



Cite this: *Soft Matter*, 2025, 21, 4498

Temperature induced migration of interacting charged colloidal particles: an irreversible thermodynamics approach

J. K. G. Dhont ^{*a} and W. J. Briels ^{*ab}

The migration of particles induced by spatial gradients in temperature is commonly referred to as thermophoresis, thermodiffusion, thermal diffusion, or the (Ludwig-)Soret effect. The force on colloidal particles that drives such a migration depends on the response to variations in temperature, both of single particles and of interactions between particles. A distinction can thus be made between single-particle and collective contributions to the thermophoretic force experienced by a colloidal particle. There is as yet no systematic theory for thermophoresis of charged colloids that accounts for the collective contribution due to interactions between charged colloids. In a previous study, we developed an irreversible thermodynamics approach for uncharged colloids [J. K. G. Dhont and W. J. Briels, *J. Colloid Interface Sci.*, 2024, **666**, 457]. In the present study we extend this approach to account for interactions between charged colloids, which includes additional fluxes of ions. Enslavement of ion fluxes to the relatively slowly evolving concentration profile of the colloids, and an approximate evaluation of the heat-of-transfer, leads to microscopic, particle-based expressions for the thermodiffusion coefficient and the Soret coefficient. In addition, an explicit expression for the macroscopic thermoelectric field is derived, which gives rise to a thermoelectrophoretic force. A comparison to existing experimental thermophoresis experiments is presented.

Received 27th March 2025,
Accepted 30th April 2025

DOI: 10.1039/d5sm00319a

rsc.li/soft-matter-journal

1 Introduction

The very first study on temperature-gradient induced mass transport stems from Ludwig in 1856, who referred to the phenomenon as “hydrodiffusion”. In a one-page report (in German), a single measurement is performed on a sodium sulphate solution.¹ About two decades later, quite extensive and systematic studies were published by Soret (in French) on various types of salts.^{2–4} Since then, many experiments have been performed on other types of molecular systems. With the advent of microfluidics, single-particle imaging, and several different types of optical techniques, thermodiffusion of macromolecular systems gained scientific interest over the last few decades. Overviews of these techniques and/or experimental results on many different macromolecular systems can be found, for example, in ref. 5–11.

Accompanying these experimental developments, a large body of theoretical work specifically aiming at colloidal

suspensions has been put forward. The main focus of this previous theoretical research is concerned with thermodiffusion of single colloidal particles, in which case the concentration of colloids is sufficiently low to neglect contributions arising from interactions between the colloids. Single-particle theories and experiments include the contribution of an electric double layer of charged colloids to thermodiffusion,^{12–21} of Marangoni-related interfacial forces,^{22–24} and of solvated uncharged colloids.^{25,26}

As yet, there is no systematic theory that accounts for the contribution to thermodiffusion due to interactions between charged colloids. There are only a few theoretical studies of the effect of inter-colloidal interactions on thermodiffusion. In ref. 27 and 28, the force between charged colloids is assumed to be given by the spatial gradient of a temperature dependent mean-field potential. As will be discussed later, however, the force due to interactions is non-conservative. In ref. 8, 24 and 29–31, the force of a colloid is related to the spatial derivative of the equation-of-state pressure (which is referred to in these references as the osmotic pressure). As will be shown, this expression omits the contribution from the heat-of-transfer.

The only published experimental thermophoresis data for charged colloids where interaction effects are probed are on micellar sodium dodecyl sulphate (SDS) systems^{12,30–32} and

^a Institute of Biological Information Processing IBI-4, Forschungszentrum Jülich, 52428 Jülich, Germany. E-mail: j.k.g.dhont@fz-juelich.de

^b Computational Chemical Physics, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands. E-mail: w.j.briels@utwente.nl



charged silica spheres.³³ As for the uncharged sticky-sphere colloids,³⁴ a strong concentration and temperature dependence due to colloid–colloid interactions is found. Due to the lack of full characterization of these systems, an accurate quantitative comparison to the present theory is not possible. The experiments on micellar SDS systems can only be compared to some extent to the present theory.

In all of the abovementioned experiments and theories, a prescribed and time independent externally imposed temperature gradient is applied. In the irreversible thermodynamics approach described in this paper we will also consider the situation where such an externally imposed temperature is present.

The present study is solely concerned with the effects of colloid–colloid interactions on thermophoresis. For single-colloidal particle thermophoresis, interactions between solvent and solute molecules with a colloidal particle surface are highly significant. The corresponding interfacial thermophoretic phenomenon renders the irreversible thermodynamics approach discussed in the present study not meaningful for single-particle thermophoresis. We do, however, include single-particle thermophoretic forces in our theory as an unspecified additional contribution to those resulting from colloid–colloid interactions. In a comparison of our theory to experiments, the single-particle contribution must be obtained from either a specific theory for single-particle thermophoresis (see the references above), or from an extrapolation of experimental data to zero colloid concentration.

Fig. 1 is an overview of the content of this study. The thermophoretic force on a charged colloid particle due to colloid–colloid interactions is derived in Section 2. As indicated in Fig. 1, the derivation consists of several consecutive steps, starting from Onsager's irreversible thermodynamics flux–force relations, which are formulated in Section 2.1. In the first step 2.2 the fluxes of solvent molecules and small ions are related to that of the colloid flux. These so-called enslavement relations are used in the subsequent step 2.3 to eliminate the solvent and salt fluxes to arrive at an effective one-component flux–force relation for the double-layer-dressed colloids. In the next step 2.4, the thermophoretic force is expressed in terms of gradients of the colloid pressure (not to be confused with the osmotic pressure) and the colloid heat-of-transfer. Separating out the mechanical forces due to pressure variations allows us to derive an explicit expression for the colloid heat-of-transfer in the subsequent step 2.5. We find a contribution to the thermophoretic force on a charged colloid due to colloid–colloid interactions that has not been considered before, which we refer to as the thermophoretic interaction force. There is also an electrophoretic force due to a macroscopic electric field generated by the spatially varying temperature and colloid concentration, commonly referred to as thermoelectricity. The origin of this electric field and an expression for it is derived in Section 3. Microscopic expressions for the Soret coefficient and thermodiffusion coefficient in terms of the pair-correlation function and the pair-interaction potential are then given in Section 4, which in principle allow for a microscopic, particle-based comparison of our theory with experiments. Finally,

Section 2 Calculation of the thermophoretic force due to colloid–colloid interactions
Subsection 2.1 Onsager's flux-force relations for a four-component simple mixture: solvent molecules, two types of small ions, and big ions (the colloidal cores)
Subsection 2.2 Enslavement of fluxes of solvent and small ions by the colloid flux
Subsection 2.3 Reduction of the four-component flux-force relations to an effective one-component flux-force relation
Subsection 2.4 Expression for the thermophoretic force on a dressed colloid in terms of the colloid pressure and the heat-of-transfer
Subsection 2.5 Explicit expression for the heat-of-transfer leading to the final expression for the thermophoretic force on a colloid including contributions from colloid–colloid interactions
Section 3 Collective thermoelectricity
Section 4 Explicit expression for the Soret coefficient and the thermodiffusion coefficient for interacting charged colloids
Section 5 Comparison with experiments on SDS micellar systems

Fig. 1 An overview of the steps taken to arrive at an expression for the thermophoretic force due to colloid–colloid interactions, and subsequent sections in this paper.

Section 5 conducts a comparison with experiments, and Section 6 contains a summary and conclusion.

2 The forces acting on a colloid in concentration and temperature gradients

In this section we calculate the contribution to the thermophoretic force on a charged colloidal particle in a salt solution that originates from its interactions with other colloids. Single-particle contributions, which are due to the response of degrees of freedom of the electric double layer (and possibly a solvation layer, a grafted polymer brush, adsorbed surfactants, ...) to the temperature gradient are not explicitly specified.

For simplicity, we consider two types of ions being present: mono-valent positive ions which dissociated from the surfaces of the colloids and those resulting from added salt, while the mono-valent negatively charged ions originate solely from added salt. For many types of charged colloids the positive



ions are H^+ -ions. In an electro-neutral homogeneous suspension the $\pm$ -ion number concentrations $\rho_{\pm}$ are thus equal to,

$$\begin{aligned}\rho_+ &= \rho_0 + Z\rho_c, \\ \rho_- &= \rho_0,\end{aligned}\quad (1)$$

where ρ_0 is the number concentration of added salt, $Z > 0$ is the number of negatively charged colloid surface groups, and ρ_c is the number concentration of colloids.

In classic irreversible thermodynamics, the system is subdivided into volume elements which are sufficiently large to be considered as thermodynamic systems by themselves, but small enough so that concentrations and temperatures do not substantially vary within the volume elements. These homogeneous volume elements are assumed to be in internal equilibrium. Hereafter, we shall refer to these volume elements as “irreversible thermodynamics volume elements”.

2.1 Irreversible thermodynamics approach

As a first step, as indicated in Fig. 1, the basic irreversible thermodynamics flux–force relations are introduced, and the approximations made in the further development of the theory are specified.

In order to quantify the thermophoretic force on a colloid that is due to interactions between the colloids we start from the fundamental Onsager flux–force relations,^{35–39}

$$\begin{pmatrix} \mathbf{J}_c \\ \mathbf{J}_s \\ \mathbf{J}_+ \\ \mathbf{J}_- \\ \mathbf{J}_U \end{pmatrix} = \begin{pmatrix} L_{cc} & L_{cs} & L_{c+} & L_{c-} & L_{cU} \\ L_{sc} & L_{ss} & L_{s+} & L_{s-} & L_{sU} \\ L_{+c} & L_{+s} & L_{++} & L_{+-} & L_{+U} \\ L_{-c} & L_{-s} & L_{-+} & L_{--} & L_{-U} \\ L_{Uc} & L_{Us} & L_{U+} & L_{U-} & L_{UU} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}_c \\ \mathbf{F}_s \\ \mathbf{F}_+ \\ \mathbf{F}_- \\ \mathbf{F}_U \end{pmatrix}, \quad (2)$$

where $\mathbf{J}_c$ is the particle-number flux of colloidal particles, $\mathbf{J}_s$ of solvent molecules, $\mathbf{J}_{\pm}$ are the number fluxes of $\pm$ -ions, and $\mathbf{J}_U$ is the flux of internal energy. The fundamental forces are equal to,

$$\begin{aligned}\mathbf{F}_c &= -T\nabla\frac{\mu_c}{T} - Ze\mathbf{E}, \\ \mathbf{F}_s &= -T\nabla\frac{\mu_s}{T}, \\ \mathbf{F}_{\pm} &= -T\nabla\frac{\mu_{\pm}}{T} \pm e\mathbf{E}, \\ \mathbf{F}_U &= T\nabla\frac{1}{T},\end{aligned}\quad (3)$$

with $\mu_{c,s,\pm}$ the chemical potentials of the colloids, solvent and ions, respectively, and where T is the temperature. The flux–force relations are valid for linear order in local spatial gradients. These relations remain valid, however, in the presence of large global variations, in which case the Onsager coefficients L_{ij} are functions of the local thermodynamic variables.⁴⁰ Furthermore, $\mathbf{E}$ is the macroscopic electric field that is due to colloid concentration and temperature gradients. As will be discussed in Section 3, the origin of this electric field is solely due to the spatial variation of the Donnan potential, to within

the approximations set out in the classic Poisson–Boltzmann approach.

The Onsager flux–force relations in eqn (2) and (3) relates to a mixture of ions, solvent molecules, and bare colloids (without the presence of an electric double layer, but just a core which carries charges), and therefore has the same standing as for simple mixtures. In particular, the Onsager coefficients satisfy the symmetry relations $L_{ij} = L_{ji}$.

The approximations that we will make concerning the behaviour of the solvent and the salt ions are much the same as those made in the classic Poisson–Boltzmann theory for charged colloids.⁴¹ Apart from excluded volume interactions, which prevent solvent molecules (and salt ions) to penetrate the cores of the colloids, solvent molecules do not interact with the colloids in any other way. Salt ions do not occupy volume, and do not interact with the solvent molecules. In addition, salt ions behave as an ideal gas in a homogeneous solution that is everywhere electro-neutral. The ions only interact with each other through the electric field that they generate due to locally unequal concentrations of $\pm$ -ions leading to a violation of local electroneutrality. The solvent is assumed to be incompressible and therefore is fully packed in the sense that each solvent molecule occupies a fixed volume v_s , independent of salt and colloid concentration, which will be referred to as “the volume of a solvent molecule”. In thermodynamic terms this means that the partial molar volume of solvent is assumed constant. The number concentration of solvent molecules within bulk salt solution is thus equal to $1/v_s$, which is of course different from the thermodynamic concentration N_s/V of solvent in a suspension (with N_s the number of solvent molecules and V the volume of the system). The difference between the two concentrations is due to the volume that is occupied by the colloids. The cores of the colloids are assumed incompressible, and the volume v_c of the core is constant, similar to the solvent molecules.

