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Phoresis in fluids

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This paper presents a unified theory of phoretic phenomena in single-component fluids. Simple formulas are given for the phoretic velocities of small inert force-free non-Brownian particles migrating through otherwise quiescent single-component gases and liquids and animated by a gradient in the fluid's temperature (thermophoresis), pressure (barophoresis), density (pycnophoresis), or any combination thereof. The ansatz builds upon a recent paper [Phys. Rev. E **84**, 046309 (2011)] concerned with slip of the fluid's mass velocity at solid surfaces—that is, with phenomena arising from violations of the classical no-slip fluid-mechanical boundary condition. Experimental and other data are cited in support of the phoretic model developed herein.

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I. INTRODUCTION

Despite our exclusive focus on phoretic-particle movement through single-component fluids, we begin by considering the phenomenon of barodiffusion or pressure-driven diffusion in binary mixtures [1–3]. The phenomenon arises when a pressure gradient ∇p applied to a quiescent binary mixture whose temperature and composition are uniform throughout gives rise to mass fluxes of both species $\mathbf{j}_i$ $(i = 1,2)$—these representing the respective barycentric diffusion fluxes of species 1 and 2 relative to the mixture's mass velocity $\mathbf{v}_m$ (with the latter velocity being zero in the present quiescent fluid case). These species fluxes exist despite the absence from the fluid of both concentration gradients (that would otherwise give rise to molecular diffusion [4]) and temperature gradients (which would otherwise give rise to thermal diffusion [5]). Pressure diffusion is important, for example, in connection with the use of ultracentifuges to separate colloidal or polymer molecules from the solvent in which they are dissolved or are dispersed [1,3].

In the absence of body forces acting upon either of the binary species, the constitutive equations for the barycentric fluxes are [1,2]

$$\mathbf{j}_1^{(p)} = \rho D^{(p)} \nabla \ln p, \tag{1a}$$

$$\mathbf{j}_2^{(p)} = -\rho D^{(p)} \nabla \ln p, \tag{1b}$$

in which $D^{(p)} \geqslant 0$ is the pressure diffusion coefficient and wherein $\mathbf{j}_1^{(p)} + \mathbf{j}_2^{(p)} = \mathbf{0}$ owing to the fluid being macroscopically at rest (i.e., quiescent: $\mathbf{v}_m = \mathbf{0}$). $D^{(p)}$ is proportional to the binary diffusion coefficient D appearing in Fick's law [4] and depends *inter alia* upon the composition of the mixture as well [1,2,6]. As $D^{(p)}$ has the units of a diffusivity, the ratios $\mathbf{j}_1^{(p)}/\rho = \mathbf{U}$ and $\mathbf{j}_2^{(p)}/\rho = -\mathbf{U}$ each have the units of a velocity $\mathbf{U}$. Barodiffusion of both species is represented collectively by the relation [1],

$$\mathbf{U} = D^{(p)} \nabla \ln p, \tag{2}$$

where the species velocity $\mathbf{U}$ is measured relative to the mixture's mass velocity $\mathbf{v}_m$, namely, the velocity appearing in the continuity equation,

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

For some authors, the word "barophoresis," constituting part of the subject matter of the present paper, is merely a synonym for the word "barodiffusion." Schimpf and Semenov [7] take exception to that view. They argue that the two constitute separate subjects, noting that barodiffusion involves a collective phenomenon resulting from the Brownian motions of a group of molecules as directionally biased by the pressure gradient, whereas, barophoresis—like all phoretic motions—involves the directionally biased deterministic motion of but a single non-Brownian macroscopic particle animated by the externally imposed pressure gradient. Terminologically, these two subjects are the respective counterparts of the better-known phenomena of thermal diffusion [5] and thermophoresis [8], wherein the driving force for both then is a temperature gradient ∇T rather than a pressure gradient.

That said, despite the large amount of literature on barodiffusion in mixtures and in contrast with its thermal diffusion or thermophoresis counterpart, we are unaware of any literature concerned with the subject of barophoresis as a single-component phenomenon. Despite this lack of a prior history, in this paper [see Eq. (32)], we argue that not only does the theoretical possibility of barophoresis exist, but that the particle's barophoretic velocity $\mathbf{U}$ through an otherwise quiescent fluid obeys a relation analogous to Eq. (2), namely,

$$\mathbf{U} = \alpha \kappa \nabla p, \tag{4}$$

at least when the particle is both force free and physicochemically inert with respect to its interactions with the fluid. In the above,

$$\alpha = \frac{k}{\rho \hat{c}_p}, \tag{5a}$$

and

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \tag{5b}$$

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are, respectively, the fluid's thermometric diffusivity and compressibility coefficients wherein k is the thermal conductivity and $\hat{c}_p$ is the isobaric specific heat.

