Elementary kinematical model of thermal diffusion in liquids and gases

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An elementary hydrodynamic and Brownian motion model of the thermal diffusivity D_T of a restricted class of binary liquid mixtures, previously proposed by the author, is given a more transparent derivation than originally, exposing thereby the strictly kinematic-hydrodynamic nature of an important class of thermodiffusion separation phenomena. Moreover, it is argued that the solvent's thermometric diffusivity α appearing in that theory as one of the two fundamental parameters governing D_T should be replaced by the solvent's (isothermal) self-diffusivity D_S. In addition, a corrective multiplier of $O(1)$ is inserted to reflect the general physicochemical noninertness of the solute relative to the solvent, thus enhancing the applicability of the resulting formula $D_T = \lambda D_S \beta$ to "nonideal" solutions. Here, β is the solvent's thermal expansivity and λ is a term of $O(1)$, insensitive to the physicochemical nature of the solute (thus rendering D_T primarily dependent upon only the properties of the solvent). This formula is, on the basis of its derivation, presumably valid only under certain idealized, albeit well-defined, circumstances. This occurs when the solute molecules are: (i) large compared with those of the solvent; and (ii) present only in small proportions relative to those of the solvent. When the solute is physicochemically inert, it is expected that $\lambda = 1$. When these conditions are met, the resulting thermal diffusivity of the mixture is, in theory, independent of any and all properties of the solute. Moreover, because β is algebraically signed, the thermal diffusivity can either by positive or negative, according as the solvent expands or contracts upon being heated. This formula for D_T is compared with available experimental data for selected binary liquid mixtures. Reasonable agreement is found in almost all circumstances with λ near unity, the more so the higher the temperature, especially when the solute-solvent mixture properties closely approximate those where agreement would be expected and conversely. Finally, it is pointed out that for the restricted circumstances described, the formula $D_T = \lambda D_S \beta$ is equally credible for gases. Here, based on gas-kinetic theory, it is possible to furnish the theoretical value of λ. Overall, while spanning a range of about five orders of magnitude, the D_T values given by this elementary formula are shown to apply with reasonable accuracy to: (i) liquids (including circumstances for which D_T is negative) as well as gases; (ii) all combinations of solvents and solutes tested (the latter including, for example, polymer molecules and metallic colloidal particles); and (iii) all sizes of solute molecules, from angstroms to submicron.

I. INTRODUCTION

Considerable theoretical and practical interest has recently arisen [1,2] in regard to thermal diffusion and thermophoresis in liquids, embracing a variety of different solvents and solutes. Included among these solutes are colloidal particles [3–9], nanoparticles [10–12], polymers [13–17], micelles [9,18,19], metallic colloidal particles [4], DNA [20], proteins [21], and other biological molecules [22], as well as a host of other entities (e.g., magnetic particles as one of the species of a ferrofluid [10,23]), all representing macromolecules with regard to their Brownian movements in liquid solvents. To a lesser extent, interest also exists in smaller solute molecules, closer in size to those of the solvent [24–29], which formerly represented the focus of thermodiffusion research [2,25]. The growing wealth of liquid-phase thermal diffusion experiments performed on these systems has revealed a number of interesting features, including the unexpected facts that solute migration may undergo a reversal in direction with changes in temperature [9,21] or composition [24,27,30] and that the thermal diffusion coefficient for polymeric solutions is independent of molecular weight and molecular configuration [1], the former extending over at least a several thousandfold range of molecular weights.

In contrast with such behavior in liquids, gases [31,32] behave in a relatively benign manner. Whereas the theory underlying thermodiffusion phenomena in gaseous continua has been well understood for almost a century, owing largely to the pioneering theoretical work of Enskog and Chapman in the case of thermal diffusion (as summarized in the monograph of Chapman and Cowling [32]) and, in the case of thermophoresis, by the work of Epstein [33] in 1929, comparably satisfactory predictive theories for liquids are currently lacking [1]. Indeed, until recently [6], the fact that thermophoresis could occur in liquids had apparently never been unequivocally demonstrated, earlier claims to this effect apparently notwithstanding [34].

Together with Bielenberg, the writer recently co-authored an elementary theory [35] of thermal diffusion. Among other things, that work offered an explanation for the unexpected liquid-phase Soret sign reversal observed in a dilute aqueous solution near the temperature of 4 °C [7], at which water has its maximum density. It also rationalized the molecular weight- and configuration-independent thermal diffusivity observed in polymer solutions [1], at least for those polymer-solvent mixtures whose properties approximate the conditions cited in the Abstract. Concurrently, the theory furnished correct order-of-magnitude estimates for the thermal diffusivities D_T of nonionic and nonpolar binary liquid mixtures, in addition to correctly predicting experimentally observed trends with regard to the dependence of D_T upon temperature and composition. The present contribution both simplifies

and amplifies that theory, while significantly improving the accuracy of its predictions by modifying two of its precepts: namely, (i) replacing the solvent's thermometric diffusivity α originally appearing therein by the solvent's (isothermal) self-diffusivity D_S; and (ii) introducing a nonideality factor λ so as to allow for the solute's lack of inertness relative to that of the solvent. The first of these two changes reflects the recent theoretical recognition [36–38] that thermal fluctuations constitute the fundamental mechanism animating thermodiffusion processes.

A. Diffuse volume flux

Elementary, in-principle, Ludwig- [39] Soret- [40] type experiments, aimed at measuring the thermal diffusivities of liquid-phase mixtures, entail steady-state measurements performed upon a confined (binary) miscible fluid mixture subjected to an externally imposed temperature gradient in the absence of gravity. This configuration results in a steady, nonuniform spatial distribution of the two species within the fluid, with the larger-size or higher-molecular-weight species (the "solute") often, but not always, concentrated in the colder regions of the fluid. Subsequent measurement of this spatial distribution furnishes the Soret coefficient S_T, a property of the mixture. When coupled with knowledge of the mixture's Fick's-law binary diffusivity D, this allows calculation of the mixture's thermal diffusivity D_T via the formula $D_T = S_T D$. In general, each of the three mixture properties appearing in the latter expression is a function of temperature, pressure, and composition, each possessing the same value for both species comprising the mixture [41,42].

Of particular interest to us in what follows is that of establishing the functional dependence of D_T upon the properties of both the solvent and solute in mixtures which are dilute with respect to the solute. In this context we begin by first considering the seemingly uninteresting limiting case in which the solute is wholly absent from the mixture, while the resulting solute-free solvent is subjected to a steady, externally-imposed temperature gradient. This arrangement gives rise to a time-independent inhomogeneous solvent density field $\rho = \rho(T)$, with $T = T(\mathbf{x})$ and hence $\rho = \rho(\mathbf{x})$ each a function of position $\mathbf{x}$ within the confined liquid.

Explicitly, consider a quiescent single-component fluid (the "solvent") confined within the one-dimensional region $(0 < x < L, \ -\infty < y < \infty, \ -\infty < z < \infty)$ bounded between two indefinitely extended heat-conducting walls, respectively situated at $x = 0$ and L, which are 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 [43,44]. The effects of gravity, which might otherwise cause a free-convection flow as a consequence of the temperature gradient, are assumed to be either wholly absent or negligible. The system's physical configuration is such that, at steady state, the confined solvent is host to an elementary one-dimensional heat conduction process, during which no mass motion of the fluid occurs. This state of rest is expressed by the relation

$$\mathbf{v}_m = \mathbf{0}, \tag{1}$$

where $\mathbf{v}_m$ refers to the fluid's mass velocity appearing in the general unsteady-state continuity equation $\partial \rho / \partial t + \boldsymbol{\nabla} \boldsymbol{\cdot} (\rho \mathbf{v}_m)$

$= 0$, with ρ the mass density and t the time. As a consequence of Eq. (1) the linear momentum and continuity equations, in combination, presumably result in the pressure being uniform throughout the fluid: $p = $ const.

During the steady-state heat conduction process, internal energy flows diffusively, but not convectively, through the fluid; that is, energy transport occurs without mass motion, corresponding to the circumstances described by Eq. (1). According to an unorthodox, volume-based view of the nature of fluid "motion" proposed by the author [45], this Fourier-law-driven diffuse energy flow $\mathbf{q} = -k\boldsymbol{\nabla}T$ (with k the thermal conductivity) gives rise to a diffusive flux or "flow" of volume accompanying the heat flow through the fluid. The possibility of a *diffuse* volume flow—as opposed to a *convective* volume flow (the latter representing the mode by which volume is usually thought to be exclusively transported)—is novel, apparently not having been explicitly proposed in the literature prior to its introduction in Ref. [45]. While the concept of volume "flowing" in the absence of an accompanying mass flow may seem strange, even impossible, especially in a single-component fluid, it needs to be recognized that volume, viewed as an extensive thermodynamic property of a fluid body, is simply a *nonmaterial* property of that body. As such, volume is no different than any other extensive nonmaterial property, be the latter internal energy, momentum, species mass, electric charge, entropy, etc. (whether or not a conserved property), all of which are capable of being transported purely diffusively—i.e., nonconvectively—through space, as explicitly embodied in constitutive equations such as Fourier's, Newton's (rheological), Fick's, Ohm's, etc., laws, respectively.

According to volume transport theory [45], the diffuse volume flux density $\mathbf{j}_v$ accompanying the Fourier heat flux density $\mathbf{q}$ through a single-component fluid, either liquid or gas, is given constitutively at a point $\mathbf{x}$ thereof by the expression $\mathbf{j}_v = -\rho D_v \boldsymbol{\nabla} \hat{v}$, where the non-negative scalar phenomenological coefficient D_v is the fluid's "volume diffusivity" and $\hat{v} = 1/\rho$ is the specific volume. Expressed alternatively, entirely in terms of the density, one has that

$$\mathbf{j}_v = D_v \boldsymbol{\nabla} \ln \rho. \tag{2}$$

A subsidiary goal of the present analysis is to present convincing experimental evidence to support our eventual contention that the solvent's volume diffusivity coefficient appearing in Eq. (2) is equal to solvent's self-diffusion coefficient D_S—explicitly, that $D_v = D_S$. As will be seen in Sec. VI, this empirical relation is philosophically independent of its use in our subsequent analysis of thermal diffusion phenomena; rather, since diffuse volume transport is not itself directly measurable, thermal diffusion represents only one of several possible experimental schemes capable of furnishing data to test our contention that $D_v = D_S$.

Given the presumed constancy of the pressure throughout the steady-state Soret apparatus, the solvent's single-component equation of state $\rho = \rho(p, T)$ furnishes the isobaric expression $\boldsymbol{\nabla} \ln \rho = -\beta \boldsymbol{\nabla} T$, in which

$$\beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p \tag{3}$$

is the solvent's coefficient of thermal expansion or thermal expansivity. Equation (2) thus adopts the form

$$\mathbf{j}_v = -D_v\beta\boldsymbol{\nabla}T. \tag{4}$$

As noted in Eq. (1), no mass flow occurs in the present circumstances. More generally, however, in circumstances where a nonzero mass flux $\mathbf{n}_m$ exists, the *total* volume flux $\mathbf{n}_v$ of fluid, in addition to possessing a diffuse portion $\mathbf{j}_v$, also possesses a convective portion $\mathbf{n}_m\hat{v}$ [45]. Here, with $d\mathbf{S}$ a space-fixed directed element of surface area at a fixed point $\mathbf{x}$ of the fluid, the quantities $d\mathbf{S}\cdot\mathbf{n}_m$ and $d\mathbf{S}\cdot\mathbf{n}_v$, respectively, represent the mass and volume flowing per unit time across $d\mathbf{S}$. Hence, in general,

$$\mathbf{n}_v = \mathbf{n}_m\hat{v} + \mathbf{j}_v. \tag{5}$$

By virtue of being a volume flow per unit area per unit time, $\mathbf{n}_v$ possesses the units of a velocity. As such, the latter flux density $\mathbf{n}_v$ is often designated as representing the fluid's *volume velocity* [41,42], here represented by the symbol $\mathbf{v}_v$ [45]. By definition, the mass flux $\mathbf{n}_m$ is related to the fluid's mass velocity $\mathbf{v}_m$ by the expression $\mathbf{n}_m = \rho\mathbf{v}_m$. Accordingly, Eq. (5) is frequently expressed in the alternative form $\mathbf{v}_v = \mathbf{v}_m + \mathbf{j}_v$, the latter formula serving to relate the fluid's respective volume and mass velocities.

