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Collective thermo-electrophoresis of charged colloids

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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.

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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 see 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,

$$u = -D_T \nabla T, \tag{1}$$

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 48000 base pairs, that 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-nanometer 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 valency of the macroions, collective effects may occur at low dilution, that is, for particle dispersion with negligible pair potential and polymer solutions where neighbor 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],

$$u = -\mu_T \nabla T + \mu E. \tag{2}$$

The first term arises from the local particle-solvent interactions in a non-uniform temperature. As first pointed out by Ruckenstein [17], the temperature gradient deforms the electric double layer and induces a pressure gradient opposite to ∇T. The resulting thermoosmotic surface flow toward higher T drives the particle to the cold side; the overall picture is similar to electroosmotic effects in an electric field [18]. The coefficient $\mu_T \propto \varepsilon\zeta^2/\eta T$ depends on the ζ-potential, and 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 (2), which accounts for the Seebeck effect of the charged solution or, in other words, for electrophoresis in the thermoelectric field E with the mobility $\mu = \varepsilon\zeta/\eta$. Due to their temperature dependent solvation forces, ions migrate along or opposite to 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 $E = -\psi\nabla T/T$; see Fig. 1. The thermopotential parameter ψ is related to the Seebeck coefficient $S = -\psi/T$; for electrolytes S attains values of several 100μV/K, which is by 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 non-linear 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

$$J = -D\nabla n + nu, \tag{3}$$

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

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

$$J_\pm = -D_\pm \left(\nabla n_\pm + 2n_\pm \alpha_\pm \frac{\nabla T}{T} \mp n_\pm \frac{eE}{k_B T} \right) \tag{4}$$

comprise normal diffusion with coefficients $D_\pm$, thermal diffusion with the reduced Soret parameters $\alpha_\pm$, and electrophoresis with the Hückel mobility for monovalent ions. In (3) and (4) we have added an electric field term; it is important to note that 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 non-uniform 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 $\alpha_\pm$ 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 [31]; 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.

TABLE I: Reduced Soret coefficient $\alpha_\pm$ of several salt ions at room temperature. The values of the heat of transport $Q^*_\pm$ are taken from Ref. [31]. The parameters $\alpha_\pm$ are calculated from $\alpha_\pm = Q^*_\pm / 2k_B T$.

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

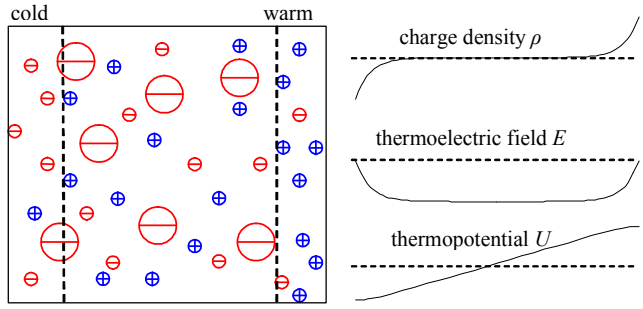

FIG. 1: Thermoelectric effect in a colloidal suspension of charged particles in salt solution. In the example presented, the Soret parameters are such that negative and positive ions accumulate at the cold and warm boundaries, respectively. In the left panel, vertical dashed lines indicate the thickness 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 E, and the thermopotential U; dashed lines indicate the zero of the ordinate. Note the non-zero surface charges at the cold and hot boundaries. The present paper discusses the bulk behavior only, where $\rho = 0$ and where E is constant.