Equation (4) will be seen to apply to both gases and liquids. In the case of ideal gases, for which $\kappa = 1/p$, we, thus, obtain

$$\mathbf{U} = \alpha \nabla \ln p. \tag{6}$$

(See also Secs. IV B and IV C.) This expression for the barophoretic velocity in a single-component fluid is, obviously, the analog of the barodiffusion velocity (2) in a two-component mixture in which the thermometric diffusivity α is the counterpart of $D^{(p)}$, the pressure diffusivity. Our paper is, initially, devoted to deriving the barophoretic velocity formula, Eq. (4). Subsequently, we seek its extension to the more general case of pycnophoresis [9].

A. Phoresis as a topic of general interest

Viewed as a generality encompassing all classes of gradients, phoresis is a phenomenon whereby, as a consequence of a driving force arising from an inhomogeneity, in some attribute of the particle-free (undisturbed) fluid—namely, the fluid's temperature, pressure, or density—a small inert particle moves relative to the fluid's local undisturbed mass velocity $\mathbf{v}_m$ that would exist at the point presently occupied by the particle were the particle not to be present. Thermophoresis [8], which is driven by a temperature gradient, constitutes the prime example of phoretic motion. (Electrophoresis, driven by gradients in electric potential, though a better-known phoretic phenomenon, does not constitute an example of this class of phoretic processes since it does not occur in single-component fluids.)

II. SLIP OF THE FLUID'S MASS VELOCITY IN SINGLE-COMPONENT FLUIDS

As will be shown in this paper, pycnophoresis [9], occurring in single-component fluids, is caused by a slip of the fluid's mass velocity along the particle's surface [10] with the slip driven by the existence in the fluid of a density gradient $\nabla\rho$. The latter can arise, for example, from a temperature gradient, resulting in thermophoresis, or from a pressure gradient in a (compressible) isothermal fluid, giving rise to the phenomenon of barophoresis.

The general theory underlying our model of phoretic phenomena is a natural outgrowth of our paper on bi-velocity hydrodynamics [11] when combined with our recent proposal [10] of a general formula for the slip velocity of mass along a solid surface. Bi-velocity theory amends the Navier-Stokes-Fourier (NSF) equations by incorporating therein a second independent velocity, the fluid's volume velocity $\mathbf{v}_v$ [12], supplementing the fluid's mass velocity $\mathbf{v}_m$. Also amended is the classical no-slip boundary condition at solid surfaces, which is changed from no-slip of the mass velocity in the NSF case to no-slip of the volume velocity in the bi-velocity (amended NSF) case [10].

The volume velocity is defined constitutively by its role in the thermodynamic rate-of-working term $\nabla \cdot (\mathbf{P} \cdot \mathbf{v}_v)$ appearing in the conservation equation [11] governing the transport of energy. In bi-velocity theory, the difference between the mass and the volume velocities is represented by the relation,

$$\mathbf{v}_v - \mathbf{v}_m = \mathbf{j}_v, \tag{7}$$

in which the diffuse volume flux $\mathbf{j}_v$, defined by the above expression, obeys the constitutive equation,

$$\mathbf{j}_v = \alpha \nabla \ln \rho. \tag{8}$$

The latter applies to both gases and liquids. In combination, the above expressions give

$$\mathbf{v}_v - \mathbf{v}_m = \boldsymbol{\alpha} \nabla \ln \rho. \tag{9}$$

This relation is applicable throughout the fluid including on its bounding surfaces, whether these surfaces are solid or otherwise.

The manner in which Eq. (9) enters into the fluid mechanics of phoretic motion stems from the fact that the physically appropriate [10] tangential velocity boundary condition to be imposed upon solutions of the amended NSF bi-velocity equations at the solid surface ∂V of the phoretic particle is one of no slip of the fluid's volume velocity,

$$(\mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}) \cdot (\mathbf{v}_v - \mathbf{U}) = \mathbf{0} \quad \text{on } \partial V, \tag{10}$$

or, what is equivalent,

$$(\mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}) \cdot (\mathbf{v}_m - \mathbf{U}) = -\alpha \nabla_s \ln \rho \quad \text{on } \partial V. \tag{11}$$

Here, $\mathbf{I}$ is the dyadic idemfactor, $\hat{\mathbf{n}}$ is a unit outer normal vector on ∂V, and $\nabla_s = (\mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}) \cdot \nabla$ is the surface-gradient operator. $\mathbf{U}$ is the velocity of the solid. By characterizing Eq. (11) as being physically appropriate is simply meant that it accords with all of the experimental data, however limited, with which it has, thus far, been compared (while, at the same time, not violating any known physical law).

In addition to this tangential velocity boundary condition, the standard normal velocity boundary condition is [13]

$$\hat{\mathbf{n}} \cdot (\mathbf{v}_m - \mathbf{U}) = 0 \quad \text{on } \partial V. \tag{12}$$

This boundary condition specifies the impenetrability of the particle's surface to mass flow. In combination with Eq. (10), this gives

$$\mathbf{v}_m - \mathbf{U} = -\alpha \nabla_s \ln \rho \quad \text{on } \partial V, \tag{13}$$

showing that the fluid's mass velocity can slip at the surface of the solid only when the fluid is compressible.

