



HAL
open science

Thermoelectric effect of charged colloids in the Hückel limit

Julien Morthomas, Alois Würger

► **To cite this version:**

Julien Morthomas, Alois Würger. Thermoelectric effect of charged colloids in the Hückel limit. European Physical Journal E: Soft matter and biological physics, 2008, 27, pp.425. 10.1140/epje/i2008-10410-8 . hal-00340777

HAL Id: hal-00340777

<https://hal.science/hal-00340777>

Submitted on 22 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.

Thermoelectric effect on charged colloids in the Hückel limit

Julien Morthomas and Alois Würger

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

We study the thermophoretic coefficient D_T of a charged colloid. The non-uniform electrolyte is characterized in terms of densities and diffusion currents of mobile ions. The hydrodynamic treatment in the vicinity of a solute particle relies on the Hückel approximation, which is valid for particles smaller than the Debye length, $a \ll \lambda$. To leading order in the parameter a/λ , we find that the coefficient D_T consists of two contributions, a dielectrophoretic term proportional to the permittivity derivative $d\epsilon/dT$, and a Seebeck term, i.e., the macroscopic electric field induced by the thermal gradient in the electrolyte solution. Depending on the particle valency, these terms may take opposite signs, and their temperature dependence may result in a change of sign of thermophoresis, as observed in several recent experiments.

PACS numbers: 66.10.C, 82.70.-y, 47.57.J-

I. INTRODUCTION.

Microfluidic devices and their applications rely to a large extent on the possibility to precisely control transport phenomena in colloidal suspensions [1]. Besides electrophoresis, which is the best known and widely used physical mechanism [2], a suspended particle may be driven by a concentration gradient of an ionic or molecular solute, or a non-uniform temperature. In charged colloids, transport is essentially due to the coupling of the applied external field to the electric double layer at the particle-fluid interface [3].

The forces underlying electrophoresis and diffusio-phoresis are described in a simple physical picture [3, 4], and their dependence on the properties of solvent and solute is rather well understood. A more complex situation occurs for motion driven by thermal forces, where a temperature gradient results in the single-particle velocity

$$\mathbf{u} = -D_T \nabla T. \quad (1)$$

Typical values of the coefficient D_T are of the order of a few $\mu\text{m}^2\text{K}^{-1}\text{s}^{-1}$ [5–7]. Thermal diffusion in dielectric binary or ternary molecular liquids [8–10] is determined by the competition of entropy and short-ranged dispersion forces; with appropriately chosen atom-atom potentials, numerical simulations of the molecular dynamics account for several observed dependencies [10–12] and in particular permit to separate the chemical contribution [11].

Transport in charged colloidal systems involves electric forces operating on the scale of the Debye screening length, which takes values between one and hundreds of nanometers. If electrophoresis is readily obtained from an external field acting on the electric-double layer [3], and diffusio-phoresis from the osmotic pressure in a concentration gradient, the physical origin of the thermal forces is less obvious. In fact, Eq. (1) arises from the superposition of several contributions of comparable magnitude. Besides the temperature gradient, any solvent parameter that depends on temperature, such as Debye screening length, permittivity, or salinity, may affect the thermally driven motion.

In the last few years, a host of experimental data provided clear evidence that the thermophoretic coefficient D_T of charged colloids may change its sign upon a variation of temperature or salinity. This was first observed for an aqueous solutions of lysozyme protein, where the macromolecular solute diffuses to the warm at low temperatures, and to the cold at higher T [13]. The transport coefficient goes through zero at T^* , which is close to room temperature and depends weakly on salinity. Later on, this behavior was confirmed for polystyrene beads [14–17], micelles of ionic surfactants [16], DNA [18], and coated Ludox particles [19], with cross-over temperatures T^* ranging from 5 to 40 °C.

Similar observations were reported upon changing the electrolyte composition. The thermophoretic mobility of latex nanoparticles was shown to depend on the quantity of added salt and in particular on the pH value of the electrolyte solution [14]. For lysozyme protein solution at room temperature, a change of sign of D_T occurred when increasing the NaCl content [13].

As first suggested in [14], the negative sign of thermophoretic coefficient of colloidal suspensions is related to a Seebeck or thermoelectric effect: The thermal gradient results in a non-uniform diffusion of positive and negative ions, depending on their heat of transport, or ionic Soret coefficient; this induces a macroscopic electric field E_∞ that drives the suspended particles in one direction or in the other, depending on their surface charge and on the sign E_∞ . The temperature dependence of the thermal transport coefficient and its change of sign have been explained in terms of the competition of this Seebeck effect with that of the non-uniform salinity and dielectrophoresis [20].

Transport coefficients describe the linear response to a non-equilibrium situation created by an applied field [21]. For a charged colloid, their explicit calculation relies on evaluating how the external field affects the cloud of counterions that screens the surface charge of a suspended particle. We briefly recall the basic results for the electrophoretic mobility $\mu = u/E_{\text{ext}}$, where u is the particle velocity u and E_{ext} the applied electric field [22]. If the particle size a exceeds the Debye length λ , the

Helmholtz-Smoluchowski relation $\varepsilon\psi_0/\eta$ gives the mobility as the ratio of the surface potential ψ_0 and the solvent permittivity ε and viscosity η . In the opposite case of small particles, the Hückel limit results in $\mu = \frac{2}{3}\varepsilon\psi_0/\eta$, which differs merely by a factor $\frac{2}{3}$. It turns out instructive to rewrite the mobility in terms of the surface charge density $\sigma = Q/4\pi a^2$. In the weak-coupling or Debye-Hückel limit, the surface potential $\psi_0 = (\lambda/\sigma\varepsilon)a/(a + \lambda)$ is a linear function of σ but depends on the ratio of screening length and particle size. Inserting in the above expressions for the mobility,

$$\mu = \frac{\sigma}{\eta} \times \begin{cases} \lambda & \text{for } \lambda \ll a, \\ \frac{2}{3}a & \text{for } a \ll \lambda, \end{cases} \quad (2)$$

one finds that μ is proportional to the shorter of the lengths λ and a .

The variation of the thermophoretic coefficient D_T with the solvent and solute parameters, and in particular with particle size and Debye length [6, 18, 19, 23], has been intensely debated in recent years. Theoretical work mostly relies on low-Reynolds number hydrodynamics [24–31]. Except for Ref. [31], these works rely on the boundary-layer approximation, valid in the limit of large particles $\lambda \ll a$, and which is the usual basis for describing capillary flow and colloidal transport [3]. Derjaguin et al. considered thermoosmosis in terms of the enthalpy flow close to the wall of a pore [24]. By adapting the Helmholtz-Smoluchowski electrophoretic mobility and using the picture of a thermal Marangoni force at the particle surface, Ruckenstein argued that the thermophoretic coefficient should be proportional to the square of the surface potential [25]; for weak coupling this implies that D_T is quadratic in the Debye length and independent of a . This was confirmed by explicitly solving Stokes's equation for a thermal force with no-slip boundary conditions [26–29], whereas hydrodynamic slippage results in a linear law [7, 30]. As an alternative to the hydrodynamic approach, the phenomenological charging-energy model was studied by several authors [18, 32–35].