Consistent with Eq. (1), $\mathbf{n}_m = \mathbf{0}$ in the present steady-state, confined-fluid case. Consequently, Eqs. (4) and (5) furnish the expression

$$\mathbf{n}_v = -D_v\beta\boldsymbol{\nabla}T. \tag{6}$$

The ability of the solvent to diffusively transport volume in the presence of a temperature gradient is seen from this expression to depend critically upon its (isobaric) compressibility, as embodied in its thermal expansivity β.

In the present Soret apparatus, the temperature T obeys the energy conservation equation $\boldsymbol{\nabla}\cdot(k\boldsymbol{\nabla}T)=0$. Hence, when k can be regarded as sensibly constant (as is true *a priori* for sufficiently small temperature gradients), the temperature gradient will be uniform throughout the fluid at the value $\boldsymbol{\nabla}T = -\hat{\mathbf{x}}(T_h - T_c)/L = \text{const}$, with $\hat{\mathbf{x}}$ a unit vector in the x direction.

II. THERMOPHORESIS OF A SINGLE PARTICLE

Equation (6) provides the fundamental basis for our eventual calculation of the thermal diffusivity D_T of a binary mixture formed by dissolving or dispersing a small amount of solute in the confined solvent. Imagine for the moment that a single, physicochemically inert, macroscopic (i.e., non-Brownian) particle is inserted into the quiescent, undisturbed solvent which is undergoing the volume flow (6). Elementary fluid-mechanical theories [46], based upon simultaneously solving the continuity, linear momentum, and energy equations subject to the usual no-slip boundary condition on the particle surface for the specified physical circumstances (namely, no net mass flow far from the particle, a

prescribed temperature difference $T_h - T_c$, a mass-impermeable particle surface, etc.), lead to the theoretical prediction that the particle will simply remain at rest within the fluid, with heat flowing via conduction around the particle (and, possibly, through it as well, were the particle to be heat conducting). Experiment, however, teaches otherwise. In particular, the macroscopic particle is observed to move towards one or the other of the two walls. This occurs in the case of both gases and liquids, as recently reviewed by Brenner and Bielenberg [47], the resulting single-particle motion being termed thermophoresis.

That the particle moves, rather than remaining at rest, arises from the fact that the traditional no-slip boundary condition along the solid particle surface is violated as a consequence of the existence of a temperature gradient in the fluid proximate thereto [47]. In the case of gases, such "thermal creep" was first identified and analyzed by Maxwell [48–50] in 1879 on the basis of gas-kinetic theory [32]. Maxwell's macroscopic slip boundary condition was subsequently employed by Epstein [33] in 1929 to explain, purely hydrodynamically, the origin of thermophoretic particle motion in gases, without having to discuss the molecular basis of such motion. An alternative hydrodynamic explanation [38,51,52] advanced to explain thermophoretic particle motion in both gases and liquids argues that a particle is simply entrained [53] in the solvent's flux field $\mathbf{n}_v$ and hence moves through space at the solvent's volume velocity $\mathbf{v}_v$, provided that the particle is physicochemically "inert." This solvent-based conveyance of the particle is formally equivalent, mathematically, to supposing that it is the fluid's volume velocity, rather than the mass velocity, which does not slip at the particle's surface. From either point of view, Eq. (6) shows that in such circumstances the inert entrained particle will be transported through space by the fluid at a velocity $(\mathbf{U}_p)_{\text{inert}} = -D_v\beta\boldsymbol{\nabla}T$. Importantly, this velocity is seen to be independent of the particle's size, shape, and physicochemical constitution. In a related context [37] this velocity is referred to as the "drift velocity" of the (undisturbed, particle-free) solvent, a purely molecular transport property of the nonisothermal solvent.

In circumstances where the thermophoretic particle is not inert with respect to the fluid in which it is immersed, we insert a noninertness or nonideality $O(1)$ coefficient λ into the preceding relation to reflect this fact, thus obtaining the more general relation

$$\mathbf{U}_p = -\lambda D_v\beta\boldsymbol{\nabla}T \tag{7}$$

for the velocity of the non-Brownian particle. The general notion of "inertness" is discussed in Ref. [52]. For example, in the case of gases, a macroscopic (i.e., non-Brownian) particle ceases to be "inert" when it possesses a nonzero thermal conductivity k_p. In that case, one has for a spherical particle that [47] $\lambda = [1 + (k_p/2k)]^{-1}$, where, as before, k is the solvent's thermal conductivity. Thus, as later observed in Sec. VII, the fact that λ is found both theoretically and experimentally to be less than unity [as well as being of $O(1)$] in the case of gases could be empirically rationalized in terms of this noninertness factor, although the notion of assigning a thermal conductivity to the "interior" of a single molecule of

the solute in an attempt to obtain quantitative agreement with the gaseous data would clearly be irrational.

III. SOLUTE TRANSPORT IN THE BINARY SYSTEM

A. Dilute solution of solute macromolecules

Consider a binary solution composed of a solute (species "1") and solvent (species "2"). Denote by w_i ($i=1,2$) the mass fraction of species i and by $\rho_i = \omega_i \rho$ the mass of species i per unit volume of solution. Of special interest is the limiting case where the size of the solute molecules greatly exceeds that of the solvent molecules. This circumstance enables the solvent to be viewed as a viscous hydrodynamic continuum relative to the discrete, effectively macromolecular, solute particles—as in the case of the Sutherland- [54] Einstein [55] classical Brownian-motion model of the (isothermal) diffusion of colloidal solute molecules in a liquid solvent. We further suppose these solute particles, regarded as Brownian, to be present only in relatively modest proportions, enabling each such "macromolecule" to be regarded as effectively interacting only with the solvent molecules, but not with each other. In this dilute solute limit the undisturbed particle-free solvent volume flux—$\mathbf{n}_{v2}$ say—will remain substantially unaffected by the presence of the solute molecules, from which it follows from Eq. (6) that $\mathbf{n}_{v2} = -\lambda (D_v)_2 \beta_2 \boldsymbol{\nabla} T$.

The density ρ_1 denotes the mass of solute per unit volume of solution. Concomitantly, in these dilute solutions, it represents the solute mass per unit volume of pure solvent. Accordingly, upon regarding each solute molecule as being individually entrained in this solvent flow, it follows that the rate per unit time per unit area at which solute mass is being transported through space accompanying this solvent volume flow is $\mathbf{n}_{v2}\rho_1 \equiv -\lambda(D_v)_2\beta_2\rho_1\boldsymbol{\nabla} T$. In the context of our "drift-velocity" notion [37], the latter represents the hypothetical solute flux that would ensue were the solute macromolecules to be devoid of Brownian motion by virtue of their being regarded as macroscopic particles. This missing diffusive attribute is subsequently reintroduced into the analysis by recognizing that the preceding deterministic solute mass flux is opposed by a diffusive mass flux stemming from the previously neglected Brownian motion, the latter given by Fick's law for the entrained solute molecules as $-\rho D \boldsymbol{\nabla} w_1$, in which D is the (isothermal) binary diffusivity. The sum

$$\mathbf{n}_1 = -\lambda(D_v)_2\beta_2\rho w_1 \boldsymbol{\nabla} T - \rho D \boldsymbol{\nabla} w_1 \qquad (8)$$

thus furnishes the *net* solute mass flux in the net mass flux-free Soret apparatus.

B. Calculation of the thermal diffusivIty

In a barycentric reference frame [41,42], for which choice mass serves as the convective carrier of extensive physical properties, the diffuse mass fluxes $\mathbf{j}_i$ ($i=1,2$) of the respective solute and solvent species in the present isobaric case are given by the constitutive expression ([42] p. 359)

$$\mathbf{j}_1 = -D_{T,12}\rho w_1 w_2 \boldsymbol{\nabla} T - D_{12}\rho \boldsymbol{\nabla} w_1, \qquad (9)$$

together with a similar expression for species 2, such that, by definition, $\mathbf{j}_1 + \mathbf{j}_2 = \mathbf{0}$. In the counterpart of Eq. (9) for the

solvent species, $D_{T,12} = -D_{T,21} \equiv D_T$, with $D_T > 0$ the thermal diffusion coefficient; moreover, $D_{12} = D_{21} \equiv D > 0$ is the ordinary binary mutual diffusion coefficient. Since, from Eq. (1), there is no *net* mass flow in present circumstances, it follows that the diffusive mass fluxes $\mathbf{j}_i$ of the two species are the same as their respective total mass fluxes $\mathbf{n}_i$ [56].

In the present dilute solute case we have that $w_2 \approx 1$ in Eq. (9). Consequently, in this limit, the total mass flux of solute is

$$\mathbf{n}_1 = -D_T \rho w_1 \boldsymbol{\nabla} T - D\rho \boldsymbol{\nabla} w_1. \qquad (10)$$

Comparison of the latter with Eq. (8), which is equally applicable in this same dilute solute limiting circumstance, furnishes the fundamental relation $D_T = \lambda(D_v)_2\beta_2$. On the understanding that in the subsequent text D_v and β refer to the respective properties of the pure solvent, we can for simplicity suppress the solvent-based subscript 2 affixed to these thermal properties and write that

$$D_T = \lambda D_v \beta. \qquad (11)$$

This limiting expression for the mixture's thermal diffusivity, which was derived here using purely kinematical arguments, is closely related to that originally obtained by Bielenberg and Brenner [35] (see also Sec. VII of Ref. [37]), albeit with the noninertness factor λ now included and with the solvent's thermometric diffusivity α_2 appearing in their expression here replaced by the more phenomenologically neutral symbol $(D_v)_2 \equiv D_v$. By the word "neutral" is meant that we have not yet committed ourselves to any particular constitutive relation between the phenomenological coefficient D_v appearing in Eq. (2) and the physical properties of the solvent (ultimately, its self-diffusivity D_S). In contrast to our purely kinematical derivation of Eq. (11), Bielenberg and Brenner [35] used dynamical arguments in their derivation, including invoking the *ad hoc* assumption of a Boltzmann distribution of solute molecules within the Soret apparatus, despite the fundamentally nonequilibrium nature of the nonisothermal Soret steady state.

C. Proposed comparison of Eq. (11) with experimental data

A *quantitative* comparison of Eq. (11) with experimental D_T data (in the sense of establishing that λ is indeed insensitive to the nature of the solute as well as being of order unity) obviously requires knowledge of the solvent's volume diffusivity D_v. However, knowledge of the functional dependence of D_v upon the properties of the solvent is itself a separate and distinct issue, one currently under development and for which no general consensus yet exists owing to the newness of the concept of diffuse volume transport [45] underlying Eq. (2). While this quantitative issue of the viability of the ultimate relationship $D_T = \lambda D_S \beta$ based upon the further hypothesis that $D_v = D_S$ will ultimately be discussed in Secs. VI and VII, it nevertheless proves convenient to initially assess the purely *qualitative* agreement of the less restrictive relation $D_T = \lambda D_v \beta$ with experiment in order to clearly distinguish the present thermal diffusion theory [as thus far embodied in Eq. (11)] from the issue of whether the additional relation $D_v = D_S$ is also valid, in the sense of being supported

by experimental data. After all, the question of the viability of the latter relation is independent of that of Eq. (11) itself, since the possibility exists that Eq. (11) may be correct, whereas the relation $D_v = D_S$ may be wrong.

By purely *qualitative* agreement with experiment is meant, *inter alia*, establishing whether or not thermal diffusion experiments performed in dilute solute solutions support the notion, implicit in Eq. (11), that D_T depends predominantly upon the solvent, being—for a given solvent—insensitive to the physicochemical nature of the particular solute. According to the proposed qualitative test of Eq. (11), experimental D_T values obtained for a given solvent should all be approximately the same, provided that conditions (i) and (ii) described in the Abstract are met. Of course, such a test does not furnish the λ value itself. As such, the test which is carried out below in Secs. IV and V does not impact upon whether λ is of $O(1)$, since it does not require knowledge of the solvent's volume diffusivity D_v. Only later, in Secs. VI and VII, following the further hypothesis that $D_v = D_S$, is the magnitude of λ established for specified solute-solvent pairs.

