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Temperature-induced migration of electro-neutral interacting colloidal particles

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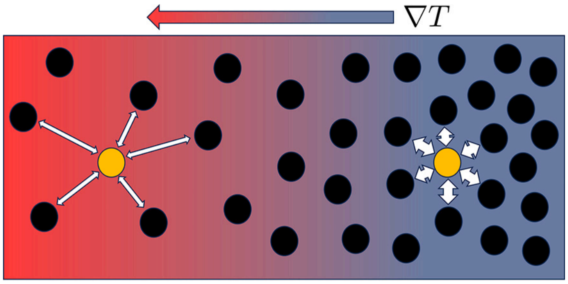
GRAPHICAL ABSTRACT



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

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ABSTRACT

Migration of colloidal particles induced by temperature gradients is commonly referred to as thermodiffusion, thermal diffusion, or the (Ludwig-)Soret effect. The thermophoretic force experienced by a colloidal particle that drives thermodiffusion consists of two distinct contributions: a contribution resulting from internal degrees of freedom of single colloidal particles, and a contribution due to the interactions between the colloids. We present an irreversible thermodynamics based theory for the latter collective contribution to the thermophoretic force. The present theory leads to a novel "thermophoretic interaction force" (for uncharged colloids), which has not been identified in earlier approaches. In addition, an N-particle Smoluchowski equation including temperature gradients is proposed, which complies with the irreversible thermodynamics approach.

A comparison with experiments on colloids with a temperature dependent attractive interaction potential over a large concentration and temperature range is presented. The comparison shows that the novel thermophoretic interaction force is essential to describe data on the Soret coefficient and the thermodiffusion coefficient.

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1. Introduction

Thermodiffusion of colloids has mostly been studied at very low concentrations where interactions between colloids can be neglected. These experiments, theories, and simulations probe single-particle thermophoretic forces, which are due to the response of internal degrees of freedom of, for example, an electric double layer in case of charged colloids [1–11], a solvation layer [12–15], or adsorbed surfactant molecules [11,16,17]. Theoretical approaches are quite specific, depending on the type of internal degrees of freedom that respond to a temperature gradient. General considerations on the single-particle level concerning interface phenomena can be found in Refs. [18–20].

Much less is known about the effect of interactions between colloids on their thermodiffusive behavior. Experimentally, a strong increase of the Soret and thermodiffusion coefficients due to colloid-colloid interactions is found in Ref. [21] for suspensions of charged silica spheres at low ionic strength. For charged polystyrene spheres, a similar strong contribution due to the interactions to the thermodiffusion coefficient results in an increase of 15% relative to the single-particle value, even at a concentration as low as 2.3 wt% [4]. In Refs. [3,22], experimental data on concentrated dispersions of an ionic sodium dodecyl sulfate (SDS) micellar system at various ionic strengths are reported, together with an attempt to quantitatively interpret these data (which will be discussed in some detail in section 4). Moreover, a strong ambient temperature dependence due to colloid-colloid interactions for the same system is found in Ref. [23]. The thermophoretic experiments on electro-neutral uncharged sticky colloidal spheres in Ref. [24] reveal both a pronounced concentration and ambient temperature dependence of the Soret coefficient and thermodiffusion coefficient. These experimental data, which span a wide ranges of concentration and temperature, will be compared to the theory developed in the present paper in sections 4 and 5.

There are only very few theoretical studies on the effect of intercolloidal interactions on thermodiffusion. In Refs. [25–27], the interaction force between charged colloids is assumed to be given by the spatial gradient of a temperature dependent mean-field interaction potential. The thermophoretic force between colloids with excluded volume interactions is stated in Refs. [28,29] to be proportional to the spatial derivative of an effective chemical potential. These approaches will be discussed in subsection 2.3 in some detail. One of the present authors (JKGD) derived expressions for the thermodiffusion coefficient for colloids with excluded volume interactions to leading order in concentration in Ref. [30] on the basis of thermodynamic arguments and in Ref. [31] to leading order in concentration for hard-spheres assuming the validity of a temperature-gradient modification of the well-known Smoluchowski equation. There has been valid criticism [32], however, on the purely thermodynamic treatment in Ref. [30], concerning the way in which entropic contributions have been accounted for. Moreover, as will be shown in the present paper, there is an additional thermophoretic force that has not been accounted for in Ref. [31], or any of the above mentioned theoretical approaches.

It is the purpose of this paper to develop a theory for the contribution of inter-colloidal interactions to the thermophoretic force experienced by electro-neutral, uncharged colloids. A contribution to the thermophoretic force due to interactions is predicted, which has not been considered before. This newly predicted force will be shown to be essential to describe the experimental data on the Soret coefficient and the thermodiffusion coefficient in Ref. [24] on colloids with a temperature dependent attractive interaction potential, over a wide range of temperature and concentration.

The thermodiffusion coefficient and the Soret coefficient as used throughout this paper are defined as follows. The flux of the number of colloids will be written as,

$$\mathbf{J}_c = -D_c \nabla \rho_c - D_T \nabla T\,, \tag{1}$$

where D_c is the collective diffusion coefficient, D_T is the thermodiffusion coefficient, ρ_c is the number concentration of colloids, and T the temperature. For a closed system, the flux vanishes in the stationary state. In such a stationary state, the Soret coefficient is defined as,

$$S_T = -\frac{1}{\rho_c}\frac{d\rho_c/dz}{dT/dz} = \frac{1}{\rho_c}\frac{D_T}{D_c}\,, \tag{2}$$

where gradients are assumed to extend along the z-direction. The Soret coefficient can be regarded as a thermophoretic response function, as it connects the concentration gradient resulting from a temperature gradient per unit temperature gradient.

This paper is organized as follows. An expression for the thermophoretic force is derived on the basis of linear irreversible thermodynamics in section 2. Before the theory is presented, this section begins with a summary of all the approximations and assumptions that will be made, detailed justifications of which are discussed in Appendix A. Assuming incompressibility of the solvent and colloids, and temperature independent partial molar volumes, the force on a colloidal particle in a concentration and temperature gradient is expressed in terms of spatial gradients of an effective chemical potential and the heat-of-transfer in subsection 2.1. In subsection 2.2, gradients of the effective chemical potential are expressed in terms of pressure gradients. The thus obtained identification of the pressure-driven forces allows for the determination of an approximate expression for the heat-of-transfer in subsection 2.3, leading to a contribution to the total thermophoretic force due to colloid-colloid interactions that has not been identified in earlier theories. We refer to this force as *the thermophoretic interaction force*. Microscopic expressions for the various contributions to the total force on colloidal particles in terms of integrals of the pair-correlation function are given in section 3. These expressions allow for a microscopic comparison of the theory for the Soret coefficient and experiments in section 4. Subsection 4.1 describes the experimental colloidal system of sticky hard spheres, and subsection 4.2 contains the comparison with theory. It turns out that the newly predicted thermophoretic interaction force is essential to describe the experimental data. In section 5 the mobility is specified, and the resulting expression for the thermodiffusion coefficient is compared with experiments on the same colloidal system. On the basis of the obtained expression for the thermophoretic force on a colloid, a Smoluchowski equation that also applies to non-isothermal systems is proposed in section 6.

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

Here, we present a linear-irreversible thermodynamics approach to obtain the total force on a colloidal particle due to concentration- and temperature gradients. Of special interest is the thermophoretic force that results from interactions between the colloids.

Before embarking on the theory, we present first a list of approximation and assumptions that will be made, the justifications of which are given in Appendix A:

(1) Gravitational forces on the colloids that either lead to sedimentation or buoyancy are not explicitly included. These forces add to the forces that are explicitly discussed, and may be included in all equations below. For the experiments that we discuss these forces are irrelevant.
(2) Partial molar volumes of the colloids and the solvent molecules are assumed to be independent of pressure, concentration, and temperature.
(3) The total pressure is assumed to be independent of position.
(4) The number of solvent molecules, residing in thin solvation layers around the surfaces of all colloids, and which interact directly with them, is negligible compared to the number of molecules within the bulk solvent.

(5) Bulk solvent attains equilibrium quasi-instantaneously for each configuration of the colloids.
(6) The force on a colloidal particle due to heat conduction in the absence of mass transport will be neglected.

2.1. Irreversible thermodynamics approach

The purpose of this subsection is to derive an effective one-component flux-force relation, which is given in eqs. (10), (11), and obtain from that eq. (15) for the force on a colloidal particle in terms of the heat-of-transfer, which is defined in eq. (17).

For the two-component system consisting of uncharged colloids and solvent molecules, the fundamental Onsager relations are formulated in terms of the colloidal-particle number flux $\mathbf{J}_c$, the number flux $\mathbf{J}_s$ of solvent molecules, and the flux $\mathbf{J}_U$ of internal energy U [33–37],

$$\begin{aligned}\mathbf{J}_c &= L_{cc}\,\mathbf{F}_c + L_{cs}\,\mathbf{F}_s + L_{cU}\,\mathbf{F}_U\,,\\ \mathbf{J}_s &= L_{sc}\,\mathbf{F}_c + L_{ss}\,\mathbf{F}_s + L_{sU}\,\mathbf{F}_U\,,\\ \mathbf{J}_U &= L_{Uc}\,\mathbf{F}_c + L_{Us}\,\mathbf{F}_s + L_{UU}\,\mathbf{F}_U\,,\end{aligned} \tag{3}$$

where $L_{ij} = L_{ji}$ are the as yet unknown Onsager coefficients, and the flux-driving single-particle forces are equal to,

$$\begin{aligned}\mathbf{F}_c &= -T\,\nabla\frac{\mu_c}{T}\,,\\ \mathbf{F}_s &= -T\,\nabla\frac{\mu_s}{T}\,,\\ \mathbf{F}_U &= T\,\nabla\frac{1}{T}\,,\end{aligned} \tag{4}$$

with T the temperature, μ_s the chemical potential of the solvent molecules, and μ_c that of the colloids. Throughout this paper, fluxes are formulated in terms of number of particles instead of mass, so that $\mathbf{F}_{c,s}$ are the forces acting on a single colloidal particle and solvent molecule, respectively. A formulation in terms of mass fluxes is necessary when combined with convection as described by the Navier-Stokes equation. Here we consider only diffusive particle displacements, in the absence of macroscopic flow. The results that are thus obtained for forces on colloids can nevertheless be used in a more general description that includes macroscopic flow. We note that hydrodynamic interactions come into play when connecting the forces to fluxes, and are thus implicit in the Onsager coefficients. Hydrodynamic interactions are explicitly accounted for in the derivation of an expression for the thermodiffusion coefficient in section 5, and the extension of the Smoluchowski equation to include temperature gradients in section 6.

To account for gravity (either leading to sedimentation or buoyancy), the additional corresponding force $-\nabla(\Delta m\,\mathbf{g}\cdot\mathbf{r})$ could be added to the force $\mathbf{F}_c$ on a colloidal particle in eq. (4), where Δm is the different in the mass of a colloidal particle and an equal volume of solvent, $\mathbf{g}$ is the earth gravitational acceleration, and $\mathbf{r}$ is the position of the colloid. As discussed in Appendix A point (1), the effect of gravity can be neglected for the experiments with which the theory will be compared.

Note that different notations are used for the energy flux by different authors. We employ the same notation as in Refs. [35,37], except that we write $\mathbf{J}_U$ for the energy flux where they use $\mathbf{J}_q$. This saves us from using a (double) prime when introducing the measurable heat flux.

The colloidal particles as well as the solvent will be considered incompressible. We therefore assume that the partial molar volumes v_c of a colloidal particle and v_s of a solvent molecule do not depend on concentrations and pressure. As mentioned in the beginning of this section, it will furthermore be assumed in the following that these partial molar volumes are independent of temperature (see also Appendix A point (2)). The number concentration of solvent molecules within bulk solvent is thus equal to $1/v_s$, not to be confused with the thermodynamic solvent concentration N_s/V, with N_s the number of solvent molecules within a suspension of volume V.

