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Thermophoresis of confined colloids in the near-contact limit

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In a recent Letter [Phys. Rev. Lett. **116**, 138302 (2016)] Würger calculated the thermophoretic velocity of a colloidal sphere towards a solid boundary due to an imposed temperature gradient perpendicular to that wall in the limit where the particle-wall separation distance h is small compared to the particle radius a. Würger obtained the approximation $u/u_0 = 3(h/a)[\ln(a/h) - 2.25]$ for the particle velocity u towards the wall, u_0 being the corresponding velocity in the bulk. In deriving that approximation an *ad hoc* procedure was employed to circumvent the calculation of a diverging integral that emerges in the course of a lubrication analysis. We show here how to systematically address this problem, obtaining the approximation $u/u_0 = 3(h/a)[\ln(a/h) + 0.1087]$.

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In a recent Letter Würger [1] calculated the thermophoretic velocity of a colloidal sphere (radius a) towards a solid wall due to the imposed temperature gradient applied perpendicular to that wall. Focusing upon the limit where the particle-wall separation distance h is small, $h \ll a$, and using a lubrication approximation in the $O(h)$-wide narrow gap, Würger obtained the approximation $u/u_0 = 3(h/a)[\ln(a/h) - \frac{9}{4}]$ for the particle velocity u towards the wall, u_0 being the corresponding velocity in an unbounded domain.

In integrating the gap pressures Würger [1] encountered a logarithmic divergence that frustrated a straightforward calculation. The appearance of such a divergence in the asymptotic evaluation of integrals typically represents a borderline case where the leading-order contribution is neither local nor global [2]. In the context of the near-contact limit considered in Ref. [1], this divergence indicates that the local contribution of pressures in the narrow gap must be supplemented by a comparable global contribution of stresses acting on the particle boundary outside the gap. A similar situation was encountered in the classical hydrodynamic analysis of particle motion parallel to a nearby solid wall [3,4], where the leading-order approximation to the resistance coefficient, consisting of a logarithmically large term and an $O(1)$ term,[1] represents the action of stresses over the entire particle boundary.

Rather than proceeding in that fashion, Würger [1] circumvented the logarithmic divergence by replacing the lubrication-scale approximation of the particle boundary by its exact form while otherwise retaining the lubrication approximation of the governing equations. Since this *ad hoc* procedure does not properly account for the particle-scale flow problem it cannot provide the correct leading-order approximation. The above-cited approximation is accordingly erroneous.[2]

In this paper we show how to systematically obtain the appropriate leading-order approximation for the particle velocity. We consider the same physical problem addressed by Würger [1], who assumed that the thermal problem is unaffected by the presence of the wall and disregarded thermal slip on the wall. Würger [1] claims that this model is reasonable provided the thermal properties of the wall are similar to those of the liquid, and we take this assertion as granted. (See, however, our concluding remarks.) The problem thus amounts to the calculation of particle drift due to a prescribed

[1]Following the standard approach in asymptotic analysis [2], logarithmically large terms are considered on par with $O(1)$ terms.

[2]The main part of Ref. [1] is concerned with the interpretation of Soret-effect data and in particular with their size dependence. I make no judgment here regarding the effect of the error upon that interpretation.

