Single-particle Thermal Diffusion of Charged Colloids : Double-layer theory in a temperature gradient.

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Abstract

The double-layer contribution to the single-particle thermal diffusion coefficient of charged, spherical colloids with arbitrary double-layer thickness is calculated and compared to experiments. The calculation is based on an extension of the Debye-Hückel theory for the double-layer structure that includes a small temperature gradient. There are three forces that constitute the total thermophoretic force on a charged colloidal sphere due to the presence of its double layer : (i) the force $\mathbf{F}_W$ that results from the temperature dependence of the internal electrostatic energy W of the double layer, (ii) the electric force $\mathbf{F}_{el}$ with which the temperature-induced non-spherically symmetric double-layer potential acts on the surface charges of the colloidal sphere and (iii) the solvent-friction force $\mathbf{F}_{sol}$ on the surface of the colloidal sphere due to the solvent flow that is induced in the double layer because of its asymmetry. The force $\mathbf{F}_W$ will be shown to reproduce predictions based on irreversible-thermodynamics considerations. The other two forces $\mathbf{F}_{el}$ and $\mathbf{F}_{sol}$ depend on the details of the temperature-gradient induced asymmetry of the double-layer structure which can not be included in an irreversible-thermodynamics treatment. Explicit expressions for the thermal diffusion coefficient

1

are derived for arbitrary double-layer thickness, which complement the irreversible-thermodynamics result through the inclusion of the thermophoretic velocity resulting from the electric- and solvent-friction force.

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1 Introduction

The thermal diffusion coefficient of colloidal particles consists, to a good approximation, of additive contributions from single-particle properties and contributions stemming from interactions between colloids [1]. Single-particle contributions relate to the response of the solvation layer, the structure of the solid core material and the electric double-layer to a temperature gradient. As far as the electric double layer is concerned, there are three forces acting on a colloidal sphere. First of all, the internal electrostatic energy W of the double layer changes with temperature, which results in a force that will be denoted here as $\mathbf{F}_W$. This force will be referred to as the *internal force*, since it originates from the internal energy of the double layer. As will be shown, to leading order in temperature gradients, it is sufficient to consider the *spherically symmetric* double layer to calculate $\mathbf{F}_W$. The temperature-induced change of the structure of the double layer does not contribute to this force to leading order in gradients. There are two more contributions to the total thermophoretic force, which are related to the temperature-induced asymmetry of the double-layer structure. The temperature-induced asymmetric charge distribution within the double layer results in a displacement of the center-of-charge of the double layer as compared to that of the colloidal sphere. This results in an *electric force* $\mathbf{F}_{el}$ of the double layer on the surface charges of the colloidal sphere. In addition, the asymmetry of the double-layer structure gives rise to electric body forces that set the solvent in motion. The friction forces on surface elements of the core of the colloidal sphere due to this flow leads to an additional *solvent-friction force* $\mathbf{F}_{sol}$. The total thermophoretic force $\mathbf{F} = \mathbf{F}_W + \mathbf{F}_{el} + \mathbf{F}_{sol}$ on the colloidal sphere is the driving force for thermal diffusion.

The temperature-gradient induced double-layer asymmetry can be understood within a first, crude intuitive approach as follows. The Debye screening length is temperature dependent, both explicitly and through the dielectric constant of the solvent. The Debye length thus differs on the cold and warm side of

2

the colloidal sphere. This induces an asymmetry in the charge distribution and the electric potential.

The available theories on the contribution of the electrical double layer to the single-particle thermal diffusion coefficient can roughly be divided into two groups : theories where the temperature-induced asymmetry of the double-layer structure is neglected (such as theories based on irreversible thermodynamics where local equilibrium is assumed) and theories where the detailed double-layer structure is considered on the basis of equations for charge density, electrical potential and solvent flow. Previous work within these two classes of theories are summarized below.

An explicit expression for the Soret coefficient, as far as the double-layer contribution is concerned, has recently been derived by one of the present authors (JKGD) [2] on the basis of an irreversible-thermodynamics approach. Here, the quasi-static force necessary to move a double layer against a temperature gradient has been shown to be proportional to the temperature derivative of the reversible work to build up the double layer. For spherically symmetric double layers and within the Debye-Hückel approximation, this work is equal to $\frac{1}{2}Q\Phi_s$, where Q is the total charge on the surface of the colloid and Φ_s is its surface potential. This leads to the following expression for the Soret coefficient of colloidal spheres with radius R and an ambient Debye length κ^{-1} [2],

$$
\begin{aligned}
T\,S_T \;=\; & 1 + \frac{1}{4}\left(\frac{4\,\pi\,l_B^2\,\sigma}{e}\right)^2 \frac{\kappa\,R}{(1+\kappa\,R)^2}\left(\frac{R}{l_B}\right)^3 \left\{1 - \frac{d\ln\epsilon}{d\ln T}\left(1 + \frac{2}{\kappa\,R}\right)\right\} \\
& + \left(\frac{4\,\pi\,l_B^2\,\sigma}{e}\right)^2 \frac{1}{1+\kappa\,R}\left(\frac{R}{l_B}\right)^3 \frac{d\ln Q}{d\ln T}\,,
\end{aligned}
\tag{1}
$$

where ϵ is the dielectric constant of the solvent, $e > 0$ the elementary charge and $l_B = \beta\,e^2/4\,\pi\,\epsilon$ is the Bjerrum length (with $\beta = kBT$, where kB is Boltzmann's constant and T is the temperature). The combination $4\pi l_B^2\sigma/e$ is the number of elementary charges on a fictitious sphere with radius l_B with the same charge density σ as the colloids. As will be shown, this expression for the Soret coefficient corresponds to the internal force $\mathbf{F}_W$ mentioned above. For thin double layers, the electric double layer and the charged surface of the colloidal particle can be considered as constituting a capacitor [3]. This capacitor model leads to an expression for the Soret coefficient that corresponds to eq.(1) for very thin double layers (where $\kappa R \gg 1$), without the temperature dependence of the surface charge (i.e. when $d\ln Q/d\ln T = 0$). Bringuier and Bourdon [4] and Fayolle et al. [5] propose an expression for the single

particle thermal diffusion coefficient in terms of the temperature derivative of the total internal energy, based on arguments within a statistical mechanics approach that is put forward by van Kampen [6]. Disregarding the temperature dependence of the dielectric constant of the solvent and of the total charge, the resulting expression for the Soret coefficient is in agreement with eq.(1) for arbitrary Debye lengths (taking the limit $E \rightarrow \infty$ in eq.(13) in ref.[4], where E is the energy related to thermally activated desorption of ions from the surface of the colloids, renders the total charge independent of temperature). The positive correspondence between the results obtained in ref.[2] and in refs.[4, 5] is quite satisfactory, since the approaches are rather different. In addition to the single-particle Soret coefficient, ref.[5] also discusses interaction contributions, which will not be addressed in the present paper.

The above mentioned theories essentially neglect the temperature-induced asymmetry of the double layer. Such an asymmetry will certainly lead to additional contributions to the Soret coefficient as given in eq.(1).

An expression for the thermophoretic velocity is derived in ref.[7], with explicit reference to the double-layer structure, in case of thin double layers and very small colloidal particles. For the very small (metal) colloidal particles under consideration in ref.[7], the thermophoretic force is essentially equal to the body force on fluid elements of the dispersion, where the colloidal particles are considered as being part of an effective fluid. The analysis is based on the Navier-Stokes equation with a gradient in the pressure generated by the charge distribution close to the surface of the particle. The temperature-gradient induced asymmetry of the electric potential is assumed to be given by a rather simple form, that probably applies for very thin double layers, but is not systematically derived from an extension of the Debye-Hückel theory that includes a temperature gradient. In ref.[7], the emphasis is on metal particles, where the local temperature variation around the particle is of crucial importance. In the present paper, we shall neglect differences in thermal conductivity of the solvent and the colloidal core that result in such non-linear temperature variations in the neighbourhood of the colloidal particle. A combined theory, where both finite-sized particles and double layers *and* differences in thermal conductivities of the solvent and the solid core material of the colloids are considered remains a challenge. Progress could be made by combining the ideas from ref.[7] for thin double layers and those presented in the present paper. What is also neglected

4

in the present paper is the effect of macroscopic pressure gradients that are set up in the bulk solvent due to temperature gradients. These pressure gradients are discussed in ref.[8]. Comparing typical values for the thermal diffusion coefficient as obtained from eq.(1) and the typical values corresponding to such macroscopic pressure gradients (see eqs.(26,31) in ref.[8]), shows that the latter can indeed be neglected. This may of course be different for neutral, non-charged colloids. In a similar approach, Morozov [9] considers thermal diffusion in case of very thin double layers and small colloids, where the dispersion is again described as an effective fluid. As mentioned above, the bulk body force acting on the effective fluid (see eq.(7) in ref.[9]) can then be directly connected to the thermophoretic force on colloidal particles. A general formalism for single-particle thermal diffusion of colloids is developed in ref.[10]. Here, a colloidal particle is assumed to act with a force on the surrounding solvent, which force is added to the Navier-Stokes equation that describes the solvent flow around the colloidal sphere. The thermophoretic force is then taken equal to minus the total force with which the colloidal particle acts onto the surrounding fluid (and possibly ions) plus the friction force as a result of solvent flow (see their eq.(11)). In the explicit evaluation of these forces for charged colloids in their section 5.2, the temperature-induced deformation of the double-layer structure is included. However, the resulting expression (47) in ref.[10] for the Soret coefficient, which is very similar to the result for thin double layers as obtained by Rückenstein [11], is by a factor $\kappa R/4$ off from the irreversible-thermodynamics result in eq.(1) in case of thin double layers. It predicts a quadratic dependence of the Soret coefficient on the Debye screening length for thin double layers and constant charge, which disagrees with eq.(1) for $\kappa R \gg 1$, and is at variance with experiments on polystyrene colloids [3]. The additional contributions to the Soret coefficient in eq.(1) that arise from temperature-gradient induced deformation of the double layer, as calculated in the present paper, are also quite different from the result in eq.(47) of ref.[10]. This discrepancy may have the following origin. The local body force of the colloidal particle on fluid elements is equal to $-\sum_\alpha \rho_\alpha z_\alpha \nabla \Phi_c$, where Φ_c is the potential that is generated by the surface charges of the colloidal sphere (here, the sum ranges over all ions of species α with valency z_α and number concentration ρ_α). In ref.[10], however, the potential is taken equal to the *total* electric potential, which arises from surface charges of the colloid *and* from charges within the double layer. Since the total force on the double layer in a temperature gradient is not necessarily

zero, this might explain the discrepancy.

In short, within the approaches taken in refs.[2]-[6], the temperature-induced deformation of the double layer is neglected. In approaches where the temperature-induced deformation of the double-layer structure and the resulting flow within the double layer is accounted for [7]-[11], only thin double layers and often very small colloids have been considered (with the exception of ref.[10]). *In the present paper we consider finite sized colloidal particles with an arbitrary double-layer thickness, where spatial variations of the fluid flow and charge distribution in all three dimensions within the double layer are analyzed. The three dimensional temperature-induced asymmetry of the double layer is systematically derived from an extended Debye-Hückel theory.*

Experimental results on polystyrene colloids [3] and a micellar system [12] are shown in ref.[2] to agree with the irreversible-thermodynamics prediction (1). This seems to indicate that the forces $\mathbf{F}_{el}$ and $\mathbf{F}_{sol}$ due to double-layer deformation are of minor importance. The electric force $\mathbf{F}_{el}$ results from forces on the surface charges of the colloidal sphere while the solvent-friction force $\mathbf{F}_{sol}$ is due to electric body forces on double-layer charges. Since free surface charges and ion charges within the double layer are dielectrically screened through polarization of the solvent, these forces are small for highly polarizable solvents like water. As will be shown, these two forces are typically by a factor ϵ_0/ϵ smaller than the internal force $\mathbf{F}_W$ due to dielectric screening (with ϵ_0 and ϵ the dielectric constants of vacuum and the solvent, respectively). Since $\epsilon_0/\epsilon \approx 1/78$ for water, this explains the good agreement of the irreversible-thermodynamics prediction in eq.(1) with experiments. The additional contributions to thermal diffusion are therefore only relevant in relatively apolar solvents. However, as will be shown, the internal force vanishes for very thin double-layer thickness, while the forces due to the asymmetry of the double layer remain finite. This is due to the temperature dependence of the dielectric constant, leading to an asymmetric dielectric screening of charges. The contribution of the asymmetric double-layer structure to the thermal diffusion coefficient can thus be dominant in case of very thin double layers even in highly polarizable solvents.

