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Thermodiffusion of interacting colloids. II. A microscopic approach

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A microscopic approach is presented to describe the contribution to the thermal diffusion coefficient of colloids due to intercolloidal particle interactions. An exact expression for the leading-order virial coefficient of the thermal diffusion coefficient of interacting colloidal spheres is derived in terms of the intercolloidal pair-interaction potential and hydrodynamic interaction functions. This general expression is explicitly evaluated for hard-core interactions and for spheres with a short-ranged attractive potential. The derivation is based on a Smoluchowski equation that is generalized to include temperature gradients. For short-ranged attractive potentials, a negative Soret coefficient is predicted under certain conditions, when the depth of the attraction increases with increasing temperature. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1633547]

I. INTRODUCTION

Diffusive mass transport can be induced solely by gradients in temperature. This phenomenon is commonly referred to as thermodiffusion or the Soret effect, or sometimes the Ludwig–Soret effect, since Ludwig actually found the effect for the first time, but published only a single-page report on his findings,[1] contrary to Soret.[2] A few decades later, some theory was developed for gases and very dilute solutions on a semiempirical basis.[3–6] For more concentrated systems, irreversible thermodynamics, partly based on Onsager's work,[7] has been used to describe thermodiffusion (see Refs. 8 and 9 and references therein). A more elaborate, microscopic theory for binary fluid mixtures has been proposed by Bearman *et al.*,[10] where the point of departure is the binary Liouville equation. A similar microscopic approach for thermodiffusion of a single polymer chain, based on the Smoluchowski equation, has been suggested by Khazanovich.[11] Khazanovich, however, used the Smoluchowski equation for systems with a spatially constant temperature, thus missing some of the explicit temperature gradient contributions. These contributions will be included in the present treatment of interacting colloids. Thermodiffusion of noninteracting polymers has also been analyzed by Luettmer-Strathmann,[12] partly analytically and partly by simulations, on the basis of a regular solution grid model. Depending on the interaction parameters, diffusion of the polymer chain to cold or hot regions is predicted. Thermodiffusion of magnetic/charged colloids has been considered by Morozov.[13,14] Interactions between the colloids are not taken into account in this work. So far as I know, there is in fact no microscopic theory on thermodiffusion available for concentrated macromolecular solutions which describes the effect of interactions between the macromolecules.

In Ref. 15, the preceding paper, hereafter referred-to as Paper I, thermodiffusion of interacting colloidal spheres is discussed on the basis of statistical thermodynamics and force balance. The thermal diffusion coefficient is expressed in terms of the pair-interaction potential between the colloidal spheres. This approach does not allow inclusion of the important effects of hydrodynamic interactions. Quantitatively correct numerical values for virial coefficients can only be obtained through a microscopic approach, rather than a statistical thermodynamics approach. *The present paper aims at the development of a microscopic theory for thermodiffusion as far as contributions due to intercolloidal interactions are concerned*. The first step in such a microscopic approach is the derivation of a Smoluchowski equation that is valid for systems in which the temperature is not constant but varies with position. The results from Paper I are necessary ingredients to obtain the relevant Smoluchowski equation. The second step is to integrate this equation to obtain an equation of motion for the colloidal number density, including temperature gradients. This leads to expressions for the thermal diffusion coefficient in terms of the pair-interaction potential and hydrodynamic interaction functions.

The thermal diffusion coefficient consists of two additive contributions, one arising from specific interactions between surface groups of the colloidal particles with the solvent and one arising from intercolloidal particle interactions. For charged colloids, the ionic cloud can also contribute to single colloidal particle thermodiffusion. Comparing experimental results with the present theoretical predictions thus requires one to subtract the thermal diffusion coefficient at infinite dilution from that of the measured diffusion coefficient at finite concentration (see Sec. VI in Paper I for a more detailed discussion).

For small gradients in concentration ρ and temperature T and small deviations from their mean values, the mass flux is simply a linear combination of the gradients $\nabla\rho$ and ∇T. The resulting mass conservation equation then takes the form

$$\frac{\partial}{\partial t}\rho = D\nabla^2\rho + D_T\nabla^2 T, \tag{1}$$

where D and D_T are referred to as the collective and thermal diffusion coefficient, respectively. In the preceding paper on

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[a)] Electronic mail: j.k.g.dhont@fz-juelich.de thermodiffusion of colloids,[15] the following expressions for the collective and thermal diffusion coefficient were found:

$$D=D_0\beta\frac{\partial\Pi(\rho,T,\mu_s)}{\partial\rho},\quad D_T=D_0\beta\frac{\partial\Pi(\rho,T,\mu_s(T,s))}{\partial T},\tag{2}$$

where D_0 is the Einstein translational diffusion coefficient of a freely noninteracting colloidal sphere, $\beta=1/k_BT$, with k_B Boltzmann's constant and T the temperature, and Π is the osmotic pressure, which is a function of the colloid number density ρ, temperature, and the chemical potential μ_s of the pure solvent with which the suspension is in osmotic equilibrium. Here, the temperature derivative includes the temperature dependence of the chemical potential μ_s, which is therefore written as a function of T and the remaining independent variables s.

As explained in detail in Paper I, Eq. (1) is only valid to leading order in both gradients and deviations from colloid number density and temperature from their mean values. Otherwise, the right-hand side of Eq. (1) would, among other contributions, include terms $\sim\nabla^2\nabla^2\rho$ (higher order gradients) and $\sim\nabla T\cdot\nabla\rho$, $\sim\nabla T\cdot\nabla T$ (higher order deviations from mean values).

The transport coefficients D and D_T can be expressed in terms of microscopic quantities, using the fact that the osmotic pressure is equal to

$$\Pi(\rho,T,\mu_s)=\rho k_BT-\frac{2\pi}{3}\rho^2\int_0^\infty dRR^3g^{\mathrm{eq}}(R|\rho,T)\frac{dV(R|T)}{dR},\tag{3}$$

where g^{eq} is the (equilibrium) pair-correlation function, and V is the pair-interaction potential of mean force. This potential of mean force is the potential energy between colloidal spheres, averaged with respect to the phase-space coordinates of the solvent molecules. Due to this averaging, the pair potential is implicitly dependent on temperature (and the chemical potential μ_s), as discussed in detail in Paper I. Part of the temperature dependence of the pair-correlation function originates from the implicit temperature dependence of the potential of mean force. For low concentrations of colloidal spheres

$$g^{\mathrm{eq}}(R|T)=\exp\{-\beta V(R|T)\},\tag{4}$$

which, upon substitution into Eqs. (3) and (2), leads to expressions for the diffusion coefficients in terms of the pair-interaction potential that are valid to leading order in concentration. It is shown in Paper I that the implicit temperature dependence of the pair-interaction potential of mean force can give rise to negative Soret coefficients, implying diffusion to hot regions. In the present paper, *exact expressions for the leading-order virial coefficients for D and D_T will be derived, including both direct and hydrodynamic interactions*.

This paper is organized as follows: In Sec. II, a Smoluchowski equation that is valid for systems in which the temperature varies with position is derived. This equation of motion is integrated in Sec. III, leading to exact expressions for the leading-order virial coefficients. Model calculations for hard spheres and for spheres where on top of the hard-core interaction a very short-ranged attractive potential is present, are given in Sec. IV. Section V contains a summary and conclusions.

A constant, time-independent temperature profile is considered here. In a typical experiment such a temperature profile is switched on at time $t=0$, say, after which it is maintained. Starting at $t=0$, the density will then develop inhomogeneities under the influence of the stationary temperature profile, which can be detected by optical means. Clearly, the diffusion coefficients calculated by assuming a constant temperature profile are the same coefficients which describe processes in nonstationary temperature profiles.

II. THE SMOLUCHOWSKI EQUATION FOR SPATIALLY VARYING TEMPERATURE

For systems with constant temperature, the Smoluchowski equation can be derived from the binary Liouville equation for the colloidal spheres and the solvent molecules.[16,17] As far as I know, there has been no attempt to derive the Smoluchowski equation for systems with spatially varying temperature on a similar, microscopic basis. Here, such a Smoluchowski equation is derived in a semiempirical manner, demanding that the thermal diffusion coefficient is indeed given by Eq. (2). It turns out that only the Brownian force needs to be modified relative to systems with homogeneous temperature in order to incorporate temperature gradients. The temperature dependence of the pair potential gives rise to additional, explicit temperature-gradient contributions in a trivial way.

