Soret Motion of a Charged Spherical Colloid

Seyyed Nader Rasuli[1,2,*] and Ramin Golestanian[3,+]

[1]*School of the Physics, Institute for Theoretical Physics and Mathematics (IPM), P.O. Box 19395-5531, Tehran, Iran*
[2]*Institute for Advanced Studies in Basic Sciences, Zanjan 45195-1159, Iran*
[3]*Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom*

The thermophoretic motion of a charged spherical colloidal particle and its accompanying cloud of counterions and coions in a temperature gradient is studied theoretically. Using the Debye-Hückel approximation, the Soret drift velocity of a weakly charged colloid is calculated analytically. For highly charged colloids, the nonlinear system of electrokinetic equations is solved numerically, and the effects of high surface potential, dielectrophoresis, and convection are examined. Our results are in good agreement with some of the recent experiments on highly charged colloids without using adjustable parameters.

Introduction.—A temperature gradient applied to a fluid mixture causes relative transformation of its components: some condensing in the hotter and some in the colder side. This phenomenon, known as the Soret effect or thermophoresis, has been studied for nearly 150 years [1] and has been observed in a variety of systems [2–7]. While the existence of such a *response* can be well formulated in the framework of nonequilibrium thermodynamics [8], in many cases its microscopic nature remains poorly understood [9–14]. The manifestation of this effect in charged colloidal solutions is particularly puzzling: while it is usually observed that colloids condense in the colder side, experiments with opposite results also exist [2] and it appears that the tendency could change with the variation of salt concentration and temperature [3,4].

In a pioneering work in 1981, Ruckenstein suggested a model for Soret motion of a single charged colloidal particle [9]. Using Boltzmann distribution for ion densities and the Debye-Hückel approximation for the electrostatic potential, he was able to solve the hydrodynamics equations and find the drift velocity of a colloid in a temperature gradient. The 2002 experiment by Piazza and Guarino on sodium dodecyl sulfate (SDS) micelles solutions provided an opportunity for verification of this model [3]. The SDS micelles in the experiment were highly charged, as they had an estimated saturated structural charge of $Z \simeq 75$ (in electronic unit) [15] and a radius of $a = 2.5$ nm, and the thickness of their double layer—as set by the Debye length—varied between 0.4–2.5 nm [3]. The experiment was therefore outside the region of validity of Ruckenstein's theory, which was restricted to weakly charged colloids with thin double layers. Piazza and Guarino showed that it was possible to get a reasonable fit to the experimental data for the dependence of the Soret coefficient on the salt concentration using Ruckenstein's formula, provided they assumed an increased radius of $a = 3.5$ nm and a reduced charge of $Z = 17$ [3]. The apparent smaller charge of the colloid could be interpreted as the renormalized charge as described by Alexander *et al.* [16].

However, this attribution is not entirely justified as the concept of effective charge is defined through the asymptotic form of the electrostatic potential of the colloid far away from its surface [16], while Ruckenstein's model deals with the electric field inside the thin double layer. In fact, the value of the effective charge $Z = 17$ used by Piazza and Guarino is obtained from measurements on intercolloidal interactions [15], and electrophoretic observation on SDS micelles does not seem to confirm this value [17]. More recently, Putnam *et al.* performed experiments on highly charged $T4$ lysozymes and found results that do not seem to be explained satisfactorily by any of the existing theories on single-colloid thermophoresis [7]. Another recent experiment by Duhr and Braun [5] probed charged particles with low surface potentials and found a new scaling relation for Soret motion of charged colloid which does not agree with Ruckenstein's prediction. They showed that it is possible to explain their observations, using the Gibbs enthalpy of the charged colloid [5] (or the irreversible work needed to construct it [12]). The controversy was later clarified to some extent but the work of Astumian [13], who suggested that while Ruckenstein's model deals with the deterministic steady motion of a charged colloid, the theory by Duhr and Braun addresses its fluctuation-induced stochastic motion, which is a separate contribution, and a complete picture should involve both of these aspects simultaneously.

Here, we focus on the deterministic motion of a charged spherical particle in a temperature gradient, and consider both weakly charged and highly charged cases taking into account effects such as the temperature dependence of solvent electric permittivity, convection, and nonequilibrium coion or counterion redistribution. We examine the behavior of the system using Debye-Hückel approximation for weakly charged colloids, and provide an analytical result for colloid drift velocity with *arbitrary* double-layer thicknesses. For highly charged colloids, we solve the nonlinear set of coupled equations numerically, and find that the Soret coefficient has a nonmonotonic dependence

on the surface (zeta) potential of the colloids, an effect that has been indeed observed by Putnam *et al.* [7]. We also examine the relative importance of various contributions in the different regimes. For the experiment with SDS micelles [3], we show that our systematic approach can yield results in reasonable agreement with the experimental data, using a realistic bare value for the micellar charge.