Experimental and theoretical confirmation of this mass velocity boundary condition at solid surfaces is discussed in Ref. [10], primarily for the case of gases. Agreement in circumstances where the density gradient in Eq. (13) arises from an isobaric temperature gradient ∇T was confirmed [8] using data for the thermophoretic velocity of small non-heat-conducting particles. Agreement in circumstances where the density gradient arose from an isothermal pressure gradient ∇p was confirmed using data obtained for pressure-driven compressible flows in microchannels [14,15].

A. Tangential-velocity boundary condition

Equation (10), representing the boundary condition imposed on the fluid's volume velocity at a solid surface, only furnishes the tangential boundary condition. However, the solution of bi-velocity boundary-value problems also requires knowledge of the normal component of the volume velocity. In previous cases [10] relating to experimental confirmation of Eq. (10), this normal velocity boundary condition was automatically supplied by the nature of the physical arrangements of the experiment itself, rather than being independently imposed upon $\mathbf{v}_v$.

Explicitly, data for the thermophoretic experiments used to confirm Eq. (10) were limited to the case of non-heat-conducting particles (or, equivalently, insulated particles), for which the temperature boundary condition at the particle surface required that

$$\hat{\mathbf{n}} \cdot \nabla T = 0 \quad \text{on } \partial V. \tag{14}$$

For the isobaric case, where the density depends only upon temperature but not pressure, one has that

$$\nabla \rho = -\rho \beta \nabla T, \tag{15}$$

where

$$\beta = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{16}$$

is the coefficient of thermal expansion of the fluid. As such, Eq. (14) requires that

$$\hat{\mathbf{n}} \cdot \nabla \rho = 0 \quad \text{on } \partial V. \tag{17}$$

On the other hand, upon applying Eq. (9) at the solid boundary and subsequently multiplying that result scalarly by $\hat{\mathbf{n}}$ yields $\hat{\mathbf{n}} \cdot (\mathbf{v}_v - \mathbf{U}) = (\alpha/\rho)\hat{\mathbf{n}} \cdot \nabla \rho$ on ∂V in which we have used Eq. (12). Together with Eq. (17), we, thus, find that

$$\hat{\mathbf{n}} \cdot (\mathbf{v}_v - \mathbf{U}) = 0 \quad \text{on } \partial V. \tag{18}$$

Consequently, for the thermophoretic case, the temperature boundary condition (14) furnishes the boundary condition (18) to be imposed upon the normal component of the volume velocity at the solid surface. In other words, a thermally insulated solid surface is impermeable to volume flow, just as it is to mass flow under more general circumstances, as set forth in Eq. (12).

Next, consider the details surrounding the isothermal pressure-driven microchannel gas flow data [14,15] that were used to confirm the volume velocity-based no-slip boundary condition (10). In isothermal circumstances, density is a function only of pressure, whence it follows that:

$$\nabla \rho = \rho \kappa \nabla p, \tag{19}$$

where κ is the coefficient of compressibility (5b). The confirming experiments, which took place between flat plates, were interpreted by the confirming researchers [14,15] as one-dimensional flows. In that circumstance, the pressure was uniform across the channel's cross section, requiring *inter alia* that

$$\hat{\mathbf{n}} \cdot \nabla p = 0 \quad \text{on } \partial V. \tag{20}$$

In conjunction with Eq. (19), this makes $\hat{\mathbf{n}} \cdot \nabla \rho = 0$ on ∂V as also was the case for the thermophoretic data in Eq. (17). In turn, Eq. (18) again is seen to apply.

For both the thermal- and the pressure-data sets, the normal component of the volume velocity relative to the walls is, thus, seen to vanish as set forth in Eq. (18). While this boundary condition is seen to apply in, at least, several instances, it is, however, not valid in all circumstances. For example, were the thermophoretic particle to be heat conducting, heat would flow from the fluid into the particle across its surface in which case, the vanishing heat flux boundary condition (14) would no longer apply. In turn, Eq. (18) would not apply. Similarly, in the isothermal case, where pressure constitutes the driving force, Eq. (18) again is seen generally to be inapplicable, e.g., for pressure-driven flows in converging or diverging ducts. There, the flow is no longer one dimensional. As a consequence, pressure, which is now no longer uniform across a cross section, is incapable of being characterized by the single symbol $\hat{\mathbf{n}}$ as was previously true in Eq. (20).