The difference in the relatively slow dynamics of the large colloids in comparison to the fast dynamics of the much smaller ions and solvent molecules will be shown below to enable the reduction of the Onsager flux–force relations(2) to an effective two-component system, involving only the colloid flux and the heat flux, evidently with forces that differ from those in eqn (3).

These assumptions constitute a minimal (Poisson–Boltzmann type) model which allows us to derive an explicit expression for the thermophoretic force on charged colloids resulting from interactions between them.

2.2 Enslavement of solvent and ion fluxes

In the next step in the derivation of the thermophoretic force as indicated in Fig. 1, we discuss how the solvent flux and ion fluxes instantaneously adapt to the relatively slowly evolving colloid concentration profile. The solvent flux $\mathbf{J}'_s$ defined in eqn (4) and the ion fluxes $\mathbf{J}'_{\pm}$ defined in eqn (15) will be argued as vanishing due to enslavement. This sets the relation between the solvent and ion fluxes, and the colloid flux.

As discussed in ref. 42, the displacement of a colloid is accompanied by an opposite displacement of v_c/v_s solvent



molecules. The corresponding trivial contribution $-(v_c/v_s)\mathbf{J}_c$ to the solvent flux is accounted for by introducing an effective solvent flux,

$$\mathbf{J}'_s = \mathbf{J}_s + \frac{v_c}{v_s}\mathbf{J}_c. \quad (4)$$

Fluxes are defined relative to the volume-fixed frame, for which,

$$v_s\mathbf{J}_s + v_c\mathbf{J}_c = \mathbf{0}. \quad (5)$$

For the incompressible system under consideration, fluxes are thus measured relative to a position fixed to that of a closed sample cell. It thus follows that $\mathbf{J}'_s$ is zero. This implies that the solvent flux responsible for the relaxation of the corresponding pressure gradients relaxes to zero instantaneously. We note that this results in zero fluxes only for closed systems, where the system boundary is impenetrable for solvent molecules.

Due to the fast dynamics of the ions relative to that of the much larger colloids, the macroscopic concentration profiles of the ions (quasi) instantaneously adapt to the slowly changing concentration profile of the colloids. The ion concentrations are therefore enslaved, and henceforth referred to as $\rho_{\pm}^{\text{ens}}$. The superscript “ens” is used to indicate that this is the ion concentration profile under the assumption that the ion concentration profiles fully adapt to the colloid’s concentration profiles.

To obtain the two ion fluxes in terms of the colloid flux, two equations are needed that connect the concentration of the ions to that of the colloids.

First, the stationary state that the ions (quasi) instantaneously attain in a closed system for a given configuration of the colloids corresponds to zero ion fluxes. As for the solvent, ion fluxes vanish in their stationary state in a closed system, since the system boundaries are impenetrable for the ions. A zero flux implies a vanishing total force on the ions, which is the result of two counter-acting forces. There is a force due to the variation in the equation-of-state pressure of the ions. Since within a Poisson–Boltzmann approach the pressure of the ions is that of an ideal gas, the corresponding force per unit volume on the $\pm$ -ions is equal to $-\nabla[\rho_{\pm}k_B T/(1 - \varphi)]$, where $\rho_{\pm}$ is the thermodynamic concentration of ions (number of ions per unit volume of suspension), and k_B is the Boltzmann constant. Note that this equation holds on length scales comparable to the dimensions of irreversible thermodynamics volume elements. Furthermore,

$$\varphi = v_c\rho_c, \quad (6)$$

is the volume fraction of colloids. Note that $\rho_{\pm}/(1 - \varphi)$ is the concentration of ions within the solvent surrounding the colloids, which is the concentration that determines the ion-pressure. There is also an electrostatic force per unit volume equal to $\pm\rho_{\pm}e\mathbf{E}$, with $e > 0$ the elementary charge, and $\mathbf{E}$ the thermoelectric field (see Section 3 for a detailed discussion concerning the thermoelectric field). The total force vanishes,

and hence,

$$\nabla\left[\frac{\rho_{\pm}^{\text{ens}}k_B T}{1 - \varphi}\right] = \pm\rho_{\pm}^{\text{ens}}e\mathbf{E}. \quad (7)$$

As mentioned before, $\rho_{\pm}^{\text{ens}}$ denotes the ion concentrations that are instantaneously adapted to the colloid concentration profile (hence the superscript “ens” referring to enslavement). The thermophoretic force experienced by the ions is included in the temperature derivative that is implicit on the left hand-side: in the absence of colloids and a vanishing electric field, the above equation implies ion-Soret coefficients equal to $S_T^{\text{ion}} = 1/T$, which complies with the ideal gas behavior of the ions within a Poisson–Boltzmann approximation.⁴¹

The second equation needed to connect the concentration of the ions to that of the colloids is the Poisson equation on length scales larger than the size of the irreversible thermodynamics volume elements,

$$\nabla \cdot [\epsilon_s \mathbf{E}] = -eZ\rho_c + \rho_e^{\text{ens}}, \quad (8)$$

with $\rho_e^{\text{ens}} = e(\rho_+^{\text{ens}} - \rho_-^{\text{ens}})$ the charge density due to unequal concentrations of ions, and where, as before, $Z > 0$ is the number of negative surface charges carried by a single colloid, and where ρ_c is the spatially varying number concentration of colloids. Furthermore, ϵ_s is the dielectric constant of the solvent, which is kept inside the divergence operator to account for its temperature-gradient induced spatial variation.

As will be shown in Appendix A, the two eqn (7) and (8) imply local electro neutrality within each irreversible thermodynamics volume elements, that is,

$$\rho_+ - \rho_- = Z\rho_c. \quad (9)$$

The divergence of the electric field on the left hand-side of eqn (8) is shown in Appendix A to be relevant only at the walls of the sample container.

It is furthermore shown in Appendix A that eqn (7) and (8) imply the following enslavements relations,

$$\begin{aligned} \mathbf{J}_-^{\text{ens}} &= -[ZF(\alpha) + \rho_{\text{salt}}^{\text{free}}v_c]\mathbf{J}_c, \\ \mathbf{J}_+^{\text{ens}} &= [Z - \{ZF(\alpha) + \rho_{\text{salt}}^{\text{free}}v_c\}]\mathbf{J}_c. \end{aligned} \quad (10)$$

For brevity, the function F is introduced,

$$F(\alpha) = \frac{1}{2 + \alpha}, \quad (11)$$

where the parameter $\alpha > 0$ is defined as,

$$\alpha = \frac{N_+^{\text{coll}}}{N_{\text{salt}}^{\text{salt}}} = \frac{Z\rho_c}{\rho_0}, \quad (12)$$

which is the ratio of the number of positive ions N_+^{coll} that dissociated from the colloid’s surfaces, and the number of positive ions $N_{\text{salt}}^{\text{salt}}$ originating from added salt, within the corresponding irreversible thermodynamics volume element. Provided that the global variation of ρ_c and ρ_0 are small, the concentrations ρ_c and ρ_0 on the right hand-side in eqn (12) can be obtained from their ambient values, that is, in that case $\rho_c = N_c/V$ and $\rho_0 = N_{\text{salt}}/V$, with N_c and N_{salt} the total number of colloids and



dissolved salt molecules in the volume V of the sample container. Furthermore,

$$\rho_{\text{salt}}^{\text{free}} = \frac{2 + 2\alpha}{2 + \alpha} \frac{\rho_0}{1 - \varphi}. \quad (13)$$

As will be shown below, this is the concentration of salt within the solvent surrounding the colloids.

The interpretation of eqn (10) for the enslaved ion fluxes is as follows. The contribution $-\rho_{\text{salt}}^{\text{free}} v_c \mathbf{J}_c$ accounts for the trivial displacement of salt in the opposite direction of the colloids, just like for the solvent molecules in eqn (4). If there is no salt added, in which case $\alpha \rightarrow \infty$ and $\rho_0 \rightarrow 0$, the above results in eqn (10) reduce to $\mathbf{J}^{\text{ens}} = \mathbf{0}$, which complies with the fact that there are no negatively charged ions present, and $\mathbf{J}_+^{\text{ens}} = Z\mathbf{J}_c$, which implies that a colloid drags all its counter ions along with it. In the opposite situation when $\alpha \ll 1$, we have the leading order $\mathbf{J}_{\pm}^{\text{ens}} = [\pm(1/2)Z - \rho_{\text{salt}}^{\text{free}} v_c] \mathbf{J}_c$. The first contribution $\pm(1/2)Z$ is in accordance with colloids that drag along their electric double layer as predicted by standard linear Poisson–Boltzmann theory for a single spherical colloid. As already mentioned, the second term $-\rho_{\text{salt}}^{\text{free}} v_c \mathbf{J}_c$ accounts for the displacement of salt contained in a volume v_c in the opposite direction of a colloid. No linearization with respect to the potential within the double layer around the colloids has been made, so that the result in eqn (10) is valid within the realm of a non-linear Poisson–Boltzmann approach. In addition, the above relations are valid also for non-spherical colloids.

That $\rho_{\text{salt}}^{\text{free}}$ in eqn (13) is the salt concentration that does not involve the ions within the double layers that are dragged along with the colloids can be seen as follows: According to eqn (10), the expression between square brackets is equal to the number $N_{\pm}$ of $\pm$ -ions that is displaced along with a single colloid,

$$\begin{aligned} N_- &= -ZF(\alpha) - \rho_{\text{salt}}^{\text{free}} v_c, \\ N_+ &= Z - ZF(\alpha) - \rho_{\text{salt}}^{\text{free}} v_c, \end{aligned} \quad (14)$$

where a minus sign indicates displacement in the opposite direction of the colloids. The concentrations $\rho_{\pm}^{\text{free}}$ of ions that do not involve such colloid-enslaved ions are therefore equal to $\rho_{\pm}^{\text{free}} = \rho_{\pm} - N_{\pm} \rho_c$. From $\rho_- = \rho_0$, $\rho_+ = \rho_0 + Z\rho_c$, and eqn (12)–(14) it is found that $\rho_+^{\text{free}} = \rho_-^{\text{free}}$, both being equal to the right hand-side of eqn (13), which is therefore the salt concentration $\rho_{\text{salt}}^{\text{free}}$ of free salt within the solvent outside the cores of the colloids.

Since we are interested in fluxes on time scales larger than relaxation times of ions, there are no ion fluxes other than those enslaved by the colloids. It follows that the fluxes,

$$\begin{aligned} \mathbf{J}'_- &= \mathbf{J}_- + [ZF(\alpha) + \rho_{\text{salt}}^{\text{free}} v_c] \mathbf{J}_c, \\ \mathbf{J}'_+ &= \mathbf{J}_+ - [Z - \{ZF(\alpha) + \rho_{\text{salt}}^{\text{free}} v_c\}] \mathbf{J}_c, \end{aligned} \quad (15)$$

vanish. These definitions of the primed fluxes will be needed in the subsequent subsection to eliminate the solvent and ion fluxes from the original Onsager relations (2), in order to reduce the number of flux–force relations to an effective one-component system.

2.3 Reduction of the Onsager flux–force relations

In this subsection, corresponding to the next step in our derivation in Fig. 1 vanishing of the fluxes in eqn (4) and (15) due to enslavement is used to derive an effective one-component colloid flux–force relation (see eqn (22)), which contains the as yet unknown modified Onsager coefficients $\mathcal{L}$. This allows (as for any one-component system) to express the total force $\mathbf{F}$ in eqn (25) in terms of the effective chemical potential ν in eqn (20), the effective partial molar enthalpy in eqn (21), and the heat-of-transfer q^* in eqn (26). The latter is the as yet unknown quantity. This total force is due to spatial gradients in temperature and colloid concentration, and also contains single-particle thermophoretic forces.

