

Colloid transport in nonuniform temperature

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The aim of this paper is to set up a theoretical framework for obtaining the thermodiffusion (or Soret) coefficient of a colloid in a carrier liquid. It is first argued that the expression of the particle-current density in nonuniform temperature cannot be derived from a theoretical formula valid for an isothermal solution. Then the kinetic theory of Brownian motion is used to derive an expression for the current density properly accounting for thermodiffusion. The cases of free and interacting particles are treated, and the thermodiffusion current pertinent to an ideal solution adds up with a current driven by a temperature- and concentration-dependent potential. Accordingly, a general explicit formula for the thermodiffusion coefficient is obtained. Practical use of the framework is illustrated on simple specific models of a colloid in a solvent. Large Soret coefficients of both signs are calculated for realistic values of the physicochemical parameters, in qualitative agreement with published experimental data.

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I. INTRODUCTION

Thermodiffusion (also called the Soret or Ludwig-Soret effect) is a phenomenon where a mass flow is induced by a gradient of temperature in a complex (at least binary) one-phase system, generally a liquid. It was observed for the first time almost 150 years ago [1–5]. To describe this effect briefly, let us consider a single-phase material made of two or more components, such as a colloidal system where grains or nanoparticles are dispersed in a carrier fluid, characterized by a volume fraction ϕ of one of the components. If this initially homogeneous material is submitted to a thermal gradient, a concentration current is sometimes observed which is parallel to the thermal gradient: this is the Soret effect. It is characterized by the so-called Soret coefficient S_T , such that [6] $D_m S_T$ is the opposite of the ratio of the volume-fraction current density to the temperature gradient (D_m is the mass diffusion coefficient). The alternative definition $S_T^* = S_T / \phi$ is also encountered. The effect is also observed in gases and in solids [4,7]. After studies on the thermodiffusion of dissolved polymers, the Soret effect has been recently studied in colloids [8–11] and this paper will mainly focus on the Soret effect in these asymmetric binary systems where nanoparticles are dispersed in a carrier liquid. After a first use of conventional hydrodynamic techniques with a thermodiffusion flow cell [12,13], optical methods such as small-angle Rayleigh scattering [14,15], beam deflection [16,17], and forced Rayleigh scattering [18–22] have proved to be interesting tools for studying thermodiffusion in binary liquids. In gases and ordinary liquids, we have $10^{-5} < S_T^* < 10^{-3} \text{ K}^{-1}$ (Ref. [23]), in liquid metals $S_T^* \approx 10^{-3} \text{ K}^{-1}$ (Ref. [24]) and in polymeric solutions $S_T^* \approx 0.5 \text{ K}^{-1}$ (Ref. [20]).

Recently, values of S_T^* from -0.25 to $+0.17 \text{ K}^{-1}$ have been reported in magnetic colloidal systems, or ferrofluids [25,26]. They are colloidal suspensions of magnetic iron-oxide nanoparticles dispersed in a carrier liquid [27,28]. They can be divided into two main groups, ionic or surfactant, depending on the interparticle repulsion used to avoid aggregation. In the case of an electrostatic repulsion (ionic

ferrofluid [29]), the particle surface is charged with H^+ or OH^- ions, or with ionic ligands, whereas in the case of a steric interaction the nanoparticle is coated with surfactant molecules (surfactant ferrofluid). In addition to the magnitude of thermodiffusion in these materials, another interesting effect is that both signs are found for the Soret coefficient by varying the type of ferrofluid (ionic or surfactant), the solvent, or the nature of the coating material, while they keep the same magnetic core. For instance, the samples in Refs. [26] and [30] have the following constitutions. (i) In the ionic samples, maghemite-core (Fe_3O_4) nanoparticles are dispersed in water; they are either citrated, with a negative surface charge, or acidic, with a positive surface charge (V207Cit and V207NO₃, respectively). (ii) In the surfactant samples, the nanoparticles have the same maghemite core as ionic samples, but they are coated with becostatne[®]-surfactant molecules and dispersed in cyclohexane.