As such, it appears in the general case that, while the tangential volume velocity boundary condition (10) might apply under any and all circumstances, the same could not be true of the normal volume-velocity boundary condition (18). Evidently, there is no universal boundary condition that specifies the value of $\hat{\mathbf{n}} \cdot (\mathbf{v}_v - \mathbf{U})$ on ∂V under any and all circumstances. However, there does exist a special, but important class of conditions for which it appears possible to specify the normal volume-velocity boundary condition independently of the specific flow circumstances. This occurs with regard to specifying the normal component of $\mathbf{v}_v$ at the surface of an inert particle as discussed in the next section.

B. Inert force-free particles

We define as an inert particle, one for which no exchange of heat or other form of energy between the fluid and the particle is possible. In what follows, we argue with respect to the boundary conditions to be imposed upon $\mathbf{v}_v$, that, in addition to requiring satisfaction of the zero tangential volume-velocity boundary condition (10), satisfaction of the zero normal volume-velocity boundary condition (12) also is required. Were this to prove to be the case, the combination of normal and tangential conditions, Eqs. (18) and (10), would result in the overall velocity requirement that

$$\mathbf{v}_v - \mathbf{U} = \mathbf{0} \quad \text{on } \partial V. \tag{21}$$

In support of the above relation, we return to the argument that originally [10] spawned the tangential boundary condition formula (10). That argument was based upon the fact that, thermodynamically, the rate at which work is being performed by the surrounding fluid on a rigid immobile body (a solid particle in the present case) immersed in that fluid is given in the absence of body forces by the expression,

$$\dot{W} = -\oint_{\partial V} d\mathbf{S} \cdot \mathbf{P} \cdot (\mathbf{v}_v - \mathbf{U}). \tag{22}$$

Here, $\mathbf{P}$ is the pressure tensor and $d\mathbf{S} = \hat{\mathbf{n}}\, dS$ is a directed element of surface area. As the particle is force free, this requires that

$$\oint_{\partial V} d\mathbf{S} \cdot \mathbf{P} = \mathbf{0}. \tag{23}$$

It was argued in that earlier paper [10] that energetic inertness required *inter alia* that no work be performed by the surroundings on the particle, while recognizing that this requirement was not inconsistent with the tangential component of the volume velocity being zero as in Eq. (10). The latter condition then was proposed as a hypothesis whose consequences need to be tested against experimental data prior to its acceptance. The proposal then was confirmed by the thermophoretic and microchannel flow data [10] alluded to earlier in this paper. Left unanswered at the time was the question of the boundary condition to be imposed upon the normal component of the relative volume velocity $\mathbf{v}_v - \mathbf{U}$? Of course, we could have speculated (subject to subsequent experimental tests) that this condition might be that given by Eq. (12) since, as a consequence of Eq. (21), that choice is consistent with the vanishing of the rate of work in Eq. (22). However, attempting to concurrently test two independent hypotheses against the same experimental data set seemed inappropriate. Moreover, the tangential-velocity hypothesis might still prove to be applicable even if work was being performed such that the integral (22) did not vanish. In any event, the special nature of the thermophoretic and one-dimensional microchannel data enabled us to test the tangential-velocity hypothesis independent of addressing the normal-velocity hypothesis.

III. PHORETIC-PARTICLE VELOCITIES IN SINGLE-COMPONENT FLUIDS

A. Pycnophoretic velocity

Pycnophoresis [9] is a compound word derived from the Greek $\pi\upsilon\kappa\nu\acute{o}\varsigma$ (*puknos*), meaning “dense” and from the Greek $\varphi\acute{o}\rho\varepsilon\sigma\iota\varsigma$ (*phoresis*), meaning “act of carrying.” The following subject matter pertaining thereto deals with the migration of a single force-free small (albeit non-Brownian) solid particle through an otherwise quiescent single-component fluid under the influence of a density gradient $\nabla\rho$. As subsequently discussed in Secs. IV B and IV C, thermophoresis and barophoresis represent special cases of pycnophoresis wherein the density gradient arises from respective temperature and pressure gradients.

As shown in the Appendix, when the physicochemically inert phoretic particle is force free and the fluid in which it is immersed is at rest at infinity such that the only fluid motion that need be addressed is that generated by movement of the particle itself, the phoretic velocity of the particle is found to be

$$\mathbf{U} = \alpha\nabla \ln \rho. \tag{24}$$

This relation is meant to be understood in the following sense: The velocity $\mathbf{U}_0$ of a small particle (instantaneously occupying some point $\mathbf{x}_0$ in the fluid) measured relative to the fluid’s undisturbed mass velocity $(\mathbf{v}_m)_0$ at that point is given by the expression $\mathbf{U}_0 = (\alpha/\rho_0)(\nabla\rho)_0$, where ρ_0 refers to the density of the undisturbed fluid evaluated at the position in the fluid currently occupied by the particle.

