

Collective thermoelectrophoresis of charged colloids

Arghya Majee and Alois Würger

Laboratoire Ondes et Matière d'Aquitaine, Université Bordeaux I and Centre National de la Recherche Scientifique, 33405 Talence, France

(Received 25 June 2010; revised manuscript received 19 January 2011; published 10 June 2011)

Thermally driven colloidal transport is, to a large extent, due to the thermoelectric or Seebeck effect of the charged solution. We show that, contrary to the generally adopted single-particle picture, the transport coefficient depends on the colloidal concentration. For solutions that are dilute in the hydrodynamic sense, collective effects may significantly affect the thermophoretic mobility. Our results provide an explanation for recent experimental observations on polyelectrolytes and charged particles and suggest that for charged colloids collective behavior is the rule rather than the exception.

DOI: [10.1103/PhysRevE.83.061403](https://doi.org/10.1103/PhysRevE.83.061403)

PACS number(s): 83.80.Hj, 47.57.jd, 66.10.C-

I. INTRODUCTION

Transport in macromolecular or colloidal dispersions is mainly driven by interface forces [1–4]. Because of the rather short-ranged flow pattern induced in the surrounding fluid, these forces do not result in hydrodynamic interactions, in contrast to diffusion and sedimentation. As a consequence, nearby beads hardly experience each other and their transport velocity is independent of concentration [5]; for the same reason, free-solution electrophoresis of polyelectrolytes does not depend on the molecular weight [6,7]. Similar results have been obtained for thermal diffusion of high polymers [8–11].

Recent experiments on thermophoresis in charged colloids, however, dress a rather different picture and indicate that the single-particle description fails in several instances: Contrary to expectation, the transport velocity due to a temperature gradient,

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

was found to depend on the volume fraction of particle dispersions and on the chain length N of macromolecular solutions. (i) Data on sodium polystyrene sulfonate (NaPSS) [12] and single-stranded DNA [13] at constant polymer content but variable N reveal that the mobility D_T becomes smaller for larger molecules; e.g., in the range from 50 to 48 000 base pairs, the mobility of DNA decreases by a factor of 5. These findings are obtained at low concentration where the molecular mean distance is much larger than the gyration radius. (ii) Regarding particle suspensions, experiments on 70-nm silica beads [14] and 26-nm latex spheres [15] in a weak electrolyte show that at a volume fraction of 2%, D_T is significantly reduced with respect to the zero-dilution value.

In the present work we show that these experimental findings arise from an interaction mechanism that has been overlooked so far, i.e., the collective thermoelectric response of the composite system. By treating the salt ions and the dispersed colloid on an equal footing, we find that both the thermoelectric field and the mobility D_T vary with the colloidal concentration. Depending on the electrolyte strength and the valence of the macroions, collective effects may occur at low dilution, that is, for particle dispersion with a negligible pair potential and polymer solutions where neighboring chains do not overlap.

Thermally driven motion of charged colloids is very sensitive to the solvent composition. From previous work it

emerges that two rather different mechanisms contribute to the velocity [15,16],

$$\mathbf{u} = -\mu_T \nabla T + \mu \mathbf{E}. \quad (2)$$

The first term arises from the local particle-solvent interactions in a nonuniform temperature. As pointed out by Ruckenstein [17], the temperature gradient deforms the electric double layer and induces a pressure gradient opposite ∇T . The resulting thermo-osmotic surface flow toward higher T drives the particle to the cold side; the overall picture is similar to electro-osmotic effects in an electric field [18]. The coefficient $\mu_T \propto \varepsilon \zeta^2 / \eta T$ depends on the ζ potential, the solvent permittivity ε , and viscosity η ; different prefactors occur in the limits of small and large particles [17–25]. This form agrees rather well with the observed salinity dependence [26], yet fails in view of the strong variation with T reported for various systems [12,13], thus suggesting the existence of an additional, so far poorly understood contribution to μ_T .

The present work deals with the second term in Eq. (2), which accounts for the Seebeck effect of the charged solution or, in other words, for electrophoresis in the thermoelectric field \mathbf{E} with the mobility $\mu = \varepsilon \zeta / \eta$. Due to their temperature-dependent solvation forces, ions migrate along or opposite the thermal gradient. As a consequence, surface charges develop at the cold and warm boundaries of the vessel and give rise to a macroscopic electric field $\mathbf{E} = -\psi \nabla T / T$ (see Fig. 1). The thermopotential parameter ψ is related to the Seebeck coefficient $S = -\psi / T$; for electrolytes S attains values of several 100 $\mu\text{V/K}$, which is one to two orders of magnitude larger than in common metals [27].

