

Different measures for characterizing the motion of molecules along a temperature gradient

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We study the motion of a Brownian particle in a medium with inhomogeneous temperature. In the overdamped regime of low Reynolds numbers, the probability distribution function (PDF) of the particle is obtained from the van Kampen diffusion equation [J. Phys. Chem. Solids **49**, 673 (1988)]. The thermophoretic behavior is commonly described by the Soret coefficient, a parameter that can be calculated from the steady-state PDF. Motivated by recent advances in experimental methods for observing and analyzing single nanoparticle trajectories, we here consider the time-dependent van Kampen equation from which the temporal evolution of the PDF of individual particles can be derived. We analytically calculate the PDF describing dynamics driven by a generalized thermophoretic force. Single-particle statistics are characterized by measures such as the mean displacement (drift) and the probability difference between moving along and against the temperature gradient (bias). We demonstrate that these quantities do not necessarily have the same sign as the Soret coefficient, which causes ambiguity in the distinction between thermophilic and thermophobic response (i.e., migration in and against the direction of the temperature gradient). The different factors determining the thermophoretic response and their influence on each measure are discussed.

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I. INTRODUCTION

The motion of molecules induced by a temperature gradient is commonly referred to as thermophoresis, thermodiffusion, or the Soret effect. Since its discovery in liquid mixtures more than a century and a half ago [1,2], the phenomenon of thermophoresis has been experimentally observed in aqueous solutions containing colloidal particles, micelles, polymers, proteins, and DNA molecules (see extensive review in Ref. [3]). Several studies have shown thermophoresis to be a promising tool for manipulating and concentrating biomolecules in solutions [4–6], which has even led to the speculations that it may play a role in the accumulation of nucleotides required for molecular evolution of early life [7].

In this work we theoretically study the thermal diffusion of colloidal particles which, in general, is a much stronger effect than thermophoresis in simple molecular mixtures. The relevant length and time scales of the colloidal particles are orders of magnitude larger than those of the embedding solvent, and hence the solvent may be treated as an effective medium. The thermal motion of the colloidal particle is driven by stresses induced on its surface by the surrounding fluid [8–10]. These forces are balanced by viscous drag forces when the particle attains a steady-state velocity [11]. Thermophoresis can therefore be treated as a mass transport process, which, for dilute suspensions (low concentration, c) can be phenomenologically described by the continuity equation $\partial_t c = -\vec{\nabla} \cdot \vec{J}$, with the particle flux \vec{J} given by [12]

$$\vec{J} = -D\vec{\nabla}c - cD_T\vec{\nabla}T. \quad (1)$$

The first term on the right-hand side of Eq. (1) describes regular diffusion due to concentration gradients, where D is

the Fickian diffusion coefficient. The second term describes an additional contribution to the flux resulting from the temperature gradient, $\vec{\nabla}T$, with D_T termed the thermal diffusion coefficient. When a closed system reaches a steady state, the flux vanishes and a concentration gradient is established that satisfies

$$\vec{\nabla}c = -cS_T\vec{\nabla}T, \quad (2)$$

where $S_T = D_T/D$ is called the Soret coefficient. For $S_T > 0$, the colloids tend to accumulate on the colder side of the system, displaying thermophobic behavior. Conversely, for $S_T < 0$, the migration is toward the hotter side, which is termed thermophilic motion.

The sign and magnitude of S_T are hard to predict since they depend on multitude of interactions and influences. Importantly, S_T may exhibit a pronounced temperature dependence and, quite interestingly, it tends to change its sign close to room temperature in many colloidal systems [13]. Experimental measurements of S_T are typically based on the application of a thermal gradient in a diffusion cell and using indirect optical methods to quantify the concentration gradients induced by thermal diffusion [3]. Recently, it became possible to measure thermophoretic forces on a single colloidal particle confined in submicrometer regions with a nearly uniform temperature gradient (and an overall small temperature difference) [14]. Moreover, we can now study not only the steady-state probability distribution of the particle, but also follow its trajectory to relaxation [15]. These advances in experimental methods call for a better understanding of the problem of a single-particle diffusion in a temperature gradient.