Since the density gradient is the driving force for this phoretic motion, in Eq. (24), it is appropriate to refer to $\mathbf{U}$ as being the particle’s pycnophoretic velocity. The formula is valid for both liquids and gases. A key attribute of this velocity, which makes it uniquely different from any other particulate formula in physics, is the fact that it is independent of the particle’s size, mass, density, and shape, as well as of the particle’s physicochemical attributes. Indeed, no aspect of the particle’s existence enters into the formula since the quantities appearing in Eq. (24) pertain to properties of the fluid alone.

B. Thermophoretic velocity

When the undisturbed fluid is isobaric, the particle’s phoretic movement is driven solely by a temperature gradient. It, thus, follows upon introduction of Eq. (15) into Eq. (24) that

$$\mathbf{U} = -\alpha\beta\nabla T. \tag{25}$$

This is the thermophoretic velocity of the inert particle with the expression being valid for both liquids and gases. For the case of ideal gases, for which $\beta = 1/T$, the above becomes

$$\mathbf{U} = -\alpha\nabla \ln T. \tag{26}$$

To compare this result with existing theoretical and experimental data bearing thereon, we first rewrite the above in the form

$$\mathbf{U} = -\frac{\upsilon}{\mathrm{Pr}}\nabla \ln T, \tag{27}$$

in which υ is the fluid’s kinematic viscosity and

$$\mathrm{Pr} = \upsilon/\alpha \tag{28}$$

is the Prandtl number, which is $O(1)$ for gases [4].

1. *Experimental confirmation of the thermophoretic-velocity formula*

By way of comparison with Eq. (27), Epstein [16] considered the case of a spherical particle of radius a immersed in an otherwise quiescent unbounded gas subject to a uniform undisturbed steady-state temperature gradient ∇T in a gas. He solved the incompressible creeping-flow [17] NSF mass, momentum, and energy equations for a fluid at rest at infinity and satisfying Maxwell’s [18] thermal-creep boundary condition, namely [compare with Eq. (11)],

$$(\mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}})\cdot(\mathbf{v}_m - \mathbf{U}) = C_s\upsilon\nabla_s \ln T \quad \text{on } \partial V. \tag{29}$$

Epstein found that a heat-conducting force-free particle would move through the fluid with velocity,

$$\mathbf{U} = -\lambda C_s\upsilon\nabla \ln T, \tag{30}$$

where $\lambda = 1/(1 + k_s/2k)$ is a dimensionless parameter given functionally by Epstein in terms of the thermal conductivity ratio k_s/k in which k_s is the thermal conductivity of the particle. The dimensionless $O(1)$ creep coefficient C_s is Maxwell’s [18] thermal-creep coefficient for dilute gases, whose precise value [19] depends upon whether the gas molecules are reflected from the particle’s surface diffusely, specularly, or otherwise. Epstein’s thermophoretic velocity formula (30) has been confirmed broadly by many experimentalists [20] and theoreticians [21,22].

In the limiting nonconducting particle case where $k_s/k \ll 1$ or, equivalently, when the particle is insulated such that no heat is exchanged with the fluid—effectively rendering the particle inert—one has that $\lambda = 1$ [16]. In that case, Epstein's more general result (30) reduces to

$$\mathbf{U} = -C_s \upsilon \nabla \ln T. \tag{31}$$

It is not possible to decide, on purely theoretical grounds, whether molecules are reflected specularly, diffusely, or otherwise from the particle's surface. Over that range of possibilities, C_s varies, theoretically, between 3/4 and 1.15 [19]. Furthermore, Prandtl numbers [4] for different gases generally vary between 2/3 and 1, depending upon whether the entraining gas is monatomic, diatomic, or polyatomic. Thus, for a given particle and fluid pair, the inability to decide, theoretically, upon the appropriate value of C_s, when considered in conjunction with the above-cited range of Prandtl number values for different gases, leads to the declaration that Eqs. (27) and (31) are indistinguishable, from which we conclude that they are one and the same.

As thermophoresis is seen to be merely a special case of pycnophoresis, the above-cited agreement noted between theory and experiment for thermophoretic-particle motion offers implicit evidence in support of the more broadly based pycnophoretic-velocity formula (24). Moreover, phenomenologically speaking, given the one-to-one [16] linkage between Maxwell's [18] thermal-creep boundary condition (29) and Epstein's experimentally confirmed thermophoretic-velocity formula (31), it appears virtually certain that our general view of all phoretic motions as originating from slip of the fluid's mass velocity at solid surfaces is correct. Such slip also is the case for electrophoretic-particle motion [22], which is, however, not a single-component phenomenon.

In contrast with this slip-based view, a number of other researchers [23,24] regard phoretic motions as originating from the existence of special solid-fluid physicochemical stresses at the surface of the solid particle (although, admittedly, these explanations generally are not advanced in the context of single-component fluids). Such explanations cannot, however, explain the size independence of the particle's phoretic velocity [whose independence is also implicit in Epstein's formula (31)] since the effect of such physicochemical surface forces must vanish in the limit of zero particle size.

