Three-particle contribution to sedimentation and collective diffusion in hard-sphere suspensions

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The virial expansion of the collective mobility (sedimentation) coefficient is considered for hard sphere suspensions at equilibrium. The term of the second order in volume fraction, which involves three-particle hydrodynamic interactions, is calculated with high accuracy. To achieve that we represent the collective mobility coefficient as the sum of convergent integrals over particle configurations. In this way the short-wave-number limit $k \to 0$ is avoided. Moreover, an efficient numerical procedure is applied to evaluate the hydrodynamic interactions. The algorithm is based on the multipole expansion, corrected for lubrication. The method allows us to analyze contributions to the collective mobility coefficient from different configurations of three particles and to select the dominant part. This suggests a general approximation scheme. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1484380]

I. INTRODUCTION

In the last few decades there has been a wide interest[1–11] in investigations of structure, transport properties, and microhydrodynamics of suspensions. One of the fundamental problems is sedimentation, that is how a suspension moves under a given force field, e.g., gravity. The basic quantity in description of this process is the sedimentation velocity U, which is the averaged velocity of suspended particles, measured with respect to the mean suspension velocity.[12,13] Actually, the quantity of interest is the dimensionless ratio of U and U_0, where U_0 is the velocity, with which a single particle would move in the suspending fluid under the given force field in absence of any other particles. This ratio is called the collective mobility (or sedimentation) coefficient K,[13]

$$K = \frac{U}{U_0}. \tag{1}$$

The coefficient K is also needed to describe the macroscopic diffusion, since the collective diffusion coefficient D_c is given as[2,13,14]

$$D_c = K \frac{D_0}{S(0)}, \tag{2}$$

where $S(0)$ is value of the structure factor for $k=0$, D_0 is the single particle diffusion coefficient, related to the temperature T, the Boltzmann constant k_B and the single particle mobility μ_0 by the Einstein's relation,[15] that is, $D_0 = k_B T \mu_0$. For a sphere of radius a, immersed in a Stokes fluid of viscosity η, $\mu_0 = (6\pi\eta a)^{-1}$. The basic issue has been to determine how the sedimentation coefficient depends on the suspension concentration. This concentration is usually expressed in terms of the dimensionless volume fraction ϕ, equal to the volume of all the particles, divided by the total volume of the suspension.

Both the sedimentation coefficient K and the collective diffusion D_c have been extensively investigated experimentally. The collective diffusion has been studied by the dynamic light scattering (see, for example, Refs. 16–20). The sedimentation has been analyzed by various methods, among others, in ultracentrifuge,[17,18] for fluidized beds,[21] and for suspensions settling under gravity by particle tracking,[22,23] by visual observation of sedimenting boundaries,[24,25] and by an acoustic technique.[26] The concentration dependence of the sedimentation coefficient, $K(\phi)$, has been measured for the whole range of volume fractions, up to the phase transition.[25]

There exists also numerical simulations of the sedimentation coefficient for various concentrations, in particular via numerical solutions to the Stokes equations with periodic boundary conditions[27,28] and via a discretized (lattice) Boltzmann equation (see, e.g., Refs. 20, 29). The numerical results agree with the experimental data.

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There has been a large interest in theoretical derivation of the concentration dependence of the sedimentation coefficient. The main problem has been related to evaluation of the equilibrium average of the mobility matrix. That is, in a naive approach to this problem, there would appear infinities due to integration of the long-range hydrodynamic interactions. There are two main methods how to tackle this problem. The first one[2,30,31] is based on averaging the Fourier transform of the mobility matrix, and then taking the limit $k \to 0$. Although in this procedure divergences do not appear, but in practice it is cumbersome to perform calculations for many small values of k, if the mobility matrix is obtained numerically.[32] An alternative is to derive a finite expression for the sedimentation coefficient by a direct averaging of the microscopic expressions for the mobility matrix. The key point in this approach is to evaluate velocities of sedimenting particles with respect to the mean velocity of the whole suspension (particles plus fluid).[12,33] In practice, it means separating out from the mobility matrix all those terms, which contribute towards the mean velocity of the suspension. For small concentrations, such a procedure was performed by Batchelor,[12,13] and in general case, by Felderhof,[34–36] Nozières,[37] and Noetinger.[38] In the following, such a regularization scheme will be outlined and applied.

In this work we concentrate on theoretical investigation of a suspension made of identical spheres of equal radii a, immersed in the Stokes fluid. We assume that the suspension particles interact with each other as hard spheres. The volume fraction ϕ of such a suspension is given as

$$\phi = \tfrac{4}{3}\pi a^3 n, \tag{3}$$

where the number density $n = N/V$ is the number of particles per unit volume. There have been attempts to evaluate theoretically the dependence of K on the volume fraction in the whole range of ϕ, with the use of various methods (see, e.g., Refs. 39–42). When the concentration is not very high, one may use as the method the virial expansion of the collective mobility coefficient, that is the expansion of K in powers of the volume fraction,

$$K = 1 + \lambda_c \phi + b_c \phi^2 + \cdots. \tag{4}$$

In this paper we concentrate on this approach. The procedure to evaluate the two-particle coefficient λ_c was developed by Batchelor in Ref. 12, where also the numerical value $\lambda_c = -6.55$ was given. Later a systematic method to represent the two-particle hydrodynamic interactions with the use of expansion in inverse powers of the interparticle distance R has been developed and applied to the sedimentation problem. To evaluate λ_c, Felderhof[43] and Fijnaut[44] approximated the two-particle mobility matrix by taking into account all the terms up to R^{-7}, and get $\lambda_c = -6.44$. With 150 terms in the expansion, more accurate value of $\lambda_c = -6.546 \pm 0.001$ was obtained in Ref. 45.