II. THERMOPHORETIC MOBILITY

We consider a dispersion of negatively charged particles or macromolecules of valency $-Z$ and concentration n , in a monovalent electrolyte solution of ionic strength n_0 with a constant temperature gradient ∇T . According to the general formulation of nonlinear thermodynamics, the currents of colloid and salt ions are linear functions of generalized forces [28]; the latter can be expressed through thermal and concentration gradients. The current of colloidal macroions is given by

$$\mathbf{J} = -D \nabla n + n \mathbf{u}, \quad (3)$$

TABLE I. Reduced Soret coefficient α_{\pm} of several salt ions at room temperature. The values of the heat of transport Q_{\pm}^* are taken from Ref. [30]. The parameters α_{\pm} are calculated from $\alpha_{\pm} = Q_{\pm}^*/2k_B T$.

Ion	Q_i^* (kJ/Mol)	α_i
H ⁺	13.3	2.7
Li ⁺	0.53	0.1
K ⁺	2.59	0.5
Na ⁺	3.46	0.7
OH ⁻	17.2	3.4
Cl ⁻	0.53	0.1

where the first term on the right-hand side accounts for normal diffusion and the second term for transport with the drift velocity [Eq. (2)].

The densities of small ions account for the counterions released by the colloidal particles and the added salt. The mobile ion currents

$$\mathbf{J}_{\pm} = -D_{\pm} \left(\nabla n_{\pm} + 2n_{\pm} \alpha_{\pm} \frac{\nabla T}{T} \mp n_{\pm} \frac{e\mathbf{E}}{k_B T} \right) \quad (4)$$

comprise normal diffusion with coefficients D_{\pm} , thermal diffusion with the reduced Soret parameters α_{\pm} , and electrophoresis with the Hückel mobility for monovalent ions. In Eqs. (3) and (4) we have added an electric-field term; it is important to note that \mathbf{E} is not an external field but arises from the kinetics of the mobile charges and is proportional to the applied temperature gradient. A similar phenomenon occurs in a nonuniform electrolyte, where the electric field is proportional to the salinity gradient and to the difference of the ionic diffusion coefficients D_{\pm} [2,29].

The numbers α_{\pm} describe the drift of positive and negative salt ions in a temperature gradient. The values for the most common ions have been determined by Agar from thermopotential measurements of electrolyte solutions [30]; our notation and Agar's heat of transport Q_{\pm}^* are related through $\alpha_{\pm} = Q_{\pm}^*/2k_B T$. Typical values range from $\alpha \approx 0$ for Li⁺ to $\alpha \approx 3$ for OH⁻; those of the most common ions are given in Table I.

A. Steady state

Equations (3) and (4) provide the currents as functions of the generalized thermodynamic forces, that is, of the concentration and temperature gradients [28]. We are interested in the steady state characterized by

$$\mathbf{J}_{\pm} = 0 = \mathbf{J}. \quad (5)$$

For later use we give the resulting relation for the electric field. Inserting the drift velocity of Eq. (2) and superposing the three equalities of Eq. (5) such that the concentration gradients result in the gradient of the charge density, $\nabla \rho = e\nabla(n_+ - n_- - Zn)$, and collecting terms proportional to \mathbf{E} and ∇T , one has

$$\mathbf{E} = e \frac{2n_+ \alpha_+ - 2n_- \alpha_- - ZnT \mu_T / D}{\epsilon \kappa^2} \frac{\nabla T}{T} + \frac{\nabla \rho}{\epsilon \kappa^2}, \quad (6)$$

with the shorthand notation $\kappa^2 = e^2(n_+ + n_- + ZnT \mu_T / D) / \epsilon k_B T$.

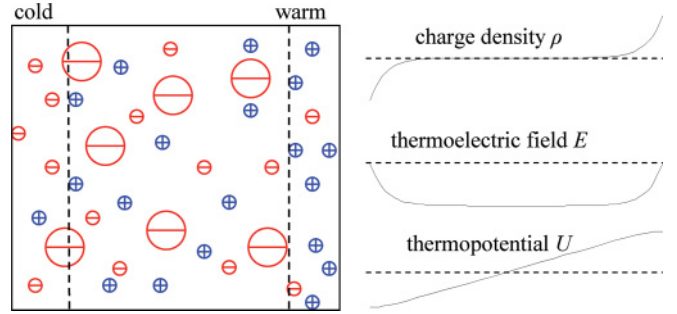


FIG. 1. (Color online) Thermoelectric effect in a colloidal suspension of charged particles in salt solution. In the example presented, the Soret parameters are such that negative and positive ions accumulate at the cold and warm boundaries, respectively. In the left panel, vertical dashed lines indicate the thickness of the surface layers of about one Debye length λ . This schematic view exaggerates the surface layers, which are much thinner in real systems. The right panel shows the spatial variation of the net charge density ρ , the thermoelectric field \mathbf{E} , and the thermopotential U ; dashed lines indicate the zero of the ordinate. Note the nonzero surface charges at the cold and hot boundaries. The present paper discusses the bulk behavior only, where $\rho = 0$ and \mathbf{E} is constant.

