Thermodiffusion of Charged Colloids : single-particle diffusion

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Abstract

An expression for the single particle thermal diffusion coefficient of a charged colloidal sphere is derived on the basis of force balance on the Brownian time scale in combination with thermodynamics. It is shown that the single particle thermal diffusion coefficient is related to the temperature dependence of the reversible work necessary to build the colloidal particle, including the core, the solvation layer and the electrical double layer. From this general expression, an explicit expression for the contribution of the electrical double layer to the single particle thermal diffusion coefficient is derived in terms of the surface charge density of the colloidal sphere, the electrostatic screening length and its core-radius, to within the Debye-Hückel approximation. This result is shown to explain experimental data, both for thin and thick double layers. In addition, a comparison with other theories is made.

1 Introduction

Spherical colloids are excellent model systems to gain understanding concerning the microscopic mechanism that underlies collective diffusion and thermal diffusion. The coupling of a temperature gradient to diffusion in a multi-component mixture was for the first time observed 150 years ago in salt solutions by Lugwig [1]. Up to a decade ago, thermal diffusion of simple molecular systems has been extensively studied. Due to the recent development of new experimental techniques to probe thermal diffusion, macromolecular systems have become of increasing interest. In recent years, several experimental [2, 3, 4, 5, 6] and theoretical [7, 8, 9, 10] studies are devoted to the determination of the thermal diffusion coefficient D_T of macromolecules, micelles and colloids. Here, one should differentiate between highly diluted and concentrated solutions. For very dilute systems the thermal diffusive behaviour is dominated by single particle properties, related to the core-material, the electric double layer and solvation layer. For concentrated systems, in addition to single particle properties, interactions between the macromolecules need to be considered. In the present paper, *the contribution of the electric double layer to the single particle thermal diffusion coefficient will be considered.*

In two earlier papers of one of the present authors [9, 10], the contribution to the thermal diffusion coefficient of colloids that arises from colloid-colloid interactions has been discussed. In the present paper we consider very dilute suspensions where these interactions do not contribute. There is one section in ref.[9], however, where the single particle thermal diffusion coefficient is claimed to vary like the temperature derivative of the chemical potential of the "complexed colloidal particle", which includes the solvation layer and electrical double layer. As shown in the present paper, however, this is not correct. It will be shown that instead of the chemical potential, the reversible work to create such a complexed colloidal particle is the important quantity.

When gradients in concentration and temperature and deviations from their mean values are small, the phenomenological equation of motion for the number density ρ of a given species that incorporates temperature induced diffusion is of the form,

$$\frac{\partial}{\partial t}\,\rho(\mathbf{r},t) \;=\; D\,\nabla^2\,\rho(\mathbf{r},t) \;+\; D_T\,\nabla^2\,T(\mathbf{r},t)\;, \tag{1}$$

where D is the collective diffusion coefficient and D_T is the thermal diffusion coefficient. The thermal diffusion coefficient describes the coupling of a spatially varying temperature $T(\mathbf{r}, t)$ and the density of a given species. Equation (1) will be derived in the present paper from thermodynamic arguments and force balance on the Brownian time scale, leading to explicit expressions for the thermal diffusion coefficient D_T. These expressions are explicitly evaluated as far as the electrical double layer contributions are concerned in terms of charge, core radius and Debye screening length. The theoretical prediction will we compared to experiments on a micellar system [11] and a colloidal system of polystyrene particles of varying sizes [12]. Moreover, our analysis will be compared to other recent theories on charged colloids [7, 8, 13].

2 The Basic Idea for the Calculation of D_T for Colloids

Starting point for the explicit calculation of the thermal diffusion coefficient of colloids is the continuity equation for the number density $\rho(\mathbf{r}, t)$ of colloidal spheres,

$$\frac{\partial}{\partial t}\,\rho(\mathbf{r}, t) \;=\; -\,\nabla \cdot \left[\, \mathbf{v}(\mathbf{r}, t)\, \rho(\mathbf{r}, t) \,\right] \;, \tag{2}$$

where ∇ is the gradient operator with respect to position $\mathbf{r}$ and $\mathbf{v}$ is the thermally averaged translational velocity of a colloidal sphere. The velocity of a colloidal particle will be calculated on the basis of thermodynamic arguments. This can be done on the diffusive time scale (typically of the order of a few nano seconds), where inertial forces on colloidal spheres can be neglected. The non-inertial forces thus add up to zero, which is known as "force balance" [14],[15]. There are generally two non-inertial forces to be distinguished : the force $\mathbf{F}$ that arises from direct, non-hydrodynamic interactions between colloidal particles and its surroundings in a concentration and temperature gradient and the force $\mathbf{F}^h$ due to hydrodynamic friction of the colloidal sphere with the solvent. Hydrodynamic interactions between colloidal spheres need not be considered here for single particle diffusion (for interacting colloids these hydrodynamic interaction contributions can be included on the basis of the Smoluchowski equation as discussed in ref.[10]). The hydrodynamic force is then proportional the velocity of the sphere,

$$\mathbf{F}^h(\mathbf{r}, t) \;=\; -\gamma\, \mathbf{v}(\mathbf{r}, t) \;, \tag{3}$$

where γ is the friction coefficient. In case of a charged colloidal particle, the electrolyte contribution to the friction coefficient is at most of the order of a few percent. Electrolyte friction will therefore be neglected, so that the friction coefficient is simply equal to the friction coefficient of the core with the solvent,

$$\gamma \;=\; 6\,\pi\,\eta_0\,R\;, \tag{4}$$

where η_0 is the shear viscosity of the solvent and R the radius of the colloidal spheres. Force balance implies that,

$$\mathbf{0} \;=\; \mathbf{F}(\mathbf{r},t)+\mathbf{F}^h(\mathbf{r},t)\;. \tag{5}$$

From eqs.(5) and (3) is follows that,

$$\mathbf{v}(\mathbf{r},t) \;=\; \mathbf{F}(\mathbf{r},t)/\gamma\;. \tag{6}$$

An equation of motion for the colloid density is thus obtained from eqs.(2,6) once an expression for $\mathbf{F}$ is found. This force will be obtained from thermodynamics, and will turn out to be equal to a linear combination of gradients in colloid density and temperature, rendering eq.(2) of the form in eq.(1). This then leads to expressions for the thermal diffusion coefficient of a colloidal particle.

The force can be obtained from thermodynamics as follows. Like in ref.[9], the system under consideration is divided into subsystems, which will be referred to here after as "boxes". These boxes are assumed to be large enough to be able to treat them as thermodynamic systems on their own. Each box can be regarded in internal equilibrium when gradients in density and temperature are small enough to assure a very slow evolution of the global colloid concentration and a slow heat transport. Gradients are supposed to be sufficiently small so that the largest internal relaxation time of a box is small compared to mass and heat transport times. Consider two neighbouring boxes $'1'$ and $'2'$. Their volumes are equal to V, while the prescribed and fixed temperature in box 1 is equal to T and in box 2 equal to $T+\delta T$. There are N_1^c colloidal particles in box 1 and N_2^c in box 2. For simplicity we shall consider the case where only H^+-ions dissociate from the surfaces of colloids and where an acid HA is added to the solution, which completely dissociates in H^+ and A^-. The final expression for the thermal diffusion coefficient is also valid for other types of ions. The number of H^+-ions in a box is denoted as N_1^+ for box 1 and N_2^+ for box 2. Likewise, the number of A^--ions is denoted as N_1^- and N_2^-, and the number of solvent molecules in box 1 and 2 is denoted as N_1^s and N_2^s, respectively. We have to calculate the reversible work δw^{rev} necessary to displace, in a quasi-static manner, δN^c colloidal spheres from box 1 to box 2. That is, an external force that is infinitesimally less in amplitude than the force $-\mathbf{F}$ acts on the colloidal spheres, which are then quasi-statically transported in the direction in which they will diffusive if no external force would be present. The reversible work,

$$\delta W^{rev} \;=\; \delta w^{rev}/\delta N^c \;, \tag{7}$$

per moved colloidal particle is related to the force $\mathbf{F}$ which we set out to calculate as,

$$\delta W^{rev} \;=\; -\mathbf{L}\cdot\mathbf{F} \;, \tag{8}$$

where $\mathbf{L}$ is the distance between the centers of box 2 and box 1, which is the distance over which the colloidal particles are displaced when moved from box 1 to box 2. Hence,

$$\mathbf{F} \;=\; -\nabla\, W^{rev}(\mathbf{r}) \;=\; -\left[\frac{\partial W^{rev}}{\partial \rho}\,\nabla\rho + \frac{\partial W^{rev}}{\partial T}\,\nabla T\right] \;. \tag{9}$$