Although the Soret effect was discovered more than one century ago, a physical understanding of it is not fully achieved. The purpose of this paper is to develop a simple framework allowing to envision the Soret effect in colloids on the microscopic scale. We shall start from the expression of the current density of colloidal particles in the presence of a nonuniform temperature. Generally speaking, if a medium is not homogeneous, the expression of the particle-current density \mathbf{j} (in $\text{s}^{-1} \text{ m}^{-2}$) as a functional of the particle density n (in m^{-3}) cannot [31] be obtained by uncritically plugging a position dependence into a ready-made homogeneous expression. Most frequently, the ready-made expression of \mathbf{j} is either phenomenological (e.g., Fick's diffusion law supplemented with a drift term) or (if it is theoretical) such that it tends to minimize the free energy of the system. Such a thermodynamic rule is not applicable in the case of a non-uniform temperature, and a new structure for the current is expected. This state of affairs is encountered in the thermoelectric effect where an electric conductor is subjected to a temperature gradient, and an extra current proportional to **grad** T flows in addition to the familiar drift and diffusion currents. A kinetic-theoretical calculation of the current in a particular model for the conducting medium [32,33] shows

that the extra current cannot be obtained from extending the isothermal drift-diffusion formula for \mathbf{j} . In view of this, a reliable treatment of the analogous Soret problem cannot be expected to have general validity unless it is borne out in kinetic theory. The fact that a particular mechanism recently succeeded in accounting for a Soret effect in micellar solutions [34] does not ensure its general validity. This is why Sec. II recalls the kinetic theory of Brownian motion and derives an expression for \mathbf{j} in a variable-temperature medium. The case of free colloidal particles is treated in Sec. II A, and the formula for the thermodiffusion coefficient in the general case is given in Sec. II C. No specific model of the colloid or the solvent is assumed so far. Section III illustrates the framework on specific, simple examples showing that strong Soret effects of both signs can be obtained, with the correct order of magnitude. The versatility of the framework is demonstrated, and conclusions are drawn in Sec. IV.

II. BROWNIAN MOTION IN NONUNIFORM TEMPERATURE

A. Current equation for independent particles

A colloidal particle in a solution undergoes Brownian motion due to the many collisions with light surrounding molecules. The kinetic theory was put forth by Smoluchowski and reviewed by Chandrasekhar [35] (also see Balian [36] for a detailed account). The joint distribution $f(\mathbf{r}, \mathbf{p}, t)$ of the position \mathbf{r} and the momentum $\mathbf{p} = M\mathbf{v}$ of the colloid obeys the Kramers equation,

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = \gamma \frac{\partial}{\partial \mathbf{p}} \cdot \left(\mathbf{p}f + MkT \frac{\partial f}{\partial \mathbf{p}} \right), \quad (1)$$

where $\mathbf{F}(\mathbf{r}, t)$ is an applied force, M is the mass of the colloidal particle, γ is the frequency of collision with the surrounding medium, and T is the temperature of that medium. This is a linear Boltzmann equation describing the evolution in phase space of a massive particle in an underlying passive medium. The basic properties of Eq. (1) are well known, and are briefly recalled now. First, the differential, instead of integral, nature of the scattering operator [right-hand side of Eq. (1)] reflects the fact that the colloid-medium collisions entail quasicontinuous changes of \mathbf{p} in the limit of infinitely light solution particles. Second, the joint distribution

$$f(\mathbf{r}, \mathbf{p}, t) = n(\mathbf{r}, t) (2\pi MkT)^{-3/2} \exp\left(-\frac{\mathbf{p}^2}{2MkT}\right) \quad (2)$$

makes the right-hand side of Eq. (1) vanish, and the left-hand side vanishes in the absence of \mathbf{F} if the density $n(\mathbf{r}, t)$ is homogeneous and independent of time. This is the homogeneous equilibrium state, in which the medium imposes its temperature to the colloid. In the presence of $\mathbf{F} = -\mathbf{grad} U$, $\partial f / \partial t = 0$ if $n(\mathbf{r}, t) \propto \exp[-U(\mathbf{r})/kT]$. This is the sedimentation equilibrium in the presence of gravity.