Fluxes will be defined relative to a volume-fixed reference frame, which for the incompressible system under consideration reflects the experimental situation where the position of the sample cell is fixed with respect to the observer. Within the volume-fixed reference we have,

$$v_s\,\mathbf{J}_s + v_c\,\mathbf{J}_c \;=\; \mathbf{0}\,. \tag{5}$$

When a colloid is displaced, a number of $v_c/v_s \gg 1$ of solvent molecules is displaced in the opposite direction. There is thus a trivial contribution to the solvent flux equal to $-(v_c/v_s)\,\mathbf{J}_c$. The remaining contribution to the solvent flux is equal to,

$$\mathbf{J}'_s \;=\; \mathbf{J}_s + \frac{v_c}{v_s}\,\mathbf{J}_c \;=\; \mathbf{0}\,, \tag{6}$$

where the latter equality follows from eq. (5).

Due to the high degree of incompressibility, the pressure p relaxes towards a position independent value on a time scale during which the positions of the colloids are essentially unchanged, so that,

$$\nabla p \;=\; \mathbf{0}\,. \tag{7}$$

Such adjustment of the pressure is entirely due to the flux $\mathbf{J}'_s$, which thus vanishes for strictly incompressible systems within the volume-fixed frame of reference. Apart from defining the frame of reference, eq. (6) expresses that for a fully packed, strictly incompressible system, there is no flux of solvent molecules in addition to that trivially associated with colloid displacements as mentioned above. A justification of the validity of eq. (7) is given in Appendix A point (3).

In case there is a difference between the specific mass density of the colloidal core and the solvent, there is a mass flux relative to the volume fixed frame. The diffusive nature of this mass flux is due to the dominance of the friction force with the solvent experienced by a colloid over their inertial forces. The momentum of a colloid due to friction relaxes on a time scale of the order of a few nanoseconds, during which the colloid's displacement is a very small fraction of its own size. Equations of motion for the colloid concentration that are coarse grained over a time interval of a few nanoseconds are therefore independent of the mass of the colloids, rendering equations of motion for the colloid concentration purely diffusive (provided that spatial gradients in the total pressure, as well as external shearing and tensile force are absent).

The flux $\mathbf{J}_U$ is most conveniently replaced by the heat flux [35–37],

$$\mathbf{J}_q \;=\; \mathbf{J}_U - h_s\,\mathbf{J}_s - h_c\,\mathbf{J}_c\,, \tag{8}$$

where,

$$h_s \;=\; \frac{\partial H(N,N_s,p,T)}{\partial N_s}\,, \tag{9}$$

is the solvent partial molar enthalpy, with H the enthalpy (as a function of the number N of colloids, the number N_s of solvent molecules, the pressure p and temperature T), and similar for h_c. The heat flux $\mathbf{J}_q$ is some times referred to as "the flux of measurable heat" (and is denoted in Ref. [35] by $\mathbf{J}''_q$). Transforming the Onsager flux-force relations in eqs. (3), (4) in terms of the new fluxes $\{\mathbf{J}_c, \mathbf{J}'_s, \mathbf{J}_q\}$, and subsequently eliminating the solvent force $\mathbf{F}_s$ using eq. (6), leads to,

$$\begin{aligned}\mathbf{J}_c &= \mathcal{L}_{cc}\,\mathbf{F}'_c + \mathcal{L}_{cq}\,\mathbf{F}_q\,,\\ \mathbf{J}_q &= \mathcal{L}_{qc}\,\mathbf{F}'_c + \mathcal{L}_{qq}\,\mathbf{F}_q\,,\end{aligned} \tag{10}$$

where the new forces are equal to,

$$\begin{aligned}\mathbf{F}'_c &= -T\,\nabla\frac{\nu}{T} + T\,h\,\nabla\frac{1}{T}\,,\\ \mathbf{F}_q &= T\,\nabla\frac{1}{T}\,.\end{aligned} \tag{11}$$

Here, the "effective chemical potential" is given by,

$$\nu \;=\; \mu_c - \frac{v_c}{v_s}\,\mu_s\,, \tag{12}$$

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

$$h \,=\, h_c - \frac{v_c}{v_s}\, h_s \,. \tag{13}$$

The new Onsager coefficients $\mathcal{L}$ can be expressed in terms of the original coefficients L in eq. (3), and also obey Onsager’s symmetry relations.

It follows from eqs. (10), (11) that the colloid flux for isothermal transport is equal to $\mathbf{J}_c = -\mathcal{L}_{cc}\,\nabla\nu$, which is in accord with the well-known expression $\mathbf{F}'_c = -\nabla\nu$ for the total force on a colloid for such isothermal systems. The mobility for isothermal colloid transport is therefore equal to $\mathcal{L}_{cc}$, so that,

$$\mathbf{J}_c \,=\, \mathcal{L}_{cc}\,\mathbf{F} \,, \tag{14}$$

with $\mathbf{F}$ the total force acting on a colloidal particle, including thermophoretic contributions. It is thus found from eq. (10) for the colloid number flux, eq. (11) for the forces, and eqs. (12), (13) for the effective partial molar quantities, that,

$$\mathbf{F} \,=\, -\nabla\nu - \frac{1}{T}\Big(q^\star + T\,s\Big)\nabla T \,, \tag{15}$$

where the “effective partial molar entropy” is equal to,

$$s \,=\, s_c - \frac{v_c}{v_s}\, s_s \,, \tag{16}$$

with $s_{c,s}$ the partial molar entropies (similarly defined as the partial molar enthalpy in eq. (9)), and where it is used that $h_{c,s} = \mu_{c,s} + T\,s_{c,s}$. Furthermore, the so-called *heat-of-transfer* is equal to,

$$q^\star \,=\, \frac{\mathcal{L}_{cq}}{\mathcal{L}_{cc}} \,, \tag{17}$$

which has the following well-known interpretation [35–37]. For a constant temperature it follows from eqs. (10), (11) that $\mathbf{J}_c = \mathcal{L}_{cc}\,\mathbf{F}'_c$ and $\mathbf{J}_q = \mathcal{L}_{qc}\,\mathbf{F}'_c$, and hence, $\mathbf{J}_q = q^\star\,\mathbf{J}_c$ ($T =$ constant). This equation shows that $q^\star$ is the heat that is transported per colloidal particle at constant temperature, hence the nomenclature “heat-of-transfer”. We adopt throughout this paper the proposed nomenclature in Ref. [35], making a distinction between the “heat-of-transfer” and the “energy-of-transfer”. The $q^\star$ includes heat transfer of a volume v_c of solvent that is displaced in the direction opposite to the colloid displacement. Note, however, that the heat-of-transfer includes both single-particle as well as collective properties.

2.2. The force in terms of the colloid pressure

The determination of an (approximate) expression for the heat-of-transfer, which will be discussed in the next subsection, requires an expression for the force in eq. (15) in terms of spatial gradients of the colloid pressure, which is the pressure due to the presence of the colloids. This alternative expression for the force is given in eq. (22).

Spatial variations of the total pressure p vanish due to incompressibility (see eq. (7) and it’s justification in Appendix A point (3)). It will be shown below that the pressure gradient that is relevant for the force on the colloids relates to the contribution p_c of the colloids to the total pressure. This pressure will henceforth be referred to as *the colloid pressure*. The colloid pressure p_c should not be confused with the osmotic pressure Π, which is commonly determined from meniscus-height experiments. As will be shown below, $\nabla p_c = \nabla\Pi$ only for mass transport under isothermal conditions.

Starting point is the Gibbs-Duhem relation for the colloidal two-component dispersion,

$$0 \,=\, \Big[\, s_s\,\rho_s + s_c\,\rho_c \Big]\, dT + \rho_s\, d\mu_s + \rho_c\, d\mu_c - dp \,, \tag{18}$$

where, as before, $s_{s,c}$ are the partial molar entropies of the solvent and the colloids, respectively, $\rho_s = N_s/V$ is the number concentration of solvent molecules, $\rho_c = N_c/V$ that of the colloids, and p is the pressure.

On the basis of the virial theorem, it is shown in Appendix B that the total pressure p can be expressed as,

$$p \,=\, p_c + p_s \,, \tag{19}$$

with p_c and p_s the contributions to the pressure of the colloids and the solvent molecules, respectively. The colloid equation-of-state pressure p_c is the pressure of an effective single-component colloid system. Excluded volume interactions and short-ranged interactions (for example, those resulting from solvation layers and/or the presence of thin layers of grafted polymers) are accounted for in the colloid equation-of-state. In the derivation of eq. (19) it is used that only a negligible number of solvent molecules (residing within the colloid’s solvation layers) interact with the colloids (see Appendix A point (4) where this is discussed in more detail). Similarly, p_s is the equation-of-state pressure of pure solvent.

Using that $\rho_s\, v_s + \rho_c\, v_c = 1$, it is readily found that eq. (18) can be rewritten as,

$$\begin{aligned} 0 = \frac{1}{v_s}\left[\, s_s\, dT + d\mu_s - v_s\, dp_s \right] \\ + \rho_c\, s\, dT + \rho_c\, d\nu - dp_c \,. \end{aligned} \tag{20}$$

As elaborated in Appendix A point (5), the bulk solvent between the colloids is assumed to quasi-instantaneously equilibrate to the relatively slowly varying positions of the colloids. Therefore, the relation between dT, $d\mu_s$, and dp_s is given by the Gibbs-Duhem relation, according to which the first term in eq. (20) vanishes. It follows that,

$$0 \,=\, \rho_c\, s\, dT + \rho_c\, d\nu - dp_c \,, \tag{21}$$

which can be regarded as an effective one-component Gibbs-Duhem relation for the colloids. The colloids thus behave like a one-component system with a partial molar entropy s, chemical potential ν, and pressure p_c. According to eq. (21) there are only two independent intensive variables, so that s, ν and p_c shall henceforth be regarded as functions of ρ_c and T.

As before, the infinitesimally small changes in the effective Gibbs-Duhem relation (21) can be interpreted as the differences between adjacent volume elements, so that elimination of $d\nu$ in favor of dp_c in eq. (15) leads to,

$$\mathbf{F} = -\frac{1}{\rho_c}\,\nabla p_c - \frac{q^\star}{T}\,\nabla T \,. \tag{22}$$

The first term on the right hand-side is the average mechanical force, experienced by the colloids, due to gradients in both the colloid concentration and temperature (see Appendix C). The second term in eq. (22) is a purely thermophoretic force (being proportional to ∇T), which contains both single-particle forces as well as forces due to temperature dependent interactions between the colloids, as will be discussed in the next subsection. The latter interaction contribution to the thermophoretic force has not been identified before, and requires a closure relation for the heat-of-transfer.

The first term on the right hand-side, with p_c replaced by the osmotic pressure, has been suggested before in Refs. [17,38–40]. Some care should be taken, however, by simply replacing p_c by the experimentally measured osmotic pressure Π^{exp} obtained from meniscus height measurements. The connection between p_c and Π^{exp} is as follows. Consider an osmotic equilibrium between the colloidal suspension and a reservoir of pure solvent, which are separated by a membrane that is only permeable for the solvent molecules. Let s^0_s, μ^0_s, and p^0_s denote the partial molar entropy, chemical potential, and pressure within the osmotic reservoir, respectively. For *isothermal* particle transport, it follows from the Gibbs-Duhem relations for the bulk solvent between the colloids ($d\mu_s = -v_s\, dp_s$) and in the pure solvent in the osmotic reservoir ($d\mu^0_s = -v_s\, dp^0_s$), together with $d\mu_s = d\mu^0_s$, that $dp_s = dp^0_s$. In this case $dp_c \equiv d\Pi^{exp}$, where $\Pi^{exp} = p - p^0_s$ is the standard definition of the osmotic pressure, which is the experimental osmotic pressure as determined from meniscus-height measurements. For *non-isothermal* particle transport, $dp_s \neq dp_s^0$, since in the respective Gibbs-Duhem relations $s_s\, dT \neq s_s^0\, dT$, and hence $dp_c \neq d\Pi^{exp}$. Since dp_c is only equal to $d\Pi^{exp}$ for isothermal particle transport, contrary to non-isothermal transport, we will henceforth refer to p_c as *the colloid pressure*.