Model.—We consider an ionic solution of different species with concentration C_i and valence q_i, which create an electrostatic potential ϕ through Poisson's equation $-\vec{\nabla} \cdot \varepsilon \vec{\nabla} \phi = 4\pi \sum_i q_i C_i$. This solution is subject to a gradient in temperature which causes ε to change in space. We consider weakly varying temperature fields, so we use linear response theory to study the deformation of the double layer and solvent flow. The Soret motion of a charged colloid is a steady motion which means that in the colloid framework we should look for a stationary solution for the fluid velocity field $\vec{V}$. This fluid velocity is governed by the Navier-Stokes equation and the incompressibility constraint $\vec{\nabla} \cdot \vec{V} = 0$. In the limit of low Reynolds number, this yields the stationary Stokes equation $-\eta \nabla^2 \vec{V} = -\vec{\nabla} P - \vec{\nabla} \phi \sum_i q_i C_i + \vec{f}$. Here η is the viscosity of the solvent and P is its pressure. The body force $\vec{f}$ is the dielectrophoretic force, which comes from the net force experienced by electric dipoles of water molecules because of spatial variation in the electric field [18]. It reads [19]: $\vec{f} = \vec{\nabla}(\frac{\varepsilon-1}{8\pi}|\vec{E}|^2) - \frac{1}{8\pi}|\vec{E}|^2\vec{\nabla}\varepsilon$, where $\vec{E} = -\vec{\nabla}\phi$. The first term in this expression is a complete derivative and can be absorbed in the fluid pressure (i.e., $P \rightarrow P - \frac{\varepsilon-1}{8\pi}|\vec{E}|^2$). Assuming that the solvent is incompressible (i.e., $\rho = \rho_0$), changes in its permittivity $\varepsilon(\rho_0, T)$ are due to the temperature gradient only: $-\frac{1}{8\pi}|\vec{E}|^2\vec{\nabla}\varepsilon = \alpha\frac{\varepsilon}{8\pi}|\vec{E}|^2\frac{\vec{\nabla}T}{T}$, where $\alpha = -\partial \ln\varepsilon/\partial \ln T$ is about 1.35 for water at room temperature [20]. Finally, each ion species is subject to a conservation law $\vec{\nabla} \cdot \vec{J}_i = 0$, with ionic current density:

$$\vec{J}_i = -D_i\vec{\nabla}C_i - \mu_i C_i q_i\vec{\nabla}\phi + \vec{V}C_i - D_i C_i S_T^{\text{ion}}\vec{\nabla}T, \quad (1)$$

where μ_i is the ith type of ion mobility and $D_i = \mu_i k_B T$ is its diffusivity. S_T^{ion} is the coion or counterion Soret coefficient. Here we only focus on 1:1 electrolytes, so we assume that coions and counterions have equal Soret coefficients [21].

In the absence of any temperature gradient and fluid motion, Eq. (1) is simplified to its first two terms. Then, $C_i = C_0 \exp[-q_i\phi/k_B T]$ yields $\vec{J}_i = 0$, and satisfies $\vec{\nabla} \cdot \vec{J}_i = 0$. In the presence of a temperature gradient, however, not only do we have to consider all of Eq. (1) terms, but we also note that a Boltzmann weight form for C_i no longer makes $-D_i\vec{\nabla}C_i - \mu_i C_i q_i\vec{\nabla}\phi$ vanish; instead, it yields $-D_i C_i(q_i\phi/k_B T^2)\vec{\nabla}T$. We suggest to use the following form: $C_i = C_0 \exp[-\frac{q_i\phi}{k_B T} - (T - T_0)S_T^{\text{ion}} + (\frac{T-T_0}{T_0})\Omega_i]$, where Ω_i measures the deviation of the concentration from a Boltzmann weight form, and it contains contribu-

tions from the convective term in Eq. (1) as well as the aforementioned term of $-D_i C_i(q_i\phi/k_B T^2)\vec{\nabla}T$.