In a nonequilibrium state, f cannot be given by Eq. (2) where the equal probabilities of \mathbf{p} and $-\mathbf{p}$ entail a vanishing current. However, it is physically clear that f keeps very close to equilibrium if the collision frequency γ is very large:

the medium tends to thermalize the particle. And it is mathematically clear from Eq. (1) that, if $\gamma \rightarrow +\infty$, f asymptotically approaches equilibrium solution (2). The distribution f can be obtained from an expansion in powers of γ^{-1} which has been carried out by van Kampen [37] in the case that both the medium temperature $T(\mathbf{r})$ and the collision frequency $\gamma(\mathbf{r})$ are inhomogeneous. From f , the current density

$$\mathbf{j} = \int \int \int (\mathbf{p}/M) f(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{p} / h^3 \quad (3)$$

(h is Planck's constant) is calculated to be, to order $1/\gamma$,

$$\mathbf{j} = \mu[\mathbf{F} - \mathbf{grad}(kT)]n - D \mathbf{grad} n. \quad (4)$$

In Eq. (4) $\mu = 1/M \gamma$ has the meaning of a mobility (response to a force \mathbf{F}), and $D = kT/M \gamma$ that of the diffusivity (response to an inhomogeneity in density). The Nernst-Einstein relation $D = kT\mu$ naturally ensues from the expansion of the kinetic equation (1).

Equation (4) can be arrived at in a different way. Whenever the collisions of the particle with the environment are weakly inelastic, an alternative Fokker-Planck formalism [38] is applicable. In the case of an energy-independent scattering time $\tau = 1/\gamma$, and if the force \mathbf{F} derives from a potential energy U , an Onsager-type expression is obtained,

$$\mathbf{j} = Dn \left[\mathbf{grad} \left(\frac{-\tilde{\mu}}{kT} \right) + \left(U + \frac{5}{2}kT \right) \mathbf{grad} \left(\frac{1}{kT} \right) \right], \quad (5)$$

where $D = kT\tau/M$, and $\tilde{\mu} = kT \ln[nh^3/2(2\pi MkT)^{3/2}] + U$ is the chemical potential of a perfect gas (or ideal solution) of classical particles subjected to a potential U . Elementary algebra shows that Eqs. (4) and (5) are equivalent to each other.

There are other variants of Eq. (4), each of which has its physical content. For example, it may be rewritten as

$$\mathbf{j} = \mu[\mathbf{F}n - \mathbf{grad}(nkT)], \quad (4')$$

and one recognizes the local osmotic pressure $\Pi(\mathbf{r}) = kT(\mathbf{r})n(\mathbf{r})$ of the solute. The quantity in square brackets is the force per unit volume entailing a flow \mathbf{j} of solute. The variety of settings of the current equation has been the source of debates which have been reviewed elsewhere [31]. Correspondingly, there is some ambiguity as to the definition of the Soret component of the current, and this is dealt with in Sec. II C.

B. Interacting particles

The linearity of the kinetic equation with respect to f expresses the independence of the motions of two colloidal particles. In practice, our solutions are not very dilute if the volume fraction $\phi = 4\pi nR^3/3$ reaches a few percent, and inter-particle interactions are expected which it is desirable to account for. In order to keep within a one-particle framework, some kind of mean-field approach is necessary. Much can be learned from the Debye-Hückel-Onsager theory of ion transport in semi-dilute solutions of electrolytes where the drift velocity of an ion is affected by the presence of nearby

ions of unlike and like signs. The interaction is described by means of an interaction energy [39] (sometimes termed ‘‘correlation energy’’)

$$U_c = \frac{1}{2} q \varphi', \quad (6)$$

where q is the ion’s charge and φ' is the electric potential due to the ionic atmosphere surrounding the ion. In the presence of an applied electric potential V , the current density in an isothermal solution, $\mathbf{j} = \mu[-\mathbf{grad}(qV)]n - D \mathbf{grad} n$ in the dilute case, becomes

$$\mathbf{j} = \mu[-\mathbf{grad}(qV + U_c)]n - D \mathbf{grad} n \quad (7)$$

in the semidilute range. As $\mathbf{grad} U_c = (\partial U_c / \partial n) \mathbf{grad} n$, Eq. (7) can be rewritten as

$$\mathbf{j} = \mu[-\mathbf{grad}(qV)]n - D_e \mathbf{grad} n, \quad (8)$$

where D_e is an effective diffusivity related to the bare diffusivity D by

$$D_e = D[1 + (n/kT)(\partial U_c / \partial n)]. \quad (9)$$

In Eq. (7) the interaction changed the drift component of the current, while in Eq. (8) the interaction modifies the diffusion component of the current through an effective, concentration-dependent diffusivity D_e . That concept is used in the physical chemistry of electrolytes [40] and colloids [41], and it accounts for the fact that D_e/μ departs from the Nernst-Einstein value kT .