Note that the effective partial molar entropy can be regarded as the partial molar entropy of the colloids with the constraint $N_s = (V - v_c N_c)/v_s$, since,

$$\frac{\partial S(N_c, N_s = (V - v_c N_c)/v_s, p, T)}{\partial N_c} = s(\rho_c, T)\,. \tag{23}$$

A similar consideration holds for the effective chemical potential ν.

Also note that for a mono-component gas or compressible fluid, the so-called "thermomolecular pressure difference" $\Delta P/\Delta T = -q^\star/(v T)$, with ΔP the pressure difference in the stationary state induced by a temperature difference ΔT, and with $v = 1/\text{concentration}$ (see eqs. (19)–(21) in chapter III of Ref. [35]). This result is formally reproduced by eq. (22) (with $\mathbf{F} = \mathbf{0}$ in the stationary state), but with P replaced by p_c. This confirms the earlier conclusion, that the colloids can formally be considered as a one-component system with pressure p_c.

2.3. An approximate expression for $q^\star$ and the resulting total force

As a last step to obtain an explicit expression for the force on a colloidal particle from eq. (22), in this subsection an approximate expression for the heat-of-transfer is derived, which is given in eq. (26). The heat-of-transfer contains a contribution for single colloids and a contribution due to the temperature dependence of the interactions between colloids. This leads to an expression for the total force given in eq. (31).

The heat flux consists of two distinct parts. There is a heat flux due to mere heat conduction, and there is a heat flux associated with particle transport. In obtaining an expression for $q^\star$, the force on a colloidal particle due to mere heat conduction will be neglected (which is further discussed in Appendix A point (6)).

Although we shall not need it to derive an expression for $q^\star$, a word on the distinction between mere heat conduction and heat transport associated with particle transport is in order. The heat flux $\mathbf{J}_q^{cond}$ due to mere heat conduction is the heat flux in case $\mathbf{J}_c = \mathbf{0}$, which implies that $\mathbf{F}'_c = -q^\star\, \mathbf{F}_q$, so that $\mathbf{J}_q^{cond} = (\mathcal{L}_{qq} - q^\star \mathcal{L}_{qc})\,\mathbf{F}_q$. The heat flux $\mathbf{J}_q^{coll}$ solely due to the transport of colloids is thus equal to $\mathbf{J}_q^{coll} = \mathbf{J}_q - \mathbf{J}_q^{cond} = q^\star\, \mathbf{J}_c$ (also when $T \neq$ constant), which is in accordance with the earlier discussed physical meaning of $q^\star$ in otherwise isothermal systems, being equal to the amount of heat transported by a single colloidal particle.

Now consider two boxes of macroscopic extent, each with a constant volume, and each containing a colloidal dispersion of the same concentration, in internal equilibrium. The case of constant pressure will be briefly discussed below. Both boxes are thermally isolated, where the temperature of the left box at position z (hereafter referred to as "box I") is T, and the box on the right ("box II") at position $z + \delta z$ has temperature $T + \delta T$, where δT is (infinitesimally) small compared to the ambient temperature T. The thermal isolation of the two boxes prevents mere heat conduction, and fixes the temperature gradient $\delta T/\delta z$. Pulling a single colloidal particle quasi-statically from box I to box II, changes the internal energy u of the combined system of the two boxes by $\delta u = -\Delta F_T\, \delta z$, where ΔF_T is the thermophoretic force. A change of the temperature of both boxes, as a result of the work performed, can be neglected, since the colloidal particle under consideration is embedded in an arbitrary large amount of suspension. The contribution to the thermophoretic force due to work against the pressure p_c experienced by the colloids is already accounted for by the first term on the right hand-side in eq. (22) for the total force, and should therefore not be included in δu to obtain an expression for the second term $\sim \nabla T$ in eq. (22) (hence the notation ΔF_T). The remaining contribution to δu is therefore the difference in the internal energy of a single colloidal particle at $T + \delta T$ and T. Recall, that the internal energy contains both single-particle as well as collective contributions. The additional thermophoretic force $\Delta \mathbf{F}_T$ is thus equal to,

$$\Delta \mathbf{F}_T \equiv -\frac{q^\star}{T}\,\nabla T = -\frac{\partial u}{\partial T}\,\nabla T\,, \tag{24}$$

where now u is understood to be equal to the thermodynamic internal energy carried by a single colloidal particle.

Since only a negligible number of solvent molecules interact directly with the colloids, as discussed in Appendix A point (4), the internal energy of the suspension can be written as a sum two single-component internal energies $U = U_c + U_s$ of the colloids U_c and solvent molecules U_s. On the other hand, $U = N\,u_c + N_s\,u_s$, with u_c and u_s the partial molar internal energies of the colloids and solvent molecules, respectively (defined similarly as the previous partial molar quantities). It follows that u_c and u_s are nothing but the single-particle internal energies, so that u is nothing but the "effective partial molar internal energy",

$$u = u_c - \frac{v_c}{v_s}\,u_s\,, \tag{25}$$

where, as before, the second term accounts for the opposite displacement of solvent. From $\partial u/\partial T = T\,\partial s/\partial T$, it thus follows from eqs. (24), (25) that,

$$q^\star = T\,\frac{\partial u(\rho_c, T)}{\partial T} = T^2\,\frac{\partial s(\rho_c, T)}{\partial T}\,. \tag{26}$$

There are two contributions to the temperature dependence of the internal energy u carried by a single colloidal particle. There is (i) a contribution due to the internal energy resulting from interactions with neighboring colloidal particles, and (ii) a single-particle contribution, related to the thermal properties of the core of a colloidal particle (and more generally to the presence of an electric double layer, a hydration layer, and a polymer brush grafted to the surfaces of the colloidal particle, as mentioned before). The interest in the present paper is in the former colloid-colloid interaction contribution.

For the colloid-colloid interaction contribution we write,

$$\Delta \mathbf{F}_T^{int} = -f_{int}(T)\,\nabla T\,, \tag{27}$$

with,

$$f_{int} = \frac{\partial u_{int}(\rho_c, T)}{\partial T}\,, \tag{28}$$

where u_{int} is the interaction energy of a single colloidal particle with its neighbors, which will be specified explicitly in the next section in terms of the colloid-colloid interaction potential. We shall henceforth refer to this force as the *thermophoretic interaction force*.

As mentioned earlier, single-particle contributions are quite specific for different types of colloidal particles. The single-particle thermophoretic force ΔF_T^{single} will not be specified here, and will be simply denoted, similarly to eq. (28) for the thermophoretic interaction force, as,

$$\Delta \mathbf{F}_T^{single} = -f_{single}(T)\,\nabla T\,, \tag{29}$$

with,

$$f_{single} = \frac{\partial u_{single}}{\partial T}\,, \tag{30}$$

where the internal energy u_{single} corresponding to the degrees of freedom of a single colloid is understood to include the opposite displacement of a volume v_c of solvent. Here, the value of f_{single} is determined from experimental thermophoretic data extrapolated to zero concentration. In addition to thermodynamic contributions, there are in general additional contributions to f_{single}, that can not be described on the basis of thermodynamics alone [20,32,35,41,42]. For charged colloids, for example, the temperature-gradient induces deformation of the electric double layer as well as electro-osmotic solvent flow, both of which contribute to the single-particle thermophoretic force. For experiments under constant pressure, the internal energy should be replaced by the enthalpy, leading to an additional contribution to the single-particle force due to pV-work, that is due to the difference between the thermal expansion coefficients of pure solvent and the core of the colloids.

It is thus finally found that,

$$\mathbf{F} = -\frac{1}{\rho_c}\frac{\partial p_c}{\partial \rho_c}\nabla \rho_c - \left[\frac{1}{\rho_c}\frac{\partial p_c}{\partial T} + f_{single} + f_{int}\right]\nabla T\,, \tag{31}$$

where p_c and f_{int} are functions of ρ_c and T. Microscopic expressions for p_c and f_{int} are discussed in the next section, which allow for a detailed comparison of the prediction for the force in eq. (31) to experimental results in sections 4 and 5. There is an additional force $-\nabla(\Delta m\,\mathbf{g}\cdot\mathbf{r})$ due to gravity that should be added to the total force $\mathbf{F}$ in case such forces are relevant (see the comments in Appendix A point (1)).

The colloid-colloid interaction energy u_{int} includes both excluded volume interactions, and for example, interactions mediated by the solvation layers and/or a thin layer of grafted polymers. The latter is the case for the experimental system to which the theory will be applied, leading to temperature dependent attractive interactions. The relation $U^\star = \nu$ that is assumed in Refs. [28,29] corresponds to $q^\star = -T\,s$ (note that in these references the quantity q, in their notation, corresponds to $-U^\star$ according to the proposed nomenclature in Ref. [35], which we adopted here). According to eq. (15) this leads to $\mathbf{F} = -\nabla\nu$, and leads to a Soret coefficient that contains derivatives of ν instead of p_c. In Refs. [25–27], the driving force for colloid transport is solely attributed to the temperature and concentration dependence of the interaction energy of the colloids (denoted here as u_{int}), which implies that $\mathbf{F} \sim (\partial u_{int}/\partial \rho_c)\nabla\rho_c + (\partial u_{int}/\partial T)\nabla T$, and leads to a Soret coefficient that solely contains derivatives of u_{int}. These predictions are at odds with eqs. (27), (28), (31), and in particular lead to expressions for the Soret coefficient that fundamentally differ from that found in the present paper (see section 4).

3. Microscopic expressions for the colloid pressure and thermophoretic interaction force

So far no assumption has been made concerning the geometry of the colloidal particles. The expression for the force in eq. (31) is equally valid for, for example, rod-like and spherical colloids. The microscopic expressions discussed below are restricted to spherical colloids.

The colloid pressure p_c in terms of the equilibrium colloid-colloid pair-correlation function g^{eq}, assuming pair-wise additivity of the total interaction potential, reads [43] (see also Appendix B),

$$p_c(\rho_c, T) = \rho_c\,k_B T - \frac{2\pi}{3}\rho_c^2\int_0^\infty dR\,R^3\,g^{eq}(R)\,\frac{dV(R)}{dR}\,, \tag{32}$$

where R is the distance between two colloidal particles, and $V(R)$ is the pair-interaction potential. The use of the *equilibrium* pair-correlation function is justified by the irreversible-thermodynamics assumption that each volume element is in internal equilibrium. Note that the pair-correlation function g^{eq} is a function of the local concentration ρ_c, while it is also depends on the local temperature in case the pair-interaction potential V is temperature dependent.

The internal interaction energy of a single colloidal particle u_{int} in eq. (28) due to interactions with the remaining colloids is equal to (again assuming pair-wise additivity of the total interaction potential),

$$u_{int} = \frac{1}{N_c}\sum_{i>j}^{N_c} < V(|\mathbf{r}_i - \mathbf{r}_j|) >\,, \tag{33}$$

where $<\cdot>$ denotes the ensemble average with respect to the colloidal particle's position coordinates $\{\mathbf{r}_j \mid j = 1, \cdots, N_c\}$. The prefactor $1/N_c$ accounts for the fact that the interest is in the average interaction energy of a single colloid. Just as for the colloid pressure in eq. (32), the ensemble average is evaluated at the local concentration and temperature. Expressing the average in terms of an integral over the pair-correlation function, the amplitude of the thermophoretic interaction force is found to be equal to (see eq. (28)),

$$f_{int} = 2\pi\rho_c\frac{\partial}{\partial T}\int_0^\infty dR\,R^2\,g^{eq}(R)\,V(R)\,. \tag{34}$$

As for the colloid pressure, g^{eq} is the equilibrium pair-correlation function for an otherwise isothermal and homogeneous system at the local density and temperature.