C. Barophoretic velocity

For the case where the fluid is isothermal such that the particle's phoretic movement is generated solely by a pressure gradient, it follows upon the introduction of Eq. (19) into Eq. (24) that

$$\mathbf{U} = \alpha\kappa \nabla p. \tag{32}$$

This is the barophoretic velocity of the particle, valid for both liquids and gases. This velocity obviously will be very small for liquids since then, $\kappa \approx 0$. For the case of ideal gases, for which $\kappa = 1/p$, the above becomes

$$\mathbf{U} = \alpha \nabla \ln p. \tag{33}$$

This relation bears a strong resemblance to the pressure diffusion equation (2) despite their very different realms of applicability; explicitly, our barophoresis formula (33) is applicable only to single-species fluids, whereas, the barodiffusion formula (2) applies only to multispecies fluids.

The existence of barophoresis as a stand-alone subject, worthy of study in a single-component fluid context appears, previously, not to have been discussed.

By way of example, consider a small inert external body-force-free particle immersed in an ideal gas undergoing a rigid-body rotation (relative to an inertial system) at an angular velocity $\mathbf{\Omega}$. Owing to the action on the particle of the resulting pressure gradient [13], $\nabla p = \rho\Omega^2\mathbf{R}$ (where $\mathbf{R}$ is the position vector relative to the axis of rotation), the particle migrates radially outward toward the higher density region at a speed given by the expression,

$$U = \frac{2\eta\Omega^2}{p\mathrm{Pr}} R_0, \tag{34}$$

with η as the fluid's viscosity. At low pressures, the viscosity of gases is sensibly independent of pressure. Accordingly, the particle's barophoretic speed can become appreciable. For example, for oxygen at 300 K ($\eta = 2.063 \times 10^{-5}$ Pas; $\mathrm{Pr} = 0.68$), a rotation rate of 10 000 rpm, and a pressure of 10^{-3}atm, a particle situated 1 cm from the axis will move with a speed of 0.223 cm/s.

Regarding possible experiments designed to study the existence of barophoresis, it is important to note that the particle's barophoretic velocity is independent of the particle's mass. On the other hand, the centrifugal forces acting on a particle in a centrifuge depend upon its mass. As such, any experiment designed to test the viability of Eq. (34) needs to take account of that fact. Fortunately, in the course of extrapolating barophoretic data to zero-particle size, the effect of the particle's mass goes to zero in comparison with the barophoretic effect. While such an experiment is possible in principle, as a practical matter, it might be difficult to maintain the background density gradient in a 10 000-rpm centrifuge.

IV. DISCUSSION

A. Phoretic wind

From Eq. (24) in conjunction with Eqs. (7) and (8), it follows that

$$\mathbf{U} = \mathbf{v}_\upsilon. \tag{35}$$

This relation may be interpreted as representing the fact that a small inert particle may be used in the capacity of a tracer of the fluid's volume velocity $\mathbf{v}_\upsilon$. Viewed alternatively, by recasting the volume velocity in the role of the fluid's phoretic wind, Eq. (35) also may be interpreted as stating that the particle simply is entrained in that wind. In contrast, a dye introduced into the fluid in the role of a tracer monitors the fluid's mass velocity $\mathbf{v}_m$. Having independent techniques available for separately measuring the fluid's mass and volume velocities, while also being able to measure the fluid's density, offers the promise of a direct test of bi-velocity hydrodynamic theory [11] based upon the fundamental equation (9).

Because the theory outlined here is valid only for single-component fluids, further research encompassing mixtures would be necessary in order to establish whether measurement of the velocity $\mathbf{U}$ of a small inert solid tracer particle in an otherwise quiescent fluid mixture undergoing transport wherein coupling effects exist (e.g., thermal diffusion, osmosis, diffusiophoresis, barodiffusion, etc.) would coincide with the fluid's volume velocity $\mathbf{v}_v$. While theoretical formulas based on Boltzmann's gas-kinetic theory [6] are currently available [25–27] for the fluid's volume velocity in low-pressure multicomponent gases (wherein concentration, temperature, and pressure gradients coexist, resulting in coupling phenomena), the author is unaware of any experimental measurements of the fluid's tracer velocity $\mathbf{U}$ in such systems to compare against these volume-velocity formulas. Moreover, even were such experimental tracer velocity data available, the complexity of the phenomenological coefficients appearing in Shavaliyev's solution [25] of Boltzmann's equation [6] for dilute monatomic gases—the only case for which phenomenological data are available—would appear to preclude an unequivocal comparison of $\mathbf{U}$ with $\mathbf{v}_v$.