Starting point for a microscopic derivation of the expressions (2) is the Smoluchowski equation for spherical colloidal particles. This is an equation of motion for the probability density function (pdf) P of the position coordinates $\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}$ of all N colloidal spheres in the system under consideration.[16–18] The equation of motion for P is a conservation equation

$$\frac{\partial}{\partial t}P(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)=-\sum_{i=1}^{N}\nabla_i\cdot[\mathbf{v}_iP],\tag{5}$$

where $\mathbf{v}_i$ is the translational velocity of sphere i, and ∇_i is the gradient operator with respect to the position coordinate $\mathbf{r}_i$ of the ith sphere. The equation of motion (1) can be found from the Smoluchowski equation, noting that

$$\rho(\mathbf{r},t)=NP(\mathbf{r},t)\equiv N\int d\mathbf{r}_2\cdots\int d\mathbf{r}_NP(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N,t).\tag{6}$$

For this purpose, the translational velocity of each colloidal sphere must be expressed in terms of the colloidal particle position coordinates.

In the case of homogeneous solvents, for the typically low Reynolds numbers and slow dynamics of colloidal spheres, the translational velocity $\mathbf{v}_i$ is determined by the forces $\mathbf{F}_j^h$ that the solvent exerts on the spheres j as (the superscript "h" stands for "hydrodynamic")

$$\mathbf{v}_i = -\frac{1}{\gamma}\sum_{j=1}^{N} \mathbf{M}_{ij}\cdot\mathbf{F}_j^h . \tag{7}$$

The modified mobility tensors $\mathbf{M}_{ij}$ connect the translational velocity of sphere i with the force $\mathbf{F}_j^h$ that the solvent exerts on sphere j. These tensors account for the fact that a moving sphere induces a flow field in the solvent which affects other particles in their motion. Such interactions are referred to as "hydrodynamic interactions." Furthermore, $\gamma = 6\pi\eta_0 a$ (with η_0 the shear viscosity of the solvent and a the radius of the colloidal spheres) is the friction coefficient of a single sphere with an otherwise quiescent solvent. Without hydrodynamic interactions (HI) there is no coupling between $\mathbf{v}_i$ and $\mathbf{F}_j^h$ for $i \neq j$, and Stokes law holds for each sphere

$$\mathbf{F}_j^h = -\gamma\mathbf{v}_j \quad (\text{no HI}). \tag{8}$$

This is equivalent to

$$\mathbf{M}_{ij} = \hat{\mathbf{I}}\delta_{ij} \quad (\text{no HI}), \tag{9}$$

where $\hat{\mathbf{I}}$ is the identity tensor and δ_{ij} the Kronecker delta.

The temperature dependence of the shear viscosity gives rise to terms in the equation of motion (1) which are $\sim\nabla T\cdot\nabla\rho$ and $\sim\nabla T\cdot\nabla T$. These terms are of second order in deviations from density and temperature from their mean values. Equation (1) is valid only to leading order in these deviations. To leading order in these deviations, the temperature dependence of the solvent properties can thus be neglected. This allows one to consider hydrodynamic interactions as if the solvent were homogeneous, that is, Eq. (7) can be used for thermodiffusion where the known approximations for the modified mobility tensors for homogeneous systems can be used, and the temperature dependence of γ can be omitted. It would be a formidable task to calculate hydrodynamic interaction functions in the case of strong temperature gradients, where flow and pressure fields propagate through a timely evolving, inhomogeneous solvent.

On the diffusive time scale, where the solvent phase-space coordinates and the momentum coordinates of the colloidal spheres have relaxed, the inertial force on each colloidal sphere is very small. There is thus force balance between (i) the force $\mathbf{F}_j^h$ that the fluid exerts on the jth sphere; (ii) the force $\mathbf{F}_j^I$ that results from direct interactions with other spheres; and (iii) the Brownian force $\mathbf{F}_j^{\mathrm{Br}}$. For a system of constant temperature, the interaction force is equal to

$$\mathbf{F}_j^I = -\nabla_j\Phi \quad (\text{constant temperature}), \tag{10}$$

where $\Phi \equiv \Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N|T)$ is the total potential of the assembly of colloidal particles. This is a potential of mean force, since it is averaged with respect to the degrees of freedom of the solvent molecules. As discussed in detail in Paper I, this potential is generally temperature dependent. The temperature dependence in Eq. (10) denotes the implicit temperature dependence including that of the chemical potential of the solvent. In the case of spatially varying temperature, the simple form (10) must be adjusted as follows: First, assume pairwise additivity, that is

$$\phi(\mathbf{r}_1,\ldots,\mathbf{r}_N|T) = \sum_{n<m} V(r_{nm}|T),$$

$$\mathbf{F}_j^I = -\nabla_j\sum_{n\neq j} V(r_{nj}|T), \tag{11}$$

where V is the pair potential of mean force, which depends on the distance $r_{nm} = |\mathbf{r}_n - \mathbf{r}_m|$ of just two colloidal particles. This approximation is valid for spheres with short-ranged interactions, that is, a potential where the range of the additional potential to the hard-core potential has a range that is small compared to the radius of the core. It is also a good approximation in many cases where the range of the additional potential is long ranged. When the range R_V of the pair potential is small in comparison to the length scale on which the temperature varies, the temperature can be taken equal to the local temperature, that is, the temperature at the position in between the colloidal spheres n and m. Hence, T in the pair potential in Eq. (11) for the force is equal to $T((\mathbf{r}_j+\mathbf{r}_n)/2)$. For small gradients, this local temperature can be expanded as (with $\mathbf{r}_{nj} = \mathbf{r}_n - \mathbf{r}_j$)

$$T\left(\frac{\mathbf{r}_j+\mathbf{r}_n}{2}\right) = T(\mathbf{r}_j) + \frac{1}{2}\mathbf{r}_{nj}\cdot\nabla_j T(\mathbf{r}_j). \tag{12}$$

For small deviations $\delta T(\mathbf{r}) \equiv T(\mathbf{r}) - T$ from the mean temperature T of the entire system, one can thus write the interaction force as

$$\mathbf{F}_j^I = -\sum_{n\neq j}\nabla_j V(r_{jn}|T) - \sum_{n\neq j}\left[\delta T(\mathbf{r}_j) + \frac{1}{2}\mathbf{r}_{nj}\cdot\nabla_j T(\mathbf{r}_j)\right] \times \frac{\partial}{\partial T}\nabla_j V(r_{jn}|T). \tag{13}$$

The expression for the Brownian force as known for systems with a constant temperature must be modified to include temperature gradients. To see how the Brownian force must be modified, consider an ideal system of noninteracting spheres, for which $N=1$ and $\Phi=0$, and Eq. (8) for the hydrodynamic force applies. In that case we have from force balance, $\mathbf{F}^h + \mathbf{F}^{\mathrm{Br}} = \mathbf{0}$, so that $\mathbf{v} = \mathbf{F}^{\mathrm{Br}}/\gamma$. From Eqs. (5) and (6), it is readily found that

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -\nabla\cdot\left[\frac{1}{\gamma}\mathbf{F}^{\mathrm{Br}}\rho(\mathbf{r},t)\right], \quad (\rho\to 0). \tag{14}$$

On the other hand, the osmotic pressure of an infinitely dilute dispersion is equal to $\Pi = \rho k_B T$, so it follows from Eqs. (1) and (2) that

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = \nabla\cdot\left[\frac{k_B T}{\gamma}\nabla\rho(\mathbf{r},t) + \frac{k_B\rho}{\gamma}\nabla T(\mathbf{r})\right], \quad (\rho\to 0). \tag{15}$$

As discussed before, the temperature dependence of the prefactors $D_0 = k_B T/\gamma$ and $k_B\rho/\gamma$ leads to terms $\sim\nabla T\cdot\nabla\rho$ and $\sim\nabla T\cdot\nabla T$. These terms are of second order in deviations $\delta\rho(\mathbf{r},t) = \rho(\mathbf{r},t) - \rho$ of the density and $\delta T(\mathbf{r}) = T(\mathbf{r}) - T$ of the temperature from their mean values ρ and T, respectively. In arriving at Eq. (15), these prefactors of the gradient terms are taken inside the divergence, which is thus allowed to leading order in deviations from mean values. Comparing

(14) and (15), it follows that, to leading order in deviations of density and temperature from their mean values

$$\mathbf{F}^{\mathrm{Br}} = -k_B T \nabla \ln\{\rho(\mathbf{r},t)\,T(\mathbf{r})\}. \tag{16}$$