In order to determine the four unknowns ∇n_{\pm} , ∇n , and \mathbf{E} , the three equations (5) need to be completed by a fourth condition. It is provided by Gauss's law

$$\text{div} \mathbf{E} = \rho / \epsilon, \quad (7)$$

which relates \mathbf{E} and the charge density $\rho = e(n_+ - n_- - Zn)$ and thus closes the above set of equations.

B. Small-gradient approximation

Equations (5) and (7) are nonlinear in the concentrations and thus cannot be solved as they stand. The salt and colloid concentrations vary very little through the sample; the relative changes $\delta n/n$ and $\delta n_{\pm}/n_{\pm}$ between the hot and cold boundaries are proportional to the reduced temperature difference $\delta T/T$. Since in experiment the ratio $\delta T/T$ is much smaller than unity, we may safely replace the concentrations n and n_{\pm} in the coefficients of Eq. (6) with constants \bar{n} and \bar{n}_{\pm} ; the latter are defined as the colloidal and salt concentrations at $\nabla T = 0$.

Formally, this small-gradient approximation corresponds to neglecting terms that are quadratic in small quantities ∇n_{\pm} , ∇n , \mathbf{E} , and ∇T . This approximation has been used, more or less explicitly, in previous works on the thermoelectric effect [30,31] and in recent applications in colloidal thermophoresis [15,16,32]. Moreover, various works on the osmotic flow driven by externally imposed gradients of charged solutes resort to the same approximation, albeit with the salinity change ∇n_0 instead of the temperature gradient [2,29,33].

C. Bulk thermoelectric field

The relations in Eqs. (5)–(7) describe both the bulk properties of a macroscopic sample and boundary effects such as the surface charges that develop at the hot and cold boundaries (see Fig. 1). The thickness of the surface layer is given by the Debye length and thus in the range 1–100 nm. This

is much smaller than the sample size. Thus we discard surface effects and discuss the bulk behavior only; a full evaluation including surface effects is given in the Appendix.

In a macroscopic sample the net charge density vanishes because of the huge electrostatic energy. With

$$\rho_{\text{bulk}} = 0,$$

Gauss's law [Eq. (7)] imposes a constant electric field whose explicit expression is readily obtained from Eq. (6),

$$\mathbf{E} = -\psi \frac{\nabla T}{T}, \quad (8)$$

with the shorthand notation for the coefficient of $\nabla T/T$,

$$\psi = -e \frac{2\bar{n}_+ \alpha_+ - 2\bar{n}_- \alpha_- - Z\bar{n} T \mu_T / D}{\varepsilon \bar{\kappa}^2},$$

and $\bar{\kappa}^2 = e^2(\bar{n}_+ + \bar{n}_- + Z\bar{n} T \mu_T / D) / \varepsilon k_B T$. Note that we have used the small-gradient approximation and replaced the colloidal and ion concentrations with their mean values. Although it is not always mentioned explicitly, the argument of zero bulk charge density has been used in previous works on the Seebeck effect of electrolytes [15,16,30–32] and, more generally, for colloidal transport in nonequilibrium situations involving thermal or chemical gradients [2,29,33].

D. Zero-dilution limit

We briefly discuss the case of a very dilute suspension where the colloidal charges are negligible for the electrostatic properties. Putting $n \rightarrow 0$ in the electric field [Eq. (8)], we have $\psi_0 = -(\alpha_+ - \alpha_-) k_B T / e$ and

$$\mathbf{E}_0 = (\alpha_+ - \alpha_-) \frac{k_B \nabla T}{e}.$$

This expression has been used previously in [15,16,31,32]. Note that the parameter κ^{-1} reduces to the usual expression of the Debye screening length.