The flux–force relations (2) are reformulated in terms of the fluxes $\mathbf{J}'_{s,\pm}$ in eqn (4) and (15), without yet setting these equal to zero, and the heat flux,

$$\mathbf{J}_q = \mathbf{J}_U - h_+ \mathbf{J}_+ - h_- \mathbf{J}_- - h_s \mathbf{J}_s - h_c \mathbf{J}_c, \quad (16)$$

where the partial molar enthalpies of the ions are defined as,

$$h_{\pm} = \frac{\partial H(N_c, N_s, N_-, N_+, p, T)}{\partial N_{\pm}}, \quad (17)$$

and similarly for the partial molar enthalpies h_s and h_c for the solvent and colloids, respectively. In terms of these fluxes, the Onsager relations (2) become,

$$\begin{pmatrix} \mathbf{J}_c \\ \mathbf{J}'_s \\ \mathbf{J}'_+ \\ \mathbf{J}'_- \\ \mathbf{J}_q \end{pmatrix} = \begin{pmatrix} L'_{cc} & L'_{cs} & L'_{c+} & L'_{c-} & L'_{cq} \\ L'_{sc} & L'_{ss} & L'_{s+} & L'_{s-} & L'_{sq} \\ L'_{+c} & L'_{+s} & L'_{++} & L'_{+-} & L'_{+q} \\ L'_{-c} & L'_{-s} & L'_{-+} & L'_{--} & L'_{-q} \\ L'_{qc} & L'_{qs} & L'_{q+} & L'_{q-} & L'_{qq} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}'_c \\ \mathbf{F}'_s \\ \mathbf{F}'_+ \\ \mathbf{F}'_- \\ \mathbf{F}_q \end{pmatrix}, \quad (18)$$

with Onsager coefficients that differ from those in eqn (2). By construction, the new Onsager coefficients are symmetric.^{37,38} The new forces are equal to,

$$\begin{aligned} \mathbf{F}'_c &= -T \nabla \frac{\nu}{T} + Th \nabla \frac{1}{T}, \\ \mathbf{F}'_s &= -T \nabla \frac{\mu_s}{T} + Th_s \nabla \frac{1}{T}, \\ \mathbf{F}'_{\pm} &= -T \nabla \frac{\mu_{\pm}}{T} + Th_{\pm} \nabla \frac{1}{T} \pm e\mathbf{E}, \\ \mathbf{F}_q &= T \nabla \frac{1}{T}. \end{aligned} \quad (19)$$

The “effective chemical potential” ν is defined as,

$$\nabla \frac{\nu}{T} = \nabla \frac{\mu_c}{T} - \frac{v_c}{v_s} \nabla \frac{\mu_s}{T} + Z \nabla \frac{\mu_+}{T} - [ZF + \rho_{\text{salt}}^{\text{free}} v_c] \nabla \frac{\mu_- + \mu_+}{T}, \quad (20)$$

and the “effective partial molar enthalpy” h is equal to,

$$h = h_c - \frac{v_c}{v_s} h_s + Zh_+ - [ZF + \rho_{\text{salt}}^{\text{free}} v_c] (h_- + h_+). \quad (21)$$

This new set of Onsager relations is completely equivalent to the original Onsager relations and therefore describes the same physical phenomena. In this respect we mention that although



the electric field has disappeared from the force $\mathbf{F}'_c$, it is still in principle present in the colloid flux through the contribution $(L'_{c+} - L'_{c-})\mathbf{E}$.

As discussed in the previous subsection, we set $\mathbf{J}'_s = \mathbf{0} = \mathbf{J}'_{\pm}$, which is a consequence of enslavement. This allows elimination of the forces $\mathbf{F}'_s$ and $\mathbf{F}'_{\pm}$ from the above Onsager relations (18) to arrive at an effective one-component flux-force relation,

$$\begin{pmatrix} \mathbf{J}_c \\ \mathbf{J}_q \end{pmatrix} = \begin{pmatrix} \mathcal{L}_{cc} & \mathcal{L}_{cq} \\ \mathcal{L}_{qc} & \mathcal{L}_{qq} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{F}'_c \\ \mathbf{F}_q \end{pmatrix}. \quad (22)$$

The new Onsager coefficients can be expressed, with some effort, in terms of the symmetric Onsager coefficients in the flux-force relations (18). These rather lengthy expressions show that symmetry is preserved, that is, $\mathcal{L}_{cq} = \mathcal{L}_{qc}$.

In the force $\mathbf{F}'_c$ on the colloids, the macroscopic electric field is absent, which can be understood as follows. The total charge carried by the ions within a double layer is equal to $e(N_+ - N_-) = Ze$ and therefore compensates the surface charge $-Ze$ of a colloid. This confirms the well-known fact that a dressed colloid, including its electric double layer, is uncharged. The simultaneous displacement of the colloid together with its double layer does not lead to a change of the electrostatic energy, which is the reason for the absence of the electric field in the force $\mathbf{F}'_c$.

The interpretation of eqn (21) being an effective one-component partial molar enthalpy is as follows. As mentioned before, the contribution $-\rho_{\text{salt}}^{\text{free}} v_c (h_- + h_+)$ accounts for the opposite displacement of a volume v_c of dissociated salt solution. A similar opposite displacement of solvent is accounted for by the contribution $-(v_c/v_s)h_s$. Furthermore, according to eqn (14), the number of positive ions contained within the electric double layer that is dragged along with the colloid is equal to $N_+ = Z[1 - F]$, while the number of enslaved negative ions is equal to $N_- = -ZF$ (as before, the minus sign indicates that the number of negative ions decreases upon displacement of the colloid). The electric double layer thus contributes

$$\begin{aligned} N_- h_- + N_+ h_+ &= -ZFh_- + Z[1 - F]h_+ \\ &= Zh_+ - ZF(h_- + h_+), \end{aligned}$$

to the effective partial molar enthalpy, in accordance with eqn (21).

Within the Onsager irreversible thermodynamics approach the temperature gradient and electric field induced deformation of the electric double layer is not accounted for. The enslavement relations (7) and (8) apply on length scales larger than the size of the irreversible thermodynamics volume elements, and therefore do not resolve the double layer structure around single colloids. The double layer deformation due to temperature gradients gives rise to a single-particle thermophoretic force, while the electric field induced double layer deformation gives rise to an electrophoretic force. The electrophoretic force in the present context will hereafter be referred

to as the thermoelectrophoretic force. Both the resulting single-particle force and the thermoelectrophoretic force will be added by hand: our interest here is in the effect of inter-colloidal interactions on the electrophoretic force. The thermoelectrophoretic force $\mathbf{F}_{el}$ is proportional to the electric field up to leading order in spatial gradients, and can be written as,

$$\mathbf{F}_{el} = -Ze\mu_f \mathbf{E}, \quad (23)$$

where μ_f is related to the electrophoretic mobility. The relation of μ_f to the electrophoretic mobility will be discussed in Section 4. The origin of the macroscopic electric field will be discussed, and an explicit expression for the electric field will be derived, in Section 3. We note that the temperature-gradient induced deformation of the electric double layer of a colloid contributes to the single-particle thermophoretic force. The total deformation of the double layer is the sum of the deformation due to the macroscopic electric field (thermoelectricity) and the temperature gradient (single-particle thermodiffusion).

The colloid flux is driven by the total force $\mathbf{F}$ on a single colloidal particle,

$$\mathbf{J}_c = \mathcal{L}_{cc} \mathbf{F}, \quad (24)$$

for which the following expression is found from eqn (22) for the colloid number flux and eqn (19) for the forces,

$$\mathbf{F} = -\nabla \frac{\nu}{T} - \frac{1}{T}(h + q^*)\nabla T - Ze\mu_f \mathbf{E}, \quad (25)$$

where the so-called heat-of-transfer is given by,

$$q^* = \frac{\mathcal{L}_{cq}}{\mathcal{L}_{cc}}. \quad (26)$$

The name ‘‘heat-of-transfer’’ refers to its contribution to the heat flux $\mathbf{J}_q$. From eqn (22) it is readily seen that $\mathbf{J}_q = q^* \mathbf{J}_c$ for constant temperature (excluding mere heat conduction), which leads to the well-known interpretation of q^* being equal to the heat that is transported per colloidal particle.^{37–39,42} The heat-of-transfer in the present case includes the solvent molecules and ions that are enslaved and dragged along with the colloid.

In ref. 27 and 28, the force on a colloid, including the thermophoretic force, is assumed to be given by the spatial gradient of a temperature dependent mean-field colloid–colloid interaction potential. Eqn (25), however, shows that the force contains several additional contributions, and in particular is non-conservative. Depending on the type of colloid under consideration, the temperature dependent part of the pair-interaction potential consists of an electrostatic contribution, van der Waals attractions, depletion attractions, and possible interactions between molecules grafted or adsorbed to the surfaces of the colloids.

Eqn (25) for the force is formally the same as for uncharged colloids as found in ref. 42, but now with additional contributions to ν from the ions, and with an additional thermoelectrophoretic force.

2.4 The force in terms of the colloid pressure p_c

For the derivation of an expression for the heat-of-transfer, the force in eqn (25) on a colloid is first expressed in terms of



gradients of the colloid pressure p_c instead of the chemical potential ν , which is the subsequent step in our derivation as presented in Fig. 1. The resulting expression for the force is given in eqn (34). The colloid pressure, which is related to the osmotic pressure, is the contribution of the colloids to the total pressure, as will be discussed below.

The starting point is the Gibbs–Duhem relation for the suspension, which reads,⁴³

$$0 = [h_s \rho_s + h_- \rho_- + h_+ \rho_+ + h_c \rho_c] \frac{dT}{T} + T \left[\rho_s d\frac{\mu_s}{T} + \rho_- d\frac{\mu_-^{\text{el}}}{T} + \rho_+ d\frac{\mu_+^{\text{el}}}{T} + \rho_c d\frac{\mu_c^{\text{el}}}{T} \right] - dp. \quad (27)$$

where, as before, $h_{s,\pm,c}$ are the partial molar enthalpies, $\rho_{s,\pm,c} = N_{s,\pm,c}/V$ are the thermodynamic number concentrations of the solvent, the ions, and the colloids, respectively, and p is the (total) pressure. Furthermore $\mu_{\pm,c}^{\text{el}}$ are the electro-chemical potentials,

$$\begin{aligned} \mu_{\pm}^{\text{el}} &= \mu_{\pm} \pm e\Phi, \\ \mu_c^{\text{el}} &= \mu_c - Ze\Phi, \end{aligned} \quad (28)$$

where, as before, $\mu_{\pm,c}$ are the purely chemical contributions and Φ the electric potential corresponding to the macroscopic electric field $\mathbf{E}$. We note that, on the level of the above Gibbs–Duhem relation, the colloid electro-chemical potential pertains to the bare colloids, not including the enslaved ions or solvent molecules. The macroscopic electric field will be discussed in more detail in Section 3.

The fundamental difference between colloids and mixtures of simple fluids is that for the latter the total pressure cannot be written as a sum of the equations-of-state pressures for the otherwise pure species. For such systems, there are contributions to the pressure due to interactions between the various species in the mixture. Within the present approach, the system can be considered to consist of three independent subsystems. First, we have the colloids, including their electric double layers, which interact only amongst each other. Secondly, we have solvent molecules interacting with each other, while being confined to the volume outside the colloids. Finally, the excess (dissociated) salt molecules, with concentration $\rho_{\text{salt}}^{\text{free}}$, that do not interact with the solvent, and similarly to the solvent have the same limited accessible volume.

As a consequence, the total pressure is a sum of three equation-of-state pressures, p_s of pure bulk solvent, p_{salt} of (dissociated) salt molecules, and the equation-of-state pressure p_c resulting from the colloids. The latter pressure includes the interactions between the colloids due to enslaved ions present within the electric double layers. For spherical colloids, the equation-of-state pressure p_c can be expressed in terms of an integral of the pair-correlation function and pair-interaction potential, as will be discussed in Section 4. Since within the Poisson–Boltzmann approximation the (dissociated) salt molecules behave as an ideal gas, as discussed before, their equation of state reads $p_{\text{salt}} = 2\rho_{\text{salt}}^{\text{free}} k_B T$. That the total pressure can be written as such a sum of three independent equation-of-state

pressures, can be shown similarly to that for uncharged colloids in Appendix B in ref. 42 based on the virial theorem, considering that the colloids with their double layers behave as a single species due to enslavement. Hence,

$$p = p_s + p_{\text{salt}} + p_c. \quad (29)$$

As in ref. 42, we will henceforth refer to p_c as the colloid pressure, which now includes the interactions between the colloids *via* their electric double layers.