A. The steady state

Eqs. (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

$$J_\pm = 0 = J. \tag{5}$$

For later use we give of a resulting relation for the electric field. Inserting the drift velocity (2) and superposing the three equations (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 E and ∇T, one has

$$E = e\frac{2n_+\alpha_+ - 2n_-\alpha_- - ZnT\mu_T/D}{\varepsilon\kappa^2}\frac{\nabla T}{T} + \frac{\nabla\rho}{\varepsilon\kappa^2}, \tag{6}$$

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

In order to determine the four unknowns $\nabla n_\pm$, ∇n, E, the three equations (5) need to be completed by a fourth condition; it is provided by Gauss law

$$\mathrm{div} E = \rho/\varepsilon \tag{7}$$

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

B. Small-gradient approximation

The above Eqs. (5) and (7) are non-linear 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 (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 approximations corresponds to neglecting terms that are quadratic in the small quantities $\nabla n_\pm$, ∇n, 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 resorts to the same approximation, albeit with the salinity change ∇n_0 instead of the temperature gradient [2, 29, 33].

C. Bulk thermoelectric field

The above relations (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 between one and hundred nanometers. 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

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

Gauss' law imposes (7) imposes a constant electric field; its explicit expression is readily obtained from (6)

$$E = -\psi \frac{\nabla T}{T}, \tag{8}$$

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 non-equilibrium 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 $n \to 0$ in the electric field (8) we have $\psi_0 = -(\alpha_+ - \alpha_-)\, k_B T/e$ and

$$E_0 = (\alpha_+ - \alpha_-)\,\frac{k_B \nabla T}{e}.$$

This expression has been used previously in [15, 16, 30, 32]. Note that the parameter κ^{-1} reduces to the usual exprerssion of the Debye screening length.

Inserting the thermoelectric field E in the drift velocity (2) and comparing with (2) defines the thermophoretic mobility

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

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. With the numbers of Table I, one finds the values $\psi_0 = -15$ mV and $+70$ mV for NaCl and NaOH solutions, respectively. Thus one expects D_T^0 to change its sign upon replacing one salt by the other [16]. This is confirmed by a very recent study on sodium dodecylsulfate (SDS) micelles, where the electrolyte composition $NaCl_{1-x}OH_x$ 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 E

Now we derive the main result of this paper, that is, the dependence of 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 and the salinity,

$$\phi = \frac{Z\bar{n}}{n_0}, \tag{10}$$

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

$$\xi = \frac{k_B T}{e}\frac{|\mu|}{D}. \tag{11}$$

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 (8) in terms of the dimensionless quantities ϕ and ξ, we have

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

Eq. (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 $\phi \to 0$ 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 typical values $T\mu_T \sim 10^{-9}$ m/s^2 one has $D/T\mu_T = 10^{-3}$ for micron-size particles (and polyelectrolytes of a gyration radius.of 1 μm), and $D/T\mu_T = 10^{-1}$ for 10-nanometer beads. This means that, at typical colloidal densities, the thermoelectric field is essentially determined by the macroions. The denominator in (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 E given in (8) into the drift velocity (2) and comparing with (1), we get

$$D_T = \frac{D_T^0}{1 + \frac{\phi}{2+\phi}\xi}. \tag{13}$$

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

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

The mobility and its dependence on the ratio ϕ constitute the main result of this paper. According to (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 (13) is rather similar to the dilute case discussed above (9).

A much more striking variation arises from the denominator of (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 ($N = 10^3 ... 10^6$) and colloidal particles in the range from ten nanometers to a micron, the parameter ξ takes values between 10 and 10^3. This simple estimate suggests collective effects to occur in many systems. A detailed comparison with experiment is given in the following section.

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

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

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]: Fig. 2a 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 percent. The same factor has been found in the temperature range from 15 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 (11), we have

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

The theoretical curve of Fig. 2a 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 (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 buffer shows a similar behavior; its mobility decreases by a factor of 5 over the range from N =50 to 48500 base pairs per molecule [13]. The overall DNA content was kept constant, $Nn = 50\mu$M/l, with a charge ratio $\phi = 0.05$. Eqs. (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 NaPSS 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