From the Smoluchowski equation (5) and Eq. (6), it immediately follows that on the N-particle level the Brownian force is given by

$$\mathbf{F}_j^{\mathrm{Br}} = -k_B T(\mathbf{r}_j)\nabla_j \ln\{P\,T(\mathbf{r}_j)\}. \tag{17}$$

For a spatially constant temperature, this expression for the Brownian force reduces to the well-known expression $\mathbf{F}_j^{\mathrm{Br}} = -k_B T \nabla_j \ln\{P\}$.[25,18] Force balance implies that

$$\mathbf{0} = \mathbf{F}_j^{h} + \mathbf{F}_j^{I} + \mathbf{F}_j^{\mathrm{Br}}. \tag{18}$$

This force balance equation can be used to evaluate $\mathbf{v}_i$ from Eqs. (7), (13), and (17), and the resulting expression can be substituted into the conservation equation (5) to arrive at the Smoluchowski equation

$$\begin{aligned}\frac{\partial}{\partial t} P(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) = \frac{1}{\gamma}\sum_{i,j=1}^{N} \nabla_i \cdot \mathbf{M}_{ij} \cdot \Bigg[& k_B T(\mathbf{r}_j)\nabla_j P \\ & + P \sum_{n\neq j} \nabla_j V(r_{jn}|T) + k_B P \nabla_j T(\mathbf{r}_j) \\ & + P \sum_{n\neq j} \left\{ \delta T(\mathbf{r}_j) + \frac{1}{2}\mathbf{r}_{nj}\cdot\nabla_j T(\mathbf{r}_j) \right\} \\ & \times \frac{\partial}{\partial T}\nabla_j V(r_{jn}|T) \Bigg]. \end{aligned} \tag{19}$$

This equation of motion is valid for small deviations of the temperature from its mean value and small gradients in the temperature. A first-principle derivation of Eq. (19), starting from the Liouville equation for the binary mixture of solvent molecules and colloidal particles, including temperature gradients, has not yet been explored.

III. INTEGRATION OF THE SMOLUCHOWSKI EQUATION

Using the connection (6) between P and ρ, an equation of motion of the type (1) can be derived from Eq. (19), when local equilibrium is assumed. On integration of the Smoluchowski equation, integrals with respect to the distance between particles are encountered, where in the integrand the pair-correlation function is multiplied by the pair-force ∇V and/or hydrodynamic interaction functions. The latter limit the effective integration range to a molecular distance d_m (about 10 times the size of the core of the spheres, say). When the externally imposed temperature profile is varying very slowly on the length scale set by d_m, the pair-correlation function in the integrand may be taken equal to its equilibrium form g^{eq} for a homogeneous system evaluated at the local density and temperature. There is local equilibrium since relaxation of density fluctuations with a wavelength shorter than d_m is very fast in comparison to the time needed for an appreciable change of the density in case of slowly spatially varying temperature. This is the statistical analog of thermodynamic local equilibrium. Hence, in combination with the assumption that deviations $\delta\rho$ and δT of the colloid density and temperature from their mean values are small, in the integrands of the type of integrals mentioned above, one can write (with $r_{21} = |\mathbf{r}_2 - \mathbf{r}_1|$)

$$\begin{aligned} g(\mathbf{r}_2 - \mathbf{r}_1) = {} & g^{\mathrm{eq}}(r_{21}|\rho,T) + \frac{\partial g^{\mathrm{eq}}(r_{21}|\rho,T)}{\partial T}\,\delta T\left(\frac{\mathbf{r}_2+\mathbf{r}_1}{2}\right) \\ & + \frac{\partial g^{\mathrm{eq}}(r_{21}|\rho,T)}{\partial \rho}\,\delta\rho\left(\frac{\mathbf{r}_2+\mathbf{r}_1}{2},t\right), \end{aligned} \tag{20}$$

where g^{eq} is the equilibrium pair-correlation function of a homogeneous system. The temperature dependence of g^{eq} is partly due to the implicit temperature dependence of the potential of mean force. Assuming small spatial gradients, the deviations in density and temperature can then be gradient expanded up to leading order, as in Eq. (12).

On integration of Eq. (19) with the neglect of hydrodynamic interactions, these assumptions lead to Eq. (2) for the transport coefficients (see Appendix A for mathematical details).

Hydrodynamic interactions can be included on the two-particle level, where at most two particles interact simultaneously. Together with Eq. (4) for the pair-correlation function, this gives exact leading-order virial expansions for the diffusion coefficients.

On the two-particle level, the hydrodynamic interaction tensors $\mathbf{M}_{ij}$ depend only on the relative separation $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ between spheres, and can be written as

$$\begin{aligned} & \mathbf{M}_{ij} = A_c(r_{ij})\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} + B_c(r_{ij})[\hat{\mathbf{I}} - \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}], \quad i \neq j, \\ & \mathbf{M}_{ii} = \hat{\mathbf{I}} + \Delta\mathbf{M}_{ii} \quad \text{with} \quad \Delta\mathbf{M}_{ii} = \sum_{n\neq i}^{N} \{A_s(r_{in})\hat{\mathbf{r}}_{in}\hat{\mathbf{r}}_{in} \\ & \qquad + B_s(r_{in})[\hat{\mathbf{I}} - \hat{\mathbf{r}}_{in}\hat{\mathbf{r}}_{in}]\}, \end{aligned} \tag{21}$$

where $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the unit vector along $\mathbf{r}_{ij}$ and $\hat{\mathbf{I}}$ is the unit tensor. The summation over the intermediate nth sphere for the self part of the hydrodynamic interaction tensors represents the interaction of the given ith sphere with all the remaining spheres on a pairwise additive level. The scalar functions A and B, where the indices c and s stand for "cross" ($i \neq j$) and "self," respectively, can be expanded in a power series of the inverse distance a/r_{ij}, where a is the core diameter of the spheres,[19–23]

$$A_c(r_{ij}) = \sum_{m=1}^{\infty} \alpha_c^{(m)}\left(\frac{2a}{r_{ij}}\right)^m, \quad B_c(r_{ij}) = \sum_{m=1}^{\infty} \beta_c^{(m)}\left(\frac{2a}{r_{ij}}\right)^m, \tag{22}$$

and similarly for the self functions

$$A_s(r_{ij}) = \sum_{m=1}^{\infty} \alpha_s^{(m)}\left(\frac{2a}{r_{ij}}\right)^m, \quad B_s(r_{ij}) = \sum_{m=1}^{\infty} \beta_s^{(m)}\left(\frac{2a}{r_{ij}}\right)^m, \tag{23}$$

where the numerical values of the coefficients $\alpha_{c,s}^{(m)}$ and $\beta_{c,s}^{(m)}$ are known up to very large order m.

Integration of the Smoluchowski equation, using the pairwise additive form (21)–(23) for the mobility tensors and Eq. (4) for the pair-correlation function, leads to the following expression for the collective diffusion coefficient:

$$D=D_0[1+\alpha_m\varphi+\mathcal{O}(\varphi^2)], \tag{24}$$

where $\varphi=(4\pi/3)a^3\rho$ is the volume fraction of colloidal spheres (with a the radius of the hard core), and the leading-order virial coefficient α_m is equal to (see Appendix B for mathematical details)

$$\begin{aligned}\alpha_m={}&8\exp\{-\beta V_+(T)\}[1+A^*_{c,+}-A_{c,+}]\\&+8\int_{R>2a}d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2\exp\{-\beta V(R|T)\}\\&\times\Big\{A_s(R)+A^*_c(R)+2B_s(R)+2B^*_c(R)\\&-R[1+A^*_c-A_c]\beta\frac{dV(R|T)}{dR}\Big\}.\end{aligned} \tag{25}$$

Here, $R=|\mathbf{r}_2-\mathbf{r}_1|$ is the distance between two colloidal spheres. The index "$+$" is used to indicate the contact value of functions. For example

$$V_+(T)\equiv\lim_{\epsilon\downarrow 0}V(R=2a+\epsilon|T),\quad A_{c,+}\equiv\lim_{\epsilon\downarrow 0}A_c(R=2a+\epsilon). \tag{26}$$