By inserting the thermoelectric field \mathbf{E} in the drift velocity [Eq. (2)] and comparing with Eq. (2) we obtain the definition of the thermophoretic mobility

$$D_T^0 = \mu_T + \frac{\varepsilon \zeta \psi_0}{\eta T}. \quad (9)$$

Not surprisingly, it is independent of the colloidal concentration. The parameter ψ_0 and the macroscopic thermopotential $U = \psi_0 \delta T / T$ between the hot and cold vessel boundaries are given by the steady state of the electrolyte solution. Using the values of Table I, one finds the values $\psi_0 = -15$ and 70 mV for NaCl and NaOH solutions, respectively. Thus one expects D_T^0 to change its sign upon replacing one salt with another [16]. This is confirmed by a very recent study on sodium dodecylsulfate (SDS) micelles, where the electrolyte composition $\text{NaCl}_{1-x}\text{OH}_x$ was varied at constant ionic strength [32]; increasing the relative hydroxide content x from 0 to 1 resulted in a linear variation of the Soret coefficient S_T and a change of sign at $x \approx \frac{1}{2}$ [32].

E. Collective effects on the electric field \mathbf{E}

Now we derive the main result of this paper, that is, the dependence of \mathbf{E} and D_T on the colloidal concentration and,

in the case of polyelectrolytes, on its molecular weight. As two important parameters we define the ratio of the colloidal charge density to the salinity,

$$\phi = \frac{Z\bar{n}}{n_0}, \quad (10)$$

and the ratio of the colloidal electrophoretic mobility μ to the diffusion coefficient D ,

$$\xi = \frac{k_B T |\mu|}{e D}. \quad (11)$$

In the following we assume a negative surface potential. For typical colloidal suspensions, the charge ratio is smaller than unity, $\phi \sim 0.1$, whereas the parameter ξ may exceed 10^2 .

Rewriting the coefficient ψ in Eq. (8) in terms of the dimensionless quantities ϕ and ξ , we have

$$\psi = -\frac{2(1+\phi)\alpha_+ - 2\alpha_- - \phi T \mu_T / D}{2 + \phi + \phi \xi} \frac{k_B T}{e}. \quad (12)$$

Equation (12) shows how the thermoelectric field arises from the competition of the Soret motion of the mobile ions and the colloidal solute. In the low-dilution limit $\phi \rightarrow 0$ the first term in the numerator reduces to $(\alpha_+ - \alpha_-)$, which corresponds to the response of the electrolyte solution discussed in previous work [15,16,32].

The ϕ -dependent term in the numerator becomes relevant where $\phi \sim D/T\mu_T$ and, in particular, may change the sign of ψ and thus of the thermoelectric field. With the typical value of $T\mu_T \sim 10^{-9}$ m/s² one has $D/T\mu_T = 10^{-3}$ for micron-size particles (and polyelectrolytes of a gyration radius of $1 \mu\text{m}$) and $D/T\mu_T = 10^{-1}$ for 10-nm beads. This means that, at typical colloidal densities, the thermoelectric field is essentially determined by the macroions. The denominator in Eq. (12) results in an overall decrease when augmenting the colloidal concentration.

F. Collective effects on the mobility D_T

Now we determine the steady-state thermophoretic mobility. Plugging the value of the electric field \mathbf{E} given in Eq. (8) into the drift velocity of Eq. (2) and comparing with Eq. (1), we get

$$D_T = \frac{D_T^0}{1 + \frac{\phi}{2+\phi} \xi}, \quad (13)$$

where D_T^0 is defined by Eq. (9) albeit with a modified parameter

$$\psi_0 = -\frac{(1+\phi)\alpha_+ - \alpha_-}{1 + \phi/2} \frac{k_B T}{e}. \quad (14)$$

The mobility and its dependence on the ratio ϕ constitute the main result of this paper. According to Eq. (9), the sign of D_T is determined by the competition of the bare mobility μ_T and the Seebeck term proportional to $\zeta \psi_0$. Since $\phi < 1$ in most cases, the numerator of Eq. (13) is rather similar to the dilute case discussed above [Eq. (9)].

A much more striking variation arises from the denominator of Eq. (13). For typical values of the charge ratio $\phi \sim 0.1$, collective effects set in where $\frac{1}{2}\phi\xi \sim 1$, in other words, where ξ is of the order of 20. For high polymers ($N = 10^3, \dots, 10^6$) and colloidal particles in the range from 10 nm to $1 \mu\text{m}$,

the parameter ξ takes values between 10 and 10^3 . This simple estimate suggests that collective effects occur in many systems. A detailed comparison with experiment is given in the following section.

In the limit of zero dilution $\phi \rightarrow 0$ one readily recovers the expression of Eq. (9). The opposite case of a salt-free system leads to

$$D_T = \frac{D_T^0}{1 + \xi} \quad (\phi \rightarrow \infty),$$

with ψ_0 determined by the counterions only. In view of the large values of ξ mentioned above, one expects a strong reduction of the mobility in the salt-free case.