II. VAN KAMPEN EQUATION

Consider a single Brownian particle moving in a one-dimensional medium with a temperature gradient along the x direction. In order to derive an equation for the evolution of the probability distribution function (PDF) of the particle, $P(x, t)$, one has to consider the Langevin equation of the dynamics or the corresponding Fokker-Planck equation. These equations capture both the inertial short-time and dissipative long-time regimes of the dynamics. In practice, however, only the latter is of interest for colloidal systems at low Reynolds numbers. In this so-called overdamped limit, the dynamics is depicted by a Smoluchowski-like diffusion equation that can be derived by an adiabatic elimination process of the fast relaxing momentum degree of freedom. The derivation was carried out by van Kampen for different models of diffusion in inhomogeneous media [16]. One of the cases considered by van Kampen is of a Brownian particle in a system with spatially varying temperature. The equation corresponding to this model is

$$\partial_t P(x, t) = -\partial_x J(x, t) = \partial_x \{ \mu(x) \partial_x [k_B T(x) P(x, t)] - \mu(x) f(x) P(x, t) \}, \quad (3)$$

where f is the mechanical force acting on the particle, while $T(x)$ and $\mu(x)$ denote, respectively, the coordinate-dependent temperature and mobility. The latter are related to the coordinate-dependent diffusion coefficient, $D(x)$, via Einstein’s relation $D(x) = k_B T(x) \mu(x)$, with k_B denoting the Boltzmann constant [16]. As noted by van Kampen, this is a diffusion equation, which does not follow either Itô [17] or Stratonovich [18] prescriptions for overdamped Brownian dynamics in inhomogeneous media.

It is important to note that while the nonisothermal dynamics considered here is clearly out of thermal equilibrium, the overdamped limit depicted by van Kampen equation (3) is based on the approximation that the momentum of the particle, p , is always at equilibrium with the local temperature $T(x)$, i.e., follows the Maxwell-Boltzmann distribution $\rho(p|x) \approx T(x)^{-1/2} \exp[-p^2/2mk_B T(x)]$ (where m denotes the mass of the particle). The local thermodynamics equilibrium (LTE) [12] approximation is justified when $l_b |\vec{\nabla} T|/T \ll 1$, where l_b is the ballistic distance characterizing the crossover between the inertial and diffusive regimes. Mathematically, the overdamped limit corresponds to $l_b \rightarrow 0$.

The force f in Eq. (3) includes both contributions from the thermophoretic force, as well as externally applied forces such as gravity, which can be minimized by density matching the colloid with the solvent. We will henceforth ignore all forces except for the thermophoretic one. Moreover, single-particle experiments are conducted in small systems where the applied temperature difference may be as small as a few degrees K. Assuming that the temperature gradient, $T' = dT/dx$, and the thermophoretic force are uniform throughout the small system, one may phenomenologically write that the thermophoretic force is given by [19]

$$f = C_T k_B T', \quad (4)$$

where C_T is dimensionless parameter. Using this phenomenological form in Eq. (3) and comparing with Eqs. (1) and (2),

we arrive at the following expression for the Soret coefficient [20,21]:

$$S_T = \frac{1 - C_T}{T}. \quad (5)$$

From Eq. (5) we conclude that in the absence of a mechanical thermophoretic force ($C_T = 0$), the Soret coefficient does not vanish ($S_T \neq 0$). The additional contribution to S_T is known as the ideal gas term. Explicitly, the $1/T$ term in Eq. (5) is expected because at steady state $\partial_t P(x, t) = 0$, and from van Kampen equation (3) one can easily deduce that the stationary solution is

$$P_s(x) \sim \frac{1}{T(x)} \exp \left[\int^x \frac{f(y)}{k_B T(y)} dy \right], \quad (6)$$

which, in the absence of a mechanical force ($f(x) = 0$), reduces to

$$P_s(x) \sim 1/T(x). \quad (7)$$

In Ref. [16], van Kampen notes that he has no simple explanation for the prefactor $1/T(x)$ in Eq. (6); however, in the special case $f(x) = 0$, Eq. (7) was nicely rationalized by Fayolle *et al.* [21]. They noted that the mechanical thermophoretic force vanishes in the absence of interaction between the colloidal particles and the embedding solvent, i.e., in the limit of extremely small colloidal particles that can be viewed as an ideal gas. In a closed system at steady state, the pressure of this ideal gas, $\Pi = c(x)k_B T(x)$, must be uniform (or otherwise, the gradient pressure force would act on the gas and change its distribution). Equation (7) then means that in the absence of a mechanical thermophoretic force, the ideal gas thermal collisions induce a steady-state distribution that is higher on the colder than on the hotter side. The associated Soret coefficient $S_T = 1/T > 0$ reflects the thermophobic nature of the thermal collisions (which are stronger on the hotter side, thus pushing the particle to the colder side). The Soret effect is associated with the interaction term in Eq. (5) and, in practice, this term is typically larger than the ideal gas term $|C| \gg 1$, with the exception of relatively small colloidal particles (see discussion in Appendix).