B. Equality of the single-component barophoretic diffusivity with the barodiffusion diffusivity in binary mixtures of ideal gases

Consider a dilute dispersion of colloidal barophoretic particles (viewed as large molecules in the Stokes-Einstein sense) dispersed in a gaseous solvent of much smaller molecules. In what follows, we pursue Einstein's classical Brownian motion Stokes-Einstein approach [28] with respect to using our single-particle hydrodynamic barophoretic velocity data for $\mathbf{U}$ to estimate the value of the binary barodiffusion coefficient $D^{(p)}$ in systems that are sparse in numbers of colloidal particles.

Designate the colloidal particles as species 1 and the solvent as species 2. With w_1, the mass fraction of colloidal molecules at a point of the fluid, the quantity $\rho_1 = w_1\rho$ gives the number of molecules of species 1 per unit volume at that point. The mass flux $\mathbf{j}_1^{(p)}$of species 1 then is $j_1^{(p)} \equiv \mathbf{U}w_1\rho$ where for gases, $\mathbf{U}$ is given for barophoretic motions by Eq. (33). Consequently, $\mathbf{j}_1^{(p)} = \rho\alpha w_1 \nabla \ln p$. With D as the solvent's self-diffusivity, the gas's dimensionless Lewis number [4,29] $\mathrm{Le} = \alpha/D$ is unity, at least, for monatomic Maxwell molecules.

Thus, based upon our single-component barophoretic analysis, we have that

$$\mathbf{j}_1^{(p)} = \rho D w_1 \nabla \ln p. \tag{36}$$

Comparison of this expression with Eq. (1a) for the flux of species 1 in a binary mixture provides the following estimate for the binary mixture's barodiffusion diffusivity:

$$D^{(p)} = D w_1. \tag{37}$$

To establish the accuracy of this estimate, we note that, according to Haase [1], his Eq. (4-23.11)], the pressure diffusion coefficient for an ideal binary gas mixture is

$$D^{(p)} = D\frac{(M_1 - M_2)x_1x_2}{M}. \tag{38}$$

Here, M_i and x_i, respectively, are the molecular weight and the mole fraction of species i, while $M = (x_1M_1 + x_2M_2)$ is the mean molecular weight of the mixture, and D is the mixture's binary diffusion coefficient as defined by Fick's law of molecular diffusion. Given the disproportion in the relative sizes and, hence, masses of the solute and solvent molecules, we have that $M_1 \gg M_2$, whence, the above becomes $D^{(p)} = DM_1x_1x_2/M$. However, $w_1 = M_1x_1/M$.This gives $D^{(p)} = Dw_1x_2$. As a consequence of the diluteness of the mixture with respect to the solute molecules, we have $x_1 \approx 0$, equivalently, $x_2 \approx 1$. Thus, we finally obtain

$$D^{(p)} = D w_1. \tag{39}$$

The latter barodiffusion expression is identical with the single-component barophoretically based estimate (37), provided that one confounds the solvent's self-diffusivity with the mixture's binary diffusivity.

To summarize, this accord adds further credibility not only to our general slip-based phoretic model [10], but also to the bi-velocity theory [11] as a whole.

C. Heuristic derivation of the barophoretic-velocity formula (33)

Equation (33) for the particle's barophoretic velocity through an ideal gas was derived formally by solving the pertinent hydrodynamic equations [see Eq. (A2)] subject to the tangential and normal boundary conditions (10) and (18). As seen in what follows, the formula also can be derived by nonhydrodynamic purely heuristic arguments patterned after Einstein's [28] Brownian motion Stokes-Einstein arguments for colloidal solute particles, whose physicochemical status is intermediate between that of a large molecule and a non-Brownian body that obeys the laws of hydrodynamics.

We begin by considering the case of an ideal gas in a state of thermodynamic equilibrium and, thus, obeying the hydrostatic equation,

$$\rho\hat{\mathbf{f}} = \nabla p, \tag{40}$$

wherein $\hat{\mathbf{f}}$ is the body force per unit mass of fluid (e.g., gravity). With n as the number density of molecules and m as the molecular mass, we have that $\rho = nm$, while $\mathbf{F} = m\hat{\mathbf{f}}$ is the force acting on a single molecule. With $\mathbf{U}$ as the mean velocity of a molecule moving under the influence of this force, we write that $\mathbf{U} = M\mathbf{F}$, where M is the molecule's mobility. From the Nernst-Planck-Einstein relation, $M = D/k_BT$ in which k_B is Boltzmann's constant and D is the self-diffusion coefficient. Furthermore, from the ideal gas law, $p = nk_BT$ Substitution of these several results into Eq. (40) gives

$$\mathbf{U} = D\nabla \ln p. \tag{41}$$

To the extent that the Lewis number for the gas is unity, rendering $D = \alpha$, the above accords with Eq. (33).

The advantage of this simple heuristic derivation lies in the fact that not only does it reproduce the hydrodynamically derived result for the particle's barophoretic velocity, but also that the analysis shows that velocity to be independent of the size and shape of the particle. Furthermore, the derivation has not relied upon the principles of bi-velocity hydrodynamics [11] nor upon the choice of boundary conditions. These facts add independent evidence to the correctness of the bi-velocity theory as a whole.