4. The Soret coefficient and comparison with experiments

In a closed system, like thermal cells with boundary heating and cooling, and in Thermo Diffusion Forced Rayleigh Scattering (TDFRS) experiments [44,45], the flux of colloidal particles vanishes in the stationary state, which implies that the total force on the colloidal particles vanishes. It thus follows from eq. (31) with gradients along the z-direction that the Soret coefficient as defined in eq. (2) is equal to,

$$S_T = \left[\frac{1}{\rho_c}\frac{\partial p_c}{\partial T} + f_{single} + f_{int}\right]\Big/\frac{\partial p_c}{\partial \rho_c}\,, \tag{35}$$

where the gradients refer to those in the stationary state. In the following subsection, the colloidal system used in the experiments in Ref. [24] is described, together with the theoretical model for the pair-correlation function for sticky hard spheres. This model is then used to calculate the various contributions to the Soret coefficient based on eqs. (32), (34). The model calculation is then compared in subsection 4.2 with the experimental results from Ref. [24].

4.1. System and model

The experimental data from Ref. [24] with which the theory will be compared are obtained by means of Thermo Diffusion Forced Rayleigh Scattering (TDFRS). Here, two 488 nm argon laser beams are crossed, leading to a standing interference pattern with a wavelength of (10–20) μm. A small amount of dye is added to the sample at low concentrations, which absorbs the 488 nm light, giving rise to a sinusoidal temperature profile with an amplitude of approximately 20 μK. Due to the difference in refractive index of the colloids and the solvent, thermodiffusion gives rise to a sinusoidally varying refractive index grating. The time-resolved Bragg-scattered intensity of a 632.8 nm krypton laser beam from this refractive index grating is then connected to the amplitude of the sinusoidally varying colloid concentration, and hence to the Soret coefficient and thermodiffusion coefficient. More information can be found in Refs. [24,44,45].

The system used in the experiments in Ref. [24] consists of silica colloids, the surfaces of which are chemically grafted with a brush of octadecyl alcohol (also referred to as stearyl alcohol). The solvent is toluene, which is a good solvent for octadecyl alcohol for temperatures larger than about 45 °C, in which cases the colloidal particles behave as hard spheres. At lower temperatures, the thickness of the octadecyl alcohol brush diminishes due to the decreasing quality of toluene as a solvent for octadecyl alcohol, in order to increase the number of octadecyl alcohol contacts within the brushes in favor of the octadecyl alcohol/toluene contacts. The energetically favorable octadecyl/octadecyl contacts and the diminished importance of entropic contributions to the Helmholtz free energy of overlapping polymer brushes at lower temperatures lead to short-ranged attractive interactions between the colloids. The strength of the attractive interactions increases upon lowering the temperature. The temperature dependence of that contribution to the total interaction potential leads to a significant, non-negligible contribution to the Soret coefficient through the newly introduced thermophoretic interaction force, as shown in Fig. 2.

We note that for n-dodecane as a solvent an abrupt change in the colloid-colloid interactions is observed as a function of temperature [47]. This is attributed to a transition where grafted linear octadecyl alcohol molecules at the colloid's surfaces and the similarly linear n-dodecane solvent molecules interpenetrate and form an ordered, solidified structure around the colloids [47]. For benzene as a solvent, which has a non-linear plate-like geometry, a gradual change of the interaction potential is observed [47,48]. In Ref. [24], a similar gradual change with temperature is observed with toluene as a solvent, which has a similar non-linear plate-like geometry like benzene.

The silica particles have a number-averaged radius of $a = (15.0 \pm 1.0)$ nm, with a size distribution corresponding to a standard deviation σ equal to $\sigma^2 = (0.054 \pm 0.07) \times a^2$ [24]. The volume fraction φ in a theoretical approach for mono-disperse systems is obtained from the number concentration ρ_c as $\varphi = (4\pi/3)\, a^3\, \rho_c$. The experimental volume fraction φ_{exp} as obtained by weighing is equal to $\varphi_{exp} = \varphi\, \left[1 + 3(\sigma^2/a^2)\right]$, up to leading order in σ/a, where φ is the volume fraction as obtained from the number-averaged radius a of the colloidal particles. The experimental volume fractions should therefore be reduced by a factor $\left[1 + 3(\sigma^2/a^2)\right]^{-1} = 0.86$ when comparing with theory.

The experimental system described above is an example of sticky hard-spheres (or alternatively, adhesive hard-spheres). The pair-interaction potential for such particles can be approximated by a square-well potential,

$$\begin{aligned} V(R) &= \infty & R &< 2a \\ &= U_0 & 2a < R &< 2a + \Delta \\ &= 0 & 2a + \Delta &< R\,, \end{aligned} \tag{36}$$

where $2a$ is the hard-core diameter of the colloids, and Δ and $U_0 < 0$ are the width and depth of the attractive potential, respectively. The nomenclature "sticky spheres" stems from the fact that $\epsilon = \Delta/2a$ attains very small values. The colloid pressure and pair-correlation function for such systems, on the basis of the Ornstein-Zernike equation in Percus-Yevick approximation, has been discussed by Baxter in Ref. [49], with the special choice $U_0 = k_B T \ln\{12\,\tau\,\epsilon\}$, where τ is referred to as the "stickiness parameter". This choice for U_0 leads, however, to an expression for the interaction energy that diverges as $\epsilon = \Delta/2a \downarrow 0$ for a given finite value of τ. This apparent inconsistency is resolved by using U_0 as an independent parameter instead of τ. From the above expression for Baxter's U_0 it follows that $\tau = (1/12\,\epsilon)\, \exp\{U_0/k_B T\}$, which shows that a finite τ in the limit where $\epsilon \downarrow 0$ requires the simultaneous limit of $U_0 \downarrow -\infty$. Menon et al. extended Baxter's approach that applies to the pair-potential in eq. (36) where both $\Delta/2a$ and U_0 are independent variables, reproducing the above expression for τ, and in addition showing that η (with η in Baxter's notation the hard-core volume fraction) should be interpreted as $\eta = \varphi\,(1 + 3\,\epsilon)$ with φ the hard-core volume fraction, up to leading order in ϵ [50]. These expressions for τ and $\Delta/2a$ are to be used in eq. (32) in Ref. [49] for the colloid pressure and eqs. (5), (10) for the pair-correlation function. The pressure (either obtained from the compressibility equation or the virial equation) and the pair-correlation function predicted by Baxter have been shown by computer simulations to be quite accurate, at least up to volume fractions of 0.3 [51]. The amplitude f_{int} of the thermophoretic interaction force is obtained from eq. (34) above and eq. (10b) for the pair-correlation function in Ref. [49], together with the expression of Menon et al. for the stickiness parameter [50], leading to,

$$f_{int} = \varphi\, \frac{\partial}{\partial T} \left[\, \lambda\, U_0 \,\right] . \tag{37}$$

Here, λ is related to τ and η as the smallest solution of the quadratic equation (21) in Ref. [49].

4.2. Results

In this subsection we compare the experimental data taken from Ref. [24] for the Soret coefficient as a function of concentration for various ambient temperatures to the theory. It will in particular be shown that the new thermophoretic interaction force introduced in this paper is essential to describe the experimental data.

As shown in Appendix D, the experimental Soret coefficients S_T^{exp} as defined in Ref. [24] and as defined in the present paper are connected as,

$$S_T^{exp} = \frac{1}{1 - \varphi}\, S_T\,. \tag{38}$$

Comparing the theoretical predictions in eqs. (32), (35), (37) to the experimental data for the Soret coefficient in Ref. [24] as a function of concentration and temperature, there are three adjustable parameters: f_{single}, $\epsilon = \Delta/2a$, and U_0. The amplitude of the single-particle force f_{single} determines the intercept at zero concentration for each temperature. For each separate temperature, both $d\epsilon/dT$ and dU_0/dT are additional independent fit variables. After a fit for the five different temperatures, the temperature dependence of ϵ and U_0 should be in accordance with the numerical values obtained for $d\epsilon/dT$ and dU_0/dT, respectively. Such a correspondence is obtained by iteration. Fig. 1 shows the experimental data taken from Ref. [24] as a function of concentration for various temperatures, and the thus obtained fits (the solid lines). A similar decrease of the Soret coefficient with increasing concentration for essentially hard-core colloids [13] and sticky-spheres [46] has also been found by simulations.

For the highest temperature of 50 °C the solid line in the upper panel in Fig. 1 corresponds to the theory for hard-spheres, without any attractions between the colloids. In this case there is only a single fitting parameter, which is the amplitude f_{single} of the single-particle thermophoretic force, which merely determines the intercept at zero concentration. As can be seen, the predicted concentration dependence of the Soret coefficient is in good agreement with the experiments. Attractions come into play upon lowering the temperature, where a fit according to Baxter-Menon as described above is essential. Moreover, the contribution from the novel thermophoretic interaction force in eq. (37) becomes essential. In particular, when the single-particle contribution f_{single} becomes negative, a monotonically increasing Soret coefficient is found when the thermophoretic interaction force in eqs. (27), (28) is neglected. The experimental data for attractive interactions can not be explained on the basis of the force due to gradients in the osmotic pressure in eq. (31) alone. Fig. 2 shows the importance of the thermophoretic interaction force (the solid curves) against the temperature-gradient induced osmotic contribution (the striped curves). For 50 °C, $f_{int} = 0$, while for decreasing temperature the thermophoretic interaction forces become dominant over the osmotic contribution.

The fitting results for $\epsilon = \Delta/2a$, U_0 and the stickiness parameter τ are given in Figs. 3, 4, and 5, respectively.

For the hard-sphere interaction potential at 50 °C (and higher temperatures), we have $U_0 = 0$, $dU_0/dT = 0$, and $d\epsilon/dT = 0$, while the value for ϵ, and hence for $\tau = 1/(12\,\epsilon)$, can not be obtained from the fit. Since at 50 °C (and higher temperatures) the octadecyl alcohol chains are stretched, an estimate of Δ can be obtained as follows. From the carbon-carbon and carbon-oxide bond-lengths and bond-angles it is found that the contour length of octadecyl alcohol $CH_3(CH_2)_{17}OH$ is equal to $L = 2.3$ nm. Reported persistence lengths of octadecyl alcohol are in the range of $l_p = 0.6$–0.8 nm [52–54]. From,

$$\begin{aligned} \Delta &= \int_0^L ds\, \hat{\mathbf{u}}(0) \cdot \hat{\mathbf{u}}(s) \,=\, \int_0^L ds\, \exp\left\{-L/l_p\right\} \\ &= l_p \left[1 - \exp\left\{-L/l_p\right\}\right], \end{aligned} \tag{39}$$

where it is used that the segment orientation $\hat{\mathbf{u}}(s)$ at the grafting point $s = 0$ is perpendicular to the colloid's particle surface, it is thus found that $\Delta = 0.58$–0.75 nm. This brush thickness at 50 °C corresponds to $\epsilon = \Delta/2a = 0.020$–$0.025$ and $\tau = 1/(12\,\epsilon) = 3.32$–$4.27$. The thus obtained data points are represented by ⊙ in Figs. 3, 4, and 5. As can be seen,