Returning to van Kampen equation, we notice that it also takes into account the spatial variation in the mobility, which within a small system can be approximated by

$$\mu(x) \simeq \mu_0 + \mu' x, \quad (8)$$

where μ_0 is the mobility in the middle of the cell at $x = 0$ and $\mu' = d\mu/dx$. We note here that the spatial variations in $\mu(x)$ can, in general, be further divided into two parts: those arising from the temperature dependence of the fluid viscosity [22] and those also encountered at equilibrium isothermal systems, for instance due to hydrodynamic interactions between the colloidal particle and the walls of the container [23]. As we will see below, the particle’s drift (to be mathematically defined later) depends on both T' and μ' , and one must keep in mind that these two gradients are not entirely independent of each other because of the temperature dependence of the mobility. On the other hand, non-temperature-related reasons for spatial variation in the mobility imply that μ' does not necessarily vanish when $T' = 0$.

Using Eqs. (4) and (8) [together with the expansion $T(x) \simeq T_0 + T'x$] in the van Kampen equation (3), yields the following form:

$$\partial_t P(x, t) = D_0 \left\{ \partial_x \left(1 + \frac{x\mu'}{\mu_0} \right) \partial_x \left(1 + \frac{xT'}{T_0} \right) - C_T \frac{xT'}{T_0} \partial_x \right\} \times P(x, t), \quad (9)$$

where $D_0 = D(x=0) = k_B T_0 \mu_0$. This is the van Kampen equation in the limit when (i) all forces besides the thermophoretic one are ignored, and (ii) the system is sufficiently small to justify the linear approximations of $T(x)$ and $\mu(x)$. (iii) Another assumption implied in Eq. (9) is the form (4) for the thermophoretic force.

III. PROBABILITY DISTRIBUTION FUNCTION

In a homogeneous ($\mu' = 0$) isothermal ($T' = 0$) system, Eq. (9) reduces to a simple diffusion equation, the solution

$$P(x, t) = \frac{\exp(-x^2/4D_0t)}{\sqrt{4\pi D_0t}} \left[1 + x \left\{ \frac{T'}{T_0} \left(-\frac{3}{4} + \frac{C_T}{2} + \frac{x^2}{8D_0t} \right) + \frac{\mu'}{\mu_0} \left(-\frac{1}{4} + \frac{x^2}{8D_0t} \right) \right\} \right], \quad (11)$$

which is the main result of the paper.

IV. DRIFT AND FLUX

The drift of an individual particle is characterized by the mean displacement, $\langle x \rangle$, and from the PDF (11), we find that

$$\langle x \rangle = \int_0^\infty x P(x, t) dx = \left(C_T \frac{T'}{T_0} + \frac{\mu'}{\mu_0} \right) D_0 t. \quad (12)$$

We notice that the drift does not necessarily have the same sign as C_T , which means that the average displacement of the particle is not necessarily in the same direction as the thermophoretic force. The reason for this remarkable result is an additional contribution to the drift originating from spatial dependence of the mobility. In general, the mobility of simple liquids increases with temperature, while gases exhibit an opposite trend and have mobility that decreases approximately like the square root of the temperature [24]. As noted earlier [see discussion after Eq. (8)], nonthermal effects may also contribute to μ' . Indeed, it is well known that drift is also observed in isothermal systems with nonuniform mobilities [25]. This equilibrium phenomenon has been termed spurious drift, which is misleading since it is a real effect [26]. In the isothermal case ($T' = 0$), we can use Einstein relation and Eq. (8) to write Eq. (12) in the more common form, $\langle x \rangle/t = D'$ [27], relating the drift velocity and the spatial derivative of the diffusion coefficient. Thus, our result Eq. (12) generalizes the well-known expression for the drift of Brownian particles in isothermal inhomogeneous media to nonisothermal systems.