As explained in Paper I, the temperature dependence of the pair potential of mean force includes the temperature dependence of the chemical potential of the solvent. The* on A_c and B_c in Eq. (25) means that only terms in Eqs. (21) and (22) which contribute to the divergenceless part of $\mathbf{M}_{ij}$ with $i\neq j$ are retained. The thermal diffusion coefficient can be written as

$$D_T=D_T^{(0)}+D_T^{(i)}, \tag{27}$$

where $D_T^{(0)}$ is the contribution due to explicit temperature dependencies and $D_T^{(i)}$ the contribution due to the implicit temperature dependence of both g and V. Integration of the Smoluchowski equation leads to

$$D_T^{(0)}=D_0\frac{\rho}{T}[1+\alpha_T^{(0)}\varphi+\mathcal{O}(\varphi^2)], \tag{28}$$

where the leading-order virial coefficient $\alpha_T^{(0)}$ is equal to (see Appendix B for mathematical details),

$$\begin{aligned}\alpha_T^{(0)}={}&4\exp\{-\beta V_+(T)\}\{[1+A^*_{c,+}-A_{c,+}][1+\beta V_+(T)]+A_{s,+}+A^*_{c,+}\}\\&+8\int_{R>2a}d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2\exp\{-\beta V(R|T)\}\Big\{[A_s(R)+A^*_c(R)\\&+2B_s(R)+2B^*_c(R)]\left[1+\frac{1}{2}\beta V(R|T)\right]-\frac{1}{2}R[1+A^*_c(R)-A_c(R)]\beta^2V(R|T)\frac{dV(R|T)}{dR}\\&-\frac{1}{2}R[A_s(R)+A^*_c(R)]\beta\frac{dV(R|T)}{dR}\Big\}.\end{aligned} \tag{29}$$

The implicit contribution to the thermal diffusion coefficient is equal to

$$D_T^{(i)}=D_0\frac{\rho}{T}[\alpha_T^{(i)}\varphi+\mathcal{O}(\varphi^2)], \tag{30}$$

where the leading-order virial coefficient $\alpha_T^{(i)}$ is equal to

$$\begin{aligned}\alpha_T^{(i)}={}&-4\beta T\exp\{-\beta V_+(T)\}\frac{dV_+(T)}{dT}[1+A^*_{c,+}-A_{c,+}]\\&-4\int_{R>2a}d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2\exp\{-\beta V(R|T)\}\Big\{[A_s(R)+A^*_c(R)\\&+2B_s(R)+2B^*_c(R)]\beta T\frac{\partial V(R|T)}{\partial T}+R[1+A^*_c(R)-A_c(R)]\beta T\left[\frac{\partial}{\partial T}\frac{dV(R|T)}{dR}-\beta\frac{\partial V(R|T)}{\partial T}\frac{dV(R|T)}{dR}\right]\Big\}.\end{aligned} \tag{31}$$

This concludes the microscopic derivation of the equation of motion (1), leading to microscopic expressions for the diffusion coefficients. The explicit expressions up to leading order in concentration as given above, which include hydrodynamic interactions, will be evaluated in the following section for two model potentials of mean force.

IV. MODEL CALCULATIONS

For a very dilute suspension, a "colloidal gas," virial corrections to transport coefficients can be neglected. It thus follows immediately from Eqs. (24), (27), (28), and (30) that

$$D=D_0,\quad D_T=D_0\frac{\rho}{T}. \tag{32}$$

The Soret coefficient, defined as $S_T \equiv D_T/\rho D$ (see Paper I), is thus equal to

$$S_T = 1/T. \tag{33}$$

As mentioned before, thermodiffusion induced by specific interactions between the surface of the colloidal spheres and the solvent (and possibly its ionic cloud) are not included here. Depending on the nature of the specific interactions between the surface of the colloidal spheres and solvent molecules, the Soret coefficient is different from that in Eq. (33) (as for the dilute polymer solutions as studied by Luettmer-Strathmann[12]). The Soret coefficient at infinite dilution, including these specific interactions, is discussed in more detail in Sec. VI of Paper I. Also, when these specific interactions are significant, one has $D_T \sim \rho$, so that the Soret coefficient remains concentration independent when intercolloidal particle interactions are not important. Any concentration dependence of the Soret coefficient is due to interactions between colloidal spheres.

A. Hard-sphere colloids

Besides the ideal colloidal gas discussed above, the simplest system is a suspension of hard spheres. For hard spheres, by definition, the contact value $V_+ = 0$, while $V(R|T) \equiv 0$ for $R > 2a$. Hence, from Eq. (25) (the index ''HS'' stands for ''hard spheres'')

$$\alpha_{m,\mathrm{HS}} = 8[1 + A^*_{c,+} - A_{c,+}] + 8\int_{R>2a} d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \times \{A_s(R) + A^*_c(R) + 2B_s(R) + 2B^*_c(R)\}, \tag{34}$$

while the thermal diffusion virial coefficients follow from Eq. (29)

$$\alpha^{(0)}_{T,\mathrm{HS}} = 4[1 + A_{s,+} + 2A^*_{c,+} - A_{c,+}] + 8\int_{R>2a} d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \{A_s(R) + A^*_c(R) + 2B_s(R) + 2B^*_c(R)\}, \tag{35}$$

and Eq. (31)

$$\alpha^{(i)}_{T,\mathrm{HS}} = 0. \tag{36}$$

There are two alternative approaches to approximate the hydrodynamic interaction functions. First of all, one could use a Taylor expansion with respect to the inverse distance between particles, where the coefficients of many hundreds of terms are known.[21–23] One could also use Padé-interpolation functions, which combine lubrication forms and truncated Taylor expansions (see, for example, Ref. 24). Both alternatives yield very accurate values for transport coefficients. Contact values of hydrodynamic interaction functions are exactly know from lubrication theory,[19,20]

$$A_{c,+} = 0.775, \quad A^*_{c,+} = 0.150, \quad B_{c,+} = 0.489,$$
$$B^*_{c,+} = 0.052, \quad A_{s,+} = -0.225, \quad B_{s,+} = -0.109. \tag{37}$$

It is thus found that

$$D = D_0[1 + 1.45\varphi + \mathcal{O}(\varphi^2)], \tag{38}$$

which is a well-known result first found by Batchelor,[25] and

$$D_T = D_0 \frac{\rho}{T}[1 - 0.35\varphi + \mathcal{O}(\varphi^2)]. \tag{39}$$

As before, it is assumed here that specific, temperature-dependent interactions between the surface of a colloidal sphere and the solvent can be neglected. So far, the prediction (39) has not been tested by experiment.

The values of the coefficients in Eqs. (38) and (39), 1.45 and −0.35, are significantly different from their values without hydrodynamic interactions, 8 and 4, respectively. Hydrodynamic interactions are thus quite significant, and even change the sign of the virial coefficient for D_T.

B. Colloids with short-ranged attractions

As shown in Paper I, short-ranged attractive potentials can give rise to negative thermal-diffusion coefficients. In this section we shall calculate virial coefficients for suspensions of spheres with a short-ranged attractive potential on top of the always existing core repulsion. Contrary to the calculation in Paper I, hydrodynamic interactions are accounted for, leading to quantitatively correct virial coefficients that could be verified experimentally.

Very short-ranged attractions can be modeled by the ''triangular potential''

$$V(R|T) = \epsilon(T)\frac{R - 2a - \Delta}{\Delta}, \quad \text{for } 2a \leqslant R \leqslant 2a + \Delta,$$
$$= 0, \quad \text{for } 2a + \Delta < R, \tag{40}$$

where ϵ is the temperature-dependent depth of the additional potential, with $\epsilon > 0$ for attractive potentials, and where Δ is its range, which is taken as temperature independent. Practical systems that could be modeled with such a potential are, for example, spheres coated with short polymer chains in a marginal/bad solvent for the grafted polymers, or large spheres with a van der Waals attraction due to large differences in refractive index of the spheres and the solvent. Short-range interactions are considered here, meaning that virial coefficients will be calculated to leading order in $\Delta/2a$. The width Δ of the triangular potential is thus assumed very small as compared to the core diameter $2a$ of the spheres.

