Thermophoresis in colloidal suspensions driven by Marangoni forces

Alois Würger

To cite this version:
Alois Würger. Thermophoresis in colloidal suspensions driven by Marangoni forces. Physical Review Letters, American Physical Society, 2007, 98, pp.138301. <10.1103/PhysRevLett.98.138301>. <hal-00341459>

HAL Id: hal-00341459
https://hal.archives-ouvertes.fr/hal-00341459
Submitted on 25 Nov 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Thermophoresis in colloidal suspensions driven by Marangoni forces

Alois Würger

CPMOH, CNRS–Université Bordeaux 1, 351 cours de la Libération, 33405 Talence, France

In a hydrodynamic approach to thermophoretic transport in colloidal suspensions, the solute velocity \( \mathbf{u} \) and the solvent flow \( \mathbf{v}(\mathbf{r}) \) are derived from Stokes’ equation, with slip boundary conditions imposed by thermal Marangoni forces. The resulting fluid velocity field \( \mathbf{v}(\mathbf{r}) \) significantly differs from that induced by an externally driven particle. We find in particular that thermophoresis due to surface forces is insensitive to hydrodynamic interactions. As a consequence, the thermal diffusion coefficient \( D_T \) of polymer solutions is independent of molecular weight and concentration. PACS: 66.10.Cb; 82.70.Dd; 61.25.Hq

Thermophoresis describes the flow induced by a thermal gradient in a complex fluid. This “Soret effect” has been observed for polymer solutions and suspensions of bubbles and colloidal particles [1–3]. Recent progress in microfluidics and optical detection techniques revealed surprising dependencies on material parameters of solute and solvent [4–15], and opened possible applications such as thermally driven segregation of macromolecular solutions [8, 10] and pattern formation [14].

Despite the many data available, the physical mechanisms of thermophoresis in liquids are not well understood, and there seems to be no generally accepted picture for the thermal driving forces. Particle motion in non-uniform gases is well described by kinetic theory [16, 17]. In liquids, however, surface forces are essential, and thermophoresis may be viewed as a Marangoni effect [16, 17]. In liquids, however, surface forces are essential, and thermophoresis may be viewed as a Marangoni effect [16, 17]. In liquids, however, surface forces are essential, and thermophoresis may be viewed as a Marangoni effect [16, 17].

Quite generally, phoretic transport occurs if physical parameters such as temperature or composition vary along the particle surface and induce a tangential force \( df \) on the area element \( dS \). In a mesoscopic description, the fluid is subject to an opposite stress \( -df/dS \) corresponding to the gradient of the surface energy \( \gamma \) at an idealized phase boundary \([21, 22]\); in the case of a non-uniform temperature one has

\[-df/dS = \nabla \gamma = \gamma_T \nabla \gamma / T, \quad (3)\]

where \( \nabla \gamma / T \) is the gradient parallel to the surface and \( \gamma_T = d\gamma / dT \).

Since heat propagation is much faster than particle migration, the temperature field may be taken as stationary. Starting from the overall thermal gradient of the fluid \( \nabla T = T_x e_x \) with constant \( T_x \), the heat conduction equation for a spherical particle is readily solved, and the gradient at the particle surface reads [22]

\[\nabla \gamma / T = \kappa (t \cdot \nabla T) t = -\kappa T_x \sin \theta t, \]

where \( \theta \) is the polar angle with respect to \( e_x \), and \( t \) the related tangent vector. The parameter \( \kappa = 3 \kappa_S / (2 \kappa_S + \kappa_P) \) is given by the heat conductivities of solvent and particle.