Our aim is to find the colloid drift velocity, so we focus on the Stokes equation that governs fluid velocity. The electric and dielectrophoretic forces on the right-hand side are acting as source terms that induce fluid motion. To first order in temperature changes, the source terms simplify to

$$-\vec{\nabla}\phi_0\sum_i q_i C_i^0\left[\frac{q_i\phi_0}{k_B T_0} - T_0 S_T^{\text{ion}} + \Omega_i\right]\frac{\delta T}{T_0} + \alpha\frac{\varepsilon|\vec{E}_0|^2}{8\pi}\frac{\vec{\nabla}T}{T_0}, \quad (2)$$

where $C_i^0 = C_0 \exp[-q_i\phi_0/k_B T_0]$ and $\vec{E}_0$ are the unperturbed values of ion density and electric field. Here, we have also extracted another complete derivative (i.e., $-\vec{\nabla}\sum_i q_i C_i^0\delta\phi$), which can be absorbed in the fluid pressure term [18].

Weakly charged colloids.—For $q\phi/k_B T \ll 1$, we can use the Debye-Hückel approximation and solve this system of equations analytically [18]. The drift velocity of a colloid with radius a is found as

$$\vec{V}_{\text{drift}} = \frac{-\varepsilon\phi_S^2}{48\pi}\frac{\vec{\nabla}T}{\eta T_0}\{(1 + T_0 S_T^{\text{ion}})F(\kappa a) - G(\kappa a) + \alpha[2 - F(\kappa a)]\}, \quad (3)$$

where $\phi_S = Zq/\varepsilon a(1 + \kappa a)$ is the zeta potential of the surface of the colloid and $\kappa = \sqrt{8\pi q^2 C_0/\varepsilon k_B T_0}$ is the inverse Debye length [22]. In this equation, $F(x) = 2x - 4x^2 e^{2x}E_1(2x)$ and $G(x) = \frac{x}{6}[x(1 + x)(12 - x^2)e^x E_1(x) + 8 - 11x + x^3 - 24xe^{2x}E_1(2x)]$, with $E_1(x) = \int_x^\infty e^{-s}ds/s$. Equation (3) is arranged in the form of Ruckenstein's result for colloid drift velocity [9] multiplied by a correcting factor. Each term in this correcting factor corresponds to one of the source terms in Eq. (2) [i.e., $\alpha[2 - F(\kappa a)]$ corresponds to the dielectrophoretic term, $-G(\kappa a)$ to $\Omega_i\delta T/T_0$ term, and $T_0 S_T^{\text{ion}}F(\kappa a)$ to ion Soret term]. The remaining $F(\kappa a)$ corresponds to the $-\vec{\nabla}\phi_0\sum_i q_i C_i^0[\frac{q_i\phi_0}{k_B T_0}]\delta T/T_0$ term, which corrects Ruckenstein's result [9] for arbitrary double-layer thicknesses.

The limit of a thick double layer (i.e., $\kappa a \ll 1$) or low ionic strength is particularly interesting, as for $\kappa a = 0$ we have $F(\kappa a) = G(\kappa a) = 0$ [18], and the only contribution in the correcting factor of Eq. (3) will be 2α. It means that with low ionic density, the dielectrophoretic force that is the force on water molecules [18] plays the dominant role in the phenomenon. In addition, Ruckenstein's formula will still be applicable, if we multiply it with a constant 2α, which can be presented in terms of a renormalized surface potential $\phi_S' = \sqrt{2\alpha}\phi_S$ or charge $Z' = \sqrt{2\alpha}Z$ [23].

Highly charged colloids.—The Debye-Hückel approximation is not valid for highly charged colloids and one needs to fully take account of the nonlinearity of the electrostatics. To this end, we have solved the above gov-

erning equations numerically. Figure 1(a) shows the Soret coefficient $TS_T \sim V_{\mathrm{drift}}$ as a function of κa for various values of structural charge, corresponding to the SDS micelles used in the experiment of Ref. [3]. We find that while the Soret coefficient initially increases with the structural charge—in agreement with the Debye-Hückel limit behavior where it is proportional to $\phi_S^2 \sim Z^2/(1 + \kappa a)^2$—this trend is reversed at sufficiently high values of the charge and the Soret coefficient starts to decrease until it changes sign and becomes negative. We can understand this behavior better if we track the contributions of the different source terms in Eq. (2) to the Soret coefficient. Following our analytical approach [that led to Eq. (3)], we name the contribution of $-\vec{\nabla}\phi_0 \sum_i q_i C_i^0 (q_i \phi_0/k_B T_0) \times (\delta T/T_0)$ term in Eq. (2) as the F term, that of the dielectrophoretic term as the α term, and finally that of Ω_i's as the $-G$ term [note the minus sign of $G(\kappa a)$ in Eq. (3)]. Figure 1(b) shows the relative importance of these contributions as a function of the surface potential. While for weakly charged colloids (i.e., $|q\phi_S/k_B T| \ll 1$), the α term is the dominant contribution, for $|q\phi_S/k_B T| \gtrsim 1$, the situation changes in favor of the G term, which eventually leads to negative Soret coefficient at high surface potentials. Interestingly, for the surface potentials attributed to

the SDS micelles of Ref. [3], the two terms balance each other.