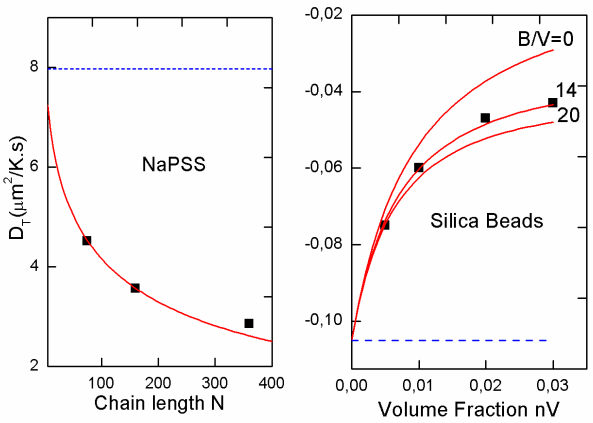

FIG. 2: Comparison with measured data. (a) Variation of D_T with the chain length N of a polyelectrolyte at fixed volume fraction. The data on 2 g/l NaPSS in a 100 mM/l NaCl solution at 30° C are taken from Iacopini et al. [12]. The solid line is calculated from Eq. (13) with the parameters as given in the main text. The dependence on N arises from the gyration radius R. (b) Volume fraction dependence of D_T of a dispersion of 70-nm silica beads in a solution of 30μM/l sulpho-rhodamine B. The data are from Ghofraniha et al. [14]; the fit curves are obtained from (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.

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 (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 [35]; for the examples studied here, it would enhance D_T in the range $N < 40$. We conclude that hydrodynamic effects may ruled out as an explanation for the reduction shown in Fig. 2a. Finally we discuss electrostatic single-particle effects. The electrophoretic mobility in saltfree solution has been found to decrease slightly at higher concentration, because of the increase of the overall ionic strength and the shorter screening length [36, 37]. 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 μM/l solution of the negatively charged dye sulpho-rhodamine B [14]. The data shown in Fig. 2b 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 (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. 2b are calculated from (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, whereas the solid lines are given by (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 [38]. To linear order in the concentration, the virial expansion for the Einstein coefficient reads as

$$D = D_0(1 + 2nB), \tag{16}$$

with the parameter

$$B = \frac{1}{2}\int dV \left(1 - e^{-\Phi/k_BT}\right).$$

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, 34]; 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. On the other hand, hydrodynamic interactions contribute a negative term $B/V \sim -6.5$ and reduce the Einstein coeffient accordingly [38]. 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 $n_0 = 30\mu$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 neglegible, 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 2mM/l ionic strength [15]; varying the volume fractions from 0.7 to 2.2 wt%, these authors observed a reduction of D_T by about 10 percent. With a valency of $Z \sim 50$ one finds that, at the highest particle concentration $n = 4\mu$M/l, the charge ratio ϕ does not exceed 10 percent.

Finally we address the concentration dependence observed by Guarino and Piazza 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 (16). In a very recent measurement, Vigolo et al. vary the electrolyte composition $\mathrm{NaCl}_{1-x}\mathrm{OH}_x$ and thus the thermal diffusion parameter of the anion in (14), $\alpha_- = (1-x)\alpha_{\mathrm{Cl}} + x\alpha_{\mathrm{OH}}$ [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. SUMMARY AND CONCLUSION

In summary, charged colloids in a non-uniform 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 (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 discussed examples 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 chosing the appropriate electrolyte and adjusting the charge ratio. With a thermal gradient of less than one Kelvin per micron, 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 to realize almost any desired spatiotemporal electric-field pattern.