Recall that the derivation of van Kampen equation (3) is based on assuming LTE in the overdamped limit. Within this approximation, the mean kinetic energy of a particle found at some coordinate x is related to the local temperature via the equipartition theorem $\langle E_k \rangle_x = \langle mv^2/2 \rangle_x = k_B T(x)/2$, where $\langle \dots \rangle_x$ denotes average at a given x . Taking the average with

of which takes the Gaussian form $P(x, t) = \exp(-x^2/4D_0t)/\sqrt{4\pi D_0t} \equiv G(x, t)$ [assuming Dirac δ -function initial condition $P(x, 0) = \delta(x)$]. For a system under a small temperature difference ($xT'/T_0 \ll 1$) and limited changes in the mobility ($x\mu'/\mu_0 \ll 1$), we may seek a linear approximate solution of the form

$$P(x, t) = G(x, t) \left[1 + xH \left(\frac{x^2}{D_0t} \right) \right], \quad (10)$$

where H is some function that can be determined in the following simple manner: (i) write H in Eq. (10) as a series expansion in the argument $y = (x^2/D_0t)$: $H = \sum_{i=0}^\infty a_n y^n$, then (ii) determine the coefficients of the expansion by substituting Eq. (10) in van Kampen equation (9), and by comparing terms of similar order in y on both sides of the equation. In this process of determining $H(y)$, we ignore the terms that are nonlinear in x . We find, $a_0 = (-3/4 + C_T/2)(T'/T_0) - 1/4(\mu'/\mu_0)$, $a_1 = 1/8(T'/T_0) + 1/8(\mu'/\mu_0)$, and $a_n = 0$ for $n > 1$, and thus write

respect to x and using Eq. (12) gives

$$\begin{aligned} & \frac{d\langle E_k(t) - E_k(t=0) \rangle}{dt} \\ &= \frac{k_B T'}{2} \frac{d\langle x \rangle}{dt} = \frac{k_B T'}{2} \left(C_T \frac{T'}{T_0} + \frac{\mu'}{\mu_0} \right) D_0. \end{aligned} \quad (13)$$

For $\mu' = 0$ (constant mobility), the particle is heated on average (i.e., gains kinetic energy) when $C_T > 0$, i.e., when the thermophoretic force drives the particle to the high-temperature side, and vice versa. This, however, may not be true when the mobility varies in space, in which case it is the sign of $C_T + (T_0\mu'/T'\mu_0)$ rather than the direction of the thermophoretic force that determines whether the particle gains or loses heat.

A common error is to confuse the above-discussed drift with the flux, defined by $J(x, t) = -D(x)\partial_x P(x, t)$. A closed system at steady state has zero flux, $J = 0$, but this does not necessarily imply that the average displacement (i.e., drift) of each individual particle must also vanish. On time scales smaller than the characteristic diffusion time across the system, particles located at different parts of the system (e.g., near the center or close to the boundaries) may have different nonvanishing displacements. This situation has been previously dubbed drift without flux in equilibrium isothermal systems [28]. Here, we consider dynamics in an open system with time-dependent flux. The tendency of particles to migrate favorably to one side may be characterized by the flux at the origin $J_0 \equiv J(x=0, t) = \sqrt{D_0}/(\pi t) [(T'/8T_0)(3 - 2C_T) + (\mu'/8\mu_0)]$. The flux at the origin causes a bias, i.e., a difference in the probability of finding the particle in the hotter and colder sides relative to its initial location. Assuming (without loss of generality) that

$T' > 0$, the bias, $\Delta(t)$, is defined by

$$\begin{aligned} \Delta(t) &\equiv \int_0^\infty P(x, t) dx - \int_{-\infty}^0 P(x, t) dx \\ &= \sqrt{\frac{D_0 t}{\pi}} \left[\frac{T'}{2T_0} (2C_T - 1) + \frac{\mu'}{2\mu_0} \right] \\ &= \frac{\langle x \rangle}{\sqrt{4\pi D_0 t}} - \sqrt{\frac{D_0 t}{4\pi}} T' S_T, \end{aligned} \quad (14)$$

with the drift, $\langle x \rangle$, and the Soret coefficient, S_T , given by Eqs. (12) and (5), respectively. Depending on the values of $T_0 \mu' / T' \mu_0$ and C_T , it now becomes clear that while Δ , $\langle x \rangle$, and $-S_T$ can all be used to characterize the response of colloidal particles to a temperature gradient, these quantities describe different features of the Soret effect, and may occasionally have different signs.