There exists a significant body of experimental liquid-phase thermal diffusion data in the literature against which Eq. (11) may be checked for consistency with the premises underlying its derivation in circumstances where these premises are, at least approximately, met. It is not our intention here to review these data in a fully systematic and comprehensive manner. Rather, in Secs. IV and V which follow, we have selectively chosen several liquid-phase data sets whose special attributes impact qualitatively upon the main issues explicit or implicit in the validity of Eq. (11) for liquids and later, quantitatively, upon its more complete formulation, where $D_v = D_S$. (Gaseous data bearing thereon are presented and discussed in Sec. VII.) More thorough and varied analyses of existing databases will be seen to be warranted by our necessarily limited findings, including the desirability of performing key systematic experiments for which no data yet exists.

IV. COMPARISON WITH LIQUID-PHASE EXPERIMENTS: (I) WATER AS THE SOLVENT

A. Dilute aqueous solutions

1. Data of Iacopini, Rusconi, and Piazza

Foremost among the pertinent data sets currently available for aqueous mixtures, and indeed the inspiration motivating our writing of the present paper, is the recent report by Iacopini, Rusconi, and Piazza [9] on thermal diffusion in dilute aqueous solutions of various high molecular weight solutes. The pertinence of their work to a test of our thermal diffusion model lies in the fact that not only did these authors measure D_T for a variety of different macromolecular solutes dissolved or dispersed in water, but that these studies were also effected over a range of temperatures including that at which water has its maximum density—namely 4 °C—and hence for which $\beta = 0$ in Eq. (11), requiring that $D_T = 0$ if our theory is to prove to be correct. It is important to recognize that this particular prediction of our theory—namely, the

temperature at which D_T reverses its algebraic sign—derives solely from the dependence of $\mathbf{j}_v$ upon $\nabla \rho$ and thus holds independently of the explicit functional dependence of the phenomenological coefficient D_v in Eq. (11) upon the physical properties of the system. Indeed, were the diffuse volume flux to simply be of the general functional form $\mathbf{j}_v = \mathbf{f}(\nabla \rho)$, not necessarily linear as in Eq. (2), and were $\mathbf{f}$ to possess the property that $\mathbf{f}(\mathbf{0}) = \mathbf{0}$, it would then be true that $\mathbf{j}_v = \mathbf{0}$ and, hence, $D_T = 0$ whenever $\beta = 0$, a conclusion transcending the other key assumptions underlying Eq. (11).

The small temperature differences involved in the experiments of Iacopini *et al.* [9] were of the order of only 0.5 °C, enabling them to obtain *temperature-specific* D_T values. This permitted these investigators to unambiguously and accurately ascertain those temperatures at which the thermal diffusivities appropriate to each solute underwent a change in algebraic sign. In turn, this ability will be seen to reflect critically upon the viability of Eq. (11) [57].

The mixture's thermal diffusivity D_T, given Eq. (11) and ostensibly applicable in circumstances for which the conditions hypothesized during its derivation are satisfied, is insensitive to the nature of the solute. Rather, its value depends primarily only upon the properties of the solvent. Moreover, because β is algebraically signed, D_T can either by positive or negative, according as the neat solvent expands or contracts upon being heated. Water, for example, has its maximum density at 4 °C (more precisely, 3.984 °C), so that β for water is either positive or negative, according as T is greater or less than 4 °C. Inasmuch as $D_v > 0$ at all temperatures (in order that the Clausius-Duhem entropy production inequality be satisfied [58]), it follows from Eq. (11) that in dilute aqueous solutions $D_T > 0$ for $T > 4$ °C and, conversely, $D_T < 0$ for $T < 4$ °C. This holds true irrespective of the physicochemical nature of the dissolved solute, at least for the class of solute molecules that fulfill the basic criteria cited in the Abstract. Moreover, again subject to this same caveat, the numerical value of D_T in dilute aqueous solutions should, according to the present theory, be essentially the same for all solute species. As will be seen in what follows, these predictions accord well with the recent experimental observations of Iacopini, Rusconi, and Piazza [9] for the case of dilute aqueous solutions in which three different solutes were dissolved, these solutes being: (i) sodium dodecyl sulfate (SDS) ionic micelles; (ii) sodium polystyrene sulfonate (NaPSS), a linear polyelectrolyte; and (iii) polystyrene latex particles (PS's) [59].

In order to distinguish these three particular solutes, terminologically, from the several other solutes on which experiments were performed by these authors (which are not further commented upon here) and which were found to display fundamentally different behavior from that described above, Iacopini *et al.* [9] refer to this class of solute molecules as "athermal." According to these authors, such systems encompass suspensions of particles interacting via screened Coulombic forces, a state presumably achieved in their experiments by dissolution in the water of small amounts of NaCl in an attempt to limit the effects of interparticle electrostatic interactions [60]. Basically, the data encompassed by the experiments of Iacopini *et al.* [9] performed on these athermal aqueous systems is, according to

TABLE I. Estimated experimental thermal diffusion parameters for various athermal solutes in water for use in Eq. (12).

Solute	$A \times 10^{12}$ $(\text{m}^2\,\text{s}^{-1}\,\text{K}^{-2})$	T^* (°C)	$D_T \times 10^{12}$ (25 °C) $(\text{m}^2\,\text{s}^{-1}\,\text{K}^{-1})$
PS[a]	0.0823	6	1.6
SDS[b]	0.138	4	2.9
NAPSS[c]			
$M_w = 15\,400$[d]	0.169	4	3.5
$M_w = 32\,900$	0.139	4	2.9
$M_w = 74\,000$	0.112	4	2.4

[a]PS=polystyrene latex particles (radius=30 nm).
[b]SDS=sodium dodecyl sulfate (ionic micelles).
[c]NaPSS=sodium polystyrene sulfonate (a linear polyelectrolyte).
[d]M_w=molecular weight.

these authors, well correlated over the temperature range from roughly 5 to 40 °C by the linear relation

$$D_T = A(T - T^*) \quad (\text{m}^2\,\text{s}^{-1}\,\text{K}^{-1}), \tag{12}$$

where the constants $A > 0$ $(\text{m}^2\,\text{s}^{-1}\,\text{K}^{-2})$ and T^* (°C) are parameters which, respectively, characterize each of the individual solutes. We have estimated these parameters for each solute from the experimental data presented graphically in their Fig. 7. The estimated values thereof are tabulated in Table I. Possible experimental uncertainties in the D_T values derived from Eq. (12) are estimated by us to be of the order of $\pm 0.1 \times 10^{-12}$ $\text{m}^2\,\text{s}^{-1}\,\text{K}^{-1}$. Also tabulated in Table I for later reference are the respective thermal diffusivity values for each solute at 25 °C, as derived from Eq. (12).

Within likely experimental error, the T^* data tabulated in Table I, corresponding to the respective temperatures at which $D_T = 0$ for each solute, accord more or less exactly with the temperature at which water has its maximum density and hence for which $\beta = 0$. In addition, the (estimated) experimental values of D_T at 25 °C for each solute are comparable in magnitude (and algebraic sign) although not exactly the same. These facts roughly support the prediction implicit in Eq. (11) that, for a specified solvent (and temperature)—water in the present case—all solutes should possess essentially the same thermal diffusivity, independently of their respective physicochemical attributes, size, configuration, etc. Of course, the validity of the latter conclusion hinges on how well these solutes are likely to fulfill the basic criteria underlying the ostensible validity of Eq. (11).

As discussed in the next two subsections, thermal diffusion data exist for dilute aqueous solutions of solutes other than those reported upon in Table I. These data generally support the predicted solute independence of D_T.

2. Data of Shiundu, Williams, and Giddings

Foremost among these other dilute aqueous solution databases is the extensive study by Shiundu et al. [4]. Their thermal diffusion data were, however, obtained by an experimental scheme very different than that employed by Iacopini et al. [9]: namely, "thermal field-flow fractionation" (thFFF)

TABLE II. Experimental thermal diffusivities of aqueous solutions[a] of various latex solute particles, and of different sizes obtained by thFFF. Data of Shiundu, Williams, and Giddings Ref. [4].

Particle diameter (μm)	Thermal diffusivity $D_T \times 10^{12}$ $(\text{m}^2\,\text{s}^{-1}\,\text{K}^{-1})$
PS[b]	
0.105	3.63
0.220	3.05
0.300	2.55
0.398	2.01
PB[c]	
0.121	3.25
0.232	2.80
0.410	1.95
0.550	1.50
PMMA[d]	
0.130	3.29
0.299	2.09
0.347	1.97
0.586	1.26

[a]The water contained 0.10 nM of tertiarybutylammoniumperchlorate as an electrolyte in order to coulombically screen the particles, thereby minimizing collective interparticle interactions.
[b]PS=polystyrene latex particles.
[c]PB=polybutadiene latex particles.
[d]PMMA=polymethylmethacrylate latex particles.

[4,5,14,44]. Except for some brief remarks, it is not our intention here to comment in detail on the accuracy of their thermal diffusivity results, especially as none of their data (or indeed any of the data reported here, other than that of Iacopini et al. [9]) pertain to the key issue of a possible change in the algebraic sign of D_T at 4 °C. The D_T data of Shiundu et al. [4] are reproduced above in Table II for those of their experiments performed without the significant addition of salts, surfactants, or buffers to the water containing the solutes to be tested. The water did, however, contain 0.1 nM of tertiarybutylammonium perchlorate (TBAP). This was added as an electrolyte in order to suppress agglomeration of the solute molecules that would otherwise occur in its absence, creating experimental complications.

Assigning an appropriate of degree of accuracy to the results of Shiundu et al. [4] is problematic for a variety of different reasons, not the least of which were the relatively large temperature differences imposed across the walls of their apparatus in relation to the strong temperature dependence of the physical properties of water, especially its thermal expansivity (cf. Table V). For example, it appears (from their Fig. 2) that the temperature difference across the gap between the walls of their thFFF channel was at least 24 °C in some of their PS experiments, while the temperature of the cold wall was systematically varied between 25 and 40 °C,

with the spacing between the channel walls of the apparatus lying somewhere between 50 and 250 μm. Since the theoretical equations underlying the interpretation of their experiments treat key fluid properties, most notably D_T and D, as being constant across the gap, this gives rise to uncertainties whose magnitudes remain to be estimated.

Owing to such temperature variations, the reported D_T values in Table II represent an average over the thFFF channel gap. Judging, for example, from the temperature dependence of the PS solute as embodied in Eq. (12) and corresponding to the A value for PS in Table I, it would appear that such uncertainties could, in fact, be comparable in magnitude to the D_T values themselves cited in Table II. Of particular note in this context is the significant difference between the values of Shiundu *et al.* [4] for aqueous PS solutions in Table II and those of Iacopini *et al.* [9] in Table I.

Questions of accuracy aside, it should be noted that the data reported in Table II endorse, at least qualitatively, the hypothesis that, for a given solvent, D_T is essentially the same for all solutes. The accompanying prediction of solute size independence in aqueous solutions based upon Eq. [11] does not appear to be comparably well satisfied by these data, which clearly suggest a systematic trend entailing a decrease in thermal diffusivity with increasing particle size. However, given the relatively large sizes of some of the particles, the question of whether the residence time in the thFFF apparatus was sufficient for the particle's translational Brownian motion to have been properly manifested needs to be explored. Given that D_T is intrinsically a *molecular* attribute (rather than a macroscopic thermophoretic attribute), thus requiring expression of the particle's Brownian motion, the possible failure of the particle's Brownian motion to be properly manifested is an issue that remains to be resolved [61].

3. Data of Chan et al.

These authors, like Shiundu *et al.* [4], also used a thFFF cell to measure the Soret coefficients S_T of dilute aqueous solutions of a series of fractionated polyethylene glycol (PEG) polymers, with the respective fractions ranging in molecular weight from about 200 to 20 000. In combination with their independent mutual binary diffusion measurements of D for these same solutions, this enabled Chan *et al.* [16] to determine D_T. These experiments showed the thermal diffusivity of the aqueous PEG solution to be independent of the PEG's molecular weight over the entire M_w range studied, averaging out to about $D_T = 5.5 \times 10^{-12}$ m^2 s^{-1} K^{-1}. Individual molecular weight-specific measurements deviated less than about $\pm 0.3 \times 10^{-12}$ m^2 s^{-1} K^{-1} from this average over the entire range of molecular weights. (This aqueous PEG D_T value is repeated in Table III.)

This PEG D_T value is somewhat larger than those of the other aqueous values tabulated in Tables I and II (over substantially the same temperature range). Moreover, the obvious consistency of these PEG data would appear to identify them as being statistically different from the other water-based data cited. Given the strongly polar natures of both the

TABLE III. Thermal diffusivities or thermophoretic mobilities D_T for several different solvents and solutes.