For the pair-interaction potential (40), the integral in Eq. (25) for α_m can be evaluated to leading order in $\Delta/2a$, leading to (the subscript ''SS'' stands for ''sticky spheres'')

$$\alpha_{m,\mathrm{SS}} = \alpha_{m,\mathrm{HS}} + 8\frac{\Delta}{2a}\{3 + 2A^*_{c,+} - 3A_{c,+} - A_{s,+} - 2B_{s,+} - 2B^*_{c,+} + \partial A^*_{c,+} - \partial A_{c,+}\}F_D(\beta\epsilon), \tag{41}$$

where $\alpha_{m,\mathrm{HS}}$ is the hard-sphere result, given in Eq. (34), and, for example, $\partial A_{c,+}$ is defined as the derivative of $A_c(R/2a)$ with respect to $R/2a$ at $R = 2a^+$. Furthermore

$$F_D(\alpha) = (1 + \alpha - \exp\{\alpha\})/\alpha. \tag{42}$$

Mathematical details are given in Appendix C. Similarly, the integral in Eq. (29) for $\alpha^{(0)}_T$ leads to

$$\alpha^{(0)}_{T,\mathrm{SS}}=\alpha^{(0)}_{T,\mathrm{HS}}+4\,\frac{\Delta}{2a}\,[\{3+2A^{*}_{c,+}-3A_{c,+}-A_{s,+}-2B_{s,+}-2B^{*}_{c,+}+\partial A^{*}_{c,+}-\partial A_{c,+}\}F^{(0)}_{T}(\beta\epsilon)+\{2A^{*}_{c,+}+2A_{s,+}-2B_{s,+}-2B^{*}_{c,+}+\partial A_{s,+}+\partial A^{*}_{c,+}\}F_{D}(\beta\epsilon)], \tag{43}$$

where

$$F^{(0)}_{T}(\alpha)=(2+\alpha+[\alpha-2]\exp\{\alpha\})/\alpha, \tag{44}$$

and Eq. (31) for $\alpha^{(i)}_{T}$ gives (note that for hard spheres, $\alpha^{(i)}_{T}=0$)

$$\alpha^{(i)}_{T,\mathrm{SS}}=4\left[\frac{T}{\epsilon}\,\frac{d\epsilon}{dT}\right]\frac{\Delta}{2a}\{3+2A^{*}_{c,+}-3A_{c,+}-A_{s,+}-2B_{s,+}-2B^{*}_{c,+}+\partial A^{*}_{c,+}-\partial A_{c,+}\}F^{(i)}_{T}(\beta\epsilon), \tag{45}$$

where

$$F^{(i)}_{T}(\alpha)=F_{D}(\alpha)-F^{(0)}_{T}(\alpha)=(-1+[1-\alpha]\exp\{\alpha\})/\alpha. \tag{46}$$

In addition to just contact values for hydrodynamic interaction functions, we now also need the first-order derivatives $\partial A^{*}_{c,+}-\partial A_{c,+}$ and $\partial A_{s,+}+\partial A^{*}_{c,+}$. The former derivative is exactly known, since only the first two terms in the inverse distance expansion (22) contribute to the difference $A^{*}_{c}(R)-A_{c}(R)$. It thus follows from the first few terms in the inverse distance expansion that $\partial A^{*}_{c,+}-\partial A_{c,+}(R)=3/8$. The second derivative is found from lubrication theory,[19,20] $\partial A_{s,+}+\partial A^{*}_{c,+}=0.095$. It is thus found that

$$D=D_0\left[1+\varphi\left\{1.45+4.50\,\frac{3\Delta}{2a}\,F_D(\beta\epsilon)\right\}\right], \tag{47}$$

$$D^{(0)}_{T}=D_0\frac{\rho}{T}\left[1+\varphi\left\{-0.35+\frac{3\Delta}{2a}(2.25F^{(0)}_{T}(\beta\epsilon)+0.08F_D(\beta\epsilon))\right\}\right], \tag{48}$$

$$D^{(i)}_{T}=D_0\frac{\rho}{T}\,2.25\varphi\left[\frac{T}{\epsilon}\,\frac{d\epsilon}{dT}\right]\frac{3\Delta}{2a}\,F^{(i)}_{T}(\beta\epsilon). \tag{49}$$

These expressions can be compared to those in Paper I, where hydrodynamic interactions are neglected.

The thermal diffusion coefficient and Soret coefficient are plotted as functions of volume fraction and temperature in Fig. 1 and Fig. 2, respectively. The parameter set for which these calculations are made is given in the figure legends. For the dotted curves, hydrodynamics is neglected. As can be seen, hydrodynamic interactions render D_T and S_T larger. Hydrodynamics thus tends to increase the concentration and decrease the temperature at which D_T changes sign.

The above expressions for the thermal diffusion coefficients are relevant to experiments, where the parameters ϵ and Δ can be determined independently through temperature-dependent dynamic light scattering measurements of D, and possibly viscosity and sedimentation experiments. The most interesting kind of particles would be those for which $d\epsilon/dT>0$, that is, for which the depth of attraction increases with temperature.

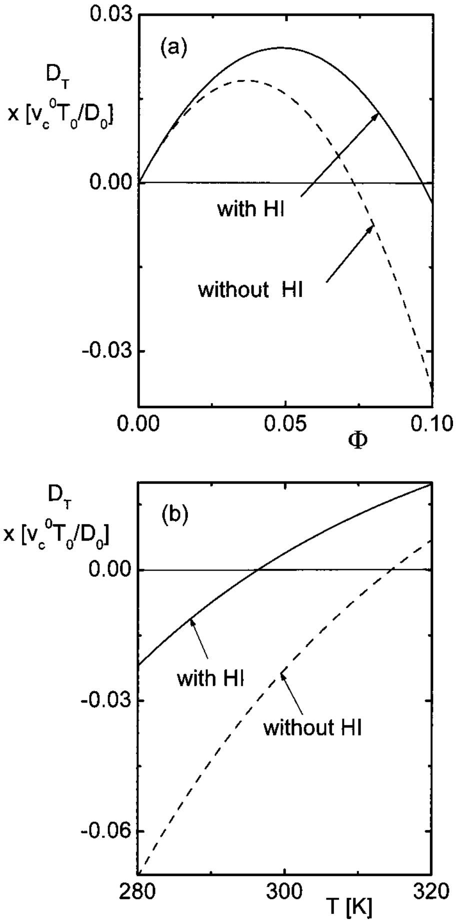

FIG. 1. (a) The thermal diffusion coefficient in dimensionless form as a function of the volume fraction of colloids. Note that $v_c^0 D_T/D_0=(\varphi/T)[1+(\cdots)\varphi]$. Here, $\Delta/2a=1/100$, $d\ln\{\epsilon\}/d\ln\{T\}=10/\beta\epsilon$ and $\beta\epsilon=5$ at room temperature $T_0=293$ K. (b) The thermal diffusion coefficient, again in dimensionless form, as a function of the temperature for $\varphi=0.1$.

V. SUMMARY AND CONCLUSION

On the basis of results obtained in Paper I, a Smoluchowski equation is proposed that is valid for systems where the temperature is spatially varying. By integration of this equation of motion, microscopic expressions for the thermal diffusion coefficient are derived. For systems where hydrodynamic interactions are important, exact results can be obtained only to leading order in concentration. For systems which are hydrodynamically very dilute, but possible thermodynamically concentrated, the thermal diffusion coefficient can be calculated from Eqs. (2) and (3) for larger concentrations, using Ornstein–Zernike type of approximations for the pair-correlation function.

There are two macromolecular systems on which systematic, concentration-dependent thermodiffusion experiments have been performed. In Ref. 26 a micellar system has been studied, and thermodiffusion of polystyrene is dis-

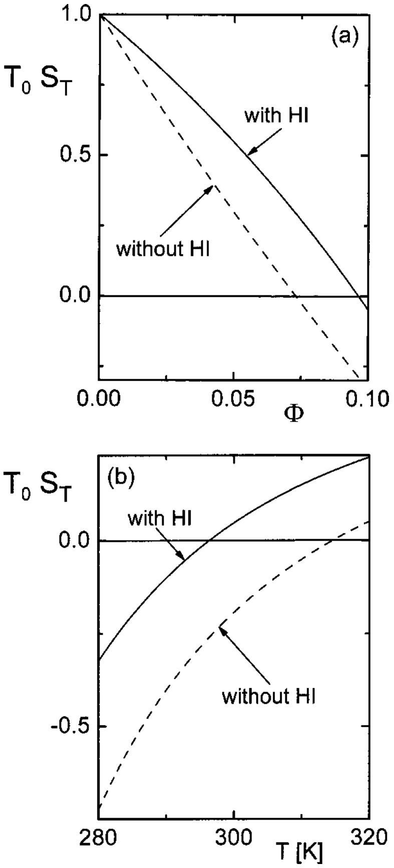

FIG. 2. The Soret coefficient as a function of concentration (a) and temperature (b). The parameters are the same as in Fig. 1.

cussed in Ref. 27, with ethyl acetate as solvent, and in Ref. 28 with toluene as solvent. Here, interactions are found to play an important role. These studies, however, do not allow for a quantitative comparison with the theory given here: interaction parameters for the micellar system are not known, and the present theory does not apply to polymers. Systematic experiments on colloids have not been done so far. A still open question is how binary colloidal mixtures of interacting spheres behave. The present approach can be extended to multicomponent colloidal systems, where the most simple system to be studied would be a hard-sphere mixture.