V. DISCUSSION AND SUMMARY

Motivated by recent single-molecule experiments for studying the behavior of macromolecules along a temperature gradient, we considered here the question of Brownian dynamics of a colloidal particle in a nonisothermal fluid. In the overdamped limit, the PDF of the particle is described by time-dependent van Kampen diffusion equation (3). Assuming a small temperature and mobility differences between the ends of the (small) system ($T'x/T_0 \ll 1$ and $\mu'x/\mu_0 \ll 1$), we considered the linear (in x) version of van Kampen equation (9) and analytically derived the solution for δ -function initial condition (11). The asymmetric PDF characterizes the general tendency of the particle to migrate in the direction of the thermophoretic force caused by the temperature gradient. However, the thermophoretic force is not the only factor determining the direction of the motion, and we have identified three different measures for the thermodiffusive response of the colloidal particle. The first measure is the Soret coefficient S_T (5), relating the concentration and temperature gradients in steady state. The Soret coefficient has been traditionally used to distinguish between thermophilic ($-S_T > 0$) and thermophobic ($-S_T < 0$) behaviors. However, we see from Eq. (5) that $-S_T$ and C_T do not necessarily have the same sign, indicating that the steady-state concentration gradient is not solely dictated by the direction of the thermophoretic force. The origin of the discrepancy are the thermal collisions, which set a concentration gradient opposite to the temperature gradient. In fact, in some recent experiments on colloidal systems it has been found that S_T exhibits a strong temperature-dependence and tends to change its sign in the vicinity of room temperature. Moreover, the magnitude of the Soret coefficient in many of these experiments is found to be of the order of $0.01\text{--}1 \text{ K}^{-1}$ [13,29]. These findings indicate that (i) the effect of the thermal collisions may sometimes be as important as the thermophoretic force that accounts for the particle-solvent interactions, and that (ii) the thermophoretic force (coefficient C_T) is sensitive to temperature variations. Due to the system-specific nature of the thermophoretic force, there is no clear explanation for its temperature sensitivity of C_T , which is likely dependent on numerous factors, e.g., the thermal expansivity of the solvent [13], the surface

functionality [15] and size [5] of the colloidal particle, and electrostatic effects [30]. In order to understand this behavior of C_T one must consider a microscopic model that takes into account some of these factor (see, e.g., the theoretical discussion in Ref. [20]). This is beyond the scope of the phenomenological discussion presented herein; however, in light of the pronounced temperature dependence of S_T , it must be reemphasized that our derivation assumes that the thermophoretic force is phenomenologically given by Eq. (4), namely assuming nonequilibrium linear response. The same linear form has been considered in other works (see, e.g., Ref. [21]), and it is consistent with the linearity of our solution for the PDF (11) with respect to T' . More generally, the variations of C_T with T can be accounted for by a Taylor expansion around T_0 : $C_T = C_T(T_0) + (dC_T/dT)\Delta T + \dots = C_T(T_0) + (dC_T/dT)T'\Delta x + \dots$, which shows that the linear approximation is valid if the total temperature difference across the experimental cell $\Delta T \simeq T'\Delta x$ is sufficiently small, i.e., if the size of the experimental setup, Δx , and the temperature gradient, T' , satisfy

$$\Delta T \simeq T' \Delta x \ll \left| \frac{C_T}{dC_T/dT} \right| \approx \left| \frac{S_T}{dS_T/dT} \right|. \quad (15)$$

In Appendix we review some experimental measurements of the Soret coefficient where the total temperature variation ΔT does not exceed a few degrees K and, thus, reasonably satisfy the above criterion.

The second quantity that can be used to characterize thermophoretic response is the drift of individual particles $\langle x \rangle$ (12), or better, the drift velocity $v = d\langle x \rangle/dt$. This measure is interesting for two reasons. First, we now have the experimental means to measure single-particle trajectories. Second, in the overdamped limit, the drift velocity is directly related to the rate of heat taken from the solvent by the particle [see Eq. (13)]. Similarly to $-S_T$, a positive (negative) value of v/T' indicates thermophilic (thermophobic) response, but these quantities are different as apparent from the comparison of Eqs. (5) and (12). Importantly, the direction of the drift is set by both directions of the thermophoretic force and the direction of the mobility gradient. Obviously, part of the mobility spatial variation can be attributed to the temperature gradient, but it is important to recall that coordinate-dependent mobility, $\mu(x)$, is also encountered in isothermal systems, i.e., in equilibrium situations. Indeed, our result Eq. (12) generalizes the expression for the drift velocity in inhomogeneous isothermal solutions.