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

V. APPENDIX

The thermoelectric field (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' law, and the electrostatic boundary conditions. Resorting to the small-gradient approximation, we replace the coefficients in (6) by their mean values and thus have

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

From Gauss's law (7) one has $\nabla\rho/\varepsilon = \nabla^2 E$ and thus obtains a differential equations for the thermoelectric field E with a constant inhomogeneity $-(\psi/T)\nabla T$,

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

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

$$E_{\mathrm{h}} = A_+ e^{\bar{\kappa}z} + A_- e^{-\bar{\kappa}z},$$

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

The electrostatic boundary conditions require that the electric field vanishes at $z = \pm\frac{1}{2}L$. Putting $E = 0$ and solving for the coefficients of E_{h}, one readily finds $A_\pm = -\frac{1}{2}E_{\mathrm{inh}}/\cosh(\bar{\kappa}L/2)$ and the thermoelectric field

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

Both 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 (8) within a few screening lengths $\bar{\kappa}^{-1}$. The parameter $\bar{\kappa}^{-1}$ takes values in the range between 1 and 100 nanometers and thus is much smaller than the size of sample L. Even in microfluidic 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 (8) and thus are irrelevant for the results of this paper.

[1] B.V. Derjaguin, N.V. Churaev, V.M. Muller, *Surface Forces*, Plenum Press, New York (1987)

[2] J.L. Anderson, Ann. Rev. Fluid Mech. **21**, 61 (1989)

[3] T. M. Squires, S. R. Quake, Rev. Mod. Phys. **77**, 977 (2005)
[4] L. Bocquet, E. Charlaix, Chem. Soc. Rev. **39**, 1073 (2010)
[5] L.D. Reed, F.A. Morrison Jr., J. Coll. Interf. Sci. **54**, 117 (1976)
[6] P.D. Grossman, J.C. Colburn (Ed.), *Capillary Electrophoresis*, Academic Press, (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, C. R. Acad. Sc. Paris, Série II **293**, 1025 (1981)
[10] S. Wiegand, J. Phys. Cond. Matt. **16**, 357 (2004)
[11] A. Würger, Phys. Rev. Lett. **98**, 138301 (2007)
[12] S. Iacopini et al., EPJ E **19**, 59 (2006)
[13] S. Duhr, D. Braun, PNAS **103**, 19678 (2006)
[14] N. Ghofraniha, G. Ruocco, C. Conti, Langmuir **25**, 12495 (2009)
[15] S.A. Putnam, 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, A. Bourdon, Phys. Rev. E **67**, 011404 (2003)
[21] S. Duhr, D. Braun, Phys. Rev. Lett. **96**, 168301 (2006)
[22] J.K.G. Dhont et al., Langmuir **23**, 1674 (2007)
[23] J.K.G. Dhont, W.J. Briels, Eur. Phys. J. E **25**, 61 (2008).
[24] J. Morthomas, A. Würger, Eur. Phys. J. E **27**, 425 (2008)
[25] S.N. Rasuli, R. Golestanian, Phys. Rev. Lett. **101**, 138301 (2008)
[26] R. Piazza, A. Guarino, Phys. Rev. Lett. **88**, 208302 (2002)
[27] D.M. Rowe, *Thermoelectrics Handbook—Macro to Nano*, CRC-Taylor & Francis, Boca Raton, (2006).
[28] S.R. de Groot, P. Mazur, *Non-equlibrium Thermodynamics*, North Holland Publishing, Amsterdam (1962)
[29] D. C. Prieve, J. Chem. Soc. Faraday Trans. 2, **83**, 1287 (1987)
[30] G. Guthrie et al., J. Chem. Phys. **17**, 310 (1949)
[31] J.N. Agar et al., J. Phys. Chem. **93**, 2082 (1989)
[32] D. Vigolo, S. Buzzaccaro, R. Piazza, Langmuir (2010)
[33] B. Abécassis et al., Nature Mat. **7**, 785 (2008)
[34] S. Fayolle et al., Phys. Rev. Lett. **95**, 208301 (2005)
[35] M. Muthukumar, Electrophoresis **17**, 1167 (1996)
[36] V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, C. Holm, Phys. Rev. Lett. **98**, 176105 (2007)
[37] M. Medrano, A.T. Pérez, L. Lobry, F. Peters, Langmuir **25**, 12043 (2009)
[38] W. Russel, D. Saville, W. Schowalter, *Colloidal Dispersions*, Cambridge University Press (1989)