III. COMPARISON WITH EXPERIMENT

We discuss Eq. (13) in view of recent experiments on colloidal suspensions. At relevant values of the charge ratio ($\phi \sim 0.1$) the numerator hardly differs from that of the dilute case. Thus in the following we focus on the reduction of D_T due to the denominator.

A. Polyelectrolytes

We start with experimental findings on polyelectrolytes at constant volume fraction but variable molecular weight. In their study of 2 g/l of NaPSS in a 100-mM/l NaCl solution, Iacopini *et al.* found a significant variation with the chain length [12]: Figure 2(a) shows the data measured at 30 °C for molecules of 74, 160, and 360 repeat units, with an overall decrease of the mobility by 40%. The same factor has been found in the temperature range from 15 °C to 35 °C.

The solid line represents collective effects arising from the denominator of Eq. (13). It has been calculated with the double-layer term in the small-bead limit, assuming the monomer to be small as compared to the Debye length ($R < \lambda$) [22–24],

$$\mu_T = -\frac{d\varepsilon}{dT} \frac{\zeta^2}{3\eta},$$

and with the Hückel-limit electrophoretic mobility $\mu = \frac{2}{3}\varepsilon\zeta/\eta$. Inserting the diffusion coefficient $D = k_B T / 6\pi\eta R$ and the Bjerrum length $\ell_B = e^2 / 4\pi\varepsilon k_B T$ in Eq. (11), we have

$$\xi = \frac{e|\zeta|}{k_B T} \frac{R}{\ell_B}. \quad (15)$$

The theoretical curve of Fig. 2(a) is calculated with the parameters $\zeta = -27$ mV, $nN = 10$ mM/l, and $\phi = 0.1$. Its variation arises only from the gyration radius $R = \ell N_K^{1-\nu} N^\nu$; we have used the usual exponent $\nu = \frac{3}{5}$, the size of a monomer $\ell = 0.4$ nm, and the number of monomers per segment $N_K = 10$. The dashed line indicates the mobility in the short-chain limit. The theoretical expression in Eq. (13) provides a good description of the reduction of D_T with increasing chain length.

As a second example, DNA in 1-mM/l Tris [tris(hydroxymethyl)aminomethane] buffer shows similar behavior; its mobility decreases by a factor of 5 over the range from $N = 50$ to 48 500 base pairs per molecule [13]. The overall DNA content was kept constant, $Nn = 50$ μ M/l, with

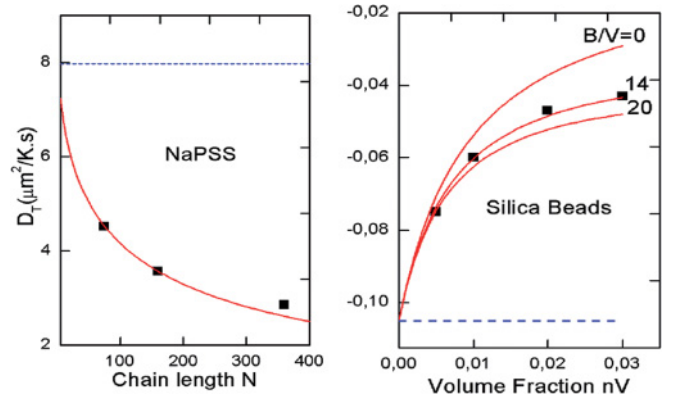


FIG. 2. (Color online) Comparison with measured data. (a) Variation of D_T with the chain length N of a polyelectrolyte at fixed volume fraction. The data on 2 g/l of Na PSS in a 100-mM/l NaCl solution at 30 °C are taken from Iacopini *et al.* [12]. The solid line is calculated from Eq. (13) with the parameters as given in the main text. The dependence on N arises from the gyration radius R . (b) Volume fraction dependence of D_T on a dispersion of 70-nm silica beads in a solution of 30 μ M/l of sulpho-rhodamine B. The data are from Ghofraniha *et al.* [14]; the fit curves are obtained from Eqs. (13) and (16), with different values of the reduced virial coefficient B/V , where $V = \frac{4}{3}\pi R^3$ is the particle volume.

a charge ratio $\phi = 0.05$. Equations (13) and (15) provide a good fit to these data, albeit with a somewhat too small exponent $\nu \approx 0.4$. In view of this discrepancy one should keep in mind the rather complex electrostatic properties of polyelectrolytes.