Substitution into eqs.(6,2) and comparing to eq.(1) leads to [16],

$$\begin{aligned} D \;&=\; D_0\,\beta\,\rho\,\frac{\partial W^{rev}}{\partial \rho} \;, \\ D_T \;&=\; D_0\,\beta\,\rho\,\frac{\partial W^{rev}}{\partial T} \;, \end{aligned} \tag{10}$$

where $D_0 = k_B T/\gamma$ is the Einstein diffusion coefficient (with k_B Boltzmann's constant). In the derivation of these expressions, only leading order terms in deviations from mean values of the density and temperature are accounted for. Terms like $\mid \nabla\rho \mid^2$ and $(\nabla T)\cdot(\nabla\rho)$ are thus neglected.

It should be noted that the definition of the thermal diffusion coefficient used in this paper complies with the equation of motion (1). Different definitions are some times used, where for example D_T in eq.(1) is replaced by $\rho\, D_T$, or $c(1-c)\, D_T$ in case of binary mixtures (with c the molar fraction of one of the species).

3 The Force on a Colloidal Sphere : heuristic considerations

Before giving a more systematic derivation of an explicit expression for the reversible work, the intuitive approach given below readily leads to the correct result.

Imagine the following pathway to move a colloidal particle from box 1 to box 2. First, a force is applied which reversibly breaks off the interface. That is, the solvation layer is forced to attain the bulk-solvent structure and ions are attached to the surface of a colloidal sphere to render it uncharged. The reversible work to do this is minus the reversible work $W_i^{rev}(T)$ involved in building up the interface at temperature T. Then the core material of the colloidal particle is reversibly heated to establish a raise in temperature of δT, which requires no work as far as the interface is concerned. The core is then moved to box 2, which requires no work as far as the interface is concerned, because the interface is simply non-existing during this displacement. Then re-structure the solvation layer and re-charge the electrical double layer, which requires work equal to $W_i^{rev}(T{+}\delta T)$. On moving the colloid from box 1 to box 2, reversible work is done against gradients in the osmotic pressure Π. For non-interacting colloids, $\Pi = \rho\, k_B T$, so that the accompanied body force is equal to $-\nabla\Pi = -k_B\, \left[T\,\nabla\rho + \rho\,\nabla T \right]$. The work per colloidal particle is thus equal to $-k_B\, \left[T\,\nabla \ln\{\rho\} + \nabla T \right]$. This work includes the displacement of an equal volume of electrolyte solution in opposite direction. Hence,

$$\mathbf{F} \;=\; -k_B T\,\nabla \ln\{\rho\} - \left[k_B + \frac{\partial W_i^{rev}(T)}{\partial T} \right] \nabla T \; . \tag{11}$$

This leads to the following expressions for the diffusion coefficients [16],

$$\begin{aligned} D \;&=\; D_0 \; , \\ D_T \;&=\; D_0 \left[\frac{\rho}{T} + \beta\,\rho\,\frac{\partial W_i^{rev}(T)}{\partial T} \right] \; . \end{aligned} \tag{12}$$

The first term within the square brackets for D_T is the "ideal gas" contribution, the second term is the contribution due to the presence of the double layer.

Besides the reversible work involving the solvation layer and the double layer, there are two additional types of internal degrees of freedom which require work : (i) to build up the structured solid colloidal material in contact with electrolyte solution in the immediate vicinity of the surface of the colloidal sphere, and (ii) work to build up the bulk solid core material of the colloidal particle including the accompanied replacement of solvent by the solid colloidal material. These two types of degrees of freedom can be incorporated in the reversible work and can simply be added in eq.(12). The bulk contribution (ii) has been discussed in detail in ref.[17].

The result (12) will be derived in the following section in a more systematic way.

4 The Force on a Colloidal Sphere : thermodynamics

The following is an extension of the discussion in ref.[10], where now the solvent molecules and ions are explicitly accounted for.

The reversible work δw^{rev} necessary to achieve the displacement of colloidal spheres from box 1 to box 2 is equal to $\delta F + S_1\,\delta T_1 + S_2\,\delta T_2$, where δF is the accompanied change in Helmholtz free energy, S_j is the entropy and δT_j the change of temperature of box j. **Here, the entropy S_1 is the entropy carried by the material that is taken from box 2 to box 1 on moving the colloids from box 1 to box 2, and $\delta T_1 = -\delta T$ is the accompanied change of temperature of that material. Similarly, S_2 is the entropy carried by the material moved from box 1 to box 2, and $\delta T_2 = \delta T$ is the temperature change of that material.** These entropic terms cancel against similar contributions in the Gibbs-Duhem relation that will be used later in our analysis (as is shown in the appendix). For brevity, we shall therefore not denote these entropic terms in equations here after. All entropic contributions of the form $S\,\delta T$ cancel at the end. Hence,

$$\delta w^{rev} \;=\; \delta F \quad (+\text{ entropic contributions})\;. \tag{13}$$

The Helmholtz free energy of each of the two boxes is a function of the number of solvent molecules, ions and colloidal particles in the box, its volume and the temperature. Let δN_j^s and $\delta N_j^{\pm}$ denote the change of the number of solvent molecules and ions (H^+ and A^-) in box j associated with an exchange of δN^c colloidal particles. The reversible work necessary for the above described process is then equal to,

$$\delta w^{rev} \;=\; \delta F \;=\; F(N_1^c-\delta N^c, N_1^s-\delta N_1^s, N_1^+-\delta N_1^+, N_1^--\delta N_1^-, V, T)$$

$$+F(N_2^c+\delta N^c, N_2^s+\delta N_2^s, N_2^+ + \delta N_2^+, N_2^- + \delta N_2^-, V, T+\delta T)$$

$$-F(N_1^c, N_1^s, N_1^+, N_1^-, V, T) - F(N_2^c, N_2^s, N_2^+, N_2^-, V, T+\delta T)\ . \tag{14}$$

Expansion of the free energies with respect to δN^c, δN_j^s and $\delta N_j^{\pm}$, using that $\partial F/\partial N_j^c = \mu_{c,j}$, with $\mu_{c,j}$ the chemical potential of the colloidal particles in box j, and similarly for the solvent molecules and the ions, gives,

$$\delta w^{rev} \;=\; \{\,\mu_{c,2}-\mu_{c,1}\,\}\;\delta N^c + \mu_{s,2}\,\delta N_2^s - \mu_{s,1}\,\delta N_1^s + \mu_2^+\,\delta N_2^+ + \mu_2^-\,\delta N_2^- - \mu_1^+\,\delta N_1^+ - \mu_1^-\,\delta N_1^-\ . \tag{15}$$

The chemical potentials appearing in eq.(15) are interpreted as follows. The chemical potential of a colloidal sphere is understood to be the difference in free energy of an uncharged colloid in its "dry state" and in the dissolved state in the suspension. It contains therefore two contributions : (i) the free energy that is released on spontaneous formation of the solvation layer and the double layer on transferring a "dry" colloidal sphere to the suspension and (ii) the gain in entropy of a colloidal sphere due to its freedom to take any position in the suspension. In particular, the gain in entropy of ions that are dissociated from the surface of a colloidal sphere is included in the chemical potential of a colloid. Similarly, the chemical potential of an added salt molecule is defined as the free energy change on dissolving a "dry" salt molecule. The separate chemical potentials μ_j^+ and μ_j^- of H^+ and A^- are therefore not independent, and will only occur in the combination $\mu_{salt,j} \equiv \mu_j^+ + \mu_j^-$, which will be referred to as "the chemical potential of a salt molecule".