Solute	ThFFF experiment?	Thermal diffusivity $D_T \times 10^{12}$ (m^2 s^{-1} K^{-1})	Reference
		SOLVENT	
		Water	
PEG[a]	Yes	5.5	[16]
Si-OH[b]	Yes	22	[6]
		Acetonitrile	
Si-OH[b]	Yes	16	[6]
Si-ODS[c]	Yes	5.2	[6]
		n-Heptane	
Si-ODS[c]	Yes	5.7	[6]
		Toluene	
POS[d]	Yes	4.1-4.2	[11]
PS[e]	No	11.5	[13,15,17]
		n-Pentane	
n-decane $x_{n\text{-decane}} = 0.20$	No	9.28±0.75	[28]
n-decane $x_{n\text{-decane}} = 0.50$	No	7.54±0.61	[28]
n-decane $x_{n\text{-decane}} = 0.80$	No	7.18±0.59	[28]

[a]PEG=polyethylene glycol (D_T was observed to be essentially independent of molecular weight over the molecular weight range from about 2×10^2 to 2×10^4).
[b]Si-OH=Hypersil 3 μm (a porous spherical silica gel).
[c]Si-ODS=Hypersil-ODS 3 μm (same as Si-OH, but coated with a monolayer of octadecyl silane).
[d]POS=polyorganosiloxane nanospheres (D_T was observed to be essentially the same for the two sphere radii studied—namely, 19 and 25 nm).
[e]PS=polystyrene (D_T was observed to be essentially independent of molecular weight over the molecular weight range from about 2×10^3 to 3×10^6).

solute and solvent in these aqueous PEG experiments, such differences might have been anticipated.

4. "Exceptional" behavior: The data of Regazzetti et al.

Regazzetti *et al.* [6,62] present thFFF-derived thermal diffusion data for dilute aqueous "suspensions" of 3-μm-diam Si-OH (porous spherical silica gel) particles. These aqueous D_T data are summarized in Table III. Because entities of this size are too large to undergo appreciable Brownian motion on the time scale of most experiments, these essentially purely macroscopic experiments constitute an important counterpoint to the previous aqueous data sets cited in Tables I and II, especially that of Iacopini *et al.* [9] in Table I.

Regazzetti *et al.* [6] refer to their thFFF-derived D_T values as "thermophoretic mobilities" rather than (true) thermal diffusivities and posit that these data (as well as their data for the other solute/solvent systems which they studied—see Table III) present, for the first time, unequivocal evidence of the phenomenon of thermophoresis in *liquids*. Previous evidence of the existence of such macroscopic thermophoretic motion in fluids had been confined exclusively to gases, the sole exception being the liquid-phase study by McNab and Meisen [34]; see the discussion of their work in Ref. [47].

By explicitly assigning a different name to the quantity D_T measured in their experiments, Regazzetti *et al.* [6] appear to give implict recognition to the fact that thermophoresis is a single-particle phenomenon pertaining to the motion of a macroscopic, non-Brownian solid body, manifested by the migration of such a particle through a single-component fluid under the influence of an externally imposed temperature gradient. As such, their choice of terminology appears meant to distinguish thermophoresis from thermal diffusion, the latter being a strictly molecular phenomenon occurring only in mixtures (solutions) of miscible species. However, since their data were obtained in a thFFF device and since the interpretation of data obtained therefrom depends crucially upon the solute particle experiencing (transverse) diffusion—both thermal and mutual—as well as upon the residence time in the device being of sufficient duration to assure the attainment of a transverse steady state [63], questions naturally arise with respect to the consistency of their thermophoreticlike experiments with the notion of thermal diffusion.

Maintaining this terminological distinction between thermal diffusion and thermophoresis is important, especially as much of the current thermodiffusion literature on liquids has tended to blur the fundamental distinction between these two phenomena. As such, especially with regard to particles whose size renders them Brownian in their behavior, as opposed to macroscopic (referring to the particulate data in Tables I and II and, later, Table IV), fundamental questions could be raised about whether thermophoretic mobilities (measured in thFFF devices) and thermal diffusivities (measured in static Soret devices) are to be regarded, unequivocally, as one and the same entity.

This issue is compounded by recent theories which, following a proposal by Ruckenstein [64], argue that the thermal diffusion of solid solute particles in liquids is analogous to the Marangoni migration of "bubbles" (droplets as well as gas bubbles [65,66]) through liquids, caused by an externally imposed temperature gradient. This solute motion is attributed to Marangoni stresses [65] at the solute particle-solvent interface stemming from the variation in the bubble's interfacial tension with temperature. Such a model of migration might possess some degree of legitimacy in the case of macroscopic solid particles were one to suppose that solid-liquid interfacial tension (including its variation with temperature) was a well-understood phenomenon, which it is not. Moreover, one might even attempt to extend this Marangoni model to the case where the particles were Brownian in size, each regarded as being a single *macromolecule* (our emphasis here being on the last syllable of the latter: namely, the phrase "molecule"). However, it does not appear, at least not

TABLE IV. Thermal diffusivities of various solute particles, and of different sizes, in acetonitrile[a] obtained by thFFF. Data of Shiundu, Williams, and Giddings Ref. [4].

Particle diameter (μm)	Thermal diffusivity $D_T \times 10^{12}$ (m^2 s^{-1} K^{-1})
PS[b]	
0.105	9.07
0.220	7.67
0.300	6.58
0.398	5.47
PB[c]	
0.121	8.21
0.232	6.57
0.410	5.21
0.550	4.03
PMMA[d]	
0.130	10.2
0.299	7.14
0.347	6.74
0.586	4.06
Palladium metal particles	
0.2±0.1	6.14
Platinum metal particles	
0.3	7.53
Silica	
0.15	5.00
0.25	4.84
0.50	3.69

[a]The acetonitrile contained 0.10 nM tertiarybutylammoniumperchlorate as an electrolyte.
[b]PS=polystyrene latex particles.
[c]PB=polybutadiene latex particles.
[d]PMMA=polymethylmethacrylate latex particles.

to us, that this model can rationalize thermal diffusion phenomena in liquids, since the latter is a strictly *molecular* phenomenon. Individual molecules, whether macromolecular or, simply, micromolecular in size, do not, after all, possess macroscopic surfaces; nor does the concept of an interfacial tension at a point lying on such a hypothetical molecular surface, much less its *local* positional variation with temperature at that point, appear acceptable as a viable concept, given that interfacial tension is a joint macroscopic property of contiguous multiphase *continua*.

That said, how do the non-Brownian themophoretic mobility Si-OH data of Regazzetti *et al.* [6] in Table III, based on water as the solvent, compare with the water-based Brownian particle and molecular data of others cited in Tables I and II? Explicitly, as noted, Regazzetti *et al.* [6]

report a value of $D_T = 22 \times 10^{-12}$ m^2 s^{-1} K^{-1} for 3-μm-diam Si-OH particles in purified water free of dissolved electrolytes. This value exceeds by a large margin those for the other water-based solutes cited in the preceding Tables I and II (as well as the PEG value in Table III). Whether the difference is to be attributed to solute size, the purity of the water, or to as yet unresolved interpretative issues associated with use of a thFFF cell, as discussed earlier, remains to be seen.

B. Summary of data for the aqueous solutions

The fact that all of the varied D_T data in Tables I–III for dilute aqueous solutions and suspensions embrace only a relative modest range of numerical values (except for the Regazzetti *et al.* [6] Si-OH data in Table III) is not inconsistent with our model-based prediction of Eq. (11) that D_T depends predominantly upon the properties of the solvent— namely, water in the present instance—at least in idealized circumstances. Inasmuch as D_v and β constitute properties of the solvent, the fact that the experimental D_T values are not identical reflects upon the fact that the (implicit) λ values vary to some extent with the choice of solute. While the requisite criteria of relative solute size and diluteness appear to have been met by these data, the strongly polar nature of water renders satisfaction of the criterion of solute inertness unlikely irrespective of nature of the solute, in which case such (implicit) variations in λ values might have been anticipated. That the explicit λ values are indeed of $O(1)$ is discussed in Sec. VI following the introduction of the hypothesis that $D_v = D_S$.

V. COMPARISON WITH LIQUID-PHASE EXPERIMENTS: (II) NONAQUEOUS SOLVENTS

The nonaqueous experimental D_T data tabulated in Tables III and IV embody a potpourri of different nonaqueous solvents and solutes dissolved or dispersed therein, the latter only for the dilute-solute case and then only for solutes whose molecules are large compared with those of the solvent. (Note that data on acetonitrile as the solvent appear in both tables.) Given the availability in the literature of D_T values for a large number of solvent/solute combinations, the limited selection of data in these tables is, as stated earlier, meant to be neither comprehensive nor systematic. In anticipation of our subsequent presentation in Sec. VI of a theory suggesting that the volume diffusivity D_v appearing in Eq. (11) is, in fact, equal to the solvent's (isothermal) self-diffusivity D_S, the limited choice of solvents displayed in these tables is further conditioned by the concomitant availability of self-diffusion data for these particular solvents. In addition, given that one of the idealizations underlying our model requires that the solvent molecules be substantially smaller in size than those of the solute (or the Brownian solute *particles* in the case of "nonmolecular" solutes), these tables embody only solute/solvent pairs for which this condition appears likely to have been satisfied.

It is evident, however, apart from the n-pentane/n-decane (P-D) mixture data [28] (Table III), that the other solute/ solvent combinations cited in these tables are unlikely to fulfill the criterion of physicochemical inertness required in order that the model be strictly applicable thereto with a value of $\lambda = 1$. Explicitly, without claiming to have performed an exhaustive search of the pertinent liquid thermal diffusion database, we were able to locate pertinent data for only this single mixture whose attributes appeared more or less certain to accurately fulfill all three basic idealizations and for which self-diffusion data were also available. (But see also Sec. VIII E, where the system benzene-cyclohexane is discussed in the context of "inertness.") In this context it is also important to note two facts: (i) the P-D mixture is the only nonaqueous solution for which the solute molecules were not macromolecular in size and hence for which use of either the Marangoni model or the thermophoretic boundary-slip model of thermal diffusion would be absurd; and (ii) the P-D combination is the only mixture appearing in Tables III and IV (apart from the PS/toluene mixture) for which the D_T values were not obtained using a thFFF device and hence for which the related issues of the magnitude of the Brownian motion or the residence time in the device were not a matter of concern.

In the interest of brevity, the D_T-related data presented in these tables and in the subsequent text summarize only the barest technical details regarding the background of the data cited. Further details relating thereto appear, of course, in the original publications cited. (Unless otherwise stated, the following data appear to refer to temperatures averaging out to about 25 °C or thereabouts, although the temperature issue for the nonaqueous solvents cited in these tables is nowhere near as critical as it was in the case of Table I, which involved water near its temperature of maximum density.) Overall, it is seen that each of these nonaqueous data sets support the hypothesis that, for a given solvent, the D_T value is essentially the same for all solutes (except the data of Regazzetti *et al.* [6] for Si-OH in acetonitrile).

The respective n-heptane and n-pentane solvent data in Table III, respectively, pertain to single, rather than multiple, solutes, and therefore neither data reflect upon the issue of the solute independence of D_T for a specified solvent. Rather, these data appear here only in connection with their subsequent role in supporting the hypothesis advanced in the next section that $D_v = D_S$, as embodied in Eq. (13).

VI. IS THE SOLVENT'S VOLUME DIFFUSIVITY D_v EQUAL TO ITS ISOTHERMAL SELF-DIFFUSIVITY D_S?

A. Experimental basis underlying the hypothesis that $D_v = D_S$ in liquids

This section focuses on making plausible the hypothesis that the solvent's volume diffusivity D_v appearing in Eq. (11) is, in fact, equal to its self-diffusivity D_S. This is accomplished by showing that $\lambda = O(1)$ for all solutes tested and that $\lambda \approx 1$ in the single case where ideality would be expected: namely, for the n-pentane/n-decane mixture. In all prior discussions of this issue of the constitutive equation for the volume diffusivity, dating back to the original development of the notion of diffuse volume transport [45], it was believed that $D_v = \alpha$ in single-component fluids (gases as

well as liquids), where $\alpha = k/\rho\hat{c}_p$ is the fluid's thermometric diffusivity, in which $\hat{c}_p$ is its isobaric specific heat. The validity of this assumption regarding α has both a theoretical and experimental basis in the case of ideal gases [52], especially those gases that could be regarded as composed of Maxwell molecules [32]. However, in such circumstances, α is essentially equal to the gas's self-diffusivity D_S [37,46]—the ratio of the two being the Lewis number—in which case one could just as well have written that D_v is equal to D_S rather than to α. The basis of our modified hypothesis lies in the recent recognition [36–38] that the diffusional flux of volume is a consequence of the existence of fluctuations and that such fluctuations are quantified in single-component fluids by their respective self-diffusivities D_S, rather than by their thermometric diffusivities α.