The reduction observed for both Na PSS and DNA cannot be explained by hydrodynamic effects. Interchain interactions are of little significance because of the low dilution. Indeed, the effective volume fraction of the polymer coils hardly attains a few percent, $nR^3 \sim 10^{-2}$; thus nearby chains do not overlap and leave both the viscosity and the diffusion coefficient unchanged. Regarding hydrodynamic interactions of beads of the same molecule, it is known that they enhance the electrophoretic mobility in Eqs. (2) and (9) with increasing chain length. Yet this effect occurs for short polyelectrolytes and saturates for chains longer than the size of the screening cloud [34]; for the examples studied here, it would enhance D_T in the range $N < 40$. We conclude that hydrodynamic effects may be ruled out as an explanation for the reduction shown in Fig. 2(a). Finally, we discuss electrostatic single-particle effects. The electrophoretic mobility in salt-free solution has been found to decrease slightly at higher concentration because of the increase of the overall ionic strength and the shorter screening length [35,36]. In the present case, however, the weight fraction of the polyelectrolyte is constant and so is the overall charge density. Thus the electrostatic properties of the solution are the same for different chain lengths.

B. Colloidal particles

Now we discuss the concentration-dependent mobility D_T that has been reported for dispersions of solid particles in weak electrolytes. Ghofraniha *et al.* studied silica particles ($R = 35$ nm) in a 30- μ M/l solution of the negatively charged dye sulpho-rhodamine B [14]. The data shown in Fig. 2(b)

reveal a significant decrease with the colloidal volume fraction; at 3% D_T is reduced to less than half of the zero-dilution value. The negative sign of the measured D_T indicates that the thermoelectric contribution $\varepsilon\psi_0\zeta/\eta T$ to Eq. (9) overtakes the Ruckenstein term [16]

$$\mu_T = \frac{\varepsilon\zeta^2}{3\eta T}.$$

The negative surface potential ζ implies that the thermopotential parameter of the sulpho-rhodamine solution is positive, $\psi_0 > 0$.

The curves in Fig. 2(b) are calculated from Eqs. (11) and (13) with $\psi_0 = 10$ mV, which is comparable to common salts and weaker than the values of NaOH and tetraethylammonium [15,32]. The rather small D_T suggests that the particles are weakly charged; we use $Z = 30$ and $\zeta = -10$ mV. The dashed line gives the mobility D_T^0 in the zero-dilution limit and the solid lines are given by Eq. (13).

In addition to the explicit concentration dependence in terms of the parameter ϕ , one has to take into account that, even at moderate colloidal volume fraction, the Einstein coefficient D is not constant. Indeed, cooperative diffusion of charged particles arises from the electrostatic pair potential $\Phi(\mathbf{r})$ and, to a lesser extent, from hydrodynamic interactions [37]. To linear order in the concentration, the virial expansion for the Einstein coefficient reads

$$D = D_0(1 + 2nB), \quad (16)$$

with the parameter

$$B = \frac{1}{2} \int dV (1 - e^{-\Phi/k_B T}).$$

For hard spheres the virial coefficient is given by the particle volume, $B = 4V$ with $V = \frac{4}{3}\pi R^3$. The electrostatic pair potential results in an effective interaction volume $V = \frac{4}{3}\pi(R + \frac{\chi}{2}\lambda)^3$, where λ is the Debye length and χ a numerical factor [26,32,38]; for small and highly charged particles in a weak electrolyte, the repulsive forces may enhance the virial coefficient by one or two orders of magnitude. In contrast, hydrodynamic interactions contribute a negative term $B/V \sim -6.5$ and reduce the Einstein coefficient accordingly [37]. Our discussion of the data of Ref. [14] is restricted to volume fractions up to 3%; at higher concentration the measured D saturates and the linear approximation ceases to be valid. In units of the particle volume V , the measured virial coefficient reads $B/V = 20$ [14]; the best fit of the mobility data is obtained with $B/V = 14$. This value is much larger than that of hard spheres and thus indicates the importance of electrostatic repulsion. The concentration of mobile charge carriers $n_0 = 30 \mu\text{M/l}$ leads to a screening length of about 50 nm. With $\chi \sim 2$ in the above expression for the effective volume, one finds a virial coefficient close to the measured value. As an illustration of the effect of collective diffusion on D_T , we plot Eq. (13) for these three values: Though the variation of D_T with B is not negligible, it is significantly weaker than that of the thermoelectric effect.

As a second experiment we mention data by Putnam and Cahill on latex beads of radius $R = 13$ nm in an electrolyte solution of 2-mM/l ionic strength [15]; by varying the volume fractions from 0.7 to 2.2 wt. %, these authors observed a

reduction of D_T by about 10%. With a valency of $Z \sim 50$ one finds that, at the highest particle concentration $n = 4 \mu\text{M/l}$, the charge ratio ϕ does not exceed 10%.

