Nonisothermal Brownian motion: Thermophoresis as the macroscopic manifestation of thermally biased molecular motion

Howard Brenner

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA
(Received 13 February 2005; published 5 December 2005)

A quiescent single-component gravity-free gas subject to a small steady uniform temperature gradient $\boldsymbol{\nabla} T$, despite being at rest, is shown to experience a drift velocity $\mathbf{U}_D = -D^* \boldsymbol{\nabla} \ln T$, where D^* is the gas's *nonisothermal* self-diffusion coefficient. D^* is identified as being the gas's thermometric diffusivity α. The latter differs from the gas's *isothermal* isotopic self-diffusion coefficient D, albeit only slightly. Two independent derivations are given of this drift velocity formula, one kinematical and the other dynamical, both derivations being strictly macroscopic in nature. Within modest experimental and theoretical uncertainties, this virtual drift velocity $\mathbf{U}_D = -\alpha \boldsymbol{\nabla} \ln T$ is shown to be constitutively and phenomenologically indistinguishable from the well-known experimental and theoretical formulas for the thermophoretic velocity $\mathbf{U}$ of a macroscopic (i.e., non-Brownian) non-heat-conducting particle moving under the influence of a uniform temperature gradient through an otherwise quiescent single-component rarefied gas continuum at small Knudsen numbers. Coupled with the size independence of the particle's thermophoretic velocity, the empirically observed equality, $\mathbf{U} = \mathbf{U}_D$, leads naturally to the hypothesis that these two velocities, the former real and the latter virtual, are, in fact, simply manifestations of the same underlying molecular phenomenon, namely the gas's Brownian movement, albeit biased by the temperature gradient. This purely hydrodynamic continuum-mechanical equality is confirmed by theoretical calculations effected at the kinetic-molecular level on the basis of an existing solution of the Boltzmann equation for a quasi-Lorentzian gas, modulo small uncertainties pertaining to the choice of collision model. Explicitly, this asymptotically valid molecular model allows the virtual drift velocity $\mathbf{U}_D$ of the light gas and the thermophoretic velocity $\mathbf{U}$ of the massive, effectively non-Brownian, particle, now regarded as the tracer particle of the light gas's drift velocity, to each be identified with the Chapman-Enskog "thermal diffusion velocity" of the quasi-Lorentzian gas, here designated by the symbol $\mathbf{U}_{\mathrm{M/M}}$, as calculated by de la Mora and Mercer. It is further pointed out that, modulo the collective uncertainties cited above, the common velocities $\mathbf{U}_D, \mathbf{U}$, and $\mathbf{U}_{\mathrm{M/M}}$ are identical to the single-component gas's diffuse volume current $\mathbf{j}_v$, the latter representing yet another, independent, strictly continuum-mechanical concept. Finally, comments are offered on the extension of the single-component drift velocity notion to liquids, and its application towards rationalizing Soret thermal-diffusion separation phenomena in quasi-Lorentzian liquid-phase binary mixtures composed of disparately sized solute and solvent molecules, with the massive Brownian solute molecules (e.g., colloidal particles) present in disproportionately small amounts relative to that of the solvent.

PACS number(s): 51.10.+y, 51.20.+d, 05.20.Jj, 05.40.Jc

I. INTRODUCTION

This paper demonstrates that, on average, the molecules of a single-component fluid which is macroscopically at rest and undergoing a steady-state heat conduction process experience a temperature gradient-induced drift velocity

$$\mathbf{U}_D = -D^* \boldsymbol{\nabla} \ln T, \tag{1}$$

with T the absolute temperature and D^* the fluid's *nonisothermal* self-diffusivity. Subsequently, in Sec. IV, we identify D^* with the fluid's thermometric diffusivity $\alpha = k/\rho \hat{c}_p$ (k=thermal conductivity, ρ=mass density, $\hat{c}_p$=isobaric specific heat); however, for the time being, D^* is simply regarded as the experimentally measured parameter that would appear in the single-component "diffusion equation"

$$\frac{\partial \rho}{\partial t} = \boldsymbol{\nabla} \cdot (D^* \boldsymbol{\nabla} \rho) \tag{2}$$

governing the unsteady-state mass density distribution in a nonisothermal isobaric heat-conducting fluid. This mass redistribution-based definition of D^* is the same as that for the more usual isothermal self-diffusivity D in a single-component fluid (with ρ in that case denoting a small deviation or fluctuation $\delta\rho$ from a state of uniform density).

Since the fluid in the case of Eq. (1) is macroscopically motionless, the drift velocity $\mathbf{U}_D$ refers not to a real velocity, namely that of a continuum fluid velocity accessible to direct experimental measurement; rather, it is a virtual velocity appearing in a physical-space Fokker-Planck [1] description of the spatiotemporal evolution of the molecular probability distribution function (see Sec. VI) in a fluid wherein $\mathbf{v}_m = \mathbf{0}$, with $\mathbf{v}_m$ the mass velocity appearing in the continuity equation

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{v}_m) = 0. \tag{3}$$

The notion of a molecular drift velocity is usually associated with the action of an externally imposed body-force field, typically gravitational or electrical in origin. Here, however, we advance the view (Sec. III) that the drift velocity $\mathbf{U}_D$ arising from the temperature gradient should be un-

derstood as arising from the action of a fictitious thermoösmotic force, $\mathbf{F} = -\boldsymbol{\nabla}\mu_T$ (per molecule), derived from a local thermochemical potential field, $\mu_T = k_b T$, where k_b is Boltzmann's constant. Like any other potential, the effect of variations in this field is such as to cause the molecules comprising the fluid continuum to migrate, on average, towards regions of lower potential energy (here, temperature), thus explaining, for example, why the density of a fluid undergoing steady-state heat conduction generally increases in the direction of diminishing temperature. Concomitantly, a similar quantitative rationalization is offered of the thermophoretic motion, not of a molecule of the gas, but rather of a macroscopic (i.e., effectively non-Brownian) particle immersed in that gas, thereby explaining the phenomenon of thermophoresis [2,3]. In that case, however, the particle's drift velocity is real, owing to the particle's lack of Brownian movement. Two independent proofs are offered of Eq. (1), one kinematical (Sec. II) and the other dynamical (Sec. III). In addition, we offer experimental thermophoretic evidence in Sec. V in support of the viability of Eq. (1) in which $D^* = \alpha$.

Section VI provides a quantitative molecular rationalization of our temperature-gradient induced drift velocity formula, at least in the case of a gas. This is accomplished by considering the quasi-Lorentzian case [[4], p. 193] of a gaseous binary mixture wherein the molecular mass m_p of the hyperdilute species (regarded as massive Brownian solute molecules or colloidal particles) is vastly greater than the molecular mass m of the light gas in whose single-component drift velocity $\mathbf{U}_D$ we are interested. The Chapman-Enskog "thermal diffusion velocity" [[4], p. 141] of the two species, representing the difference in mean velocities between the "heavy" and "light" species (in circumstances where the composition of the gas is uniform throughout and pressure gradients are absent) is identified, simply, as representing the "tracer" velocity of the single-component *particle-free* light gas when the latter is macroscopically at rest. This Boltzmann or Fokker-Planck-based quasi-Lorentzian calculation of the (thermophoretic) "particle drift velocity" $\mathbf{U}_{M/M}$, which furnishes results that accord both constitutively and phenomenologically with our main result, Eq. (1), was, in fact, effected long ago by de la Mora and Mercer [5]. They did not, however, explicitly identify this quantity as being the quasi-Lorentzian-derived "tracer velocity" [6] of the single-species light gas itself, from which the second massive Brownian species was absent.

Section VII outlines how the ideas set forth in Sec. II–VI for gases can be adapted to the case of liquids without, however, requiring a quasi-Lorentzian-type molecular-level calculation analogous to that performed for gases in Sec. VI. These calculations exploit the liquid-phase analog of the fact that the "thermal diffusion velocity" of relatively massive Brownian colloidal solute particles or molecules present in relatively small amounts in nonisothermal binary solutions (within which the solvent is macroscopically at rest) constitutes the drift velocity of the neat, particle-free, solvent. These notions are used to provide what amounts to an elementary hydrodynamic theory of Soret separation phenomena [7] for an important class of binary liquid-phase mixtures. This class includes dilute polymer solutions, wherein

the thermal diffusion coefficient D_T is observed experimentally to depend only upon the physical properties of the solvent, independently of those of the solute, including the latter's molecular size, mass, configuration, and physicochemical constitution—a result predicted by our quasi-Lorentzian liquid-phase theory.

Finally, Sec. VIII elaborates on key aspects of the preceding calculations, including raising—but not answering—fundamental questions involving the relationship between our hydrodynamic tracer-velocity calculations [3,8,9], the latter dependent upon macroscopic boundary conditions, and our comparable kinetic-molecular, interpenetrating continua model, calculations of this same tracer-velocity in single-species gases, as outlined in Sec. VI, for which the issue of boundary conditions appears to be irrelevant.

II. ELEMENTARY CALCULATION OF THE DRIFT VELOCITY OF A SINGLE-COMPONENT GAS

Consider a quiescent single-component ideal gas confined within the region $0 < x < L$ bounded between two indefinitely extended heat-conducting walls respectively situated at $x = 0$ and $x = L$ while permanently maintained at the respective "hot" and "cold" temperatures T_h and T_c ($T_h > T_c$) by virtue of their intimate contact with heat reservoirs [10–13]. The confined gas is assumed to undergo a steady-state one-dimensional heat conduction process. (We deliberately limit attention, at least initially, to single-component fluids so as to avoid the complications resulting from thermal diffusion, i.e., Soret separation phenomena [4,14], that would otherwise arise from the existence of a temperature gradient in a multicomponent fluid.) A key feature of the subsequent analysis lies in the fact that the pressure p is constant throughout the quiescent gas as a consequence of the linear momentum equation.

It will be supposed that the system is not too far from thermodynamic equilibrium. This allows us, where necessary, to use the gas's equilibrium equation of state, as well as other pertinent thermodynamic parameters (including the equilibrium definition of the fluid's thermodynamic or absolute temperature) in order to bring the analysis to fruition. Explicitly, we limit ourselves to situations wherein the temperature difference between the walls is relatively small, such that $\gamma := (T_h - T_c)/T_o \ll 1$ for T_o any temperature lying in the range $T_c < T_o < T_h$. In such circumstances, local variations in the thermal conductivity k of the isobaric gas with temperature may be neglected. Accordingly, the (algebraically signed) temperature gradient may be regarded as essentially uniform throughout the fluid at the value $dT/dx = -(T_h - T_c)/L = \text{const}$, thus satisfying the steady-state energy equation $d^2 T/dx^2 = 0$, which thus possesses the solution

$$T(x) = T_h - (T_h - T_c)x/L. \tag{4}$$

According to the ideal gas law,

$$p = k_b \rho T/m, \tag{5}$$

with m the molecular mass and $\rho = nm$ the mass density, wherein n is the number density of molecules. It follows

from Eq. (5) together with the position independence of the pressure p in present circumstances that $\rho(x)T(x)=$const. As such, the steady-state temperature nonuniformity (4) in the heat-conducting gas is accompanied by corresponding mass- and number-density nonuniformities, $\rho=\rho(x)$ and $n=n(x)$, with a preponderance of the total number N of confined molecules in the gap, $N=\int_0^L n(x)dx$ (per unit wall area), situated near to the cold wall. In effect, the temperature gradient dT/dx is accompanied by a corresponding molecular number density gradient, dn/dx.