Also suggested by Eq. (12) is that for $\mu' = 0$, the temperature gradient causes a nonvanishing drift vanishing drift only when $C_T \neq 0$, i.e., only in the presence of a thermophoretic force, but not due to thermal collisions (fluctuations) that are also influenced by the temperature gradient. This can be understood by noting that the stochastic noise term in the Langevin equation depicting the dynamics of the particle has a zero mean, even for multiplicative (state-dependent) noise (see discussion in Ref. [27]).

Finally, the third quantity defined here is the bias Δ (14), measuring the probability difference of moving along and against the temperature gradient. Similarly to the previously discussed measures, a positive (negative) value of Δ/T' may indicate thermophilic (thermophobic) response. From Eq. (14)

we infer that the bias may be expressed as a linear combination of $\langle x \rangle$ and $-S_T$ and, thus, the value of this quantity is influenced by all three factors of asymmetry discussed in the work, namely the thermophoretic force, the spatial dependence of the mobility, and thermal collision effect.

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APPENDIX: ANALYSIS OF EXPERIMENTAL DATA

We begin by noting that a key assumption in our theoretical analysis is the form of Eq. (4), stating a linear relationship between the thermophoretic force and the temperature gradient. This form is consistent with the frequently used linear-response theory for nonequilibrium systems. As discussed in the main text, the strong variations of S_T with temperature reported in many experimental studies [13,14,29] restrict the validity of the linear form Eq. (2) to small systems where the total temperature difference, ΔT , applied across the experimental setup satisfy criterion (15). Reviewing the experimental data, it can be concluded that the linear approximation holds reasonably well in many setups where ΔT does not exceed a few degrees K. [Some noticeable exceptions include: (i) Ref. [15] where the ΔT was as high as 30 K, but in that work S_T was found to be temperature independent. (ii) the measurements of S_T for large colloidal particles of size $2.5 \times 10^{-1} \mu\text{m}$ reported in [29] exhibiting exceptionally strong variations in S_T over a temperature range smaller than 5K which, in fact, calls for care in the interpretation of the experimental data.]

The distance, Δx , across which the temperature difference, ΔT (of order of a few degrees K), is applied, varies from $h \approx 500 \mu\text{m}$ in older experiments [29] to $h \approx 10 \mu\text{m}$ in more recent ones [14,15]. Thus, the experimental range of the temperature gradient is roughly $3 \times 10^{-3} - 3 \times 10^{-1}$. As these experiments are conducted around room temperature $T \approx 300 \text{ K}$, we find that $l_T^{-1} \equiv T'/T_0 \approx 10^{-5} - 10^{-3} \mu\text{m}^{-1}$. Furthermore, the range of experimental values for the Soret coefficient varies from $|S_T| \approx 10^{-2} \text{ K}^{-1}$ for micellar solution, globular proteins and small colloidal particles ($a \approx 10^{-2} \mu\text{m}$) [3] to $|S_T| \approx 1 \text{ K}^{-1}$ for large colloidal particles ($a \approx 2.5 \times 10^{-1} \mu\text{m}$) [29]. (A noticeable exception is Ref. [14] where $|S_T| \approx 50 \text{ K}^{-1}$ was measured for large colloidal particles of diameter $a \approx 2.5 \mu\text{m}$.) Recalling that $C_T \simeq (1 - T_0 S_T)$ (5), we can deduce from this relationship that the experimental range of the thermophoretic force coefficient is $-10^3 \lesssim C_T \lesssim 10^3$.

The confinement of the particle in a thin slit between two plates leads to strong variations in the mobility due to hydrodynamic interactions between the Brownian particle and the walls of the cell. The hydrodynamic effect overshadows the additional (nonequilibrium) contribution to μ' due to the temperature variation, which is typically negligible because of the smallness of ΔT . From theoretical considerations [23,31] we can estimate that the relative variations in the mobility, $\Delta\mu/\mu_0 \approx a/h$, where a is the diameter of the colloidal

particle. Therefore, the inverse length $l_\mu^{-1} \equiv \mu'/\mu_0 \approx a/h^2$. Experimentally, colloids of diameter $a \approx 2.5 \times 10^{-2} - 2.5 \mu\text{m}$ have been studied, corresponding to a wide range of values $l_\mu^{-1} \approx 10^{-6} - 10^{-2} \mu\text{m}^{-1}$.