Given the identification of fluctuations as the driver for the diffuse transport of volume [36–38], together with the fact that fluctuations exist in both gases and liquids, it thus seems reasonable to introduce the hypothesis that, for *both* states of matter, one should have that

$$D_v \overset{?}{=} D_S. \tag{13}$$

Despite the existence of a fluctuation-based rationale behind Eq. (13), the presence of the question mark surmounting the equality sign is meant to suggest that this relation should be regarded objectively as constituting a strictly empirical phenomenological hypothesis, one to be ultimately justified or rejected on the basis of the agreement of its consequences with experiment. However, this caveat notwithstanding, Eq. (13) will be seen in Sec. VII to possess a sound gas-kinetic theoretical basis in the case of gases, to the extent that an explicit quantitative formula, one that accords with experiment, can be derived expressing λ in terms of the gas's molecular properties.

Experimental verification of Eq. (13) requires designing an appropriate experimental protocol meant to measure the phenomenological coefficient D_v appearing in Eq. (2). In fact, this issue possesses two distinct aspects, since it has to be established concurrently that the diffusive volume flux is, functionally, linearly dependent upon $\nabla\rho$, all other things being equal. Given that volume is a nonmaterial property of a fluid, such questions cannot be lightly approached, no more than was internal energy or momentum the particular extensive property to be measured, each of which is equally nonmaterial in nature. And one can neither see, feel, taste, smell, nor otherwise sense, directly, such abstract nonmaterial properties. Experience in such matters, whether experimental or merely philosophical, teaches that one has necessarily to approach such issues *indirectly*, since thermodynamically extensive nonmaterial properties cannot be directly measured in experiments. And this imposition of an *indirect* measurement scheme, in turn, necessitates relying upon the validity of subsidiary hypotheses. Thus, as will be seen, a nontrivial chain of reasoning necessarily underlies any attempt to confirm Eq. (13).

In the present thermal diffusion context and in light of the closing remarks of the preceding paragraph, it is important to recognize that the necessity for confirming the validity of the constitutive equation (2) for the diffuse volume flux, irrespective of subsequently establishing the functional dependence of D_v upon the solvent's properties, rationally precedes establishing the validity of Eq. (11) for D_T. That is, were Eq. (2) to be proved wrong, Eq. (11) could not then possibly be correct under any circumstances. As such, the question of the correctness of Eq. (13) is independent of its possible use in connection with Eq. (11). Stated explicitly, the introduction of Eq. (13) into Eq. (11), so as to obtain the relation

$$D_T \overset{?}{=} \lambda D_S \beta, \tag{14}$$

does not provide a rigorous test of the validity of Eq. (13), *per se*, inasmuch as the failure of Eq. (14) to agree with experiment (with λ of order unity) could still be attributed, for example, to a lack of physicochemical inertness of the solute, despite Eq. (13) being true. After all, Eq. (13) has nothing whatsoever to do with the presence of a solute in the solvent. On the other hand, were Eq. (14) found to accord with experimental thermal diffusivity measurements, especially in circumstances where the solute could be regarded as substantially inert with respect to its physicochemical interaction with the solvent, this would then be a strong indicator of the correctness of the more basic relation (13). This lengthy preface brings us, therefore, to the stage of effecting a comparison of the predictions of Eq. (14) with the data in Tables I–IV.

Effecting a comparison of our fluctuation theory perspective with experiment is tantamount to calculating the value of λ for each data point in Tables I–IV, enabling us thereby to establish how close this parameter is to unity. Operationally, however, rather than compiling λ values for each entry, we have simply tabulated in Tables V and VI theoretical values of the defined quantity

$$D_T^* := D_S \beta \tag{15}$$

for each solvent listed in Tables I–IV, based upon the known thermal expansivity and self-diffusivity of each at the temperatures of interest. The λ value for each solvent (and solute) for which data are tabulated in Tables I–IV can then be obtained from the relation

$$\lambda = \frac{D_T}{D_T^*} \tag{16}$$

for any or all of the individual D_T entries in Tables I–IV. However, rather than doing so in detail, we believe that it will suffice on the part of the reader to simply mentally compare the experimental D_T values tabulated in Tables I–IV with the respective calculated D_T^* values in Tables V and VI for each specified solvent. The disparity or agreement between these two sets of numbers for the given solvent then provides a simple overview of how well our underlying fluctuation-based notion of thermal diffusion accurately reflects the physics of the phenomenon.

TABLE V. Properties of liquid water at 1 atm and various temperatures used to calculate the hypothetical thermal diffusivity D_T^* of solutes dissolved or dispersed in water.

Temperature (°C)	Thermal expansivity[a] $\beta \times 10^3$ (K^{-1})	Self-diffusivity[b] $D_S \times 10^9$ (m^2 s^{-1})	Hypothetical thermal diffusivity for $\lambda=1$ $D_T^* \times 10^{12}$ (m^2 s^{-1} K^{-1})
0	−0.0681	1.10	−0.075
1	−0.0501	1.14	−0.0571
3.984	0.0000	1.26	0.000
4	0.00027	1.26	0.00034
5	0.0160	1.30	0.0208
10	0.0880	1.53	0.135
15	0.151	1.77	0.267
20	0.207	2.02	0.418
25	0.257	2.30	0.591
30	0.303	2.59	0.785
35	0.346	2.91	1.01
40	0.385	3.24	1.25
45	0.422	3.59	1.51
50	0.458	3.96	1.81
60	0.523	4.75	2.48
70	0.584	5.62	3.28
80	0.641	6.56	4.20
90	0.696	7.57	5.27
100	0.750	8.67	6.50

[a]Reference [96].
[b]Reference [97].

B. Comparison of theory and experiment: Is $\lambda=O(1)$ for all solute-solvent combinations?

Based upon the experimental data available for both the self-diffusivity and thermal expansivity of water over a range of temperatures, the last column of Table V presents the hypothetical thermal diffusivity D_T^* defined by Eq. (15), arbitrarily representing the idealized $\lambda=1$ limiting value of the theoretical D_T value for the case of perfectly inert solutes dissolved or dispersed in water. Table VI presents the corresponding data (at 25 °C) for the four nonaqueous solvents cited in Tables III and IV.

1. Water as the solvent

Consider, first, the aqueous experimental D_T data in Tables I and II (as well as the two water-based entries in Table III) in relation to the value of $D_T^*=0.59 \times 10^{-12}$ m^2 s^{-1} K^{-1} in Table V for water at 25 °C. Except for the two aqueous entries in Table III, this corresponds to values in the range $\lambda \approx 2$–6. Being of $O(1)$, these λ values are thus of the right order of magnitude. However, by virtue of encompassing a threefold range of values for the different solutes, this conclusion is not fully in accord with the hypothesis that λ should have essentially the same value for all solutes. Moreover, the aqueous Si-OH value in Table III lies significantly outside this threefold range, as too does the corresponding PEG data, although the latter to a lesser extent. This Si-OH "anomaly" could, conceivably, be a consequence

of the fact that the 3-μm-diam particles were not Brownian. In any event, given that water molecules are highly polar, the strong noninertness assumption required for Eq. (14) to be strictly applicable would seem unlikely to have been met by virtually any solute dissolved or dispersed in water. In addition to this noninertness rationalization of the departure of the Si-OH/water data of Regazzetti et al. [6] from expectations, questions arise, as earlier discussed in the context of the accuracy of the (non-temperature-specific) D_T data in Table II (as well as that of the aqueous Si-OH entry in Table III), all of which were obtained by thFFF measurements.

2. Nonaqueous solvents

Table VI presents D_T^* values for each of the four nonaqueous solvents listed in Tables III and IV. Calculation of the λ values via Eq. (16) based on the experimental D_T values appearing in these tables leads to observations and conclusions similar to those for the aqueous case, discussed above. Here again, the 3-μm Si-OH solute data of Regazzetti et al. [6] in Table III, albeit this time for acetonitrile rather than water as the solvent, deviates markedly from the other nonaqueous λ values.

Of special interest is the n-pentane/n-decane (P-D) data in Table III, since n-decane is the only solute on the list whose molecules are not macromolecular in size. Moreover, this P-D mixture D_T data [28] were not obtained in a thFFF device. Although the data in this table indicate that the

TABLE VI. Properties of various solvents used to calculate their hypothetical thermal diffusivities D_T^*.

Thermal expansivity[a] $\beta \times 10^3$ (K^{-1})	Self-diffusivity $D_S \times 10^9$ (m^2 s^{-1})	Hypothetical thermal diffusivity for $\lambda = 1$ $D_T^* \times 10^{12}$ (m^2 s^{-1} K^{-1})
	SOLVENT	
	Toluene[b,c]	
1.05	2.66	2.8
	Acetonitrile[d]	
1.35	4.34	5.9
	n-Heptane[e,f]	
1.24	3.12	3.9
	n-Pentane[f]	
1.58	5.5	8.7

[a]Reference [98].
[b]Reference [99].
[c]Reference [100].
[d]Reference [101].
[e]Reference [102].
[f]Reference [103].

n-decane solute concentrations employed in the experiments were insufficiently small to have achieved the "dilute" solute status presumably necessary for Eq. (14) to be strictly applicable, the relatively modest variation of D_T with n-decane concentration nevertheless encourages extrapolation of the data to zero solute concentration in order to estimate the limiting dilute solution value of D_T. In turn, given the magnitude of the experimental uncertainties in the data, it does not appear overly presumptuous to conclude that our theory is not in disagreement with the P-D data, since the extrapolated λ value is very close to the theoretically expected value of $\lambda = 1$ for thermodynamically "ideal" mixtures.

3. Theoretical basis underlying Eq. (13) in the case of liquids

From a theoretical point of view, the posited validity of Eq. (13) rests on the fundamental role played by fluctuations in the notion of diffuse (i.e., nonconvective) volume transport [45]. This fluctuation-based role can be seen most clearly by considering the closely related case of mutual mass diffusion in *isothermal* thermodynamically ideal binary fluid mixtures, both gaseous and liquid. In this purely isothermal context, wherein thermal gradients play no role in contemplating fluctuations (thus excluding α from consideration as a possibly relevant variable in the analysis) and hence for which the fluctuations are associated exclusively with fluctuations in composition, volume transport theory [45] teaches that the diffusional volume flux is given, unequivocally, by the expression $\mathbf{j}_v = D\boldsymbol{\nabla} \ln \rho$, with D the Fick's-law binary mutual diffusion coefficient—in which case comparison with Eq. (2) yields $D_v = D$. Thus, in contrast with the single-component relation (13), there exists no

doubt of the correctness of identifying the fluid's volume diffusivity D_v with its diffusivity D in the isothermal two-component case [67]. The suggested analogy here between the two-component isothermal relation $D_v = D$ and its single-component nonisothermal counterpart, $D_v = D_S$, is self-evident, given that, in both cases, fluctuations constitute the sole source of the diffuse volume transport process.

Other seemingly compelling reasons exist for belief in the validity of Eq. (13). These can be seen from a recent analysis [37] of the nonisothermal isobaric density distribution $\rho = \rho(\mathbf{x})$ prevailing within a confined single-component fluid (either gas or liquid) at rest between two parallel walls while undergoing one-dimensional steady-state Fourier heat conduction in the absence of gravity. It was argued in that context that this nonuniform density distribution could be envisioned as representing a kinematical mass balance between a flux $\mathbf{U}n$ of molecules being conveyed in a piggyback mode preferentially towards one of the two walls as a result of the prevailing temperature gradient, while being opposed by a back-diffusion flux of molecules, $-D'\boldsymbol{\nabla}n$, as a consequence of the ensuing gradient in the molecular number density n. Here, $\mathbf{U}$ is the fluid's "drift velocity" and D' its so-called nonisothermal self-diffusivity [37]. Inasmuch as $\rho = mn$, with m the molecular mass, this flux balance leads immediately to the relation $\mathbf{U} = D'\boldsymbol{\nabla} \ln \rho$ in single-component nonisothermal fluids. By then identifying $\mathbf{U}$ with the fluid's volume velocity $\mathbf{v}_v$ [the latter equal to the fluid's diffuse volume flux $\mathbf{j}_v$ in present circumstances wherein Eq. (1) applies] and further identifying D' with the fluid's *isothermal* self-diffusivity D_S, one thus recovers the posited relation (13) as a consequence of Eq. (2). While the original derivation [37] dealt only with gases, in which case D' was identified with α, the kinematical balance scenario clearly applies equally to liquids, in which case it is more natural to identify D' with the liquid solvent's self-diffusivity D_S.