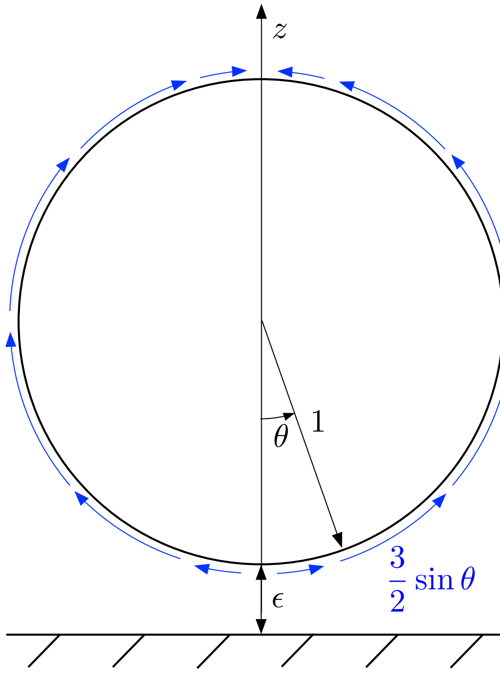

FIG. 1. Schematic of the problem. The dimensionless slip velocity is $\frac{3}{2}\sin\theta$, with θ being the indicated polar angle.

axisymmetric distribution of slip along the particle. In what follows we consider a *stationary* particle. Once the force on such a particle is evaluated, the thermophoretic velocity of a freely suspended force-free particle is readily obtained using the known mobility coefficients for motion perpendicular to a boundary [5]. This approach is more convenient than that adopted in Ref. [1].

Our asymptotic analysis is conveniently carried out using a dimensionless formulation. We normalize lengths by a, velocities by u_0, and the fluid pressure p by $\mu u_0/a$, with μ being the liquid viscosity. We employ the cylindrical coordinates r and z with $r = 0$ being the symmetry axis passing through the particle center and $z = 0$ the wall boundary. The radial and axial components of the velocity field are respectively denoted by v_r and v_z. The flow is governed by the continuity and Stokes equations, far-field decay, and no slip at $z = 0$. It is driven by a tangential slip of magnitude $3r/2$ along the particle boundary, directed away from the wall (see Fig. 1). Expressed in terms of the cylindrical velocity components, this condition reads

$$v_r = \tfrac{3}{2}r(1+\epsilon - z), \quad v_z = \tfrac{3}{2}r^2, \tag{1}$$

where $\epsilon = h/a$ is the dimensionless gap width. Our interest lies in the hydrodynamic force F (normalized by $\mu a u_0$) acting on the particle in the z direction.

An alternative formulation of the flow problem makes use of the stream function ψ, defined by

$$v_r = \frac{1}{r}\frac{\partial \psi}{\partial z}, \quad v_z = -\frac{1}{r}\frac{\partial \psi}{\partial r}. \tag{2}$$

This function is governed by the fourth-order differential equation

$$E^4\psi = 0, \tag{3}$$

where

$$E^2 = \frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}. \tag{4}$$

On the wall it satisfies impermeability and no slip,

$$\psi = \frac{\partial \psi}{\partial z} = 0 \quad \text{at } z = 0. \tag{5}$$

On the particle boundary it satisfies impermeability, $\psi = 0$, as well as the inhomogeneous condition

$$\frac{\partial \psi}{\partial r} = -\frac{3r^3}{2}, \tag{6}$$

representing the imposed slip (1). The far-field velocity decay necessitates that $\psi \ll |\mathbf{x}|^2$ as $|\mathbf{x}| \to \infty$, where $\mathbf{x} = \hat{\mathbf{e}}_r r + \hat{\mathbf{e}}_z z$ is the position vector.

In our dimensionless formulation the pertinent fields are functions of the single geometric parameter ϵ. We now proceed to the near-contact limit $\epsilon \ll 1$. The narrow gap separating the particle from the wall is analyzed using the rescaled coordinates

$$R = \frac{r}{\epsilon^{1/2}}, \quad Z = \frac{z}{\epsilon}, \tag{7}$$

whereby the particle boundary becomes $Z = H(R) + O(\epsilon)$ in which $H = 1 + R^2/2$. The slip condition (1) implies that the radial velocity v_r is $O(\epsilon^{1/2})$. The continuity equation in conjunction with the impermeability to flow of the wall and particle boundaries then dictates an $O(\epsilon)$ axial velocity, while the radial momentum balance implies that the pressure is $O(\epsilon^{-1})$. We therefore postulate the lubrication scaling

$$v_r = \epsilon^{1/2} V_r(R,Z) + \cdots, \quad p = \epsilon^{-1} P(R,Z) + \cdots. \tag{8}$$