The small-particle limit $a \ll \lambda$ has so far attracted little attention, although it is relevant for molecular solutes and for nanoparticles in weak electrolytes where the Debye length may attain hundreds of nanometers. Extending our previous work [20], the present paper deals with thermophoresis of small particles, by paying particular attention to the role of the non-uniform electrolyte. In Sect. 2 we give the densities and currents of salt ions and particles; for small Peclet numbers the coupled diffusion equations reduce to the fluid flow around a suspended particle. This hydrodynamic problem is addressed in Sect. 3; we derive the force density exerted by a suspended particle on the surrounding fluid and determine the fluid velocity. In Sect. 4 the transport coefficient D_T is evaluated in weak-coupling or Debye-Hückel approximation. Finally we discuss several aspects of small-particle thermophoresis and compare our results with recent experiments.

II. DIFFUSION IN NON-EQUILIBRIUM SYSTEMS

On a fundamental level, thermal diffusion is driven by the principle of minimum entropy production [21]. The resulting phenomenological equations provide a complete description for the heat and particle currents; they do not, however, relate the transport coefficients to the physical and chemical properties of the system. In order to express thermally driven transport in terms of the system parameters, one needs to start from the diffusion equations for the components and to derive the forces from their interactions potentials.

In principle heat and particule currents are coupled. Since heat diffusion is much faster than particle motion, the temperature follows instantaneously and takes in a given profile $\delta T(\mathbf{r})$ around the particle. Local temperature modulations occur if the heat conductivities of solute and solvent differ significantly [26]. Except for metal particles, this effect is of little relevance and will be discarded here. Throughout this paper we assume a constant temperature gradient

$$\nabla T = T_x \mathbf{e}_x$$

along the x -axis.

A. Electrolyte solution

We start with a discussion of an electrolyte solution of monovalent ions of charge $q_i = z_i e$ with number densities n_i . Their current densities comprise normal diffusion, thermal diffusion, and a term accounting for a macroscopic electric field [36–38],

$$\mathbf{J}_i = -D_i \left(\nabla n_i + n_i \frac{Q_i^*}{k_B T^2} \nabla T - n_i \frac{q_i \mathbf{E}_\infty}{k_B T} \right), \quad (3)$$

where the Einstein coefficients $D_i = k_B T / (6\pi\eta a_i)$ are defined by Fick's law $-D_i \nabla n_i$, and the thermal diffusion current depends on the heat of transport Q_i^* . The latter determine the thermoelectric field \mathbf{E}_∞ , as derived below.

We discuss the stationary state $\mathbf{J}_i = 0$, where the currents vanish and the electric field has reached a constant value. For later convenience we define the salinity

$$n_0 = \frac{1}{2} \sum_i n_i, \quad (4)$$

the reduced ionic Soret coefficient in terms of the heat of transport

$$\alpha_i = \frac{Q_i^*}{2k_B T}, \quad (5)$$

and the reduced Soret and Seebeck coefficients of the electrolyte solution, as the mean values of α_i and $z_i \alpha_i$, weighted with the number densities n_i ,

$$\alpha = \sum_i \alpha_i \frac{n_i}{n_0}, \quad \delta\alpha = \sum_i z_i \alpha_i \frac{n_i}{n_0}. \quad (6)$$

The macroscopic charge separation reads as

$$\rho_\infty = \sum_i q_i n_i.$$

The stationary state implies overall conditions of zero particle current $\sum_i \mathbf{J}_i = 0$ and zero charge current $\sum_i q_i \mathbf{J}_i = 0$; inserting the above quantities and using the valencies $z_i = \pm 1$ for positive and negative ions, we obtain the relations

$$\begin{aligned} 0 &= \nabla n_0 + \alpha n_0 \frac{\nabla T}{T} - \frac{\mathbf{E}_\infty}{2k_B T} \rho_\infty, \\ 0 &= \frac{\nabla \rho_\infty}{2e} + \left(\delta\alpha \frac{\nabla T}{T} - \frac{e\mathbf{E}_\infty}{k_B T} \right) n_0. \end{aligned}$$

The salinity gradient ∇n_0 and the thermoelectric field \mathbf{E}_∞ arise from the tendency of the ions to diffuse to cold or warm regions of the solution, as expressed by the relative values of their heat of transport Q_i^* . Both ∇n_0 and \mathbf{E}_∞ are macroscopic quantities that are independent of the system size. The charge density ρ_∞ , however, vanishes throughout a macroscopic system, except for a screening layer at the boundaries.

Setting $\rho_\infty = 0$ relates the salinity gradient and the thermoelectric field \mathbf{E}_∞ to the thermal gradient,

$$\frac{\nabla n_0}{n_0} = -\alpha \frac{\nabla T}{T}, \quad \frac{e\mathbf{E}_\infty}{k_B T} = \delta\alpha \frac{\nabla T}{T}, \quad (7)$$

and points out the physical meaning of the reduced Soret and Seebeck coefficients α and $\delta\alpha$. With typical values for the ionic heat of transfer $Q_i^* \sim$ a few kJ/Mol [39], one finds that the dimensionless quantities α and $\delta\alpha$ are of the order of unity.

There is a close analogy to the thermoelectric effect of charge carriers in solid-state physics, where the Seebeck coefficient is defined as the ratio of the induced voltage and the temperature difference $S = \Delta\psi/\Delta T$; for an electrolyte solution this ratio takes the value $E_\infty/T_x = \delta\alpha k_B/e \sim 10^{-4}$ V/K. This implies that the macroscopic electrostatic potential $e\Delta\psi$ of a single ion is much smaller than its thermal energy.

B. Charged colloidal suspensions

Now we add particles to the electrolyte solution. Their charge Q is screened by a cloud of counterions and a depletion of co-ions within one Debye length; the spherical symmetry of this screening cloud is broken by the non-uniform temperature, salinity $n_0(T)$, and permittivity $\varepsilon(T)$. The gradients of these macroscopic parameters and the thermoelectric field \mathbf{E}_∞ result in thermal forces on the charged fluid and in a flow field $\mathbf{v}(\mathbf{r})$ around each particle.

The ion densities are subject to the electric field $\mathbf{E} = -\nabla\psi$ of the particle; in principle we have to consider the superposition of local and macroscopic fields

$\mathbf{E} + \mathbf{E}_\infty$. The surface potential of the particle is of the order $\psi \sim k_B T/e$ and decays on the scale of the Debye length λ , resulting in $E \sim k_B T/e\lambda$. A rough estimate shows that the local field $E \sim 10^7$ V/m is by several orders of magnitude larger than the thermoelectric field $E_\infty \sim k_B T_x/e$, which attains 10^2 V/m for a thermal gradient $T_x = 1$ K/micron. A similar argument shows that the salinity gradient is much smaller than the change in ion densities occurring in the boundary layer.

As a consequence, the Seebeck and Soret effects are insignificant on short scales, and the thermoelectric field and the salinity gradient may be neglected when discussing the ion densities close to the particle. Thus the ion currents in the boundary layer comprise a convection term due to the fluid flow $\mathbf{v}(\mathbf{r})$, and diffusion in the local electric field,

$$\delta\mathbf{J}_i = \delta n_i \mathbf{v} - D_i \left(\nabla \delta n_i - \delta n_i \frac{q_i \mathbf{E}}{k_B T} \right), \quad (8)$$

where the δn_i are the excess ion densities with respect to their values n_i in the pure electrolyte discussed above.