In this Letter we start from the hydrodynamic boundary conditions at the particle-liquid interface, derive the velocity field \( \mathbf{v}(\mathbf{r}) \) of the fluid around a particle driven by the surface force (3), and then obtain the thermodiffusion coefficient \( D_T \). Surface forces lead to a slip velocity at the interface, i.e., a jump in the tangential velocity component, whereas the normal component is continuous,

\[\mathbf{n} \cdot \mathbf{v}_{t=a} = \mathbf{n} \cdot \mathbf{u}. \quad (4)\]

Since there is no external force acting on the particle, the integrated surface stress vanishes [19],

\[\int dS \sigma \cdot \mathbf{n} = 0. \quad (5)\]

There is one more boundary condition that depends on the properties of the solid-fluid interface. In the stationary state, the Marangoni force \( \nabla \gamma \) is counterbalanced by the off-diagonal component of the surface stress [22],

\[t \cdot (\sigma \cdot \mathbf{n} + \nabla \gamma) = 0. \quad (6)\]
Now we determine the velocity field \( \mathbf{v}(r) \) of the fluid close to a spherical particle of radius \( a \) which moves at a velocity \( \mathbf{u} = u \mathbf{e}_x \). We transform to the reference frame in which the particle is at rest, i.e., \( \dot{u} = 0 \) and \( \mathbf{v}(r) = \mathbf{v}(r) - \mathbf{u} \). At small Reynolds numbers, the steady state flow is well described by the Stokes equation \( \eta \nabla^2 \mathbf{v} = \nabla P \) with \( \nabla \cdot \mathbf{v} = 0 \) and the solvent viscosity \( \eta \). From Ref. \[22\] we take the solution \( \mathbf{v} = \mathbf{v}_n + \mathbf{v}_b \) in spherical coordinates,

\[
\dot{v}_r = -u \cos \theta \left( 1 - 2 \alpha \frac{a}{r} + 2 \beta \frac{a^3}{r^3} \right), \quad (7a)
\]

\[
\dot{v}_\theta = u \sin \theta \left( 1 - \alpha \frac{a}{r} - \beta \frac{a^3}{r^3} \right). \quad (7b)
\]

The radial and tangential unit vectors \( \mathbf{n} = r/r \) and \( \mathbf{t} = \mathbf{n}/\partial \theta \) satisfy \( \alpha_x = \cos \theta \mathbf{n} - \sin \theta \mathbf{t} \). The hydrodynamic pressure reads \( P(r) = P_0 + 2a \cos \theta (\eta \alpha a/r^2) \), and the parameters \( u, \alpha, \beta \) have to be determined from the boundary conditions (4–6).

The condition of zero radial velocity (4) gives \( 1 - 2 \alpha + 2 \beta = 0 \). The stress tensor \( \sigma = \sigma' - P \) consists of the shear-induced dissipative term \( \sigma' \) and the isotropic hydrodynamic pressure \( P \). At the interface \( r = a \), the relevant entries of the former read \[22\]

\[
\sigma_{rr}'' = 2 \eta \frac{\partial v_r}{\partial r}, \quad \sigma_{\theta \theta}' = \eta \left( \frac{\partial v_\theta}{\partial r} - \frac{v_r}{r} \right). \]

Writing the total stress in (5) as \( \sigma \cdot \mathbf{n} = n \sigma_{rr} + t \sigma_{\theta \theta} \), inserting \( \sigma_{rr} = \sigma''_{rr} - P \) and \( \sigma_{\theta \theta}' \), and integrating over the surface, one finds \( 1 - 5 \alpha + 2 \beta = 0 \). With the above relation \( 1 - 2 \alpha + 2 \beta = 0 \) one has

\[
\alpha = 0, \quad \beta = -\frac{1}{2}.
\]

Back transformation to the laboratory frame \( \mathbf{v}(r) = \mathbf{v}(r) + \mathbf{n} \) yields the fluid velocity

\[
\mathbf{v}(r) = u \frac{a^3}{r^3} \left( \frac{1}{2} \sin \theta \mathbf{t} + \cos \theta \mathbf{n} \right), \quad (8)
\]

with the origin at the center of the particle.

We still have to determine the phoretic velocity \( u \). The balance (6) of the stress \( \sigma_{\theta \theta}' \) and the Marangoni force \( \nabla \cdot \gamma T_k T_x/a \) \( \sin \theta \mathbf{t} \) readily gives \( 3u/a = -\gamma T_k T_x/\eta \). Thus the particle velocity reads

\[
u = -\frac{a \gamma T_k}{3 \eta} T_x. \quad (9)
\]

We note the most striking features of the solution (8,9).