An effective one-component Gibbs–Duhem relation for the colloids can now be derived as follows. Within the Poisson–Boltzmann approximation, the ions do not occupy any volume, so that $\rho_c \nu_c + \rho_s \nu_s = 1$. Furthermore using eqn (1) and (9), imposing ion-enslavement, it follows that $\rho_+ - Z\rho_c = \rho_0$ and $\rho_- = \rho_0$, with ρ_0 the spatially varying salt concentration that would have existed in the absence of the colloids. In addition,

$$\rho_0 + \rho_c ZF + \rho_c \nu_c \rho_{\text{salt}}^{\text{free}} = \rho_{\text{salt}}^{\text{free}}, \quad (30)$$

which follows from the definition of $\rho_{\text{salt}}^{\text{free}}$ in eqn (13), as well as $F = 1/(2 + \alpha)$ with $\alpha = Z\rho_c/\rho_0$. Using these relations, together with eqn (20) and (21) in order to eliminate $d(\nu_c/T)$ and h_c in favour of $d(\nu/T)$ and h , it is found, with some effort, that the suspension Gibbs–Duhem relation (27) can be rewritten as,

$$\begin{aligned} 0 &= \frac{1}{\nu_s} h_s \frac{dT}{T} + \frac{1}{\nu_s} d\frac{\mu_s}{T} - dp_s \\ &+ \rho_{\text{salt}}^{\text{free}} (h_- + h_+) \frac{dT}{T} + \rho_{\text{salt}}^{\text{free}} d\frac{\mu_- + \mu_+}{T} - dp_{\text{salt}} \\ &+ \rho_c h \frac{dT}{T} + \rho_c d\frac{\nu}{T} - dp_c. \end{aligned} \quad (31)$$

As mentioned earlier, each irreversible thermodynamics volume element is in internal equilibrium, and the solvent molecules and salt do not interact with each other nor with the colloids (except for exclusion of volume). The relation between variations of temperature, chemical potential, and the pressure for the solvent and the salt between the volume elements are therefore given by their corresponding Gibbs–Duhem relations. The first two lines in the suspension Gibbs–Duhem relation (31) therefore vanish (note that $1/\nu_s$ is the solvent number concentration in bulk, outside the cores of the colloids). We thus arrive at the following effective one-component Gibbs–Duhem relation for the colloids,

$$0 = \rho_c h \frac{dT}{T} + \rho_c d\frac{\nu}{T} - dp_c. \quad (32)$$

Since the infinitesimal differences can be related to the differences between the irreversible thermodynamics volume elements, the above Gibbs–Duhem relation implies that,

$$\frac{\nabla \nu}{T} = -h \frac{\nabla T}{T} + \frac{1}{\rho_c} \nabla p_c, \quad (33)$$

from which eqn (25) for the force can be rewritten as,

$$\mathbf{F} = -\frac{1}{\rho_c} \nabla p_c - \frac{q^*}{T} \nabla T - Ze\mu_r \mathbf{E}, \quad (34)$$



Except for the thermoelectrophoretic force, this expression for the force is formally identical to that for uncharged colloids.⁴² However, both the colloid pressure and the heat-of-transfer now include the enslaved ions, that is, the electric double layer that is dragged along with the colloid. The earlier proposed expressions for the force in ref. 8, 24 and 29–31 do not include the contribution arising from the heat-of-transfer, while p_c is referred to as the osmotic pressure (although the correct equation-of-state pressure is used in these references in its virial expression, as will be further discussed in Section 5).

It is important to realize that the colloid pressure p_c is not the osmotic pressure Π , which is commonly defined as the excess pressure of the suspension with respect to a salt reservoir with a separating membrane that is permeable for solvent molecules and salt ions. For example, for low colloid concentrations and for ideal salt solutions $p_c = \rho_c k_B T$, while $\Pi = [\rho_c + \rho_- + \rho_+ - 2\rho_{\text{salt}}^R] k_B T$, with $\rho_{\pm}$ the ion concentrations within the suspension and ρ_{salt}^R the number concentration of salt in the reservoir.^{44,45}

Note that the heat-of-transfer q^* is responsible for the Dufour effect, where transport of particles gives rise to a temperature gradient.

2.5 Expression for the heat-of-transfer and the total thermophoretic force

As the last step in Fig. 1 to arrive at an explicit expression for the thermophoretic force, the remaining unknown quantity needed to fully specify the total force in eqn (34) is the heat-of-transfer q^* . In this subsection, an explicit expression for the heat-of-transfer is derived. The expression for q^* in eqn (37) contains the internal energy u per colloidal particle, which is an additive contribution u_{int} due to colloid–colloid interactions and u_{single} from single colloids. This finally leads to eqn (39), where f_{int} and f_{single} are defined in eqn (38).

The derivation of an expression for the heat-of-transfer follows the same lines of reasoning as for uncharged colloids in ref. 42. First, the force on a colloid due to mere heat conduction (without particle transport) is neglected. The motivation for this approximation is that microstructural ordering of the colloids, contrary to simple liquids, is not affected by mere heat conduction (heat conduction in the absence of particle transport) since colloids behave in that respect as macroscopic objects. Secondly, the forces on the colloids due to pressure gradients as a result of gradients in concentration and temperature need not be considered in the calculation of the heat-of-transfer, since these forces are already included in the first term on the right hand-side in eqn (34) for the force. In fact, the force has been expressed in terms of the pressure in favour of the chemical potential to render the calculation of the heat-of-transfer feasible.

As in ref. 42 we consider two irreversible thermodynamics volume elements which are thermally isolated from their surroundings and from each other. We next pull, by means of an external force balancing the force in eqn (34) a colloid from one volume element to the other. By isolation of the volume elements, we have excluded the possibility of mere heat

conduction. The work done by the external force then consists of work against pressure gradients and work needed to change the thermodynamic internal energy u per colloid. Therefore,

$$-\frac{q^*}{T} \nabla T = -\frac{\partial u}{\partial T} \nabla T \equiv \Delta \mathbf{F}_T, \quad (35)$$

where $\Delta \mathbf{F}_T$ denotes the thermophoretic force responsible for the changing internal energy. As before, displacing a single colloid implies displacing enslaved solvent and ions, so that

$$\delta u = \delta u_c - \frac{v_c}{v_s} \delta u_s + Z \delta u_+ - [Zf + \rho_{\text{salt}}^{\text{free}} v_c] \delta(u_- + u_+). \quad (36)$$

The interpretation of each of the terms on the right hand-side is the same as that discussed for the effective molar enthalpy in Section 2.3. It thus follows that,

$$q^* = T \frac{\partial u(\rho_c, T)}{\partial T}. \quad (37)$$

The variation of the effective partial molar internal energy comprises an additive contribution δu_{int} from interactions between neighbouring colloids and a single-particle contribution δu_{single} , that is, $\delta u = \delta u_{\text{int}} + \delta u_{\text{single}}$. The single-particle contribution is understood to include the internal energy involving the earlier discussed opposite displacement of a volume v_c of solvent molecules and salt.

For convenience we introduce the abbreviations,

$$\begin{aligned} f_{\text{int}} &= \frac{\partial u_{\text{int}}}{\partial T}, \\ f_{\text{single}} &= \frac{\partial u_{\text{single}}}{\partial T} + f_0. \end{aligned} \quad (38)$$

In addition to the contribution to the single-particle thermophoretic force that follows from eqn (37) for q^* , we introduced f_0 in the above expression for f_{single} . This additional contribution accounts for effects such as solvent flow induced by the interface between the solvent and the solid core of the colloids.²² For charged colloids, for example, it is well-known that electro-osmotic flow plays a role in addition to the temperature dependence of the internal thermodynamic energy u_{single} of the electric double layer. To leading order in spatial gradients, such phenomena do not give rise to additional colloid–colloid interaction forces.

We thus find,

$$\mathbf{F} = -\frac{1}{\rho_c} \frac{\partial p_c}{\partial \rho_c} \nabla \rho_c - \left[\frac{1}{\rho_c} \frac{\partial p_c}{\partial T} + f_{\text{single}} + f_{\text{int}} \right] \nabla T - Ze\mu_f \mathbf{E}, \quad (39)$$

where both p_c and f_{int} are functions of just two variables ρ_c and T , as is evident from the effective one-component Gibbs–Duhem relation in eqn (32).

In the comparison to experiments, f_{single} is determined from thermophoretic data extrapolated to zero concentration. In addition to the purely thermodynamic contribution to f_{single} in eqn (38), there are in general contributions that cannot be described on the basis of thermodynamics alone, due to temperature-gradient induced solvent flow.^{19,37,46–49}

The above expression for the force is formally identical to that for uncharged colloids.⁴² The new aspect of the current



discussion is that the ions which are dragged along with the colloids, which give rise to additional interactions between the colloids, are fully accounted for through the colloid pressure and the thermophoretic interaction force. Eqn (39) is more general than just for uncharged colloids.

In the following section an explicit expression for the macroscopic electric field is derived, which then specifies the thermoelectrophoretic force in eqn (39).

3 The macroscopic electric field: Donnan and Seebeck contributions to thermoelectricity

The phenomenon in which an electric field arises as a result of a temperature gradient is commonly referred to as thermoelectricity. There are two mechanisms for colloidal suspensions giving rise to thermoelectricity. One mechanism arises from concentration gradients of the colloids (also in the absence of a temperature gradient) and one from temperature gradients (also in the absence of colloid concentration gradients). Both mechanisms will be discussed below.

First, the local Donnan electric potential within an irreversible thermodynamics volume element is defined as the volume averaged electric potential of a unit charge. That potential depends on the concentration of the colloids, and thus varies between volume elements, giving rise to a Donnan electric field. In a closed system, there are oppositely charged layers formed at the opposite (uncharged) walls of the sample container. These thin charged layers on either side of the container lead to the Donnan electric field, even though the bulk system is locally electro-neutral (see also the discussion at the end of Appendix A). This is very similar to the electric field that exists in an isothermal diffusion-sedimentation equilibrium of charged colloids.^{50,51}

The second contribution to the macroscopic electric field is due to the disproportional accumulation of different species of ions at the walls of the sample container as a result of their different thermophoretic mobilities.^{31,52–57} This mechanism is similar to the Seebeck effect in solid state physics, where electrons accumulate at the walls of a conducting material (see, for example, ref. 58). That contribution to the electric field is therefore referred to as the Seebeck electric field. Within the Poisson–Boltzmann approximation used in the present approach, the $\pm$ -ions have identical Soret coefficients being equal to $1/T$ so that the Seebeck electric field in our approach is absent.

We note that within the present approach, an additional external electric field will not give rise to an additional electrophoretic force. Enslavement implies complete electrode polarization: double layers are present at the walls of the sample container which compensate the externally applied charge, leading to a zero additional macroscopic field within the bulk of the suspension. In electrophoresis experiments, enslavement of the ion concentration profiles must therefore be avoided. This is accomplished by using a large distance between the

electrodes (which enhances the time to establish electrode polarization), and switching the direction of the external field before electrode polarization kicks in (see, for example, ref. 59 and references therein).

An expression for the macroscopic Donnan electric field can be obtained by subtraction of the two eqn (7) for the $\pm$ -ions, and using that $\nabla\rho_+ = \nabla\rho_- + Z\nabla\rho_c$ which follows from local electro-neutrality as discussed in Section 2.2, leading to,

$$\mathbf{E} = \frac{\alpha}{2 + \alpha} \frac{1}{e} \frac{k_B T}{1 - \varphi} \left[\frac{1}{1 - \varphi} \frac{\nabla\rho_c}{\rho_c} + \frac{\nabla T}{T} \right], \quad (40)$$

where, as before, $\alpha = Z\rho_c/\rho_0$, with $\rho_0 = \rho_-$ is the spatially varying local thermodynamic number concentration of negative salt ions (see eqn (1)), and φ is the volume fraction of colloids. Eqn (40) for the Donnan electric field in the presence of a temperature gradient has not been derived before. The contribution $\sim \nabla T$ to the Donnan electric field stems from the temperature dependent structure of the electric double layers of the colloids.

The thermoelectrophoretic force in eqn (23) is thus equal to,

$$\mathbf{F}_{el} = \mu_\rho \nabla\rho_c + \mu_T \nabla T, \quad (41)$$

where,

$$\begin{aligned} \mu_\rho &= -\mu_c \frac{Z^2}{2\rho_0 + Z\rho_c} \frac{k_B T}{(1 - \varphi)^2} \\ \mu_T &= \mu_\rho (1 - \varphi) \frac{\rho_c}{T}. \end{aligned} \quad (42)$$

where it is used that $\alpha = Z\rho_c/\rho_0$ (see eqn (12)).