In principle, the ion densities and currents are obtained from the coupled diffusion equation for δn_i and the hydrodynamic equation for \mathbf{v} . A detailed study of the opposite case $Pe > 1$ has been given for particles driven by the strong concentration gradient of an adsorbing neutral solvent [4]. In the present case, however, convection is negligible, and the problem simplifies significantly. The reason is that, even for large thermal gradients, thermophoretic transport velocities are at most of the order 10^{-6} m/s; the corresponding Peclet number for ion diffusion, $Pe = v\lambda/D_i$, hardly attains values of 10^{-3} . This means that convection is much slower than diffusion and does not affect the ion densities,

Thus we neglect convection effects and assume that the ion distributions follow instantaneously the particle and motion. To zeroth order in the thermal perturbation, that is when neglecting the temperature gradient, the ion densities are obtained from $\nabla \delta n_i - \delta n_i q_i \mathbf{E}/k_B T = 0$, which is readily integrated,

$$\delta n_i = n_i (e^{-q_i \psi/k_B T} - 1). \quad (9)$$

At distances beyond a few Debye lengths from the particle, its potential ψ vanishes due to screening, and so does δn_i . The fluid flow carries a net ion current

$$\delta\mathbf{J}_i = \delta n_i \mathbf{v}.$$

For a negatively charged colloidal particles one has $\psi < 0$, resulting in an excess density of positive ions and a depletion of negative ones, $\delta n_+ > 0 > \delta n_-$. As a consequence, the effective convection currents take opposite directions, thus carrying in the vicinity of the particle permanently charge along the thermal gradient. At larger distances they decay rapidly; the charge current $\sum_i q_i \delta\mathbf{J}_i$ is equilibrated by diffusion, as expressed by the small Peclet number.

C. Particle diffusion

According to Eq. (1) the thermally driven particle current of a colloidal suspension of number density $N(\mathbf{r})$ reads $N\mathbf{u} = -ND_T\nabla T$. Adding normal diffusion with Fick's law $-D\nabla N$ results in

$$\mathbf{J} = -D\nabla N - ND_T\nabla T. \quad (10)$$

The drift velocity of the particle is given by the fluid flow at its surface,

$$\mathbf{u} = \mathbf{v}|_{r=a}.$$

Thus calculation of the thermal diffusion coefficient D_T reduces to solving the fluid flow driven by thermal forces.

III. HYDRODYNAMICS

Transport in colloidal suspensions is described by relating the particle velocity to the applied forces; the coefficients are calculated by equilibrating the driving force and the hydrodynamic stress of the fluid [22]. Stationary states and mechanical equilibrium of inhomogeneous systems are discussed in Chapter V of [21].

Like in most micron-scale flows, the Reynolds number of thermally driven motion is small, and the stationary fluid velocity in the vicinity of the particle is determined by Stokes' equation

$$\eta\nabla^2\mathbf{v} = \nabla(P_0 + nk_B T) - \mathbf{f}_0, \quad (11)$$

where η is the solvent viscosity and the right-hand side depends on ion densities (9). We have separated the hydrostatic pressure P_0 of the pure electrolyte and the pressure of the excess density of mobile ions,

$$n = \sum_i \delta n_i.$$

A. Double-layer forces

The electric force density \mathbf{f}_0 acting on the charged fluid comprises two independent parts [40, 41],

$$\mathbf{f}_0 = \nabla \cdot \mathcal{T} + \rho\mathbf{E}_\infty;$$

the divergence of the Maxwell stress tensor \mathcal{T} describes the force exerted by the charged particle surface, and the second term accounts for the coupling of the charge density ρ to an external electric field \mathbf{E}_∞ . With known properties of the gradient $\mathbf{E} = -\nabla\psi$ of the particle's electrostatic potential [40, 41], the divergence of the Maxwell tensor can be written as

$$\nabla \cdot \mathcal{T} = -\frac{1}{2}E^2\nabla\varepsilon + \rho\mathbf{E},$$

where ε is the solvent permittivity and where

$$\rho = \sum_i q_i \delta n_i$$

is a shorthand notation for the charge density of mobile ions in the screening cloud. Because of $E_\infty \ll E$, the contribution of the macroscopic field to the dielectrophoretic term is negligible.

It turns out convenient to add the osmotic pressure to the electric forces,

$$\mathbf{f} = -\frac{1}{2}E^2\nabla\varepsilon + \rho\mathbf{E} - \nabla(nk_B T) + \rho\mathbf{E}_\infty, \quad (12)$$

resulting in

$$\eta\nabla^2\mathbf{v} = \nabla P_0 - \mathbf{f}. \quad (13)$$

A somewhat different route is taken in studies on diffusiophoresis [3], i.e., for neutral solutes adsorbing on the particle surface, where the right-hand side of (13) is written in terms of the total pressure $P = P_0 + nk_B T$ and the force $\mathbf{f}_0 = -\nabla\Phi$ arising from the particle-solute van der Waals attraction Φ . A thermal gradient, however, gives rise to a rather intricate force density (12), that comprises terms of different physical origin and that does not derive from a potential. The screened electrostatic potential ψ is an effective quantity that depends on the entropy of the mobile ions; thus it is in any case impossible to distinguish potential and entropic forces, and we find it more convenient to include the osmotic pressure gradient in the force density \mathbf{f} .

Eq. (12) gives the force density as a function of the quantities describing the electric double-layer and of the thermoelectric field. In a uniform electrolyte, the Poisson-Boltzmann mean-field expression (9) results in $\mathbf{f} = 0$. Treating the thermal gradient as a perturbation, we insert the unperturbed ion distribution function (9) in the expression for \mathbf{f} and expand all terms to linear order in the gradients of the slowly varying solvent parameters.

We start with the particle's electric field and the ion pressure, $\rho\mathbf{E} - \nabla(nk_B T)$. The Poisson-Boltzmann mean-field expressions (9) give $\rho = -2en_0 \sinh \hat{\psi}$ and $n = 2n_0(\cosh \hat{\psi} - 1)$, with the reduced potential $\hat{\psi} = e\psi/k_B T$. Spelling out the pressure gradient we find

$$\nabla(nk_B T) = nk_B \nabla T + nk_B T \frac{\nabla n_0}{n_0} + \rho\psi \frac{\nabla T}{T} - \rho\nabla\psi.$$

The last term cancels its counterpart $\rho\mathbf{E} = -\rho\nabla\psi$ in (12), and we are left with

$$\mathbf{f} = -(\rho\psi + nk_B T) \frac{\nabla T}{T} - \frac{E^2}{2} \nabla\varepsilon + nk_B T \frac{\nabla n_0}{n_0} + \rho\mathbf{E}_\infty. \quad (14)$$

Note that the gradient of the electrostatic potential $\nabla\psi$ has disappeared.