VII. THERMAL DIFFUSION IN GASES

A. Application of the theory to gases

While we have thus far emphasized thermal diffusion in liquids, there is nothing in the derivation of Eq. (14) to prevent its being applied to *gaseous* binary mixtures, provided only that the basic criteria entering into its derivation are satisfied. What is of interest in this context is the fact that satisfactory theories of thermal diffusion in gases have existed for almost a century, following the pioneering work of Enskog and Chapman [32]. Moreover, since these theories are much broader in scope than is Eq. (14), comparison of the respective predictions of the two can provide potentially useful insights into the limitations of our more specialized theory, at least when applied to gases. The hope, of course, is that some of the conclusions thereby gleaned may carry over to the case of liquids, where no comparably satisfactory general theory currently exists to suggest the limitations of Eq. (14).

In effecting the proposed comparison of Eq. (14) with experimental results for gases, it needs to be borne in mind that the quantity termed the thermal diffusivity in the gas-phase literature, and there designated by the same symbol D_T

TABLE VII. Experimental thermal diffusivities D_T and calculated λ values at 300 K for H_2–noble-gas mixtures in the limit where the mole fraction of the specified noble gas solute approaches zero.

Noble gas	Reciprocal thermal diffusion factor[a] $(\alpha_T)^{-1}$	Mutual diffusion coefficient[b] $D \times 10^5$ $(m^2\,s^{-1})$	Thermal diffusivity[c] $D_T \times 10^7$ $(m^2\,s^{-1}\,K^{-1})$	$\lambda = \dfrac{D_T}{D_T^*}$
Ne	2.75	11.76	1.43	0.30
Ar	2.11	8.24	1.30	0.28
Kr	1.92	7.24	1.26	0.27
Xe	1.75	6.23	1.19	0.25

[a]This corresponds to c_0 in the notation of Dunlop *et al.* Ref. [69].
[b]This corresponds to D_{12}^0 in the notation of Dunlop *et al.* Ref. [69].
[c]Calculated from the expression $D_T = \alpha_T D/T$.

as here, is really equivalent to our TD_T [with the gas-phase thermal diffusivity possessing the dimensions of a true diffusivity, namely (length)^2/time]. Accordingly, in order to avoid confusion in what is to follow, we affix a prime to the gaseous thermal diffusivity symbol, writing it as D_T', so that $D_T' \equiv TD_T$, with D_T the thermal diffusion coefficient appearing throughout the present paper, including in what follows. The gas-phase thermal diffusivity D_T' is rarely used in practice to quantify thermodiffusion effects [31,32]. Rather, preference favors use of the so-called thermal diffusion factor α_T, a dimensionless quantity defined as $\alpha_T = D_T'/D \equiv TS_T$ and thus related to the Soret coefficient $S_T = D_T'/DT \equiv D_T/D$ [68].

Binary mixtures composed of gaseous H_2 (as the "solvent") admixed with each of the noble gases Ne, Ar, Kr, and Xe (as the respective "solutes") [69] represent candidates likely to approximate all the criteria necessary for the applicability of Eq. (14). Accurate experimental data for α_T and D at a common temperature, and in the dilute solute concentration limit needed to evaluate D_T for each of these mixtures, are provided by Dunlop *et al.* [69] over an extensive range of temperatures. Their data at 300 K are summarized in Table VII together with the values of D_T calculated therefrom for each noble gas. It should be noted from these data that, independently of the numerical value of the volume diffusivity D_v, our theoretical prediction that this "tracer" thermal diffusivity should be the same for all inert solutes (at least those whose molecules are large relative to those of the solvent) is borne out by these data, at least approximately.

The self-diffusivity of gaseous hydrogen at this temperature is (approximately) $D_S = 1.4 \times 10^{-4}$ m^2 s^{-1} ([32] p. 267). Since $\beta = 1/T$ for ideal gases—namely, H_2 in the present case—Eq. (15) furnishes the value $D_T^* = 4.7 \times 10^{-7}$ m^2 s^{-1} K^{-1} at 300 K. In turn, from Eq. (16), this yields the λ values shown in the last column of Table VII for each noble-gas solute. The next subsection shows that these values of λ (including the fact that λ is essentially the same for all solutes) accord well with theoretical expectations based upon the gas-kinetic theory analysis of de la Mora and Mercer [70].

B. Gas-kinetic theory prediction of the value of λ

de la Mora and Mercer's [70] quasi-Lorentzian analysis neatly complements our present purely continuum-level

transport arguments by explicitly identifying and quantifying the molecular-level factors that need to be considered in establishing the magnitude (as well as the algebraic sign) of λ in the case of gases. Their work was recently reviewed by the present writer [37] in a context not wholly dissimilar from that addressed here. A remarkable feature of their analysis, and one in complete accord with our theory, is that when a large disparity exists between the respective molecular masses in a binary gaseous mixture and when the mixture is dilute in the heavier species (the "solute"), corresponding collectively to a so-called quasi-Lorentzian mixture [32,37], the thermal diffusivity D_T of the mixture depends only upon the transport properties of the lighter of the two species (namely, the "solvent").

As summarized in Ref. [37] and as reexpressed in our present notation, the calculations of de la Mora and Mercer lead to the relation $D\alpha_T = C_{M/M}v$, where D and α_T are, respectively, the mutual diffusion coefficient and thermal diffusion factor, as already defined, while v is the kinematic viscosity of the light species. The dimensionless $O(1)$ $C_{M/M}$ coefficient, referring to the light gas, is given by the expression

$$C_{M/M} = \frac{3}{2}\left(3\frac{\Omega_{12}^*}{\Omega_{11}^*} - \frac{5}{2}\right), \qquad (17)$$

where the above Ω integrals are those tabulated in the Appendix to the book by Hirschfelder *et al.* [71]. Values of $C_{M/M}$ calculated therefrom are tabulated in Ref. [37] for various collisional potential-energy models, including Lennard-Jones 6-12, square-well, hard-sphere, etc., over a wide range of reduced temperatures T^* (with $C_{M/M}$ attaining asymptotic values as $T^* \to \infty$ of 0.517 in the Lennard-Jones case and 0.75 in both the square-well and hard-sphere cases).

In terms of our present notation, $D_T = C_{M/M}v/T$. Alternatively, since $\beta = 1/T$ for ideal gases, this can be written in the form of Eq. (14), wherein

$$\lambda = C_{M/M}Sc, \qquad (18)$$

in which $Sc = v/D_S$ is the Schmidt number for the light-gas solvent, with D_S the latter's self-diffusivity. As such, the work of these authors provides a theoretical molecular basis for Eq. (14), at least in the case of gases, including establish-

ing the functional dependence of the nondimensional $O(1)$ coefficient λ upon the properties of the solvent.

The hydrogen-noble gas data of Dunlop *et al.* [69] in Table VII provides a basis for judging the accuracy of the de la Mora–Mercer analysis. In Eq. (18) the Schmidt number for H_2 is about Sc=0.73 [46]. For purposes of estimating $C_{M/M}$ we adopt the Lennard-Jones 6-12 potential. The Lennard-Jones parameter for H_2 is ε/k_b=38.0 K (with k_b Boltzmann's constant) ([46] p. 864). At 300 K this corresponds to a reduced temperature of $T^*=k_b T/\varepsilon$=7.89 and thus to the value $C_{M/M}\approx 0.48$ for the Lennard-Jones potential case. Similarly, one obtains $C_{M/M}$=0.39 for the modified Buckingham 6-Exp12 potential case [37]. As such, the respective theoretical λ values for these two intermolecular models are λ=0.35 and 0.26. These values are seen to accord quite well with the range of experimental values tabulated in Table VII [72].

VIII. DISCUSSION AND CONCLUSIONS

A. Review of prior theories applicable to both liquids and gases

The only other recent work known to us that also proposes a theory of thermal diffusion which is applicable to *both* liquids and gases is that of Kempers [73]. Indeed, his theory also addresses solids. Since Kempers' paper reviews earlier theories, we confine our review of the pertinent literature entirely to his paper.

Kempers' theory, like ours, is applicable only to binary mixtures. [74] However, a separate theory of Kempers, although not concerned with the Soret effect, deals with ternary molecular diffusion processes in isothermal mixtures. However, apart from both addressing the Soret effect, our theories appear to have nothing in common. They even differ slightly in their respective goals, since our theory is aimed at predicting the thermal diffusion coefficient D_T, whereas Kempers' theory aims at predicting the thermal diffusion factor, $\alpha_T=D_T T/D$. Moreover, where our model addresses only dilute solutions, Kempers' theory is not similarly restricted. Furthermore, in order to predict D_T, our theory requires no knowledge whatsoever of the solute's physicochemical properties, only those of the solvent: namely, its self-diffusivity D_S and thermal expansivity β—properties readily available in handbooks and in the archival literature. In contrast, predictions of Kempers' thermal diffusion factor α_T require knowledge of the mixture's thermodynamic properties (derived in part from a modification of the Soave equation of state for the mixture), as well as knowledge of the thermal diffusion factor α_T^0 that would exist in the mixture's ideal gas state, the latter derivable from gas-kinetic theory. According to Kempers, a test of his theory against the experimentally measured Soret effect in 18 liquid and gaseous mixtures showed agreement generally to within a factor of about two over four decades of α_T values, although not in all cases. Of course, in the case of (low pressure) gases, a major portion of this observed agreement merely represents the fact that the dominant contribution stems from the ideal gas contribution α_T^0 derived from Chapman-Enskog theory, which is known to accurately mirror experimental values. Viewed from an over-

all perspective, Kempers' theory requires *a priori* data on the equilibrium and kinetic properties of the mixture itself. In contrast, our theory does not require any mixture data (except, of course, if one wishes to attempt to predict the non-inertness λ factor in our model).

Among other things Kempers' model has been tested only for situations in which the solute and solvent molecules are both of ordinary size, thus addressing only so-called molecular fluids. As such, in contrast with our model, which has been shown to furnish reasonably accurate Soret predictions for solutes encompassing the entire molecular-size spectrum, Kempers' theory has not been tested for either macromolecular (i.e., polymeric) or colloidal solutes, although he states that such applications are possible in principle. Moreover, as discussed in Section VIII F, our theory appears to have some degree of legitimacy in the case of ionic solutes, in apparent contrast with Kempers' model.

B. Orders of magnitude of the thermal diffusivities of liquids and gases

As seen from Tables I–IV, except under unusual circumstances (such as arises in the case of water at temperatures near to its maximum density, where D_T=0) and irrespective of the particular solute-solvent combination being considered, virtually all of the experimental liquid-phase thermal diffusivity values are of the order of $D_T=O(10^{-12})$ m^2 s^{-1} K^{-1}, at least in the dilute solutions considered. The same is true of much of the other liquid-phase thermal diffusivity values available in the literature which we have examined but not explicitly cited here. This magnitude is entirely consistent with Eq. (14) and owes to the facts that: (i) thermal expansivities for most ordinary liquids lie in the range of about $\beta=O(10^{-3})$ K^{-1} to within a multiple of $O(1)$ [Ref. "a" in Table VI]; and (ii) the self-diffusivities of these same liquids obey, at least approximately, the Stokes-Einstein-Sutherland diffusion relation [54,55] $D_S=k_b T/3\pi\eta_2 d_2$, where η_2 and d_2 are, respectively, the solvent's viscosity and molecular diameter. Since the molecular sizes of common mobile liquids tend not to differ too much from one another, and for circumstances where these liquids possess normal viscosities (thus excluding exceptionally high-viscosity solvents like glycerine), typical liquid-phase self-diffusivities are of the order of $D_S=O(10^{-9})$ m^2 s^{-1} to within a multiple of $O(1)$ (cf. Tables V and VI). Use of these β and D_S estimates in Eq. (14) shows why D_T values for liquids tend to be clustered around the $O(10^{-12})$ m^2 s^{-1} K^{-1} value cited [75].