The additive contribution ΔS_T to the Soret coefficient related to the forces $\mathbf{F}_{el}$ and $\mathbf{F}_{sol}$, is found in the present paper to be equal to,

$$T \, \Delta S_T \;=\; \frac{\epsilon_0}{\epsilon} \, \frac{\beta \, Q^2}{16 \, \pi \, \epsilon \, R} \, \left[\chi \, \kappa \, R - \frac{d \ln \epsilon}{d \ln T} \left(\frac{1}{2} - 3 \, \kappa \, R \right) \right] , \tag{2}$$

6

for thick double layers, where $\kappa R \ll 1$, up to order $\mathcal{O}((\kappa R)^2 \ln\{\kappa R\})$, and,

$$T \, \Delta S_T \; = \; \frac{\epsilon_0}{\epsilon} \, \frac{\beta \, Q^2}{24 \, \pi \, \epsilon \, R} \, \frac{d \ln \epsilon}{d \ln T} \left(1 - \frac{1}{2 \, \kappa \, R} \right) , \tag{3}$$

for thin double layers, where $\kappa R \gg 1$, up to order $\mathcal{O}((1/\kappa R)^2)$. Here, χ is a parameter that describes the effect of thermal diffusion of the co- and counter ions. In case the ions reached their thermal stationary state during the measurement of the Soret coefficient of the colloidal sphere, the parameter χ is equal to 2. In the other extreme case where such a stationary state is not reached, and the ion concentration outside the double layer is uniform, the parameter χ is equal to 1. The latter is the case when thermal diffusion of the small ions has not been effective during a measurement of the Soret coefficient of the colloidal sphere. The expression for ΔS_T that is valid for arbitrary double-layer thickness is somewhat more involved and is given in section 8. As mentioned above, ΔS_T is proportional to ϵ_0/ϵ, due to dielectric screening of free charges.

This paper is organized as follows. The various forces that act on a single charged colloidal sphere are discussed in more detail in section 2. The fundamental equations and the corresponding boundary conditions which govern the temperature-induced asymmetry of the double-layer structure are formulated in section 3. On the basis of these governing equations, the well-known Debye-Hückel theory for the double layer structure is generalized in section 4 to include a temperature gradient. Here the temperature-gradient induced asymmetric charge distribution and potential are calculated to leading order in temperature gradients. From the double-layer potential and charge distribution, the forces $\mathbf{F}_W$, $\mathbf{F}_{el}$ and $\mathbf{F}_{sol}$ will be calculated explicitly in sections 5, 6 and 7, respectively. The Soret coefficient is computed from the total force in section 8 and is compared to experiments.

We will assume an externally imposed, time-independent temperature profile $T(z)$ that varies in the z-direction. The thermal conductivity of the solvent and the core of the colloidal sphere is supposed to be not very different, so that the externally imposed temperature gradient in the z-direction is essentially not affected by the presence of the colloidal sphere. Differences in thermal conductivity between solvent and colloid core material results in a more complicated temperature profile in the vicinity of the sphere, which complicates the analysis considerably, especially for extended double layers. Furthermore we will assume that the charges on the surface of the colloidal sphere originate from fully dissociated chemical groups, so

that the free surface charge is independent of temperature. The effects arising from differences in thermal conductivity and variable surface charge density can be included in the present theory, but is outside the scope of the present paper.

Throughout this paper we will use the following notation convention : when a z-dependence is not denoted explicitly, the quantity is meant to denote its value at the ambient temperature. For example, $\epsilon(z)$ is the dielectric constant which is z-dependent due to the temperature gradient that extends in the z direction, and ϵ denotes its constant value in the absence of the temperature gradient at the ambient temperature (like in the above expressions (1)-(3)) . Similarly T is the homogeneous temperature in the absence of gradients in temperature.

2 Forces Acting on the Charged Colloidal Sphere

There are three forces acting on a charged colloidal sphere in a temperature gradient. The origin of these forces is schematically depicted in Fig.1.

First of all, the temperature dependence of the internal electrostatic energy W of the double layer and surface charges gives rise to a force $\mathbf{F}_W$, which is referred to as the *internal force*. The origin of this force can be understood as follows. A particle that moves under the action of an external field, where the energy of the particle is specified by an external potential $\Phi_{ext}(\mathbf{r})$, experiences a force equal to $-\nabla\Phi_{ext}(\mathbf{r})$. The common assumption here is that the internal degrees of freedom of the particle on which the external field acts are *not* affected by the field (like a permanent dipole in an electric field). The expression $-\nabla\Phi_{ext}(\mathbf{r})$ for the force, however, remains valid also when the external field *does* affect internal degrees of freedom (like a non-permanent, electric-field induced dipole in an electric field). In this case, the potential energy $\Phi_{ext}(\mathbf{r})$ must include the change in energy that complies with the changes of the internal degrees of freedom (in case of an induced dipole, the strength of the dipole is affected by the external electric field, which leads to a change of the potential energy of the dipole). In the present case of thermodiffusion there is a change of the internal energy of the colloid when it is displaced, due to the change of the local temperature (see Fig.1a). The internal degrees of freedom of the "colloidal complex" respond to a change in temperature. The role of the *external* potential Φ_{ext} is now played by the *internal* energy W of the "colloidal complex".

Since forces are related to work, the change of the internal energy on displacement of a colloidal particle is actually the work that is involved to achieve that displacement. The work to achieve this displacement, in turn, is equal to the difference in the work to build up the "colloidal complex" after and before its displacement. Hence, the force $\mathbf{F}_W$ is equal to $-\nabla W$, with W the work that is necessary to build up the "colloidal complex", starting from a given, temperature-independent reference state. To within linear order in gradients, this work is reversible work since then local equilibrium can be assumed. As far as the double-layer contribution is concerned, this is the reversible work to build up the double layer and the surface charge distribution (see also reference [2]). The reversible work to build up the double layer and surface charge distribution can be calculated through a quasi-static "charging process" [13], where the free charge surface density on the sphere is build up from 0 to its final value σ. The work involved to charge the "colloidal complex" is nothing but the electrostatic energy that is stored in the double layer and the surface charges. Hence,

$$\mathbf{F}_W = -\frac{dW}{dT}\nabla T ,\tag{4}$$

where W is the internal electrostatic energy W of the double layer and surface charges. The charging process for the calculation of W is described in detail in section 5.

Secondly, the temperature gradient will induce an asymmetry in the double-layer charge distribution. This is due to the temperature dependence of the double-layer thickness. On the colder side of the colloidal sphere the Debye screening length is larger as compared to the warmer side. As a result, the center-of-charge of the double layer does no longer coincide with the center-of-charge of the surface-charge distribution of the colloidal sphere. This results in an *electric force* $\mathbf{F}_{el}$ of the double layer on the surface charges of the sphere (see Fig.1b). Due to the asymmetry of the double-layer potential, the electric field inside the core of the colloidal sphere is non-zero. Electric forces on the charged surface of the colloid therefore arise from both the electric field just outside the sphere, within the solvent, and inside the core of the colloidal sphere. As shown in appendix A, the resulting electric force on the surface charges of the colloidal sphere is equal to,

$$\mathbf{F}_{el} = \frac{1}{2}\oint_{\partial V} dS\, \sigma_t(\mathbf{r})\left[\mathbf{E}^+(\mathbf{r}) + \mathbf{E}^-(\mathbf{r})\right] ,\tag{5}$$
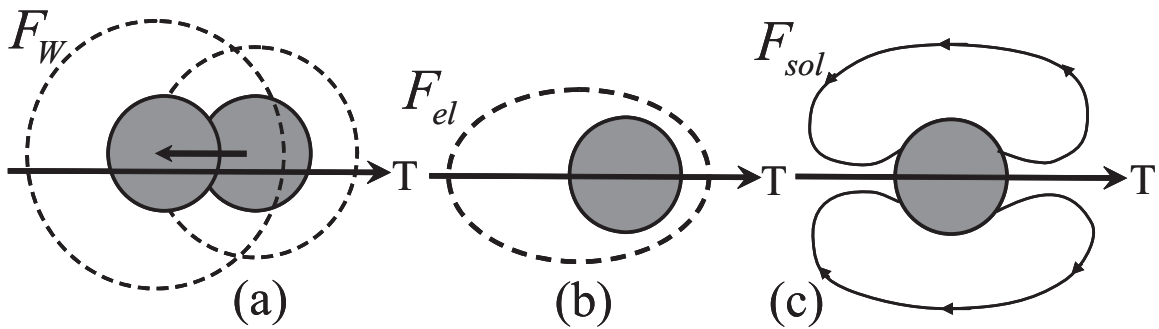
9

Figure 1: The three forces acting on a charged colloidal sphere in a temperature gradient. (a) The internal force $\mathbf{F}_W$ due to the change of the double-layer structure on displacement of the sphere. The dashed lines indicate the extent of the unperturbed double-layer at the ambient temperature, that is, the temperature at the origin of the colloidal sphere. (b) The electric force $\mathbf{F}_{el}$ that is due to the non-spherically symmetric double-layer structure. The dashed line indicates the asymmetry of the double layer. (c) The solvent-friction force $\mathbf{F}_{sol}$ is due to the solvent flow that is induced by electric body forces arising from the asymmetry of the double-layer structure. The lines indicate solvent flow lines.

where the integration ranges over the surface area ∂V of the sphere (with dS an infinitesimally small surface area element) and σ_t is the total surface charge density, including both free- and polarization-induced charges. Furthermore, $\mathbf{E}^+$ is the limiting electric field on approach of the surface of the colloidal sphere from outside the sphere, and $\mathbf{E}^-$ is the limiting field on approach of the surface from inside the sphere.

The total surface charge density σ_t includes the charges near the surface of the colloidal sphere which arise due to polarization of solvent molecules in the direct vicinity of the ionized surface groups of the colloidal sphere. The electric force in eq.(5) is thus actually the force on the sphere plus the solvation layer (excluding salt ions contained in it). The assumption therefore is that the electric forces on the solvation layer are fully transmitted to the colloidal sphere.

Thirdly, due to the asymmetry of the charge distribution, electric body forces will set the solvent in motion. Without a temperature gradient, the radial electric body forces are counter balanced by pressure gradients, and no flow is induced. In case of an asymmetric double layer, however, pressure gradients alone can not balance electric body forces within the double layer. Shear forces due to (low Reynolds-number) flow are now necessary to counter balance the electric body forces. This solvent flow acts with a

solvent-friction force $\mathbf{F}_{sol}$ on the surface of the sphere (see Fig.1c). This force is equal to,

$$\mathbf{F}_{sol} = -\oint_{\partial V} dS\, \mathbf{f}(\mathbf{r}) , \qquad (6)$$

where $\mathbf{f}$ is the force per unit area that the surface of the colloidal sphere exerts onto the solvent.

The total thermophoretic force $\mathbf{F}_T$ can thus be written as,

$$\mathbf{F}_T = \mathbf{F}_W + \mathbf{F}_{el} + \mathbf{F}_{sol} . \qquad (7)$$

The explicit calculation of the electric force $\mathbf{F}_{el}$ and friction force $\mathbf{F}_{sol}$ requires a detailed analysis of the temperature-gradient induced asymmetry of the charge distribution and potential, which will be discussed in subsequent sections.

There is an additional electric force due to the flow-induced deformation of the unperturbed potential and charge distribution within the double layer. This force can be neglected, since flow-induced displacements of ions are small in comparison to their diffusive displacements. The double-layer structure is therefore essentially unaffected by convective perturbations as a result of fast relaxation of the double-layer structure. A more detailed argument for the neglect of this force is given in the beginning of section 8.

3   The Fundamental Equations and Boundary Conditions

In subsection 3.1 we will discuss the fundamental equations that describe the double-layer structure in the presence of a temperature gradient. The boundary conditions to these differential equations are formulated in subsection 3.2.