With the above definitions of chemical potentials, the changes $\delta N_j^{\pm}$ are changes solely due to transport of $H^+ - A^-$ pairs, that is, of salt molecules. It follows from electro neutrality that $\delta N_j^+ = \delta N_j^-$, which will be denoted simply as δN_j^{salt}. This is the change of the number of salt molecules in box j. Hence, from eq.(15),

$$\delta w^{rev} \;=\; \{\,\mu_{c,2}-\mu_{c,1}\,\}\;\delta N^c + \mu_{s,2}\,\delta N_2^s - \mu_{s,1}\,\delta N_1^s + \mu_{salt,2}\,\delta N_2^{salt} - \mu_{salt,1}\,\delta N_1^{salt}\ . \tag{16}$$

The number of solvent molecules and the number of ion pairs $H^+ - A^-$ that is transported is connected to the number of colloidal particles that are moved from box 1 to box 2. On moving a colloidal particle from box 1 to box 2, an equal volume of electrolyte solution will be moved from box 2 to box 1, when thermal expansion of colloidal material and solvent is neglected. The total number of bulk solvent molecules within the volume of a colloidal sphere in box j is equal to $v_c^0\, \rho_{s,j}^0\, \delta N^c$, where v_c^0 is the volume occupied by the core of a single colloidal sphere and $\rho_{s,j}^0$ is the bulk concentration of solvent in box j, that is, the concentration of solvent outside the solvation layer. The molar volume v_c^0 of the colloids is taken independent of the colloid concentration and temperature, as indicated by the superscript "0". The molar volume v_c^0 is to a good approximation simply equal to the volume of a colloidal sphere, where the relatively small differences due to thermal expansion of the colloidal material are neglected. There is an excess number of molecules Γ^s within the solvation layer that is attached to each colloidal sphere. The free energy connected to the formation of this solvation layer is already incorporated in the chemical potential of a colloidal particle, as discussed above. The changes of the number of solvent molecules δN_j^s in eq.(16) do therefore not include the excess amounts of solvent molecules within the solvation layers. Hence,

$$\delta N_j^s \;=\; -v_c^0\, \rho_{s,j}^0\, \delta N^c\;. \tag{17}$$

This equation allows to express δN_j^s in eq.(16) in terms of δN^c. A similar relation can be derived for the change of the number of ions. Hence, just as for the solvent molecules we have,

$$\delta N_j^{salt} \;=\; -v_c^0\, \rho_{salt,j}^0\, \delta N^c\;, \tag{18}$$

where $\rho_{salt,j}^0$ $(= \rho_\pm^0)$ is the number concentration of ion pairs (=salt molecules) outside the double layer.

Substitution of eqs.(17,18) into eq.(16) gives,

$$\delta w^{rev}/\delta N^c \;=\; \mu_{c,2} - \mu_{c,1} - v_c^0\, \left[\rho_{s,2}^0\, \mu_{s,2} - \rho_{s,2}^0\, \mu_{s,1} + \rho_{salt,2}^0\, \mu_{salt,2} - \rho_{salt,1}^0\, \mu_{salt,1}\right]\;, \tag{19}$$

or, in obvious notation,

$$\delta w^{rev}/\delta N^c \;=\; \delta\mu_c - v_c^0\, \delta\Big[\rho_s^0\, \mu_s\Big] - v_c^0\, \delta\Big[\rho_{salt}^0\, \mu_{salt}\Big]\;. \tag{20}$$

Here, the δ's refer to the differences between box 2 and box 1.

The expression (20) includes both single particle- and interaction-contributions. In order to separate these two contributions, the chemical potential of the solvent molecules and the ions within the suspension are defined through an osmotic equilibrium. That is, we shall imagine each box to be in osmotic equilibrium with a reservoir of electrolyte solution with the corresponding temperature, where the membrane is permeable for solvent and ions, but not for colloids. **The physics behind the introduction of such a reservoir is as follows. The dynamics of the small species (the solvent molecules and the ions) are much faster as compared to the colloidal particles. These small species are therefore always in equilibrium with the field imposed by the instantaneous configuration of colloidal particles. In particular, the small species inside the solvation layer and the double layer are in equilibrium with the small species outside these layers. The solvent molecules and ions outside the solvation layer and double layer are now formally regarded as an osmotic reservoir.** The Gibbs-Duhem relation for the suspension reads (entropic contributions are again not denoted here since these cancel against the entropic contributions in eq.(13), as shown in the appendix)),

$$0 \;=\; V\,\delta p - N^c\,\delta\mu_c - N^s\,\delta\mu_s - N^{salt}\,\delta\mu_{salt}\ , \tag{21}$$

where p is the mechanical pressure within the suspension with volume V . Note that, as for eq.(19), the differences δ refer to the differences between box 2 and box 1. Since differences between the two boxes are (infinitesimally) small, the number N^c of colloidal particles in eq.(21) is "the average" of the number of particles in the two boxes, and similarly for the other extensive quantities. The corresponding Gibbs-Duhem relation for differences between the reservoirs of boxes 2 and 1 is,

$$0 \;=\; V^r\,\delta p_r - N^s_r\,\delta\mu_s - N^{salt}_r\,\delta\mu_{salt}\ , \tag{22}$$

where a sub- or super-script "r" of "reservoir" is added to indicate that these quantities relate to the osmotic reservoir. This index is missing on μ_s and μ_{salt}, since these are equal in the suspension and the osmotic reservoir. Since the osmotic pressure is defined as,

$$\Pi \;=\; p \;-\; p_r\ . \tag{23}$$

it follows from eqs.(21,22) that,

$$\delta\mu_c \;=\; \frac{1}{\rho}\,\delta\Pi + \frac{1}{\rho}\,\left(\,\rho_{s,r} - \rho_s\,\right)\,\delta\mu_s + \frac{1}{\rho}\,\left(\,\rho_{salt,r} - \rho_{salt}\,\right)\,\delta\mu_{salt}\ , \tag{24}$$

where $\rho = N^c/V$ and $\rho_{salt} = N^{salt}/V$ are the number density of colloids and salt molecules, respectively. Substituting this expression for $\delta\mu_c$ into eq.(19) leads to,

$$\begin{aligned} \delta w^{rev}/\delta N^c \;&=\; \frac{1}{\rho}\,\delta\Pi - v_c^0\,\delta\left[\,\rho_s^0\;\mu_s\,\right] - v_c^0\,\delta\left[\;\rho_{salt}^0\,\mu_{salt}\right] \\ &\quad+\frac{1}{\rho}\;(\,\rho_{s,r}-\rho_s\,)\;\delta\mu_s+\frac{1}{\rho}\;(\,\rho_{salt,r}-\rho_{salt}\,)\;\delta\mu_{salt}\;. \end{aligned} \tag{25}$$

The number density ρ_s^0 of solvent molecules outside the solvation layer is different from the "thermodynamic" density $\rho_s = N^s/V$ in the suspension. There is an excess number of molecules Γ^s within the solvation layer that is attached to each colloidal sphere. This excess amount of solvent molecules in the solvation layer of a colloidal sphere is defined as,

$$\Gamma^s \;=\; \int_{r>R} d\mathbf{r}\;\left(\rho_s(r)-\rho_s^0\right)\;, \tag{26}$$

where $\rho_s(r)$ is the local solvent molecule concentration at a radial distance r from the center of a colloidal sphere. The Gibbs-dividing surface is defined here such that the adsorbed amount of solid colloidal core material is zero. Since the total number $V\rho_s$ of solvent molecules is equal to $N^c\Gamma^s + (V - N^c v_c^0)\rho_s^0$, it follows that,

$$\rho_s \;=\; \rho\,\Gamma^s + (1-\varphi)\,\rho_s^0\;, \tag{27}$$

where $\varphi = v_c^0\rho$ is the volume fraction of colloids.