In order to calculate the gas's drift velocity, we adopt a strategy analogous to that followed by Einstein [15] in his classical sedimentation-equilibrium analysis of isothermal Brownian motion, which ultimately resulted in the celebrated Stokes-Einstein equation for the diffusion coefficient of a colloidal particle, the latter regarded as a massive molecule of one of the two chemical species present in a binary liquid-phase solution. Now, however, instead of using *a priori* knowledge of the colloidal-species Stokes-law sedimentation velocity arising from differences in density between the two species to calculate the binary diffusivity D of the colloidal molecule, we invert Einstein's scheme by using Eq. (1) to calculate the fluid's drift velocity $\mathbf{U}_D$ from *a priori* knowledge of the nonisothermal self-diffusivity D^*. In addition, in a further departure from Einstein's original scheme, we deal here with gases rather than liquids.

As in Einstein's [15] ansatz, we regard the nonuniform steady-state distribution of molecules, $n=n(x)$, across the gap between the two walls as reflecting a balance between a temperature-cum-density-gradient induced drift flux, $U_D n$, of molecules towards the cold wall, and the self-diffusion Brownian flux, $-D^* dn/dx$, of molecules away from that wall, the latter tending to redistribute the molecules uniformly throughout the gap. Since there is no net flux of molecules during the steady-state heat conduction process, it follows that $U_D=D^* d\ln n/dx$. Written in vector form, the latter is equivalent to

$$\mathbf{U}_D = D^* \nabla \ln \rho. \qquad (6)$$

In the particular case of ideal gases, for which $\rho T=$const throughout the gap during the isobaric heat conduction process, the preceding immediately yields Eq. (1).

III. DYNAMIC/THERMODYNAMIC OSMOTIC INTERPRETATION OF THE GAS'S DRIFT VELOCITY $\mathbf{U}_D$

The preceding derivation of Eq. (1) embodied purely kinematical heat-conduction arguments, whereby, at steady state, a drift flux of molecules from hot to cold animated by a temperature gradient is balanced by an equal and opposite diffusive flux arising from the molecular number-density gradient. While such purely kinematical arguments similarly characterized Einstein's [15] original analysis of isothermal chemical species fluxes in a gravity field, he also provided an alternative, dynamical and thermodynamic view of the phenomenon, involving the use of so-called osmotic forces engendered by species chemical potential gradients. His arguments involved the notion of gravity forces being balanced by fictitious mechanoösmotic "forces" $\mathbf{F}_i=-\nabla\mu_i$ ($i=1, 2$) in

a binary solution, the latter virtual forces—thermodynamic in origin—and deriving from mechanochemical species potentials, $\mu_i(y_i)$, arising from the existence of gradients ∇y_i in species mole fractions y_i. This section offers a philosophically comparable dynamical derivation of Eq. (1) based upon the notion of a fictitious thermoösmotic "force," $\mathbf{F}=-\nabla\mu_T$, emanating from a temperature-dependent thermochemical potential, $\mu_T(T)$. In our case, a temperature gradient ∇T within a fluid of uniform density will be seen to take the place of Einstein's species gradient ∇y_i within a fluid of uniform temperature as the origin of the osmotic force.

As in Sec. II, consider a one-dimensional steady-state heat-conduction process occurring in a single-component gas confined to the region $0<x<L$. Now, however, that we incorporate the effect of gravity acting in the same direction as the temperature gradient, namely in the negative x direction (so that with $\mathbf{g}$ Earth's gravity vector, we have that $\mathbf{g}=-\hat{\mathbf{x}}g$, where $\hat{\mathbf{x}}$ is a unit vector in the positive x direction and $g>0$ is the magnitude of the gravity field). Thus the hotter of the two walls at $x=0$ is situated at the bottom of the apparatus. While this configuration is potentially unstable owing to the colder fluid being on top, instability does not set in until the magnitude $(T_h-T_c)/L$ of the temperature gradient exceeds a certain critical value attained at a Rayleigh number of Ra$=g\beta\Delta L^3/\nu\alpha=1708$, the threshold value for the onset of convection in the classical Rayleigh-Bénard problem [16]. Here, $\beta=-(\partial\ln\rho/\partial T)_p$ is the coefficient of thermal expansion (which for ideal gases is $\beta=1/T$), $\Delta=T_h-T_c$ is the temperature difference, $\nu=\eta/\rho$ is the kinematic viscosity (with η the shear viscosity) and, as before, α is the thermometric diffusivity. Our previous assumption that $\beta\Delta\equiv\gamma\ll 1$ will be seen to assure hydrodynamic stability for physically reasonable choices of system parameters—a fact which will subsequently be confirmed for the particular set of circumstances to be described.

In purely isothermal circumstances the action of gravity is to cause the confined gas to be densest at the bottom wall, $x=0$. On the other hand, were gravity to be absent during the heat-conduction process, the gas would then be densest at the cold upper wall, $x=L$. When operating concurrently, each effect tends to nullify the other. In particular, it will be seen that for a specified gas and for a given plate spacing L it becomes possible to choose the temperature difference Δ such that the gas's density will actually be uniform throughout the gap, $0<x<L$. For the present steady-state heat-conduction process occurring in the presence of gravity, the hydrostatic equation requires that $\nabla p=\rho\mathbf{f}^e$, where $\mathbf{f}^e=\mathbf{g}$ is the external body force per unit mass. Thus when ρ is independent of position (and $\mathbf{g}$ is taken to be constant, independent of vertical position x), it follows that the local pressure gradient dp/dx is constant through the gas, and possesses the value $dp/dx=-(p_h-p_c)/L=-\rho g=$const. On the other hand, as earlier discussed, for sufficiently small temperature gradients, such that $\gamma\ll 1$, the temperature dependence of the gas's thermal conductivity k may be neglected, whence the local temperature gradient dT/dx is constant throughout the gas at the value $-(T_h-T_c)/L=$const, as in Eq. (4). With $R=k_b N$ the universal gas constant and $M_w=mN$ the gas's molecular weight, in which N is Avogadro's number, it thus follows

from the ideal gas law (5) written in molar, rather than molecular, units that for the present uniform density case the required temperature gradient must be of magnitude

$$\frac{T_h - T_c}{L} = g\frac{M_w}{R}. \tag{7}$$

For example, in the case of hydrogen ($M_w = 2.016$ kg/kg-mol) with $g = 9.81$ m/s^2 for Earth's gravity field, and $R = 8.315 \times 10^{-3}$ kg m^2/s^2 kg-mol K, this yields a temperature gradient of 2.40×10^{-3} K/m. For a gap of, say, $L = 10$ cm, and for a mean temperature of $T_o = 300$ K ($v = 1.095 \times 10^{-4}$ m^2/s, $\alpha = 1.554 \times 10^{-4}$ m^2/s [17]) this yields a Rayleigh number of Ra$=0.46$, which is well below the critical threshold at which convective instability would be initiated. As such, the proposed configuration of "cold above hot" is seen to be stable in gases over a wide range of operating conditions.

When the density of the gas is uniform throughout, the hydrostatic equation becomes $\mathbf{f}^e = \nabla(p/\rho)$. Consequently, in the ideal gas case, it follows from Eq. (5) that the hydrostatic equation may be written as

$$\mathbf{F}^e = \nabla(k_b T), \tag{8}$$

where $\mathbf{F}^e = m\mathbf{g}$ is the force exerted by Earth's gravity on a molecule. Write $\mathbf{F}^e = -\nabla V_g$ where, to within an arbitrary additive constant, $V_g = -m\mathbf{g}\cdot\mathbf{x} \equiv mgx$ (with $\mathbf{x} = \hat{\mathbf{x}}x$ the position vector) is the gravitational potential energy of the molecule at the elevation x. If we then define (again to within an arbitrary constant)

$$\mu_T = k_b T, \tag{9}$$

Eq. (8) is seen to be equivalent to the relation

$$V_g + \mu_T = \text{const.} \tag{10}$$

With μ_T designated as being the "thermochemical potential energy" of a molecule, Eq. (10) states that the sum of the gravitational and thermochemical potentials is constant throughout the uniform density gas, analogous to the corresponding situation prevailing in an isothermal multicomponent mixture, where, at thermodynamic equilibrium (and hence steady state), the sum of the gravitational ($m_i g$) and thermodynamically ideal isothermal species molecular chemical potential ($\mu_i = k_b T \ln y_i + \text{const}$) energies is constant throughout the uniform temperature system [18].

Use of the appellation "thermochemical potential" to describe the quantity $k_b T$ appears apt. Explicitly, this terminology is consistent with the generic effect of a potential being of such a nature as to tend to cause a body (a molecule in the present case) to move from a region of high potential to one of low potential—namely, from high to low temperature in the present instance, such as occurs literally in the case of the thermophoretic motion of a particle in a gas. [This is equally true in the case of liquids, as discussed in Sec. VII; see Eqs. (39) and (50).] In this sense, the exponent appearing in the expression $\exp(-\frac{1}{2}mu^2/k_b T)$ serving to characterize the local Maxwellian equilibrium distribution of molecular velocities

$\mathbf{u}$ in a spatially homogeneous gas [4,19] may be interpreted as representing the ratio of the gas's local kinetic energy to its local "thermal potential energy."

Each of the molecules confined between the hot and cold walls is, on average, at rest despite the force of gravity, $\mathbf{F}^e = m\mathbf{g}$, striving to drive each molecule towards the lower plate, $x = 0$, and hence incidentally, the hot wall. From the point of view of a hypothetical force balance, involving an equal and opposite force, say $\mathbf{F}$, acting upon each molecule such as to nullify the effect of gravity, this requires that $\mathbf{F} + \mathbf{F}^e = \mathbf{0}$. Accordingly, it would thus appear from Eq. (8) as if, on time average, a force

$$\mathbf{F} = -\nabla\mu_T \tag{11}$$

acts on each molecule. The quantity $\mathbf{F}$ defined by Eq. (11) is not a real force, since, were gravity to be absent, the quantity $\nabla\mu_T$ would not, by itself, possess independent dynamical significance with regard to the application of Newton's laws of motion to the instantaneous motion of a given molecule. As such, following terminology initiated by Einstein [15] during the course of his isothermal sedimentation-equilibrium analysis, Eq. (11) should be understood as being a virtual or "osmotic" force, here termed the "thermoösmotic force."

Were this force to be regarded as being real rather than virtual, its action would, by definition, result in a molecule moving in the direction of the cold wall with a velocity $\mathbf{U}_M = M^*\mathbf{F}$, where M^* is the molecule's nonisothermal hydrodynamic mobility. Use of the Nernst-Planck-Einstein relation $D^* = k_b T M^*$ relating the molecule's (self-)diffusivity to its mobility (here assumed equally applicable to the nonisothermal case), together with Eqs. (11) and (9), thus leads to the relation

$$\mathbf{U}_M = -D^*\nabla\ln T. \tag{12}$$

Comparison with Eq. (1) shows that $\mathbf{U}_M \equiv \mathbf{U}_D$. Equation (12) for the gas's "thermophoretic" migration velocity, which we have here derived via dynamical arguments and interpreted by invoking a thermodynamic analogy, is, of course, identical to that derived in Sec. II by purely kinematical arguments. As such, our respective kinematic and dynamic formulations of the notion of a drift velocity are seen to be consistent with one another.