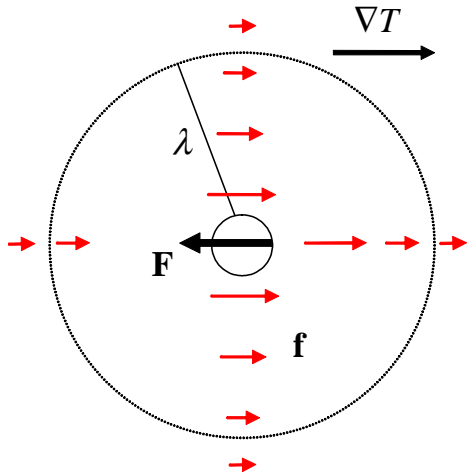


FIG. 1: Schematic view of a charged particle of radius a , and its screening cloud with Debye length $\lambda \gg a$. Except for the immediate vicinity of the particle, the force field \mathbf{f} exerted by the particle on the fluid is parallel to the thermal gradient. The Hückel approximation relies on the counterforce \mathbf{F} on the particle

Eq. (14) constitutes the general expression for the force density in a non-uniform electrolyte, consisting of the external electric field \mathbf{E}_∞ and the gradients of the slowly varying quantities temperature, permittivity, and salinity. It relies on Poisson-Boltzmann mean-field theory and linear-response approximation; the latter assumes a sufficiently weak electric field, $\rho E_\infty \ll k_B T/a$, and that the solvent parameters T , ε , n_0 vary little on the scale of the particle, $\nabla \ln T \ll 1/a$, etc. These conditions are satisfied in all experimental situations.

Now we turn to the dielectric force proportional to the permittivity gradient $\nabla \varepsilon$. With the logarithmic derivative

$$\tau = -\frac{d \ln \varepsilon}{d \ln T} \quad (15)$$

one has

$$-\frac{1}{2} E^2 \nabla \varepsilon = \frac{\tau}{2} E^2 \nabla T.$$

The remaining contributions to Eq. (14) describe the Soret and Seebeck effects of the electrolyte solution. The former accounts for a non-uniform salinity n_0 , and the latter for a charge separation that occurs if the thermal diffusion strengths of positive and negative ions are not the same [36, 39, 42]. Inserting the dimensionless quantities $\tau, \alpha, \delta\alpha$ in (12) we obtain the force density on the fluid as a linear function of the thermal gradient,

$$\mathbf{f} = \left(\frac{\tau \varepsilon E^2}{2k_B T} - \frac{\rho \psi}{k_B T} + (\alpha - 1)n + \delta\alpha \frac{\rho}{e} \right) k_B \nabla T. \quad (16)$$

This force arises from the interactions at the solid-fluid interface. As a consequence, the total force on the colloidal particle and its screening cloud vanishes, and there

is a counterforce

$$\mathbf{F} = -\int dV \mathbf{f} \quad (17)$$

exerted by the charged fluid on the particle.

B. Fluid velocity

Stokes' equation (13) with the force density (16) cannot be solved as it stands. For small particles,

$$a \ll \lambda,$$

the velocity field can be obtained in two particular cases, (i) at short distances close to the particle surface, $r - a \ll \lambda$; (ii) at large distances well beyond the Debye length $r \gg \lambda$. These approximations rely on the fact that the force density is spread over an interaction volume of the order λ^3 , much larger than the particle volume.

(i) At distances much shorter than the Debye length, the velocity is determined by the counter-force \mathbf{F} acting on the particle [22]. This corresponds to the Hückel limit of electrophoresis; the solution is given by [43]

$$\mathbf{v}(\mathbf{r}) = \frac{1}{8\pi\eta r} \left((1 + \mathbf{P}_r) + \frac{a^2}{r^2} \left(\frac{1}{3} - \mathbf{P}_r \right) \right) \cdot \mathbf{F}, \quad (18)$$

with the projection $\mathbf{P}_r = \hat{\mathbf{r}}\hat{\mathbf{r}}$ on the radial direction $\hat{\mathbf{r}} = \mathbf{r}/r$. Note that this result is valid for $r - a \ll \lambda$ only. On the particle surface $r = a$, the terms in \mathbf{P}_r cancel each other, and $\mathbf{u} = \mathbf{v}|_{r=a}$ takes the value

$$\mathbf{u} = \frac{\mathbf{F}}{6\pi\eta a}. \quad (19)$$

For no-slip boundary conditions, the velocity field is continuous at the interface, and \mathbf{u} is the particle velocity. Eq. (19) could be obtained equally well by equilibrating the force \mathbf{F} on the particle with the Stokes drag $-6\pi\eta a \mathbf{u}$.

(ii) At distances well beyond the Debye length, $r \gg \lambda$, the size of the particle and the boundary conditions at its surface are irrelevant. Thus the fluid velocity may be written as the superposition of the flow engendered by the point force \mathbf{F} and that on the mobile ions in the screening cloud,

$$\mathbf{v}(\mathbf{r}) = \mathbf{G}(\mathbf{r}) \cdot \mathbf{F} - \int dV' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}(\mathbf{r}'),$$

where the Oseen tensor

$$\mathbf{G}(\mathbf{r}) = \frac{1}{8\pi\eta r} (1 + \mathbf{P}_r)$$

plays the role of a Green function associated with Stokes' equation [44]. This expression provides a basis for expanding the velocity field in inverse powers of the distance r . At lowest order we replace the Oseen tensor with $\mathbf{G}(\mathbf{r})$; then the surface and volume terms cancel and we

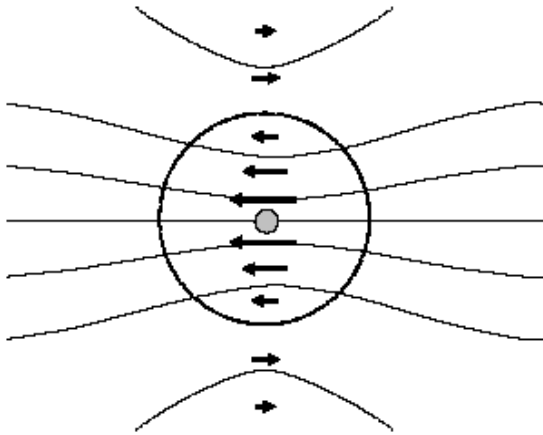


FIG. 2: Schematic view of the fluid velocity $\mathbf{v}(\mathbf{r})$ around a particle moving to the left. The Debye length is indicated by the dashed line; the flow pattern (18) in the interaction volume ($r < \lambda$) differs significantly from that at large distances, as given by Eq. (20).

find that there is no velocity contribution $\mathbf{v} \sim 1/r$. The leading correction is obtained by expanding $\mathbf{G}(\mathbf{r} - \mathbf{r}')$ to third order in $1/r$; the fluid flow reads

$$\mathbf{v}(\mathbf{r}) = \frac{R^2}{8\pi\eta r^3} \left(\mathbf{P}_r - \frac{1}{3} \right) \mathbf{F}, \quad (r \gg \lambda), \quad (20)$$

where the quantity R^2 is defined through the integral

$$R^2 = \frac{1}{F} \int dV r^2 f(r),$$

with $\mathbf{f}(r) = f(r)\mathbf{e}_x$ and $\mathbf{F} = F\mathbf{e}_x$.

Fig. 2 gives a schematic view of the fluid velocity resulting from Eqs. (18) and (20). At distances within one Debye length, the particle drags the fluid with a velocity $v \sim 1/r$ similar to what happens in sedimentation. At larger distances, the fluid close to the symmetry plane moves in the opposite direction; its velocity decays as $v \sim 1/r^3$.