Due to electro-neutrality of the colloidal surface plus its double layer, the excess amount of H^+ ions is equal to $-Z$, where Z is the valency of a colloidal sphere (including the sign of the charge). In the present case, where H^+ ions dissociate from the surface, Z is a negative number. The number of adsorbed salt molecules Γ^{salt} in a single double layer is thus equal to,

$$\Gamma^{salt} \;=\; \Gamma^- \;=\; \Gamma^+ + Z\;, \tag{28}$$

where,

$$\Gamma^{\pm} \;=\; \int_{r>R} d\mathbf{r}\;\left(\rho_{\pm}(r)-\rho_{\pm}^0\right)\;, \tag{29}$$

are the excess amounts of H^+ or A^- ions in the double layer. Here, $\rho_{\pm}(r)$ is the local number concentration of H^+ and A^- around a colloidal sphere, which can be calculated within the scope of the

Debye-Hückel theory for small surface potentials. Similarly as for solvent molecules, the thermodynamic concentration of salt is equal to,

$$\rho_{salt} \;=\; \rho\,\Gamma^{salt} + (1-\varphi)\,\rho^0_{salt}\;, \tag{30}$$

where $\rho^0_{salt} = \rho^0_{\pm}$ is the concentration of salt molecules outside the double layer.

The chemical potential of solvent molecules away from a colloidal particle, outside the solvation layer, is equal to that of the osmotic reservoir. The concentration ρ^0_s of such solvent molecules is therefore equal to the concentration $\rho_{s,r}$ of solvent molecules in the reservoir for incompressible solvents. With the neglect of the small contribution of thermal expansion of bulk material (so that $\delta\rho^0_s = 0$), using eq.(27), gives,

$$-v^0_c\,\delta\left[\,\rho^0_s\,\mu_s\,\right] + \frac{1}{\rho}\,(\,\rho_{s,r} - \rho_s\,)\,\delta\mu_s \;=\; -\Gamma^s\,\delta\mu_s\;. \tag{31}$$

Similarly, the concentration ρ^0_{salt} outside the double layer is equal to the salt concentration $\rho_{salt,r}$ in the osmotic reservoir, so that it follows from eq.(30) that,

$$-v^0_c\,\delta\left[\,\rho^0_{salt}\,\mu_{salt}\,\right] + \frac{1}{\rho}\,(\,\rho_{salt,r} - \rho_{salt}\,)\,\delta\mu_{salt} \;=\; -\Gamma^{salt}\,\delta\mu_{salt}\;. \tag{32}$$

Substitution of eqs.(31,32) into eq.(25) gives,

$$\delta w^{rev}/\delta N^c \;=\; \frac{1}{\rho}\,\delta\Pi - \Gamma^s\,\delta\mu_s - \Gamma^{salt}\,\delta\mu_{salt}\;. \tag{33}$$

This result can be written in an alternative form with the use of the Gibbs-adsorption equation,

$$-\Gamma^s\,\delta\mu_s - \Gamma^{salt}\,\delta\,\mu_{salt} \;=\; 4\,\pi\,R^2\,\delta\gamma \,+\, S_i\,\delta T\;, \tag{34}$$

where R is the radius of a colloidal sphere, γ is the surface tension and S_i is the entropy of a single interface between the colloidal material and the electrolyte solution, including the solvation layer and double layer. As before, the location of the Gibbs-dividing surface is chosen such that the amount of adsorbed solid colloidal material vanishes. The surface tension γ is well defined both for thin and thick double layers. Since $4\pi R^2\gamma$ is equal to the free energy of the interface, it follows that,

$$-\Gamma^s\,\delta\mu_s - \Gamma^{salt}\,\delta\,\mu_{salt} \;=\; \delta W^{rev}_i\;. \tag{35}$$

where W_i^{rev} is the reversible work involved in building up a single interface, including the solvation layer and the electrical double layer. The reversible work $W^{rev} = \delta w^{rev}/\delta N^c$ necessary to move a single colloidal sphere (see eq.(8)) thus follows from eqs.(33,35) as,

$$\delta W^{rev} \;=\; \frac{1}{\rho}\,\delta\Pi + \delta W_i^{rev}\;. \tag{36}$$

The first term on the right hand-side describes the energy necessary to displace a colloidal particle against gradients in the osmotic pressure. The second term is related to the work that is involved in changing the temperature of a solvation layer and a double layer, and of the immediate surface of the colloidal sphere.

For very dilute suspensions, where colloidal spheres do not interact with each other, $\Pi = \rho\, k_B\, T$. From eqs.(10,36) the following expressions for the diffusion coefficients are then found,

$$\begin{aligned} D &= D_0\,, \\ D_T &= D_0\left[\frac{\rho}{T} + \beta\,\rho\,\frac{\partial W_i^{rev}(T)}{\partial T}\right]\,, \end{aligned} \tag{37}$$

which reproduces eq.(12).

The interaction contributions to the osmotic pressure [10],[9] should be added to the above results for concentrated colloids.

As mentioned before, what has been neglected are the degrees of freedom associated with the bulk material of the core of a colloidal particle. The reversible work that is required to build up the solid bulk core material of a colloidal sphere (and the accompanied displacement of solvent) can simply be added to the work in eq.(37).

5 The Double Layer Free Energy and Reversible Work

In order to compare the prediction (12,37) for the thermal diffusion coefficient to experiments, the reversible work W_i^{rev} involved in creating an interface must be expressed in terms of, for example, salt concentration and the radius of the colloidal sphere. In the present section only the double layer contribution W_{dl}^{rev} to the interface work is considered.

It will be assumed that the dielectric constant within the core of a colloidal sphere is constant and that there are no charges inside the core of the colloidal particle, that is, all charges are assumed to be located on its surface.

When the dielectric constant within the core of the colloidal particle is homogeneous, independent of position, the surface charge σ is proportional to the radial derivative of the electric potential Φ at the surface of the colloidal particle, that is, at the radial distance $r = R$, with R the radius of the colloidal sphere, $\sigma = -\epsilon \frac{d\Phi(r)}{dr}_{|r=R}$, with ϵ the dielectric constant of the solvent. For moderate electric surface potentials, the electric potential Φ within the double layer is equal to [18],

$$\Phi(r) \;=\; \Phi_s \, \frac{exp\{-\kappa\,(r-R)\}}{r/R} \quad , \quad (\, r \geq R\,)\, , \tag{38}$$

where $\Phi_s = \Phi(r = R)$ is the surface potential and,

$$\kappa \;=\; \sqrt{\frac{e^2}{k_B T \epsilon}\, \sum_j \rho_j^0\, z_j^2}\; , \tag{39}$$

is the reciprocal Debye length, with $e > 0$ the elementary charge, k_B Boltzmann's constant, ρ_j^0 the number density of ions of species j outside the double layer, which carry z_j elementary charges.

The surface potential can be expressed in terms of the total charge $Q = 4\pi R^2 \sigma$ on a colloidal sphere from the relation between the charge density and the radial derivative of the potential at the colloidal surface as mentioned above,

$$\Phi_s \;=\; \frac{Q}{4\pi\epsilon\, R}\, \frac{1}{1+\kappa\, R}\; . \tag{40}$$

For some colloidal particles (like carboxyl-modified polystyrene) the surface groups are fully dissociated, whereas for other systems (like bare silica) the surface groups are only partially dissociated, depending on the pH.