3.1   Fundamental equations

The flux $\mathbf{j}_\alpha = \rho_\alpha \mathbf{v}_\alpha$ of ions of species α (with ρ_α the number density and $\mathbf{v}_\alpha$ the thermally averaged velocity) consists of two parts : a convective part due to solvent flow (of which the origin will be discussed later) and a part due to the force $\mathbf{F}_\alpha$ that the surroundings exert on an ion,

$$\mathbf{v}_\alpha(\mathbf{r},t) = \mathbf{v}_s(\mathbf{r},t) + \frac{1}{\gamma_\alpha}\mathbf{F}_\alpha(\mathbf{r},t) , \qquad (8)$$

where $\mathbf{v}_s$ is the solvent velocity and γ_α is the friction coefficient of an ion with solvent. The force $\mathbf{F}_\alpha$ on an ion of species α has two contributions. The force due to the electric potential Φ that is set up by the

charges on the surface of the sphere as well as the charge distribution within the double layer. This force is equal to $-z_\alpha e \nabla \Phi(\mathbf{r}, t)$, where z_α is the valency of the ions of species α and $e > 0$ is the elementary charge. The second force is the Brownian force $\mathbf{F}_\alpha^{Br}$. In the presence of a temperature field $T(\mathbf{r})$, this force is equal to $-k_B T(\mathbf{r}) \nabla \ln\{T(\mathbf{r}) \rho_\alpha(\mathbf{r}, t)\}$ [6],[14]. From eq.(8) one thus finds,

$$\mathbf{j}_\alpha(\mathbf{r}, t) = \left\{ \rho_\alpha(\mathbf{r}, t) \mathbf{v}_s(\mathbf{r}, t) - \frac{\rho_\alpha(\mathbf{r}, t)}{\gamma_\alpha} \left[z_\alpha e \nabla \Phi(\mathbf{r}, t) + k_B T(\mathbf{r}) \nabla \ln\{T(\mathbf{r}) \rho_\alpha(\mathbf{r}, t)\} \right] \right\} . \tag{9}$$

The equation of motion for the ion densities therefore reads,

$$\begin{aligned}
\frac{\partial \rho_\alpha(\mathbf{r}, t)}{\partial t} &= -\nabla \cdot \mathbf{j}_\alpha(\mathbf{r}, t) \\
&= \nabla \cdot \frac{1}{\gamma_\alpha} \left\{ -\gamma_\alpha \rho_\alpha(\mathbf{r}, t) \mathbf{v}_s(\mathbf{r}, t) + z_\alpha e \rho_\alpha(\mathbf{r}, t) \nabla \Phi(\mathbf{r}, t) + k_B \nabla \left[T(\mathbf{r}) \rho_\alpha(\mathbf{r}, t) \right] \right\} . \tag{10}
\end{aligned}$$

The interest here is in stationary solutions of this equation of motion, where all quantities are independent of time. In one dimension, a solution exists for which the fluxes in eq.(9) are zero (such solutions are discussed by van Kampen in ref.[6]). In higher dimensions, however, it is easily verified that no stationary solutions exist for which the fluxes vanish. In the present case we therefore have to solve the full stationary form of the equation of motion (10),

$$0 = \nabla \cdot \left\{ -\gamma_\alpha \rho_\alpha(\mathbf{r}) \mathbf{v}_s(\mathbf{r}) + z_\alpha e \rho_\alpha(\mathbf{r}) \nabla \Phi(\mathbf{r}) + k_B \nabla \left[T(z) \rho_\alpha(\mathbf{r}) \right] \right\} , \tag{11}$$

where the temperature dependence of the ion-friction coefficients γ_α has been neglected. The temperature is assumed to vary only along the z direction with constant spatial increments,

$$T(z) = T + C_T z , \tag{12}$$

where C_T is the constant temperature gradient dT/dz, and T is the temperature at the origin of the sphere. The spatial temperature variation in the vicinity of the sphere is more complicated when there is a substantial difference between the thermal conductivity of the solvent and the core material of the colloidal sphere. Such a temperature variation complicates the analysis considerably, especially for thick double layers. As already mentioned in the introduction, we will assume here that the thermal conductivity of the solvent and the sphere are essentially equal. The effects of different thermal conductivities need additional consideration and is outside the scope of the present paper.

The fluid flow velocity $\mathbf{v}_s$ in eq.(11) has two distinct contributions. The flow is set in motion due to electric body forces that are active within the double layer and there will be a flow around the colloid due to its thermophoretic drift velocity. These flows will distort the structure of the double layer and therefore contribute to the total force on the core of the colloidal sphere. In the beginning of section 8, however, it is argued that the resulting forces can be neglected. Without these convective distortions of the double-layer structure eq.(11) reduces to,

$$0 \; = \; \nabla \cdot \left\{ \, z_\alpha \, e \, \rho_\alpha(\mathbf{r}) \, \nabla \Phi(\mathbf{r}) + k_B \, \nabla \left[\, T(z) \, \rho_\alpha(\mathbf{r}) \, \right] \right\} \; , \tag{13}$$

This equation describes the temperature-induced deformation of the double layer.

Without a temperature gradient, eq.(13) is solved by setting fluxes $\mathbf{j}_\alpha$ equal to $\mathbf{0}$. This immediately leads to the classic Boltzmann connection between the density and the potential [13],

$$\rho_{\alpha,0}(r) \; = \; \rho_{\alpha,0} \, \exp\{-z_\alpha e \, \Phi_0(r)/k_B \, T\} \quad , \quad \text{no temperature gradients} \; , \tag{14}$$

where $\rho_{\alpha,0}$ is the concentration of ion species α outside the double layer. The indices $'0'$ on $\rho_{\alpha,0}(r)$ and $\Phi_0(r)$ are used to indicate the absence of a temperature gradient. The analog of the Boltzmann relation (14) between ion concentrations and the potential in the presence of a temperature gradient will be obtained from eq.(13) in subsection 4.1.

To derive a closed expression for the ion concentrations and electric potential, the relation between ion concentrations and potential must be used in the Poisson equation,

$$\nabla \cdot \left\{ \, \epsilon(z) \, \nabla \Phi(\mathbf{r}) \, \right\} \; = \; - \, \rho(\mathbf{r}) \quad , \quad \text{for} \quad r > R \; , \tag{15}$$

where $\epsilon(z)$ is the dielectric constant of the solvent, which is z-dependent due to its temperature dependence. Furthermore, ρ is the charge density, which is connected to the ion concentrations as,

$$\rho(\mathbf{r}) \; = \; \sum_\alpha z_\alpha \, e \, \rho_\alpha(\mathbf{r}) \; , \tag{16}$$

where the summation ranges over all ion species.

Contrary to the spherically symmetric case in the absence of a temperature gradient, the potential inside the colloidal sphere is non-zero, both due to the temperature dependence of the dielectric constant

ϵ_c of the core material of the sphere and due to the asymmetry of the potential outside the sphere. Since the bulk-core material of the colloid contains no free charges, the potential $\Phi^{(i)}$ inside the sphere follows from the Poisson equation (15) with $\rho = 0$,

$$\nabla \cdot \left\{ \epsilon_c(z) \nabla \Phi^{(i)}(\mathbf{r}) \right\} = 0 \quad , \quad \text{for} \quad r < R , \tag{17}$$

This potential should be well-behaved also at the origin.

The integration of the two Poisson equations and matching to the appropriate boundary conditions (as will be discussed in section 4), constitute an extension of the classic Debye-Hückel theory to include the effect of temperature gradients.

3.2 Boundary conditions

Without a temperature gradient, where the potential is spherically symmetric, the relevant boundary condition relates to the discontinuous jump of the normal component of the electric field across the surface of colloidal sphere due to its surface charges,

$$\epsilon \left[\hat{\mathbf{n}} \cdot \nabla \Phi_0(r) \right]_{r=R} = -\sigma \quad , \quad \text{no temperature gradient} . \tag{18}$$

Here, $\hat{\mathbf{n}} = \mathbf{r}/r$ is the unit normal to the surface of the sphere, pointing away from the origin, and σ is the free surface charge density. The potential in this boundary condition is the potential just outside the core of the sphere, within the solvent. When the dielectric constant of the core of the sphere is constant, the potential inside the core is identically equal to zero, and therefore plays no role in the boundary condition (18). In the presence of a temperature gradient, however, the potential inside the sphere is non-zero. This is due to the non-spherically symmetric potential outside the sphere as well as the spatial variation of the dielectric constant of the sphere due to its temperature dependence. The generalized boundary condition is found from eqs.(15,17),

$$\hat{\mathbf{n}} \cdot \nabla \left[\epsilon(z) \Phi(\mathbf{r}) - \epsilon_c(z) \Phi^{(i)}(\mathbf{r}) \right] = -\sigma \quad , \quad \text{at} \quad r = R , \tag{19}$$

If the free surface charge is due to fully dissociated chemical groups, it is independent of temperature and thus independent of position.

A second boundary condition relates to the continuity of the tangential component of the electric field across the surface of the sphere,

$$\hat{\mathbf{t}} \cdot \nabla \left[\Phi(\mathbf{r}) - \Phi^{(i)}(\mathbf{r}) \right] \; = \; 0 \quad , \quad \text{at} \quad r = R \,, \tag{20}$$

where $\hat{\mathbf{t}}$ is a unit vector tangential to the surface of the colloidal sphere.

The third boundary condition involves a zero normal component of the flux of ions through the surface of the colloidal sphere. From the stationary form of eq.(9) with a z-dependent temperature it follows that,

$$\hat{\mathbf{n}} \cdot \left[z_\alpha \, e \, \nabla\Phi(\mathbf{r}) + k_B T(z) \nabla \ln\{T(z)\, \rho_\alpha(\mathbf{r})\} \right] \; = \; 0 \quad , \quad \text{at} \quad r = R \,. \tag{21}$$

The conditions (20,21) play no role in the standard Debye-Hückel theory, but are important when a temperature gradient is present.

4 Double-Layer Structure within Debye-Hückel Approximation

In this section we extend the well-known Debye-Hückel theory for the double-layer structure to include effects of a small temperature gradient, where the thermal conductivity of the solvent is assumed to be essentially equal to that of the core material of the colloid.

We shall require that the relative temperature change over distances of the order of the extent $R + \kappa^{-1}$ of the "colloidal complex" is small, where R is the radius of the colloid and κ^{-1} is the Debye-screening length, which is given by [13],

$$\kappa^2 \; = \; \frac{e^2}{k_B \, T \, \epsilon} \sum_\alpha \rho_{\alpha,\,0} \, z_\alpha^2 \,, \tag{22}$$

with ϵ the dielectric constant of the solvent and $\rho_{\alpha,\,0}$ the ion concentration outside the double layer in the absence of a temperature gradient. The dimensionless parameter,

$$\Gamma \; \equiv \; \frac{C_T}{(R^{-1} + \kappa)\, T} \; = \; \frac{\kappa \, R}{1 + \kappa \, R} \frac{C_T}{\kappa \, T} \,, \tag{23}$$

is thus assumed to be a small. An expansion with respect to Γ is equivalent to an expansion in terms of temperature gradients.

Within the Debye-Hückel approach taken in the present paper, the second small parameter is the value of the potential energy of a small ion in comparison to its kinetic energy, that is, the parameter,

$$\Lambda \; \equiv \; |\, \frac{z_m \, e \, \Phi_s}{k_B \, T} \,| \,, \tag{24}$$

is the second small parameter in our analysis, where $|\, z_m \,|$ is the largest ion valency and Φ_s is the surface potential of the colloidal sphere.

The theory presented here is valid up to leading order in these two small parameters.

In subsection 4.1 we formulate the relation between the ion concentrations and the electric potential, which extends the Boltzmann formula (14) to include temperature gradients. In subsection 4.2 the Poisson equations are integrated.

4.1   Relation between ion densities and potential

The analog to the Boltzmann relation eq.(14) between ion densities and the electric potential in the presence of a temperature gradients must be obtained from $\nabla \cdot \mathbf{j}_\alpha = 0$ instead of simply setting $\mathbf{j}_\alpha = \mathbf{0}$ as for a homogeneous temperature. The ion flux is now non-zero, and can be written as,

$$\mathbf{j}_\alpha(\mathbf{r}) \; = \; \nabla \times \mathbf{A}(\mathbf{r}) \,, \tag{25}$$

where $\mathbf{A}$ is a vector field. This field can be expressed in terms of the flux by standard methods [15],

$$\mathbf{A}(\mathbf{r}) \; = \; \frac{1}{4\pi} \int d\mathbf{r}' \; \frac{\nabla' \times \mathbf{j}_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,, \tag{26}$$

provided that $\nabla \cdot \mathbf{A} = 0$, which can always be achieved by addition of an irrelevant term of the form $\nabla f(\mathbf{r})$ to $\mathbf{A}$. Combining eqs.(25) and (26) gives,

$$\mathbf{j}_\alpha(\mathbf{r}) \; = \; \frac{1}{4\pi} \nabla \times \int d\mathbf{r}' \; \frac{\nabla' \times \mathbf{j}_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{27}$$

Substitution of eq.(9) for the flux, with the neglect of the small convective contribution, leads to the following integro-differential equation that connects the ion densities with the electric potential,

$$z_\alpha \, e \, \rho_\alpha(\mathbf{r}) \, \nabla\Phi(\mathbf{r}) + k_B \nabla \left[T(z) \, \rho_\alpha(\mathbf{r}) \right] \; = \; \frac{z_\alpha \, e}{4\pi} \nabla \times \int d\mathbf{r}' \; \frac{[\nabla' \rho_\alpha(\mathbf{r}')] \times [\nabla' \Phi(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} \,. \tag{28}$$

The square brackets in the integrand are used to indicate the limitation of the action of the gradient operators ∇' on $\mathbf{r}'$. This is an integro-differential equation that replaces the Boltzmann connection eq.(14) when temperature gradients are present.