The response to a given temperature gradient in terms of the resulting colloid concentration gradient in the stationary state, which is often probed in experiments, is quantified by the Soret coefficient S_T , which is defined as,

$$\frac{\nabla\rho_c}{\rho_c} = -S_T \nabla T. \quad (43)$$

The Donnan electric field in eqn (40) in the stationary state can be rewritten as,

$$\mathbf{E} = -\frac{\alpha}{2 + \alpha} \frac{k_B}{e} \frac{1}{1 - \varphi} \left[\frac{TS_T}{1 - \varphi} - 1 \right] \nabla T. \quad (44)$$

Although this is the Donnan electric field, one can formally define the Seebeck coefficient S_e in the stationary state as $\mathbf{E} = S_e \nabla T$. From the above expression for the electric field, the following relation between the Soret coefficient and the Seebeck coefficient is obtained as

$$S_e = -\frac{\alpha}{2 + \alpha} \frac{k_B}{e} \frac{1}{1 - \varphi} \left[\frac{TS_T}{1 - \varphi} - 1 \right]. \quad (45)$$

For non-interacting colloids and without colloid-internal degrees of freedom contributing to single-particle thermophoresis, we have $S_T = 1/T$, and hence $S_e \sim \varphi/(1 - \varphi)^2$. For very dilute suspensions, the Seebeck coefficient is therefore, as expected, solely due to single-particle contributions to the colloid's Soret coefficient.



An expression for the macroscopic electric field in the stationary state is proposed in ref. 57 on the basis of a Nernst–Planck approach. In this approach the variation of the Donnan potential as a consequence of the varying colloid concentration and temperature is not included. In addition, the heat-of-transfer for the colloids is not accounted for. A relatively large increase of the Seebeck coefficient is experimentally observed in ref. 60 upon adding colloids to an electrolyte solution, which might be due to the Donnan electric field in eqn (40).

There are some studies on thermoelectricity of suspensions of colloids with added salt which indicate that once colloids accumulate at the container walls, specific interactions with the wall lead to a significant change of the thermoelectric potential.^{61,62} The details of such electrode-specific interactions are as yet unclear.

4 The Soret and thermodiffusion coefficient

Here, microscopic expressions for the Soret coefficient S_T (defined in eqn (43)) and the thermodiffusion coefficient D_T (see eqn (49)) will be discussed. This allows in principle for a particle-based evaluation of S_T and D_T as far as the collective contributions are concerned. The single-particle contribution f_{single} in eqn (39) for the force requires a separate theoretical approach for each different type of colloid particles.

In typical closed systems, like for example in cells with thermalized boundaries, as well as in thermodiffusion forced Rayleigh scattering (TDFRS) experiments,^{63,64} the colloid flux vanishes in the stationary state. A vanishing flux implies a vanishing force on the colloidal particles. It thus follows from eqn (39) and (41)–(43) that

$$S_T = \left[\frac{1}{\rho_c} \frac{\partial p_c}{\partial T} + f_{\text{single}} + f_{\text{int}} - \mu_T \right] / \left[\frac{\partial p_c}{\partial \rho_c} - \rho_c \mu_\rho \right]. \quad (46)$$

The coefficients μ_ρ and μ_T will be specified in terms of the electrophoretic mobility μ_{el} below (see eqn (53)).

Eqn (39) for the force, and hence the above expression for the Soret coefficient, is valid for any type of geometry of the core of the colloids, spherical, rod-like, plate-like, or otherwise. For spherical colloids, for which the theory will be compared to experiments below, a particle-based approach is feasible, based on the expressions,^{42,65}

$$p_c(\rho_c, T) = \rho_c k_B T - \frac{2\pi}{3} \rho_c^2 \int_0^\infty dR R^3 g^{\text{eq}}(R) \frac{dV(R)}{dR}, \quad (47)$$

$$f_{\text{int}} = 2\pi \rho_c \frac{\partial}{\partial T} \int_0^\infty dR R^2 g^{\text{eq}}(R) V(R),$$

where $V(R)$ is the pair-interaction potential between the colloids, and $g^{\text{eq}}(R)$ is the equilibrium pair-correlation function which specifies the probability to find two colloids a distance R apart. The pair-correlation is understood to be evaluated at a local temperature and colloid concentration.

The transient dynamics in reaching the stationary state is governed by the phenomenological diffusion equation,

$$\frac{\partial \rho_c(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{J}_c = \nabla \cdot [D_c \nabla \rho_c + D_T \nabla T], \quad (48)$$

where D_c is collective diffusion coefficient, and D_T is the thermodiffusion coefficient. Eqn (24) and (39) lead to the following expressions for these diffusion coefficients,

$$D_c = \mathcal{L}_c \left[\frac{1}{\rho_c} \frac{\partial p_c}{\partial \rho_c} - \mu_\rho \right],$$

$$D_T = \mathcal{L}_c \left[\frac{1}{\rho_c} \frac{\partial p_c}{\partial T} + f_{\text{single}} + f_{\text{int}} - \mu_T \right]. \quad (49)$$

From the well-known expression for the collective diffusion coefficient of spherical colloids in the absence of thermoelectricity,^{66–69} it immediately follows that the mobility $\mathcal{L}_{cc}$ is equal to

$$\mathcal{L}_{cc} = D_0 \rho_c \beta H_0, \quad (50)$$

where $D_0 = k_B T / 6\pi \eta_s a$ is the Stokes–Einstein–Sutherland diffusion coefficient for non-interacting colloids (η_s is the solvent shear-viscosity), $\beta = 1/k_B T$, and the hydrodynamic mobility function is defined as (with $\hat{\mathbf{k}} = \mathbf{k}/k$ the unit vector in the direction of the wave vector $\mathbf{k}$),

$$H_0 = \frac{1}{N_c} \lim_{k \rightarrow 0} \left\langle \sum_{i,j=1}^{N_c} \left(\hat{\mathbf{k}} \cdot \frac{\mathbf{D}_{ij}}{D_0} \cdot \hat{\mathbf{k}} \right) \exp\{i\mathbf{k} \cdot [\mathbf{r}_i - \mathbf{r}_j]\} \right\rangle_0. \quad (51)$$

Here, $\langle \cdot \rangle_0$ denotes the equilibrium average with respect to the position coordinates $\{\mathbf{r}_i | i = 1, 2, \dots, N_c\}$ of the colloids, and the tensors $\mathbf{D}_{ij}$ specify hydrodynamic interactions between the colloids.^{66–69} Note that H_0 is a function of the local colloid concentration and temperature through the probability density function with respect to which the average $\langle \cdot \rangle_0$ in eqn (51) is taken. We note that a non-zero wave vector $\mathbf{k}$ has a significance in light, X-ray, and neutron scattering experiments, being related to the wave length and scattering angle.^{66–69}

We note that the expression for the collective diffusion coefficient is the short-time coefficient, whereas the diffusion coefficient in eqn (49) is the long-time diffusion coefficient. It is well-known, however, that the zero-wavevector limit of the short-time collective diffusion coefficient is essentially equal to the long-time diffusion coefficient.^{70–72}

The relation between μ_f in eqn (23) and the electrophoretic mobility μ_{el} is as follows. By definition, $\mathbf{v} = \mu_{\text{el}} \mathbf{E}$, $\mathbf{v}$ being the field-induced velocity of a colloid. The colloid flux due to that velocity is $\mathbf{J}_{\text{el}} = \rho_c \mathbf{v} = \rho_c \mu_{\text{el}} \mathbf{E}$. On the other hand, from eqn (23) and (24), $\mathbf{J}_{\text{el}} = \mathcal{L}_{cc} \mathbf{F}_{\text{el}} = -\mathcal{L}_{cc} Z e \mu_f \mathbf{E}$, and hence,

$$\mu_f = -\frac{\rho_c}{\mathcal{L}_{cc} Z e} \mu_{\text{el}} = -\frac{1}{D_0 \beta H_0 Z e} \mu_{\text{el}}. \quad (52)$$

The relation between the coefficients μ_ρ and μ_T in eqn (46) for the Soret coefficient, according to eqn (42) and (52), thus reads



(using that $\beta = 1/k_B T$),

$$\mu_\rho = \frac{\mu_{el}}{D_0 H_0} \frac{Z \rho_c}{2 \rho_0 + Z \rho_c} \frac{1}{e \rho_c} \frac{(k_B T)^2}{(1 - \phi)^2}, \quad (53)$$

$$\mu_T = \mu_\rho (1 - \phi) \frac{\rho_c}{T}.$$

Well-known expressions for the electrophoretic mobility μ_{el} on the single-particle level in terms of the surface charge Z and the salt concentration ρ_0 exist. It should be noted, however, that colloid–colloid interactions give rise to a concentration dependence of the electrophoretic mobility, for which simulation data are available for particular system parameters (see ref. 73–76 and references therein).

The above expressions for the Soret coefficient and the thermodiffusion coefficient allow in principle for a microscopic, particle-based test of the validity of the theory for spherically shaped colloids.

5 Comparison with experiments

For a detailed comparison of the theory with experiments, a set of thermophoretic data as a function of the colloid concentration, temperature, and salt concentration is required, preferably with a characterization of the temperature and salt-concentration dependence of the pair-interaction potential (similar to the uncharged colloids in ref. 42). Such data are unfortunately not available for charged colloids. The most complete set of thermophoretic data of charged colloids that allow a comparison to the theory to some extent concerns micellar sodium dodecyl sulfate (SDS) suspensions.

It is stated in ref. 31 that for the micellar SDS suspensions under consideration no significant thermoelectric contributions to experimental Soret coefficients are found, which is in accordance with the present theory, as shown in Appendix B.

In ref. 12, 30 and 31 the Soret coefficient for SDS micelles is reported as a function of the NaCl concentration at a fixed temperature. Here, it is found that $1/S_T$ varies linearly with the micellar concentration for various NaCl salt concentrations, up to micellar concentrations of about 20 g dm^{-3} . The slope of these curves can be determined from eqn (46) for the Soret coefficient.

First, it follows from eqn (46), by neglecting thermoelectricity,³¹ that the single-particle Soret coefficient S_T^0 is equal to

$$S_T^0 = \frac{1}{T} \left[1 + \frac{f_{\text{single}}}{k_B} \right], \quad (54)$$

so that the Soret coefficient can also be written as,

$$S_T = \left[\frac{1}{\rho_c} \frac{\partial}{\partial T} \{ p_c - \rho_c k_B T \} + k_B T S_T^0 + f_{\text{int}} \right] / \frac{\partial p_c}{\partial \rho_c}. \quad (55)$$

Expanding both the numerator and the denominator to leading order in concentration, using that $p_c = k_B T \rho_c [1 + B_2 \rho_c]$, where

$$B_2 = 2\pi \int_0^\infty dR R^2 [1 - \exp\{-V(R)/k_B T\}], \quad (56)$$

is the second virial coefficient, leads to,

$$S_T = \frac{S_T^0}{1 + 2B_2 \rho_c} \left[1 + \frac{\rho_c}{T S_T^0} \left\{ B_2 + T \frac{dB_2}{dT} + \frac{f_{\text{int}}^0}{k_B} \right\} \right], \quad (57)$$

with (see eqn (47)),

$$f_{\text{int}}^0 = \lim_{\rho_c \rightarrow 0} \frac{f_{\text{int}}}{\rho_c} = 2\pi \frac{\partial}{\partial T} \int_0^\infty dR R^2 \exp\{-V(R)/k_B T\} V(R), \quad (58)$$

considering $g^{\text{eq}}(R) = \exp\{-V(R)/k_B T\}$ at low concentrations. The linear dependence of $1/S_T$ on the micellar SDS concentration that is found in ref. 12, 30, and 31 suggests that the term in the numerator involving the curly brackets in eqn (57) is small compared to unity. Expanding the corresponding term in the expression for $1/S_T$ up to leading terms in concentration leads to

$$\frac{1}{S_T} = \frac{1}{S_T^0} [1 + k \rho_c], \quad (59)$$

where,

$$k = 2B_2 - \frac{1}{T S_T^0} \left\{ B_2 + T \frac{dB_2}{dT} + \frac{f_{\text{int}}^0}{k_B} \right\} \quad (60)$$

$$\equiv 2B_2 + \Delta k.$$

The coefficient k is not to be confused with the wave vector in eqn (51).

The term in the curly brackets has not been included in the data interpretation in ref. 12, 30 and 31. In ref. 12 and 30 a typical ratio $k/2B_2$ was approximately equal to 2, while in ref. 31 a typical ratio close to 1 was reported.