The flow pattern $\mathbf{v}(\mathbf{r})$ is of limited interest for thermophoresis of spherical particles, where the transport velocity is given by Eq. (19). For macromolecules, however, the drag flow (20) within one Debye length results in hydrodynamic interactions between nearby units, which may significantly enhance the transport coefficient.

IV. TRANSPORT COEFFICIENT

For arbitrary surface charge density, the electrostatic potential ψ cannot be given in closed form. Thus we evaluate the force F in Debye-Hückel approximation, where

$$\psi = \frac{Ze}{4\pi\epsilon r} \frac{e^{-(r-a)/\lambda}}{1 + a/\lambda}.$$

This weak-coupling expression is valid as long as the electrostatic potential $e\psi$ of an ion is smaller than the thermal energy. Expanding the charge density and the excess ion density to quadratic order in ψ , and using the Debye length $\lambda^2 = 1/(8\pi n_0 \ell_B)$ with the Bjerrum length $\ell_B = e^2/(4\pi\epsilon k_B T)$, we obtain

$$\rho = -\frac{\epsilon\psi}{\lambda^2}, \quad n = \frac{\epsilon\psi^2}{2\lambda^2 k_B T}.$$

Then the force acting on the particle is given by

$$\frac{F}{k_B T_x} = \int dV \left(\frac{\tau\epsilon E^2}{2k_B T} + \frac{(\alpha + 1)\epsilon\psi^2}{2\lambda^2 k_B T} - \frac{\delta\alpha\epsilon\psi}{e\lambda^2} \right). \quad (21)$$

Evaluating the electric field $E = -d\psi/dr$, defining the surface potential $\psi_0 = \psi(a)$, and changing to the variable $\xi = (r - a)/a$, the volume integral is readily performed,

$$F = 2\pi a \epsilon \psi_0^2 \left(\tau + (\tau + \alpha + 1) \frac{a}{2\lambda} \right) \frac{T_x}{T} - 4\pi a \epsilon \psi_0 \delta\alpha \left(1 + \frac{a}{\lambda} \right) \frac{k_B T_x}{e}, \quad (22)$$

Finally we calculate the quantity R^2 that determines the fluid velocity at large distances. If the Seebeck coefficient is small, one has $R^2 = a\lambda(\frac{1}{2} + (\alpha + 1)/\tau)$, whereas in the opposite case we find $R^2 = 6\lambda^2$.

Eqs. (12) and (19) relate the thermophoretic coefficient to the force on the particle,

$$D_T = \frac{F}{6\pi\eta a T_x}.$$

Inserting the explicit form (22) we have

$$D_T = \frac{\epsilon}{3\eta T} \left\{ \psi_0^2 \left(\tau + \frac{a}{2\lambda} (\tau + \alpha + 1) \right) - \psi_0 \frac{2k_B T}{e} \delta\alpha \left(1 + \frac{a}{\lambda} \right) \right\}, \quad (23)$$

with the coefficients τ and $\delta\alpha$ as defined in (15) and (6). When retaining only leading terms in a/λ , one has

$$D_T = \frac{\epsilon}{3\eta T} \left(\tau \psi_0^2 - 2\delta\alpha \frac{k_B T}{e} \psi_0 \right) \quad (a \ll \lambda).$$

Inserting the surface potential of small particles $\psi_0 = Ze/4\pi\epsilon a$, we obtain the coefficient as a function of the valency,

$$D_T = \frac{k_B}{12\pi\eta a} \left(\tau Z^2 \frac{\ell_B}{a} - 2\delta\alpha Z \right). \quad (24)$$

As a most striking feature, D_T is independent of the Debye length. The only terms contributing to thermally driven transport are the dielectrophoretic force and the thermoelectric field, that are proportional to $\tau = -(T/\epsilon)d\epsilon/dT$ and to $\delta\alpha$, respectively. For water, the permittivity derivative takes the value $\tau = 1.4$ at

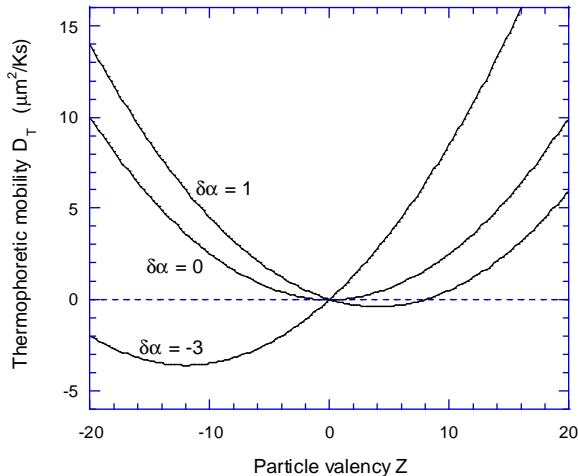


FIG. 3: Thermophoretic mobility as a function of the valency Z for $\delta\alpha = 1; 0; -3$. We have used $\ell_B = 0.7$ nm, $a = 3$ nm, $\tau = 1.4$, and $\eta = 10^{-3}$ Pa s.

room temperature. Thus the dielectrophoretic contribution to D_T is positive. The Seebeck term may be positive or negative, depending on the signs of the thermoelectric coefficient $\delta\alpha$ and the valency Z . In Fig. 3 we plot the thermophoretic mobility as a function of Z for different values of $\delta\alpha$. For comparison we give values for different electrolyte solutions, as calculated from measured ion Soret coefficients: $\delta\alpha = 0.6$ for NaCl, $\delta\alpha = -2.7$ for NaOH, and $\delta\alpha = 2.6$ for HCl [20]. The curves of Fig. 3 show a qualitative behavior similar to that reported in [20] for large particles. Due to the weaker charges, the absolute values of D_T shown here are by about one order of magnitude smaller.

V. DISCUSSION

A. Approximations

The coefficient D_T in the present work has been derived in Debye-Hückel approximation, contrary to our previous analysis based on boundary-layer approximation [20]. This additional approximation is imposed by the fact that in the small-particle or Hückel limit ($a \ll \lambda$), the screened electrostatic potential ψ can not be calculated for arbitrary charge. Thus Eq. (24) relies on the weak-coupling assumption for the ratio of the electrostatic potential of an elementary charge and the thermal energy,

$$\frac{e\psi_0}{4k_B T} = \frac{Z\ell_B}{4a} = \frac{Z}{Z^*} < 1, \quad (25)$$

i.e., the weak-coupling approach is justified as long as the valency is smaller than the effective value $Z^* = 4a/\ell_B$

[45]. The relation to the dimensionless coupling parameter $\hat{\sigma} = 2\pi\sigma\lambda\ell_B$ introduced in [20] is given by $\hat{\sigma} = 2Z/Z^*$. Highly charged macroions of nanometer size do not necessarily satisfy the weak-coupling assumption, e.g., for coated Ludox particles ($a = 12$ nm, $Z = 50\dots 100$) [19] one finds the ratio $Z/Z^* \sim 1$, and for micelles of the ionic surfactant SDS ($a = 3$ nm, $Z \sim 40$) [6] one has $Z/Z^* \sim 2.5$.