As an Ansatz for the relation between the density and potential we write,

$$\rho_\alpha(\mathbf{r}) = \rho_{\alpha,0} \exp\left\{-\frac{z_\alpha e\,\Phi(\mathbf{r})}{k_B\,T(z)}\right\} \exp\left\{F(\mathbf{r})\right\} . \tag{29}$$

A non-zero value for F describes the deviation from local equilibrium, where the form (14) that is valid in the absence of a temperature gradient would hold locally. Equation (28) can be rewritten as,

$$
\begin{aligned}
\nabla_R F(\mathbf{R}) &= -\left(1 + \frac{T}{T(Z)}\,\zeta_\alpha(\mathbf{R})\right)\nabla_R \ln T(Z) \\
&\quad + \frac{1}{4\pi}\frac{T}{T(Z)}\frac{1}{\rho_\alpha(\mathbf{R})}\,\nabla \times \int d\mathbf{R}'\,\rho_\alpha(\mathbf{R}')\,\frac{\left[\nabla_R' F(\mathbf{R}') + \frac{T}{T(Z')}\,\zeta(\mathbf{R}')\,\nabla_R' \ln T(Z')\right] \times \left[\nabla_R' \zeta(\mathbf{R}')\right]}{|\mathbf{R}-\mathbf{R}'|} ,
\end{aligned}
\tag{30}
$$

where $\zeta_\alpha(\mathbf{r}) = z_\alpha e\Phi(\mathbf{r})/k_B T$, and where the dimensionless distances $\mathbf{R} = \kappa\mathbf{r}$ and $\mathbf{R}' = \kappa\mathbf{r}'$ are introduced with κ the inverse Debye-screening length in the absence of a temperature gradient. Furthermore, Z and Z' are the z-components of $\mathbf{R}$ and $\mathbf{R}'$, and ∇_R and ∇_R' are the gradient operators with respect to $\mathbf{R}$ and $\mathbf{R}'$, respectively. Since $|\zeta_\alpha|$ is equal or smaller than the small parameter Λ in eq.(24), and $\kappa^{-1}|\nabla \ln T|$ is of the order of the small parameter Γ in eq.(23), while F is of the order Γ, it follows that the two terms in the integrand on the right hand-side are $\mathcal{O}(\Gamma\Lambda)$ and $\mathcal{O}(\Gamma\Lambda^2)$, respectively. To linear order in both Λ and Γ, the integral on the right hand-side in eq.(30) can therefore be neglected. The first term on the right hand-side simply reduces to $-\nabla_R \ln T(Z)$ up to $\mathcal{O}(\Lambda\Gamma)$. Hence, in terms of the original coordinates we have,

$$\nabla F(\mathbf{r}) + \nabla \ln T(z) = 0 , \tag{31}$$

to linear order in Λ and Γ, so that $F(\mathbf{r}) = C - \ln T(z)$, where C is an integration constant. Since for a uniform temperature, Φ takes the form (14), and outside the double layer where $\Phi = 0$ the density $\rho_\alpha(\mathbf{r})$ must be equal to $\rho_{\alpha,0}$, it follows from eq.(29) that $C = \ln T$, and hence $\exp\{F(\mathbf{r})\} = T/T(z)$. To leading order in temperature gradients and for small potentials, the connection between the ion density and electric potential thus takes the form,

$$\rho_\alpha(\mathbf{r}) = \frac{T}{T(z)}\,\rho_{\alpha,0}\,\exp\left\{-z_\alpha e\,\Phi(\mathbf{r})/k_B\,T(z)\right\} . \tag{32}$$

17

This in the analogon of the Boltzmann relation (14) between ion densities and the potential in case of a small temperature gradients and small potentials.

The prefactor $T/T(z)$ of the local Boltzmann exponential in eq.(32) has the following interpretation. Thermodiffusion of the small ions outside the double layer is described, within the present framework, by eq.(13) with Φ set equal to 0. It follows from that expression for the flux of ions, that in the stationary state,

$$\rho_\alpha(\mathbf{r}) \; = \; \frac{T}{T(z)} \, \rho_{\alpha,0} \; . \tag{33}$$

This reproduces eq.(32) for $\Phi = 0$, as it should. The conclusion is that the prefactor $T/T(z)$ in eq.(32) is the result of thermal diffusion of the small ions, which are supposed to have achieved their stationary state during the measurement of the thermal diffusion coefficient of the colloidal sphere.

Under certain experimental conditions, the small ions may not achieve a stationary state during a measurement, in which case the concentration of the small ions outside the double layer is not given by eq.(33) but is constant and equal to $\rho_{\alpha,0}$. In that case, the prefactor $T/T(z)$ in eq.(32) should be omitted. A possible reason that the stationary state for the small ions is not achieved during a measurement is that the sample container is relatively large, so that is takes a long time for the small ions to reach a stationary state. In a Thermal Diffusion Forced Rayleigh Scattering (TDFRS) experiment, the small ions reach a stationary state on a time scale that is very small as compared to the time it takes for significant colloid displacements. The typical pitch of the temperature grating is about $10 \; \mu m$, and small-ion displacements of this order are very fast as compared to sub-micron displacements of the colloids. This is different for particle-tracking microscopy experiments. Here the linear dimensions of the sample volume is of the order of mm's, so that small ions need a relatively long time to establish thermal equilibrium. During the measurement of sub-micron displacements of the colloids, the small ions will not have established thermal equilibrium. In an experiment where only the stationary state is probed, the parameter χ is of course equal to 2. To distinguish between the two cases, the parameter χ is introduced as,

$$\rho_\alpha(\mathbf{r}) \; = \; \left(\frac{T}{T(z)}\right)^{\chi-1} \, \rho_{\alpha,0} \, \exp\left\{-z_\alpha e \, \Phi(\mathbf{r})/k_B \, T(z)\right\} \; . \tag{34}$$

According to the above discussion we have,

$$
\begin{aligned}
\chi \;=\; & 1 \quad \text{homogeneous ion concentrations outside the double layer ,} \\
\;=\; & 2 \quad \text{small ions reached their thermal stationary state .}
\end{aligned}
\tag{35}
$$

Note that in case $\chi = 1$, eq.(34) corresponds to a local equilibrium Boltzmann distribution of ions.

For larger temperature gradients and/or larger potentials, the integro-differential equation (28) must be solved together with the Poisson equations. This seems a formidable task that is probably not amenable to analytical treatment.

4.2 The temperature-induced asymmetric part of the potential

The charge density and electric potential within the double layer follow from eq.(34) and the Poisson equation (15). The z-dependence of the dielectric constant $\epsilon(z)$ is due to the temperature gradient, so that $\nabla \epsilon = (d\epsilon/dT)\nabla T(z)$ and hence, from eqs.(12,23),

$$
\epsilon(z) \;=\; \epsilon \left[1 + \Gamma \, \frac{1 + \kappa R}{\kappa R} \, \frac{d \ln \epsilon}{d \ln T} \, \kappa z \right] ,
\tag{36}
$$

to leading order in temperature gradients. Using eqs.(34,16) gives, to leading order in temperature gradients and the potential $z_\alpha e \Phi / k_B T$,

$$
\nabla^2 \Phi(\mathbf{r}) \;=\; \kappa^2 \left(\frac{T}{T(z)} \right)^{\chi} \Phi(\mathbf{r}) - \Gamma \, \frac{1 + \kappa R}{R} \, \frac{d \ln \epsilon}{d \ln T} \left[\kappa^2 \left(\frac{T}{T(z)} \right)^{\chi} z \, \Phi(\mathbf{r}) + \frac{\partial \, \Phi(\mathbf{r})}{\partial z} \right] .
\tag{37}
$$

We now write $\Phi = \Phi_0 + \Phi_1$, where Φ_0 is the potential for a constant temperature T and where Φ_1 is the contribution due to the temperature gradient, which is of the order Γ as compared to Φ_0. The leading order potential Φ_0 satisfies the Poisson-Boltzmann equation for a homogeneous temperature (this is eq.(37) in the absence of temperature gradients),

$$
\nabla^2 \Phi_0(r) \;=\; \kappa^2 \, \Phi_0(r) .
\tag{38}
$$

The solution of eqs.(38,18) that tends to zero outside the double layer is the well-known Yukawa potential,

$$
\Phi_0(r) \;=\; \frac{Q}{4 \pi \epsilon} \, \frac{\exp\{\kappa R\}}{1 + \kappa R} \, \frac{\exp\{-\kappa r\}}{r}
\tag{39}
$$

19

where $Q = 4\pi\sigma R^2$ is the total free charge on the surface of the colloidal sphere.

Equation (37) can now be expanded to leading order temperature gradients to obtain the following inhomogeneous differential equation for Φ_1,

$$\left(\nabla^2 - \kappa^2\right)\Phi_1(\mathbf{r}) = \Gamma\frac{Q}{4\pi\epsilon R}\exp\{\kappa R\}\frac{\partial}{\partial z}\left\{\left[\chi + \frac{d\ln\epsilon}{d\ln T}\right]\kappa\exp\{-\kappa r\} - \frac{d\ln\epsilon}{d\ln T}\frac{\exp\{-\kappa r\}}{r}\right\}. \quad (40)$$

We approximated here,

$$\left(\frac{T}{T(z)}\right)^\chi - 1 \approx -\chi\frac{C_T}{T}z = -\chi\Gamma\frac{1+\kappa R}{\kappa R}\kappa z, \quad (41)$$

to leading order in temperature gradients, that is for small values of Γ.

The potential $\Phi^{(i)}$ inside the core of the sphere satisfies the Poisson equation (17). Noting that $\Phi^{(i)}$ is first order in Γ, a similar expansion with respect to temperature gradients as above leads to,

$$\nabla^2\Phi^{(i)}(\mathbf{r}) = 0 \quad, \quad \text{for} \quad r < R. \quad (42)$$

Since this potential should be well-behaved at the origin, the solution of the Poisson equation that is appropriate to the present problem is,

$$\Phi^{(i)}(\mathbf{r}) = C^{(i)}z \quad, \quad \text{for} \quad r < R, \quad (43)$$

where $C^{(i)}$ is an integration constant.

The solution of the differential equation (40) for Φ_1 and the determination of integration constants are discussed in appendix B. The temperature-induced asymmetric part of the potential is most conveniently written as,

$$\Phi_1(\mathbf{r}) = \Gamma\frac{Q}{16\pi\epsilon R}\exp\{-\kappa(r-R)\}\left\{\chi + \frac{d\ln\epsilon}{d\ln T}\left(1 - \frac{2}{\kappa r}\right) - A\left(\frac{R}{r}\right)^3(1+\kappa r)\right\}\kappa z, \quad (r \geq R), \quad (44)$$

where the constant A is equal to,

$$A = \frac{\chi\left(\kappa R - 1 + \frac{\epsilon_c}{\epsilon}\right) + \frac{d\ln\epsilon}{d\ln T}\left\{1 + \kappa R + \frac{\epsilon_c}{\epsilon}\left(1 - \frac{2}{\kappa R}\right)\right\}}{2 + 2\kappa R + (\kappa R)^2 + \frac{\epsilon_c}{\epsilon}(1 + \kappa R)}. \quad (45)$$

The potential inside the core is written as,

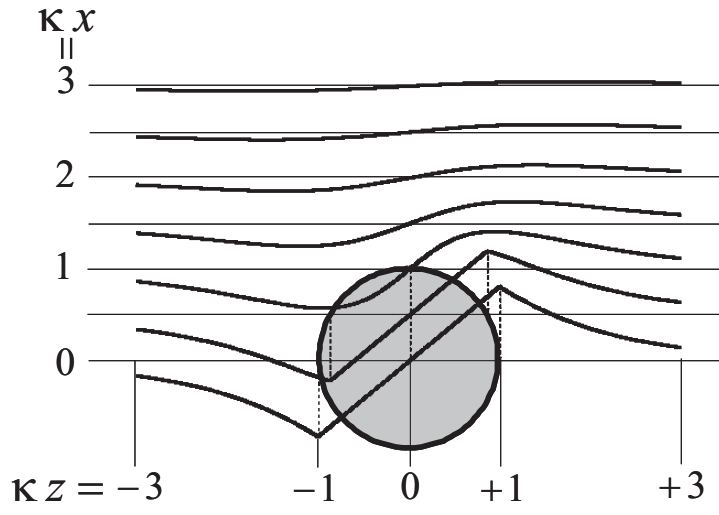$$\Phi^{(i)}(\mathbf{r}) = \Gamma\frac{Q}{16\pi\epsilon R}B\kappa z \quad, \quad (r \leq R), \quad (46)$$

20

Figure 2: The asymmetric part of the electric potential (44-47) in the xz-plane. The thick lines are plots of the potential as a function of κz (as indicated by the number on the horizontal axis) for various values of κx (as indicated by the numbers on the vertical axis). Each curve corresponds to a fixed value of κx from 0 to 3 in steps of 0.5. The temperature increases with z. Here, $\kappa R = 1$, $\Gamma = 0.1$, $\chi = 2$, $d\ln\epsilon/d\ln T = -1.34$ and $\epsilon_c/\epsilon = 1$.

where B is a constant equal to,

$$
B = \frac{\chi\left(3 + 2\kappa R\right) - \frac{d\ln\epsilon}{d\ln T}\left(3 + 2\kappa R + \frac{4}{\kappa R}\right)}{2 + 2\kappa R + (\kappa R)^2 + \frac{\epsilon_c}{\epsilon}\left(1 + \kappa R\right)} . \tag{47}
$$

It is easily confirmed that the potential is continuous across the surface area of the sphere, that is, $\Phi(\mathbf{r}) = \Phi^{(i)}(\mathbf{r})$ for $r = R$.