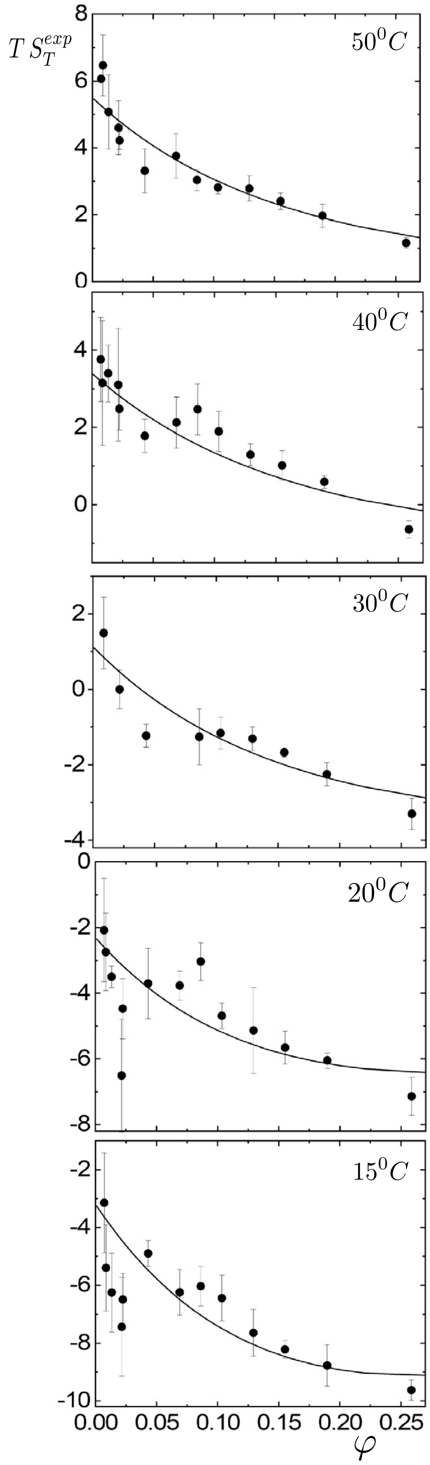

Fig. 1. Experimental results for $T \times S_T^{exp}$ as a function of the volume fraction for different temperatures (from top to bottom, 50, 40, 30, 20, and 15 °C). The solid curves are fits, using the Baxter-Menon colloid pressure and pair-correlation function. The volume fractions are corrected for polydispersity, as mentioned in subsection 4.1. The experimental data are taken from Ref. [24]. Courtesy of Prof. S. Wiegand.

these data points are in accordance with the data obtained at lower temperatures (the corresponding dashed lines in Figs. 3 and 5 represent extrapolations by eye). Phase separation occurs at $T = 3$ °C [24] and for $\tau = 0.1$ [51], which point is shown by the symbol ⊙ in the left lower part of Fig. 5. Again, this additional data point is in line with the extrapolated data by eye obtained from the thermodiffusion data.

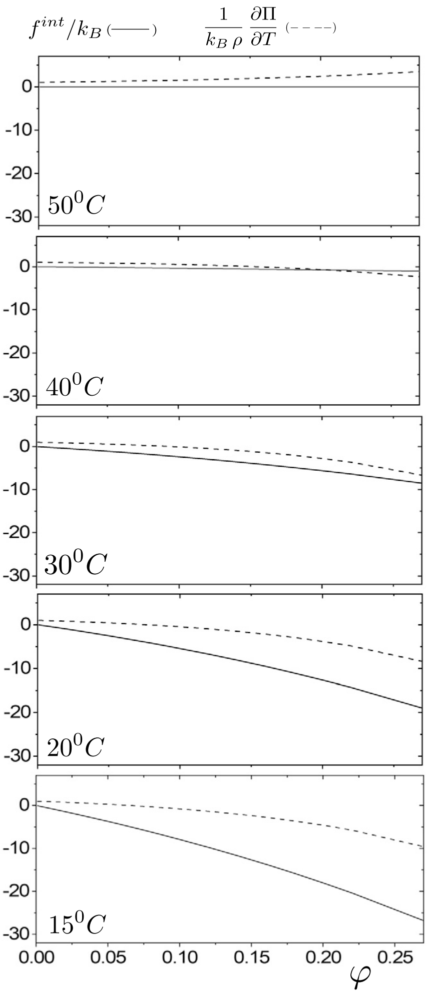

Fig. 2. A comparison of the amplitudes of the thermophoretic interaction force f_{int}/k_B (solid curves) and the force $(1/k_B\rho_c)\partial p_c/\partial T$ (the dashed curves) due to the temperature dependence of the colloid pressure, as a function of concentration for different temperatures, as indicated in the various panels. For 50 °C, $f_{int}/k_B = 0$. All plots are given on the same scale, to compare variations between the different temperatures.

Fig. 6 shows the temperature dependence of the single-particle amplitude f_{single} in eq. (29). As can be seen, f_{single} increases with increasing temperature, which implies an increasing tendency to migrate to regions of lower temperature with increasing solvent quality. The increase of f_{single} with increasing quality of the solvent is also seen in simulations [13]. A (semi-)quantitative interpretation of the temperature dependence of f_{single} requires an analysis that is beyond the scope of the present paper.

5. The thermodiffusion coefficient and comparison with experiments

According to eq. (1) for the flux,

$$\frac{\partial \rho_c(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}_c = \nabla \cdot \left[D_c \, \nabla \rho_c + D_T \, \nabla T \right] , \tag{40}$$

together with eqs. (14), (31), the collective diffusion coefficient and the thermodiffusion coefficient are equal to,

$$D_c = \mathcal{L}_{cc} \, \frac{1}{\rho_c} \, \frac{\partial p_c}{\partial \rho_c} \, ,$$

$$D_T = \mathcal{L}_{cc} \left[\frac{1}{\rho_c} \, \frac{\partial p_c}{\partial T} + f_{single} + f_{int} \right] . \tag{41}$$

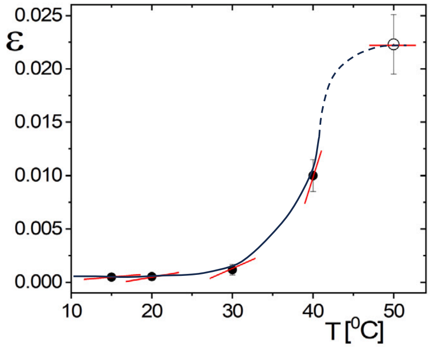

Fig. 3. $\epsilon = \Delta/2a$ as a function of temperature. The short red lines indicate the slopes obtained from the fits. The point at 50 °C for hard-spheres is obtained from the estimated linear extent of octadecyl alcohol in a good solvent. The solid curve is a guide-to-the-eye, the dashed line is an extrapolation by eye to the estimated point at 50 °C.

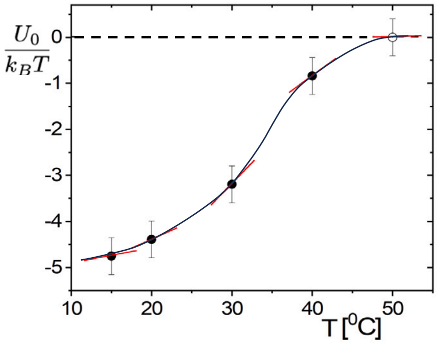

Fig. 4. The depth of the square-well potential as a function of temperature. The short red lines indicate the slopes obtained from the fits. The solid curve is a guide-to-the-eye. The dashed line is the zero-line, above which the colloids behave as hard spheres.

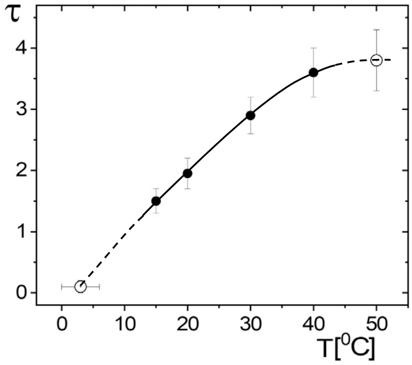

Fig. 5. The stickiness parameter τ as a function of temperature. The point at 50 °C is obtained from the estimated linear extent of octadecyl alcohol in a good solvent. The point at the lowest temperature corresponds to the temperature and τ where phase separation sets in [24,51]. The solid curve is a guide-to-the-eye, the dashed lines are extrapolations by eye to the estimated points at 3 and 50 °C.

These expressions describe long-time diffusive processes. However, as is well-known, the zero-wavevector limit of the short-time collective diffusion coefficient differs only by a few percent from the long-time diffusion coefficient [55–57]. We can therefore rely on literature on short-time collective diffusion for D_c in the zero-wavevector limit [58–60]. Within this approximation we find,

$$\mathcal{L}_{cc} \; = \; D_0\,\rho_c\,\beta\,H_0\,, \tag{42}$$

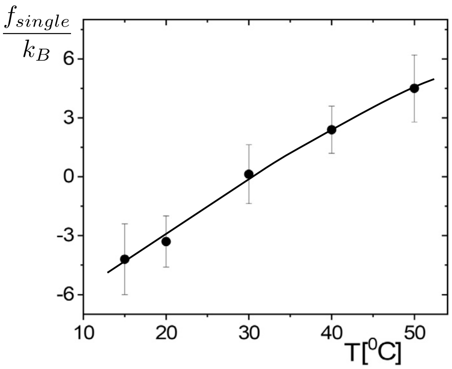

Fig. 6. The single-particle thermophoretic force f_{single}/k_B as a function of temperature. The solid curve is a guide-to-the-eye.

where $D_0 = k_BT/6\pi\eta_s a$ is the Stokes-Einstein-Sutherland free diffusion coefficient (with η_s the shear-viscosity of the solvent), where $\beta = 1/k_BT$, and where the *hydrodynamic mobility function* is equal to (with $\hat{\mathbf{k}} = \mathbf{k}/k$),

$$H_0 = \frac{1}{N_c}\lim_{k\to 0}\left\langle \sum_{i,j=1}^{N_c}\left(\hat{\mathbf{k}}\cdot\frac{\mathbf{D}_{ij}}{D_0}\cdot\hat{\mathbf{k}}\right)\exp\left\{ i\,\mathbf{k}\cdot\left[\mathbf{r}_i-\mathbf{r}_j\right]\right\}\right\rangle_0 . \tag{43}$$

Here, $< \cdot >_0$ denotes the equilibrium average with respect to the position coordinates $\{\mathbf{r}_i \mid i = 1, 2, \cdots N_c\}$ of the colloids, while the tensors $\mathbf{D}_{ij}$ specify the hydrodynamic interactions between the colloids. Note that H_0 is a function of ρ_c and T through the probability density function with respect to which the average $< \cdot >_0$ in eq. (43) is taken.

Unfortunately, there is no accurate analytical expression for H_0 for adhesive hard-sphere systems, so that a comparison with the data in Ref. [24] is only possible for the highest temperature. A good approximation for H_0 for stick boundary conditions up to high volume fractions for colloids which solely interact through excluded volume interactions reads [61],

$$\begin{aligned} H_0 &= 1 - 6.55\,\varphi \\ &\quad\times\left[1 - 3.35\,\varphi + 7.43\,\varphi^2 - 10.03\,\varphi^3 + 5.88\,\varphi^4\right]. \end{aligned} \tag{44}$$

The concentration dependence of the thermodiffusion coefficient D_T^{exp} as obtained experimentally in Ref. [24] is related to the theoretical D_T as defined in the present paper as (see Appendix D),

$$D_T^{exp} = \frac{1}{\rho_c\,(1-\varphi)}\,D_T\,. \tag{45}$$

Furthermore, the collective diffusion coefficient D_0^{exp} at infinite dilution as measured by light scattering is related to the monodisperse diffusion coefficient $D_0(\bar{a})$ for particles with the number average radius $\bar{a}$ as $D_0^{exp} = D_0(\bar{a})\,[1 - 5(\sigma^2/\bar{a}^2)] = 0.73 \times D_0(\bar{a})$ (see subsection 4.1). In comparing the experiments with theory, the ratio D_0/D_0^{exp} is therefore taken equal to $1/0.73$ in order to correct for polydispersity.