To obtain numerical values for k , we need values for S_T^0 , B_2 , dB_2/dT , and f_{int}^0 . Values for S_T^0 can be directly obtained from extrapolation of data in ref. 12 and 30 for $1/S_T$ to zero micellar SDS concentration. The results are given in Fig. 2, for 25°C at which the thermophoretic experiments were performed. Values

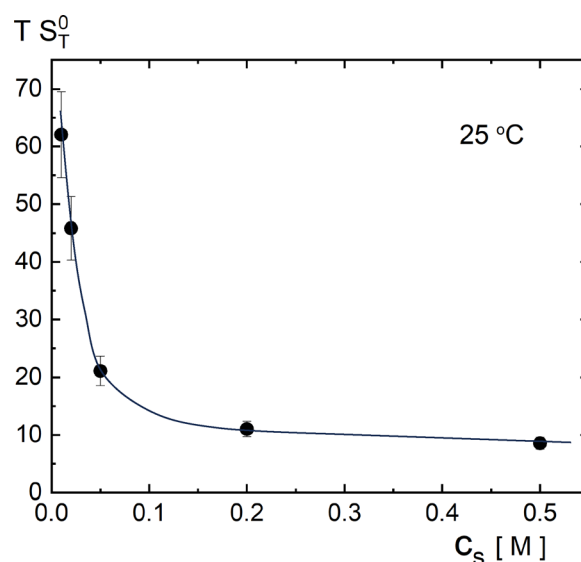


Fig. 2 $T S_T^0$ as a function of the salt concentration in moles NaCl per dm^3 . These data are obtained from Fig. 1 in ref. 30 by linear extrapolation. The ambient temperature is 25°C . The solid line is a guide to the eye.



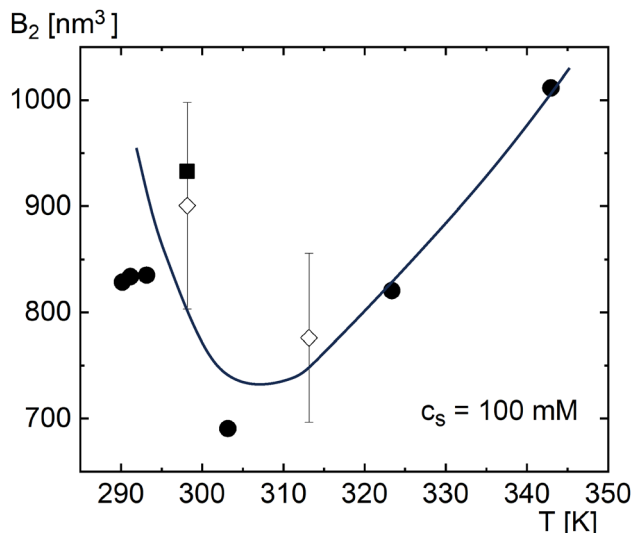


Fig. 3 The second virial coefficient as a function of temperature at a NaCl concentration of 100 mM obtained from data in ref. 78 ($\diamond$), ref. 77 ($\blacksquare$), and ref. 79 ($\bullet$). The solid line is a guide to the eye.

for B_2 and dB_2/dT can be obtained from independent light scattering data in ref. 77–79, albeit for a single NaCl concentration of 100 mM. How to obtain the second virial coefficients B_2 in units of nm^3 from those reported in ref. 77–79 is discussed in Appendix C. The resulting second virial coefficient B_2 in units of nm^3 is given in Fig. 3 as a function of temperature for a salt concentration of 100 mM. Independent values for f_{int}^0 are not available. However, the amplitude f_{int}^0 can be expressed in terms of the second virial coefficient up to leading order in $V_{\text{el}}/k_{\text{B}}T$ (with V_{el} the electric contribution to the pair-interaction potential), which leads to $f_{\text{int}}^0/k_{\text{B}} = B_2 + TdB_2/dT$, and hence,

$$\frac{\Delta k}{2B_2} = -\frac{1}{TS_{\text{T}}^0} \left[1 + T \frac{d \ln B_2}{dT} \right].$$

Accepting this estimate, the numerical value of k for 25 °C and an NaCl concentration of 100 mM can be obtained from Fig. 2 and 3, although numerical errors are quite substantial. From Fig. 2 it is found, for $T = 298 \text{ K}$, that $1/(TS_{\text{T}}^0) = 0.071 \pm 0.015$, and from Fig. 3, $Td \ln B_2/dT = -(6.3 \pm 2.7)$. It thus follows that $\Delta k/2B_2 = 0.38 \pm 0.30$. In ref. 12 and 30 it was reported that $\Delta k/2B_2 = 1$, with an equally large experimental error, while in ref. 31 a smaller value was found. The above theoretical estimate is therefore in agreement with those experiments, although error margins are quite substantial.

In ref. 32 the Soret coefficient for the same micellar SDS system is reported as a function of temperature for two NaCl concentrations (10 and 20 mM), and for two surfactant concentrations (10 and 20 g dm^{-3}). As discussed in the Appendix C, this allows in principle for the determination of numerical values for k in eqn (60) as a function of temperature for the two salt concentrations from eqn (59). The necessary independent information for the temperature- and salt-concentration dependence of the micellar molar mass and critical micellar concentration (cmc) can be found in ref. 77–80. As discussed in

Appendix C, the substantial variation of reported values for the molar mass and cmc as a function of temperature does not allow for a (semi-) quantitative comparison. Note the quite substantial variation of reported data on micellar systems is also reflected in the variation between B_2 's taken from ref. 77–79 as plotted in Fig. 3.

As mentioned above, there are at present no experimental thermophoresis data available where the colloid concentration, temperature, and ionic strength are systematically varied, together with a characterization of the colloids concerning their size and effective surface charge. Such data would allow for a quantitative comparison to our theory, similar to that for uncharged colloids in ref. 42.

6 Summary and conclusions

We present an irreversible thermodynamics analysis of the thermodiffusion of charged colloids, focussing on the effect of colloid–colloid interactions. This is an extension of our earlier work on uncharged colloids.⁴² The starting points are the irreversible thermodynamics flux–force relations in eqn (2) and (3) for the colloids, solvent molecules, and ions. Due to the relatively fast dynamics of the solvent molecules and ions as compared to the colloids, the spatially varying solvent and ion concentrations quasi instantaneously adjust to the relatively slowly varying colloid's concentration profile. This allows us to derive enslavement relations, where the fluxes of solvent molecules and ions are proportional to the colloid flux (see eqn (4) and (15)), with vanishing $\mathbf{J}'_{\text{s},\pm}$. This in turn allows reducing the flux–force relations to the effective one-component colloid flux–force relation in eqn (19) and (22). Subsequently this leads to the expression (25) for the force on a single colloid, which contains the still unknown heat-of-transfer. The Onsager irreversible thermodynamics approach does not account for deformation of the electric double layers of the colloids due to the macroscopic electric field. The corresponding thermoelectrophoretic force in eqn (23) is therefore added by hand in eqn (25) for the total force. After expressing the force on a colloidal particle in terms of spatial gradients of the colloid pressure (see eqn (34), an approximate expression for the heat-of-transfer is derived (see eqn (37)), which contains both single-particle and collective contributions. The approximation involves neglecting pure heat conduction (that is, heat conduction in the absence of colloid migration), which is argued to be a good approximation due to the relatively large size of the colloids. The total force in eqn (39) is valid for arbitrary core geometries (spherical, rod-like, plate-like, *etc.*) and arbitrary surface charge density. It consists of a single-particle thermophoretic force, a term proportional to the spatial gradient of the colloid pressure, a thermoelectrophoretic force, and a thermophoretic force that we refer to as the thermophoretic interaction force. In a closed system, the stationary state implies a zero flux and hence a zero force, which leads to the explicit expression (46) for the Soret coefficient. An expression for the mobility, valid for spherical colloids, is then derived, which leads to an explicit



expression for the thermodiffusion coefficient (see eqn (49)–(51)). The coefficients μ_p and μ_T in the expression (46) for the Soret coefficient and eqn (49)–(51) for the diffusion coefficients, which account for the thermoelectrophoretic force, are expressed in terms of the electrophoretic mobility in eqn (53), for the derivation of which the expression (44) for the macroscopic electric field is essential. The colloid–colloid interaction contributions to the Soret and thermodiffusion coefficients can be expressed in terms of integrals of the pair-interaction potential and the pair-interaction function (see eqn (47)), which are valid for spherical colloids). This allows in principle a particle-based, microscopic comparison of the theory with experiments.

The main results are summarized in Section 4: the Soret coefficient is given in eqn (46) (where μ_p and μ_T specify the contributions from electrophoresis, which are given in eqn (53)), and the collective and thermodiffusion coefficients are given in eqn (49) and (50) (where H_0 is the hydrodynamic mobility function, which is defined in eqn (51)).

To within the Poisson–Boltzmann approximations that were made, and assuming enslavement of the ion concentrations, there is a macroscopic electric field that is given in eqn (44). This expression for the macroscopic electric field is a necessary input to quantify the thermoelectrophoretic force in eqn (23). The electric field is solely due to the spatial variations of the Donnan potential, which is very similar to the field that exists in an isothermal diffusion–sedimentation equilibrium for charged colloids.^{50,51}

That the force on a colloid in a temperature gradient is proportional to spatial gradients of the colloid pressure has been suggested before in ref. 8, 24 and 29–31, albeit without further justification and without inclusion of the thermophoretic interaction force. The force on a colloid is argued in ref. 27 and 28 to be proportional to gradients of the mean-field colloid–colloid interaction potential, which resembles the present thermophoretic interaction force that originates from the heat-of-transfer. Forces due to gradients of the colloid pressure are not included in these latter papers. Moreover, a term proportional to the concentration derivative of the colloid–colloid interaction potential appears in ref. 27 and 28 that is absent within our theory. The theory presented here provides a systematic approach that leads to the force in eqn (39) that contains contributions resulting from gradients of the colloid pressure (like in ref. 8, 24 and 29–31), as well as the gradient of the colloid–colloid interaction potential as far as its temperature dependence is concerned (like in ref. 27 and 28, except that there the concentration derivative of the colloid–colloid interaction energy should be omitted).

The colloid pressure p_c in eqn (47) should not be confused with the osmotic pressure Π . The colloid pressure is the contribution to the total suspension pressure originating from the presence of the colloids in a closed system. The osmotic pressure on the contrary is the excess pressure of the suspension with respect to an osmotic reservoir, with a membrane that is permeable for both solvent molecules and ions. This is most explicitly seen from the expression $\Pi = (\rho_c + \rho_- + \rho_+ - 2\rho_{\pm}^R)k_B T$ for the osmotic pressure at low colloid concentrations,^{44,45} for which $p_c = \rho_c k_B T$.

A comparison of the theory with experiments for uncharged colloids requires data where the concentration and temperature are systematically varied ref. 34 and 42. For charged colloids, where also the ionic strength is varied, are not available. The only experiments that allow for a comparison to some extent are those conducted on a micellar sodium dodecyl sulphate (SDS) system.^{12,30–32} In these references the inverse Soret coefficient (without the contribution from the thermophoretic interaction force) is expanded to leading order in concentration. In that case, apart from the single-particle contribution, the only unknown parameter that is left is the second-order virial coefficient originating from the colloid pressure. For such micellar SDS systems additional information is necessary, such as the temperature and concentration dependence of the molar mass and the critical micellar concentration. The limited available data and the variation of such data between different publications^{77–80} unfortunately renders a conclusive quantitative comparison not feasible. We presented a comparison that indicates that the thermophoretic interaction force could explain differences between second-virial coefficients obtained from thermophoresis experiments as described above^{12,30–32} and those obtained by independent light scattering experiments.^{77–80}

Experiments on well-defined charged colloids where the colloid concentration, ionic strength, temperature, and possibly the colloid's charge are systematically varied are required for a conclusive comparison with the theory. A particle-based comparison would also provide access to knowledge of the pair-interaction potential and the pair-correlation function.

The results obtained here for charged colloids are applicable to other types of colloids as well. The analysis is equally valid in case there are additional colloid–colloid direct interactions, on top of the excluded-volume and double-layer interactions, due to for example, van der Waals attractions and/or an uncharged polymer brush grafted to the surface of the colloids. Furthermore, for the additional presence of relatively small solutes, their enslavement can be assumed just as for ions.