IV. IDENTIFICATION OF D^* WITH α

In this section we demonstrate that the gas's nonisothermal self-diffusivity is equal to its thermometric diffusivity:

$$D^* = \alpha. \tag{13}$$

In order to prove this contention, imagine that both walls of the apparatus within which the steady-state heat conduction process of Sec. II is being conducted are suddenly insulated, trapping all of the system's initial energy within. Eventually, of course, the confined (and now energetically isolated) gas in the region $0 < x < L$ will attain steady uniform values of its temperature, density, and pressure. In the interim, however, the gas will undergo an unsteady-state transport process in

which, among other things, the density will change with time: $\partial \rho / \partial t \neq 0$. In accordance with the continuity equation (3) an unsteady mass flow $\mathbf{v}_m(x,t)$ necessarily accompanies this temporal density change.

The relation existing between the gas's respective volume velocity $\mathbf{v}_\nu$ and mass velocity $\mathbf{v}_m$ for the ensuing one-dimensional flow is [20]

$$\nu_\nu = \nu_m + j_\nu, \quad j_\nu = \alpha \, \partial \ln \rho / \partial x, \tag{14}$$

with j_ν the diffusive flux density of volume. When the fluid obeys the adiabatic law of isobarically additive volumes and where dissipative effects in the energy equation are negligible compared with conduction effects (corresponding to a small Brinkman number [21]), the volume velocity satisfies the quasi-incompressible equation of state, $\nabla \cdot \mathbf{v}_\nu = 0$ [20]. In the present one-dimensional case this requires that $\partial v_x / \partial x = 0$. Integration gives $\nu_\nu = f(t)$, independently of x. Now, since the walls are insulated for $t > 0$, it follows that $\partial T / \partial x = 0 (\forall \, t > 0)$ at $x = (0, L)$. The adiabatic law of isobarically additive volumes is satisfied by ideal gases, from which it follows that $d\hat{v}/dT = \text{const}$, with $\hat{v} = 1/\rho$ the specific volume. Accordingly, in present circumstances the vanishing temperature gradient boundary conditions imposed at the walls translates into equivalent boundary conditions imposed on the density gradient, namely $\partial \rho / \partial x = 0 (\forall \, t > 0)$ at $x = (0, L)$. Moreover, since the walls are impermeable to mass, it also follows that $\nu_m = 0 (\forall \, t > 0)$ at $x = (0, L)$. Consequently, Eq. (14) requires that $\nu_\nu = 0 (\forall \, t > 0)$ at $x = (0, L)$. Given that ν_ν is a function only of time, this necessitates that $\nu_\nu = 0 (\forall \, t > 0 \text{ and } \forall \, x)$. It follows from the latter condition in conjunction with Eq. (14) that $\nu_m = -\alpha \, \partial \ln \rho / \partial x$. Finally, substitution of this expression into Eq. (3) gives

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left(\alpha \frac{\partial \rho}{\partial x} \right) \tag{15}$$

[see Eq. (2.34) of Ref. [20]]. Comparison with Eq. (2) confirms the validity of Eq. (13).

Equation (15) was derived by invoking the boundary condition that the walls were insulated. However, since Eq. (15) is a differential equation, applicable at each point of the fluid, any conclusions derived therefrom must necessarily prove to be independent of this boundary condition (as well as of the specific conditions characterizing the initial steady state of the system prior to perturbing the system). The route that we chose to follow in demonstrating the validity of Eq. (15) was dictated by expediency, since it provided the simplest scheme for deriving that equation. However, the validity of Eq. (15) can be demonstrated under much more general circumstances—beginning, for example, by disturbing the steady-state temperature field (4) by, say, permanently changing the temperature of the hot wall from T_h to $T_h + \delta T_h$ (where δT_h is a small constant), while, say, keeping T_c fixed for all time, and subsequently following the temporal response of the perturbed density field $\rho(x,t)$ from its initial distribution, $\rho(x,0) = \text{const}/T(x,0)$, where $T(x,0)$ is given by Eq. (4). This would entail appropriately linearizing the respective mass, momentum, and energy equations governing the resulting single-component single-phase convec-

TABLE I. Values of the Lewis number calculated from experimental values of the Schmidt and Prandtl numbers at 0 °C.

Gas	Schmidt number $Sc = \nu/D$	Prandtl number $Pr = \nu/\alpha$	Lewis number $Le = Sc/Pr = \alpha/D$
Ne	0.73	0.66	1.11
A	0.75	0.67	1.12
H_2	0.73	0.71	1.03
N_2	0.74	0.71	1.04
O_2	0.74	0.72	1.03
CH_4	0.70	0.74	0.95
CO_2	0.71	0.75	0.95

tive heat transfer process. While we do not present the details of this perturbation scheme, when carried to fruition it serves to confirm Eq. (15), with $\delta \rho$ appearing in place of ρ.

Having established the validity of Eq. (13), it follows that Eq. (1) may be written as

$$\mathbf{U}_D = -\alpha \nabla \ln T. \tag{16}$$

V. COMPARISON WITH EXPERIMENTAL DATA

A. Preliminaries

Prior to comparing Eq. (16) with experimental data it proves convenient to recast the latter in an alternative form. In this context we define the dimensionless drift coefficient

$$C_D := \frac{\alpha}{\nu} \left(\equiv \frac{1}{Pr} \right), \tag{17}$$

in which $Pr = \nu/\alpha$ is the fluid's Prandtl number [21]. Equation (16) thus furnishes the following expression for the drift velocity:

$$\mathbf{U}_D = -C_D \nu \nabla \ln T. \tag{18}$$

Physical property-based values of C_D derived from its definition, Eq. (17), are tabulated in Table I of Ref. [8] for a number of common monatomic, diatomic, and polyatomic gases at 0 °C and atmospheric pressure. All of these values are seen to lie in the range $1.16 < C_D < 1.50$ (see also the penultimate column of Table I). The main point on which to focus with respect to the purely theoretical equation (18) is its constitutive form, wherein the gas's molecular drift velocity $\mathbf{U}_D$ is proportional to $\nu \nabla \ln T$, with the numerical value of the $O(1)$ phenomenological drift coefficient C_D lying in a relatively narrow range for a wide variety of gases.

B. Thermophoretic velocity of macroscopic particles in gases

Thermophoresis [2,3] is a phenomenon whereby a macroscopic non-Brownian particle, typically spherical, moves through an otherwise quiescent fluid undergoing heat conduction under the influence of a steady temperature gradient. The standard correlation for the thermophoretic velocity $\mathbf{U}$ [2,3] of macroscopic non-heat-conducting particles [22] in gases in the continuum region of small Knudsen numbers is

given by the experimental and theoretical formula [22,23]

$$\mathbf{U} = -C_s \nu \nabla \ln T. \tag{19}$$

Maxwell's [11] thermal creep coefficient C_s appearing therein is a dimensionless $O(1)$ phenomenological constant about which much has been written [3]. Depending upon the value of the dimensionless accommodation coefficient quantifying the interaction between the surface of the particle and the gas molecules impinging thereon, C_s is predicted theoretically [25] to lie in the range $3/4 \leqslant C_s \leqslant 3/2$, at least when the Boltzmann gas-kinetic theory intermolecular binary collision model employed in the calculation involves so-called Maxwell molecules [4,19]. The lower and upper limits cited correspond respectively to diffuse and specular reflection of the gas molecules from the particle surface.

Other molecular models, such as rigid-elastic spheres, yield slightly different values for C_s [19]. As such, the phenomenological coefficient appearing in Eq. (19) is generally regarded as being an experimentally adjustable parameter. Nevertheless, experiments involving a variety of different gases and particles of widely ranging physicochemical properties do not indicate a large variation in their respective C_s values, nor do such data reveal any systematic trends with regard to the possibility of such functional dependences. Talbot *et al.*'s [26] experimental value of $C_s \approx 1.17$, which is frequently cited, is also supported by the experimental and theoretical work of others (cf. Ref. [27]), although the experiments of other investigators, as well as alternative theories, suggest an uncertainty of perhaps as large as ±0.3 (our estimate), including, as mentioned, the possibility [8,27] that the exact value of C_s may depend upon the joint properties of the gas and particle, rather than having the same value for all gas-particle combinations.

Epstein's [23] theoretical model of thermophoresis, which underlies the correlation of experimental data embodied in Eq. (19), is based upon abandoning the conventional no-slip tangential velocity boundary condition normally imposed upon the fluid at the particle surface, in favor of a "thermal creep" slip condition due to Maxwell [11], while solving the incompressible creeping flow [28] and energy equations for the velocity of a force- and torque-free (spherical) particle moving through a fluid at rest at infinity, and there subjected to a uniform temperature gradient. The appearance of Maxwell's C_s slip coefficient in Epstein's [23] thermophoretic velocity formula, Eq. (19), originates in its role as the proportionality coefficient in Maxwell's linear relation between the magnitude of the thermal-creep-induced slip velocity along the particle surface and the surface temperature gradient prevailing thereon [11,12,29].

Perhaps the most notable feature of Eq. (19) lies in the fact that the particle's thermophoretic velocity $\mathbf{U}$ is independent of its size. This surprising attribute, coupled with Eq. (19)'s obvious constitutive equivalence to Eq. (18), as well as the theoretical and experimental indistinguishability, $C_D \approx C_s$, of the respective phenomenological coefficients appearing in each, raises the interesting question as to why the particle's macroscopic thermophoretic velocity $\mathbf{U}$ should not then qualify as being the *particle-free* gas's drift velocity $\mathbf{U}_D$? Explicitly, the hypothesis being proposed is

$$\overset{?}{\mathbf{U} = \mathbf{U}_D}. \tag{20}$$

Given the experimental and theoretical uncertainties in the value of Maxwell's [11] thermal creep coefficient C_s, including its possible dependence upon both the individual and composite physicochemical properties of the gas (e.g., monatomic or polyatomic) and particle (the latter in the form of such factors as the accommodation coefficient, surface roughness, etc.), it is not possible to state with assurance whether the proposed empirical equality (20) constitutes an exact relation embodying an important fundamental physical truth, or is merely a fortuitous contextual coincidence.

In attempting to identify the literal velocity $\mathbf{U}$ of a single non-Brownian body moving through an otherwise quiescent gas with the corresponding virtual drift velocity $\mathbf{U}_D$ of an average molecule of that gas, it is useful to recall that the drift velocity of a tagged molecule of the neat gas appearing in the Fokker-Planck equation [1] is the deterministic velocity with which that molecule would move under the action of a force, *were its Brownian motion to be miraculously suppressed*. As such, since $\mathbf{U}_D$ is a *deterministic* velocity, there is no logical contradiction in suggesting that these two velocities are, in fact, physical manifestations of the same phenomenon, namely the neat gas's (nonisothermal) Brownian motion. However, since $\mathbf{U}_D$ is not susceptible to direct experimental measurement, proof of this assertion requires either a molecular theory [4,19] or an appropriate simulation. The first of these two routes is followed in Sec. VI.

In suggesting the gas's nonisothermal (biased) Brownian motion to be the underlying source of the macroscopic thermophoretic particle movement, it is interesting to compare the neat gas's nonisothermal self-diffusivity, $D^* \equiv \alpha$, with its *isothermal* self-diffusion counterpart, say D, since the latter is, by definition, undeniably a manifestation of Brownian motion in the traditional sense. For the ratio of these two self-diffusivities we have that

$$\frac{D^*}{D} = \text{Le}, \tag{21}$$

where $\text{Le} = \alpha/D$ is the Lewis number [21]. Expressed alternatively, $\text{Le} = \text{Sc}/\text{Pr}$, in which $\text{Sc} = \nu/D$ is the Schmidt number. Since, $\text{Pr} = 2/3$ and $\text{Sc} = 3/4$ [4,21] for monatomic Maxwell molecule gases, it follows for such gases that $\text{Le} \approx 1.1$. From this point of view, nonisothermal Brownian motion in gases differs only slightly in intensity from its isothermal counterpart, an intuitively satisfying result, especially as we have confined ourselves to the case of small temperature gradients. Values of the Lewis number for other classes of gases, derived from the tabulation in Table I (data taken from Table 1.2-3 of Ref. [30]), confirm the numerical closeness of the respective nonisothermal and isothermal self-diffusivities for a variety of gases, while revealing that no systematic trend exists with regard to which of the two diffusivities is the more intense as regards its Brownian movement.