The thus obtained comparison with experimental results for $T \times D_T^{exp}/D_0^{exp}$ is shown in Fig. 7 for 50 °C, corresponding to hard spheres. The solid curve corresponds to the theory, where the parameters from the fit of the Soret coefficients in Fig. 1 has been used without any further fitting parameters. To within the quite large experimental errors, there is agreement between the experiments and theory.

6. Fokker-Planck approaches

There are a number of studies [62–68] aimed at the derivation of Fokker-Planck equations for the probability density function (pdf) of the phase-space coordinates of spherical colloidal particles in the presence of a temperature gradient. Integration of the Fokker-Planck equation that includes both the position coordinates and velocities of the colloids

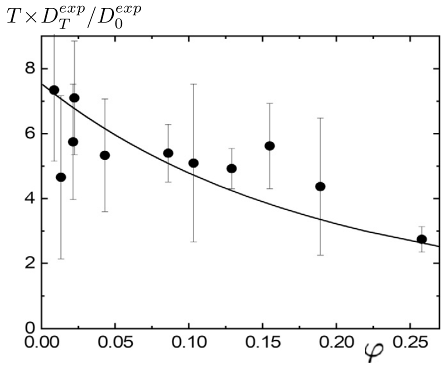

Fig. 7. Experimental results for $T \times D_T^{exp}/D_0^{exp}$ as a function of the volume fraction for 50 °C). The solid curve corresponds to the theoretical prediction, without any fitting parameters.

with respect to the relatively fast velocities leads to a Fokker-Planck equation for the pdf of the position coordinates only, which is commonly referred to as a Smoluchowski equation. Subsequent integration of the Smoluchowski equation with respect to all position coordinates, except for one, in principle leads to an equation of motion for the colloid concentration, and hence to expressions for the collective diffusion and thermodiffusion coefficients.

Specific interactions between a colloid and the surrounding solvent molecules have been included in a single-particle Fokker-Planck equation in Ref. [62]. The resulting single-particle thermodiffusion coefficient is stated to be proportional to the “heat drag coefficient” which is equal to a time-integral over a correlation function, for which, however, no explicit expression is given. The thermophoretic contribution from the ideal colloid pressure $p_c = \rho_c\, k_B T$ for non-interacting colloids has been found here as well, which has also been discussed in Refs. [63,64] without considering further specific interactions with solvent molecules. A combination of statistical mechanical and kinetic methods, as well as irreversible thermodynamics for a single colloid is discussed in Ref. [65], where a Fokker-Planck equation is derived that essentially reproduces the results in Ref. [62]. A similar approach is subsequently used in Ref. [66] to include interactions between the colloids, which are characterized by two variables: the “thermal acceleration coefficient” and the “friction coefficient”. Both variables are related to unspecified Onsager coefficients. A Fokker-Planck equation and accompanied hydrodynamic equations of motion are derived in Refs. [67,68] where various contributions are formulated in terms of local thermal averages and correlation functions which would require further analysis in order to obtain the thermodiffusion coefficient in terms of the local temperature and colloid concentration. A Smoluchowski equation that is applicable to non-isothermal systems, which contains only known phase functions without unspecified coefficients, has not been derived so far.

An extension of the well-known Smoluchowski equation for an equilibrium NVT-system [59,60,69–75] to account for the presence of an externally imposed temperature gradient up to linear order can be obtained by simply adding the purely thermophoretic forces as obtained in subsection 2.3 to the existing forces in the NVT-system without a temperature gradient. This leads to (here is understood that $N = N_c$ is the total number of colloids),

$$\frac{\partial}{\partial t} P_N = \sum_{i,j=1}^{N} \nabla_i \cdot \left[\beta\, \mathbf{D}_{ij}\right] \cdot \left[k_B T_j \nabla_j P_N + P_N \nabla_j \Psi \right. \\ \left. + \left\{ P_N \left[k_B + f_{single}(T_j) \right] + \frac{\partial}{\partial T}\left(P_N \frac{\Psi}{N} \right) \right\} \nabla_j T_j \right] , \qquad (46)$$

where P_N is the pdf for the position coordinates of the assembly of N colloids, the tensors $\mathbf{D}_{ij}$ account for the hydrodynamic interactions between the colloids (the same tensors appear in eq. (43)), which are functions of all the position coordinates, and Ψ is the total interaction energy due to colloid-colloid interactions. Furthermore, ∇_j is the gradient operator with respect to the position coordinate $\mathbf{r}_j$ of the j^{th} colloidal particle, and $T_j = T(\mathbf{r}_j)$. The newly suggested force in the above Smoluchowski equation is the thermophoretic interaction force $\sim \partial (P_N\, \Psi/N)/\partial T$.

The equation of motion (40), (41) for the colloid concentration can be obtained by integration of the above Smoluchowski equation, again assuming pair-wise additivity of the total interaction potential, and pre-averaging of the hydrodynamic tensors, that is, employing the approximation,

$$\beta\, \mathbf{D}_{ij} \approx \delta_{ij}\, \hat{\mathbf{I}}\, M(\rho_c(\mathbf{r}_i, t), T(\mathbf{r}_i))\,, \qquad (47)$$

where δ_{ij} is the Kronecker delta and $\hat{\mathbf{I}}$ is the identity tensor. The ρ and T dependence of the function M requires additional considerations, and will be specified below. The intuition behind hydrodynamic pre-averaging is that hydrodynamic interactions are long-ranged, so that many colloids interact simultaneously with each given colloid. Upon integration, the resulting integral over the direct interaction force $\sim P_N\, \nabla_j \Psi$ in eq. (46) can be expanded to leading order in gradients of the colloid concentration and temperature (mathematical details are given in Appendix C). Subsequently, the same reasoning in section 5 to arrive at eq. (42) for the mobility can be employed to show that $M = D_0\, \beta\, H_0$.

7. Summary and conclusion

Little is known about the effect of inter-colloidal interactions on their thermophoretic behavior. We present a systematic approach for electro-neutral, uncharged colloids that predicts a thermophoretic force due to inter-colloidal interactions that has not been identified before. This force is given in eqs. (27), (34), which we referred to as the *thermophoretic interaction force*.

The total thermophoretic force on a colloidal particle consists of two parts: (i) a single-particle contribution that result from the temperature-gradient response of the internal degrees of freedom of, for example, an electric double layer, a surface-grafted polymer brush, adsorbed surfactants, a solvation layer, and the core of the colloid, and (ii) a contribution that arises from interactions between the colloids. For electro-neutral, uncharged colloids, it is shown by means of a linear irreversible thermodynamics approach that the total force on a colloid due to concentration and temperature gradients is equal to the spatial gradient of an effective, single-component chemical potential plus a purely thermophoretic contribution (see eq. (15)). From an effective one-component Gibbs-Duhem relation, the gradients of the effective chemical potential can be expressed in terms of gradients of the colloid pressure (see eq. (22)), which for isothermal systems is equal to spatial gradients of the osmotic pressure as obtained experimentally from meniscus-height measurements. The remaining purely thermophoretic contribution to the force is proportional to the heat-of-transfer. With the neglect of mere heat conduction, eq. (22) for the force allows for the determination of an expression for the heat-of-transfer, being equal to the temperature derivative of the effective partial molar internal energy (see eq. (26)). The heat-of-transfer is thus shown to entail the two contributions mentioned above, corresponding to a single-particle internal energy and an internal energy due to colloid-colloid interactions. The latter contribution to the thermophoretic force has not been considered in previous theories. The various contributions to the Soret coefficient in eq. (35) and the thermodiffusion coefficient in eqs. (41), (42) are expressed in terms of integrals over the colloid-colloid pair-correlation function. This allows for a particle-based comparison of the theory with experiments on suspensions of sticky hard spheres over a wide range of concentration and temperature. It is shown that the newly predicted contribution to the thermophoretic force is essential to describe the experimental data.

Equation (22) has been suggested before, with the omission of the heat-of-transfer, and without further justification, in Refs. [17,38–40].

Since the new thermophoretic interaction force originates from the heat-of-transfer, these references therefore miss that contribution to the thermophoretic force. There is no previous systematic theory for the contribution of colloid-colloid interactions to the Soret coefficient and thermodiffusion coefficient at high concentrations.

The experiments on well-characterized, uncharged colloids in Ref. [24] span a wide range of concentration and temperature, which is essential for a detailed comparison with the theory. No other similar data on uncharged systems are available in literature. This is different for the experimental data on concentrated dispersions of an ionic sodium dodecyl sulfate (SDS) charged micellar system at various ionic strengths reported in Refs. [3,22]. The experimental data for the Soret coefficient are fitted according to $S_T = S_{T,0}/(1+2B_2\rho_c)$, where $S_{T,0}$ is the Soret coefficient at zero concentration, and the denominator relates to the first order in concentration expansion of $\partial p_c/\partial \rho_c$, with B_2 the second virial coefficient. Comparing to eq. (35), the concentration dependence of both $(1/\rho_c)(\partial p_c/\partial T)$ and f_{int} are neglected. The obtained virial coefficients differ by a factor of about 2 from those obtained by independent light scattering experiments [76] (as correctly stated by the authors of Refs. [3,22]). Moreover, a strong temperature dependence of the Soret coefficient due to interactions for the same system is found in Ref. [23].

Suspensions of concentrated system of charged colloids are outside the scope of the present paper. The gradients in ion concentrations induced by the colloid concentration gradient (like in sedimentation experiments [77,78]), as well as the thermophoretic motion of the ions, both contribute to the migration force of the colloids, which therefore requires additional considerations as compared to electro-neutral colloids. Charged colloids will be addressed in a forthcoming publication, where ions are taken into account within the same approach as developed here for uncharged colloids.

For charged colloids, the expression (30) for the single-particle thermophoretic force neglects contributions from temperature-gradient induced deformation of the electric double layer and the resulting electro-osmotic flow. These additional forces, however, are small for polar solvents like water [9]. To within a linear Boltzmann approximation the internal energy of the electric double layer is equal to $u_{single} = Q\,\Psi_s/2$, with Q the surface charge and Ψ_s the surface potential. The resulting expression for the single-particle Soret coefficient obtained from eq. (30) is in agreement with experiments on charged spherical colloids [11,79] and rod-like colloids [80]. In general, however, there are additional contributions to the single-particle thermophoretic force in eq. (30).

CRediT authorship contribution statement

J.K.G. Dhont: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **W.J. Briels:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: J.K.G. Dhont reports financial support, article publishing charges, and statistical analysis were provided by Research Centre Jülich. J.K.G. Dhont reports a relationship with Research Centre Jülich that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Approximations and assumptions

In this appendix we motivate the approximations and assumptions listed in the beginning of section 2:

(1) *Gravitational forces on the colloids that either lead to sedimentation or buoyancy are not explicitly included. These forces add to the forces that are explicitly discussed, and may be included in all equations below. For the experiments that we discuss these forces are irrelevant.*

That such forces are not relevant for the colloidal system and experimental technique under consideration as described in subsection 4.1 can be seen as follows. First of all, concentration gradients due to thermophoresis in the experiments used are perpendicular to those caused by gravitational forces, and only a sinusoidal concentration profile due to thermophoresis is probed. The effect of gravitational forces on the experimental results can therefore only be significant through the variation of the ambient colloid concentration over length scales of the order of the height of the sample volume, within which the laser beams are crossed, approximately $h \approx 1$ mm. Since the specific mass density of toluene is equal to 900 kg/m^3 and that of colloidal silica 2200 kg/m^3, we have $\Delta m = (4\pi/3)\,a^3 \times 1300$ kg $= 1.8\times 10^{-20}$ kg. Hence, $\Delta m\, g\, h/k_BT \approx 0.004$. The relative difference of the ambient colloid concentration within the probed sample volume is therefore about 0.4%, and can be safely neglected.