The main assumption in our treatment of the ions is conform those made in the classic Poisson–Boltzmann approach of charged colloids.⁴¹ The ions are assumed to behave as an ideal gas, and only respond to the (mean) electric field that is generated by the colloid's surface charges and the unequal $\pm$ -ion concentrations within the double layers. This is a crucial assumption for the formulation of eqn (7), which is one of the equations to obtain the ion-enslavement relations. This equation is also at the origin of the expression (40) for the macroscopic electric field. Including interactions between the ions would be an important generalization of the theory towards very high salt concentrations.

Data availability

All data are displayed within the paper.

Conflicts of interest

There are no conflicts to declare.



Appendices

A: Derivation of the enslavement relations

First, we rewrite eqn (7), as,

$$\frac{1}{\rho_{\pm}^{\text{ens}}} \nabla \left[\frac{\rho_{\pm}^{\text{ens}} k_B T}{1 - \varphi} \right] = \pm e \mathbf{E}. \quad (61)$$

Adding the equation for the $\pm$ ions eliminates the electric field, and leads to

$$\frac{1}{\rho_+^{\text{ens}}} \nabla \left[\frac{\rho_+^{\text{ens}} k_B T}{1 - \varphi} \right] + \frac{1}{\rho_-^{\text{ens}}} \nabla \left[\frac{\rho_-^{\text{ens}} k_B T}{1 - \varphi} \right] = \mathbf{0}. \quad (62)$$

Performing the differentiation gives,

$$\frac{k_B T}{1 - \varphi} \left[\frac{1}{\rho_+^{\text{ens}}} \nabla \rho_+^{\text{ens}} + \frac{1}{\rho_-^{\text{ens}}} \nabla \rho_-^{\text{ens}} + \frac{2}{T} \nabla T + \frac{2}{1 - \varphi} \nabla \varphi \right] = \mathbf{0}, \quad (63)$$

and hence,

$$\nabla \ln \rho_+^{\text{ens}} + \nabla \ln \rho_-^{\text{ens}} + \nabla \ln T^2 - \nabla \ln(1 - \varphi)^2 = \mathbf{0}. \quad (64)$$

It thus follows that,

$$\nabla \left[\frac{\rho_-^{\text{ens}}(\mathbf{r}, t) \rho_+^{\text{ens}}(\mathbf{r}, t) T^2(\mathbf{r})}{[1 - \varphi(\mathbf{r}, t)]^2} \right] = \mathbf{0}. \quad (65)$$

As before, the superscript “ens” refers to enslavement. Note that we consider throughout this paper a time independent, externally imposed temperature gradient, so that $T \equiv T(\mathbf{r})$ is independent of time. Since eqn (65) holds for all times, we also have,

$$\nabla \left[\frac{\rho_-^{\text{ens}}(\mathbf{r}, t + \delta t) \rho_+^{\text{ens}}(\mathbf{r}, t + \delta t) T^2(\mathbf{r})}{[1 - \varphi(\mathbf{r}, t + \delta t)]^2} \right] = \mathbf{0}, \quad (66)$$

where δt is an infinitesimally change of the time. During the time interval $(t, t + \delta t)$, the colloid concentration profile changes from $\rho_c(\mathbf{r}, t)$ to $\rho_c(\mathbf{r}, t) + \delta \rho_c(\mathbf{r}, t)$ and the ion concentrations change from $\rho_{\pm}^{\text{ens}}(\mathbf{r}, t)$ to $\rho_{\pm}^{\text{ens}}(\mathbf{r}, t) + \delta \rho_{\pm}^{\text{ens}}(\mathbf{r}, t)$. Subtracting eqn (65) and (66) this leads to, up to leading order in the changes of the concentrations (not denoting the position and time dependencies for brevity),

$$\nabla \left\{ \frac{T^2}{(1 - \varphi)^2} \times \left[\rho_-^{\text{ens}} \delta \rho_+^{\text{ens}} + \rho_+^{\text{ens}} \delta \rho_-^{\text{ens}} + 2 \frac{\rho_-^{\text{ens}} \rho_+^{\text{ens}}}{1 - \varphi} \delta \varphi \right] \right\} = \mathbf{0}. \quad (67)$$

Since linear irreversible thermodynamics assumes from the outset small spatial gradients, and $\delta \rho_{\pm}^{\text{ens}}$ and $\delta \varphi$ are by definition infinitesimally small differences, products of gradients with either $\delta \rho_{\pm}^{\text{ens}}$ or $\delta \varphi$ can be neglected, so that eqn (67) leads to

$$\nabla \left[\rho_-^{\text{ens}} \delta \rho_+^{\text{ens}} + \rho_+^{\text{ens}} \delta \rho_-^{\text{ens}} + 2 \frac{\rho_-^{\text{ens}} \rho_+^{\text{ens}}}{1 - \varphi} \delta \varphi \right] = \mathbf{0}. \quad (68)$$

The combination within the square brackets is thus a function of time only. Dividing by $\rho_-^{\text{ens}} \rho_+^{\text{ens}}$ and using that $\varphi = v_c \rho_c$ thus gives,

$$\frac{1}{\rho_-^{\text{ens}}} \delta \rho_-^{\text{ens}} + \frac{1}{\rho_+^{\text{ens}}} \delta \rho_+^{\text{ens}} + \frac{2v_c}{1 - \varphi} \delta \rho_c = \delta F(t), \quad (69)$$

where $\delta F(t)$ is the infinitesimally small change of the as yet unknown function $F(t)$ during the time interval δt . That $\delta F(t) = 0$ can be shown as follows. Since $\delta \rho_{\pm}^{\text{ens}} = \delta t (\partial \rho_{\pm}^{\text{ens}} / \partial t) = -\delta t \nabla \cdot \mathbf{J}_{\pm}^{\text{ens}}$ and similarly $\delta \rho_c = -\delta t \nabla \cdot \mathbf{J}_c$, while the fluxes are linear in gradients, eqn (69) can be written as,

$$\nabla \cdot \left[\frac{1}{\rho_-^{\text{ens}}} \mathbf{J}_-^{\text{ens}} + \frac{1}{\rho_+^{\text{ens}}} \mathbf{J}_+^{\text{ens}} + \frac{2v_c}{1 - \varphi} \mathbf{J}_c \right] = \frac{\delta F(t)}{\delta t}, \quad (70)$$

up to linear order in gradients, where products of two gradients are neglected. Due to the impermeability of the boundary of the system (the wall of the sample container) for ions and colloids, the components of fluxes normal to the boundary vanish. Therefore, according to Gauss' integral theorem, the integral over the volume of the system of the left hand-side of eqn (70) vanishes. The integral on the right hand-side is equal to $(\delta F(t) / \delta t) \times V$, with V as the volume of the system. It thus follows F is independent of time, so that δF in eqn (69) vanishes, and hence,

$$\frac{1}{\rho_-^{\text{ens}}} \delta \rho_-^{\text{ens}} + \frac{1}{\rho_+^{\text{ens}}} \delta \rho_+^{\text{ens}} + \frac{2v_c}{1 - \varphi} \delta \rho_c = 0. \quad (71)$$

The number-concentration increments $\delta \rho_{\pm, c}$ are directly correlated with their corresponding fluxes. Enslavement implies that each colloid drags along with it, in the same direction, a proportional amount of positive and negative ions. These amounts of $\pm$ -ions that are dragged along with a single colloid correspond to are specified by eqn (71) as $\delta \rho_{\pm}^{\text{ens}} / \delta \rho_c = -\rho_{\pm}^{\text{ens}} [2v_c / (1 - \varphi)]$. Since the ions are dragged along with the colloids, it follows directly from eqn (71) that

$$\frac{1}{\rho_-^{\text{ens}}} \mathbf{J}_-^{\text{ens}} + \frac{1}{\rho_+^{\text{ens}}} \mathbf{J}_+^{\text{ens}} = -\frac{2v_c}{1 - \varphi} \mathbf{J}_c. \quad (72)$$

In order to obtain the second enslavement relation, we calculate $\nabla \cdot [\varepsilon_s \mathbf{E}]$ from eqn (7) and compare the result to eqn (8). Subtraction of the eqn (7) for ρ_+^{ens} and ρ_-^{ens} leads to the following expression for the electric field,

$$\mathbf{E} = \frac{1}{e^2 (\rho_+^{\text{ens}} + \rho_-^{\text{ens}})} \nabla \left[\frac{\rho_{\pm}^{\text{ens}} k_B T}{1 - \varphi} \right]. \quad (73)$$

Within linear irreversible thermodynamics, products of two gradients are neglected. Multiplication of eqn (73) with ε_s then leads to

$$\nabla \cdot [\varepsilon_s \mathbf{E}] = \frac{1}{1 - \varphi} \kappa^{-2} \left[\nabla^2 \rho_{\pm}^{\text{ens}} + \frac{\rho_{\pm}^{\text{ens}}}{1 - \varphi} \nabla^2 \varphi + \frac{\rho_{\pm}^{\text{ens}}}{T} \nabla^2 T \right], \quad (74)$$

where κ^{-1} is the Debye screening length,

$$\kappa^2 = \frac{2e^2 \mathcal{I}}{\varepsilon_s k_B T}, \quad (75)$$

with $\mathcal{I}$ the ionic strength,

$$\mathcal{I} = \frac{1}{2} [\rho_+^{\text{ens}} + \rho_-^{\text{ens}}]. \quad (76)$$

Within the present setting, contrary to the classic Poisson-Boltzmann theory for single charged colloids, both the Debye length and the ionic strength are position dependent quantities



that vary between irreversible thermodynamics volumes and are thus related to the macroscopically varying ion concentrations. Each term on the right hand-side of eqn (74) is of the form $\kappa^{-2}\nabla^2(\cdot)$, which is the second order gradient contribution in a Taylor expansion of $(\cdot)$ over a distance equal to the Debye length κ^{-1} . Since the Debye length is of the order of the size of a colloid, these terms constitute the spatial variation of $(\cdot)$ within irreversible thermodynamics volume elements. The Onsager irreversible thermodynamics approach, $(\cdot)$ is assumed constant within irreversible thermodynamics volume elements which contain many colloids. The terms on the right hand-side of eqn (74) are therefore of no significance within the present irreversible thermodynamics approach. In other words, the variation of $(\cdot)$ over distances comparable to the size of a single colloid is negligible as compared to the change of $(\cdot)$ over distances comparable to the size of irreversible thermodynamics volume elements. Within the bulk of the system, we thus find that

$$\rho_+^{\text{ens}} - \rho_-^{\text{ens}} = Z\rho_c, \quad (77)$$

which implies local electro neutrality to leading order in spatial gradients. A small change $\delta\rho_c$ thus leads to changes $\delta\rho_{\pm}^{\text{ens}}$ equal to

$$\delta\rho_+^{\text{ens}} - \delta\rho_-^{\text{ens}} = Z\delta\rho_c, \quad (78)$$

and hence, similarly as discussed just below eqn (71),

$$\mathbf{J}_+^{\text{ens}} - \mathbf{J}_-^{\text{ens}} = Z\mathbf{J}_c. \quad (79)$$

Combining eqn (72) and (79) it is found that,

$$\mathbf{J}_{\pm}^{\text{ens}} = \left[\pm \frac{\rho_{\pm}^{\text{ens}}}{\rho_-^{\text{ens}} + \rho_+^{\text{ens}}} Z - \frac{\rho_-^{\text{ens}} \rho_+^{\text{ens}}}{\rho_-^{\text{ens}} + \rho_+^{\text{ens}}} \frac{2v_c}{1 - \varphi} \right] \mathbf{J}_c. \quad (80)$$

According to eqn (1) for the (position dependent) concentration profiles $\rho_{\pm}^{\text{ens}}$ that exists under enslavement and the corresponding position dependent concentration ρ_0 , together with the definitions in eqn (11)–(13); this can be rewritten in the final form given in eqn (10).

We note that the right hand-side of eqn (74) cannot be neglected in the Poisson equation to describe sample container wall effects. In an isothermal sedimentation–diffusion equilibrium, for example, similar contributions lead to thin charged layers of ions at the sample container walls with an extent of the order of the Debye length, within which $\kappa^{-1}\nabla(\cdot)$ cannot be neglected.⁵⁰ No approximation is made, however, neglecting these wall effects to correctly describe the electric field within the bulk of the system (see also the discussion section in ref. 51).