Acceptance of the hypothesis embodied in Eq. (20) as an equality would lead, naturally, to the physical interpretation of the phenomenon of thermophoresis in gases (at least in the case of nonconducting particles) as constituting a state of

motion in which the macroscopic particle is simply passively entrained in the "flowing" (particle-free) gas, despite the absence therefrom of mass motion, $\mathbf{v}_m = \mathbf{0}$. From this perspective, prior to introducing the particle therein, the gas undergoing steady-state heat conduction—while not moving in the sense of macroscopic mass movement—is, nevertheless, imagined to be "flowing" [8,9]. And it is this pre-existing state of flow which subsequently entrains and otherwise shepherds the particle following the latter's introduction into the quiescent gas. As regards terminology, we are here using the word "flow" unaccompanied by mass motion in the manner conventionally employed in the case of heat (or energy) flowing purely by conduction, without concomitant mass movement. Such flow is understood to be diffusive rather than convective.

This same issue of the passive entrainment of the macroscopic thermophoretic particle by a fluid seemingly at rest has already surfaced earlier [8,9], albeit in a rather different, nonmolecular, continuum-hydrodynamic, context involving the diffuse volume current

$$\mathbf{j}_v = -\alpha \, \nabla \ln T \qquad (22)$$

[see Eq. (14)]. The fact that the neat gas's drift and volume velocities, $\mathbf{U}_D$ and $\mathbf{v}_v \equiv \mathbf{j}_v$, respectively (the latter in the present case, where $\mathbf{v}_m = \mathbf{0}$), are, in fact, synonymous (irrespective of whether either is, in fact, the thermophoretic velocity $\mathbf{U}$ of a macroscopic particle) provides an alternative way of viewing both phenomena.

VI. GAS-KINETIC CALCULATION OF THE THERMAL DRIFT VELOCITY OF A HEAVY MOLECULE IN A LIGHT GAS: TRACER VELOCITY OF THE LIGHT GAS

A. Thermal drift velocity

de la Mora and Mercer [5] solved the Boltzmann equation for a rarefied binary gas mixture characterized both by disparate molecular masses and diluteness of the more massive species (the so-called quasi-Lorentz-gas case [[4], p. 193]) when subjected to a temperature gradient. In particular, they calculated the average force on a "heavy" molecule (corresponding to a Brownian particle of mass m_p) in a background gas of "light" molecules (mass m) for the limiting case where (i) the ratio of the molecular masses tends to zero, $m/m_p \to 0$; (ii) the binary mixture is dilute in the heavy species, $n_p/n \to 0$, where the n's represent the respective number densities; (iii) the light gas is not too far from equilibrium; and (iv) the light gas is macroscopically at rest [31]. Their results were interpreted in terms of the following Fokker-Planck equation governing the heavy Brownian particle molecular distribution function $f_p(\mathbf{u}_p, \mathbf{x}, t)$ when this species is admixed with the light gas in circumstances wherein the comparable light-gas species distribution function $f(\mathbf{u}, \mathbf{x}, t)$ [cf. Eq. (29)] is rendered slightly nonuniform by the temperature gradient:

$$\frac{\partial f_p}{\partial t} + \nabla \cdot (f_p \mathbf{u}_p) = J_p. \qquad (23)$$

In the latter, $\mathbf{u}_p$ is the velocity, $\mathbf{x}$ the position vector, and $f_p(\mathbf{u}_p)$ the density of Brownian particles in the phase space of

its variables. For the source term appearing on the right-hand side of the above, resulting from interactions with the light gas molecules, they obtained

$$J_p = \frac{k_B T}{D} \frac{\partial}{\partial \mathbf{u}_p} \cdot \left[(\mathbf{u}_p - D\alpha_T \nabla \ln T) f_p + \frac{k_B T}{m_p} \frac{\partial f_p}{\partial \mathbf{u}_p} \right], \qquad (24)$$

where D and α_T are, respectively the Chapman-Enskog [4] binary diffusion coefficient and thermal-diffusion factor. de la Mora and Mercer [5] note that the new term appearing in the latter expression, above and beyond the usual isothermal Fokker-Planck expression for the same limiting circumstances, corresponds exactly to Chapman and Cowling's [[4], p. 142] "diffusion velocity," $\bar{\mathbf{u}}_p - \bar{\mathbf{u}} \equiv \bar{\mathbf{U}}_p - \bar{\mathbf{U}} = -D\alpha_T \nabla \ln T$, representing the difference in mean molecular species velocities between the heavy and light species due solely to the temperature gradient (i.e., corresponding to circumstances where ordinary molecular diffusion and pressure diffusion are absent).

As de la Mora and Mercer observe, this velocity can be attributed to the action of a net thermal force $\mathbf{F}_p = -(D\alpha_T \nabla \ln T)/M_p$ acting, on average, upon a molecule of the heavy species, in which M_p is the mobility of the Brownian particle. This mobility is related to the mixture's binary diffusion coefficient D by the Nernst-Planck-Einstein equation, $M_p = D/k_b T$. Thus, equivalently [32],

$$\mathbf{F}_p = -\alpha_T \nabla (k_B T). \qquad (25)$$

de la Mora and Mercer refer to the thermal diffusion velocity as the "particle drift velocity," an appellation to which we fully subscribe, whence we write

$$\mathbf{U}_{M/M} = -D\alpha_T \nabla \ln T, \qquad (26)$$

where the subscript distinguishes their drift velocity from our earlier drift velocity expressions for both $\mathbf{U}_D$ and $\mathbf{U}$. The respective formulas derived by de la Mora and Mercer for D and α_T via their solution of the Boltzmann equation for the present quasi-Lorentzian, near-equilibrium, case are such that their product is given by the formula

$$D\alpha_T = \frac{3}{2} \frac{S_b}{S_B} v. \qquad (27)$$

In the above, v is the kinematic viscosity of the light gas, and

$$S_b = \int_0^\infty dc \, c^5 (c^2 - 5/2) \exp(-c^2) Q_1(c),$$

$$S_B = \int_0^\infty dc \, c^5 (-c^2) \exp(-c^2) Q_1(c), \qquad (28)$$

in which $Q_1(c) = 2\pi \int_0^\pi \sigma(\theta, c)(1 - \cos \theta) \sin \theta \, d\theta$, wherein σ is the differential scattering cross section for heavy-light collisions, and θ is the scattering angle appearing in Boltzmann's collision integral [4]. The Q_1 values depend upon the particular collision model adopted. The appearance of the integrals (28) in de la Mora and Mercer's theory derives from the fact that the slightly nonuniform light-gas molecular distribution function $f(\mathbf{u})$ is, following Chapman and Cowling [4], and in absence of net motion of the light gas [31], taken to be

TABLE II. Calculation of $C_{M/M}$ for various collision potential models

T^*	Lennard-Jones 6–12 potential[a]	Sutherland inverse 6th power potential[b]	Square-well potential[c]		Modified Buckingham 6-exp. potential[d]	
			$1/R=0.4$	$1/R=0.8$	$\alpha=12$	$\alpha=15$
			$C_{M/M}$			
0.50	−0.370	0.315	0.077	0.656	−0.073	0.019
1.00	0.015	0.386	0.097	0.647	−0.042	0.045
2.50	0.296	0.556	0.321	0.644	0.235	0.302
5.00	0.443	0.662	0.520	0.675	0.370	0.434
10.0	0.503	0.713			0.409	0.480
50.0	0.517				0.389	0.490
100	0.517				0.397	0.508
∞	0.517	0.750	0.750	0.750		

[a]Lennard-Jones: $\varphi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$.

[b]Sutherland:
$$\varphi(r)=\begin{cases}\infty & (r<\sigma),\\ -cr^{-6} & (r>\sigma).\end{cases}$$

[c]Square-well:
$$\varphi(r)=\begin{cases}\infty & (r<\sigma),\\ -\varepsilon & (\sigma<r<R\sigma),\\ 0 & (r>R\sigma).\end{cases}$$

[d]Modified Buckingham:
$$\varphi(r)=\begin{cases}\varepsilon\{6\alpha^{-1}\exp[\alpha(1-r/r_m)]-(r/r_m)^6\}/(1-6\alpha^{-1}) & (r\geq r_{max}),\\ \infty & (r\leq r_{max}).\end{cases}$$

In the latter expression, r_{max} is the value of r for which $\varphi(r)$, as given by the upper relation, has a (spurious) maximum. The ratio r_{max}/r_m is given by the smallest root of the transcendental equation $(r_{max}/r_m)^7\exp[\alpha(1-r_{max}/r_m)]=1$.

$$f(\mathbf{u})=n\left(\frac{m}{2\pi k_b T}\right)^{3/2}\exp(-c^2)[1-\boldsymbol{\varepsilon}\cdot\mathbf{c}(c^2-5/2)], \quad (29)$$

in which $\boldsymbol{\varepsilon}=6(m/2k_bT)^{1/2}\upsilon\boldsymbol{\nabla}\ln T$ is the nondimensional temperature gradient, assumed small ($|\boldsymbol{\varepsilon}|\ll1$), and $c=|\mathbf{c}|$, in which $\mathbf{c}=\mathbf{u}(m/2k_bT)^{1/2}$. Of course in the absence of the temperature gradient, namely when $\boldsymbol{\varepsilon}=\mathbf{0}$, the gas is uniform, whence the distribution (29) is Maxwellian. As such, subject to the caveat that $|\boldsymbol{\varepsilon}|\ll1$, this distribution function represents but a small departure from equilibrium, arising as a consequence of the temperature gradient.

The integrals (28) are related to integrals $\Omega^{(l,s)*}(T^*)$ defined in Hirschfelder, Curtiss, and Bird [[30], p. 527] and tabulated by them for different collision models and for various reduced temperatures $T^*=k_bT/\varepsilon$, where ε is the parameter appearing in the intermolecular potential energy function $\varphi(r)=\varepsilon f(r/\sigma)$, where r is the separation distance between the centers of the colliding molecules and σ the collision diameter. In turn, these Hirschfelder $et\ al.$ Ω integrals are identical to comparable integrals defined by Chueca, Fernandez-Feria, and de la Mora [33], namely

$$\Omega_{ls}^*(T^*)=\frac{2}{(s+1)!}\int_0^\infty\exp(-x^2)x^{2s+3}Q_l^*(xT^{*1/2})dx, \quad (30)$$

whose notation we prefer to follow here. In terms of this notation, $S_b/S_B=3\Omega_{12}^*/\Omega_{11}^*-5/2$. As noted by Hirschfelder

$et\ al.$ [[30], p. 528], the ratio $\Omega_{12}^*/\Omega_{11}^*$ (represented in several instances by the symbol C^* in Hirschfelder $et\ al.$) is very nearly unity in most cases. Accordingly, $S_b/S_B=O(1)$, whence from Eq. (27) $D\alpha_T=O(\upsilon)$, a general conclusion confirmed by Stolovitzky [35].