Although we shall not need it in Sec. III, a word about the mobility μ is in order. In a homogeneous isothermal solution subjected to an external force $\mathbf{F} = -\mathbf{grad} U$, the current density \mathbf{j} consists of a pure drift term $\mu \mathbf{F}n$, and the drift velocity is $\mathbf{v}_d = \mu \mathbf{F}$. If the solution is characterized by a viscosity η , and if the particle’s radius R is much larger than the typical molecular dimensions, μ is given by the Stokes formula, namely,

$$\mu = 1/6\pi\eta R. \quad (10)$$

If the particle carries an electric charge Q , and if an electric field $\mathbf{E} = -\mathbf{grad} V$ is applied to the solution, the drift velocity is written $\mathbf{v}_d = \mu_E \mathbf{E}$, where μ_E (in $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$) is termed the electrophoretic mobility [42]. The latter quantity should not be identified with $Q\mu$. This comes about because the electric field acts *both* on the large particle and on the ionic cloud (of charge $-Q$) screening the particle. The particle and the cloud are respectively subjected to the forces QE and $-QE$. In the strong screening limit, the ionic cloud lies very near the particle, and then the viscosity of the fluid transmits part of the force $-QE$ to the particle, entailing an electrophoretic mobility weaker than $Q\mu$ by a factor $3\lambda_D/2R \ll 1$ (λ_D is the screening length defined in Sec. III A). In the weak screening limit, the typical size of the ionic cloud very much exceeds R , and then μ_E is identical with $Q\mu$. In what follows, the knowledge of μ is not necessary as it does not appear in the expression of the Soret coefficient.

C. Expression of the Soret mobility

We return to Eq. (4) where we take for U an internal potential energy instead of an external one like qV . The internal U is due to the interaction of the colloid with its surrounding, either the small ions copresent in the solution or the other colloidal particles. If not only the density n , but also the temperature T is inhomogeneous,

$$\mathbf{grad} U = (\partial U / \partial n)_T \mathbf{grad} n + (\partial U / \partial T)_n \mathbf{grad} T, \quad (11)$$

assuming no explicit position dependence in U . As a result, the current density may be written on the pattern of Ref. [26], namely,

$$\mathbf{j} = -\mu_s(\mathbf{grad} kT)n - D_e \mathbf{grad} n, \quad (12a)$$

where the effective diffusivity D_e defined according to Eq. (9) should be identified with D_m introduced in Sec. I, and

$$\mu_s = \mu\{1 + [\partial U / \partial (kT)]_n\} \quad (12b)$$

is the so-called Soret mobility. In Ref. [26] μ_s is compared to $\mu_e \equiv D_e/kT$, and the ratio μ_s/μ_e is accessed experimentally; it is related to the Soret coefficient S_T^* by $\mu_s/\mu_e = TS_T^*$. From Eqs. (9) and (12b), the theoretical expression for the mobility ratio is

$$\mu_s/\mu_e = \frac{1 + [\partial U / \partial (kT)]_n}{1 + (n/kT)(\partial U / \partial n)_T}. \quad (13)$$

In the absence of a potential energy, $\mu_s = \mu$ and $S_T^* = 1/T$ are positive: the colloids are dragged towards lower temperatures. It is sometimes said that the particles accumulate in regions of smaller agitation. In the presence of a temperature-dependent U , the tendency to go to lower temperatures may be strengthened or reversed by the interaction. Thus, μ_s/μ_e or S_T^* brings information on the interaction undergone by the colloid. Section III studies toy-model examples showing (i) how to use the theoretical machinery, and (ii) that strong Soret mobilities of both signs are possible.