APPENDIX: DEMONSTRATION THAT EQ. (24) RENDERS THE PHORETIC PARTICLE FORCE FREE

Equation (9) is valid everywhere, including at the particle surface. When combined with Eq. (35), this makes

$$\mathbf{v}_m = \mathbf{U} - \boldsymbol{\alpha}\boldsymbol{\nabla} \ln \boldsymbol{\rho} \quad \text{on } \partial V, \tag{A1}$$

as in Eq. (13). When the particle is spherical and the fluid at infinity is at rest, Eq. (6.7) of Ref. [30] shows that the hydrodynamic force on a spherical particle of radius a in a fluid of viscosity η undergoing an incompressible creeping flow generated by the particle's motion can be expressed directly in terms of the prescribed mass velocity field at the surface of the particle by the expression,

$$\mathbf{F} = -\frac{3\eta}{2a}\int_{r=a} (\mathbf{v}_m)_{r=a} dS. \tag{A2}$$

As such, in the limit where the particle is small, we have, with the use of Eq. (A1), that

$$\mathbf{F} = -\frac{3\eta}{2a}\int_{r=a} [\mathbf{U} - \alpha\boldsymbol{\nabla} \ln \rho]_0 dS.$$

The condition that the particle be force free is, thus, synonymous with the vanishing of the above integrand,

$$\mathbf{U} = \alpha\boldsymbol{\nabla} \ln \rho. \tag{A3}$$

Our analysis, therefore, confirms that satisfaction of Eq. (24) is consistent with the particle being force free.

Although Eq. (A3) was derived by considering the case of a spherical particle, the result can be shown [8] to be independent of the particle's shape. The explanation for this lies in the fact that the particle's phoretic velocity is, according to our elementary theory, a function only of the fluid in which the particle is immersed, independent of any property of the particle itself, including its size, shape, and physicochemical constitution.

It is important to note that, by use of Eq. (A2), we have applied the boundary condition (A1) [or, equivalently Eq. (21)] not toward the solution of the bi-velocity hydrodynamic equations for a compressible fluid [11] but rather to the original NSF equations for an incompressible fluid. While this appears to be inconsistent, the singular-perturbation thermophoretic analysis of Brenner and Bielenberg [8] as well as the corresponding thermal transpiration analysis of Bielenberg and Brenner [31]—both involving solving the bi-velocity equations subject to no slip of the volume velocity at solid surfaces—show that no inconsistency exists. In effect, it proves consistent, mathematically, to solve the original NSF equations [13] rather than the bi-velocity equations [11], provided that one solves these equations subject to the bi-velocity volume-velocity boundary condition (21). Insofar as the accuracy of the overall solution scheme is concerned, in this asymptotic limit, the relative importance of the contribution of $\mathbf{j}_v$ to the boundary condition dominates over that of its contribution to the bi-velocity differential equations themselves [11].

1. Alternative view

With regard to the comments of the last paragraph, there is a rather different view that can be taken concerning our phoresis calculations, one that is not keyed either to bi-velocity theory or to the concept of a volume velocity. This involves: (i) regarding the boundary conditions (12) and (13) imposed upon $\mathbf{v}_m$ at the surface of the particle to purely be empirical in nature, having nothing to do with bi-velocity theory; and (ii) applying these boundary conditions [together with requiring the vanishing of $\mathbf{v}_m$ at infinity and the satisfaction of the force-free requirement (21)] to the traditional NSF incompressible creeping flow equations, rather to any amended versions thereof. This scheme constitutes a well-posed hydrodynamic boundary-value problem and is tantamount to what actually has been performed in connection with our use of Eqs. (A2) and (23) to derive the phoretic-velocity formula (24). In fact, this is exactly the route taken by Epstein [16] (who knew nothing of bi-velocity theory) in his derivation of the widely accepted [8] thermophoretic-velocity formula (31) based upon Maxwell's thermal-creep boundary condition (29). As such, our pycno-, thermo-, and barophoretic-velocity formulas may be regarded as classical creeping flow hydrodynamic results, provided that one accepts the tangential-velocity boundary condition (11) on a purely empirical basis in terms of solutions based thereon furnishing theoretical predictions that accord with experimental data. And that modest view is no different in principle from the current practice of empirically accepting the validity of the classical no-slip boundary condition,

$$(\mathbf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}) \cdot (\mathbf{v}_m - \mathbf{U}) = \mathbf{0} \quad \text{on } \partial V,$$

in the traditional hydrodynamics of incompressible fluids.

Thus, while we do not retreat from our belief in the viability of bi-velocity theory, adoption of this pragmatic empirical attitude would enable skeptics of that theory to accept our slip-based model phoretic-velocity predictions without having to subscribe to the bi-velocity theory as a whole.

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