For purposes of comparing the quasi-Lorentzian drift velocity (26) with earlier estimates for the single-component drift velocity of the light gas, it is convenient to rewrite Eq. (26) as

$$\mathbf{U}_{M/M}=-C_{M/M}\upsilon\boldsymbol{\nabla}\ln T, \quad (31)$$

where $C_{M/M}$ is a dimensionless coefficient of $O(1)$ defined as

$$C_{M/M}=\frac{3}{2}\left(3\frac{\Omega_{12}^*}{\Omega_{11}^*}-\frac{5}{2}\right). \quad (32)$$

Based upon Hirschfelder $et\ al.$'s Ω-integral tabulations in their Appendix, Table II furnishes values of $C_{M/M}$ for various choices of potentials and reduced temperatures. The requisite inequality $|\boldsymbol{\varepsilon}|\ll1$ will obviously be more accurately satisfied the higher is the temperature. Accordingly, we have restricted the tabulation in Table II to the range $0.5\leq T^*<\infty$, representing the higher reduced temperatures for which values of the pertinent integrals are available.

In addition to the values of the $O(1)$ coefficient $C_{M/M}$ tabulated in Table II for the indicated temperatures and potentials, it is also of interest to consider the simple case

where the molecules are modeled as rigid elastic spheres. In this context, we note that the more general case where the molecules are regarded as point centers of repulsion corresponds to the potential $\varphi(r) = Kr^{-\delta}$, where K and δ are constants, the latter termed the index of repulsion [[30], p. 31]. The value $\delta = 4$ corresponds to the case of Maxwell molecules, whereas the rigid elastic sphere case corresponds to $\delta = \infty$. More properly, the latter rigid impenetrable-sphere case is represented by the potential

$$\varphi(r) = \begin{cases} \infty & (r < \sigma), \\ 0 & (r > \sigma). \end{cases} \tag{33}$$

As noted by Riesco-Chueca *et al.* [33], $\Omega_{12}^*/\Omega_{11}^* = 1 - (2/3)\delta^{-1}$ for the point center-of-repulsion case. Thus upon setting $\delta = \infty$ in the latter we obtain [35]

$$C_{\text{M/M}} = 0.75 \quad \text{(rigid elastic spheres)}. \tag{34}$$

Equation (31), derived from gas-kinetic theory, gives the drift velocity of massive Brownian molecules in a dilute solution thereof when "dissolved" in an ordinary gaseous solvent undergoing steady-state heat conduction (and which is thus at rest during the ensuing gaseous Soret-type binary separation phenomenon). Among other things, one of the remarkable aspects of the formula (31) is that this velocity is wholly independent of any properties of the massive Brownian solute particles, be they the molecule's size, shape, molecular weight, chemical constitution, or concentration (provided that the solution is sufficiently dilute). Indeed, the macroscopic velocity (31) depends solely on the microscopic properties of the solvent, the latter as embodied in the intermolecular forces acting between the solvent molecules and thus entering into the collision integral (such forces thus being implicit in the respective values of the phenomenological coefficient $C_{\text{M/M}}$ and the kinematic viscosity).

Equally striking is the fact that the molecularly derived Eq. (31) is identical in its constitutive form to the experimentally confirmed formula (19) for the thermophoretic velocity **U** of a single macroscopic (i.e., non-Brownian) particle moving through the otherwise quiescent light-gas continuum (of kinematic viscosity ν) under the influence of an externally imposed temperature gradient. It also needs to be recalled in this context that the experimental correlation (19) was derived by Epstein [23] using purely macroscopic hydrodynamics, and that it was based upon Maxwell's [11] macroscopic thermal creep, slip-velocity boundary condition, assuming the particles to be spherical. On the other hand, the molecularly derived (temperature-dependent) coefficients $C_{\text{M/M}}$ appearing in Table II, as well as the temperature-independent value indicated in Eq. (34) for rigid elastic spheres, differ somewhat from the experimentally-observed phenomenological values noted earlier in connection with Eq. (31). One is thus faced with an issue not dissimilar from that identified by the question mark surmounting the equality sign in Eq. (20).

Explicitly, given the obvious uncertainty in the value of the model-dependent coefficient $C_{\text{M/M}}$, together with comparable uncertainties in the experimental coefficients C_s, is the seeming equality,

$$\overset{?}{\mathbf{U}_{\text{M/M}} = \mathbf{U}}, \tag{35}$$

to be viewed merely as being possibly yet another coincidence, or does it have deeper physical significance? The question is compounded not only by the uncertainties in the respective values of C_s and $C_{\text{M/M}}$, but equally by questions as to the role, if any, of the conductivity ratio k_s/k [22] in relating Epstein's [23] theoretical analysis of the phenomenon of thermophoresis to experiment. In a similar vein, issues of interpretation also arise with regard to Maxwell's [11] theoretical thermal creep boundary condition, whose calculation underlies the numerical value of the slip coefficient C_s. Whereas Maxwell modeled his calculation by assuming diffuse reflection of his Maxwellian gas molecules from the particle surface, thereby obtaining the value $C_s = 3/4$, later researchers [19,25] generalized the issue by adding the notion of an accommodation coefficient to the mix, thereby rendering the theoretical value of C_s dependent upon the accommodation coefficient.

B. Tracer velocity of the light gas

Independently of whether or not Eq. (35) represents a bona fide physical relation between the kinetic-molecular velocity $\mathbf{U}_{\text{M/M}}$ of the (relatively) massive Brownian particle(s) and the hydrodynamic velocity **U** of a macroscopic particle, or is simply a fortuitous coincidence, the fact remains that $\mathbf{U}_{\text{M/M}}$ is, by definition, the "tracer velocity" of the *particle-free* light gas! After all, a (non conducting) tracer is simply an inert, passive, effectively non-Brownian particle added to a flowing fluid in order to monitor the latter's velocity through space (independently of the animating source of the fluid's motion—e.g., the temperature gradient in the present case). This view of what constitutes a tracer accords with that expressed, for example, by Kincaid *et al.* [6] in their discussion of quasi-Lorentzian transport phenomena. As discussed elsewhere [9], when conducting an appropriate tracer experiment aimed at measuring the velocity of a fluid, one must be assured that the addition of the tracer does not disturb the very fluid motion that one is attempting to measure. Normally, this would involve conducting a series of tracer-particle velocity measurements using a sequence of ever smaller, albeit non-Brownian, tracers, and subsequently extrapolating the recorded particle velocity vs particle-size measurements to zero particle size. However, since the particle velocity $\mathbf{U}_{\text{M/M}}$ given by Eq. (31) is already independent of particle size, no such passage to the limit is required in order to interpret this massive Brownian particle velocity as being the light gas's tracer velocity.

Superficially, it appears strange that the light gas can have a "velocity" since the gas is macroscopically at rest as regards its mass motion. But, as explained earlier, this drift velocity constitutes a virtual velocity, rather than describing the literal motion of an object through space, at least when a steady state is achieved by both species. On the other hand, consider the unsteady, initial-value case, where molecules of the heavy species are introduced impulsively and locally into the particle-free light gas in the neighborhood of a single point of the gas, and under circumstances where the light gas

is initially in a steady-state heat conduction mode. In this situation the Brownian molecules would presumably be seen to move, on average, deterministically through space during the course of undergoing redistribution, enroute towards eventually attaining a non-uniform, non-equilibrium, steady-state Brownian particle distribution appropriate to an expected steady Soret-type distribution (see Sec. VII B for the comparable liquid-phase non uniform colloidal particle distribution). Presumably, these massive molecules would initially, before their own Brownian motion was sensibly manifested, move stochastically towards the cold wall at a velocity $\mathbf{U}_{M/M}$, behaving on average as if each was a truly *macroscopic* body, simply moving thermophoretically through the light gas.

In this sense, were one to imagine the Brownian molecules (but not those of the light gas) to be photochromic, fluorescent, or otherwise rendered visible against the light-gas background, thus enabling them to be collectively thought of as a "dye," this initially localized dye spot would be seen to move through the fluid at the velocity $\mathbf{U}_{M/M}$. This allows a collective "tracer" interpretation to be assigned to the observed movement of the heavy species, different from the effective single-tracer particle view discussed in the preceding paragraph. Nevertheless, the resulting tracer velocity would be the same in both cases. Of course, this latter deterministic movement would be observed only initially. Eventually, the significance of the velocity $\mathbf{U}_{M/M}$ would change from literal to virtual when the appropriate Soret-like steady-state distribution of both the heavy and light molecular species was achieved.

Given that the Brownian tracer molecules possess mass, one might think that, as a result of their initial movement through the light gas, this would compromise the assumption that the light gas remains macroscopically at rest. However, because the number density of Brownian molecules is disproportionately small everywhere relative to that of the light gas (as quantified by the assumption that $n_p/n \ll 1$), no sensible mass motion of the light gas would be expected to occur in the proposed impulsive quasi-Lorentzian unsteady-state experiment, despite the concomitant tracer redistribution. That is, matters can always be arranged such the dual inequalities $m_p \gg m$ and $n_p/n \ll 1$ satisfy the composite inequality $n_p m_p/nm \ll 1$, resulting in a vanishingly small mass fraction of Brownian particles, and thus incurring no sensible macroscopic motion of the light gas.

In summary of the conclusions of this subsection, despite uncertainties in the values of the respective phenomenological coefficients $C_{M/M}$ and C_D, we believe that sufficient evidence has been advanced herein to indicate the likely correctness of the following molecularly and macroscopically based equality:

$$\mathbf{U}_{M/M} \overset{?}{=} \mathbf{U}_D, \tag{36}$$

where $\mathbf{U}_D$ is the drift velocity of the light gas, given by Eq. (16). Like the earlier equalities which were likewise surmounted by a question mark, further efforts, especially in regard to the values of the respective phenomenological C coefficients appearing in the several drift velocity formulas,

are required to establish whether or not Eq. (36) is a bona fide physical equality.

VII. LIQUIDS

A. Temperature gradient-induced single-species drift velocity in liquids

With only slight modifications, the purely kinematical arguments of Sec. II can easily be extended to (single-component) liquids. In particular, Eq. (6) derived via an elementary kinematical flux balance, appears as equally applicable to liquids as it does to gases. Given that $\mathbf{\nabla}\ln\rho = -\beta\mathbf{\nabla}T$ for a single-component isobaric fluid, either gas of liquid, it follows immediately from Eqs. (6) and (13) that

$$\mathbf{U}_D = -\alpha\beta\,\mathbf{\nabla}\,T. \tag{37}$$

In the particular case of ideal gases, where $\beta = 1/T$, the above reduces to Eq. (16). Equation (37), which is presumably applicable to both liquids and gases undergoing steady-state heat conduction, accords with its volume velocity-based counterpart [3,8,9] $\mathbf{v}_\nu = -\alpha\beta\mathbf{\nabla}T$ for such circumstances.

Equation (37) provides an opportunity to establish the analog of the thermoösmotic potential (9) for single-species liquids, at least those which obey the adiabatic law of isobarically additive volumes [20], $(\partial\hat{\nu}/\partial T)_p = C = $const, with C temperature independent. In such circumstances $\alpha\beta = kC/\hat{c}_p$. Since the thermal conductivity k has already been assumed to be constant, it follows that $\alpha\beta = $const upon supposing the specific heat to also be temperature independent. As such, in place of Eq. (37) we may write

$$\mathbf{U}_D = -\mathbf{\nabla}(\alpha\beta T). \tag{38}$$

With $\mathbf{F}$ a thermoösmotic force acting on a molecule of the liquid as in the case of gases in Sec. III, we find upon again writing $\mathbf{F} = \mathbf{U}_D/M^*$, while supposing the mobility to be sensibly independent of temperature, that $\mathbf{F} = -\mathbf{\nabla}(\alpha\beta T/M^*)$. Upon again invoking the Nernst-Planck-Einstein relation $M^* = D^*/k_b T$ relating mobility and diffusivity, and upon once again adopting the relation $D^* = \alpha$ relating the liquid's nonisothermal self-diffusivity to its thermometric diffusivity, the preceding relation may be written in the form of Eq. (11), in which the thermochemical potential now has the form

$$\mu_T = \chi k_b T, \quad \chi = \beta T. \tag{39}$$

The dimensionless coefficient χ is unity for ideal gases, whence the above relation, which is equally applicable to both liquids and gases, properly reduces to Eq. (9) in the gaseous case. Typical values of the thermal expansion coefficient β for liquids are of the order of 10^{-3}–10^{-4} K^{-1}, whence χ values at room temperature will not generally depart much from unity. As such, the thermochemical potential μ_T for typical liquids will not generally differ too much from the gaseous $k_b T$ value.