The free energy of a colloidal particle is, by definition, the change in free energy on immersion of a colloid in its "dry state" into the dispersion. This free energy is either the Helmholtz free energy under constant volume or the Gibbs free energy under constant pressure. Before immersion, the colloidal particle is not solvated and surface groups are not dissociated. On immersion, the colloidal particle will gain entropy since it is free to move through the dispersion, the surface of the particle will be solvated and ions will be released from the surface while building up the double layer. The free energy to built up the double layer consists of two parts : (i) the free energy that it takes to create the ion cloud around the colloid and to charge its surface, which can be calculated via a "charging process", and (ii) the gain in entropy on release of ions from the surface of the colloidal particle on charging the surface. These two contributions have been discussed in detail in chapter 3 of the classic book of Verwey and Overbeek [18]. The charging process costs an energy in the form of reversible work W_{dl}^{rev} equal to,

$$W_{dl}^{rev} \;=\; \tfrac{1}{2}\, Q\, \Phi_s \;. \tag{41}$$

The change in free energy due to release of ions from the surface is equal to $-Q\,\Phi_s$. The double layer free energy F_{dl} (relative to the "dry" colloidal particle) is thus equal to,

$$F_{i,dl} \;=\; -\tfrac{1}{2}\, Q\, \Phi_s \;. \tag{42}$$

The free energy of the double layer must be negative, since otherwise the double layer would be unstable : the free energy would be lowered by de-charging the colloidal particle if the free energy were positive. The reversible work is thus equal but opposite in sign to the free energy, as a result of the entropic contribution due to the release of ions from the colloid surface.

Note that, according to eq.(42), the contribution γ_{dl} of the double layer to the interfacial tension is equal to,

$$\gamma_{dl} \;=\; -\frac{1}{8\,\pi\, R^2}\, Q\,\Phi_s \;=\; -\frac{\epsilon}{2\,R}\,(1+\kappa R)\,\Phi_s^2 \;, \tag{43}$$

within the Debye-Hückel approximation, where in the second line eq.(40) has been used. For thin double layers this reduces to $\gamma_{dl} = -\epsilon\kappa\Phi_s^2/2$, which is the expression that is used in, for example, refs.[11],[19] (in Gaussian units).

6 Explicit Expression for the Soret Coefficient

Explicit expressions for the double-layer contribution to the single particle diffusion coefficient are obtained by substitution of eqs.(39-41) into eq.(37). Again neglecting small contributions from thermal expansion, it is found that the double-layer contribution to the Soret coefficient $S_T^{(dl)} = D_T/\rho\, D$ is given by,

$$T\, S_T^{(dl)} \;=\; 1+\frac{1}{4}\,\beta\, Q\, \Phi_s\, \frac{\kappa\, R}{1+\kappa\, R}\left\{1-\frac{d\ln\epsilon}{d\ln T}\left(1+\frac{2}{\kappa\, R}\right)\right\}+\beta\, Q\, \Phi_s\, \frac{d\ln Q}{d\ln T}\;. \tag{44}$$

The "ideal gas" contribution (the first term on the right-hand side in eq.(44)) stems from work against the osmotic pressure, where additional terms should be accounted for when inter-colloidal interactions become important at higher concentrations (see refs.[10, 9]). The last term in this equation is only important when the total charge on the colloidal spheres is temperature dependent. This is generally the case for colloidal particles where the surface groups are only partially dissociated.

In order to compare with experiments, where the dependence of the Soret coefficient on the Debye length $\lambda_{DH} = \kappa^{-1}$ and the radius R of the colloidal spheres is probed, eq.(44) is more conveniently written as,

$$\begin{aligned} T\, S_T^{(dl)} \;=\;& 1+\frac{1}{4}\left(\frac{4\,\pi\, l_B^2\,\sigma}{e}\right)^2 \frac{\kappa\, R}{(1+\kappa\, R)^2}\left(\frac{R}{l_B}\right)^3\left\{1-\frac{d\ln\epsilon}{d\ln T}\left(1+\frac{2}{\kappa\, R}\right)\right\} \\ &+\left(\frac{4\,\pi\, l_B^2\,\sigma}{e}\right)^2 \frac{1}{1+\kappa\, R}\left(\frac{R}{l_B}\right)^3\frac{d\ln Q}{d\ln T}\;, \end{aligned} \tag{45}$$

where $l_B = \beta\, e^2/4\,\pi\,\epsilon$ is the Bjerrum length (which is 0.71 nm for water at room temperature). This result is valid for arbitrary Debye screening lengths. Note that the dimensionless combination $4\pi l_B^2\sigma/e$ is the number of unit charges on a fictitious sphere with radius l_B with the same charge density as the colloids. As will be seen in section 7, where a comparison with experiments is made, the values that this dimensionless group takes varies from about 0.01 for polystyrene spheres to 1 for SDS micelles. The temperature dependence of the dielectric constant can not be neglected, since for water at room temperature $d\ln\epsilon/d\ln T = -1.34$.

7 Comparison with Experiments and other Theories

In this section we shall compare the theoretical predictions in eq.(45) with experiments on two different types of systems : carboxyl-modified polystyrene spheres of various radii but equal charge density [12] and (ii) a SDS micellar solution [11]. In particular the salt-concentration dependence of the Soret coefficient will be discussed as well as its colloid size dependence. The polystyrene spheres are always large compared to the Debye length, while for the micellar system the Debye length is comparable or larger than the size of the micelles. The table gives the parameters for the two systems that are needed for a quantitative comparison.

A comparison with experiments on colloidal polystyrene spheres with identical surface chemistry but differing radii is given in Fig.1, where data are taken from ref.[12]. Here, the Soret coefficient is plotted against the Debye-Hückel screening length $\lambda_{DH} = \kappa^{-1}$. The surface charge density of the spheres as measured with electrophoresis is equal to $\sigma = 4500\ e/\mu m^2$, and hence $4\pi l_B^2 \sigma/e = 0.029$. Since the surface groups for these particles are fully dissociated, the charge is independent of temperature, that is $dQ/dT = 0$. The Bjerrum length for water at room temperature is 0.71 nm and $d\ln\{\epsilon\}/d\ln\{T\} = -1.34$.

The only adjustable parameter in a comparison of experimental values for the Soret coefficient and eq.(45) is the offset for zero Debye length, which is related to the contribution of the solvation layer to the reversible work W_i^{rev} to create an interface, and the contribution associated with the degrees of freedom within the bulk solid core material of the colloidal sphere. The solid curves in Fig.1 correspond to eq.(45) with $dQ/dT = 0$. As can be seen, the agreement with the experiments is quite reasonable, both for the salt-concentration dependence of the Soret coefficient and for the dependence on the radii of the colloids.

The variation of the offset in Fig.1 with the radius of the colloidal spheres indicates that the solvation layer is the main additional contribution to the single-particle Soret coefficient, and that the contribution from colloidal bulk-material is much less important. This is analyzed in more detail in ref.[20].

Thermodiffusion of SDS micellar particles has been explored in ref.[11]. These particle are much

Table : system parameters

System	Radius $[nm]$	σ	$4\pi l_B^2 \sigma/e$	$d\ln\epsilon/d\ln T$	$l_B\ [nm]$
Polystyrene	550/250/100	4500 $e/\mu m^2$	0.029	-1.34	0.71
SDS micelles	2.7	0.218 e/nm^2	1.38	-1.34	0.71