B: The significance of thermoelectrophoretic forces

An estimate of the significance of thermoelectrophoretic forces can be made on the basis of data provided in ref. 31 and 77–80: $a \approx 2.5$ nm, $Z \approx 17$ (less than the number of monomers due to physical adsorption of ions), $B_2 \approx 8.2 \times 10^{-25}$ m³, and the dimensionless electrophoretic mobility $\tilde{\mu}_{\text{el}} = (6\pi\eta_s a/e)\mu_{\text{el}} = 3Z/[2(1 + \kappa a)]$ is equal to 7 (where $\kappa a = 2.6$). Furthermore,

$dB_2/dT \approx -14 \times 10^{-27}$ m³ K, and $f_{\text{single}}/k_B = 13$ (see eqn (54) and Fig. 2 for 100 mM salt). To within the second virial approximation it follows that, for $T = 298$ K, $(1/k_B T)(\partial p_c/\partial \rho_c) \approx 1 + 24\varphi$, and $(1/\rho_c k_B)(\partial p_c/\partial T) + f_{\text{single}}/k_B \approx 14 - 52\varphi$. In addition, $H_0 \approx 1$, so that, $\rho_c \mu_\rho/k_B T \approx \mu_T/k_B \approx 290\varphi/(2\rho_0 v_c + 17\varphi)$. For the 100 mM salt solution $\rho_0 v_c \approx 4$, so that it follows that, $(\partial p_c/\partial \rho_c)/(\rho_c \mu_\rho) \approx (1 + 24\varphi)(8 + 17\varphi)/290\varphi$ and $(\partial p_c/\partial T + \rho_c f_{\text{single}})/(\rho_c \mu_T) \approx (14 - 52\varphi)(8 + 17\varphi)/290\varphi$. The micellar SDS concentrations correspond to volume fractions $0.002 < \varphi < 0.02$, so that $6 < (\partial p_c/\partial \rho_c)/(\rho_c \mu_\rho) < 37$ (the 6 for $\varphi = 0.02$ and 37 for $\varphi = 0.002$), and $46 < (\partial p_c/\partial T + \rho_c f_{\text{single}})/(\rho_c \mu_T) < 460$ (the 460 for $\varphi = 0.02$ and 46 for $\varphi = 0.002$). The above lower limit of 6 is most probably about a factor 2 larger, since the μ_{el} decreases with increasing concentration. Thermoelectric contributions can thus be safely neglected against those from pressure gradients and single-particle forces for the micellar SDS system under consideration.

C: Converting experimental second virial coefficients to B_2

The experimental determination of the second virial coefficient and the molar mass M of colloids by means of static light scattering experiments is based on the following relation involving the (inverse) Rayleigh ratio $R(k \rightarrow 0)$, which goes back to Debye,⁸¹

$$\frac{Kc}{R(k \rightarrow 0)} = \frac{1}{M} + 2Bc, \quad (81)$$

where K is a constant, c is the colloid concentration in units g ml⁻¹. Furthermore, B is the second virial coefficient in units ml mol g⁻², which is proportional to the second virial coefficient B_2 in eqn (56). To obtain the proportionality constant between B and B_2 , it is noted that (see, for example, ref. 69, Section 3.5),

$$\frac{Kc}{R(k \rightarrow 0)} = \frac{1}{M}[1 + 2B_2\rho_c]. \quad (82)$$

Comparing the two expressions above, and using that $\rho_c[\text{\#colloids per m}^3] = (N_{\text{Av}}/M)10^6 c$ [g ml⁻¹], leads to,

$$B_2 = (M^2/N_{\text{Av}})10^{-6}B, \quad (83)$$

where B_2 is understood to have the unit m³, M is expressed in units g mol⁻¹, and the unit of B is already mentioned above. Experimental light scattering data for B are given in Fig. 4.^{77–79} The necessary temperature and salt-concentration dependence of the molar mass of SDS micelles, required to convert experimental values for B into B_2 , are given in Fig. 5 and 6, respectively, where the data are taken from the same references. These plots are used to generate Fig. 3 for B_2 versus temperature for $c_s = 100$ mM in the main text.

Also note that relation (3a) in ref. 78 implies that the numerical values for k_1 in Tables I and II in that reference (for 25 and 40 °C, respectively) are related to B as $k_1 = 2MB$. Alternatively, B_2 can also be obtained from ref. 78 without the use of their eqn (3a), using the values for k_1 and the aggregation numbers m in Tables I and II (with the molecular weight of a single surfactant equal to $M_1 = 288$ g mol⁻¹), together with the relation $k_1' = 2B_2 = k_1/\bar{v}$. The specific volume $\bar{v}$ of a micelle is obtained from the data for the radii in Tables III and IV in



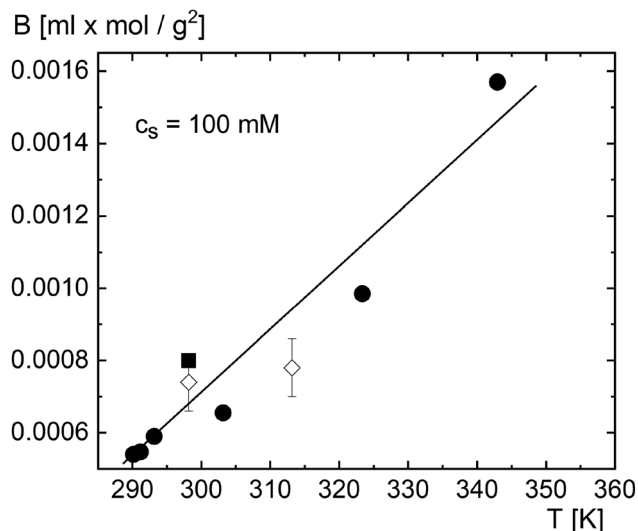


Fig. 4 The second virial coefficient B as defined in eqn (81) in units of ml mol g^{-2} for a NaCl concentration of $c_s = 100 \text{ mM}$, as a function of temperature. The data points $\bullet$ are taken from ref. 79, the points are from ref. 78, and the point $\blacksquare$ is taken from ref. 77. Note that the definition of the second virial coefficient k_1 in eqn (3a) in ref. 78 differs by a factor of 2 M from the definition of the second virial coefficient B in ref. 77 and 79.

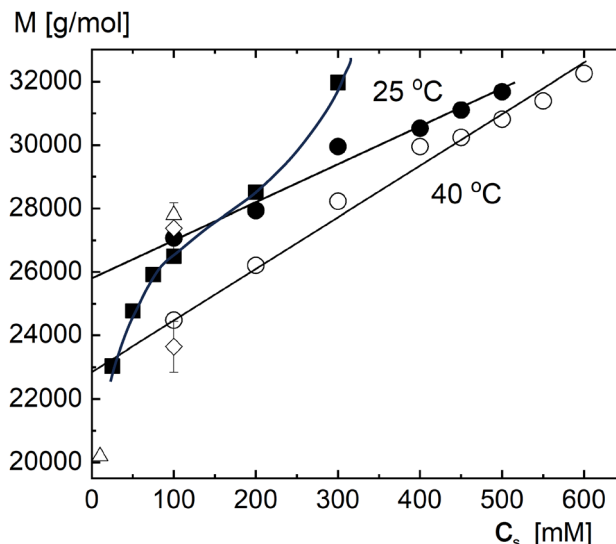


Fig. 6 The molar mass as a function of NaCl concentration for two temperatures. The data points $\bullet$ and $\circ$ are taken from ref. 78, for 25 and 40 °C, respectively. The points $\blacksquare$ for 25 °C are taken from ref. 77. The two points $\diamond$ are obtained by interpolation of the data in Fig. 5 from ref. 79 to 25 and 40 °C. The points $\triangle$ for 25 °C are from ref. 82. The solid lines are guides to the eye.

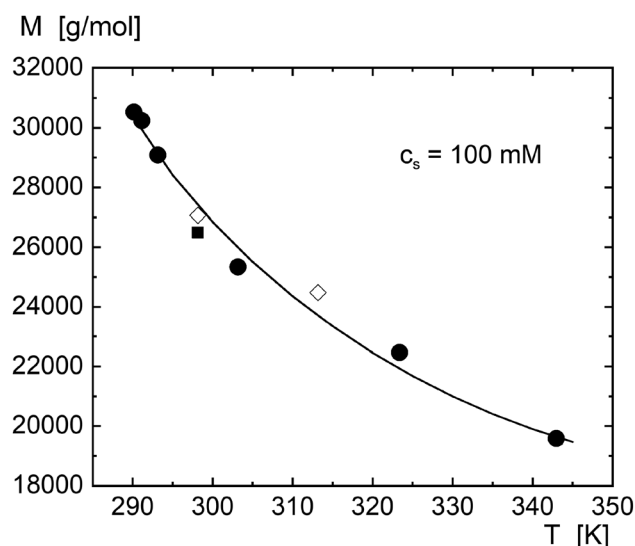


Fig. 5 The molar mass of SDS micelles as a function of temperature at a salt concentration of 100 mM. The data points $\bullet$ are taken from ref. 79, the two points $\diamond$ from ref. 78, and the single point $\blacksquare$ from ref. 77.

ref. 78, using that $\bar{v} = [N_{\text{AV}}/(mM_1)]v_c$. The thus obtained numerical values for B_2 are the two data points $\diamond$ in Fig. 3.

For a given temperature and salt concentration, eqn (59) predicts that,

$$k = \frac{S_T^{(1)} - S_T^{(2)}}{\rho^{(2)}S_T^{(2)} - \rho^{(1)}S_T^{(1)}}, \quad (84)$$

where the superscripts refer to two different micellar concentrations. Fig. 2 in ref. 32 allows in principle to obtain k as a function of temperature for the two salt concentrations 10

and 20 mM. To this end, however, the concentration in units g dm^{-3} must be converted to the number of colloids ρ_c per unit volume, for which the molar mass is needed for the two salt concentrations as a function of temperature. Furthermore, the total surfactant concentration in terms of which Fig. 2 in ref. 32 is plotted, should be corrected for the cmc to obtain the concentration of the surfactant in the micellar form.

Without salt, the cmc is equal to $(2.30 \pm 0.15) \text{ mg ml}^{-1}$ within the temperature range of 15–30 °C.⁸³ In ref. 79, for a NaCl concentration of 100 mM, the cmc concentration of $(0.41 \pm 0.01) \text{ mg ml}^{-1}$ is also found to be independent of the temperature within the temperature range of 17–30 °C. One can therefore safely assume that the cmc is independent of temperature within the temperature range of interest. For 25 °C the cmc is equal to 1.50 mg ml^{-1} for a NaCl concentration of 10 mM, and 0.43 mg ml^{-1} for 100 mM,⁸² and is found to vary from 2.65 to 0.53 mg ml^{-1} for salt concentrations varying from 10 to 100 mM in ref. 77. These data are plotted in Fig. 7, and are thus taken to be independent of temperature. For the salt concentrations of 10 and 20 mM it is found from Fig. 7 that $\text{cmc} = (1.57 \pm 0.10) \text{ mg ml}^{-1}$ and $(1.35 \pm 0.10) \text{ mg ml}^{-1}$, respectively. The molar mass on the contrary is a function of temperature, as shown in Fig. 5 and 6. For a salt concentration of 100 mM, the data for the molar mass in Fig. 6 are in quite good agreement between the various reported values. For the salt concentrations of 10 and 20 mM used in the temperature dependent thermophoretic measurements in ref. 32, however, there is quite a significant variation between the reported values for the molar mass. It turns out that this variation leads to quite large errors in the expression (84) for k , and thus prevents us from a comparison of the experimental data in ref. 32 with theory.

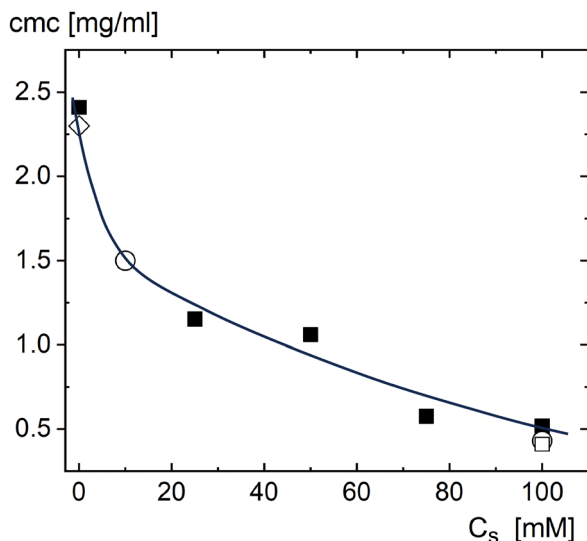


Fig. 7 The cmc, which is essentially constant within the temperature range 15–30 °C, as a function of NaCl concentration. The data points ■ are taken from ref. 77, the points ◇ from ref. 83, □ from ref. 79, and the points ○ from ref. 82. The solid line is a guide to the eye.

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