontinuum sources. The credibility thereby conferred upon our purely continuum volume-velocity hypothesis is further enhanced by the fact that our unconventional \mathbf{v}_v -based no-slip condition Eq. (5) is, following the introduction of Eq. (12) into the boundary condition $\mathbf{I}_s\cdot\mathbf{v}_v=\mathbf{0}$ on ∂V_s , seen to be constitutively identical to Maxwell’s mass-velocity-based slip condition (18), with the two expressions differing only in their respective $O(1)$ phenomenological coefficients C_s and C'_s . As discussed in detail elsewhere [26], this agreement between our purely continuum, \mathbf{v}_v -based, model of mass slip along the surface of the sphere and Maxwell’s [4] original model thereof, embodied in Eq. (18), strongly suggests that the attribution of thermophoretic particle movement to *noncontinuum* phenomena, an assignation implicitly embodied in Epstein’s Eq. (17), is inappropriate. This conclusion accords with the independent reassignment by other researchers [27] of the $O(\text{Kn}^2)$ noncontinuum Burnett thermal stress terms [28,2] to the $O(\text{Kn})$, NS fluid-mechanical level, a topic extensively reviewed in Ref. [26].

C. Tracer velocity

The arguments favoring Eq. (2) over Eq. (3) are further augmented by recognizing that Eq. (15) [and its experimentally confirmed counterpart [16–18] for gases, Eq. (17), with $C_s\approx 1.17$] is independent of the size of the particle. As such, the particle’s thermophoretic velocity (15) qualifies as constituting the tracer or Lagrangian velocity $\mathbf{v}_l:=\left(\partial\mathbf{x}/\partial t\right)_{\mathbf{x}_0}$ of the *undisturbed* fluid, namely, the fluid from which the velocity-monitoring tracer particle is absent. In other words, our claim is that Eq. (15), representing the velocity through space of a passive (i.e., non-heat-conducting), non-Brownian tracer particle—the latter constituting a *point-size* foreign object entrained in the “flowing” fluid—is, in fact, physically, the velocity $\mathbf{v}=\mathbf{v}_l$ of the particle-free fluid continuum at a point \mathbf{x} along the trajectory $\mathbf{x}=\mathbf{x}(\mathbf{x}_0,t)$. The latter curve denotes the spatiotemporal path of a hypothetical “fluid particle,” wherein \mathbf{x} denotes the current position in space at time t of the particular infinitesimal fluid particle that at an earlier time $t=0$ was situated at the spatial position \mathbf{x}_0 . This fluid-particle/tracer-particle velocity interpretation, $\mathbf{v}_l=\mathbf{U}$, is further supported by the fact that according to theory [15] (see also the Appendix), \mathbf{U} is independent of the tracer particle’s shape as well as of the latter’s orientation in space relative to the direction of that of the externally imposed vector ∇T_0 . (Certainly, in order to qualify physically as a tracer of the undisturbed fluid motion, it would surely be required that the fluid’s velocity \mathbf{v}_l be independent of the shape of the particle serving to measure this velocity.) Our conclusions regarding particle size and shape independence appear to be confirmed by independent calculations [29], revealing that the thermophoretic velocities of simulated soot particles are “remarkably insensitive to aggregate size and morphology.”

By definition, a fluid’s tracer velocity through space is necessarily given by the expression $\mathbf{v}_l=\mathbf{U}$, with \mathbf{U} the veloc-

ity of a passive, effectively point-size, material tracer particle. As such, in contrast to the continuum fluid's *aphysical* velocities, namely, \mathbf{v}_m and \mathbf{v}_v (respectively representing disguised mass- and volume-flux densities or current densities \mathbf{n}_m/ρ and \mathbf{n}_v , as discussed in [6]), the fluid's tracer velocity \mathbf{v}_l represents the actual physical velocity \mathbf{v} of the fluid through space, as objectively monitored by the entrained tracer's space-time trajectory $\mathbf{x}=\mathbf{x}(\mathbf{x}_0, t)$. From Eq. (12), the fluid's undisturbed "motion" in the present, wall-bounded, temperature gradient animation case, corresponding to the seemingly static-fluid, pure heat conduction case $\mathbf{v}_m=\mathbf{0}$ is $\mathbf{v}_v=-(kC/\hat{c}_p)\nabla T$. Since the latter is seen to be identical to \mathbf{U} , as given by Eq. (15), and, hence, to \mathbf{v}_l , one has that $\mathbf{v}_l=\mathbf{v}_v$, at least in present circumstances. Accordingly, this latter conclusion is equipollent to the more physically meaningful relation