B. Ludwig-Soret effect in quasi-Lorentzian liquid-phase mixtures

Imagine that a single nonconducting *colloidal* solute particle is introduced into the neat solvent (either liquid or gas)

confined in the space between the hot and cold walls. By the term "colloidal," following Einstein [15], we refer to a foreign particle whose size is much larger than that of a molecule of the solvent, but which is nevertheless sufficiently small to undergo some degree of Brownian motion. Were the colloidal particle miraculously freed physically of this stochastic attribute, it would respond to the imposed temperature gradient in the deterministic manner of an ordinary non-Brownian (i.e., macroscopic) body. As such, it would move through the fluid with the size-independent thermophoretic velocity (38) of such a body. In what follows we pursue the consequences of the tentative hypothesis that Eq. (20) holds not only for gases but also for liquids, a subject discussed in Refs. [8,9] in the context of the theoretical volume velocity relation $\mathbf{v}_\nu = \mathbf{U}$ [3]. Thus, subject to experimental confirmation, we suppose that the size-independent drift velocity $\mathbf{U}_C$ of the colloidal particle through space is given by the expression

$$\mathbf{U}_C = -\mathbf{\nabla}(\alpha_S \beta_S T),\qquad(40)$$

with α_S the liquid solvent's thermometric diffusivity and β_S its thermal expansivity.

1. Probability density

Eventually, such a hypothetical non-Brownian colloidal particle would strike the cold wall and come to rest there. However, owing to its Brownian motion, a real colloidal particle, rather than coming eventually to rest, will permanently wander about in stochastic fashion within the solvent, in a manner quantified jointly by its diffusivity D_C and drift velocity $\mathbf{U}_C$. This stochastic motion is governed by the Fokker-Planck equation [1] $\partial P_C/\partial t + \partial J_C^{(P)}/\partial x = \delta(x-x_0)\delta(t)$ for the colloidal particle's conditional probability density $P_C(x,t|x_0,0)$, with $J_C^{(P)} = U_C P_C - D_C \partial P_C/\partial x$ the probability current of colloidal particles. (The presence of the Dirac delta function assures satisfaction of the normalization condition $\int_0^L P_C dx = 1$.)

Setting $J_C^{(P)} = 0$ gives rise to the steady-state unconditional probability distribution function

$$P_C(x) = \frac{\mathrm{Pe}}{L}\frac{\exp(\mathrm{Pe}\,x/L)}{\exp(\mathrm{Pe})-1},\qquad(41)$$

in which

$$\mathrm{Pe} = \frac{U_C L}{D_C}\qquad(42)$$

is a Peclét number. The mean position $\bar{x} = \int_0^L x P_C(x)dx$ of the particle relative to the hot wall situated at $x=0$ is

$$\frac{\bar{x}}{L} = \frac{1}{1-\exp(-\mathrm{Pe})} - \frac{1}{\mathrm{Pe}}.\qquad(43)$$

In the limiting cases where $\mathrm{Pe}\to 0$ and $\mathrm{Pe}\to\infty$, Eq. (43) properly asymptotes to the respective values $\bar{x}/L\to 1/2$ and $\bar{x}/L\to 1$, as would be expected on physical grounds.

As regards the value of the diffusivity D_C entering into the above calculation, in the case of spherical particles of radius a it is to be expected on the basis of the (isothermal)

Stokes-Einstein relation that, at least approximately,

$$D_C = \frac{k_b T}{\lambda 6\pi\eta_S a},\qquad(44)$$

with λ a dimensionless coefficient, possibly dependent upon slip [36] as well as upon the presence of the temperature gradient. In the above, η_S is the solvent viscosity.

2. Soret separation phenomena in quasi-Lorentzian binary liquid-phase mixtures

The preceding analysis applies to the case of a single colloidal solute particle dispersed in the liquid solvent. Suppose, however, that the solvent now instead contained a large number of such solute molecules, albeit present in such small concentrations that solute-solute hydrodynamic and colloidal interaction forces could both be neglected compared with solute-solvent interactions. In such circumstances, kinematical arguments similar to those employed in Sec. II can be applied to the resulting distribution of dispersed colloidal particles. Explicitly, with $n_C(x)$ the local number density of solute molecules present at a point in the fluid mixture during the steady-state one-dimensional heat conduction process taking place in the confined space between the hot and cold reservoirs, one would expect to be able to apply Einstein-like "sedimentation-equilibrium" ideas to calculate the distribution of colloidal particles therein. Here, however, in contrast with the analogous isothermal binary liquid-phase case treated by Einstein [15], the forces exerted on the colloidal particles are now thermoösmotic in nature rather than gravitational.

The situation as described above corresponds to a steady-state solute (and concomitant solvent) flux balance, wherein the thermoösmotic flux $U_C n_C$ of solute molecules driven by the temperature gradient towards the cold wall is balanced by an equal and opposite diffusion flux $-D_C dn_C/dx$, the latter tending to redistribute the solute uniformly throughout the solvent. As in the case of the single-component formula (6) (wherein $\rho = mn$), this results in present circumstances in the formula

$$U_C = D_C d\ln n_C/dx.\qquad(45)$$

Integration gives

$$n_C(x) = n_C(0)\exp\left(\frac{U_C x}{D_C}\right),\qquad(46)$$

where $n_C(0)$ is a constant whose value is determined by the fact that the total number N_C of solute molecules (per unit area) permanently present in the space between the hot and cold walls is $N_C = \int_0^L n_C(x)dx$. Of course, because we have neglected particle-particle interactions among the effectively point-size colloidal molecules, Eq. (46) is formally equivalent in its physical content to Eq. (41) governing the single-particle probability density function $P_C(x)$, the relationship between them being $n_C(x)/N_C = P_C(x)$.

Substitution of Eq. (40) into Eq. (46), in conjunction with assumed constancy of the temperature gradient dT/dx throughout the binary mixture, yields the relation

$$n_C(x) = n_C(0)\exp\left(\frac{\alpha_S\beta_S}{D_C}\frac{T_h - T_c}{L}x\right)$$

$$\equiv n_C(0)\exp\left\{\frac{\alpha_S\beta_S}{D_C}[T(0) - T(x)]\right\}, \qquad (47)$$

in which Eq. (4) has been invoked in the last step of the above. Having regarded the mixture of solute and solvent as a *binary* solution, albeit composed of species of disparate molecular size, Eq. (47) provides a quantitative rationalization of the Ludwig-Soret effect in liquids, whereby the mere existence of a temperature gradient in a two-component liquid mixture results in a nonuniform steady-state distribution of each species—the respective species in the present case being the colloidal particles and solvent [37].

This scheme for rationalizing Soret-separation thermal diffusion phenomena has already been addressed elsewhere [7]. To compare those results with comparable results obtainable from the current scheme, we note from Eq. (47) upon supposing the combination of parameters appearing therein to be sensibly independent of temperature [as already noted for the product $\alpha_S\beta_S$ in connection with Eq. (38)] that

$$\boldsymbol{\nabla}\ln n_C \equiv -(\alpha_S\beta_S/D_C)\,\boldsymbol{\nabla}\,T.$$

However, in terms of weight fractions, $w_C = (n_C m_C)/(n_C m_C + n_S m_S) \approx n_C m_C/n_S m_S$, with the latter asymptotic result valid in the dilute colloidal solutions of interest to us here, namely $w_C \ll 1$. Thus, we have that $\boldsymbol{\nabla}\ln w_C \approx -(\alpha_S\beta_S/D_C)\boldsymbol{\nabla}T \times (w_C \ll 1)$. In the case of thermal diffusion occurring in binary solutions in the absence of external forces and pressure gradients, the mass diffusion flux of species 1 relative to the mass-velocity of the mixture as a whole is given by the expression [38]

$$\mathbf{j}_1 = -\rho w_1 w_2 D_{T,12}\nabla T - \rho D_{12}\,\boldsymbol{\nabla}\,w_1$$

$$= -\rho w_1 w_2\left[D_{T,12}\,\boldsymbol{\nabla}\,T + D_{12}\,\boldsymbol{\nabla}\left(\frac{w_1}{1 - w_1}\right)\right]$$

together with a similar expression for the second species, such that, by definition, $\mathbf{j}_1 + \mathbf{j}_2 = \mathbf{0}$. In the expression for the second species, $D_{T,12} = -D_{T,21} \equiv D_T$, in which $D_T > 0$ is termed the thermal diffusion coefficient, and in which $D_{12} = D_{21} \equiv D > 0$ is the ordinary binary diffusion coefficient. Thus, when a Soret-type steady-state exists in the one-dimensional binary colloid-solvent system undergoing heat transfer in the absence of external forces, the respective flux balances $\mathbf{j}_1 = \mathbf{j}_2 = \mathbf{0}$ between thermal diffusion and ordinary diffusion require that term in square brackets appearing above is zero. Since D is common to both species, we have notationally that $D \equiv D_C$ in dilute colloidal solutions. Consequently, in such solutions the Soret steady-state balances furnish the relation

$$\boldsymbol{\nabla}\ln w_C \approx -(D_T/D_C)\,\boldsymbol{\nabla}\,T\,(w_C \ll 1)(x_C \ll 1).$$

Comparison of the latter with its counterpart displayed above reveals that in dilute colloidal solutions the thermal diffusion coefficient is given asymptotically by the expression

$$D_T \approx \alpha_S\beta_S. \qquad (48)$$

This accords with the comparable expression for the thermal diffusion coefficient in dilute colloidal liquid-phase mixtures obtained previously [7].

The conclusions derived from Eq. (48) were shown in Ref. [7] to accord reasonably well with experimental data for the thermal diffusion coefficient D_T in dilute binary polymer solutions. The quantitative extent of the disagreement was only modestly greater than the degree of uncertainty in the experimental data itself and of the respective uncertainties introduced upon assuming: (i) the applicability of the law of additive volumes; (ii) the thermodynamic ideality of the solutions; (iii) that the conductivity ratio k_s/k factor can be disregarded; and (iv) that the polymer concentration was sufficiently small to be able to neglect polymer-polymer interactions. (Given the ability of linear polymers chains to become entangled, the latter was probably the weakest of these assumptions.) As discussed in Ref. [7], such agreement was interpreted as offering implicit support for the volume velocity approach to thermophoretic motion in liquids. Since the single colloidal particle analysis leading to Eq. (48) was shown in Sec. V to be consistent with the fact that $\mathbf{U}_C \equiv \mathbf{v}_\nu$ (albeit demonstrated there only for the case of gases), we regard such agreement as providing indirect experimental evidence favoring the hypothesis made in the opening paragraph of this subsection, following Eq. (44), and underlying the proposed extension of our drift velocity theory from that for single particles to two-component interpenetrating liquid-phase continua. Of course, the comparable gas-phase analysis of Sec. VI offers further general support for the hypothesis.