III. ILLUSTRATION OF THE FRAMEWORK

A. Sensitivity to temperature

Consider that the colloids are spherical objects of radius R and of charge $Q = Ne$ in a solution containing a number density c of monovalent ions (of charge $\pm e$). The number density n of the colloidal particles is taken to be so small that they do not interact with each other. The Debye-Hückel theory of electrolytes gives the following value for the electric potential created by the ionic cloud at the surface of Q ,

$$\varphi' = -Q/4\pi\epsilon(R + \lambda_D), \quad (14)$$

where

$$\lambda_D = (\epsilon kT/2ce^2)^{1/2} \quad (15)$$

is the screening length, and ϵ denotes the dielectric permittivity of the solvent. (We use SI units throughout.) In Eq. (6), where the ion’s potential energy U is $\frac{1}{2}Q\varphi' = -Q^2/8\pi\epsilon(R$

+ λ_D), the ion's self-energy $Q^2/8\pi\epsilon R$ has been removed. While this is justified for a point charge such as Cl^- or Na^+ , it is inappropriate in the case of a complex object whose charge and even radius may depend on the state of the environment. Indeed, it is *not* the interaction energy $\frac{1}{2}Q\phi'$, but the total energy $U = \frac{1}{2}Q\phi$, where $\phi = Q/4\pi\epsilon R + \phi'$ is the total electric potential, that accounts for the solubility of polyions [39]. Likewise, in a nonuniform temperature, if the charge Q depends on T owing to a chemical equilibrium between the colloid surface and the solution, the self-energy also varies with T . For definiteness, suppose that $Q = Q_0[1 - \exp(-E/kT)]$, that is to say, Q decreases with increasing temperature according to a thermally activated desorption mechanism. Then the total energy

$$U = Q^2\lambda_D/8\pi\epsilon R(R + \lambda_D) \quad (16)$$

depends on temperature through Q and λ_D (neglecting the temperature dependence of the permittivity):

$$\frac{\partial U}{\partial(kT)} = -2 \frac{E}{kT} \frac{\exp(-E/kT)}{1 - \exp(-E/kT)} \frac{U}{kT} + \frac{R}{2(R + \lambda_D)} \frac{U}{kT}. \quad (17)$$

The first term in $\partial U/\partial(kT)$, due to $(\partial U/\partial Q)_{\lambda_D}$, is negative, while the second one, due to $(\partial U/\partial \lambda_D)_Q$, is positive. In water at 300 K, if $\lambda_D = 30$ nm (ionic strength 10^{-4} mol/L), $R = 7$ nm and $N = 100$, $U/kT = 417$, and $\mu_S/\mu \approx -780$ as $E/kT \ll 1$. For $E = 4kT$, $\mu_S/\mu \approx -40$. Finally, for $E \gg kT$ (Q does not vary with T), $\mu_S/\mu \approx +40$. From this toy model, it is clear that strong Soret mobilities of both signs are possible in colloidal systems. In Ref. [26] the experimental values of μ_S/μ_e found in ionic ferrofluids are -22 ($V207\text{NO}_3$), -55 ($V207\text{Cit}$), and -137 ($S184$). Recent measurements show that positive Soret coefficients in ionic ferrofluids are possible, too [30]. Since Sec. III B will show that μ_S/μ_e is usually of the order of μ_S/μ , the simple mechanism studied here is a plausible candidate. There is no need to invoke [43] a thermal conductivity mismatch between particle and solvent combined with a dielectrophoretic force which was experimentally shown to be negligible [26]. It should be noted that U is proportional to the square of the colloid charge, meaning that the knowledge of polydispersity is mandatory for quantitative interpretation of the thermodiffusion data, and this is contemplated for future work.

B. Sensitivity to density

The interaction energy discussed above takes into account the interaction between the colloid and the solvent. It does not depend on the colloid density, as the colloid-colloid interaction is dismissed. Such an assumption is too restrictive at the volume fractions usually considered in most experiments, and we show what happens when van der Waals forces between two colloidal particles are accounted for.