Static properties of strongly charged particles ($Z > a/\ell_B$) are well described by Debye-Hückel theory with the effective valency Z^* and a corresponding potential ψ^* [45]. This does not necessarily hold true for the transport properties. Close to the particle the electric field varies as $E \sim 1/r^2$; thus the volume integral (21) of the force F is dominated by the range close to the particle surface $r \sim a$, where the effective-valency potential ψ^* works less well. Still, all quantities are smooth functions of the ratio Z/Z^* ; thus one expects that the present results describe the qualitative behavior even for $Z > Z^*$.

The non-uniform electrolyte properties are treated in linear perturbation theory. In particular, the force density (12) has been evaluated by inserting the isotropic ion distribution (9). In most experiments the thermal gradient is very weak indeed. Finally, the hydrodynamics have been solved in the Hückel limit $a \ll \lambda$. A comparison with the results from the opposite case of large particles is given below.

B. Comparison with the case $\lambda \ll a$

The present work deals with the small-particle limit $a \ll \lambda$. In order to compare with the opposite case we write the weak-coupling result of [20] in terms of the surface potential $\psi_0 = e\sigma\lambda/\varepsilon$,

$$D_T = \frac{\varepsilon}{3\eta T} \left(\frac{\tau + \alpha + 1}{4} \psi_0^2 - 3\delta\alpha \frac{k_B T}{e} \psi_0 \right). \quad (26)$$

Formally, Eqs. (23) and (26) are rather similar and differ merely in prefactors.

The relative factor $\frac{2}{3}$ of the Seebeck effect has the same origin as that of the electrophoretic mobility in (2). In physical terms, it arises from the distortion of the electric field by the permittivity jump at the particle-liquid interface. In the boundary layer close to large particles ($\lambda \ll a$), the permittivity contrast $\varepsilon/\varepsilon_P \gg 1$ enhances the parallel electric field by a factor $3\varepsilon/(2\varepsilon + \varepsilon_P) \approx \frac{3}{2}$. In the present case ($\lambda \gg a$), however, this distortion is irrelevant in most of the interaction volume $\sim \frac{4}{3}\pi\lambda^3$ and the electric field is well approximated by its macroscopic value \mathbf{E}_∞ . By the same token, we have neglected the discontinuity of thermal conductivity at the particle-fluid interface, which modifies the normal and parallel components of the thermal gradient [26].

Regarding the term in (26) that is quadratic in the surface potential, the factor $\frac{1}{4}(\tau + \alpha + 1)$ indicates that the dielectrophoretic term $\sim \tau$, the electrolyte Soret effect \sim

α , and the charge term, contribute equally to the thermal force. For the case considered in the present work, $a \ll \lambda$, the dielectrophoretic contribution dominates in (21). This is due to the fact that, close to the particle surface, the electric field is of the order $E \sim \psi/a$, resulting in $E^2 \sim \psi^2/a^2$ which is much larger than the charge and pressure terms $\rho\psi \sim \psi^2/\lambda^2$ and $k_B T n \sim \psi^2/\lambda^2$.

C. Variation with particle size

The present work deals with the small-particle limit ($a \ll \lambda$) and thus completes previous work relying on the boundary layer approximation that is valid for large particles [20, 24–29]. As a function of the surface potential, the electrophoretic mobility differs merely by a numerical factor $\frac{2}{3}$. The corresponding weak-coupling expressions for the thermophoretic coefficients, Eqs. (23) and (26), show a similar structure. Significant discrepancies arise, however, when considering the dependence of the surface potential on Debye length and particle size.

Since in many instances particles of different size but equal surface charge density $\sigma = Z/(4\pi a^2)$ are considered, we rewrite the Debye-Hückel surface potential as

$$\psi_0 = \frac{Q}{4\pi\epsilon a(1+a/\lambda)} = \frac{\sigma e}{\epsilon} \frac{a\lambda}{a+\lambda}. \quad (27)$$

For small particles this form reduces to $\psi_0 = \sigma ea/\epsilon$ and results in the thermophoretic coefficient

$$D_T = \frac{1}{3\eta T} \left(\tau \frac{(\sigma ea)^2}{\epsilon} - 2\delta\alpha k_B T \sigma a \right), \quad (a \ll \lambda).$$

Thus at constant σ the dielectrophoretic term varies with the square of the particle size, whereas the thermoelectric one is linear in a . In the opposite case of large particles the surface potential $\psi_0 = \sigma e\lambda/\epsilon$ is independent of the particle size, and so is the transport coefficient D_T .

We summarize the variation of the two contributions to (26) with particle size and Debye length, by splitting the thermophoretic coefficient as $D_T = C_0 + C_S$. The thermoelectric or Seebeck contribution shows a linear dependence on the smaller of the two lengths a, λ ,

$$C_S = -\frac{2\delta\alpha k_B \sigma}{3\eta} \times \begin{cases} a & \text{for } a \ll \lambda, \\ \frac{3}{2}\lambda & \text{for } \lambda \ll a. \end{cases} \quad (28)$$

This behavior is identical to that of the electrophoretic mobility μ given in (2). This does not come as a surprise, since the Seebeck effect describes the electric field induced by the charge separation of the electrolyte solution.

The remainder, that is the dielectrophoretic, osmotic, and charge terms vary with the square of the smaller length scale,

$$C_0 \propto \frac{\sigma^2 e^2}{3\eta\epsilon T} \times \begin{cases} a^2 & \text{for } a \ll \lambda, \\ \lambda^2 & \text{for } \lambda \ll a, \end{cases} \quad (29)$$

with numerical prefactors of the order unity.

Eqs. (28) and (29) reveal a rather different behavior in the limiting cases of large and small particles. The difference arises from the fact the thermoelectric effect, like electrophoresis, is linear in the surface potential, whereas the dielectric and Soret contributions to thermophoresis vary with its square.

D. Comparison with previous work

The stationary state of a non-uniform system is determined by requiring mechanical equilibrium [21]. Yet this general principle is not readily applied to complex systems with multiple interactions, where the transport coefficient shows subtle dependencies on the physical parameters of solute and solvent. If mesoscopic solutes induce local flows of the solvent, the stationary state is determined by requiring that viscous and thermal forces cancel. The main difficulty resides in properly determining the thermal forces that act on the solute particle.

Recent theoretical studies took two different approaches. The first one relies on solving Stokes' equation in the vicinity of a solute particle, with a force field comprising the pressure and electric forces on the fluid; the formal framework is analogous to the common treatment of electrophoresis and similar phenomena [3]. This route has been taken in Refs. [20, 24–31] mostly for ($\lambda \ll a$); the present work deals with small particles ($a \ll \lambda$), corresponding to the Hückel limit of electrophoresis [22]. The recent Ref. [31] derives an expression that is valid in both limits; in the Hückel limit, the result for the transport velocity corresponds to our Eq. (23) for $\delta\alpha = 0$, i.e., without the thermoelectric effect. Finally we note that the first term $-(\rho\psi + nk_B T)\nabla \ln T$ of the force density (14) is proportional to the enthalpy flow carried by the charged fluid, which has first been considered by Derjaguin et al. [24] in their study of thermoosmotic transport through a pore.