The above expressions (44-47) constitute the extension of the well-known Debye-Hückel approximation for the double-layer potential when a small gradient in temperature is present. The asymmetric part of the potential is plotted in xz-plane in Fig.2 for $\kappa R = 1$, $\Gamma = 0.1$, $\chi = 2$, $d\ln\epsilon/d\ln T = -1.34$ and $\epsilon_c/\epsilon = 1$.

5 The Internal Force $\mathbf{F}_W$

The internal electrostatic energy W is calculated by means of a charging process, where the free surface charge density of the colloidal particle is quasi-statically build up from 0 to its final value σ. During charging, the surface charge density is equal to $\lambda\sigma$, where λ varies from 0 to 1. The change in electrostatic energy by increasing the surface charge density by an infinitesimal amount $d\sigma = \sigma\,d\lambda$ is equal to,

$$
\delta W = \sigma \oint_{\partial V} dS\, \Phi(\mathbf{r}\,|\,\lambda)\,d\lambda , \tag{48}
$$

21

where $\Phi(\mathbf{r} \mid \lambda)$ is the electric potential at point $\mathbf{r}$ when the surface charge density is equal to $\lambda \sigma$. The free surface charges are assumed here to be uniformly distributed over the surface of the sphere. Inhomogeneous charge distributions can arise when chemical groups are not fully dissociated and the dissociation constant is temperature dependent. Here we assume the chemical groups to be fully dissociated. To within the Debye-Hückel approximation for small potentials, the potential $\Phi(\mathbf{r} \mid \lambda)$ corresponding to a surface charge density $\lambda \sigma$ is equal to $\lambda \Phi(\mathbf{r})$, with $\Phi(\mathbf{r})$ the electrostatic potential of the fully charged sphere. Hence, from eq.(48),

$$W = \sigma \int_0^1 d\lambda \, \lambda \oint_{\partial V} dS \, \Phi(\mathbf{r}) = \frac{1}{2} \sigma \oint_{\partial V} dS \, \Phi(\mathbf{r}) \,. \tag{49}$$

In case of a system containing free bulk charges instead of free surface charges, this charging procedure, in combination with Poisson's equation and a partial integration, leads to the classic expression $W = \frac{1}{2} \int d\mathbf{r} \, \rho(\mathbf{r}) \, \Phi(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r} \, \epsilon(\mathbf{r}) \mid \nabla \Phi(\mathbf{r}) \mid^2$, where ρ is the free charge density and ϵ is the dielectric constant. For dielectric media, this result is generally valid also for high potentials due to the linearity of the Maxwell equations. The fundamental difference with the present case of double layers is that charges within the double layer are induced during charging of the surface of the colloidal sphere in a way that is governed by Boltzmann statistics, in addition to electrostatics. This statistical-mechanics aspect of the charge density within the double layer destroys the linear relation ship between surface charge density and surface potential, except when potentials are low enough to linearize the Boltzmann exponent. The result (49) is therefore only valid within the Debye-Hückel approximation. To leading order in temperature gradients, the potential in eq.(49) can be taken equal to the surface potential $\Phi_{0,s}$ of the unperturbed, spherically symmetric double-layer. It thus follows from eqs.(4,49) that,

$$\mathbf{F}_W = -\frac{1}{2} \nabla T \frac{d}{dT} [Q \Phi_{0,s}] \,, \tag{50}$$

to leading order in temperature gradients. Here, $Q = 4\pi R^2 \sigma$ is the total free charge on the sphere with radius R. This expression for the force reproduces the irreversible-thermodynamics prediction in ref.[2].

The well-known Debye-Hückel connection between the total free charge Q of the sphere due to dissociated chemical surface groups and the unperturbed surface potential follows from eq.(39) as,

$$\Phi_{0,s} = \frac{Q}{4\pi \epsilon R} \frac{1}{1 + \kappa R} \,, \tag{51}$$

22

For a fixed free surface charge density, independent of temperature, eq.(50) for the internal force thus gives,

$$\mathbf{F}_W = -\frac{\nabla T(z)}{T} \frac{Q^2}{24\,\pi\,\epsilon\,R} \left\{ H_1^W(\kappa\,R) - \frac{d\ln\epsilon}{d\ln T}\,H_2^W(\kappa\,R) \right\}, \tag{52}$$

where the functions H_1^W and H_2^W are equal to,

$$\begin{aligned}
H_1^W(x) &= \frac{3\,x}{2\,(\,1+x\,)^2}, \\
H_2^W(x) &= \frac{3\,(\,2+x\,)}{2\,(1+x)^2}.
\end{aligned} \tag{53}$$

These functions are plotted in Fig.3a,b. In the derivation of this result it is used that (see eq.(22) for the inverse Debye length),

$$\frac{d\,\kappa}{dT} = -\frac{\kappa}{2\,T} \left\{ 1 + \frac{d\ln\epsilon}{d\ln T} \right\}. \tag{54}$$

For water, $d\ln\epsilon/d\ln T = -1.34$, so that the Debye length increases with decreasing temperature. This is why in Fig.1b the distorted double layer has a larger extent at lower temperatures and why in Fig.1a the dotted circle, which marks the thickness of the double layer, is larger for the displaced sphere towards lower temperatures.

The expressions (52,53) reproduce the irreversible-thermodynamics prediction for the thermophoretic force [2], provided the total free charge Q is independent of temperature.

6   The Electric Force $\mathbf{F}_{el}$

In order to calculate the electric force in eq.(5), the total surface charge density σ_t which includes free surface charges and solvent polarization charges, is expressed in terms of the electrostatic potential as (as before, ϵ_0 is the dielectric constant of vacuum),

$$\sigma_t(\mathbf{r}) = -\epsilon_0\,\hat{\mathbf{n}} \cdot \left\{ \nabla\Phi(\mathbf{r}) - \nabla\Phi^{(i)}(\mathbf{r}) \right\} = \sigma\,\frac{\epsilon_0}{\epsilon} - \epsilon_0\,\hat{\mathbf{n}} \cdot \left\{ \nabla\Phi_1(\mathbf{r}) - \nabla\Phi^{(i)}(\mathbf{r}) \right\}, \tag{55}$$

where in the second equation the boundary condition (18) for the unperturbed potential is used. Furthermore, $\hat{\mathbf{n}}$ is the unit normal on the surface of the colloidal sphere pointing into the solvent. To first order

in temperature gradients, the electric force (5) is thus equal to,

$$\mathbf{F}_{el} = -\sigma \frac{\epsilon_0}{2\,\epsilon} \oint_{\partial V} dS \left\{ \nabla\Phi_1(\mathbf{r}) + \nabla\Phi^{(i)}(\mathbf{r}) \right\} + \frac{\epsilon_0}{2} \oint_{\partial V} dS\, \hat{\mathbf{n}} \cdot \left\{ \nabla\Phi_1(\mathbf{r}) - \nabla\Phi^{(i)}(\mathbf{r}) \right\} \nabla\Phi_0(r)\,, \qquad (56)$$

where it is used that $\nabla\Phi_0 \sim \mathbf{r}/r$, so that the corresponding surface integral vanishes. The first term on the right hand-side is the force on the free surface charges where the polarization shielding of the charge is accounted for by the factor ϵ_0/ϵ, while the second term is the force on non-uniformly distributed polarization charges. From the expressions (44-47) for the potentials and using that $\nabla\Phi_0(r) = -(\mathbf{r}/r)\,(\sigma/\epsilon)$ on the surface of the sphere, it is found with some effort that,

$$\mathbf{F}_{el} = -\frac{\nabla T}{T} \frac{\epsilon_0}{\epsilon} \frac{Q^2}{24\,\pi\,\epsilon\,R} \left\{ \chi\, H_1^{el}(\kappa\,R) - \frac{d\ln\epsilon}{d\ln T}\, H_2^{el}(\kappa\,R) \right\}\,, \qquad (57)$$

where the functions H_1^{el} and H_2^{el} are equal to,

$$
\begin{aligned}
H_1^{el}(x) &= \frac{x\,(3+2x)\left\{2 + \frac{\epsilon_c}{\epsilon}\right\}}{2\,(1+x)\left\{2 + 2x + x^2 + \frac{\epsilon_c}{\epsilon}\,(1+x)\right\}}\,, \\
H_2^{el}(x) &= \frac{8 - 2x - 4x^2 - 4x^3 + \frac{\epsilon_c}{\epsilon}\,(4 - x - 2x^2)}{2\,(1+x)\left\{2 + 2x + x^2 + \frac{\epsilon_c}{\epsilon}\,(1+x)\right\}}\,.
\end{aligned}
\qquad (58)
$$

The interpretation of the prefactor ϵ_0/ϵ in eq.(57) for the electric force is that the total charge on which the potential acts is dielectrically screened. Free charges are effectively diminished by a factor ϵ_0/ϵ due to polarization of the solvent.

The functions H_1^{el} and H_2^{el} are plotted in Fig.3c,d (for $\epsilon_c/\epsilon = 0, 1$ and 10). As can be seen, $H_1^{el} = 0$ both for very thin and thick double layers, while $H_2^{el} = 2$ for thick double layers and $H_2^{el} = -2$ for thin double layers. For very thin double layers there is an asymmetry in the total surface charge density due to the temperature dependence of the dielectric constant, resulting in a non-zero thermophoretic force.