The binary interaction energy, in the large-distance ($r \gg R$) limit, is

$$u_{12}(r) = -16AR^6/9r^6, \quad (18)$$

where $A > 0$ is Hamaker's constant [42]. The collective interaction energy between a colloid labeled 1 (located at $r = 0$) and colloids labeled 2 is approximately given by

$$U_1 \approx \int_{2R}^{+\infty} u_{12}(r)n4\pi r^2 dr \quad (19)$$

if the conditional density of colloids 2 in the presence of colloid 1 is equal to n for all $r > 2R$. [In actual fact, short-distance repulsion usually lowers the conditional density near $r = 2R$, but there the true $u_{12}(r)$ is larger than given by Eq. (18).] One obtains

$$U_1 = -8\pi AR^3 n/27. \quad (20)$$

From Eq. (9b), it is clear that $\partial U_1/\partial n < 0$ yields a negative contribution to D . Such antidiffusion expresses the tendency to coagulation, and the relative correction to the diffusivity is $-(2/9)(A\phi/kT)$. Taking a typical value $A = 5 \cdot 10^{-20}$ J in water [42] and $R = 7$ nm, the measured value of diffusivity, based on interpreting the forced Rayleigh scattering data on the basis of Eq. (12a), differs from the value D at infinite dilution by a relative correction $(D_e - D)/D \approx -2.5\phi$.

Similarly, the short-distance repulsion caused by the overlap of the ionic clouds entails a *positive* contribution to the diffusivity. In the limit $R \gg \lambda_D$, the Derjaguin-Landau-Verwey-Overbeek theory gives [42]

$$u'_{12}(r) = (N^2 \ell kT/8R) \ln\{1 + \exp[-(r - 2R)/\lambda_D]\}. \quad (21)$$

where $\ell = e^2/4\pi\epsilon kT$ is the Bjerrum length. Calculating U'_1 according to Eq. (19), letting $u = (r - 2R)/\lambda_D$, and neglecting $u\lambda_D$ in front of $2R$ in the integrand for $u \leq 1$ yield

$$U'_1 = 2\pi n N^2 \ell kTR \lambda_D \int_0^{+\infty} \ln(1 + e^{-u}) du, \quad (22)$$

or, equivalently,

$$U'_1/kT = (\pi^2/8)\phi N^2 \ell \lambda_D/R^2. \quad (23)$$

In water at 300 K, and for $N = 100$, $\phi = 1\%$, $R = 7$ nm, and $\lambda_D = 0.7$ nm, the diffusivity correction is $+120\%$. Equation (23) is quantitatively valid insofar as $U'_1/kT < 1$; more precisely, the total (attractive+repulsive) function $u_{12}(r) + u'_{12}(r)$ should not exceed kT . Otherwise the conditional density is significantly reduced by the potential barrier near $r = 2R$, and the integrand of Eq. (19) has to be multiplied by $\exp(-[u_{12}(r) + u'_{12}(r)]/kT)$.

A final remark is in order. If the Hamaker constant depends on temperature, $\partial U_1/\partial(kT) \propto \partial A/\partial T$ contributes to μ_S/μ . In the Lifshitz theory [42], $A \propto T$ if the temperature dependence of the dielectric permittivities is neglected, so that the contribution is $U_1/kT = -2A\phi/9kT \approx -2.5\phi$. At $\phi = 1\%$, this is very small compared to the contribution examined in Sec. III A. The reason is that U_1 is small in thermal (kT) units and does not exhibit a pronounced sensitivity to temperature, while the electrostatic interaction energies of Sec. III A are large in thermal units. The repulsive contribu-

tion U'_1 is $1.2kT$ in the example considered above, and the relative contribution to the Soret mobility is $\partial U'_1/\partial(kT) = +0.6$.

IV. CONCLUSION

In this paper, we have devised a general framework aimed at accounting for the thermodiffusion of colloids. Unlike previous workers, we have not relied on extensions of ready-made isothermal expressions of the current density. Starting from the kinetic theory of Brownian motion in nonuniform temperature, we obtained (i) the nanoparticle-current equation used in interpreting the experimental data, and (ii) theoretical formulas for the diffusion and thermodiffusion coef-

ficients. Our derivation takes into account the colloid-solvent and colloid-colloid interactions through the potential energy of one colloidal particle. That energy depends on the kind of solution considered (aqueous or nonpolar solvent, ionic or surfactant colloid), and is calculable from the physicochemical data. The framework is not restricted to very dilute solutions. As such, it can be of broad interest beyond the particular area where it was devised. Finally, preliminary toy-model calculations performed in that framework prove that large Soret coefficients of both signs can be obtained, in qualitative agreement with published experimental data. Further data are being obtained [30], and we plan to interpret them within this framework.

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