In a second approach, the thermal force is obtained as the gradient of a single-particle Gibbs potential, or charging energy [18, 32–35],

$$U = \frac{1}{2} Q \psi_0 = \frac{Q^2}{8\pi\epsilon a(1+a/\lambda)}, \quad (30)$$

where we used (27) and the total charge $Q = Ze$. Its spatial variation arises from the implicit dependence on the temperature gradient, and is used to define the force

$$\mathbf{F}_c = -\nabla U = -\frac{dU}{dT} \nabla T.$$

The thermophoretic velocity is obtained by equilibrating the driving force with the Stokes drag, $\mathbf{F}_c + 6\pi\eta a \mathbf{u} = 0$. The resulting Soret coefficient $S_T = (dU/dT)/k_B T$ had been evaluated by several authors [18, 32–35]; the complete temperature derivative has been calculated only recently [34, 35].

In order to facilitate comparison with our Eq. (23), we rewrite the Soret coefficient $S_T = \bar{D}_T/D$ given in [34, 35] in our notation, use $D = kT_B/6\pi\eta a$, and expand in powers of a/λ ,

$$\bar{D}_T = \frac{\varepsilon\psi_0^2}{3\eta T} \left(\tau + \frac{a}{2\lambda} (1 - 3\tau) + 2 \frac{d \ln Q}{d \ln T} \right).$$

The leading term in τ is identical to that of (23); there is a slight difference in the linear correction, whereas the charge derivative $d \ln Q/d \ln T$ is absent both in the force density (14) and in the transport coefficient (23). Thus the present approach confirms the leading dielectric contribution $\bar{D}_T = (\varepsilon\psi_0^2/3\eta T)\tau$ obtained previously from the charging-energy model [34, 35].

E. Temperature dependence

As a most striking finding, recent experiments revealed a strong temperature dependence of the thermophoretic coefficient and, in several cases, a change of sign from negative D_T at lower T to positive values at higher temperatures. We discuss the parameters appearing in Eqs. (23) and (24) in view of these experimental findings.

Seebeck and Soret coefficients. Both coefficients α and $\delta\alpha$ are given by the difference of the ionic Soret strengths α_i , which in turn are determined by heat of transport Q^* of the charge carriers [36, 39]. Typical values are of the order of a few kJ/Mol. A particularly strong effect occurs for acids and protonated solvents, the heat of transfer of protons $Q_{H^+}^* = 13.3$ kJ/M or hydroxide $Q_{OH^-}^* = 17.2$ kJ/Mol being significantly larger than that of most salts [39, 42]. The value of $Q_{H^+}^*$ corresponds to a heat of transfer per proton of about $5k_B T$ or 100 meV.

The heat of transfer Q^* accounts for the energy carried by the mobile ions and their interactions with the solvent molecules; specific-ion and hydration effects result in an intricate temperature and concentration dependence, the theoretical comprehension of which is far from satisfactory. Partly because of the relevance for large-scale thermohaline circulation, there are a number of experimental studies on the Soret coefficients α of solutions of alkali halides and salts of divalent cations as calcium and magnesium [46–51]. At standard pressure, measured values are in the range $-1 < \alpha < 3$. For alkali chlorides, α is negative at low T and goes through zero at a temperature T_0 that lies between 0 and 25 °C, depending on concentration and the size of the cation. In this temperature range the slope of the Soret coefficient takes the value $d\alpha/dT \sim 0.03$ K⁻¹; a stronger variation has been reported for solutions of Na₂SO₄ and CaCl₂ [49].

Several recent experimental studies on thermophoresis fix the acidity of the solution by adding buffers like Tris/HCl, CAPS/NaOH, or NaAcO [13–18]. The few available data suggest that these molecular ions show a strong thermoelectric effect, possibly due to the protons of their aliphatic parts; the data of Ref. [14] illustrate

the crucial role of the electrolyte composition for thermally driven transport.

Permittivity. The logarithmic derivative of the permittivity varies from $\tau = 1.25$ at 0 °C to $\tau = 1.5$ at 50 °C [53]. Its temperature derivative $d\tau/dT \sim 0.003$ K⁻¹ is by one order of magnitude smaller than that of the Soret coefficient of alkali chlorides.

Viscosity. The viscosity of water decreases from $\eta = 1.3 \times 10^{-3}$ Pa·s at 10 °C to 0.55×10^{-3} Pa·s at 50 °C [53]. Since the thermophoretic coefficient is proportional to the inverse viscosity, one expects an increase of D_T with rising temperature; this is confirmed by numerical simulations for nanoparticles [12]. The logarithmic derivative at 25 °C takes the value $d \ln \eta/dT \sim -0.02$ K⁻¹.

Thermal expansion of the solvent. Above the melting point, the density ρ of water decreases, goes through a minimum at $T = 4$ °C, and increases monotonically at higher temperature. The Soret coefficient of aqueous alkali chloride solution is strongly correlated with the thermal expansivity of the solvent [48], and similar observations have been made for the thermophoretic mobility of colloidal suspensions [16, 52]. The present work suggests that the correlation of D_T with the thermal expansion of water originates from the thermoelectric effect. Indeed, according to Eq. (23) D_T depends through $\delta\alpha$ linearly on the ionic Soret parameters.

Comparison of the permittivity derivative $d\tau/dT \sim 0.003$ K⁻¹ with that of the Soret coefficient of alkali halides, $d\alpha/dT \sim 0.03$ K⁻¹, strongly suggest that ion transport is much more sensitive to temperature than the thermal expansion and the dielectric properties of the solvent. Assuming $\alpha(T)$ and $\delta\alpha(T)$ to show similar slopes with respect to T , one is led to the conclusion that the Seebeck effect is most likely responsible for the change of sign reported for several colloids. Although the temperature dependence of the viscosity is of the same order of magnitude, it provides an overall factor and thus cannot affect the sign of D_T .

VI. SUMMARY

Recent experiments on suspensions of macromolecules and nanoparticles [13–18] reported a strong temperature dependence and a change of sign of the coefficient D_T . The role of the thermoelectric effect has been pointed out in Ref. [14], and a quantitative study of the dielectric, Soret, and Seebeck contributions to D_T has been given in [20] for the case of large particles. The present work deals with the opposite case, that is the Hückel limit. As the most striking feature, thermally driven motion results from the competition of several terms; the strong temperature dependence of the electrolyte coefficients α and $\delta\alpha$ may cause a change of sign. We summarize the main results of the present work.

(i) The thermal force Eq. (14) comprises the osmotic pressure and the enthalpy carried by the charged fluid, the dielectric force proportional to the permittivity gradi-

ent, a chemiphoretic term involving the salinity gradient, and the Seebeck contribution. Thus thermophoresis is driven by the gradients of the solvent parameters (temperature, permittivity, salinity) and the thermoelectric field E_∞ , all of which can be related to the thermal gradient. Note that derivatives of the particle's charge or of the viscosity do not appear in (14).

(ii) According to Eq. (23) thermophoresis of small particles does not depend on the Soret coefficient α of the electrolyte solution, but is entirely determined by the logarithmic derivative τ of the permittivity and the thermoelectric coefficient $\delta\alpha$. The leading corrections $\mathcal{O}(a/\lambda)$ are proportional to $(1 + \tau + \alpha)$ and $\delta\alpha$. For $\delta\alpha = 0$ these results confirm those of Ref. [31].