7 The solvent-friction force $\mathbf{F}_{sol}$

Since fluid elements within the double layer are charged and experience an electric field, a body force acts on these volume elements. If the mechanical coupling between the individual small ions and fluid molecules is complete, the body force on a fluid element at position $\mathbf{r}'$ is equal to $-\rho_t(\mathbf{r}')\nabla'\Phi(\mathbf{r}')$, where ρ_t is the total charge density. This charge density includes both free charges due to different concentrations
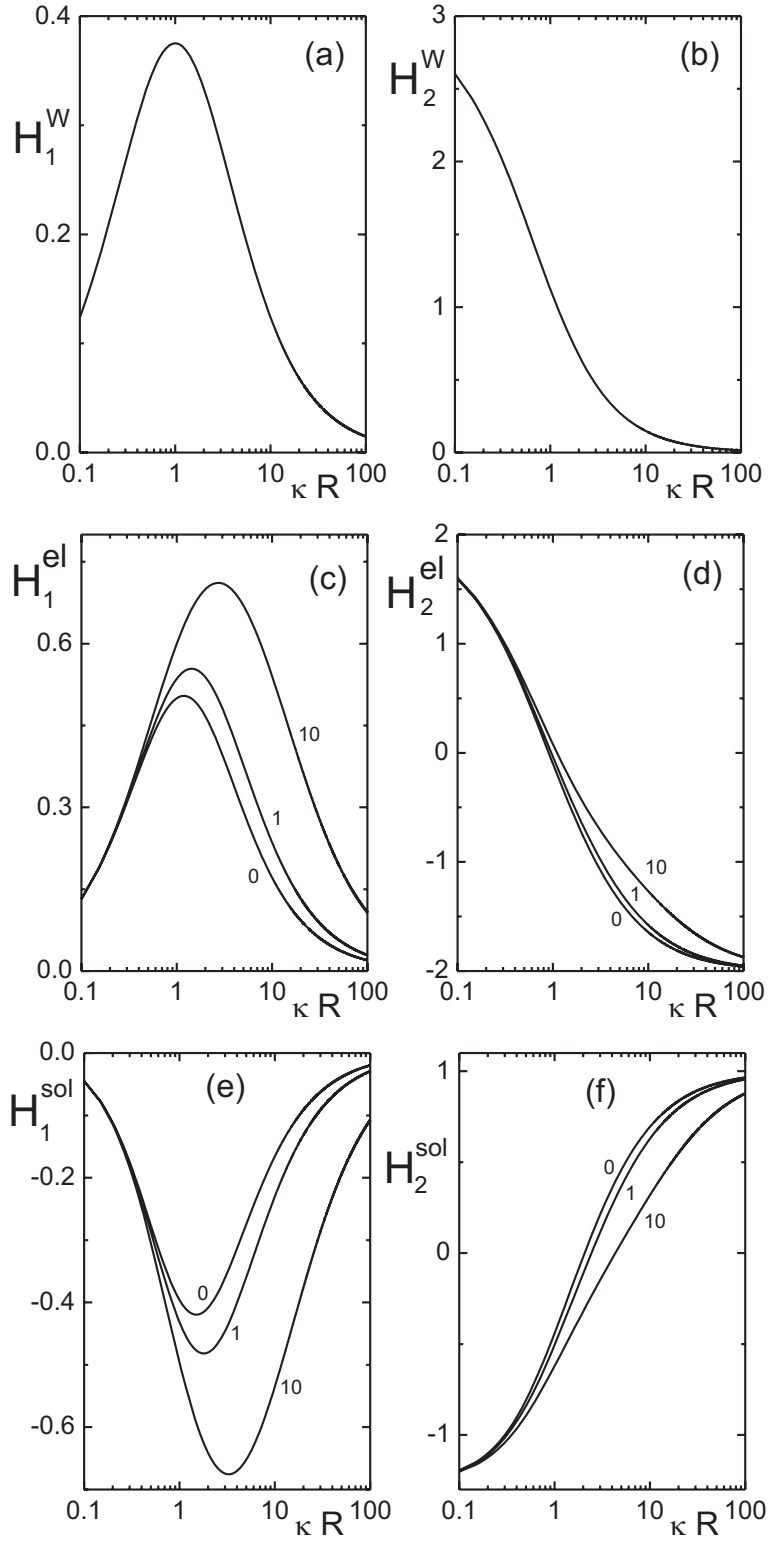
Figure 3: The functions (a) H_1^W, (b) H_2^W (see eq.(53)), (c) H_1^{el}, (d) H_2^{el} (see eq.(58)), (e) H_1^{sol} and (f) H_2^{sol} (see eq.(67)), for $\epsilon_c/\epsilon = 0$, 1 and 10, as indicated in the figures. Note that H_1^W and H_2^W are independent of ϵ_c/ϵ.

25

of small ions and charges due to polarization of the solvent. Once a fluid flow is set up, friction with the surface of the colloidal sphere leads to forces with which surface elements act onto the fluid. Let $\mathbf{f}(\mathbf{r}')$ denote the force per unit area with which a surface element on the sphere's surface at $\mathbf{r}'$ acts on the fluid. For the small Reynolds numbers under consideration here, and on the diffusive time scale, the fluid flow velocity at a point $\mathbf{r}$ (with $r > R$) in the stationary state is given by,

$$\mathbf{v}(\mathbf{r}) = -\int_{r'>R} d\mathbf{r}'\, \mathbf{T}(\mathbf{r}-\mathbf{r}') \cdot [\,\rho_t(\mathbf{r}')\,\nabla'\Phi(\mathbf{r}')\,] + \oint_{\partial V} dS'\, \mathbf{T}(\mathbf{r}-\mathbf{r}') \cdot \mathbf{f}(\mathbf{r}') \quad, \quad r \geq R\,, \tag{59}$$

where $\mathbf{T}$ is the Oseen tensor,

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_0\,r}\left[\hat{\mathbf{I}} + \frac{\mathbf{r}\,\mathbf{r}}{r^2}\right]\,, \tag{60}$$

with η_0 the shear viscosity of the solvent, $\hat{\mathbf{I}}$ is the identity and $\mathbf{r}\,\mathbf{r}$ is the dyadic product of $\mathbf{r}$. This expression for the solvent flow velocity can be regarded as the "integral form of the Navier-Stokes equation", since the friction forces $\mathbf{f}$ are functions of velocity gradients (at the surface of the colloid). The variation of the solvent viscosity due to temperature variations can be neglected to leading order in temperature gradients, since all the forces are already of first order in temperature gradients. For the same reason, the variation of the viscosity due to spatial variations of ion-concentration can be neglected.

The force $\mathbf{F}_{sol}$ that the solvent exerts on the sphere is given in eq.(6). The integral over the surface forces $\mathbf{f}$ can be obtained directly from eq.(59), without having to calculate the full velocity profile, as follows. We follow here a different route to calculate the friction force as compared to Teubner [16] in connection with electrophoresis, where a generalization of the hydrodynamic reciprocal theorem has been employed to cast the total solvent-friction force into a tractable form. Here, we use a convenient mathematical identity that involves a surface integral of the Oseen tensor. Since for stick boundary conditions we have $\mathbf{v}(\mathbf{r}) = \mathbf{0}$ for $\mathbf{r} \in \partial V$, it follows from eq.(59) after integration with respect to $\mathbf{r}$ over ∂V, that,

$$\oint_{\partial V} dS' \oint_{\partial V} dS\, \mathbf{T}(\mathbf{r}-\mathbf{r}') \cdot \mathbf{f}(\mathbf{r}') = \int_{r'>R} d\mathbf{r}' \oint_{\partial V} dS\, \mathbf{T}(\mathbf{r}-\mathbf{r}') \cdot [\,\rho_t(\mathbf{r}')\,\nabla'\Phi(\mathbf{r}')\,]\,. \tag{61}$$

The integral of the Oseen tensor over the surface area of the sphere with its center at the origin is equal to [17],

$$\mathbf{M}(\mathbf{r}') \equiv \frac{3\eta_0}{2R}\oint_{\partial V} dS\, \mathbf{T}(\mathbf{r}-\mathbf{r}') = \frac{3}{4}\left[\frac{R}{r'} + \frac{1}{3}\left(\frac{R}{r'}\right)^3\right]\hat{\mathbf{I}} + \frac{3}{4}\left[\frac{R}{r'} - \left(\frac{R}{r'}\right)^3\right]\frac{\mathbf{r}'\,\mathbf{r}'}{r'^2}\,, \quad \text{for } r' \geq R\,. \tag{62}$$

26

Note that "monopole terms" $\sim 1/r'$ appear in this expression. These monopole terms are due to the non-zero *hydrodynamic* force on the core of the particle. Hence, from eqs.(6,61),

$$\mathbf{F}_{sol} = -\int_{r>R} d\mathbf{r}\, \rho_t(\mathbf{r})\, \mathbf{M}(\mathbf{r}) \cdot \nabla \Phi(\mathbf{r}) \,. \tag{63}$$

Note that this force vanishes when the charge density and potential are spherically symmetric. Without temperature variations, pressure gradients are set up in the solvent that compensate the electrical forces. In the presence of temperature gradients, the asymmetry of the double-layer structure requires friction forces, and hence solvent flow, to compensate the electric forces.

In order to obtain the force due to friction with the solvent, it is not necessary to calculate the entire flow field $\mathbf{v}(\mathbf{r})$ around the sphere. It would be interesting to calculate the full flow field and measure it, for example by trapping a large colloidal sphere in an organic solvent (in order to obtain extended double layers) and using small fluorescent colloidal probes to visualize the flow field.

Using that $\epsilon_0 \nabla^2 \Phi = -\rho_t$ and $\nabla \cdot (\epsilon \nabla \Phi) = -\rho$, it follows that,

$$\rho_t(\mathbf{r}) = \rho(\mathbf{r}) \frac{\epsilon_0}{\epsilon} + \epsilon_0 \left[\nabla \ln \epsilon(z)\right] \cdot \left[\nabla \Phi(\mathbf{r})\right] \,. \tag{64}$$

To first order in temperature gradients and within the Debye-Hückel approximation, it follows from eqs.(34,22) that this equation can be written as,

$$\rho_t(\mathbf{r}) = -\epsilon_0 \kappa^2 \left[\Phi_0(\mathbf{r}) + \Phi_1(\mathbf{r})\right] + z \frac{C_T}{T}\left[\epsilon_0 \kappa^2 \chi \Phi_0(\mathbf{r}) + \epsilon_0 \frac{d\ln\epsilon}{d\ln T}\frac{1}{r}\frac{d\Phi_0(r)}{dr}\right] \,. \tag{65}$$

Substitution of eqs.(39,44,45,62) into eq.(63) gives, after a lengthy calculation,

$$\mathbf{F}_{sol} = -\frac{\nabla T}{T}\frac{\epsilon_0}{\epsilon}\frac{Q^2}{24\pi\epsilon R}\left\{\chi H_1^{sol}(\kappa R) - \frac{d\ln\epsilon}{d\ln T} H_2^{sol}(\kappa R)\right\} \,, \tag{66}$$

where the functions H_1^{sol} and H_2^{sol} are equal to,

$$
\begin{aligned}
H_1^{sol}(x) &= -\frac{x}{(1+x)^2}\left[\frac{3}{2}E(x) + \frac{x\left\{4 + x + 2\frac{\epsilon_c}{\epsilon}(1+x)\right\}}{2\left\{2 + 2x + x^2 + \frac{\epsilon_c}{\epsilon}(1+x)\right\}}\right]\,, \\
H_2^{sol}(x) &= \frac{x}{(1+x)^2}\left[\frac{3}{2}E(x) - \frac{10 + 30x + 17x^2 + 4x^3 - 4x^4 + \frac{\epsilon_c}{\epsilon}(5 + 15x + 10x^2)}{4x\left\{2 + 2x + x^2 + \frac{\epsilon_c}{\epsilon}(1+x)\right\}}\right]\,, \tag{67}
\end{aligned}
$$

with,

$$E(x) = 2x\,\exp\{2x\}\int_x^\infty dz\,\frac{\exp\{-2z\}}{z}\,. \tag{68}$$

27

The functions H_1^{sol} and H_2^{sol} are plotted in Fig.3e,f (for $\epsilon_c/\epsilon = 0, 1$ and 10). As for the corresponding function H_2^{el} for the electric force, the function H_2^{sol} asymptotes to a finite value, equal to 1, for thin double layers. Again, this is due to the temperature dependence of the dielectric constant, which results in an asymmetric dielectric screening of free charges. Note that the solvent friction force is typically opposite, but smaller in magnitude, as compared to the electric force.

8   The Soret Coefficient

The velocity $\mathbf{v}_c$ that the colloidal particle attains on average due to the temperature-gradient induced force $\mathbf{F}_T = \mathbf{F}_{el} + \mathbf{F}_W + \mathbf{F}_{sol}$ is equal to $\mathbf{F}_T/\gamma_c$, where γ_c is the friction coefficient of the colloidal sphere with the solvent.

Electrolyte friction effects are known to be less than 5% as compared to friction of the solvent with the core of the colloidal sphere, both experimentally [18] and theoretically [19],[20]. The friction coefficient γ_c is therefore to a good approximation equal to the Stokes friction coefficient $\gamma_c = 6\pi\eta_0 R$ of the core, where η_0 is the shear viscosity of the solvent. This approximation neglects the force that results from the convection-induced deformation of the double layer where flow is due to motion of the sphere. As discussed in sections 2 and 3, the deformation of the double layer due to the temperature-gradient induced solvent flow is similarly neglected. The corresponding force that adds to the thermophoretic force $\mathbf{F}_T$ is expected to be equally small, since, just as for the well-known electrolyte friction effect, this force is due to convection-induced deformation of the double layer.