A similar nonmonotonic behavior has recently been observed by Putnam *et al.* for lysozyme proteins with various surface charges or potentials [7]. Figure 2(a) shows a comparison between their observed TS_T versus lysozyme surface potential, and the prediction of our theory without any adjustable parameters. In this calculation, we have ignored the contribution of the Soret coefficient of the ions, as we were not able to obtain relevant experimental values for these quantities. The encouraging agreement suggests that for highly charged colloids it will not be sufficient to treat the double layer close to the surface within the equilibrium Poisson-Boltzmann formulation, and it is necessary to fully take account of the nonlinear nonequilibrium effects in the profile of the ion cloud around the colloid.

FIG. 1 (color online). (a) TS_T vs κa for a colloid with radius $a = 2.5$ nm, but different charges. Mean temperature is $T = 25\,°C$, and we extrapolated existing data [21] to obtain (Na^+ and CL^-) ion Soret coefficient: $S_T^{\mathrm{ion}} = 0.99$–$2 \times 10^{-3}$ K^{-1} (depending on salt density). (b) Ratios of the dielectrophoretic term (α term) to the F term (dashed blue line) and G term/F term (solid red line), versus $|q\phi_S/k_B T|$, for $\kappa a = 2$. $|q\phi_S/k_B T| = 3.74$ corresponds to $Z = 50$–60, our suggested charge for a micelle in the experiment of Ref. [3]. The dash-dotted (orange) curve corresponds to when the convection term is artificially switched off.

FIG. 2 (color online). (a) Comparison of Putnam *et al.* [7] data (red solid line) for mutant $T4L$ lysozymes with $Z = +3$, $+5$, $+7$, $+9$, and $R_h \simeq 1.8$ nm, with our numerical prediction (dash-dotted green curve). (b) Comparison of the experimental data of Piazza and Guarino [3] with our theoretical prediction. Depending on salt concentration, we assume a varying micelle charge of $Z = 50$–60 [18], a varying ion Soret coefficient $S_T^{\mathrm{ion}} = 0.99$–$2 \times 10^{-3}$ K^{-1}, and a fixed ionic diffusion coefficient $D = 1.33 \times 10^9$ nm^2/s [24]. Our data is lifted by $+6.547$, to obtain the best fit with four last points. (c) Comparison of our analytic theory with Duhr and Braun data [5] for polystyrene spheres with different radii.

It is also interesting to probe the role of convection in our results. The convection term in Eq. (1) affects Ω_i's and consequently the G term. The dash-dotted (orange) curve in Fig. 1(b) shows the ratio G term/F term, with convection artificially turned off. We observe that while for $|q\phi_S/k_BT| \ll 1$ the convective term has a small effect (proportional to $|q\phi_S/k_BT|^2$ [18]), for higher surface potentials the convective motion will be non-negligible, but always finite.

We also do numerical calculation for the experiment of Piazza and Guarino, and use electrophoresis data [17] to find micelles charge [18]. The result is presented in Fig. 2(b), which only shows an agreement with the experiment for $\kappa a > 3$. Since we have established (see Fig. 1) that changing the structural charge does not lead to a better harmony, we can conclude that effects other than the ones considered here systematically should control the behavior of the system for $\kappa a < 3$.

Discussion.—The experiment performed by Duhr and Braun [5], unlike most other experiments, has been done for colloids within Debye-Hückel regime. Therefore, it is natural to expect that our analytical results should agree with its findings. Figure 2(c) compares our result [based on Eq. (3)] with its data, and does not show a satisfactory agreement. We have examined possible corrections coming from fluid slip velocity on the colloid surface and mismatch in the thermal conductivities of the colloid and the fluid, and found that they cannot improve the situation [24]. To resolve this discrepancy it has been suggested [13] that one should differentiate between the regime where hydrodynamic or deterministic components of the motion are dominant and the regime in which the system feels a local thermal equilibrium, and it is the stochastic motion which is the dominant player. It is expected that the behavior of the Soret coefficient as a function of various parameters such as the radius, temperature, etc. will be significantly different in these two regimes. This means that a theoretical formulation that can account for experiments corresponding to the hydrodynamic or deterministic regime is almost bound to fail to account for experiments in the stochastic regime as they would be mutually exclusive, a view which is also supported by recent experimental evidence [25]. Further work is needed to fully clarify this picture, ideally in the form of a theoretical formulation that includes both effects and can show the crossover from one behavior to the other in a systematic way.