Three quantities that characterize the thermophoretic response of a system are highlighted in the paper: S_T , v (the drift velocity), and Δ (the probability bias). These can be rescaled to allow direct comparison with C_T . We thus define the following dimensionless quantities:

- (i) the scaled negative Soret coefficient,

$$-\tilde{S}_T \equiv -T_0 S_T = C_T - 1;$$

- (ii) the scaled drift velocity,

$$\tilde{v} \equiv v(T_0/D_0 T') = C_T + l_T/l_\mu;$$

- (iii) the scaled bias,

$$\tilde{\Delta} \equiv \Delta \sqrt{\pi/D_0 t} (T_0/T') = C_T - 1/2 + l_T/2l_\mu,$$

where the length scales l_T and l_μ were defined in the previous two paragraphs. All of these quantities have the form $Q = C_T + A$, implying that they do not change sign at exactly the same temperature like the thermophoretic force coefficient C_T . As discussed extensively in the paper, the additional contribution to each quantity, A , arises from both a thermal collision effect (which is represented by the negative constants in the definitions of the scaled quantities) and from spatial variations in the mobility (the terms proportional to l_μ^{-1}). Let us look at a few experimental examples in order to assess the relative importance of the additional contribution, A/C_T , to the thermophoretic force.

(i) In experiments with charged micelles [13], the thermophoretic force coefficient was found to be of order $|C_T| \lesssim 10$ within the experimental temperature range ($|S_T| \approx 10^{-2} \text{ K}^{-1}$). The size of these micelles is of order of a few tens of nanometers, and the cell size in the experiments $h > 100 \mu\text{m}$. Thus, $l_T^{-1} \approx 10^{-2} \mu\text{m}^{-1}$, while $l_\mu^{-1} \approx 10^{-5} \mu\text{m}^{-1}$. We therefore conclude that in these classical experiments, the hydrodynamics effect is negligible, while the thermal collision effect is small but, nevertheless, important because the thermophoretic force is also fairly small.

(ii) When colloidal particles of diameter $a \approx 5 \times 10^{-2} \mu\text{m}$ are studied in similar diffusion cells, the thermophoretic force coefficient is typically an order of magnitude larger, $C_T \approx 10^2$ [13]. For larger colloidal particles of size $a \approx 2 \times 10^{-1} \mu\text{m}$, $C_T \approx 10^3$ [29]. Thus, in these experiments, the additional contributions to the scaled quantities defined above are vanishingly small: $A/C_T \ll 1$.

(iii) Large colloidal particles of size $a \approx 2 \times 10^{-1} \mu\text{m}$ were also studied in Ref. [5], but in a much narrower diffusion cell of height $h \approx 10 \mu\text{m}$. Here we also have $C_T \approx 10^3$, but in this case $l_T^{-1} \approx 3 \times 10^{-4} \mu\text{m}^{-1}$ and $l_\mu^{-1} \approx 5 \times 10^{-3} \mu\text{m}^{-1}$. Thus, the sign of the thermophoretic force dominates the direction of movement, but the influence of the hydrodynamic effect on the drift and the bias may be felt close to the transition temperature from thermophilic to thermophobic response.

(iv) In a recent experiment [15], a temperature-independent Soret coefficient $S_T \approx 0.2 \text{ K}^{-1}$ was measured for colloidal particles of diameter $a \approx 1 \mu\text{m}$, diffusing between

plates with spacing $h \approx 10 \mu\text{m}$ and an unusually large temperature difference $\Delta T \lesssim 30 \text{ K}$. In this setup, $C_T \approx 50$, $l_T^{-1} \approx 10^{-2} \mu\text{m}^{-1}$, and $l_\mu^{-1} \approx 10^{-2} \mu\text{m}^{-1}$. These values suggest that the thermophoretic force is the key factor in determining the diffusive behavior of the colloidal particles. Collision and hydrodynamic effects are equally important and their influence is about 1–2 orders of magnitude weaker than that of the thermophoretic force.