The leading-order momentum balance in the z direction necessitates that P is independent of Z and is accordingly a function of R alone, say, $P(R)$. Integrating the leading-order radial momentum balance $dP/dR = \partial^2 V_r/\partial Z^2$ and making use of the no-slip condition at $Z = 0$, where $V_r = 0$, and the slip condition at $Z = H$, where $V_r = 3R/2$, gives the velocity profile

$$V_r = \frac{dP}{dR}\frac{Z^2}{2} + \left(\frac{3R}{2} - \frac{H^2}{2}\frac{dP}{dR}\right)\frac{Z}{H}. \tag{9}$$

Imposing the requirement of zero net radial flux yields $dP/dR = 9R/H^2$. Integration in conjunction with the requirement $P(\infty) = 0$ [representing asymptotic matching with the $O(1)$ outer pressure] gives $P = -9/H$.

Since the gap-region area is $O(\epsilon)$, the action of the $O(\epsilon^{-1})$ pressures results in an $O(1)$ contribution to the force F. At leading order in that region, the differential area element on the particle boundary is $2\pi\epsilon\, dR$, while the outward-pointing unit vector is $-\hat{\mathbf{e}}_z$. It may thus appear as though F is given to leading order by $2\pi \int_0^\infty RP\, dR$; because of the slow large-R decay of P, however, this integral diverges logarithmically. This obstacle has led to the *ad hoc* calculation in Ref. [1].

The above divergence is actually hardly surprising since the "outer" contribution to the force from stresses acting on the remaining particle boundary is clearly $O(1)$, of the same asymptotic order as that contributed by the "inner" gap pressures. We accordingly need to account for the entire particle boundary. Towards that end we employ the following expression for the hydrodynamic force [6]:

$$F = \pi \int r^3 \frac{\partial}{\partial n}\left(\frac{E^2\psi}{r^2}\right) ds, \tag{10}$$

where $\partial/\partial n$ is the outward normal derivative and the integration is carried out over any meridian of the sphere on which ds is a length differential. Recalling that in Stokes flow the force on a particle can be obtained via integration over any closed surface that encapsulates it we choose that surface as the union of two surfaces: the portion of the plane $z = 0$ bounded by circle of radius r_∞ and a hemisphere of the same radius (both surfaces centered about the origin). Assuming, subject to *a posteriori* confirmation, that the fluid velocity decays faster than $|\mathbf{x}|^{-1}$ and considering the limit $r_\infty \to \infty$ we find that the contribution of stresses on the hemisphere goes to zero; the force on the particle is accordingly contributed solely by stresses at the plane $z = 0$, whereby (10) becomes

$$F = -\pi \int_0^\infty r^3 \frac{\partial}{\partial z}\left(\frac{E^2\psi}{r^2}\right)_{z=0} dr. \tag{11}$$

Given the no-slip condition and the continuity equation, $\partial v_z/\partial z = 0$ at $z = 0$. With the consequent vanishing of the normal viscous stress on the plane, expression (11) simply represents the force due to the pressure distribution at $z = 0$; an alternative form is then $F = 2\pi \int_0^\infty rp\, dr$, where p is evaluated at $z = 0$.

To account for both the local (gap-scale) and global (particle-scale) contributions to the force we introduce a cutoff-type parameter r^*, satisfying $\epsilon^{1/2} \ll r^* \ll 1$. The corresponding rescaled radius $R^* = r^*/\epsilon^{1/2}$ satisfies $1 \ll R^* \ll \epsilon^{-1/2}$. Consider first the local contribution $F^{(\mathrm{i})}$ from the inner region $r < r^*$. Recalling that the pressure field within the gap is independent of Z we obtain

$$F^{(\mathrm{i})} = 2\pi \int_0^{R^*} RP\, dR \sim -18\pi(2\ln R^* - \ln 2), \tag{12}$$

where the $o(1)$ asymptotic error is "algebraically small," i.e., smaller than some positive power of ϵ. Since F cannot depend upon R^*, the spurious divergence with it must be eliminated by the respective global contribution to the force from the outer region.