To within linear response to temperature gradients, the total force can be written as $\mathbf{F}_T = -A\,\nabla T$, where the amplitude A has been specified in previous sections for each of the separate forces that contribute to the total force. Hence, $\mathbf{v}_c = -(A/\gamma_c)\,\nabla T$. According to the continuity equation $\partial\rho_c/\partial t = -\nabla\cdot(\rho_c\,\mathbf{v}_c)$ for the colloidal concentration ρ_c, it follows that the contribution of temperature gradients to the continuity equation reads $\partial\rho_c/\partial t = D_T^{(dl)}\nabla^2 T(z)$, where $D_T^{(dl)} = D_0\,\rho_c\,\beta\,A$ is the double-layer contribution to the thermal diffusion coefficient (here $D_0 = k_B T/\gamma_c$ is the Einstein mass diffusion coefficient and $\beta = 1/k_B T$). In the derivation of this result it is assumed that both gradients *and* deviations from average values are small, so that terms like $[\nabla T]\cdot[\nabla\gamma_c]$ can be neglected, being of second order in deviations from average

28

values. When such deviations from spatially independent average values are not small, the velocity of the colloids can not be directly connected to the Soret coefficient, as discussed by Bringuier in ref.[21]. In that case, terms of the form $[\nabla T] \cdot [\nabla \gamma_c]$ can not be neglected. The expression that we obtain here for the thermal diffusion coefficient, however, can be used to study situations where such deviations are not small. In such cases, however, the concentration and temperature dependence of both the mass-diffusion and thermal diffusion coefficient should be accounted for in the divergence of the flux. The Soret coefficient $S_T = D_T^{(dl)}/\rho_c D_0 = \beta A$ is thus found from eqs.(57,58) for the electric force, eqs.(52,53) for the internal force and eqs.(66,67) for the solvent friction force, to be equal to,

$$T \, S_T \;=\; T \, S_T^W \;+\; \frac{\epsilon_0}{\epsilon} \, \frac{\beta \, Q^2}{16 \, \pi \, \epsilon \, R} \, \frac{\kappa \, R}{(1 + \kappa \, R)^2} \left[\chi \, G_1(\kappa \, R) - \frac{d \ln \epsilon}{d \ln T} \, G_2(\kappa \, R) \right] , \tag{69}$$

where S_T^W is the contribution to the Soret coefficient due to the temperature dependence of the internal energy W of the double layer,

$$T \, S_T^W \;=\; \frac{\beta \, Q^2}{16 \, \pi \, \epsilon \, R} \, \frac{\kappa \, R}{(1 + \kappa \, R)^2} \left[1 - \frac{d \ln \epsilon}{d \ln T} \left(1 + \frac{2}{\kappa \, R} \right) \right] . \tag{70}$$

The functions G_1 and G_2 in eq.(69) describe the contribution to the Soret coefficient due to the temperature-induced deformation of the double layer. These functions take the relatively simple form,

$$\begin{aligned} G_1(x) &= -E(x) + 1 , \\ G_2(x) &= E(x) - \frac{2}{3} \, x - 2 + \frac{1}{2} \, x^{-1} , \end{aligned} \tag{71}$$

where E is defined in eq.(68). The functions $G_j^\star \equiv x \, G_j/(1 + x)^2$ are plotted in Fig.4. Note the rather satisfying and surprisingly simple result for the total contribution of the double-layer deformation to the Soret coefficient. The functions in eq.(71) are quite simple as compared to the complicated expressions (58) and (67) for the separate contributions stemming from the electric and solvent-friction force, respectively. In particular, the dependence of the Soret coefficient on the dielectric constant ϵ_c of the core material of the colloidal sphere drops out.

To make the dependence of the Soret coefficient on the radius of the colloidal sphere explicit, one could rewrite,

$$\frac{\beta \, Q^2}{24 \, \pi \, \epsilon \, R} \;=\; \frac{1}{6} \left(\frac{4 \, \pi \, l_B^2 \, \sigma}{e} \right)^2 \left(\frac{R}{l_B} \right)^3 , \tag{72}$$
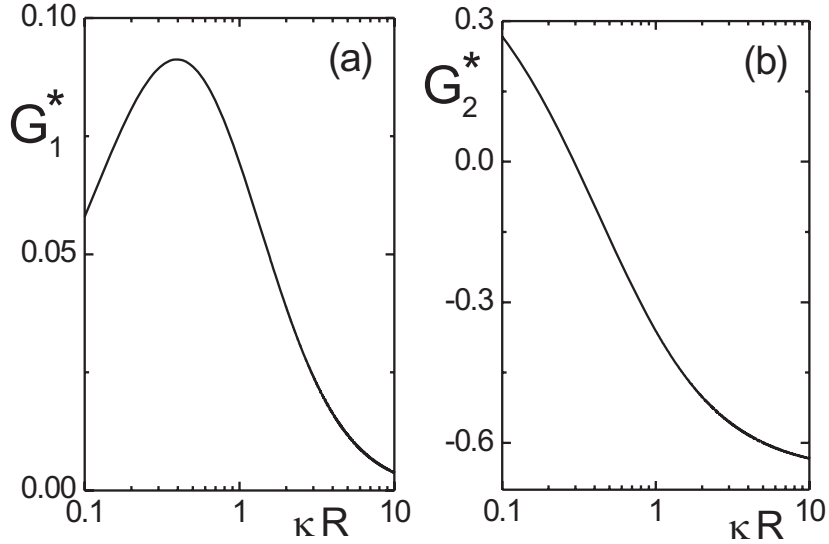
Figure 4: The functions (a) $G_2^\star(x) \equiv x\, G_1(x)/(1+x)^2$ and (b) $G_2^\star(x) \equiv x\, G_2(x)/(1+x)^2$ that determine the contributions to the Soret coefficient in eq.(69) due to the temperature-induced deformation of the double layer.

in eqs.(69,70), where $l_B = e^2/4\pi\epsilon k_B T$ is the Bjerrum length (0.71 nm for water at room temperature).

It has been shown in ref.[2] that the internal, "irreversible-thermodynamics" contribution to the Soret coefficient describes experimental data for aqueous systems quite accurately. Both the dependence of the Soret coefficient on salt concentration and the radius of the colloids are well described by S_T^W. The obvious reason for this is the high polarizability of water (for which $\epsilon_0/\epsilon = 1/78$ at room temperature), which leads to small contributions ΔS_T due to the double-layer deformation (the second term on the right hand-side in eq.(69)). However, for very thin double layers, the internal Soret coefficient S_T^W tends to zero for very thin double layers (see Fig.3a,b), whereas the deformation contribution ΔS_T remains finite (see Fig.4b). The experiments in ref.[3] are on carboxylated-modified polystyrene spheres, which are indeed very large in comparison to their double-layer thickness. The reason that S_T^W nevertheless describes these data accurately is due to the fact that ΔS_T is almost independent of the Debye length when the Debye length is small. This can be seen from the three left figures in Fig.5, where S_T^W and ΔS_T are plotted as functions of the Debye length for the three radii of the particles used in experiments in ref.[3]. A comparison of the
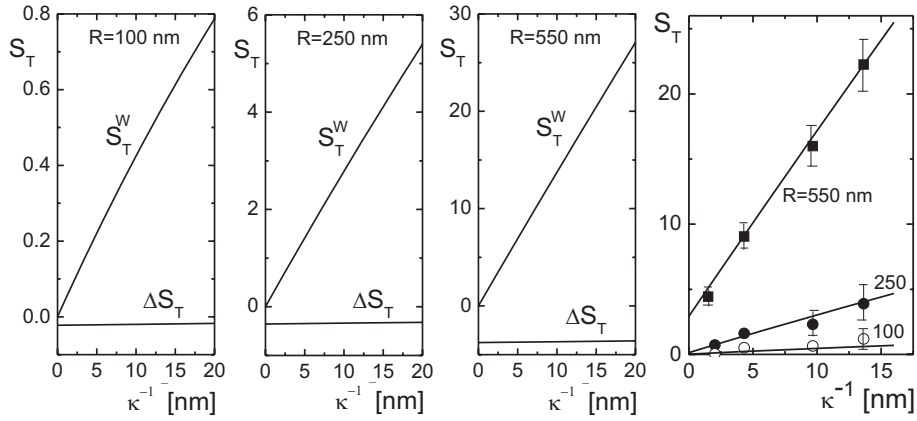
Figure 5: Left three figures : the two contributions to the Soret coefficient, S_T^W (the internal contribution) and ΔS_T (the contribution due to the temperature-induced double-layer deformation), as a function of the Debye length for three radii of the colloidal spheres, as indicated in the figures. The variables chosen here correspond to the experimental system of carboxyl-modified polystyrene spheres from ref.[3] : $l_B = 0.71 \ nm$, $4\pi l_B^2 \sigma/e = 0.029$ and $T = 298 \ K$. Most right figure : comparison of the Soret coefficient $S_T^W + \Delta S_T$ in eqs.(69-71) to experimental results. Here, $\epsilon_0/\epsilon = 1/78$. Soret coefficients are in units $1/K$.

theory to experimental data involves a single adjustable parameter, which is the intercept at zero Debye length. The whole theoretical curve can be shifted up or down for each Debye length equally, as a result of the essential salt-independent contributions due to the solvation layer and the core of the colloidal sphere. Since ΔS_T is almost independent of the salt concentration for thin double layers, this contribution results essentially in a different value for the adjustable intercept. The most right figure in Fig.5 indeed shows a perfect agreement of the experimental data with eqs.(69-71). A similar good agreement is found when only the internal contribution S_T^W is used, but the adjustable intercept is different.

9   Summary and Outlook

The single-particle thermal diffusion coefficient arising from the presence of a double layer has two distinct contributions : a contribution that is due to the temperature dependence of the internal electrostatic energy of the double layer and a contribution that is due to the temperature-gradient-induced deformation of the double layer. The former contribution can be calculated on the basis of irreversible-thermodynamics arguments, while the latter contribution requires extension of double-layer theory to include a temperature

gradient. The deformation of the double layer gives rise to two thermophoretic forces : a force with which the deformed double layer acts on the surface charges of the colloidal sphere and a force arising from friction with the solvent that is set into motion by electrical body forces. In the absence of a temperature gradient, these body forces are counter balanced by gradients in pressure, which do not set the solvent into motion. For a deformed double layer, however, the electrical body forces can not be counter balanced by pressure gradients alone, and flow will be induced, giving rise to viscous friction forces that are essential to balance the electrical body forces. The electrical forces are dielectrically screened, so that the forces due to the asymmetry of the double layer are typically a factor ϵ_0/ϵ smaller than the internal force (with ϵ_0 and ϵ the dielectric constant of vacuum and the solvent at the ambient temperature, respectively). In a highly polarizable solvent like water, experimental results can therefore be explained on the basis of irreversible thermodynamics only (see, however, the discussion at the end of section 8). The effects of the temperature-gradient induced asymmetry of the double layer are relevant in less polar solvents. Experiments on such systems have not yet been performed. For a quantitative comparison with experiments, the present theory probably needs to be extended in order to include the temperature-induced variation of the surface charge density of the colloidal sphere as a result of partial dissociation of surface groups. It would also be interesting to probe the solvent flow around a charged colloidal sphere in a temperature gradient.

Appendix A : Derivation of eq.(5)

Consider a spherical shell of thickness δ, within which there is a total charge density $\rho_t(\mathbf{r})$ (see Fig.6). This shell represents a continuum description of the interfacial layer between the bulk core material of the colloidal sphere and the bulk solvent. The total charge density ρ_t includes both free charges arising from deionized groups on the colloidal sphere and charges due to polarization of the dielectric material inside the sphere and the solvent. The electrical force on this layer is,

$$\mathbf{F}^{el} = \int_V d\mathbf{r}\, \rho_t(\mathbf{r})\, \mathbf{E}(\mathbf{r}) , \tag{73}$$

where V is the volume occupied by the shell. We assume that the force on the shell is completely transferred to the colloidal sphere, so that $\mathbf{F}^{el}$ is indeed the electric force on the sphere. The shell therefore includes the adhered solvation layer, which contributes to the total charge through its dielectric polarization. That
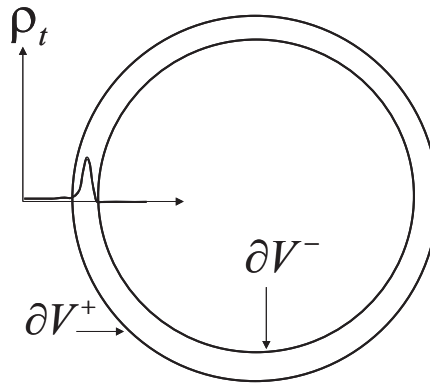
Figure 6: The charged, thin shell around the colloidal sphere that contains the surface charges from ionized chemical groups and the polarization charges from the solvation layer. The surfaces ∂V^+ and ∂V^- are the spherical surfaces within which these surface charges are contained. The distance between these two bounding surfaces is the thickness δ of the shell. The plot is a sketch of the spatial variation of the total charge density.

the hydration shell is "mechanically attached" to the colloidal particle is reminiscent of hydrodynamic stick-boundary conditions. Stresses induced by flow around the colloidal particle are not able to set the hydration shell in motion relative to the colloidal core. We will take the limit of eq.(73) where the thickness δ of the layer tends to zero, and show that this leads to eq.(5).