To conclude, in most of the above experimental examples, the magnitude of C_T is at least one order of magnitude larger

than that of other contributions (denoted collectively by A) over most of the investigated temperature range. Collision effect has influence on the Soret coefficient of small particles and micelles of diameter not larger than $5 \times 10^{-2} \mu\text{m}$, especially close to the transition temperature from thermophilic to thermophobic behavior (i.e., when C_T becomes small). The hydrodynamic interactions between the Brownian particle and the walls of the diffusion cell may influence the drift behavior of large colloidal particles ($a \gtrsim 1 \mu\text{m}$) in small cells ($h \approx 10 \mu\text{m}$).

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- [1] C. Ludwig, Stiz. Akad. Wiss. Wien, Math.-Nat. Wiss. Kl. **20**, 539 (1856).
- [2] C. Soret, Arch. Sci. Phys. Nat. Genève **2**, 48 (1879).
- [3] R. Piazza and A. Parola, *J. Phys.: Condens. Matter* **20**, 153102 (2008).
- [4] S. J. Jeon, M. E. Schimpf, and A. Nyborg, *Anal. Chem.* **69**, 3442 (1997).
- [5] S. Duhr and D. Braun, *Phys. Rev. Lett.* **97**, 038103 (2006).
- [6] H.-R. Jiang, H. Wada, N. Yoshinaga, and M. Sano, *Phys. Rev. Lett.* **102**, 208301 (2009).
- [7] P. Baaske, F. M. Weinert, S. Duhr, K. H. Lemke, M. J. Russell, and D. Braun, *Proc. Natl. Acad. Sci. USA* **104**, 9346 (2007).
- [8] E. Ruckenstein, *J. Colloid Interf. Sci.* **83**, 77 (1981).
- [9] J. L. Anderson, *Annu. Rev. Fluid Mech.* **21**, 61 (1989).
- [10] H. Brenner, *Physica A* **349**, 60 (2005).
- [11] J. Burelbach, D. Frenkel, I. Pagonabarraga, and E. Eiser, *Eur. Phys. J. E* **41**, 7 (2018).
- [12] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
- [13] S. Iacopini, R. Rusconi, and R. Piazza, *Eur. Phys. J. E* **19**, 59 (2006).
- [14] L. Helden, R. Eichhorn, and C. Bechinger, *Soft Matter* **11**, 2379 (2015).
- [15] J. Burelbach, M. Zupkauskas, R. Lamboll, Y. Lan, and E. Eiser, *J. Chem. Phys.* **147**, 094906 (2017).
- [16] N. G. van Kampen, *J. Phys. Chem. Solids* **49**, 673 (1988).
- [17] K. Itô, *Proc. Imp. Acad. Tokyo* **20**, 519 (1944).
- [18] R. L. Stratonovich, *SIAM J. Control* **4**, 362 (1966).
- [19] M. E. Widder and U. M. Titulaer, *Physica A* **154**, 452 (1989).
- [20] J. M. Sancho, *J. Stat. Phys.* **172**, 1609 (2018).
- [21] S. Fayolle, T. Bickel, and A. Würger, *Phys. Rev. E* **77**, 041404 (2008).
- [22] F. Gutmann and L. M. Simmons, *J. Appl. Phys.* **23**, 977 (1952).
- [23] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Martinus Nijhoff, Dordrecht, 1983).
- [24] D. T. Gillespie, *Markov Processes: An Introduction for Physical Scientists* (Academic Press, San Diego, 1992).
- [25] G. Volpe and J. Wehr, *Rep. Prog. Phys.* **79**, 053901 (2016).
- [26] O. Farago and N. Grønbech-Jensen, *Phys. Rev. E* **89**, 013301 (2014).
- [27] O. Farago and N. Grønbech-Jensen, *J Stat Phys* **156**, 1093 (2014).
- [28] P. Lançon, G. Batrouni, L. Lobry, and N. Ostrowsky, *Europhys. Lett.* **54**, 28 (2001).
- [29] M. Braibanti, D. Vigolo, and R. Piazza, *Phys. Rev. Lett.* **100**, 108303 (2008).
- [30] S. A. Putnam, D. G. Cahill, and G. C. L. Wong, *Langmuir* **23**, 9221 (2007).
- [31] T. Benesch, S. Yiacoumi, and C. Tsouris, *Phys. Rev. E* **68**, 021401 (2003).