The limit $\epsilon \ll 1$ at the particle scale corresponds at leading order to the particle touching the wall. The outer region is accordingly analyzed using tangent-sphere coordinates [7], defined by

$$\xi = \frac{2z}{r^2 + z^2}, \quad \eta = \frac{2r}{r^2 + z^2}. \tag{13}$$

The surfaces $\xi = \text{const}$ are spheres of radius ξ^{-1} centered about the point $\xi^{-1}\hat{\mathbf{e}}_z$; the surfaces $\eta = \text{const}$ are toroids without center opening. The wall boundary is thus given by $\xi = 0$, while the particle boundary, at leading order, is $\xi = 1$. The homogeneous wall conditions (5) become

$$\psi = \frac{\partial\psi}{\partial\xi} = 0 \quad \text{at } \xi = 0. \tag{14}$$

At $\xi = 1$, ψ satisfies the impermeability condition $\psi = 0$ as well as the slip condition [see (6)]

$$\frac{\partial\psi}{\partial\xi} = \frac{12\eta^2}{(1+\eta^2)^3}. \tag{15}$$

In addition, ψ satisfies far-field decay $\psi \ll (\xi^2 + \eta^2)^{-1}$ as $\xi^2 + \eta^2 \to 0$.

A general solution of (3) that satisfies far-field decay and the homogeneous conditions at $\xi = 0$ and $\xi = 1$ is

$$\psi = \eta(\xi^2+\eta^2)^{-3/2} \int_0^\infty A(s)\left\{\left[1 + \xi\left(\frac{s}{\tanh s} - 1\right)\right]\sinh(\xi s) - s\xi\cosh(\xi s)\right\} J_1(\eta s) ds, \tag{16}$$

where J_1 is the Bessel function of the first kind and order unity. Imposing the inhomogeneous condition (15) yields, upon making use of the well-known properties of Hankel transforms [8],

$$A(s) = \frac{12se^{-s}\sinh s}{s^2 - \sinh^2 s}. \tag{17}$$

At large distances, where both ξ and η are small, ψ behaves like $\eta^2\xi^2(\eta^2+\xi^2)^{-3/2}$ or, equivalently, $r^2z^2/|\mathbf{x}|^5$. The associated velocity field, which decays as $|\mathbf{x}|^{-3}$, confirms our *a priori* neglect leading to (11). Inspection of the inner limit $\eta \to \infty$ of the outer solution (16) and (17) reveals that it trivially matches the gap flow calculated above.

Now, on $\xi = 0$,

$$\frac{\partial}{\partial z} = \frac{\eta^2}{2}\frac{\partial}{\partial \xi}, \quad dr = -\frac{2}{\eta^2}d\eta, \tag{18}$$

so the outer contribution to (11) is

$$F^{(o)} = -\pi \int_0^{\eta^*} r^3 \frac{\partial}{\partial \xi}\left(\frac{E^2\psi}{r^2}\right)_{\xi=0} d\eta, \tag{19}$$

where $\eta^* = 2/r^*$ ($\gg$1) [see (13)] or, equivalently,

$$\eta^* = \frac{2}{\epsilon^{1/2}R^*}. \tag{20}$$

Upon transforming to tangent-sphere coordinates and making use of the homogenous conditions (14) we obtain

$$F^{(o)} = -\frac{\pi}{2}\int_0^{\eta^*} \eta^3 \left(\frac{\partial^3\psi}{\partial\xi^3}\right)_{\xi=0} d\eta. \tag{21}$$

Substitution of (16) yields

$$F^{(o)} = \pi \int_0^{\eta^*} d\eta\, \eta \int_0^{\infty} ds\, s^3 A(s) J_1(\eta s). \tag{22}$$

Our goal is to calculate this integral to leading order in the limit $\eta^* \gg 1$.