$$\mathbf{v} = \mathbf{v}_l. \quad (19)$$

In this expression, the strictly *dynamical* concept of the diffuse transport of momentum [the latter as embodied in the presence of \mathbf{v} in Newton's viscosity law Eq. (1)] is formally reunited with the strictly *kinematical* notion (as embodied in \mathbf{v}_l) of the movement through space of the object transporting that momentum [namely, the fluid particle traversing the trajectory $\mathbf{x}=\mathbf{x}(\mathbf{x}_0, t)$]. In assessing the philosophical import of Eq. (19) on the subject of fluid mechanics, one needs to be consciously aware of the fact that the thermophoretic particle tracer motion, as quantified by \mathbf{U} , does not represent the motion of a foreign object *through* the fluid but, rather, the motion of this object *with* the fluid, i.e., an object entrained in the already "flowing" fluid [cf. Eq. (14)] and hence simply moving through space at the local velocity \mathbf{v}_l of the fluid continuum [30].

V. CLOSURE

A. Other experimental evidence favoring Eq. (2) over Eq. (3)

The experimental data advanced in this paper in support of the viability of the relation $\mathbf{v}=\mathbf{v}_v$ address only the phenomenon of thermophoresis. However, other equally credible experimental evidence exists favoring Eq. (2) over Eq. (3). In the case of gases, these additional experimental data include thermal transpiration [22] in single-component fluids and diffusio-phoresis [31] in isothermal, compositionally inhomogeneous, binary fluid mixtures (cf. [13]). In these other classes of experiments the use of Eq. (2) leads to results that accord well with experiments in gases. Similar agreement with experiment (albeit of a less rigorously founded nature) is observed when Eq. (15) is applied to rationalize *liquid-phase* thermal diffusion data [32] involving the Soret effect [10].

B. Theoretical evidence in favor of Eq. (2)

Purely theoretical evidence pointing to the viability of Eq. (2) over Eq. (3) is summarized in Ref. [26]. The latter paper also presents formal arguments based upon the contribution of Burnett's [2,28] thermal stress terms to the viscous stress tensor \mathbf{T} Eq. (1), over and above the classical \mathbf{v}_m -based New-

ton's law deviatoric stress relation $\mathbf{T}=2\mu\overline{\nabla\mathbf{v}_m}+\kappa\mathbf{I}\nabla\cdot\mathbf{v}_m$.

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APPENDIX: ELEMENTARY CALCULATION OF THE THERMOPHORETIC VELOCITY OF A NONCONDUCTING SPHERE

1. Spherical particles

Consider velocity and pressure fields (\mathbf{v}, p) satisfying the generic incompressible creeping flow and continuity equations (9) and (8), in which \mathbf{v} is the field appearing in both the deviatoric stress tensor (1) and the no-slip boundary condition (5). According to Faxen's theorem [19] for such flows satisfying a zero vector velocity boundary condition on the sphere, namely, $\mathbf{v}=\mathbf{0}$ on ∂V_s , the hydrodynamic force \mathbf{F} exerted by the fluid on a solid sphere of radius a translating with velocity \mathbf{U} when immersed in an incompressible creeping flow, say $\{\mathbf{v}^{(0)}, p^{(0)}\}$, satisfying Eqs. (9) and (8) far from the sphere, is given by the expression

$$\mathbf{F} = 6\pi\mu a \left[(\mathbf{v}^{(0)} - \mathbf{U}) + \frac{a^2}{6\mu} \nabla p^{(0)} \right]_o. \quad (A1)$$

The corresponding torque \mathbf{L}_o is

$$\mathbf{L}_o = 8\pi\mu a^3 \left[\frac{1}{2} \nabla \times \mathbf{v}^{(0)} - \mathbf{\Omega} \right]_o, \quad (A2)$$

in which $\mathbf{\Omega}$ is the sphere's angular velocity. The subscript "o" appended to the above expressions connotes evaluation of the indicated quantities at the center o of the fluid space presently occupied by the sphere. Accordingly, a force- and torque-free sphere will, in the absence of wall effects associated with the nonzero nature of the size ratio a/L , translate quasistatically with a velocity

$$\mathbf{U} = \mathbf{v}_o^{(0)} + \frac{a^2}{6\mu} \nabla p_o^{(0)} \quad (A3)$$