As discussed in Sec. VI of Paper I, the single-particle contribution of the thermal diffusion coefficient should be subtracted from the measured diffusion coefficient in order to obtain the contribution due to interactions between the colloidal particles. Apart from the ideal colloidal-gas contribution, there may be substantial contributions to the thermal diffusion coefficient of a noninteracting colloidal sphere as a result of specific interactions between colloid surface groups and solvent molecules. For the micellar system used in Ref. 26, these single-particle contributions are experimentally shown to be quite significant.

APPENDIX A: DERIVATION OF EQ. (2) FROM EQ. (19)

Here, we shall show that the adapted Smoluchowski equation (19), which includes spatial temperature variations, indeed assures that the thermodynamic results (2) are recovered for any concentration. The results (2) are derived in Paper I, where the thermodynamic approach does not allow inclusion of hydrodynamic interactions.

With the neglect of hydrodynamic interactions, $\mathbf{M}_{ij}$ takes the simple form (9). Substitution of this form into the Smoluchowski equation (19), integration with respect to $\{\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N\}$, and using Eq. (6), yields (with $\mathbf{r}_{21}=\mathbf{r}_2-\mathbf{r}_1$ and $r_{12}=|\mathbf{r}_{21}|$)

$$\frac{\partial\rho(\mathbf{r}_1,t)}{\partial t}=I_1+I_2+I_3+I_4+I_5, \tag{A1}$$

with

$$\begin{aligned}
I_1&=\frac{N}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N k_BT(\mathbf{r}_1)\nabla_1 P, \qquad I_2=\frac{N(N-1)}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N P\nabla_1 V(r_{12}|T),\\
I_3&=\frac{N}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N k_B P\nabla_1 T(\mathbf{r}_1),\\
I_4&=\frac{N(N-1)}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N P\,\delta T(\mathbf{r}_1)\frac{\partial}{\partial T}\nabla_1 V(r_{12}|T),\\
I_5&=\frac{N(N-1)}{2\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N P[\mathbf{r}_{21}\cdot\nabla_1 T(\mathbf{r}_1)]\frac{\partial}{\partial T}\nabla_1 V(r_{12}|T),
\end{aligned} \tag{A2}$$

where it is assumed that the colloidal spheres are identical. Note that according to Gauss's integral theorem, all terms with $i\neq 1$ in the Smoluchowski equation do not contribute. To leading order in gradients and deviations from mean values, the integrals I_1 and I_3 are easily seen to be equal to

$$I_1=\frac{k_BT}{\gamma}\nabla_1^2\rho(\mathbf{r}_1,t)=D_0\nabla_1^2\rho(\mathbf{r}_1,t), \tag{A3}$$

$$I_3=\frac{k_B\rho}{\gamma}\nabla_1^2 T(\mathbf{r}_1)=D_0\frac{\rho}{T}\nabla_1^2 T(\mathbf{r}_1). \tag{A4}$$

The second integral can be written as

$$I_2=\frac{1}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t)\nabla_1 V(r_{12}|T), \tag{A5}$$

where the pair-correlation function g is defined as

$$P(\mathbf{r}_1,t)P(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t) \equiv P_2(\mathbf{r}_1,\mathbf{r}_2,t)\equiv \int d\mathbf{r}_3\cdots\int d\mathbf{r}_N P(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\cdots,\mathbf{r}_N,t), \tag{A6}$$

where P_1 and P_2 are the one- and two-particle probability density functions, respectively. Now write (with $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ and $r_{12}=|\mathbf{r}_{12}|$)

$$\begin{aligned}\rho(\mathbf{r},t)&=\rho+\delta\rho(\mathbf{r},t),\\ T(\mathbf{r})&=T+\delta T(\mathbf{r}),\\ g(\mathbf{r}_1,\mathbf{r}_2,t)&=g^{\mathrm{eq}}(r_{12}|\rho,T)+\delta g(\mathbf{r}_1,\mathbf{r}_2,t),\end{aligned} \tag{A7}$$

where ρ, T, and g^{eq} are the mean number density, temperature, and the equilibrium pair-correlation function, respectively, while $\delta\rho$, δT, and δg are the corresponding small, spatially varying quantities. The small deviation δg of the pair-correlation function from its local equilibrium form g^{eq} is given by Eq. (20). Substitution of Eq. (A7) into Eq. (A5), linearization with respect to deviations, and omitting integrals of odd functions of $\mathbf{r}_{12}$ which vanish, leads to (for brevity, the density and temperature dependencies of g and V are omitted)

$$I_2=\frac{\rho}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\left[\rho\,\frac{\partial g^{\mathrm{eq}}(r_{12})}{\partial\rho}\,\delta\rho\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}\right)+\rho\,\frac{\partial g^{\mathrm{eq}}(r_{12})}{\partial T}\times\delta T\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}\right)+g^{\mathrm{eq}}(r_{12})\,\delta\rho(\mathbf{r}_2,t)\right]\nabla_1 V(r_{12}). \tag{A8}$$

Next, the following leading-order gradient expansions are used:

$$\begin{aligned}\rho(\mathbf{r}_2,t)&=\rho(\mathbf{r}_1,t)+\mathbf{r}_{21}\cdot\nabla_1\rho(\mathbf{r}_1,t),\\ \rho\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2},t\right)&=\rho(\mathbf{r}_1,t)+\frac{1}{2}\mathbf{r}_{21}\cdot\nabla_1\rho(\mathbf{r}_1,t),\end{aligned} \tag{A9}$$

and similarly for the temperature. Substitution into Eq. (A8), using that $\nabla_1 V=\hat{\mathbf{r}}_{12}dV(r_{12})/dr_{12}$ with $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/r_{12}$, transforming to the integration variable $\mathbf{r}_{12}$, and using that for arbitrary functions $f(r_{12})$

$$\int d\mathbf{r}_{12}\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12}f(r_{12})=\frac{4\pi}{3}\hat{\mathbf{I}}\int_0^\infty dr_{12}r_{12}^2f(r_{12}), \tag{A10}$$

it is finally found that (with $R=r_{12}$)

$$\begin{aligned}I_2=&-\frac{2\pi}{3\gamma}\nabla_1^2\rho(\mathbf{r}_1,t)\frac{\partial}{\partial\rho}\rho^2\\&\times\int_0^\infty dR R^3 g^{\mathrm{eq}}(R|\rho,t)\frac{dV(R|T)}{dR}-\frac{2\pi\rho^2}{3\gamma}\nabla_1^2T(\mathbf{r}_1)\\&\times\int_0^\infty dRR^3\frac{\partial g^{\mathrm{eq}}(R|\rho,T)}{\partial T}\frac{dV(R|T)}{dR}.\end{aligned} \tag{A11}$$

The integrands in Eq. (A2) for I_4 and I_5 are first order in δT, so that after integration with respect to $\{\mathbf{r}_3,\ldots,\mathbf{r}_N\}$, the combination $\rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t)$ can be set equal to $\rho^2g^{\mathrm{eq}}(r_{12}|\rho,T)$. Following the same procedure as described above for the evaluation of I_2, it is readily found that

$$I_4=\frac{\rho^2}{\gamma}\nabla_1\cdot\delta T(\mathbf{r}_1)\int d\mathbf{r}_2g^{\mathrm{eq}}(r_{12})\frac{\partial}{\partial T}\nabla_1V(r_{12}|T). \tag{A12}$$

Transforming to the integration variable $\mathbf{r}_{12}$, as before, it follows from the fact that $\nabla_1 V$ is an odd function of $\mathbf{r}_{12}$ that

$$I_4=0. \tag{A13}$$

Similarly, it is found that

$$I_5=-\frac{\rho^2}{2\gamma}\nabla_1\cdot\int d\mathbf{r}_2r_{12}g^{\mathrm{eq}}(r_{12})\frac{\partial}{\partial T}\frac{dV(r_{12})}{dr_{12}}\times\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12}\cdot\nabla_1T(\mathbf{r}_1). \tag{A14}$$

Transforming to the integration variable $\mathbf{r}_{12}$, performing the angular integrations using Eq. (A10), it is thus found that (again with $R=r_{12}$)

$$I_5=-\frac{2\pi\rho^2}{3\gamma}\nabla_1^2T(\mathbf{r}_1)\times\int_0^\infty dRR^3g^{\mathrm{eq}}(R|\rho,T)\frac{\partial}{\partial T}\frac{dV(R|T)}{dR}. \tag{A15}$$

Collecting results and grouping terms $\sim\nabla_1^2\rho(\mathbf{r}_1,t)$ and $\sim\nabla_1^2T(\mathbf{r}_1)$, it is easily verified that Eq. (A1) is precisely Eq. (1), with D and D_T given by Eq. (2), with Π equal to the expression in Eq. (3).