First, at the interface the fluid and the particle move in opposite directions with a finite slip velocity \( \mathbf{v}_b \), as illustrated in Fig. 1b; inserting \( \alpha, \beta \) in (7) at \( r = a \) gives \( \mathbf{v}_b = \frac{2}{3} u \sin \theta \mathbf{t} \). Second, the orientational average \( \langle \cdots \rangle = 1/(4 \pi) \int d \Omega \cdots \) of the velocity field \( \mathbf{v}(r) \) vanishes; with \( \langle \sin \theta \mathbf{t} \rangle = -\frac{3}{2} \mathbf{e}_z \) and \( \langle \cos \theta \mathbf{n} \rangle = \frac{1}{2} \mathbf{e}_z \) one finds

\[
\langle \mathbf{v}(r) \rangle = 0. \quad (10)
\]

Third, there is no "backflow"; integrating (8) over the plane \( \theta = \frac{\pi}{2} \), one obtains the fluid current \( -\pi a^2 u \mathbf{e}_x \), which exactly cancels that of the particle. Fourth, the Marangoni force does not modify the hydrodynamic pressure, one has \( P = P_0 \) everywhere.

It turns out instructive to compare (8,9) with the flow of a particle dragged by an external force \( \mathbf{F}_{ext} \) such as gravity. In this case the solid-fluid interface is homogeneous and requires stick boundary conditions \( \mathbf{v}|_{r=a} = \mathbf{u} \). In the steady state, the external force and the integrated stress cancel, \( \mathbf{F}_{ext} + \int dS \sigma \cdot \mathbf{n} = 0 \), and one has \[22\]

\[
\alpha_F = 3, \quad \beta_F = 1, \quad u_F = u_{ext}.
\]

The moving particle induces an excess hydrodynamic pressure \( P(r) - P_0 \sim 1/r^2 \) and a velocity field \( \mathbf{v}_F \) that satisfies \( \langle \mathbf{v}_F \rangle = (a/r) \mathbf{u} \) and is illustrated in Fig. 1a.

The transport coefficients \( D \) and \( D_T \) are determined from Eqs. (8,9). Writing the gradient of the osmotic pressure in (2) as \( \nabla \Pi = \Pi_r \mathbf{n} + \Pi_n \mathbf{t} \), with the shorthand notation \( \Pi_r = \partial \Pi/\partial T, \) etc., and comparing with (1), we find \( D = \mu \Pi_n \) and \( D_T = \mu T / n + \alpha \gamma T_k / 3 \Pi_n \). Since \( D \) and \( D_T \) are linear-response coefficients, the pressure derivatives \( \Pi_n \) and \( \Pi_T \) can be evaluated in the framework of equilibrium thermodynamics. In terms of the virial expansion for the pressure \( \Pi = n k_B T (1 + n B + \ldots) \), with \( B = \frac{1}{2} \int dV (1 - e^{-\frac{\gamma T k}{k_B T}}) \) and the pair potential \( v(r) \), we obtain the translational diffusion coefficient

\[
D = \mu k_B T (1 + 2 n B + \ldots), \quad (11)
\]

which turns out to be insensitive to Marangoni effects.

A more complicated expression arises for the thermal diffusion coefficient

\[
D_T = \mu k_B (1 + n B + n T B_T + \ldots) + \frac{\alpha \gamma T_k}{3 \eta}. \quad (12)
\]

The first term describes the entropic, or diffusive, contribution to thermophoresis and is always positive, whereas the second one is proportional to the Marangoni force parameter \( \gamma T \) which may take both signs. The properties of \( D \) and \( D_T \) determine directly those of the Soret coefficient \( S_T = D_T / D \).
In liquids hydrodynamic interactions are present, in addition to the electrostatic, magnetic, and steric forces accounted for by the virial coefficient \( B \). For example, particle sedimentation at a velocity \( \mathbf{u}_s \) engenders a fluid backflow \( \mathbf{v}_s \sim -\mathbf{u}_s \), where \( \phi = \frac{1}{2} \pi a^3 n \) is the volume fraction of the colloidal suspension. At small \( \phi \) the mobility varies as \( \mu(\phi) = \mu_0(1 - \zeta \phi) \), with the bare value \( \mu_0 = 1/(6\pi \eta a) \) and a numerical constant \( \zeta \sim 1 \) [23]. The resulting modification of the entropic contribution \( -\mu k_B T \) to \( D_T \) is discussed in detail in [24].