3. Thermoösmotic forces in liquid-phase mixtures

In closing this subsection we note that Eq. (47), though derived by strictly kinematical sedimentation-equilibrium-type arguments, may be given a *dynamical* interpretation. In particular, this equation can be recast into the Boltzmann-distribution-like form

$$n_C(x) = n_C(0)\exp\left\{-\frac{[\mu_C(x) - \mu_C(0)]}{k_b T}\right\}, \qquad (49)$$

in which

$$\mu_C(x) = \frac{\alpha_S\beta_S}{M_C}T(x), \qquad (50)$$

wherein we have invoked the Nernst-Planck-Einstein equation, $D_C = k_b T M_C$. Here, μ_C is interpreted as representing the "thermochemical potential" of a solute molecule in the binary solution, with the potential increasing (algebraically) in the direction of increasing temperature, at least over the range of temperatures for which $\beta_S > 0$. The fictitious thermoösmotic force $\mathbf{F}_C$ (per solute molecule) derived from the above potential, namely

$$\mathbf{F}_C := -\boldsymbol{\nabla}\mu_C, \qquad (51)$$

is thus seen to be of the form

$$\mathbf{F}_C = -\frac{\alpha_S \beta_S}{M_C} \boldsymbol{\nabla} T. \tag{52}$$

Equation (50), which played a fundamental role in our Brownian motion model of thermal diffusion phenomena in liquids [7], constitutes the two-component analog of the single-component relation (39). Consistency of Eq. (50) with the latter can be seen by noting that $M_C \equiv M_S^* = D_S^*/k_b T$ when the solute molecules become indistinguishable from those of the solvent, since D_S^* is the solvent's nonisothermal self-diffusivity. But, according to the results of Sec. IV, $D_S^* = \alpha_S$, whereupon Eq. (50) is indeed seen to be identical to Eq. (39).

A sidelight of the present calculation resides in the existence of the Boltzmann-like physical-space molecular distribution function (49), shown here to be applicable despite the distinctly nonequilibrium nature of the heat conduction process, at least when departures from equilibrium are small. In effect, Boltzmann's classical *isothermal* equilibrium distribution function is seen to remain viable in present circumstances, even though the system is not at thermodynamic equilibrium. In our previous analysis [7] we arbitrarily *assumed* the Boltzmann distribution to apply in the presence of a steady temperature gradient. The present, more rigorous, analysis supports that conjecture, at least in the case of small gradients. In a certain sense, this issue is closely related to a similar issue in the case of gases, as typified, for example, by the physical significance of Eq. (10), wherein a real potential is balanced by a thermochemical potential.

VIII. DISCUSSION

A. Boundary conditions

Issues other than those outlined in the preceding sections intrude into our attempt to establish the physically common origin of the respective single-component drift and tracer velocities, flux densities, and currents, here respectively identified by the symbols $\mathbf{U}_D, \mathbf{U}, \mathbf{v}_\nu$, and $\mathbf{U}_{M/M}$. Differences could conceivably arise from a possible distinction between the respective mobilities of macroscopic bodies and molecules in regard to the question of "stick" or "slip" boundary conditions, certainly when attempting to interpret the respective velocities $\mathbf{U}$ and $\mathbf{U}_D$ of these bodies in terms of the forces acting upon them. Thus, using molecular dynamic simulations, Schmidt and Skinner [36] confirm the molecular dynamics simulation results of other researchers with regard to the value of the coefficient c appearing in the isothermal Stokes-law resistance formula $M^{-1} = c\pi\eta a$ for the mobility of a spherical solute particle of the same radius a and mass m as that of a tagged molecule of the neat fluid. Explicitly, they find that $c = 4.5$. This differs from the Stokes-Einstein value [15] of $c = 6$ for the stick case, as well as from the perfect slip value of $c = 4$ [28]. As such, this finding raises the delicate question of whether or not, all other things being equal, the respective mobilities of non-Brownian (i.e., macroscopic) objects and Brownian molecules of the same size (and mass) can be treated on the same footing. Resolution of the possible relevance of this observation to the issues under discussion lies beyond the scope of the present work.

Intimately related to the latter issue are the following facts. Suppose we accept the value of the molecularly derived coefficient $C_{M/M}$ appearing in Eq. (34), which, incidentally, is also the value given by several other collision models in Table II, at least at large reduced temperatures. We then have from Eq. (31) that the tracer-derived drift velocity for single-component gases is $\mathbf{U}_{M/M} = -(3/4)\nu\boldsymbol{\nabla}\ln T$. On the other hand, inasmuch as Maxwell [11] determined his thermal creep coefficient to be $C_s = 3/4$, Epstein's [23] theoretical hydrodynamic calculation, based thereon, of the thermophoretic velocity of a (nonconducting) macroscopic particle moving through a gas, predicted that $\mathbf{U} = -(3/4)\nu\boldsymbol{\nabla}\ln T$. Of course, in this circumstance, the question mark is removed from Eq. (35). To the extent then that the equality $\mathbf{U} \equiv \mathbf{U}_{M/M}$ is an exact physical relation, how, precisely, is one to understand *physically* the relationship between the Maxwell-Epstein mass-slip hydrodynamic boundary condition on a macroscopic particle and the notion of a slip boundary condition on a molecule, however massive? This and other fundamental questions remain to be addressed.

B. Precursors of the notion of a drift velocity in nonisothermal fluids

Attempts by others, dating back to at least Chapman [39] in 1928, to introduce the notion of the "drift" of a massive Brownian particle caused by a temperature gradient in a fluid, either gas or liquid, are reviewed by Peskir [40]. We refer here not to the literal motion of a single Brownian particle, but rather to the average behavior of a dilute collection of such massive molecules, viewed in the context of being one of the two molecular species present in a binary solution, albeit present in such relatively small amounts that solute-solute interactions can be neglected compared with solvent-solvent and solvent-solute interactions. The latter conditions correspond to what in the cases of gases is termed a quasi-Lorentzian fluid [[4], p. 193; [6]].

Without claiming thoroughness in exploring the prior literature on the transport of Brownian particles in single-component fluids subject to temperature gradients, we note that a concept equivalent to that of our molecular drift velocity $\mathbf{U}_D$ is necessarily implicit in the nontraditional work of Streater. Thus Streater, using his nonlocal statistical dynamics-based molecular transport model [42], whose realm of applicability is said to extend beyond that of the Boltzmann equation [4,19], succeeds in identifying the presence of both Soret and Dufour effects in single-component gases composed of molecules possessing repulsive cores [43]. Such single-species effects—the former as reflected in our drift velocity (and the latter possibly by our proposed modification [20] of Fourier's law of heat conduction)—are not predicted by classical Boltzmann equation-based statistical-mechanical arguments, wherein Soret and Dufour effects are claimed [4] to be physically possible only in multicomponent mixtures.

In any event, to refer to the velocity appearing in Eq. (1) as either the *particle* or *Brownian* drift velocity, as have Chapman [39], de la Mora and Mercer [5], and others, is really a misnomer, since this quantity is actually the drift

velocity of the neat, single-component fluid. As such, the notion of a drift velocity has nothing whatsoever to do with any particle, unless the particle or Brownian entity being referred to is a molecule of the single-component fluid itself! That is, the notion of a drift velocity in the sense being referred to in this paper, is a strictly single-component concept. It is precisely that single-species connotation which distinguishes it from the notion of a drift velocity in the sense associated with the common usage of the latter term when discussing external force-driven molecularly-based velocities in connection with, say, gravitational or centrifugal sedimentation, or electrophoresis, in solutions—which processes clearly refer to two-species situations. There, the drift velocity depends, *inter alia*, upon the properties of both species, as well as upon the magnitude of the external force, rather than being an intrinsic attribute of the pure solvent.

Closely related to this issue of terminology is that of the fluid's "tracer velocity," which clearly refers to motion of the neat fluid as monitored by the addition a foreign body thereto. Confusion exists in the literature with regard to the notion of a tracer. Certainly in the case where a temperature gradient exists, the term fails to distinguish between the respective cases where the distinguishable entity being introduced, namely the tracer, is a single macroscopic (effectively non-Brownian) particle or a dye. In the former case, owing to its relative massivity, the tracer will not generally move with the mean mass velocity $\mathbf{v}_m$ of the fluid. Rather, it will move thermophoretically through the fluid owing to the presence of the temperature gradient. On the other hand, the dye, whose molecules are assumed to be comparable in size, and hence molecular mass, to those of the fluid being monitored, will, on average, move at the same mass velocity $\mathbf{v}_m$ as the solvent. Accordingly, since the latter is macroscopically at rest, the dye will presumably not move. As discussed elsewhere [9], the distinction between the respective particle-tracer and dye experiments is important in understanding precisely what is meant by the "velocity" of the fluid. In particular, is the latter a macroscopic dynamical attribute, namely the fluid's specific momentum density, or is it a macroscopic kinematical attribute, namely the fluid's mass velocity?

Demonstration via simulation of the existence of a drift velocity in single-component gases may be implicit in the recent DSMC calculations of Tysanner and Garcia [44]. These authors detected a "measurement bias" in the gas's SAM ("sample-averaged measurements") velocity from its expected zero-mean CAM ("cumulative-average measurement") value. This occurred under exactly the same steady-state heat-conduction circumstances as are addressed in our paper, namely a gas confined within a finite one-dimensional region bounded between heat reservoirs [45].

C. Mean-squared molecular displacements accompanying nonisothermal Brownian motion

Consider the situation described at the beginning of Sec. II, involving a single-component gravity-free fluid confined between two laterally unbounded isothermal walls while undergoing a steady one-dimensional heat conduction process.

Imagine that one of the molecules, initially far from either wall, is tagged, and that its motion through space is subsequently monitored over the course of time. After undergoing a sufficient number of collisions with other fluid molecules the tagged molecule will manifest Brownian motion, quantified by its mean-square displacement $\overline{(\Delta x)^2} = 2D^* \Delta t$ during a time interval Δt (provided that during this interval the particle has not collided with wall, certainly not frequently). In view of Eq. (13), we thus expect that

$$\overline{(\Delta x)^2} = 2\alpha \Delta t. \tag{53}$$

In principle, the nonisothermal Brownian motion experiment pertaining to this relation appears capable of being performed in practice or, alternatively, simulated. In any event, given the relatively small difference between the respective isothermal and nonisothermal diffusivities as reflected in the magnitudes of the Lewis numbers reported in Table I, it may not prove easy experimentally to clearly distinguish the nonisothermal self-diffusivity expected on the basis of Eq. (53) from the corresponding *isothermal* self-diffusivity, say D, that would prevail in the absence of temperature gradients.

D. Summary and commentary

This paper has introduced the notion of the existence of a drift velocity $\mathbf{U}_D$ in a single-component quiescent fluid, gas, or liquid, arising from the presence of a temperature gradient. The focus throughout was primarily on gases. The drift velocity, as given by Eq. (1), namely $\mathbf{U}_D = -D^* \nabla \ln T$ with $D^* = \alpha$ as in Eq. (13), can be traced to the gas's Brownian motion, the latter as quantified by the single-component gas's nonisothermal self-diffusion coefficient D^* acting in concert with the temperature gradient ∇T. Explicitly, Eq. (16) may be regarded as having been derived by purely kinematical, sedimentation-equilibrium-type arguments, analogous to those adopted by Einstein [15] in his analysis of isothermal Brownian motion in binary mixtures, in which, at steady state, a drift-velocity flux of molecules was balanced by an equal and opposite diffusion flux. An alternative and independent dynamic and thermodynamic derivation of Eq. (1) was presented, based upon the notion of a gradient in the gas's thermoösmotic potential, $\mu_T = k_b T$, serving as the animating force $\mathbf{F} = -\nabla \mu_T$ underlying the gas's drift velocity.