This verifies that the Smoluchowski equation (19), with the neglect of hydrodynamic interactions, reproduces the results obtained in Paper I that were obtained on the basis of thermodynamics and force balance.

APPENDIX B: INTEGRATION OF THE SMOLUCHOWKSI EQUATION

Two of the nontrivial integrals that are encountered on integration of the Smoluchowski equation (19) will be discussed in some detail. The mathematics is much like that discussed in Appendix A, except that the hydrodynamic interaction functions complicate things in a nontrivial manner.

First, consider the integral that originates from the first and third terms (the Brownian contributions) in the square brackets in Eq. (19). Due to Gauss's integral theorem, only the terms with $i=1$ survive the integration with respect to $\{\mathbf{r}_2,\ldots,\mathbf{r}_N\}$. Integration of Eq. (19) and assuming identical colloidal particles leads to the integrals

$$\begin{aligned}I=&\frac{k_BN}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N\nabla_1[T(\mathbf{r}_1)P]\\&+\frac{k_BN}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N\Delta\mathbf{M}_{11}\cdot\nabla_1[T(\mathbf{r}_1)P]\\&+\frac{k_BN(N-1)}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N\mathbf{M}_{12}\cdot\nabla_2[T(\mathbf{r}_2)P].\end{aligned} \tag{B1}$$

We shall consider here, as an example, just the last integral. The other integrals are evaluated similarly. Since $\mathbf{M}_{12}$ only depends on $\mathbf{r}_1$ and $\mathbf{r}_2$, the integration with respect to $\{\mathbf{r}_3,\ldots,\mathbf{r}_N\}$ can be done. Using the definition (A6) of the pair-correlation function, the last integral in Eq. (B1), I_3 say, is thus found to be equal to

$$I_3=\frac{k_B}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2\mathbf{M}_{12}\cdot\nabla_2[T(\mathbf{r}_2)\rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t)]. \tag{B2}$$

Note that, according to Gauss's theorem, only the divergenceless part of $\mathbf{M}_{12}$ contributes to the integral. This is important to assure convergence of the integral. Substitution of the leading order expansions (A7), linearization with respect to the deviations $\delta\rho$, δT, and δg, using Eqs. (21) and (22) for the hydrodynamic mobility tensor, gives

$$\begin{aligned}I_3=\frac{k_B}{\gamma}\nabla_1\cdot\int d\mathbf{r}_2[B_c^*(r_{12})\hat{\mathbf{I}}+(A_c^*(r_{12})-B_c^*(r_{12}))\hat{\mathbf{r}}_{12}\hat{\mathbf{r}}_{12}]\\
\cdot\nabla_2\Bigg\{\rho^2Tg^{\mathrm{eq}}(r_{12}|T)+\rho Tg^{\mathrm{eq}}(r_{12}|T)\,\delta\rho(\mathbf{r}_1,t)\\
+\rho Tg^{\mathrm{eq}}(r_{12}|T)\,\delta\rho(\mathbf{r}_2,t)+\rho^2g^{\mathrm{eq}}(r_{12}|T)\,\delta T(\mathbf{r}_2,t)\\
+\rho^2T\frac{\partial g^{\mathrm{eq}}(r_{12}|T)}{\partial T}\,\delta T\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}\right)\Bigg\}.\end{aligned} \tag{B3}$$

The coefficients A_c and B_c in Eq. (22) that contribute to the divergenceless part of $\mathbf{M}_{12}$ are denoted here as A_c^* and B_c^*, respectively. The first two terms between the curly brackets vanish upon integration, because $\nabla_2g^{\mathrm{eq}}(r_{12}|T)=\hat{\mathbf{r}}_{21}dg(r_{12}|T)/dr_{12}$, rendering the integrand an odd function of $\mathbf{r}_{12}$. Note that to within the low density approximation (4), the pair-correlation function is only temperature dependent, not density dependent. Substitution of the leading-order gradient expansions (A9), both for the density and temperature, into Eq. (B3), changing to the integration variable $\mathbf{r}_{12}$, and using Eq. (A10) for the angular integration, it is finally found that (with $R=r_{12}$)

$$\begin{aligned}I_3=&\frac{4\pi}{3}\rho D_0\frac{\rho}{T}\nabla_1^2T(\mathbf{r}_1)\int_0^\infty dRR^2\Bigg\{(A_c^*(R)+2B_c^*(R))\left(g^{\mathrm{eq}}(R|T)+\frac{1}{2}T\frac{\partial g^{\mathrm{eq}}(R|T)}{\partial T}\right)\\
&+RA_c^*(R)\left(\frac{dg(R|T)}{dR}+\frac{1}{2}T\frac{\partial}{\partial T}\frac{dg^{\mathrm{eq}}(R|T)}{dR}\right)\Bigg\}\\
&+\frac{4\pi}{3}\rho D_0\nabla_1^2\rho(\mathbf{r}_1,t)\int_0^\infty dRR^2\left\{(A_c^*(R)+2B_c^*(R))g^{\mathrm{eq}}(R|T)+RA_c^*(R)\frac{dg^{\mathrm{eq}}(R|T)}{dR}\right\}.\end{aligned} \tag{B4}$$

The two other integrals in Eq. (B1) are evaluated similarly.

Second, consider the interaction contribution corresponding to the last term in the curly brackets in Eq. (19). As in the expression (B1), this term leads to three contributions, one of which reads

$$\begin{aligned}I'=\frac{N}{2\gamma}\nabla_1\cdot\int d\mathbf{r}_2\cdots\int d\mathbf{r}_N\sum_{m\neq1}[B_s(r_{1m})\hat{\mathbf{I}}+(A_s(r_{1m})\\
-B_s(r_{1m}))\hat{\mathbf{r}}_{1m}\hat{\mathbf{r}}_{1m}]P\times\sum_{n\neq1}[\mathbf{r}_{n1}\\
\cdot\nabla_1T(\mathbf{r}_1)]\frac{\partial}{\partial T}\nabla_1V(r_{1n}|T).\end{aligned} \tag{B5}$$

First, note that $\nabla_1T(\mathbf{r}_1)$ is already first order in deviation from the mean temperature, so that on integration, $\rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,t)$ need not be expanded with respect to deviations. Second, "cross terms," where $n\neq m$, lead to contributions that are of third order in the mean number density ρ. To leading order in density, only contributions with $n=m$ need be calculated. For identical colloidal spheres, it is thus readily found that

$$\begin{aligned}I'=-\frac{2\pi}{3}\rho D_0\frac{\rho}{T}\nabla_1^2T(\mathbf{r}_1)\beta T\\
\times\int_0^\infty dRR^3A_s(R)g^{\mathrm{eq}}(R)\frac{\partial}{\partial T}\frac{dV(R|T)}{dR}.\end{aligned} \tag{B6}$$

The remaining contributions to the equation of motion for $\rho(\mathbf{r},t)$ can be evaluated similarly.