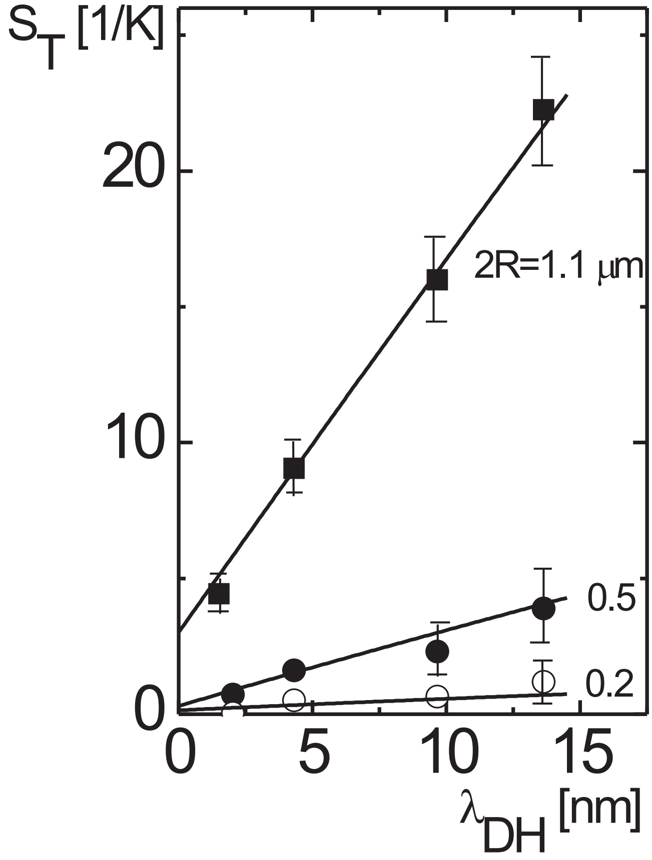

Figure 1: The Soret coefficient at room temperature $T = 298\ K$ as a function of the Debye-Hückel screening length $\lambda_{DH} = \kappa^{-1}$ for carboxyl-modified polystyrene spheres with a surface charge of $\sigma = 4500\ e/\mu m^2$, or, equivalently $4\pi l_B^2 \sigma / e = 0.029$. The radii of the spheres are 550, 250 and 100 nm, as indicated in the figure. The solid lines are the predictions from eq.(45) with $dQ/dT = 0$, and the data points are for polystyrene spheres [12]. The only adjustable parameter for each curve is the offset for zero Debye length, which is related to the solvation layer contribution and the contribution associated with the degrees of freedom within the bulk solid core material of a colloidal sphere.

smaller than the polystyrene spheres discussed above. For this system the particle radius is $R = 2.7\ nm$ and the charge density is $0.218\ e/nm^2$, and hence $4\pi l_B^2 \sigma / e = 1.38$ [21]. This system thus covers an entirely different part of parameter space as compared to the above mentioned polystyrene spheres. For the SDS micelles it is reasonable to assume that the surface groups are dissociated to an extent that allows the neglect of the temperature dependence of the charge in eq.(45). Care should be taken when comparing with these experiments with the prediction in eq.(45), since now, according to eq.(40), the dimensionless parameter $\beta e \Phi_s$ can be large, which invalidates the Debye-Hückel approach (for $\lambda_{DH} = 0.63\,nm$, $\beta e \Phi_s = 1$ and for $\lambda_{DH} = 1.07\,nm$ we have $\beta e \Phi_s = 1.5$). The above theory is thus certainly not applicable when λ_{DH} is larger than about $1\,nm$. For such small Debye lengths, the continuum Poisson-Boltzmann approach might be questionable. Nontheless, we compare the prediction in eq.(45) with the experimental data in Fig.2. As can be seen, the salt-concentration dependence of the Soret coefficient is correctly predicted for Debye lengths where the Debye-Hückel theory is valid. The theory and experimental data begin to deviate from the experimental data at a Debye length above which $\beta e \Phi_s$ becomes larger than unity, as expected. As before, the offset is an adjustable parameter. In ref.[11] it is stated that even for potentials such that $\beta e \Phi_s$ is much larger than unity, the Debye-Hückel theory is still applicable when an "effective charge" is used. In the above comparison we used the charge density as reported in ref.[21] for this system for lower potentials and refrained from using an "effective potential".

Based on a capacitor analogon with the electric-double-layer/charged-colloid system, the following expression for the Soret coefficient may be obtained [12],

$$T\, S_T^{(dl)} \;=\; 1 + \frac{1}{4} \left(\frac{4\,\pi\, l_B^2\, \sigma}{e} \right)^2 \frac{R^2}{\kappa\, l_B^3} \left\{ 1 - \frac{d \ln\{\epsilon\}}{d \ln\{T\}} \right\} \quad , \quad (\text{ from ref.[12] })\ , \tag{46}$$

where the "ideal-gas contribution" has been added. This expression is precisely the result in eq.(45) in the limit of thin double layers, where $\kappa R \gg 1$ (note that the polystyrene particles are very large in comparison to the double layer thickness). The experimental results in Fig.1 can therefore also be described on the basis of the capacitor model.

In ref.[19], an expression for the thermophoretic velocity is derived for thin double layers on the basis of a Navier-Stokes equation together with thermodynamic relations. Combining eq.(27) from

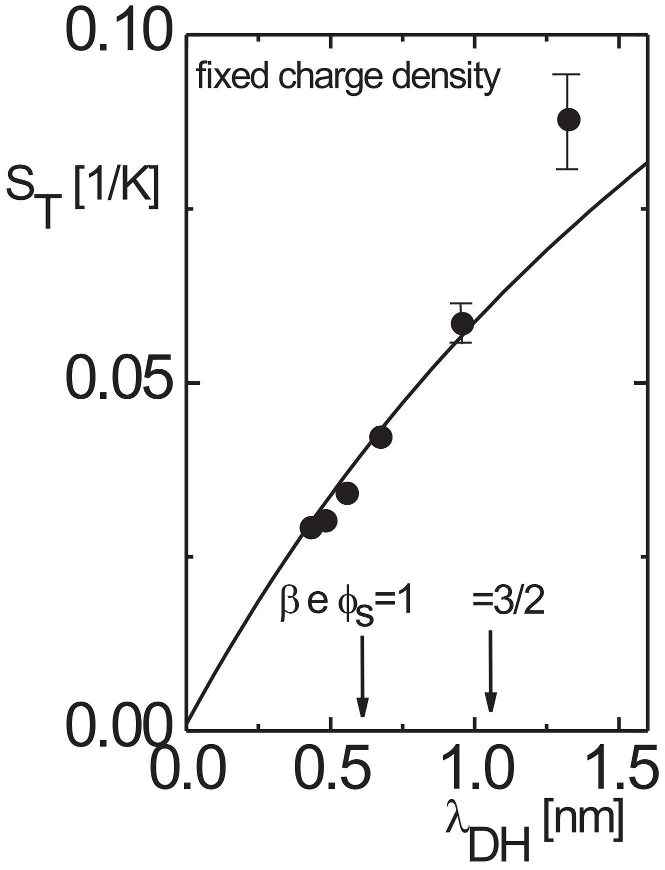

Figure 2: The Soret coefficient at room temperature $T = 298\ K$ as a function of the Debye-Hückel screening length $\lambda_{DH} = \kappa^{-1}$ for SDS micelles with a surface charge of $\sigma = 0.218\ e/nm^2$, or, equivalently $4\pi l_B^2\sigma/e = 1.38$. The radii of the spheres is $2.7\ nm$. The solid lines are the predictions from eq.(45) with $dQ/dT = 0$. The experimental data are taken from ref.[11]. As before, the only adjustable parameter is the offset at zero Debye length. The verticle arrows indicate the Debye lengths where $\beta\, e\, \Phi_s$ is 1 and 3/2, beyond which the Debye-Hückel approach becomes invalid.

ref.[19] and eq.(43) for the double-layer contribution to the surface tension with $\kappa R \gg 1$ it is found that,

$$T\,S_T^{(dl)} \;=\; 1+\frac{3\,\pi}{4}\left(\frac{4\,\pi\,l_B^2\,\sigma}{e}\right)^2\frac{R}{l_B^3\kappa^2}\quad,\quad(\text{ from ref.[19] })\;. \tag{47}$$

This expression is used in ref.[11] to interpret the experimental data on SDS micelles discussed above. It predicts that the Soret coefficient is a quadratic function of the Debye screening length. This result does not agree with our prediction in eq.(45), not for thin and also not for extended double layers. The reasons for this are (i) that it is not the free energy but only the reversible work that determines the Soret coefficient, and (ii) that eq.(47) assumes thin double layers whereas the double layer thickness for the micellar SDS system is actually comparable or larger than the size of the micelles. We therefore feel that the agreement between the proposed theory in ref.[11] with their SDS micellar data is fortuitous.