(iii) The dielectric and Seebeck contributions to D_T are of the same order of magnitude. With the permittivity derivative $\tau = 1.4$ of water at room temperature [53] and typical values for the thermoelectric coefficient of the order $\delta\alpha \sim 1$, the relative magnitude of the two terms in Eq. (24) is given by the ratio $Z\ell_B/a$. For nanoparticles this quantity is often of the order of unity;

then the two terms in Eq. (24) are comparable.

(iv) The Seebeck term takes opposite signs for positive and negative colloidal charges. Most macromolecules and nanoparticles carry negative valency $Z < 0$; then one expects normal thermophoresis ($D_T > 0$) for a positive Seebeck coefficient $\delta\alpha > 0$, whereas a negative $\delta\alpha$ favors an inverse effect ($D_T < 0$).

(v) Regarding the temperature dependence, no data seem to be available for the Seebeck coefficient $\delta\alpha(T)$. Still, measured values for the derivative $d\alpha/dT$ of the Soret coefficient provide evidence for the thermal variation of the electrolyte properties, and strongly suggest that the Seebeck effect is responsible for the change of sign reported for several colloids.

(vi) The viscosity of water varies with temperature according to $d\ln\eta/dT \sim -0.02 \text{ K}^{-1}$, and thus may significantly contribute to the T dependence of the thermophoretic coefficient. Since the viscosity is an overall factor, it does not affect the sign of D_T .

Acknowledgement. Helpful and stimulating discussions with Werner Köhler are gratefully acknowledged.

-
- [1] T.M. Squires, S.R. Quake, *Rev. Mod. Phys.* **77**, 977 (2005)
- [2] J.L. Viovy, *Rev. Mod. Phys.* **72**, 813 (2000)
- [3] J. L. Anderson, *Ann. Rev. Fluid Mech.* **21**, 61 (1989)
- [4] J. L. Anderson, D.C. Prieve, *Langmuir* **7**, 403 (1991)
- [5] W. Köhler, S. Wiegand (eds.): *Thermal Nonequilibrium Phenomena in Fluid Mixtures*, Springer (2001)
- [6] R. Piazza, A. Guarino, *Phys. Rev. Lett.* **88**, 208302 (2002)
- [7] R. Piazza, A. Parola, *J. Phys. Cond. Matt.* **15**, 153102 (2008)
- [8] J. Rauch, W. Köhler, *Macromolecules* **38**, 3571 (2005)
- [9] R. Kita, P. Polyakov, S. Wiegand, *Macromolecules* **40**, 1638 (2007)
- [10] A. Leahy-Dios et al., *J. Chem. Phys.* **122**, 234502 (2005)
- [11] P.-A. Artola, B. Rousseau, *Phys. Rev. Lett.* **98**, 125901 (2007)
- [12] G. Galliero, S. Volz, *J. Chem. Phys.* **128**, 064505 (2008)
- [13] S. Iacopini, R. Piazza, *Europhys. Lett.* **63**, 247 (2003)
- [14] S.A. Putnam, D.G. Cahill, *Langmuir* **21**, 5317 (2005)
- [15] S.A. Putnam et al., *Langmuir* **23**, 9221 (2007)
- [16] S. Iacopini, R. Rusconi, R. Piazza, *EPJ E* **19**, 59 (2006)
- [17] M. Braibanti, D. Vigolo, R. Piazza, *Phys. Rev. Lett.* **100**, 108303 (2008)
- [18] S. Duhr, D. Braun, *PNAS* **103**, 19678 (2006)
- [19] H. Ning, J.K.G. Dhont, S. Wiegand, *Langmuir* **24**, 2426 (2008)
- [20] A. Würger, *Phys. Rev. Lett.* **101**, 138302 (2008)
- [21] S.R. de Groot, P. Mazur, *Non-equilibrium Thermodynamics*, North Holland Publishing, Amsterdam (1962)
- [22] P.C. Hiemenz, R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Dekker (1997)
- [23] D. Vigolo, G. Brambilla, R. Piazza, *Phys. Rev. E* **75**, 040401 (2007)
- [24] B.V. Derjaguin, N.V. Churaev, V.M. Muller, *Surface Forces*, Plenum Press, New York (1987)
- [25] E. Ruckenstein, *J. Colloid Interface Sci.* **83**, 77 (1981)
- [26] J.C. Giddings, P.M. Shinudu, S.N. Semenov, *J. Coll. Interf. Sci.* **176**, 454 (1995)
- [27] K.I. Morozov, *JETP* **88**, 944 (1999)
- [28] A. Parola, R. Piazza, *EPJ E* **15**, 255 (2004)
- [29] S. Fayolle, T. Bickel, A. Würger, *Phys. Rev. E* **77**, 041404 (2008)
- [30] A. Würger, *Phys. Rev. Lett.* **98**, 138301 (2007)
- [31] S.N. Rasuli, R. Golestanian, *Phys. Rev. Lett.* **101**, 138301 (2008)
- [32] E. Bringuier, A. Bourdon, *Phys. Rev. E* **67**, 011404 (2003)
- [33] S. Fayolle et al., *Phys. Rev. Lett.* **95**, 208301 (2005)
- [34] J.K.G. Dhont et al., *Langmuir* **23**, 1674 (2007)
- [35] J.K.G. Dhont, W.J. Briels, *Eur. J. Phys. E* **25**, 61 (2008)
- [36] E.D. Eastman, *J. Am. Chem. Soc.* **50**, 283 and 292 (1928)
- [37] G. Guthrie et al., *J. Chem. Phys.* **17**, 310 (1949)
- [38] E. Helfand, J.G. Kirkwood, *J. Chem. Phys.* **32**, 857 (1960)
- [39] J.N. Agar et al., *J. Phys. Chem.* **93**, 2082 (1989)
- [40] J.A. Stratton, *Electromagnetic Theory*, Mc Graw-Hill, New York (1941)
- [41] L. D. Landau, E. M. Lifshitz, *Electrodynamics of Continuous Media*, Elsevier (1983)
- [42] V.N. Sokolov et al., *J. Solution Chem.* **35**, 1621 (2006)
- [43] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Elsevier, 1987).
- [44] S. Kim, S.J. Karilla, *Microhydrodynamics: Principles and Selected Applications*, Butterworth-Heinemann Boston (1991)
- [45] L. Bocquet, E. Trizac, M. Aubouy, *J. Chem. Phys.* **117**, 8138 (2002)
- [46] L.G. Longworth, *J. Phys. Chem.* **61**, 1557 (1957)
- [47] P. N. Snowdon, J. C. R. Turner, *Trans. Faraday Soc.* **56**, 1409 (1960)
- [48] D.R. Caldwell, *J. Phys. Chem.* **77**, 2004 (1973)
- [49] D.R. Caldwell, S.A. Eide, *Deep Sea Res.* **28A**, 1605 (1981)

- [50] F.S. Gaeta et al., *J. Phys. Chem.* **26**, 2967 (1982)
- [51] H. Yow, J. Lin, *J. Solution Chem.* **12**, 487 (1983)
- [52] H. Brenner, *Phys. Rev. E* **74**, 036306 (2006)

- [53] *Handbook of Chemistry and Physics*, 55th edition, CRC Press (1974)