Finally, we address the concentration dependence observed by Piazza and Guarino for the Soret coefficient $S_T = D_T/D$ of SDS micelles [26]. Its decrease with the SDS content is well described by collective diffusion according to Eq. (16). In a very recent measurement, Vigolo *et al.* varied the electrolyte composition $\text{NaCl}_{1-x}\text{OH}_x$ and thus the thermal diffusion parameter of the anion in Eq. (14), $\alpha_- = (1-x)\alpha_{\text{Cl}} + x\alpha_{\text{OH}}$ [32]. The observed linear dependence of S_T on x confirms the crucial role of the thermopotential. Unfortunately, there are no mobility data for micelles; thus at present it is not possible to determine whether their D_T is subject to collective effects similar to those of polyelectrolytes and solid beads.

IV. CONCLUSION

In summary, charged colloids in a nonuniform temperature show collective transport behavior mediated by the Seebeck effect of both colloidal and salt ions. For large particles and macromolecules, cooperative effects set in at rather low concentration, where hydrodynamic interactions are absent and where the charge ratio ϕ is much smaller than unity. The criterion for the onset of collective behavior, $\phi\xi \sim 1$ in Eq. (13), involves the ratio of the electrophoretic mobility and the Einstein coefficient; by contrast, the criterion for cooperative diffusion, $Bn \sim 1$, depends on the pair potential of the solute particles. The examples discussed suggest that the collective thermoelectric effect is generic for colloids at ordinary concentrations. This issue could be relevant for microfluidic applications of thermophoresis.

We conclude with a remark on the thermoelectric field given in Eq. (12). Both its magnitude and its sign can be tuned by choosing the appropriate electrolyte and adjusting the charge ratio. With a thermal gradient of less than 1 K/ μm , \mathbf{E} may attain values of 100 V/m. Thus the thermoelectric effect could be used for applying electric fields in microfluidic devices. Local laser heating would permit the realization of almost any desired spatiotemporal electric-field pattern.

ACKNOWLEDGMENTS

Helpful and stimulating discussions with D.G. Cahill, R. Piazza, D. Braun, and N. Ghofraniha are gratefully acknowledged.

I. APPENDIX

The thermoelectric field in Eq. (8) has been derived by using the charge neutrality of the bulk of a macroscopic sample. Here we give a derivation based on the steady state, Gauss's law, and the electrostatic boundary conditions. Resorting to the small-gradient approximation, we replace the coefficients in Eq. (6) with their mean values and thus have

$$\mathbf{E} = -\psi \frac{\nabla T}{T} + \frac{\nabla \rho}{\varepsilon \bar{\kappa}^2}.$$

From Gauss's law in Eq. (7) we have $\nabla\rho/\varepsilon = \nabla^2\mathbf{E}$ and thus obtain a differential equation for the thermoelectric field \mathbf{E} with a constant inhomogeneity $-(\psi/T)\nabla T$,

$$\mathbf{E} - \frac{\nabla^2\mathbf{E}}{\bar{\kappa}^2} = -\psi\frac{\nabla T}{T}.$$

The solution $\mathbf{E} = \mathbf{E}_{\text{inh}} + \mathbf{E}_h$ consists of two contributions. The inhomogeneous term $\mathbf{E}_{\text{inh}} = -(\psi/T)\nabla T$ accounts for the macroscopic Seebeck effect. The remaining term \mathbf{E}_h is related to surface charges at the cold and hot boundaries of the sample. The homogeneous equation $\nabla^2\mathbf{E}_h = \bar{\kappa}^2\mathbf{E}_h$ is solved by the exponential function,

$$\mathbf{E}_h = \mathbf{A}_+e^{\bar{\kappa}z} + \mathbf{A}_-e^{-\bar{\kappa}z},$$

where z is the coordinate in the direction of the temperature gradient. Its range is $-\frac{1}{2}L \leq z \leq \frac{1}{2}L$ with the sample size L .

The electrostatic boundary conditions require that the electric field vanishes at $z = \pm\frac{1}{2}L$. Setting $\mathbf{E} = 0$ and

solving for the coefficients of \mathbf{E}_h , one readily finds $\mathbf{A}_{\pm} = -\frac{1}{2}\mathbf{E}_{\text{inh}}/\cosh(\bar{\kappa}L/2)$ and the thermoelectric field

$$\mathbf{E} = -\frac{\psi}{T}\nabla T \left(1 - \frac{\cosh(\bar{\kappa}z)}{\cosh(\bar{\kappa}L/2)} \right).$$

Both \mathbf{E} and the corresponding charge density ρ are illustrated in the right panel of Fig. 1. The field vanishes at the boundaries and reaches its constant bulk value [Eq. (8)] within a few screening lengths $\bar{\kappa}^{-1}$. The parameter $\bar{\kappa}^{-1}$ takes values in the range between 1 and 100 nm and thus is much smaller than the size of sample L . Even in microfluid devices, $\bar{\kappa}L$ is, in general, larger than 10^3 .