Collecting terms and using Eq. (4) for the pair-correlation function leads to the virial expansion

$$D=D_0[1+\alpha_m\varphi+\mathcal{O}(\varphi^2)], \tag{B7}$$

where $\varphi=(4\pi/3)a^3\rho$ is the volume fraction of colloidal spheres, with a the radius of the hard core), and the leading-order virial coefficient α_m is equal to (with $R=|\mathbf{r}_2-\mathbf{r}_1|$ the distance between two colloidal spheres)

$$\alpha_m=\int_0^\infty d\left(\frac{R}{a}\right)\left(\frac{R}{a}\right)^2 \exp\{-\beta V(R|T)\}\Bigg\{A_s(R)+A_c^*(R) + 2B_s(R)+2B_c^*(R)-R[1+A_c^*-A_c]\beta\frac{dV(R|T)}{dR}\Bigg\}. \tag{B8}$$

The corresponding virial expansion for D_T is found to be given by

$$D_T^{(0)}=D_0\frac{\rho}{T}[1+\alpha_T\varphi+\mathcal{O}(\varphi^2)], \tag{B9}$$

where the leading-order virial coefficient α_T is equal to

$$\begin{aligned}\alpha_T=&\int_0^\infty d\left(\frac{R}{a}\right)\left(\frac{R}{a}\right)^2 \exp\{-\beta V(R|T)\}\Bigg\{[A_s(R)+A_c^*(R)+2B_s(R)+2B_c^*(R)]\left[1+\frac{1}{2}\beta V(R|T)\right]\\&-\frac{1}{2}R[1+A_c^*(R)-A_c(R)]\beta^2V(R|T)\frac{dV(R|T)}{dR}-\frac{1}{2}R[A_s(R)+A_c^*(R)]\beta\frac{dV(R|T)}{dR}\Bigg\}\\&-\frac{1}{2}\int_0^\infty d\left(\frac{R}{a}\right)\left(\frac{R}{a}\right)^2 \exp\{-\beta V(R|T)\}\Bigg\{[A_s(R)+A_c^*(R)+2B_s(R)+2B_c^*(R)]\beta T\frac{\partial V(R|T)}{\partial T}\\&+R[1+A_c^*(R)-A_c(R)]\beta T\left[\frac{\partial}{\partial T}\frac{dV(R|T)}{dR}-\beta\frac{\partial V(R|T)}{\partial T}\frac{dV(R|T)}{dR}\right]\Bigg\}.\end{aligned} \tag{B10}$$

As a last step, the singular behavior of the integrands at contact should be explicitly accounted for. To this end, first note that

$$\begin{aligned}\exp\{-\beta V(R|T)\}\frac{dV(R|T)}{dR}&=-\beta^{-1}\frac{d}{dR}\exp\{-\beta V(R|T)\}\\&=-\beta^{-1}\exp\{-\beta V_+(T)\}\delta(R-2a),\\&\quad\text{for } 2a-\epsilon<R<2a+\epsilon,\end{aligned} \tag{B11}$$

where δ is the one-dimensional delta distribution, ϵ is an arbitrary small distance, and

$$V_+(T)\equiv\lim_{\epsilon\downarrow 0}V(2a+\epsilon|T), \tag{B12}$$

is the contact value of the pair-interaction potential. The integral in the expression (B8) is now split into two integrals

$$\int_0^\infty dR(\cdots)=\int_{2a-\epsilon}^{2a+\epsilon}dR(\cdots)+\int_{2a+\epsilon}^\infty dR(\cdots), \tag{B13}$$

where ϵ is an arbitrary small distance. Only the first integral contains the singular contribution from the discontinuity of the potential at contact where $R=2a$. Note that, due to the exponential of the pair potential in the integrands, values of R less then $2a$ do not contribute to the integral. Using Eq. (B11) in Eq. (B13) as far as the first integral is concerned, Eq. (25) for the virial coefficient α_m follows immediately from Eq. (B8). Next, it follows from Eq. (B11) that

$$\begin{aligned}&\exp\{-\beta V(R|T)\}\left[\frac{\partial}{\partial T}\frac{dV(R|T)}{dR}-\beta\frac{\partial V(R|T)}{\partial T}\frac{dV(R|T)}{dR}\right]\\&\quad=\exp\{-\beta V_+(T)\}\left[\frac{dV_+(T)}{dT}-\frac{\beta^{-1}}{T}\right]\delta(R-2a),\\&\quad\text{for } 2a-\epsilon<R<2a+\epsilon,\end{aligned} \tag{B14}$$

where, as before, ϵ is an arbitrary small distance. Writing the integrals in Eq. (B10) as a sum of the two integrals in Eq. (B13), the singular contribution to the second integral in Eq. (B10) is easily evaluated. Note that singular contribution to the first integral in Eq. (B10) is absent. Writing α_T as a sum of terms which vanish when V is temperature independent and the rest, leads to the expressions (29) and (31) for the virial coefficients $\alpha_T^{(0)}$ and $\alpha_T^{(i)}$, respectively.

APPENDIX C: EVALUATION OF VIRIAL COEFFICIENTS FOR SHORT-RANGED POTENTIALS

As an example, we calculate α_m in Eq. (25) for the potential (40) to first order in $\Delta/2a$. The same mathematical steps can be used to evaluate $\alpha_T^{(0)}$ and $\alpha_T^{(i)}$.

First of all, the integral in Eq. (25) is written as a sum of two integrals ranging from $R\in(2a,2a+\Delta)$ and $R\in(2a+\Delta,\infty)$, respectively. For the latter integral, I' say, $V\equiv 0$, leading to

$$\begin{aligned} I' &= \int_{2a+\Delta}^{\infty} d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \{A_s(R)+A_c^*(R)+2B_s(R) \\ &\quad +2B_c^*(R)\} \\ &= \left[\int_{2a}^{\infty} - \int_{2a}^{2a+\Delta}\right] d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \{A_s(R)+A_c^*(R) \\ &\quad +2B_s(R)+2B_c^*(R)\}. \end{aligned} \tag{C1}$$

To first order in $\Delta/2a$, the second integral in Eq. (C1) is equal to

$$\frac{\Delta}{2a}\{A_{s,+}+A_{c,+}^*+2B_{s,+}+2B_{c,+}^*\}. \tag{C2}$$

In the integral mentioned in the beginning, ranging from $R \in (2a, 2a+\Delta)$, the new integration variable

$$z = \frac{R-2a}{\Delta}, \tag{C3}$$

is introduced, which now varies from 0 to 1. The expression that needs to be evaluated for the calculation of α_m thus reads

$$\begin{aligned} I &= \int_{R>2a} d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \{A_s(R)+A_c^*(R)+2B_s(R) \\ &\quad +2B_c^*(R)\} - \frac{\Delta}{2a}\{A_{s,+}+A_{c,+}^*+2B_{s,+}+2B_{c,+}^*\} \\ &\quad + \frac{\Delta}{2a}\int_0^1 dz \exp\{-\beta\epsilon(z-1)\}\left(1+\frac{\Delta}{2a}z\right)^2\left\{F\left(1 \right.\right. \\ &\quad \left.\left. +\frac{\Delta}{2a}z\right) - \beta\epsilon\frac{2a}{\Delta}\left(1+\frac{\Delta}{2a}z\right)G\left(1+\frac{\Delta}{2a}z\right)\right\}, \end{aligned} \tag{C4}$$

where

$$\begin{aligned} F(x) &\equiv A_s(x)+A_c^*(x)+2B_s(x)+2B_c^*(x), \\ G(x) &= 1+A_c^*(x)-A_c(x). \end{aligned} \tag{C5}$$

Hydrodynamic interaction functions are regarded here as functions of $R/2a = 1+(\Delta/2a)z$, rather than just R. Note that the large prefactor $2a/\Delta$ of G in Eq. (C5) originates from dV/dR. In order to obtain expressions to first order in $\Delta/2a$, we can take F in Eq. (C5) equal to its contact value F_+ at $R=2a$, while G must be expanded to leading order as

$$G\left(1+\frac{\Delta}{2a}z\right) = G_+ + \frac{\Delta}{2a}z\,\partial G_+, \tag{C6}$$

where ∂G_+ is the derivative $dG(x)/dx$ at contact. Substituting into Eq. (C4), further expanding up to linear order in $\Delta/2a$, leads to

$$\begin{aligned} I &= \int_{R>2a} d\left(\frac{R}{2a}\right)\left(\frac{R}{2a}\right)^2 \{A_s(R)+A_c^*(R)+2B_s(R)+2B_c^*(R)\} - \frac{\Delta}{2a}\{A_{s,+}+A_{c,+}^*+2B_{s,+}+2B_{c,+}^*\} \\ &\quad + \{1+A_{c,+}^*-A_{c,+}\}(1-\exp\{\beta\epsilon\}) + \frac{\Delta}{2a}\left[\{A_{s,+}+A_{c,+}^*+2B_{s,+}+2B_{c,+}^*\}\frac{\exp\{\beta\epsilon\}-1}{\beta\epsilon}\right. \\ &\quad \left. + \{3+3A_{c,+}^*-3A_{c,+}+\partial A_{c,+}^*-\partial A_{c,+}\}\frac{1+\beta\epsilon-\exp\{\beta\epsilon\}}{\beta\epsilon}\right], \end{aligned} \tag{C7}$$

where, for example, $\partial A_{c,+}$ is defined as the derivative of $A_c(R/2a)$ with respect to $R/2a$ at contact.

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