Since $\nabla \cdot \mathbf{E} = \rho_t/\epsilon_0$ (with ϵ_0 is the dielectric constant of vacuum) and $\nabla \times \mathbf{E} = \mathbf{0}$, the integrand can be written as the divergence of the Maxwell stress tensor,

$$\rho_t(\mathbf{r})\,\mathbf{E}(\mathbf{r}) \;=\; \epsilon_0\,\nabla \cdot \left\{ \mathbf{E}\mathbf{E} - \frac{1}{2}\hat{\mathbf{I}}\,|\mathbf{E}|^2 \right\}, \tag{74}$$

which allows to rewrite the force (73) in terms of two surface integrals ranging over the outer spherical surface ∂V^+ and inner surface ∂V^- as sketched in Fig.6,

$$\mathbf{F}^{el} \;=\; \epsilon_0 \oint_{\partial V^+} dS\,\hat{\mathbf{n}} \cdot \left\{ \mathbf{E}\mathbf{E} - \frac{1}{2}\hat{\mathbf{I}}\,|\mathbf{E}|^2 \right\} - \epsilon_0 \oint_{\partial V^-} dS\,\hat{\mathbf{n}} \cdot \left\{ \mathbf{E}\mathbf{E} - \frac{1}{2}\hat{\mathbf{I}}\,|\mathbf{E}|^2 \right\}, \tag{75}$$

where $\hat{\mathbf{n}}$ is the unit normal on the spherical surface pointing away from the origin. When the thickness δ vanishes, the normal components E_n of the electric fields develop a singularity,

$$E_n^+(\mathbf{r}) - E_n^-(\mathbf{r}) \;=\; \sigma_t(\mathbf{r})/\epsilon_0\,, \tag{76}$$

where the superscripts $+$ and $-$ refer to the limit of the electric field on approach of the surface of the colloidal sphere from outside and inside the sphere, respectively. Here, the total surface charge density σ_t

33

is defined such that the charge $\sigma_t \, dS$ on an infinitesimal surface element dS at $\mathbf{r}$ is equal to total charge of the corresponding volume for finite thickness δ. The tangential component E_t of the electric field remains continuous,

$$E_t^+(\mathbf{r}) - E_t^-(\mathbf{r}) \;=\; 0 \,, \tag{77}$$

Decomposing the electric fields in normal and tangential components and using eqs.(76,77) gives (with $\hat{\mathbf{t}}$ the unit tangential vector and $E_t = E_t^+ = E_t^-$),

$$\hat{\mathbf{n}} \cdot \left\{ \mathbf{E}^+ \mathbf{E}^+ - \mathbf{E}^- \mathbf{E}^- \right\} \;=\; \left\{ \hat{\mathbf{t}} \, E_t + \hat{\mathbf{n}} \left(E_n^+ + E_n^- \right) \right\} \sigma_t / \epsilon_0 \,,$$

$$(E_n^+)^2 - (E_n^-)^2 \;=\; \left(E_n^+ + E_n^- \right) \sigma_t / \epsilon_0 \,. \tag{78}$$

Substitution into eq.(75) in the limit that the shell thickness vanishes thus gives (with $\mathbf{E}_t = E_t \, \hat{\mathbf{t}}$ and $\mathbf{E}_n = E_n \, \hat{\mathbf{n}}$),

$$\mathbf{F}^{el} \;=\; \oint_{\partial V} dS \, \sigma_t(\mathbf{r}) \left\{ \mathbf{E}_t(\mathbf{r}) + \frac{1}{2} \left[\mathbf{E}_n^+(\mathbf{r}) + \mathbf{E}_n^-(\mathbf{r}) \right] \right\} . \tag{79}$$

Noting that $\mathbf{E}_t = \frac{1}{2}[\mathbf{E}_t^+ + \mathbf{E}_t^-]$ and $\mathbf{E}^{\pm} = \mathbf{E}_t^{\pm} + \mathbf{E}_n^{\pm}$ reproduces eq.(5).

Appendix B : Solution of the Poisson equations

The solution of eq.(40) can be written as $\partial \Psi(r) / \partial z$, where Ψ is a function of the magnitude $r = | \mathbf{r} |$ only. Substitution of this Ansatz into eq.(40) leads to the following ordinary differential equation for Ψ,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d \, \Psi(r)}{dr} \right) - \kappa^2 \, \Psi(r) \;=\; \Gamma \frac{Q}{4 \, \pi \, \epsilon \, R} \exp\{\kappa \, R\} \left\{ \left[\chi + \frac{d \ln \epsilon}{d \ln T} \right] \kappa \, \exp\{-\kappa \, r\} - \frac{d \ln \epsilon}{d \ln T} \frac{\exp\{-\kappa \, r\}}{r} \right\} . \tag{80}$$

The particular solution Φ_1^{par} of this differential equation is,

$$\Phi_1^{par}(\mathbf{r}) \;=\; \frac{\partial \, \Psi(r)}{\partial z} \;=\; \frac{1}{4} \Gamma \frac{Q}{4 \, \pi \, \epsilon \, R} \exp\{\kappa \, R\} \frac{\partial}{\partial z} \left\{ -\chi \, (1 + \kappa \, r) + \frac{d \ln \epsilon}{d \ln T} \, (1 - \kappa \, r) \right\} \exp\{-\kappa \, r\} . \tag{81}$$

The general solution to eq.(40) is obtained by adding to this particular solution the corresponding homogeneous solution where the right hand-side of eq.(40) is set equal to zero. According to eq.(38), all derivatives of the form $\partial^n \Phi_0(r) / \partial z^n$, for any $n \geq 0$ are homogeneous solutions of eq.(40). As will turn

out, in order to satisfy the boundary conditions, we only need the homogeneous solution with the same symmetry as the particular solution in eq.(81), that is, a solution of the form $z\,H(r)$, where $H(r)$ is a function of the length r of $\mathbf{r}$ only. The only homogeneous solution that has this type of symmetry is the one with $n = 1$. Hence,

$$\Phi_1^{hom}(\mathbf{r}) \;=\; C_1 \frac{\partial}{\partial z} \frac{\exp\{-\kappa\,r\}}{r} \;, \tag{82}$$

where C_1 is an integration constant. The total potential $\Phi_1^{par} + \Phi_1^{hom}$ is thus given by,

$$\Phi_1(\mathbf{r}) \;=\; z\,\exp\{-\kappa\,r\} \left\{ \frac{1}{4}\,\Gamma\,\frac{Q}{4\,\pi\,\epsilon\,R}\,\exp\{\kappa\,R\}\,\kappa^2 \left[\chi + \frac{d\ln\epsilon}{d\ln T}\left(1 - \frac{2}{\kappa\,r}\right)\right] - C_1 \frac{1+\kappa\,r}{r^3}\right\}. \tag{83}$$

Substitution of the form (34) into the boundary condition (21) shows that this boundary condition is of second order : a term that is first order in temperature gradients multiplied by a term that is first order in the small dimensionless electric potential. To within the present linear approximations in both temperature gradients and potential, the boundary condition (21) is therefore trivially satisfied. This is in accordance with the analysis in subsection 4.1, where the right hand-side of eq.(27) is shown to be of second order as well. The two unknown integration constants C_1 and $C^{(i)}$ are determined from the two boundary conditions (19) and (20). The boundary condition (19) can be expanded to leading order in temperature gradients as,

$$\frac{\epsilon_c}{\epsilon}\,\hat{\mathbf{n}}\cdot\nabla\Phi^{(i)}(\mathbf{r}) - \hat{\mathbf{n}}\cdot\nabla\Phi_1(\mathbf{r}) \;=\; \Gamma\,\frac{1+\kappa\,R}{\kappa\,R}\,\kappa\,\frac{d\ln\epsilon}{d\ln T}\,\hat{\mathbf{n}}\cdot\nabla\left[z\,\Phi_0(r)\right] \quad , \quad \text{at} \quad r = R\,, \tag{84}$$

where it is used that $\epsilon(z) = \epsilon + z\,C_T d\epsilon/dT$ for z not much larger than the Debye-screening length, and that $\Phi^{(i)}$ is of first order in Γ. As before, the dielectric constants for which the z-dependence is not denoted are their values at the ambient temperature T. Similarly, the boundary condition (20) reads,

$$\hat{\mathbf{t}}\cdot\nabla\left[\Phi_1(\mathbf{r}) - \Phi^{(i)}(\mathbf{r})\right] \;=\; 0 \quad , \quad \text{at} \quad r = R\,, \tag{85}$$

since the unperturbed potential $\Phi_0(r)$ does not play a role here because $\nabla\Phi_0(r) \sim \hat{\mathbf{n}}$ and $\hat{\mathbf{t}}\cdot\hat{\mathbf{n}} = 0$. The integration constants C_1 and $C^{(i)}$ are obtained from the boundary conditions (84) and (85). After a somewhat lengthy calculation it is found that,

$$C_1 = \Gamma\,\frac{Q\,\kappa\,R^2}{16\,\pi\,\epsilon}\,\exp\{\kappa\,R\}\,\frac{\chi\left(\kappa\,R - 1 + \frac{\epsilon_c}{\epsilon}\right) + \frac{d\ln\epsilon}{d\ln T}\left(1 + \kappa\,R + \frac{\epsilon_c}{\epsilon}\left[1 - \frac{2}{\kappa\,R}\right]\right)}{2 + 2\kappa\,R + (\kappa\,R)^2 + \frac{\epsilon_c}{\epsilon}\,(1+\kappa\,R)}\,, \tag{86}$$

and,

$$C^{(i)} = \Gamma \, \frac{Q \, \kappa}{16 \, \pi \, \epsilon \, R} \; \frac{\chi \, (\, 3 + 2\kappa \, R \,) - \frac{d \ln \epsilon}{d \ln T} \, (\, 3 + 2\kappa \, R + \frac{4}{\kappa \, R} \,)}{2 + 2\kappa \, R + (\kappa \, R)^2 + \frac{\epsilon_c}{\epsilon} \, (1 + \kappa \, R)} \, .$$

(87)

This concludes the determination of the integration constants, which leads to eq.(44-47) for the asymmetric

part Φ_1 of the potential

36

References

[1] S. Wiegand, J. Phys. Cond. Matter **16**, R357 (2004).

[2] J.K.G. Dhont, S. Wiegand, S. Duhr, D. Braun, Langmuir **23**, 1674 (2207).

[3] S. Duhr, D. Braun, PNAS **103**, 19678 (2006).

[4] E. Bringuier, A. Bourdon, Phys. Rev. E **67**, 011404 (2003).

[5] S. Fayolle, T. Bickel, S. Le Boiteux, A Würger, Phys. Rev. Lett. **95**, 208301 (2005).

[6] N.G. van Kampen, J. Phys. Chem. Solids **49**, 673 (1988).

[7] J.C. Giddings, P.M. Shinudu, S.N. Semenov, J. Coll. Int. Sci. **176**, 454 (1995).

[8] S.N. Semenov, M. Schimpf **69**, 011201 (2004).

[9] K.I. Morozov, J. Exp. Theor. Phys. **88**, 944 (1999).

[10] A. Parola, R. Piazza, Eur. Phys. J. E **15**, 255 (2004).

[11] E. Rückenstein, J. Coll. Int. Sci. **83**, 77 (1981).

[12] R. Piazza, A. Guarino, Phys. Rev. Lett. **88**, 208302 (2002).

[13] E.J.W. Verwey, J. Th. G. Overbeek, *Theory of the stability of lyophobic colloids* (Dover publications, New York, 1999).

[14] J.K.G. Dhont, J. Chem. Phys. **120**, 1642 (2004).

[15] LL. G. Chambers, *A course in vector analysis* (Chapman and Hall, and Science Paperbacks, New York, 1974).

[16] M. Teubner, J. Chem. Phys., **76**, 5564 (1982).

[17] J.K.G. Dhont, *An introduction to dynamics of colloids* (Elsevier, Amsterdam, 1996).

[18] G.A. Schumacher, T.G.M. van de Ven, Faraday Discuss. Chem. Soc., **83**, 75 (1987).

[19] F. Booth, J. Chem. Phys., **22**, 1956 (1954).

[20] M.G. McPhie, G. Nägele, J. Phys.: Condens. Matter **16**, S4021 (2004).

[21] E. Bringuier, Philosophical Magazine **87**, 873 (2007).