Yet thermophoresis of most colloidal suspensions is driven by surface forces, \( D_T = a\gamma T \kappa /3\eta \), and the diffusive term \( \sim \mu k_B T \) of (12) is generally small. We consider the hydrodynamic effects on the driven motion of a particle at \( \mathbf{r}_0 \) that experiences the velocity field created by its neighbors, \( \mathbf{u} = \sum_n \mathbf{v}(\mathbf{r}_n - \mathbf{r}_0) \). In a complex fluid there is no orientational order: from Eq. (10) it follows that the angular average of the drag field is zero, \( \langle \mathbf{v}(\mathbf{r}_n - \mathbf{r}_0) \rangle = 0 \). Thus each particle drifts with mean velocity \( \mathbf{u} = \omega \mathbf{e}_z \) and we conclude that thermophoresis driven by surface forces is not affected by hydrodynamic interactions.

Now we consider solutions of flexible polymers. Each molecular chain consists of \( N \) beads of effective radius \( a \) at position \( \mathbf{r}_n \); the average configuration is described by a gyration radius \( R \) that scales as \( R \sim aN^\nu \) where \( \nu \approx \frac{1}{2} \) in a good solvent and \( \nu \approx \frac{1}{3} \) for theta conditions [25]. Hydrodynamic interactions reduce the mobility to the value \( \mu = \xi / (\eta R) \) with \( \xi \sim 1 \), i.e., the polymer diffuses like a spherical particle of size \( R \) and drags a fluid volume \( \sim R^3 \), as shown in Fig. 2a. As a consequence, the diffusion coefficient \( D \) and the diffusive part \( \sim \mu k_B T \) of \( D_T \) vary with the molecular weight as \( \sim N^{-\nu} \). A totally different picture arises for surface forces, i.e., for the last term in (12). The fluid velocity induced by the migrating polymer is given by the superposition

\[
\mathbf{V}(\mathbf{r}) = \sum_n \mathbf{v}(\mathbf{r} - \mathbf{r}_n).
\]

Because of (10), the mean flow of the surrounding fluid vanishes, \( \langle \mathbf{V} \rangle = 0 \). In the frame attached to the polymer this means that Marangoni forces do not retain the fluid volume within the gyration radius. As illustrated in Fig. 2b, the fluid flows through the polymer coil without significant perturbation.

The velocity of a given monomer \( n \) is obtained by adding to the single-bead velocity \( \mathbf{u} \) the flow induced by the neighbors,

\[
\mathbf{u}_n = \mathbf{u} + \sum_{m \neq n} \mathbf{v}(\mathbf{r}_n - \mathbf{r}_m).
\]

The statistical average over the polymer configurations corresponds to performing the orientational mean (10),

\[
\langle \mathbf{u}_n \rangle = \mathbf{u}.
\]

Thus each monomer drifts with mean velocity \( \mathbf{u} \), and so does the polymer as a whole, independently of its molecular weight and its branching structure. This remarkable result had been inferred by Brochard and de Gennes from general properties of heat flow and from symmetry relations for the Onsager coefficients [26]. Here it has been derived explicitly from the zero mean flow (10) which is closely related to the absence of hydrodynamic interactions. (In contrast, hydrodynamic interactions are responsible for volume-fraction dependent mobility \( \mu(\phi) \) of colloidal suspensions and for the variation \( \mu \sim N^{-\nu} \) with the molecular weight of polymers.) A phoretic mobility \( \mu_{ph} \) may be defined through \( \mathbf{u} = \mu_{ph} \mathbf{f} \), where the force acting on a single bead is given by the surface integral of the Marangoni stress (3), \( \mathbf{f} = -\frac{8}{3} \pi a^2 \gamma T \kappa \mathbf{e}_z \). One readily finds that \( \mu_{ph} = 1/(8\pi \eta a) \) depends only on the solvent viscosity and the effective size of a monomer. Experimentally, Eq. (13) has been shown to hold for various polymers and alkanes in different solvents over a wide range of parameters [2, 4–7].