With $A(s) \sim -36/s^2$ at small s, the interior integral in Eq. (22) behaves as η^{-2} for large η. Due to the resulting logarithmic divergence of the exterior integral, it is not allowed to replace η^* by infinity in Eq. (22). We accordingly isolate the singular small-s behavior of $A(s)$ by defining

$$A(s) = \underbrace{-\frac{36}{s^2}e^{-s}}_{A_{\mathrm{I}}(s)} + \underbrace{A(s) + \frac{36}{s^2}e^{-s}}_{A_{\mathrm{II}}(s)}, \tag{23}$$

with the corresponding contributions to (22) denoted by $F_{\mathrm{I}}^{(o)}$ and $F_{\mathrm{II}}^{(o)}$, respectively. [The e^{-s} factor is introduced in Eq. (23) to ensure convergence at large s of these respective contributions.] The contribution to $F^{(o)}$ from the singular part A_{I} is

$$F_{\mathrm{I}}^{(o)} = -36\pi\left(\sinh^{-1}\eta^* - \frac{\eta^*}{\sqrt{1+\eta^{*2}}}\right) \sim -36\pi(\ln 2 + \ln\eta^* - 1), \tag{24}$$

with an $o(1)$ algebraically small asymptotic error. In calculating the contribution from A_{II} we are allowed to replace η^* by infinity to leading order, yielding

$$F_{\mathrm{II}}^{(o)} = \pi\int_0^{\infty} d\eta\,\eta \int_0^{\infty} ds\, s^3 A_{\mathrm{II}}(s) J_1(\eta s) = \pi \int_0^{\infty} ds\, s A_{\mathrm{II}}(s), \tag{25}$$

again with an $o(1)$ algebraically small error. The integral is evaluated numerically, giving

$$F_{\mathrm{II}}^{(o)} = -0.5264\pi. \tag{26}$$

Adding (12), (24), and (26) we find, using (20), that the spurious dependence upon r^* in Eqs. (12) and (24) cancels out, giving the force

$$F = 18\pi(\ln\epsilon - 3\ln 2 + 2 - 0.029) = 18\pi(\ln\epsilon - 0.1087), \tag{27}$$

with an algebraically small error. The velocity acquired by a force-free particle in the positive z direction is obtained by multiplying (27) by the appropriate mobility coefficient [normalized by $(a\mu)^{-1}$], which, up to an algebraically small error, is given by $(6\pi)^{-1}\epsilon$ (see, e.g., [9]). We therefore obtain the particle velocity

$$3\epsilon(\ln\epsilon - 0.1087), \tag{28}$$

which is to be contrasted with that obtained by Würger [1], namely, $3\epsilon(\ln\epsilon + 2.25)$.

In concluding we comment on the physical model employed by Würger [1]. By ignoring the effect of the wall upon the temperature field the problem reduces to a pure hydrodynamic calculation of particle motion due to a prescribe slip. While it was noted in Ref. [1] that the mathematical description of thermophoresis is similar to that in electrophoresis and diffusiophoresis, it appears that Würger was unaware of relevant analyses of electrophoresis perpendicular to a boundary in the near-contact limit, where the effect of the wall on the electric field and, consequently, on the ensuing slip has been accounted for [10–13]. It is interesting to note that in these problems the resulting hydrodynamic analysis typically becomes significantly *simpler*, with the leading-order phoretic force being contributed by either the inner [12] or outer [13] region (depending upon the type of wall considered). Paradoxically then, the problem identified by Würger [1], which may appear to be the simplest model of wall confinement, turns out to be the most difficult one to analyze.

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