(2) *Partial molar volumes of the colloids and the solvent molecules are assumed to be independent of pressure, concentration, and temperature.*

The volume of the solid core of the colloids and the concentration of solvent molecules (the solvent being quasi-incompressible) are essentially independent of the small pressure variations in experiments (of the order of fractions of the atmospheric pressure). As discussed above, cross-interactions can be neglected, so that partial molar volumes are also independent of the colloid concentration. We also neglect the temperature dependence of the partial molar volumes. There is, however, a contribution of the difference in the thermal expansion coefficients of the core of the colloids and the solvent, which contributes to the single-particle thermodiffusion coefficient, as discussed in subsection 2.3.

(3) *The total pressure is assumed to be independent of position.*

For typical solvents like water and toluene (the solvent that is used for the colloidal suspension to which the theory will be applied), the propagation velocity of pressure waves varies between 1000–1500 m/s. For a closed sample container with a typical size of $h = 1$ mm, the time τ_p it takes for the spatial relaxation of pressure waves induced by the motion of the colloids is therefore of the order of a µs. The distance l_T that a colloid traverses during the pressure relaxation time τ_p due to thermophoresis is equal to $l_T = (|D_T|/\rho_c)\,\tau_p|\nabla T|$, where D_T is the thermodiffusion coefficient as defined in the introduction and ρ_c is the number concentration of colloids. From the definition of the Soret coefficient in eq. (2), this can also be written as $l_T = |S_T|\,D_c\,\tau_p|\nabla T|$. The distance l_T should be much smaller than the linear dimensions of the irreversible-thermodynamics volume elements in order to assure that during the time τ_p the concentration profile does not significantly change. Since these volume elements are thermodynamic systems, a small, safe upper bound for l_T would be $10\,a$, where a is the linear dimension of a colloid. This sets an upper limit for the temperature gradient: $|\nabla T| \lesssim 10\,a/(|S_T|D_c\,\tau_p)$. For typical values of $D_c \approx (10^{-9}$–$10^{-11})$ m^2/s, $a = (5$–$500)$ nm, $|S_T| \approx (0$–$10)/T$ K^{-1}, and $T = 300$ K, it is thus found that $|\nabla T| \lesssim 10^9$ K/m. This upper bound for the validity of a quasi-instantaneous relaxation of the total pressure, during which the colloid concentration profile does not significantly change, is far beyond typical temperature gradients (less than 10^4 K/m) employed in experiments, and is most probably beyond the validity of a linear-irreversible thermodynamics approach. The temperature gradient for the experimental results discussed in sections 4 and 5 is (1–2) K/m.

(4) *The number of solvent molecules, residing in thin solvation layers around the surfaces of all colloids, and which interact directly with them, is negligible compared to the number of molecules within the bulk solvent.*

Interactions between the solvent molecules and the colloids leads to solvation layers at the surfaces of the colloids, with a thickness of a few times the linear dimension l_s of a solvent molecule. The number of solvent molecules within the solvation layers is equal to $N_{solv} = 4\pi a^2 l_s N_c / v_s$ where a is the radius of a (spherical) colloid, N_c is the number of colloids, and v_s is the volume occupied by a solvent molecule. The number of solvent molecules within the remaining bulk solvent is equal to $N_{bulk} = (1-\varphi) V / v_s$, where V is the total volume, and $\varphi = (4\pi/3)(a+l_s)^3 \rho_c$, with $\rho_c = N_c/V$. Hence, $N_{solv}/N_{bulk} = 3\,(l_s/a)\,\varphi/(1-\varphi)$ to leading order in l_s/a. This is a very small number since φ is not larger than about $1/2$, and $l_s/a \ll 1$, that is, colloids are by definition much larger than the size of the solvent molecules. A colloid is therefore considered to consist of its core plus its solvation layer with an extent that is negligible compared to the colloid size. The colloid surface may contain, for example, a thin layer of grafted polymers that contributes to the interactions between the colloids. This is the case for the experimental system to which the theory is applied in this paper. At contact of the colloids these layers give rise to temperature dependent attractive colloid-colloid interactions.

(5) *Bulk solvent attains equilibrium quasi-instantaneously for each configuration of the colloids.*

The time scale τ_{micro} on which micro-structural order of a solvent like water relaxes is of the order of pico seconds, while for colloids typical relaxation times are of the order of tens of microseconds to milliseconds (depending on the size of the colloids and their concentration). Furthermore, the displacement l_T of a colloid due to thermodiffusion during relaxation of the solvent, relative to the radius a of a colloid is equal to (see also point (3) above) $l_T/a = |S_T|\, D_c\, |\nabla T|\, \tau_{micro}/a$. For typical values (see point (3) above) and $|\nabla T| < 100$ K/m, is thus found that $l_T/a \approx (0\text{–}3)\times 10^{-21}$.

(6) *The force on a colloidal particle due to heat conduction in the absence of mass transport will be neglected.*

Mere heat conduction, in the absence of mass transport, occurs through the solvent and the colloidal cores which behave like a macroscopic solid material. Contrary to (mixtures of) simple liquids, microstructural order is therefore not affected by mere heat conduction, and is therefore neglected. Including mere heat conduction would require a molecular-based microscopic kinetic theory, which could be important for simple liquids.

Appendix B. The colloid pressure p_c

Consider a container with a fixed temperature, a fixed volume V, and a fixed number of N_c of colloids and N_s solvent molecules. We start with the well-known definition of the phase function,

$$G \equiv \frac{1}{V}\sum_{j=1}^{N_c} \mathbf{p}_j^c \cdot \mathbf{r}_j^c + \frac{1}{V_a}\sum_{j=1}^{N_s} \mathbf{p}_j^s \cdot \mathbf{r}_j^s \,, \tag{48}$$

where $\mathbf{p}_j^{c,s}$ and $\mathbf{r}_j^{c,s}$ are the momentum and position coordinates of the j^{th} colloid and solvent molecule. Just as in the standard derivation of the virial theorem, the time-derivative of G is time-averaged over a time interval that is sufficiently large to establish thermodynamic equilibrium. Assuming that G is a bounded function of time, leads to ($< \cdots >$ denotes the time averaging),

$$\begin{aligned} 0 = {} & 3\,\frac{N_c}{V} k_B T + 3\,\frac{N_s}{V} k_B T \\ & + \frac{1}{V}\sum_{j=1}^{N_c} < \mathbf{F}_j^c \cdot \mathbf{r}_j^c > + \frac{1}{V}\sum_{j=1}^{N_s} < \mathbf{F}_j^s \cdot \mathbf{r}_j^s > \\ & + \frac{1}{V}\sum_{j=1}^{N_c} < \mathbf{F}_{j,W}^c \cdot \mathbf{r}_j^c > + \frac{1}{V}\sum_{j=1}^{N_s} < \mathbf{F}_{j,W}^s \cdot \mathbf{r}_j^s > , \end{aligned} \tag{49}$$

where the equi-partition theorem for translational motion and Newton's equation of motion is used. Here, $\mathbf{F}_j^c$ is the force on the colloid due to interactions with other colloids and solvent molecules, and $\mathbf{F}_{j,W}^c$ is the force that the wall exerts on the colloid, and similar for the solvent molecules.

The force $\mathbf{F}_j^c$ and $\mathbf{F}_j^s$ on colloid j and solvent molecule j, respectively, can be written as,

$$\begin{aligned} \mathbf{F}_j^c &= \sum_{i(\neq j)=1}^{N_c} \mathbf{F}_{ji}^{cc} + \sum_{i=1}^{N_s} \mathbf{F}_{ji}^{cs} \\ \mathbf{F}_j^s &= \sum_{i(\neq j)=1}^{N_s} \mathbf{F}_{ji}^{ss} + \sum_{i=1}^{N_c} \mathbf{F}_{ji}^{sc} \,, \end{aligned} \tag{50}$$

where $\mathbf{F}_{ji}^{cc}$ is the force of colloid i on colloid j, and $\mathbf{F}_{ji}^{cs}$ is the force of solvent molecule i on colloid j, and similarly for the force on a solvent molecule.

The sum S_{cross} of the two contributions to eq. (49) arising from the "cross terms" on the right hand-side in eq. (50) can be written as,

$$S_{cross} = \frac{1}{V}\sum_{j=1}^{N_c}\sum_{i=1}^{N_s} < \mathbf{F}_{ji}^{cs} \cdot \left(\mathbf{r}_j^c - \mathbf{r}_i^s \right) > , \tag{51}$$

where it is used that $\mathbf{F}_{ij}^{sc} = -\mathbf{F}_{ji}^{cs}$. First notice that only those solvent molecules that are in the immediate vicinity of the colloid's surface act with a force on the colloid. Furthermore, the vast majority of solvent molecules interact with only a single colloid. Equation (51) can thus be simplified to,

$$S_{cross} = -\frac{N_c}{V}\sum_{i=1}^{N_s} < \mathbf{F}_{ji}^{cs} \cdot \mathbf{R}_i^s > , \tag{52}$$

where $\mathbf{R}_i^s$ is the position of solvent molecule i at the surface ∂V_j of the colloid, relative to the position coordinate of the colloid.

The position coordinate $\mathbf{R}_i^s$ of a solvent molecule that interacts with the colloid's surface is essentially equal to the position $\mathbf{R}$ of the surface element, so that,

$$< \sum_{i \in dS} \mathbf{F}_{ji}^{cs} \cdot \mathbf{R}_i^s > = < \sum_{i \in dS} \mathbf{F}_{ji}^{cs} > \cdot\, \mathbf{R} \,. \tag{53}$$

Since the colloids are much larger than the solvent molecules, the average force of solvent molecules on a surface element dS of colloid j can be written as,

$$< \sum_{i \in dS} \mathbf{F}_{ji}^{cs} > = -\hat{\mathbf{n}}\, p_s\, dS \,, \tag{54}$$

where the summation ranges over all solvent molecules in the vicinity of the surface element which act with a force on that surface element, and where $\hat{\mathbf{n}}$ is the unit surface vector pointing towards the solvent, and where p_s is contribution to the pressure of the solvent.

Using the obvious equality,

$$< \sum_{i=1}^{N_s} \mathbf{F}_{ji}^{cs} \cdot \mathbf{R}_i^s > = \oint_{\partial V_j} dS\, < \sum_{i \in dS} \mathbf{F}_{ji}^{cs} \cdot \mathbf{R}_i^s > , \tag{55}$$

it thus follows that,

$$S_{cross} = p_s \frac{N_c}{V} \oint_{\partial V_j} dS\, \hat{\mathbf{n}} \cdot \mathbf{R} = 3\,\varphi\, p_s\,, \tag{56}$$

where $\varphi = (N_c/V)v_c$ is the volume fraction of colloids, with v_c the volume of a single colloid.

Similarly the interactions with walls are found to be equal to,

$$\frac{1}{V}\sum_{j=1}^{N_s} < \mathbf{F}^{s}_{j,W} \cdot \mathbf{r}_j > = -3\,p_s$$
$$\frac{1}{V}\sum_{j=1}^{N_c} < \mathbf{F}^{c}_{j,W} \cdot \mathbf{r}_j > = -3\,p_c\,, \tag{57}$$

where p_c is contribution to the total pressure due to the interactions of the colloids with the wall of the container.

Gathering the above results for the various terms occurring on the right hand-side of eq. (49) leads to the following expression for the total pressure p,

$$p = p_c + p_s\,, \tag{58}$$

where,

$$p_c = \frac{N_c}{V}\,k_B T + \frac{1}{3\,V}\sum_{j=1}^{N_c} < \mathbf{F}^{cc}_j \cdot \mathbf{r}^c_j >\,,$$
$$p_s = \frac{N_s}{V_a}\,k_B T + \frac{1}{3\,V_a}\sum_{j=1}^{N_s} < \mathbf{F}^{ss}_j \cdot \mathbf{r}^s_j >\,, \tag{59}$$

where $V_a = V(1-\varphi)$ is the volume that is accessible to the solvent molecules.