Similar arguments based upon applying Eq. (14) to gases show that thermal diffusivities should be of the order of $D_T=O(10^{-7})$ m^2 s^{-1} K^{-1}, in accord with experimental data (cf. Table VII and other gaseous data [31,32,71]). Explicitly, based on the Stokes-Einstein-Sutherland diffusion model [54,55], self-diffusivities in gases are found to be of the order of $D_S=O(10^{-4})$ m^2 s^{-1} to within a multiple of $O(1)$ (cf. Table VII). Inasmuch as $\beta=1/T$ for ideal gases, at ordinary temperatures (e.g., T=300 K), the magnitudes of gaseous thermal diffusivities are thus seen to lie in the range indicated

TABLE VIII. λ values at different temperatures for various athermal solutes in water.

Solute	λ (25 °C)	λ (100 °C)
PS[a]	2.7	1.2
SDS[b]	4.9	2.0
NaPSS[c]		
$M_w = 15\,400$[d]	5.9	2.5
$M_w = 32\,900$	4.9	2.1
$M_w = 74\,000$	4.1	1.7

[a]PS=polystyrene latex particles (radius=30 nm).
[b]SDS=sodium dodecyl sulfate (ionic micelles).
[c]NaPSS=sodium polystyrene sulfonate (a linear polyelectrolyte).
[d]M_w=molecular weight.

above, being larger than comparable values for typical liquids by about five orders of magnitude.

C. Effect of temperature on λ

According to the theory presented here, the departure of λ from unity is a manifestation of the effects of noninertness or, equivalently, nonideality in regard to solute-solvent physicochemical interactions. It is therefore natural to expect that, all other things being equal, the higher the temperature, the closer λ should be to unity. Thus, for example, in the case of liquid water one would expect the extent of hydrogen bonding to diminish with increasing temperature, resulting in more ideal behavior by making it easier for a solute molecule to wend its way through the water by not having to "break" any bond. It is possible to test this expectation by supposing that the aqueous athermal D_T data of Iacopini *et al.* [9], summarized by Eq. (12) and covering the range from 0 to only 40 °C, can nevertheless be extrapolated to 100 °C (a quite reasonable assumption given the linearity of their data as displayed in their Fig. 7). From Table V, it is seen that at 25 °C and 100 °C, $D_T^* = 0.59 \times 10^{-12}$ m^2 s^{-1} K^{-1} and $D_T^* = 6.5 \times 10^{-12}$ m^2 s^{-1} K^{-1}, respectively, for liquid water. Using Eq. (12) to compute the respective "experimental" D_T values, Table VIII compares the respective λ values for aqueous solutions of PS, SDS, and NAPSS at these two temperatures. It is evident that the λ values for all three athermal solutes are very much closer to unity at the higher temperature, in accord with our intuitive expectations.

D. Can λ exceed unity?

According to the theory advanced here, $\lambda \rightarrow 1$ in the limiting case where the solute molecules are "inert" relative to those of the solvent. The theory does not, however, establish whether λ is greater or less than unity in circumstances where the solute fails to be inert. The data presented here suggest that, generally, $\lambda \geq 1$ in the case of liquids whereas $\lambda \leq 1$ in the case of gases. Given that the numerical value of λ derives from the issue of the entrainment of a solute particle in the solvent's volume flow, it may thus appear strange that in the case of liquids the solute molecules appear to be moving faster than those of the solvent, as implied by the fact that $\lambda > 1$. In resolving this concern it must be borne in mind that in steady-state Soret-type experiments both the solute and solvent molecules are, in fact, (on average) macroscopically at rest. In particular, the solvent "velocity" referred to in the present analysis is that of volume rather than mass [with mass motion, $(\mathbf{v}_m)_2 = (\mathbf{n}_m)_2 / \rho_2$, referring to the net movement of solvent molecules through space]. Since volume is an abstract, nonmaterial property, the notion of a "volume velocity" here should not be taken literally as referring to the movement of a material entity through space [45]. Rather, it is a normalized diffuse flux density, totally disassociated from the net *physical* movement of matter through space.

Indeed, one can define the diffuse "velocity" of any extensive physical property. Thus, if $\mathbf{j}_\psi$, say, denotes the diffuse flux density or current of any such property (representing the amount of that property per unit time crossing a unit area) at a point of a fluid (or even solid) continuum and if ψ denotes the density of the property at that point (representing the amount of the property per unit volume), then $\mathbf{v}_\psi := \mathbf{j}_\psi / \psi$ constitutes the so-called "property-specific velocity." In the case of volume, this gives $\mathbf{v}_v = \mathbf{j}_v$ for the volume velocity. Owing to the nonmaterial nature of volume, the fact that the solute's "velocity" can exceed this value, corresponding to the fact that $\lambda > 1$, does not violate any physical principle. Indeed, in steady-state Soret-type experiments, since the solute is, in fact, at rest, the notion of a solute velocity represents only a virtual or drift velocity [37]. Being thus aphysical, no contradiction to physical law resides in the fact that λ can exceed unity.

E. Benzene-cyclohexane mixtures: Another "inert" liquid-phase system?

Earlier, we indicated that the only complete liquid-phase data set of which we were aware for which "inertness" appeared intuitively likely (corresponding to $\lambda = 1$), occurred for *n*-pentane/*n*-decane mixtures. However, we have subsequently become aware of data for another such candidate mixture: namely, the system benzene-cyclohexane, with benzene serving as the "solvent" in the sense of being the smaller, lower molecular weight species, and accumulating at the warmer wall of the Soret apparatus (cf. the following references). Pertinent data for this system at 25 °C are as follows: $S_T = 1.03 \pm 0.05 \times 10^{-3}$ K^{-1} [76], $D = 2.10 \times 10^{-9}$ m^2 s^{-1} [77,78], $D_S = 2.21 \times 10^{-9}$ m^2 s^{-1} [79], and $\beta = 1.14 \times 10^{-3}$ K^{-1} [Ref. "a" of Table VI]. These respectively give $D_T = S_T D = 2.16 \times 10^{-12}$ m^2 s^{-1} K^{-1} and $D_T^* = D_S \beta = 2.52$ m^2 s^{-1} K^{-1}. Accordingly, to within experimental uncertainties (the error estimate is ours),

$$\lambda = D_T / D_T^* = 0.86 \pm 0.04.$$

The fact that λ is not closer to unity can perhaps be explained in terms of the fact that the cyclohexane molecule is not sufficiently large relative to that of a benzene molecule for the disparate size precondition to be met. Another source is, obviously, the possible failure of our intuitive expecta-

tions. That is, whereas both species are hydrocarbons, they are not members of a homogeneous chemical family. Irrespective of the reason, the fact remains that our prediction D_T^* of the thermal diffusivity D_T is in error only by about 15%. As an aside, it is interesting to note that this is the first liquid-phase mixture encountered for which the λ value is less than unity.

F. Other data in support of the sign change in D_T when $\beta=0$

Further evidence in support of the discussion in Sec. IV of the fact that in sufficiently dilute aqueous solutions D_T changes sign at 4 °C for any and all solutes is offered by the experimental data of Agar and Turner [80] for 0.01 M NaCl solutions. Thus Caldwell [81], in the context of his own data on much more concentrated NaCl solutions (0.5 N), referring to their data, states that "Extrapolation of Agar and Turner's results for much more dilute NaCl at 25 and 34.7 °C to lower temperatures suggests a change in sign at 5° or so." Caldwell's statement is offered in the context of his experimentally demonstrated belief in the existence of a strong correlation (based on the theory of Hurle and Jakeman [82]) between the Soret coefficient S_T and the mixture's thermal expansivity β. Indeed, Caldwell's 0.5 N NaCl experiments confirm a linear relation between S_T and β, although the relation is not a *direct* proportionality (i.e., such that $S_T=0$ when $\beta=0$), which, according to our theory, would be expected to apply only in dilute solutions, such as that studied by Agar and Turner [80].

Equally strong evidence in a similar context is provided by the results of Alexander [83] on the variation of the Soret coefficient with temperature in a 0.05 mol/l aqueous solution of LiCl, in which the experiments were performed in a thermogravitational column. Colombani *et al.* [84], in comparing Alexander's dilute solution data [83] with their own LiCl data in significantly more concentrated systems, point out that Alexander's data indicate that $S_T=0$ at about 3.6 °C. Within experimental error this value does not differ from the 4 °C temperature at which water has its maximum density. Colombani *et al.* [84], in relation to this observation, note that Lin *et al.* [85] attempted to explain the Soret coefficient sign change inversion by considering the change in sign of β.

These data sets extend the class of so-called athermal systems of Iacopini *et al.* [9] to now include simple electrolytes. Moreover, the above-cited authors point to the existence of a prehistory to our belief that D_T may be correlated with β.

G. Composition-dependent changes in the algebraic sign of D_T

Section IV A 1, which focuses on evidence that $D_T=0$ when $\beta=0$, deals only with changes occurring in the algebraic sign of D_T arising as the temperature is varied while keeping the mixture's composition fixed. This vanishing thermal diffusivity phenomenon has a counterpart with respect to possible changes in the algebraic sign of (the temperature-specific) D_T occurring as the mixture composition is changed while keeping the temperature fixed. Indeed, there exists a growing body of experimental literature demonstrating sign-change phenomena occurring in the latter

composition-varying case, such as arises, for example, in the case of ethanol-water mixtures [24,27,86], presumably on the basis of hydrogen bonding in these highly thermodynamically nonideal solutions. Indeed, Other examples can be found in Refs. [30,81]. On the theoretical side, Rousseau *et al.* [87], using molecular dynamics simulations, were able to explain, quantitatively, the experimentally observed change in the sign of the Soret coefficient with composition. Other theories [73,88] aim, *inter alia*, at this same goal. The source of the sign change with composition is obviously quite different from that arising from thermal expansivity. Our theory, of course, provides no insight into such phenomena since it does not deal with effects of varying composition [89].

H. Possible pressure-diffusion effects

Given the fact that steady-state Soret experiments entail no net mass motion, as embodied in Eq. (1), it has always been implicitly assumed that the pressure is uniform throughout the binary mixture, thereby eliminating the possibility of a *pressure-diffusion* contribution [90] to the species mass flux in Eq. (9). The isobaric assumption implicit in Eq. (9) hinges critically on the validity of the Navier-Stokes equations, in particular—in view of Eq. (1) indicating the absence of inertial effects—on the applicability of Newton's rheological viscosity constitutive law, wherein the velocity gradient appearing therein is that of the fluid's mass velocity $\mathbf{v}_m$. However, recent work [38,51,52], closely related to our volume-transport view of fluid motion [45] leading to Eq. (11), has suggested that the velocity whose gradient appears in Newton's viscosity law should be the volume velocity $\mathbf{v}_v$ rather than the mass velocity $\mathbf{v}_m$. To the extent that this is indeed true, a pressure gradient might then arise in the particle-free solvent as a consequence of "thermal stresses" [51,52] induced by the solvent's density-cum-temperature gradient, even in the simple one-dimensional Soret-based apparatus described in the opening paragraph of our presentation [91,92]. Because it is the divergence of Newton's viscous deviatoric stress, rather than the stress itself, which governs the resulting pressure gradient ∇p, the magnitude and direction of the latter will depend functionally upon the temperature-dependence of the solvent's viscosity, thermal diffusivity, and especially its thermal expansivity. The possible effect of such a pressure gradient upon both the theory underlying Eq. (11) and the experimental evaluation of D_T based upon the modified form of Eq. (9), which would now include a pressure-diffusion contribution [41,42], here ignored, remains to be assessed.