The thermal drift velocity $\mathbf{U}_D$ was shown to be indistinguishable, both constitutively and phenomenologically, from the experimentally and theoretically established thermophoretic velocity $\mathbf{U}$ of a finite-size, macroscopic (effectively non-Brownian), non-heat-conducting particle moving through the gas in the continuum regime of Knudsen numbers. Based upon this empirical agreement of the particle's thermophoretic velocity $\mathbf{U}$ with the gas's drift velocity $\mathbf{U}_D$ (at least to within moderate experimental and theoretical uncertainties), it was hypothesized that they both stemmed from the same molecular physics, namely the gas's thermally biased Brownian movements. Modulo some small uncertainty in the respective values of the various phenomenological coefficients, collectively represented by the symbol C appearing in the several constitutively identical expressions for the

gas's drift velocity $C\nu\nabla\ln T$, this hypothesis appears to be confirmed by the quasi-Lorentzian calculation outlined in Sec. VI. Yet another interpretation of the gas's drift velocity was provided by noting its formal equivalence with the single-component gas's purely diffusive volume velocity $\mathbf{v}_\nu \equiv \mathbf{j}_\nu$. Finally, it was pointed out that our notion of the existence of a drift velocity in a single-component fluid subjected to a temperature gradient appears as applicable to liquids as it is to gases. This was evidenced by the agreement (again, modulo modest theoretical and experimental uncertainties) of predictions based thereon with Soret-type thermal diffusion experiments performed with binary liquid-phase solutions whose solute molecules, present in only relatively small amounts, were much more massive than those of the solvent.

Overall, in circumstances where temperature gradients exist, pertinent issues have been raised with respect to the proposed equality of the fluid's tracer velocity, representing a real motion through space, and the fluid's drift velocity, which is virtual rather than real. Are the "slip" coefficients C appearing in the common constitutive expression $C\nu\nabla\ln T$

for each of these velocities the same, or are they intrinsically different? And, if the latter, how do the individual and composite physical properties of the chemical species and particle affect C? These and closely related issues point up the need for critical experiments as well as simulations to help resolve these questions.

Note added in proof: The existence in nonisothermal systems of the thermoösmotic force given by Eqs. (11) and (9) was conjectured by Landauer [R. Landauer, Physica A **194**, 551 (1993)] on the basis of an extended theory of fluctuations in nonequilibrium systems, and referred to by him as the "blowtorch effect." Others have since elaborated upon his *blowtorch* theorem [cf. Superlattices and Microsturctures **23**, Nos. 3/4, dedicated to Rolf Landauer on his 70th birthday; M. Bekele, S. Rajesh, G. Ananthakrishna, and N. Kumar, Phys. Rev. E **59**, 143 (1999); G. Stolovitzky and E. S. C. Ching, Phys. Lett. A **255**, 11 (1999); S. Fedade and M. Bekele, Eur. Phy. J. B **26**, 369 (2002).]

---

[1] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981); H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1984).

[2] G. M. Hidy and J. R. Brock, *The Dynamics of Aerocolloidal Systems* (Pergamon, Oxford, 1970); L. Waldmann and K. H. Schmitt, in *Aerosol Science*, edited by C. N. Davies (Academic Press, London, 1966) p. 137; B. V. Derjaguin and Yu. I. Yalamov, in *Topics in Current Aerosol Research*, edited by G. M. Hidy and J. R. Brock (Pergamon, Oxford, 1972) p. 2; F. Zheng, Adv. Colloid Interface Sci. **97**, 255 (2002).

[3] H. Brenner and J. R. Bielenberg, Physica A **355**, 251 (2005).

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

[5] J. Fernandez de la Mora and J. M. Mercer, Phys. Rev. A **26**, 2178 (1982).

[6] J. M. Kincaid, E. G. D. Cohen, and M. López de Haro, J. Chem. Phys. **86**, 963 (1987).

[7] J. R. Bielenberg and H. Brenner, Physica A **356**, 279 (2005).

[8] H. Brenner, Phys. Rev. E **70**, 061201 (2004).

[9] H. Brenner, Physica A **349**, 60 (2005).

[10] Lateral unboundedness is necessary so as to avoid dealing with complications arising from the presence of bounding sidewalls, on which Maxwell's thermal creep slip-velocity boundary condition [11,12] would have to be satisfied. And, due to this slip, the presence of sidewalls would give rise to a thermal transpiration [13] mass motion of the gas, even in the absence of the particle.

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

[12] D. E. Rosner and D. H. Papadopoulos, Ind. Eng. Chem. Res. **35**, 3210 (1996).

[13] J. R. Bielenberg and H. Brenner, J. Fluid Mech. (to be published).

[14] K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge, London, 1952).

[15] A. Einstein, Ann. Phys. **17**, 549 (1905); reprinted (with corrections) in *Investigations on the Theory of the Brownian Movement*, edited by R. Fürth (Dover, New York, 1956).

[16] S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability* (Oxford University Press, London, 1961); A. Manela and I. Frankel, Phys. Fluids **17**, 036101 (2005).

[17] R. F. Probstein, *Physicochemical Hydrodynamics*, 2nd ed. (Wiley, New York, 1994), pp. 14 and 19.

[18] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961); K. G. Denbigh, *The Principles of Chemical Equilibrium* (Cambridge, London, 1955).

[19] Y. Sone, *Kinetic Theory and Fluid Dynamics* (Birkhäuser, Boston, 2002).

[20] H. Brenner, Physica A **349**, 11 (2005).

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

[22] Equation (19) is valid only for non-heat-conducting particles. More generally, according to theory [3,23], the thermophoretic velocity $\mathbf{U}$ of a spherical particle of thermal conductivity k_s in a gas whose thermal conductivity is k is modified by the presence of a term $1+k_s/2k$ in the denominator of Eq. (19). In contrast with a macroscopic particle, a molecule has neither a definite "shape" nor "interior" to which a thermal conductivity k_s can be assigned. As such, our eventual comparison of the particle's thermophoretic velocity $\mathbf{U}$, Eq. (19), with the comparable formula for the gas's molecularly-based drift velocity $\mathbf{U}_D$, Eq. (18), can only be rationally affected in the case of a passive, non-heat-conducting particle. Moreover, in such circumstances, Eq. (19) holds irrespective of the particle's shape as well of its orientation relative to the temperature gradient [3,24].

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

[24] A. Mohan and H. Brenner, Phys. Fluids **17**, 038107 (2005).

[25] F. Sharipov, Eur. J. Mech. B/Fluids **22**, 133 (2003); F. Sharipov and D. Kalempa, Phys. Fluids **16**, 759 (2004); F. Sharipov, Phys. Rev. E **69**, 061201 (2004).

[26] L. Talbot, R. K. Cheng, R. W. Schefer, and D. R. Willis, J.

Fluid Mech. **101**, 737 (1980); L. Talbot, in *Rarefied Gas Dynamics*, edited by S. S. Fisher (AIAA, New York, 1981) Part 1, p. 467.

[27] B. V. Derjaguin, Ya. I. Rabinovich, A. I. Storozhilova, and G. I. Shcherbina, J. Colloid Interface Sci. **57**, 451 (1976).

[28] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Kluwer, Dordrecht, 1987).

[29] Were the classical no-slip condition to be retained in Epstein's [23] theoretical derivation of Eq. (19), corresponding to setting $C_s=0$ therein, the particle would not move. Rather, it would simply remain fixed in place. In that event the resulting transport processes scenario, with $\mathbf{U}=0$, would simply be one of steady-state heat conduction through the gas and around the immobile nonconducting particle (as well as through the particle's interior, were the latter to be heat conducting). In particular, no force would act upon the particle.

[30] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[31] de la Mora and Mercer [5] actually calculated the light-gas distribution function for the more general case where the light gas is subjected to a relatively weak shearing motion. However, in the subsequent calculations we have set their light-gas shear flow velocity V to zero, as this represents the present case of interest.

[32] This expression for the force acting on a molecule should be compared with Eq. (8), bearing in mind that the latter result, based on its derivation, is expected to be valid only in the single-component gas case. As pointed out by de la Mora and Mercer [5], α_T is of order unity for ordinary gas mixtures, perhaps implicitly suggesting that their force formula might be applicable to ordinary mixtures despite the disparity in molecular masses used in its derivation. Of course, in order to be compared with the single-component gas case, namely Eq. (8), the value of α_T must refer not to the quasi-Lorentzian disparate mass case, but rather to the isotopic case, where the two species have the same molecular mass. Experimental and theoretical values of the thermal diffusion factor α_T are available [4,14].

[33] P. Riesco-Chueca, R. Fernandez-Feria, and J. Fernandez de la Mora, Phys. Fluids **30**, 45 (1987).

[34] G. Stolovitzky, Phys. Lett. A **241**, 240 (1998); see his Eqs. (10) and (1).

[35] By way of confirming the internal consistency of the general results of de la Mora and Mercer [5], it is interesting to note that in the case of Maxwell molecules, for which $\delta=4$, one obtains $C_{\mathrm{M/M}}=0$ identically. This conclusion is consistent with the fact that Maxwell molecules are known [[4], p. 191] to furnish a zero-valued thermal diffusivity.

[36] J. R. Schmidt and J. L. Skinner, J. Chem. Phys. **119**, 8062 (2003); , J. Phys. Chem. B **108**, 6767 (2004).

[37] Explicitly, this view of the mechanical mixture as a two-species solution of molecules is based on Einstein's view [15] of the colloidal particles as solute molecules. To quote Einstein: "According to this theory [namely, the molecular-kinetic theory of heat], a dissolved molecule differs from a suspended body only in size…," as quoted with emphasis in Einstein's *Miraculous Year*, edited by J. Stachel (Princeton University Press, Princeton, NJ, 1998), pp. 86–87.

[38] S. R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics, p. 278 (North-Holland, Amsterdam, 1962). Note that the quantity designated as being the thermal diffusion coefficient in the case of gases [4,14] and identified in that case by the same symbol D_T as is used for liquids, is different from that defined here. Indeed, the two coefficients do not even have the same dimensions, typical units of D_T, respectively, being $\mathrm{cm}^2 s^{-1}$ for gases and $\mathrm{cm}^2 s^{-1} K^{-1}$ for liquids.

[39] S. Chapman, Proc. R. Soc. London, Ser. A **119**, 34 (1928).

[40] G. Peskir, Stoch. Models **19**, 383 (2003). However, this review appears to have overlooked the highly relevant contribution of de la Mora and Mercer [5], as well as the precursor and subsequent follow-up researches pertaining thereto [34,41].

[41] J. Fernandez de la Mora, Phys. Rev. A **25**, 1108 (1981); R. Fernandez-Feria and P. Riesco-Chueca, Phys. Rev. A **36**, 4940 (1987); J. Fernandez de la Mora and R. Fernandez-Feria, Phys. Fluids **30**, 740 (1987).

[42] R. F. Streater, *Statistical Dynamics* (Imperial College Press, London, 1995).

[43] R. F. Streater, Proc. R. Soc. London, Ser. A **456**, 205 (2000); Open Syst. Inf. Dyn. **10**, 3 (2003).

[44] M. W. Tysanner and A. L. Garcia, J. Comput. Phys. **196**, 173 (2004).

[45] However, the nonzero SAM velocity observed by these investigators, which arises from correlations between momentum and density fluctuations, was directed from the cold towards the hot wall, exactly opposite to the direction found by us for the virtual drift velocity.