and rotate at an angular velocity

$$\mathbf{\Omega} = \frac{1}{2} (\nabla \times \mathbf{v}^{(0)})_o. \quad (A4)$$

In the past, Faxen's laws, Eqs. (A1) and (A2), have only been applied to the usual case, where $\mathbf{v}=\mathbf{v}_m$. However, from a purely mathematical view, Faxen's laws may equally well be applied any velocity field \mathbf{v} satisfying Eqs. (9) and (8), provided that \mathbf{v} also satisfies a vanishing vector velocity boundary condition $\mathbf{v}=\mathbf{0}$ on ∂V_s . As discussed in [33], the latter condition is applicable to the choice $\mathbf{v}=\mathbf{v}_v$ for situations in which the sphere is nonconducting (and, generally, only in that case). The undisturbed volume velocity field $\mathbf{v}_v^{(0)}$ existing in the absence of the sphere is given by Eq. (14) as $\mathbf{v}_v^{(0)}=-\alpha\beta\nabla T_0=\text{const}$, in which, by definition, $\nabla T^{(0)}\equiv\nabla T_0=\text{const}$ ($\forall \mathbf{x}$). This velocity field obviously satisfies the quasi-incompressibility condition (11), namely, $\nabla\cdot\mathbf{v}_v^{(0)}=0$, since $\mathbf{v}_m^{(0)}=\mathbf{0}$ and $\nabla^2 T^{(0)}=0$. Moreover, we see that $\mathbf{v}_v^{(0)}$ also satisfies the \mathbf{v}_v -based creeping flow equations $\nabla p^{(0)}=\mu\nabla^2\mathbf{v}_v^{(0)}$, in which $\nabla p^{(0)}=\mathbf{0}$. Thus, Eq. (A3) becomes

$$\mathbf{U}=-\alpha\beta\nabla T_0. \quad (\text{A5})$$

Additionally, Eq. (A4) becomes $\boldsymbol{\Omega}=\mathbf{0}$ [34]. In the nonconducting particle limit, Eq. (A5) accords with the more general formula [15] $\mathbf{U}=-\alpha\beta[1+(k_s/2k)]^{-1}\nabla T_0$, applicable to the conducting sphere case ($k_s/k\neq 0$), and derived by solving the complete, coupled boundary-value problem for that case.

2. Nonspherical particles

Equation (A5) is applicable not only to spheres, but equally to any nonconducting particles, irrespective of their

shape and orientation. This follows from the fact that the generalization of Eq. (A1) for an arbitrarily shaped (nonrotating) particle [19,34] is $\mathbf{F}=\mathbf{M}^{-1}\cdot[(\mathbf{v}^{(0)}-\mathbf{U})+O(a/L)]_o$, where \mathbf{M} is the particle's (torque-free) mobility dyadic, a is a characteristic particle size, and L is a characteristic length appearing in the dimensionless normalization $\nabla^*=L\nabla$ of the gradient operator appearing explicitly in the undisturbed nonuniform flow $\mathbf{v}^{(0)}$ [so that the $O(a/L)$ term represents a wall effect]. Accordingly, the velocity of such a force-free body is $\mathbf{U}=\mathbf{v}_o^{(0)}+O(a/L)$. With use of Eq. (14), one thus recovers Eq. (A5). Thus, remarkably, as is more formally demonstrated in Ref. [15], irrespective of size, shape, and orientation relative to the undisturbed temperature gradient ∇T_0 , nonconducting particles will all move with the same velocity \mathbf{U} . Accordingly, provided that one interprets fluid motion physically as being the fluid's volume velocity rather than its mass velocity, Eq. (A5), expressed more generally as $\mathbf{U}\equiv(\mathbf{v}_l^{(0)})_o=(\mathbf{v}_v^{(0)})_o+O(a/L)$, simply states that any passive (i.e., nonconducting), no-slip, thermophoretically animated particle is simply entrained in the flowing fluid. Alternatively, with use of Eq. (12), this may be written more generally as

$$\mathbf{U}\equiv\mathbf{v}_l^{(0)}=\mathbf{v}_m^{(0)}-\alpha\beta\nabla T^{(0)}+O(a/L), \quad (\text{A6})$$

a result which holds in all situations wherein a temperature gradient exists in the fluid.