IX. SUMMARY AND CONCLUSIONS

A. Summary

This paper has demonstrated, *inter alia*, that a theoretical formula previously derived by us for the thermal diffusivity D_T of a dilute mixture consisting of physicochemically inert "macromolecular" solute molecules dispersed in a solvent—and requiring both dynamical and extra-thermodynamic arguments (the latter invoking an assumed Boltzmann distribution, despite the system's nonequilibrium nature)—could be

obtained alternatively by purely kinematical arguments. It was further shown that the agreement of our previous formula with liquid-phase experiments could be improved, and its realm of applicability extended so as to include gases, upon replacing the solvent's thermometric diffusivity α appearing in the original formula by the solvent's isothermal self-diffusivity D_S and by introducing a multiplicative correction factor λ to allow for deviations of the solute-solvent mixture from "inert" behavior. This led to the formula $D_T = \lambda D_S \beta$ as set forth in Eq. (14), with β the solvent's thermal expansion coefficient and λ an $O(1)$ dimensionless parameter, presumably equal to unity in the particular case of physicochemically inert, dilute, disparate-size binary mixtures, and (for a given solvent) otherwise weakly dependent upon the nature of the solute. Arguments based upon gas-kinetic theory and supported by experiments were shown to theoretically affirm this new formula. Explicitly, the quasi-Lorentzian analysis of de la Mora and Mercer [70] for gases, whose validity we have confirmed in Sec. VII by comparing its predictions with experiment, was shown to provide a rational molecular basis for Eq. (14).

Our new formula for D_T, Eq. (14), was shown on the basis of the algebraic sign of β to provide a theoretical basis for rationalizing the observed reversal in the direction of solute migration with temperature in dilute aqueous solutions at 4 °C by Iacopini *et al.* [9] for several "athermal" solutes [93]. Moreover, in accordance with our theory, the thermal diffusion data in Tables I–IV were shown to provide evidence of the insensitivity of D_T to the physical properties of the solute—be these properties its molecular size or configuration or its physicochemical constitution—as is implicit in Eq. (14). In the sole case examined, higher temperatures were shown to improve agreement between theory and experiment, in accord with expectations.

Whereas Eq. (14) was deemed applicable for only a restricted set of circumstances, comparison of its predictions with experiments that almost certainly violated these stated criteria revealed that the formula possesses an unexpected robustness [94]. The theoretically predicted thermal diffusivity of *n*-pentane/*n*-decane mixtures, the only binary liquid-phase mixture studied which would be expected to fulfill all of the basic criteria underlying our model, especially including inertness, and for which the requisite D_S, β, and dilute solution D_T data sets were also available, agreed well with experiments in the sense that it was found that $\lambda = 1$ in Eq. (14) to within the accuracy of the data. Modulo experimental uncertainties, together with the fact that the set of assumptions underlying our theory were almost certainly not met exactly by any of the liquid-phase solute-solvent systems analyzed by us (with the possible exception of this *n*-pentane/*n*-decane mixture), Eq. (14) was shown to be consistent (or, at least, not inconsistent) with the experimental D_T data for each of the several, physicochemically diverse, solute-solvent liquid-phase systems studied. Excellent agreement of the theory with experiment was also noted in the gaseous case.

B. Validity of Marangoni-like models of thermodiffusion phenomena

That Eq. (14) appears to apply to the extraordinary variety of liquid-phase dispersed solutes listed in the opening para-

graph of this paper, ranging from polymer molecules and large (albeit submicron in size) metallic colloidal particles down to solute molecules not much larger than those of the solvent (as in the *n*-pentane/*n*-decane mixture case), as well as to gases, casts doubt on the current spate of theoretical papers whose central thesis argues that thermal diffusion constitutes a surface-driven Marangoni-like phenomenon [64], arising from gradients in interfacial tension or surface energy over the surface of a *single* molecule—macromolecular, mesomolecular, or micromolecular in size—such gradients, in turn, deriving from comparable temperature gradients over its surface. Apart from the self-contradictory notion of a macroscopic temperature gradient acting over the surface of single molecule in a continuum (as well as the fact that Marangoni-induced particle velocities increase linearly with particle size [65,66]) is the fact that, for a given solvent, such interfacial effects would be expected to be strongly dependent upon the nature of the solute. Yet, for a given solvent, this predicted functional dependence upon the solute's physicochemical attributes is not supported by the data, in the sense that, experimentally, $\lambda = O(1)$ for all solute-solvent combinations and molecular size ratios examined, whether referring to liquid- or gas-phase experiments. Nor is the Marangoni-model-predicted increase in migration velocity $\mathbf{U}_M$ (and, hence, in D_T [95]) with particle size borne out by the data in Tables I, II, and IV, which, without exception, indicate, if anything, a slight *decrease* in thermal diffusivity with increasing particle size.

C. Closing remarks

A comprehensive and critical survey of the existing thermodiffusion database, as well as the undertaking of several key experiments implicitly suggested by the results of this paper, would appear to be warranted by our findings. Among other things, such studies could serve to establish definitive trends prerequisite to the creation of a more accurate thermal diffusion theory, one embodying physical attributes not addressed by the present elementary kinematical model, especially composition-dependent effects. In regard to such future work, a great deal of liquid-phase thermodiffusion data capable of serving as a useful guide in this capacity already exists in the literature. Thus, for example, Zhang *et al.* [27] provide extensive and systematic data for both the Soret coefficient and mutual diffusivity of toluene/*n*-hexane mixtures over the entire range of possible compositions, and at temperatures from 5 to 45 °C. Moreover, self-diffusion and thermal expansivity data are available for both compounds. Since the molecules of both species are about the same size, we made no attempt here to use these data to test our theory, given the latter's presumed applicability only to mixtures of disparate molecular sizes. Nevertheless, any systematic attempts to explore the limitations of the present theory should certainly take advantage of the availability of temperature-specific data of this quality, especially as these data were not obtained in a thFFF device.

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[43] Referring specifically to this arrangement is not meant to imply that this is the only type of apparatus capable of measuring S_T and/or D_T. Rather, many ingenious devices and schemes exist for effecting these measurements [1,2], an especially popular one involving thermal field-flow fractionation [3,4,14,44].

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[49] As a matter of historical interest, Maxwell's work on this subject of "slip" at solid surfaces can be traced to the intense competition at the time among prominent scientists of the era to explain the workings of the Crookes' radiometer [50]—the latter laboratory curiosity having been introduced to the public a few years earlier, in 1873.

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[53] Complete entrainment by the solvent occurs only when the particle is nonheat conducting or at least poorly conducting relative to that of the fluid [47,52].

[54] S. Sutherland, Philos. Mag. **9**, 781 (1905).

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[56] Were there to be a nonzero mass flux, corresponding to $\mathbf{v}_m \neq \mathbf{0}$, one would then have, more generally, that $\mathbf{n}_i = \mathbf{n}_m \overline{v}_i + \mathbf{j}_i$, where $\overline{v}_i$ is the species partial specific volume [41,42].

[57] In contrast, much of the other D_T data upon which we will be reporting subsequently were obtained by use of thermal field-flow fractionation techniques [3,4,14,44]. The devices used in such experiments are, at least at their present stage of development, intrinsically incapable of producing temperature-specific thermal diffusivity data (certainly not accurate data) owing to the large temperature differences necessitated by their use, and the interpretative complications arising therefrom.

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[59] As a chronological note, Bielenberg and Brenner [35], in their original derivation of Eq. (11), commenting on the preliminary

aqueous SDS Soret sign-reversal experiments reported by Piazza [7] preceding the full report of these data by Iacopini *et al.* [9], had already ascribed the experimentally observed 4 °C reversal to the fact that water has its maximum density at this temperature.

[60] A direct proportionality of the Soret coefficient S_T (and, hence, of D_T) to β in the limiting case where the particles act as a "hard wall" (corresponding to the case of "no specific particle/solvent interactions") "dispersed in a hard-sphere solvent" is said by these authors to have already been anticipated earlier by Parola and Piazza [8] based upon upon their prior theory [5].

[61] From a strictly pragmatic viewpoint, current interest in the phenomenon of thermal diffusion resides in the ability of a temperature gradient to effect the separation of solutes of different sizes from a given solvent. While D_T values are seen to vary little among different solutes (and solvents), it is the difference in their respective mutual diffusivities D (and hence in their respective Soret coefficients, $S_T = D_T/D$) which constitutes the dominant factor in effecting the separation of molecules of different sizes from the given solvent. Moreover, all other things being equal, the larger the solute molecule, the smaller its mutual diffusivity and hence the greater the effect of a temperature gradient in efficiently effecting the separation.

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[63] From Eq. (10), this corresponds to the attainment of a state wherein that component of the net solute flux which is colinear with the temperature gradient vanishes.

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[66] R. S. Subramanian and R. Balasubramanian, *The Motion of Bubbles and Drops in Reduced Gravity* (Cambridge University Press, Cambridge, England, 2001).

[67] Fick's law holds only for thermodynamically ideal fluid mixtures. Otherwise, the species chemical potential rather than the species mass fraction would appear as the driving force for molecular diffusion. As such, the relation $D_v = D$ can only be strictly valid for such ideal binary mixtures. However, since the concept of thermodynamic ideality does not arise in connection with single-component fluids, was Eq. (13) to be accepted as correct, it would not be comparably restricted to any "ideal" circumstance limitations.

[68] From de Groot and Mazur ([41] pp. 276–280), the molar flux counterpart of Eq. (9) [based on the use of a barycentric reference frame, the same frame as is also used for the mass flux in Eq. (9)] is such that the diffusive molar flux density of species 1 is given by the expression $\mathbf{J}_1 = -\rho^{-1} M_2 N^2 (n_1 n_2 D_T \boldsymbol{\nabla} T + D \boldsymbol{\nabla} n_1) \equiv \mathbf{j}_1/M_1$, where n_i and M_i are, respectively, the mole fraction and molar mass of species i ($i = 1, 2$) and N is the total number of moles per unit volume. Thus, at Soret steady state (upon symbolically regarding $\boldsymbol{\nabla}$ as the one-dimensional derivative d/dx), one has in respective mass and molar units that $S_T = -(w_1 w_2)^{-1} dw_1/dT \equiv -(n_1 n_2)^{-1} dn_1/dT$.

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

[72] As an aside, it is interesting to note that $C_{M/M}$ values for these two models of the collisional process become negative at small reduced temperatures, respectively having the values -0.370 and -0.073 at $T^* = 0.50$. While this suggests the theoretical possibility of a reverse Soret effect at very low temperatures, with the larger more massive molecules in the mixture migrating towards the hot wall, we are unaware of this inversion ever having been observed experimentally in gases.

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[75] The unexpected robustness of Eq. (14), despite the seemingly restrictive assumptions entering into its derivation, stems, at least in part, from the fact that D_T does not depend upon solute particle size or shape. As such, even were the solute molecules to cluster together owing to attractive intermolecular dispersion forces (rather than behaving individually were they to be screened coulombically), this would, according to Eq. (14), nevertheless be wholly without effect upon D_T.

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[89] Interestingly, even in the case of benzene-cyclohexane mixtures, which we intuitively regarded as possibly being "inert" in Sec. VIII E, the thermal diffusivity vs composition experimental studies of Story-Turner and Debuschewitz-Köhler [76] on this system at 25 °C reveal a change in the algebraic sign of D_T occurring at a benzene mole fraction of about 0.80.

[90] In circumstances where the pressure in not uniform, an additional flux $D_{p,12}\rho w_1 w_2 \boldsymbol{\nabla}\ln p$, arising from the pressure gradient $\boldsymbol{\nabla}p$, appears in Eq. (9), wherein $D_{p,12}=-D_{p,21}\equiv D_p$, with $D_p>0$ the pressure diffusivity ([42], p. 359).

[91] The work of Mackowski *et al.* [92] relates closely to this issue since it refers to pressure gradients arising from the higher-order Burnett-Kogan thermal stress terms appearing in the Chapman-Enskog Knudsen number expansion [32,71] of the viscous stress tensor in single-component nonisothermal gases, as discussed in Sec. IV of Ref. [52].

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[93] This statement should actually refer to the more generally valid precursor of Eq. (14)—namely, Eq. (11), which makes no assumptions, such as that embodied in Eq. (13), with respect to the constitutive equation for the volume diffusivity D_v.

[94] The unexpected robustness of Eq. (14), despite the seemingly restrictive assumptions entering into its derivation, stems, at least in part, from the fact that D_T does not depend upon solute particle size or shape. As such, even were the solute molecules to cluster together owing to attractive intermolecular dispersion forces (rather than behaving individually were they to be screened coulombically), this would, according to Eq. (14), nevertheless be wholly without effect upon D_T.

[95] The particle's Marangoni-induced solute migration velocity is related to the thermal diffusivity (i. e., the thermophoretic mobility) by the expression $\mathbf{U}_M=-D_T\boldsymbol{\nabla}T$ [3].

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