In conclusion, we have presented a systematic theoretical analysis of the Soret motion of charged colloids both in the weakly and strongly charged regimes. Using contributions from different physical sources, we have found competing tendencies that are entirely due to the nonlinearity of electrostatics and the nonequilibrium redistribution of the ion clouds around the colloid.

*rasuli@mail.ipm.ir
+r.golestanian@sheffield.ac.uk

[1] C. Ludwig, Sitzungsber. Akad. Wiss. Wien Math.-Naturwiss. Kl **20**, 539 (1856); C. Soret, Arch. Sci. **3**, 48 (1879).
[2] J. Lenglet et al., Phys. Rev. E **65**, 031408 (2002).
[3] R. Piazza and A. Guarino, Phys. Rev. Lett. **88**, 208302 (2002).
[4] S. Iacopini and R. Piazza, Europhys. Lett. **63**, 247 (2003).
[5] S. Duhr and D. Braun, Proc. Natl. Acad. Sci. U.S.A. **103**, 19 678 (2006); S. Duhr and D. Braun, Phys. Rev. Lett. **96**, 168301 (2006).
[6] C. Debuschewitz and W. Köhler, Phys. Rev. Lett. **87**, 055901 (2001); S. Wiegand, J. Phys. Condens. Matter **16**, R357 (2004).
[7] S. A. Putnam et al., Langmuir **23**, 9221 (2007).
[8] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
[9] E. Ruckenstein, J. Colloid Interface Sci. **83**, 77 (1981).
[10] K. I. Morozov, JETP **88**, 944 (1999).
[11] E. Bringuier and A. Bourdon, Phys. Rev. E **67**, 011404 (2003); B. J. de Gans et al., Phys. Rev. Lett. **91**, 245501 (2003); A. Najafi et al., Europhys. Lett. **68**, 776 (2004); S. N. Rasuli et al., J. Phys. Condens. Matter **17**, S1171 (2005); Hui Ning et al., J. Chem. Phys. **125**, 204911 (2006); A. Würger, Phys. Rev. Lett. **98**, 138301 (2007); E. Bringuier, Philos. Mag. **87**, 873 (2007).
[12] J. K. G. Dhont et al., Langmuir **23**, 1674 (2007).
[13] R. D. Astumian, Proc. Natl. Acad. Sci. U.S.A. **104**, 3 (2007).
[14] S. Fayolle et al., Phys. Rev. Lett. **95**, 208301 (2005).
[15] S. Bucci et al., Langmuir **7**, 824 (1991).
[16] S. Alexander et al., J. Chem. Phys. **80**, 5776 (1984).
[17] D. Stigter, J. Phys. Chem. **68**, 3603 (1964).
[18] See EPAPS Document No. E-PRLTAO-101-073835 for supplementary material on the details of the calculations. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[19] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Butterworth-Heinenmann, Oxford, 1984).
[20] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (Taylor and Francis, Boca Raton, FL, 2007), 87th ed.
[21] D. R. Caldwell, J. Phys. Chem. **77**, 2004 (1973); F. S. Gaets et al., J. Phys. Chem. **86**, 2967 (1982); P. N. Snowdon et al., Trans. Faraday Soc. **56**, 1812 (1960).
[22] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, England, 1988).
[23] In some practical situations, we may use the renormalized surface charge or potential for arbitrary κa's. It is because other terms in the correcting factor of Eq. (3) are usually smaller than 2α. For the experiment of Ref. [3], for instance, TS_T^{ion} varies between 0.3 and 0.6 (depending on salt density [24]), then $(1 + TS_T^{ion} - \alpha)F(\kappa a)$ and $G(\kappa a)$ are small enough that the deviation of the correcting factor from 2α is less than 20%.
[24] S. N. Rasuli and R. Golestanian (unpublished).
[25] M. Braibanti et al., Phys. Rev. Lett. **100**, 108303 (2008).