[1] In contrast with this unorthodox, purely continuum, view of thermophoretic particle movement in gases, the conventional interpretation regards the forces animating such motion as a manifestation of noncontinuum behavior, arising from so-called Maxwell slip of the gas at the particle surface, the latter deriving from the noncontinuum Burnett thermal stress terms in the Knudsen number perturbation expansion of the Boltzmann equation [2]. In the absence of slip, the classical \mathbf{v}_m -based incompressible continuum NS equations fail to predict the existence of thermophoresis.

[2] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, U.K., 1970).

[3] P. S. Epstein, *Z. Phys.* **54**, 537 (1929).

[4] J. C. Maxwell, *Philos. Trans. R. Soc. London* **170**, 231 (1879).

[5] H. Brenner, *Physica A* (to be published).

[6] Despite the terminology, \mathbf{v}_v is not strictly a "velocity" in the physical sense of quantifying the temporal motion of a *material object* through space. Rather, \mathbf{v}_v is physically (i.e., experimentally) a Eulerian flux density $\mathbf{n}_v(\mathbf{x},t)$ of volume in disguise, defined at a point \mathbf{x} of the fluid continuum, such that with $d\mathbf{S}$ a space-fixed (i.e., Eulerian) directed element of surface area at \mathbf{x} , the scalar $d\mathbf{S}\cdot\mathbf{n}_v$ represents the total volume flowing across $d\mathbf{S}$ per unit time by both convective and diffusive mechanisms [5]. Explicitly, $\mathbf{v}_v\equiv\mathbf{n}_v$. Likewise, the quantity $\mathbf{v}_m:=\mathbf{n}_m/\rho$ appearing in the continuity equation [cf. Eq. (4)] is really a (normalized) flux density of mass masquerading

as a velocity, where $d\mathbf{S}\cdot\mathbf{n}_m$ is the mass flowing per unit time across $d\mathbf{S}$. As such, in terms of their physical significance, as evidenced by the protocols quantifying their respective experimental measurements, \mathbf{v}_m and \mathbf{v}_v should both be regarded terminologically as normalized flux densities rather than as physical velocities, with the term "velocity" reserved exclusively for the fluid's tracer or Lagrangian velocity \mathbf{v}_l (see Sec. IV). The latter represents the *physical* velocity through space of a point-size, passive, non-Brownian solid particle entrained in the flowing fluid, an object whose presence does not disturb the particle-free continuum fluid motion that one is objectively attempting to measure.

[7] G. G. Stokes, *Trans. Cambridge Philos. Soc.* **8**, 287 (1845).

[8] Up to this point we have not yet explicitly set forth the constitutive equation relating \mathbf{v}_v to \mathbf{v}_m [see Eq. (12)]. However, for the case where $\mathbf{v}=\mathbf{v}_v$ it is subsequently demonstrated [cf. Eq. (11)] that Eq. (8) indeed holds for the volume velocity choice $\mathbf{v}=\mathbf{v}_v$ [5], at least in circumstances where the thermal law of adiabatically additive volumes holds [9].

[9] In physical terms, this "law" is tantamount to supposing that the volume of the uniform-temperature fluid which results upon adiabatically (and isobarically) mixing together hot and cold masses of fluid is simply the sum of the respective volumes occupied by these two fluid masses at their original temperatures [5].

[10] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed. (Wiley, New York, 2002).

- [11] Note that since $C=0$ for the \mathbf{v}_m -based incompressible fluid case $\rho=\text{const}$, corresponding to the case of isothermal flow $\nabla T=0$, one has in such circumstances from Eq. (12) that $\mathbf{v}_v = \mathbf{v}_m$. In this situation the conventional mass-velocity-based forms of Newton's viscosity law (1) and the no-slip boundary condition (5) are recovered.
- [12] D. D. Joseph and Y. Renardy, *Fundamentals of Two-Fluid Dynamics* (Springer, New York, 1992), Part I, pp. 349–361. In the case of single-component fluids undergoing heat transfer, Eq. (11) is attributed by the preceding authors (see p. 352 of their book) to V. V. Pukhnachov, University of Minnesota Institute of Mathematics and Applications Report No. 796, 1991 (unpublished); see also V. V. Pukhnachov, in Proceedings of the Eighth European Symposium on Materials and Fluid Sciences in Microgravity, Brussels, 1992 (unpublished); ESASP, 1992, pp. 157–160.
- [13] The notion of a volume velocity \mathbf{v}_v as a physical entity is well known in connection with compositionally inhomogeneous multicomponent fluids undergoing (isothermal, isobaric) mass transfer [14]; however, in the context of single-component fluids undergoing heat transfer the notion of a volume velocity \mathbf{v}_v (existing independently of \mathbf{v}_m) does not appear to be a known physical concept, although it is implicit in the work of Pukhnachov cited in Ref. [12]. To see the intimate relation existing between these two cases, we note that the analog of the convective-diffusive energy equation (10) for the isothermal isobaric binary mixture case is given by the species transport equation [10]