Bringuier and Bourdon [7] propose an expression for the thermal diffusion coefficient in terms of the temperature derivative of the total internal energy (see their eq.(13)), based on arguments that are put forward by van Kampen [22]. Disregarding the temperature dependence of the total charge, which amounts to taking the limit $E \to \infty$ in their eq.(17), where E is the energy related to thermally activated desorption of ions from the surface of the colloids, and using their expression (16) for U in their eq.(13) gives, for small colloid concentrations,

$$TS_T^{(dl)} \;=\; 1+\frac{1}{4}\left(\frac{4\,\pi\,l_B^2\,\sigma}{e}\right)^2\frac{1}{(\,1+\kappa\,R\,)^2}\,\frac{\kappa\,R^4}{l_B^3}\quad,\quad(\text{from ref.[7] with } E\to\infty \text{ and } \rho\to 0\,)\;. \tag{48}$$

Here, the temperature dependence of the total charge as well as the dielectric constant have been neglected. Within this approximation, the above expression is in accordance with our expression (45), both for thin and thick double layers. The correspondence between this single particle result for charged colloids from ref.[7] and our expression (45) for the Soret coefficient is quite satisfactory in view of the fundamentally different approaches that have been employed. For interacting systems, however, there is a difference between the general result in eq.(13) of ref.[7] and what is said in the present paper and refs.[9],[10]. According to refs.[9],[10], interaction contributions are related to temperature and density derivatives of the osmotic pressure rather than derivatives of the internal energy (for the isothermal collective diffusion coefficient this is long known). The internal energy U due to inter-colloidal interactions is introduced in ref.[7] in a rather uncontrollable manner. If the reversible work is used instead of U, and one recognizes that reversible work is done (i) against gradients in the osmotic pressure which includes interaction contributions and (ii) to build up single particle colloidal complexes, the expression that would have been obtained in ref.[7] fully agrees with the results of the present paper and refs.[9],[10].

Similar considerations as in ref.[7] based on van Kampen's work [22] lead to the correct expression for the Soret coefficient in ref.[17] (the expression between their eqs.(4) and (5)), provided that the "energy" u is interpreted as the reversible work to build up a colloidal sphere. The contribution to the reversible work associated with the bulk core material of a colloidal sphere and the displaced amount of solvent by the core has been extensively discussed in ref.[17].

8 Summary and Conclusions

On the basis of force balance on the Brownian time scale in combination with thermodynamic considerations concerning the force on a colloidal sphere resulting from gradients in concentration and temperature, it follows from the present analysis and what has been said in ref.[9] that the collective diffusion coefficient D and the thermal diffusion coefficient D_T are given by,

$$\begin{aligned} D &= D_0\,\beta\,\frac{\partial\Pi(\rho,T,\mu_s)}{\partial\rho}\,, \\ D_T &= D_0\,\beta\left[\frac{\partial\Pi(\rho,T,\mu_s(T,s))}{\partial T}+\rho\,\frac{\partial W_c^{rev}}{\partial T}\right]\,, \end{aligned} \tag{49}$$

where Π is the osmotic pressure (which is a function of the colloid number density ρ, the temperature T and the chemical potential μ_s of the solvent). In the temperature derivative of Π in the expression for D_T, the derivative also acts on the temperature dependence of the chemical potential of the solvent (the variable s represents the other variables on which μ_s depends besides the temperature). Furthermore, D_0 is the Einstein diffusion coefficient and $\beta = 1/k_BT$ (where k_B is Boltmann's constant). The first term on the right-hand side of the expression for D_T accounts for direct interactions between colloidal particles and includes the "ideal gas" contribution, while the second term is the single-particle contribution. Here, W_c^{rev} is the reversible work that is needed to build up a colloidal particle. This includes the creation of (i) the solid bulk core material of the colloid and the associated displacement of solvent, (ii) the structured layer of solid material in the immediate vicinity of the solvent, (iii) the solvation layer and (iv) the electrical double layer. The results in eq.(49) reproduce the expression for the Soret coefficient given in ref.[17] (see the equation in between their eqs.(4) and (5)), provided that the energy u is interpreted as the reversible work to build up a colloidal sphere.

What is neglected in eq.(49) is thermal expansion of colloidal core material and solvent, and more importantly, hydrodynamic interactions between the colloidal spheres. Hydrodynamic interactions become significant at higher colloid concentrations, and can be accounted for in a microscopic approach as described in ref.[10].

The single-particle contribution to the Soret coefficient related to the electric double layer is calculated within the Debye-Hückel approximation, leading to eqs.(44,45). This prediction is shown to be in accordance with experiments on polystyrene spheres (thin double layers) and micelles (thick double layers), within the parameter range where the Debye-Hückel approximation is valid. There is a single adjustable parameter when comparing with experiments where the salt concentration is varied. This is the intercept at zero Debye length, which is related to the remaining contributions to W_c^{rev} mentioned above.

Acknowledgement

This work has benefited from several discussions with Wim Briels, Eric Bringuier, Werner Köhler and Marianne Hartung, part of which resulted in the material of section 3 and the appendix.

Appendix : The Entropic Contributions

It will be shown here that the entropic contributions to eq.(13) and those arising from the Gibbs-Duhem relations for the suspension and the osmotic reservoir cancel, provided that thermal expansion is neglected and the solvent is incompressible. In ref.[9] these entropic contributions were simply omitted.

For reversible isothermal changes, the reversible work is equal to the change in free energy. The process considered here is also isothermal (since the temperature of the two boxes is fixed). However, in exchanging matter between the two boxes, this matter experiences a change in its temperature. The free energy must be corrected for these temperature changes in order to obtain the reversible work. Since the change δF in free energy is equal to $\delta F = \delta w^{rev} - S\,\delta T$, we have to add the contribution $S\,\delta T$ to the calculated δF in order to obtain the reversible work δw^{rev}.

There is a single particle contribution to the reversible work that is related to the change in temperature of matter that is exchanged. For example, the reversible work involved in building up an electrical double layer is temperature dependent. In changing the temperature of a double layer, part of the exchanged heat in order to change the temperature is therefore converted into work. This latter contribution to the reversible work is a single particle contribution which will be denoted in this appendix as δw_c^{rev} (where the subscript "c" stands for "colloid"). The total reversible work is thus written as,

$$\delta w^{rev} \;=\; \delta F + S\,\delta T + \delta w_c^{rev} \; . \tag{50}$$

The free energy and entropy are now understood to exclude the single particle internal degrees of freedom, **which relate to the solvation layer, the electrical double layer and the solid material of which the core of the colloids consists.** Changes related to these internal degrees of freedom of the "complexed colloidal particles" are lumped into the single particle contribution δw_c^{rev} to the total work. It is precisely this single particle contribution that is considered explicitly in the present paper. The **corresponding** degrees of freedom related to the electrical double layer are treated explicitly in the present paper by **explicitly** accounting for the electrolyte species that build the double layer in thermodynamic relations. In this appendix, we shall disregard these "internal degrees of freedom" of colloidal spheres **which are responsible for single-particle thermal diffusion**, and simply lump them all together into δw_c^{rev} without further specification. The similar "entropic contributions" of the form $S\,\delta T$ that are connected to the internal, single particle degrees of freedom can be treated similarly. Including these contributions would unnecessary complicate notation : all species that are involved in these internal degrees of freedom must be taken into account explicitly in all equations. We shall therefore discuss only the "interaction contributions" of the form $S\,\delta T$ of the solvent and of the colloids in this appendix. As mentioned above, contrary to the free energy in eq.(50), the change in free energy in eq.(13) in the main body of the present paper includes the internal colloidal particle degrees of freedom, which are lumped in eq.(50) into the contribution δw_c^{rev}. Here we will show that the remaining entropic contribution $S\delta T$ in eq.(50) cancels against similar contributions arising from Gibb-Duhem relations and that the change in free energy δF in eq.(50) is connected to interaction contributions (except for the "ideal gas contribution").