![Fig. 2: Fluid velocity field \( \mathbf{V}(\mathbf{r}) \) in the frame attached to a solution polymer. a) Stick boundary conditions, applying to self-diffusion and externally driven motion. Because of hydrodynamic interactions, the polymer retains a fluid volume \( \sim R^3 \). b) In the case of surface forces, there are no hydrodynamic interactions, and the fluid passing through the polymer is hardly perturbed, i.e., \( \mathbf{V} = -\mathbf{u} \) almost everywhere.](image)
\[ \gamma = \frac{1}{2} \psi_0 \varepsilon / \lambda \] and the opposite sign, \( \gamma_T = -\frac{1}{2} (\gamma / T) (1 + \tau) \) \[18\].) Eqs. \ref{12,14} correct a previous result \[15, 18, 30\] by a numerical factor \( \frac{1}{2} k = \frac{3}{2} \kappa_S / (2 \kappa_S + \kappa_P) \); for suspensions of solid nanoparticles, the solute thermal conductivity \( \kappa_P \) may significantly exceed that of the solvent and thus reduce thermophoresis \[31\].

Further contributions to \( \gamma \) are the interface tension and the energy of surfactants grafted on the particle \[13, 32\]. For most materials the interface energy decreases with temperature according to the law \( \gamma = \gamma_0 (1 - T/T_0) \) with \( \gamma_0 \sim 100 \text{ mJ/m}^2 \) and \( T_0 \sim 10^4 \text{ K} \). Adding the charge and interface energy, one obtains

\[ \gamma_T = \frac{\sigma^2 \lambda}{4 \varepsilon T (1 + \tau)} - \gamma_0 \frac{T}{T_0}, \]

(15)

For zero surface charge \( \sigma = 0 \), the interface tension term \( \gamma_0 / T_0 \sim 10^{-5} \text{J/(m}^2\text{K)} \) results in \( \gamma_T < 0 \) and in an inverse Soret effect, \( D_T < 0 \), i.e., the particles migrate to warmer regions. With typical parameters \( \sigma = 10^{-2} \text{e/nm}^2 \) and \( \lambda = 10 \text{ nm} \), the charge term \( \sigma^2 \lambda / 4 \varepsilon T \sim 10^{-4} \text{J/(m}^2\text{K)} \) dominates and leads to a positive thermodiffusion coefficient \( D_T > 0 \). This rule is qualitatively confirmed by various experiments on suspensions of micelles, polymers, and solid nanoparticles, in water and organic solvents \[9, 13, 15\]. Uncertainties arise mainly from the temperature dependence of the interface tension and from the contribution of surface coating. A quantitative description has been achieved for charged particles \[9, 15, 30\], confirming in particular the dependency on particle size and Debye length \( D_T \propto a \alpha \). For \( a > \alpha \), our previous result \( S_T \propto a^2 \lambda \) \[30\] compares favorably with several measurements, as shown in Fig. 1 of Ref. \[33\].

We briefly summarize the main results. (i) Stokes’ equation with slip boundary conditions \(4–6\) results in a flow field \( v(r) \sim 1/r^3 \) with zero orientational average. (ii) In colloidal suspensions, the Marangoni term \( \alpha \gamma T \kappa / \eta \) in general exceeds the diffusive contribution to \( D_T \). (iii) The Marangoni term is insensitive to hydrodynamic interactions and does not depend on the volume fraction \( \phi \). (iv) As a consequence, thermophoresis in polymer solutions is independent of molecular weight and concentration.

Helpful and stimulating discussions with Y. Amrouchène, W. Köhler, S.N. Semenov, and S. Wiegand are gratefully acknowledged.