$$\rho D_m w / Dt = \nabla \cdot (\rho D \nabla w),$$

where w is the mass fraction of either one of the two species, and D is the Fick's law binary diffusivity. In circumstances where the isothermal, isobaric law of additive volumes for mixtures [14] is applicable, one has that $d\hat{v} = C_* dw$, where C_* is a composition-independent constant. Since $\hat{v} = 1/\rho$, the latter gives rise to the following identity pertaining to the LHS of the above species balance equation: $\rho D_m w / Dt = \rho C_*^{-1} D_m \hat{v} / Dt \equiv -C_*^{-1} D_m \ln \rho / Dt = C_*^{-1} \nabla \cdot \mathbf{v}_m$, the last step being a consequence of Eq. (4). On the other hand, as regards the RHS of the above species transport equation, one has successively that $\rho D \nabla w = \rho C_*^{-1} D \nabla \hat{v} \equiv -C_*^{-1} D \nabla \ln \rho$. Accordingly, one finds that $\nabla \cdot (\mathbf{v}_m + D \nabla \ln \rho) = 0$. On the other hand, for such isothermal, isobaric, two-component fluid mixtures obeying both Fick's law and the law of additive volumes, the relation between the binary mixture's respective volume- and mass-average velocities is easily shown to be $\mathbf{v}_v = \mathbf{v}_m + D \nabla \ln \rho$ [5]. This result represents the two-component mass-transfer analog of the single-component heat transfer equation (12), as is readily seen by noting that in the last term of that equation one has the identity $C^{-1} \nabla T = \nabla \hat{v} = -\rho^{-1} \nabla \ln \rho$. This yields the expression $-(k C^{-1} / \hat{c}_p) \nabla T = \alpha \nabla \ln \rho$, wherein $\alpha = k / \rho \hat{c}_p$ is the fluid's thermometric diffusivity. As such, Eq. (12) is seen to adopt the form $\mathbf{v}_v = \mathbf{v}_m + \alpha \nabla \ln \rho$. This expression points up the obvious analogy existing between the respective one- and two-component volume velocities, including the fact that $\nabla \cdot \mathbf{v}_v = 0$ in both cases, the latter reflecting the applicability of the compositional law of additive volumes [5,12,14].

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- [31] J. R. Bielenberg and H. Brenner (unpublished).

- [32] J. R. Bielenberg and H. Brenner (unpublished).
- [33] Equations (A1) and (A2) apply only in circumstances where not only is the no-slip condition Eq. (5) applicable at the sphere surface ∂V_s , but so also is the vanishing normal velocity condition $\mathbf{n} \cdot \mathbf{v} = 0$ on ∂V_s ; that is, Faxen's laws depend for their validity upon the vanishing, $\mathbf{v} = \mathbf{0}$ on ∂V_s , of the complete vector velocity field \mathbf{v} at the sphere surface. Given Eq. (6), this obviously requires, *inter alia*, that $\mathbf{n} \cdot (\mathbf{v} - \mathbf{v}_m) = 0$ on ∂V_s . This condition is trivially satisfied in the case of Eq. (3). In the case of Eq. (2), where $\mathbf{v} = \mathbf{v}_v$, we see from Eqs. (12) and (13) that

the condition $\mathbf{n} \cdot \mathbf{v}_v = 0$ on ∂V_s is automatically satisfied in circumstances where the sphere is nonconducting. Accordingly, in such situations we have that $\mathbf{v}_v = \mathbf{0}$ on ∂V_s , thereby allowing Faxen's laws to be applied to the nonconducting sphere case, $\mathbf{v} = \mathbf{v}_v$.

- [34] That the particle does not rotate is a consequence of the fact that from Eq. (12) the undisturbed velocity field Eq. (14) is vorticity-free throughout the fluid, $\nabla \times \mathbf{v}_m^{(0)} = \nabla \times \mathbf{v}_v^{(0)} = \mathbf{0}$, owing to the fact that the curl of the gradient of any scalar field, here the temperature field, is identically zero.