The "entropic contribution" $S\delta T$ can be obtained by considering the exchange of matter between the two boxes in more detail. What is actually happening during thermodiffusion is that all particles drift coherently from one box to the other. Consider therefore the process where all particles from box 1 drift to box 2. During the same time span, all particles within the neighbouring box (box 0 say) diffuse to box 1 and all particles from box 2 are displaced to the neighbouring box (box 3, say). Since the gradients in concentration and temperature are constant over the length scale set by the size of the boxes, effectively $\delta N_c = N_{c,2} - N_{c,1}$ particles are moved from box 0 to box 1, from box 1 to box 2 and from box 2 to box 3. In the main text and in ref.[9], the change in free energy is calculated for a displacement of these δN_c particles from box 1 to box 2. This is sufficient to obtain an expression for the force acting on a particle, once the entropic contributions are omitted. To include the entropic contributions $S\delta T$, however, we have to consider the whole cascade of coherent displacements of colloidal particles, where it suffices to ask for the change in free energy that is required to move all particles from box 1 to box 2. The similar contributions to the change in free energy from the entire cascade of displacements can simply be added to obtain the change of free energy of the whole system.

When thermal expansion of colloidal material and solvent is neglected, the movement of colloidal spheres from box 1 to box 2 is accompanied by the movement of an equal volume of solvent from box 2 to box 1. The process is sketched in the Fig.3. The entropic contribution is now unambiguously defined as $S_s\delta T - S_l\delta T$, where S_s is the entropy of the suspension and S_l is the entropy of an equal volume of pure solvent (note that the temperature of box 1 and 2 is T and $T + \delta T$, respectively). It is very difficult to specify the entropic contributions if one considers the displacement of just a sub-collection of particles from box 1 to box 2.

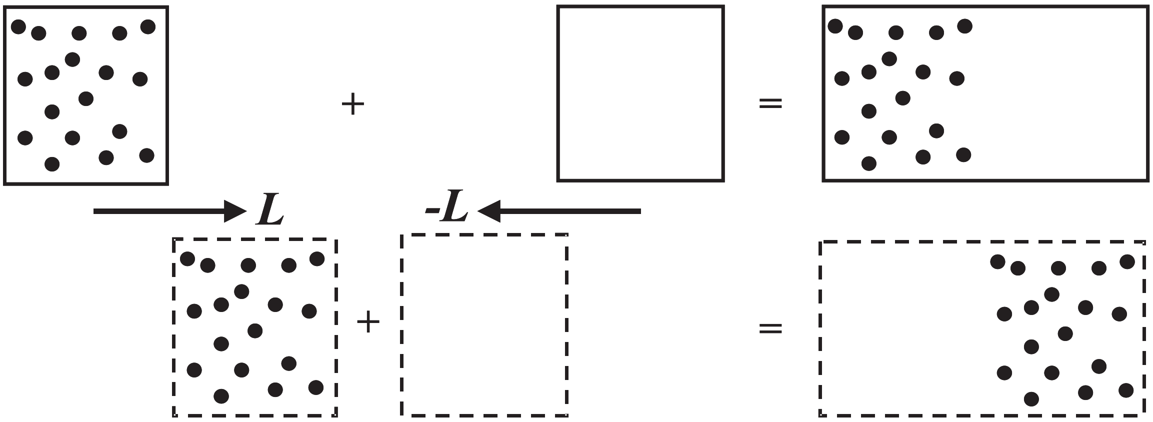

Figure 3: The left two figures depict the process of moving all colloidal particle from box 1 to box 2. The middle two figures depict the accompanied opposite displacement of pure solvent. The right two figures depict the resulting total process. Not depicted is are the colloidal particles which are also displaced simultaneously during thermodiffusion (for example from box 2 to box 3).

According to eq.(50) we thus have (with V the volume of the boxes),

$$\delta w^{rev} \; = \; \delta F + V \; [\, s_s - s_l \,] \, \delta T + \delta w_c^{rev} \; , \tag{51}$$

where s_s and s_l are the entropy of the suspension and pure solvent per unit volume.

The change in free energy $\delta F/\delta N_c$ per colloidal particle is calculated in ref.[9],

$$\delta F/\delta N_c \; = \; \delta \nu \; , \tag{52}$$

where,

$$\nu \; \equiv \; \mu_c - \frac{v_c^0}{v_s^0} \, \mu_s \; . \tag{53}$$

The δ on $\delta\nu$ now refers to the difference between box 2 and box 1.

The Gibbs-Duhem relation for the suspension reads,

$$0 \; = \; S_s \, \delta T - V \, \delta p + N_c \, \delta \mu_c + N_s \, \delta \mu_s \; , \tag{54}$$

where S_s is the entropy of the suspension, V the volume and p the mechanical pressure. The Gibbs-Duhem relation for the osmotic reservoir **(that was already introduced in section 4, just above eq.(22))** reads,

$$0 \; = \; S_r \, \delta T - V_r \, \delta p_r + N_{s,r} \, \delta \mu_s \; , \tag{55}$$

where the index "r" refers to the reservoir. It follows from these two relations and the definition of ν in eq.(53) that,

$$\delta\nu \; = \; \frac{V}{N_c}\,[\, s_r - s_s \,]\; \delta T + \frac{V}{N_c}\,\delta\Pi \; , \tag{56}$$

where s_r is the entropy of the pure solvent in the reservoir per unit volume and $\Pi = p - p_r$ is the osmotic pressure. In deriving this equation it is used that the suspension is space filling (that is $N_c v_c^0 + N_s v_s^0 = V$) and that the fluid in the reservoir is space filling (that is $N_{s,r} v_s^0 = V_r$).

Combining eqs.(51,52) and (56) thus leads to the following expression for the reversible work δW^{rev} per colloidal particle,

$$\delta W^{rev} \; = \; \frac{V}{N_c}\,[\, s_r - s_l \,]\, \delta T + \frac{V}{N_c}\,\delta\Pi + \delta W_c^{rev} \; , \tag{57}$$

where δW_c^{rev} is the single-particle reversible work for a single colloidal sphere. The entropy densities of pure liquid in the suspension (outside the solvation and double layers of the colloids) and of pure solvent in the osmotic reservoir differ from each other due to the pressure difference Π in the suspension and the osmotic reservoir. Now, according to the Gibbs-Duhem relation for the pure solvent, there are only two independent intrinsic variables. The entropy per unit volume, being an intrinsic variable, is therefore a function of two intrinsic variables only. Both s_r and s_l can thus be regarded as functions of either the intrinsic variables T, p or T, ρ_s (with $\rho_s = N_s/V$ the number concentration of pure solvent). For the same reason, the number density is a function of T and p. Hence,

$$s_r(p_r, T) - s_l(p, T) \; = \; \int_p^{p_r} dp' \, \frac{\partial s(p', T)}{\partial p'} \; = \; \int_p^{p_r} dp' \, \frac{\partial s(\rho_s(p',T),T)}{\partial \rho_s} \, \frac{\partial \rho_s(p',T)}{\partial p'} \; . \tag{58}$$

For nearly incompressible solvents, $\partial\rho_s(p',T)/\partial p'$ is very small, so that the difference in entropy density can be neglected provided that $\Pi\times$ a typical value of $\partial s(\rho_s,T)/\partial\rho_s$ is not inversely proportional to $\partial\rho_s(p',T)/\partial p'$. Since $\partial s(\rho_s,T)/\partial\rho_s = S/V - (V/N_s)\,\partial S(N,V,T)/\partial V$, and both terms on the right-hand side are perfectly well-defined also for incompressible solvents ,there is no reason for $\partial s(\rho_s,T)/\partial\rho_s$ to diverge for incompressible solvents.

This shows that the entropy contributions to the reversible work on the right-hand side of eq.(13) cancel against those arising from the Gibbs-Duhem relations for the suspension and the osmotic reservoir, provided that thermal expansion is neglected and the solvent is incompressible.

With the neglect of the entropy contribution for incompressible solvents and without the single particle contribution, we thus recover from eq.(57) the result $\delta W^{rev} = \frac{V}{N_c}\,\delta\Pi$ of ref.[9] for the interaction contribution to the reversible work per colloidal sphere.

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[16] In a comment in ref.[9] section VI, this expression for the single particle thermal diffusion coefficient was cited, except that instead of W^{rev} the chemical potential $\mu^{\star}_{cs}$ for the "complexed colloidal sphere" appears. This is not correct : only that part of the chemical potential related to reversible work appears in the expression for the single particle thermal diffusion coefficient.

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