Evaluation of the expression in eq. (59) for p_c in terms of integrals with respect to the probability density function for the position coordinates of the colloids leads to the equation-of-state in (32).

Appendix C. The average mechanical force on the colloids

The average force on a colloid due to mechanical interactions with other colloids in an inhomogeneous system is equal to,

$$\mathbf{F}_{mech} = \int d\mathbf{r}'\; \rho_c(\mathbf{r}',t)\, g(\mathbf{r},\mathbf{r}',t)\, \mathbf{F}(\mathbf{R}|T)\,, \tag{60}$$

where $g(\mathbf{r},\mathbf{r}',t)$ is the pair-correlation function, with $\mathbf{R} = \mathbf{r}' - \mathbf{r}$, and where $\mathbf{F} = -\nabla V(\mathbf{R}|T)$, with V the (generally temperature dependent) pair-interaction potential.

The integration range of the $\mathbf{r}'$-integration in eq. (60) is limited to a region of extent R_V around $\mathbf{r}$, where R_V is the range of the pair-interaction potential: $\nabla V(|\mathbf{r}-\mathbf{r}'|) = \mathbf{0}$ for $|\mathbf{r}-\mathbf{r}'| > R_V$. For these small distances, the relaxation of the pair-correlation-function is much faster as compared the time scale on which the relatively smooth colloid concentration profile is evolving. One can therefore assume that $g(\mathbf{r},\mathbf{r}',t)$ is the equilibrium pair-correlation function $g^{eq}(|\mathbf{r}-\mathbf{r}'|)$ at the instantaneous local concentration $\rho_c([\mathbf{r}+\mathbf{r}']/2,t)$ and the local temperature $T([\mathbf{r}+\mathbf{r}']/2)$. This can be regarded as the statistical mechanical analogy of the concept of local equilibrium in irreversible thermodynamics. Furthermore, spatial gradients of the colloid density are now assumed to be sufficiently small, such that,

$$\begin{aligned}&\left|\,\delta\rho_c\left(\frac{\mathbf{r}+\mathbf{r}'}{2},t\right)\right|\\ &\equiv \left|\,\rho_c\left(\frac{\mathbf{r}+\mathbf{r}'}{2},t\right) - \rho_c(\mathbf{r},t)\right| \ll \rho_c(\mathbf{r},t)\,,\end{aligned} \tag{61}$$

for $|\mathbf{r}'-\mathbf{r}| \leq R_V$, which is satisfied when the change of the relative colloid concentration over distance of the order R_V is small, that is $R_V\,|\nabla\rho_c(\mathbf{r},t)| \ll \rho_c(\mathbf{r},t)$. The same restriction on the magnitude of temperature gradients will be assumed. For such small spatial gradients, the pair-correlation function can be expanded as,

$$\begin{aligned}&g(\mathbf{r},\mathbf{r}',t)\\ &= g^{eq}(R) + \frac{\partial g^{eq}(R)}{\partial\rho_c}\,\delta\rho_c\left(\frac{\mathbf{r}+\mathbf{r}'}{2},t\right) + \frac{\partial g^{eq}(R)}{\partial T}\,\delta T\left(\frac{\mathbf{r}+\mathbf{r}'}{2}\right)\\ &= g^{eq}(R) + \frac{1}{2}\frac{\partial g^{eq}(R)}{\partial\rho_c}\,\mathbf{R}\cdot\nabla\rho_c(\mathbf{r},t) + \frac{1}{2}\frac{\partial g^{eq}(R)}{\partial T}\,\mathbf{R}\cdot\nabla T(\mathbf{r})\,,\end{aligned} \tag{62}$$

with $\mathbf{R} = \mathbf{r}' - \mathbf{r}$, and $g^{eq}(R)$ is the equilibrium pair-correlation function at the colloid concentration $\rho_c(\mathbf{r},t)$ and temperature $T(\mathbf{r})$. Note that $g^{eq}(R)$ is implicitly time dependent, since it is evaluated at the time-dependent concentration $\rho_c(\mathbf{r},t)$.

Within the same approximation,

$$\begin{aligned}&\mathbf{F}\left(\mathbf{R}\,\middle|\,T\left(\frac{\mathbf{r}+\mathbf{r}'}{2}\right)\right)\\ &= \mathbf{F}(\mathbf{R}\,|\,T(\mathbf{r})) + \frac{1}{2}\left[\frac{d}{dT(\mathbf{r})}\,\mathbf{F}(\mathbf{R}\,|\,T(\mathbf{r}))\right]\left(\mathbf{r}'-\mathbf{r}\right)\cdot\nabla T(\mathbf{r})\\ &= -\nabla_R V\left(R|T(\mathbf{r})\right) - \frac{1}{2}\left[\frac{d}{dT(\mathbf{r})}\,\nabla_R V\left(\mathbf{R}|T(\mathbf{r})\right)\right]\mathbf{R}\cdot\nabla T(\mathbf{r})\,,\end{aligned} \tag{63}$$

where ∇_R is the gradient operator with respect to $\mathbf{R}$.

For the same reason, for the slowly changing concentration as compared to the range R_V of the pair-interaction potential, the concentration $\rho_c(\mathbf{r}',t)$ in eq. (60) can similarly be written as,

$$\rho_c(\mathbf{r}',t) = \rho_c(\mathbf{r},t) + \mathbf{R}\cdot\nabla\rho_c(\mathbf{r},t)\,. \tag{64}$$

Substitution of eqs. (62), (63), (64) into the integral in eq. (60) leads, with some effort, to,

$$\begin{aligned}\mathbf{F}_{mech} &= -\int d\mathbf{r}'\;\rho_c(\mathbf{r}',t)\,g(\mathbf{r},\mathbf{r}',t)\,\nabla V(|\mathbf{r}-\mathbf{r}'|)\\ &= -\frac{1}{\rho_c}\left\{\nabla\rho_c(\mathbf{r},t)\frac{\partial}{\partial\rho_c} - \nabla T(\mathbf{r})\frac{\partial}{\partial T}\right\}\left[p_c - \rho_c\,k_B\,T\right]\\ &= -\frac{1}{\rho_c}\nabla\left[p_c - \rho_c\,k_B\,T\right]\,,\end{aligned} \tag{65}$$

where,

$$p_c(\rho_c,T) = \rho_c\,k_B T - \frac{2\pi}{3}\rho_c^2 \int dR\,R^3\,g^{eq}(R)\,\frac{dV(R)}{dR}\,, \tag{66}$$

is the virial equation-of-state for the colloid pressure, as shown in Appendix A. Here it is understood that $\rho_c = \rho_c(\mathbf{r},t)$ and $T = T(\mathbf{r})$, and that the pair-correlation function is evaluated at that colloid concentration and temperature.

Appendix D. Connection between experimental and theoretical coefficients

The number flux $\mathbf{J}_c$ of colloids as used in this paper is written as,

$$\mathbf{J}_c = -D_c\,\nabla\rho_c - D_T\,\nabla T\,, \tag{67}$$

which defines the theoretical diffusion coefficients. The following alternative expression for the flux is given in Ref. [24],

$$\mathbf{J}_c = -\frac{\bar{\rho}_c}{m_c}\,D^{\star}_c\,\nabla w - \frac{\bar{\rho}_c}{m_c}\,w(1-w)\,D^{\star}_T\,\nabla T\,, \tag{68}$$

where w is the mass fraction of colloids, $\bar{\rho}_c$ is the mass density of the suspension, and m_c is the mass of a single colloidal particle. In order to compare the diffusion coefficients $D^{\star}_c$ and $D^{\star}_T$ to the theoretical diffusion coefficients D_c and D_T, the mass fraction and mass density of the suspension in eq. (68) are rewritten in terms of the number concentration. To this end, we need to specify the mass density ρ^s_m [kg/m^3] of the solvent and ρ^c_m [kg/m^3] of the colloids. As will be shown below, only their ratio α will be of importance,

$$\alpha \;=\; \rho_m^c/\rho_m^s \;=\; \frac{m_c/v_c}{m_s/v_s}\,, \tag{69}$$

where m_s is the mass of a single solvent molecule. Using that,

$$\begin{aligned}\bar{\rho}_c &= \frac{m_c}{\alpha\, v_c}\left[1+(\alpha-1)\,\varphi\right]\,,\\ w &= \frac{m_c\rho_c}{\bar{\rho}_c} \;=\; \frac{\alpha\,\varphi}{1+(\alpha-1)\,\varphi}\,,\end{aligned} \tag{70}$$

it is readily found that the flux in eq. (68) can also be written as,

$$\mathbf{J}_c = -\left[1-w\left(1-\frac{1}{\alpha}\right)\right] D_c^{\star}\nabla\rho_c - \rho_c(1-w)\,D_T^{\star}\,\nabla T. \tag{71}$$

Comparing to eq. (67) it is thus found that,

$$\begin{aligned}D_c &= \left[1-\left(1-\frac{1}{\alpha}\right)w\right]\,D_c^{\star}\,,\\ D_T &= \rho_c\,(1-w)\,D_T^{\star}\,,\\ S_T &\equiv \frac{1}{\rho_c}\,\frac{D_T}{D_c} = \frac{1-w}{1-\left(1-\frac{1}{\alpha}\right)w}\,\frac{D_T^{\star}}{D_c^{\star}} \equiv \frac{1-w}{1-\left(1-\frac{1}{\alpha}\right)w}\,S_T^{\star}\,,\end{aligned} \tag{72}$$

which can be expressed in terms of the volume fraction, leading to,

$$\begin{aligned}D_c &= \frac{1}{1+(\alpha-1)\,\varphi}\,D_c^{\star}\,,\\ D_T &= \frac{\rho_c\,(1-\varphi)}{1+(\alpha-1)\,\varphi}\,D_T^{\star}\,,\\ S_T &= \rho_c\,(1-\varphi)\,S_T^{\star}\,.\end{aligned} \tag{73}$$

From eqs. (68), (70) the following equation of motion for w is obtained,

$$\frac{\partial w}{\partial t} = \left[1-\left(1-\frac{1}{\alpha}\right)w\right]\left[D_c^{\star}\,\nabla w + w\,(1-w)\,D_T^{\star}\,\nabla T\right]. \tag{74}$$

Despite the expression for the flux in eq. (68) given in Ref. [24], the TDFRS data are not based on the equation of motion (74) that complies with it. Instead, the equation of motion that is used reads,

$$\frac{\partial w}{\partial t} \;=\; \left[D_c^{exp}\,\nabla w + w\,(1-w)\,D_T^{exp}\,\nabla T\right], \tag{75}$$

where the experimentally obtained diffusion coefficients, and the corresponding Soret coefficient, are related to those in eq. (68), by comparing the two equations of motion above,

$$\begin{aligned}D_c^{exp} &= \left[1-\left(1-\frac{1}{\alpha}\right)w\right]\,D_c^{\star}\,,\\ D_T^{exp} &= \left[1-\left(1-\frac{1}{\alpha}\right)w\right]\,D_T^{\star}\,,\\ S_T^{exp} &= S_T^{\star}\,.\end{aligned} \tag{76}$$

The relation between these experimental coefficients with the theoretical coefficients follows from the above considerations,

$$\begin{aligned}D_c^{exp} &= D_c\,,\\ D_T^{exp} &= \frac{1}{\rho_c\,(1-\varphi)}\,D_T\,,\end{aligned} \tag{77}$$

$$S_T^{exp} = \frac{1}{1-\varphi}\,S_T\,. \tag{78}$$

These relations are used to convert theoretical coefficients to their experimental counterparts.

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