In real systems a more complex picture may emerge from the surface roughness of the boundaries, the solute size, and surface charges of other origin. Note that such additional effects do not affect the bulk electric field [Eq. (8)] and thus are irrelevant for the results of this paper.

-
- [1] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Plenum, New York, 1987).
- [2] J. L. Anderson, *Annu. Rev. Fluid Mech.* **21**, 61 (1989).
- [3] T. M. Squires and S. R. Quake, *Rev. Mod. Phys.* **77**, 977 (2005).
- [4] L. Bocquet and E. Charlaix, *Chem. Soc. Rev.* **39**, 1073 (2010).
- [5] L. D. Reed and F. A. Morrison Jr., *J. Colloid Interface Sci.* **54**, 117 (1976).
- [6] *Capillary Electrophoresis*, edited by P. D. Grossman and J. C. Colburn (Academic, New York, 1992).
- [7] J. L. Viovy, *Rev. Mod. Phys.* **72**, 813 (2000).
- [8] J. C. Giddings *et al.*, *Macromolecules* **9**, 106 (1976).
- [9] F. Brochard, P.-G. de Gennes, and C. R. Acad. Sci. Paris Ser. II **293**, 1025 (1981).
- [10] S. Wiegand, *J. Phys. Condens. Matter* **16**, 357 (2004).
- [11] A. Würger, *Phys. Rev. Lett.* **98**, 138301 (2007).
- [12] S. Iacopini *et al.*, *Eur. Phys. J. E* **19**, 59 (2006).
- [13] S. Duhr and D. Braun, *Proc. Natl. Acad. Sci. USA* **103**, 19678 (2006).
- [14] N. Ghofraniha, G. Ruocco, and C. Conti, *Langmuir* **25**, 12495 (2009).
- [15] S. A. Putnam and D. G. Cahill, *Langmuir* **21**, 5317 (2005).
- [16] A. Würger, *Phys. Rev. Lett.* **101**, 108302 (2008).
- [17] E. Ruckenstein, *J. Colloid Interface Sci.* **83**, 77 (1981).
- [18] A. Würger, *Rep. Prog. Phys.* **73**, 126601 (2010).
- [19] K. I. Morozov, *JETP* **88**, 944 (1999).
- [20] E. Bringuier and A. Bourdon, *Phys. Rev. E* **67**, 011404 (2003).
- [21] S. Duhr and D. Braun, *Phys. Rev. Lett.* **96**, 168301 (2006).
- [22] J. K. G. Dhont *et al.*, *Langmuir* **23**, 1674 (2007).
- [23] J. K. G. Dhont and W. J. Briels, *Eur. Phys. J. E* **25**, 61 (2008).
- [24] J. Morthomas and A. Würger, *Eur. Phys. J. E* **27**, 425 (2008).
- [25] S. N. Rasuli and R. Golestanian, *Phys. Rev. Lett.* **101**, 108301 (2008).
- [26] R. Piazza and A. Guarino, *Phys. Rev. Lett.* **88**, 208302 (2002).
- [27] D. M. Rowe, *Thermoelectrics Handbook—Macro to Nano* (CRC, Boca Raton, 2006).
- [28] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
- [29] D. C. Prieve, *J. Chem. Soc. Faraday Trans. 2* **83**, 1287 (1987).
- [30] J. N. Agar *et al.*, *J. Phys. Chem.* **93**, 2082 (1989).
- [31] G. Guthrie *et al.*, *J. Chem. Phys.* **17**, 310 (1949).
- [32] D. Vigolo, S. Buzzaccaro, and R. Piazza, *Langmuir* **26**, 7792 (2010).
- [33] B. Abécassis, C. Cottin-Bizonne, C. Ybert, A. Ajdari, and L. Bocquet, *Nature Mater.* **7**, 785 (2008).
- [34] M. Muthukumar, *Electrophoresis* **17**, 1167 (1996).
- [35] V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, and C. Holm, *Phys. Rev. Lett.* **98**, 176105 (2007).
- [36] M. Medrano, A. T. Pérez, L. Lobry, and F. Peters, *Langmuir* **25**, 12043 (2009).
- [37] W. Russel, D. Saville, and W. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).
- [38] S. Fayolle, T. Bickel, S. Le Boiteux, and A. Würger, *Phys. Rev. Lett.* **95**, 208301 (2005).