Evaluation of the three-particle hydrodynamic interactions is more complex than in the case of two particles, therefore until now there has been no calculation of the coefficient b_c with a comparably high accuracy as for λ_c, and this paper is a step in this direction. Beenakker and Mazur evaluated b_c in Ref. 46 (together with λ_c), however, the details of the calculations have not been published.[47] Jones, Muthukumar, and Cohen[48] kept several terms in the scattering expansion of the three-particle hydrodynamic interactions, and get $b_c = 18.27$. Clercx and Schram[32] developed a systematic approach, and get $b_c = 20.8$. They used the multipole expansion (however, without taking into account the short-range lubrication effects) to calculate numerically the three-particle mobility matrix, averaged its Fourier transform, and numerically took the limit $k \to 0$. It is hard to estimate the accuracy of results obtained in this way.

In this paper we construct a method of calculating the coefficient b_c, which allows us to control the accuracy of the final result. In order to achieve that, we correct for lubrication to speed up the slow convergence of the multipole expansion for the hydrodynamic interactions. Moreover, we use the regularization scheme without taking the Fourier transforms, and in this way we avoid uncertainty of taking the limit $k \to 0$ from numerical expressions. This work has also another goal. That is, to point out the structure of derivation and to analyze significance of contributions from different configurations of three particles.

We start in Sec. II from an outline of the algorithm, constructed by Cichocki, Felderhof, and their co-workers,[49–53] which we apply to calculate numerically hydrodynamic interactions between spheres in the Stokes flow. In this scheme (similarly as in another ones[54–58]), the multipole expansion,[6,59] which takes care of the long-distance hydrodynamic interactions, is combined with the lubrication theory, which accounts for the short-range behavior, according to the idea of Brady, Bossis, and Durlofsky,[54,55,60] with the improvements introduced in Ref. 52. Next, in Sec. III, we describe the regularization procedure,[35–38] which we use to determine the sedimentation coefficient. The key point is to calculate the particle current relative to the average suspension velocity. The scattering series is split into different structures, and the expansion of correlation functions is carried out. This method is based on direct evaluation of K, without the Fourier transformation. Then, in Sec. IV, we apply this procedure to virial expansion of the sedimentation coefficient up to the three-particle contributions. Apart from the self-diffusion coefficient[52] and the two-particle contributions, we get several new terms, corresponding to different three-particle configurations. In Sec. V we evaluate all the terms; some of them analytically, some by a series expansion of two-particle hydrodynamic functions, and the last one by the Monte Carlo method of integration over relative configurations of three particles. Finally, in Sec. VI, we identify the terms, which give the dominant contribution to the sedimentation coefficient, and we suggest a rule of approximation.

II. HYDRODYNAMIC INTERACTIONS BETWEEN MANY SPHERES: MOBILITY PROBLEM

Consider N spheres of equal radii a, which undergo external forces $\boldsymbol{\mathcal{F}}_1, \ldots, \boldsymbol{\mathcal{F}}_N$ and external torques $\boldsymbol{\mathcal{T}}_1, \ldots, \boldsymbol{\mathcal{T}}_N$ (in the following abbreviated as $\boldsymbol{\mathcal{F}}$ and $\boldsymbol{\mathcal{T}}$), and which are immersed in an incompressible fluid of viscosity η. Assume

that the Reynolds number is low and that the fluid velocity and pressure, $\boldsymbol{v}(\mathbf{r})$ and $p(\mathbf{r})$, satisfy the stationary Stokes equations,[6]

$$\eta\nabla^2\boldsymbol{v}(\mathbf{r})-\nabla p(\mathbf{r})=\mathbf{0},\quad \nabla\cdot\boldsymbol{v}=0, \tag{5}$$

with the stick boundary conditions at the particle surfaces S_i,

$$\boldsymbol{v}(\mathbf{r})=\mathbf{w_i}(\mathbf{r})\equiv\mathbf{U_i}+\boldsymbol{\Omega}_i\times(\mathbf{r}-\mathbf{r_i}),$$
$$\text{for}\ \ \mathbf{r}\in S_\mathbf{i}, i=1,\ldots,N, \tag{6}$$

where $\mathbf{r_i}$ stands for the position of the center of particle i, while $\mathbf{U}_1,\ldots,\mathbf{U}_N$ and $\boldsymbol{\Omega}_1,\ldots,\boldsymbol{\Omega}_N$ (in the following abbreviated as $\mathbf{U}$ and $\boldsymbol{\Omega}$) are the translational and the rotational velocities of all the particles.

To solve Eqs. (5)–(6), the density $\mathbf{f_i}(\mathbf{r})$ of induced forces[61–63] is introduced for each particle $i=1,\ldots,N$. These forces, located at the particle surfaces, are exerted onto the fluid by the spheres and are determined by the boundary conditions (6). The rigid body motion of the particles may be now interpreted as a fictitious fluid flow for $|\mathbf{r}-\mathbf{r_i}|\leqslant a$, which obeys the Stokes equations (5). This way Eqs. (5), with the additional source term at the r.h.s., equal to $-\sum_{i=1}^{N}\mathbf{f_i}(\mathbf{r})$, may be extended onto the whole space.[61–63] Their solution for an unbounded fluid, which is at rest at infinity, $\boldsymbol{v}(\mathbf{r})$, can be written as

$$\boldsymbol{v}(\mathbf{r})=\sum_{j=1}^{N}\int \boldsymbol{T}(\mathbf{r}-\mathbf{r}')\,\mathbf{f}_j(\mathbf{r}')d^3\mathbf{r}', \tag{7}$$

where $\boldsymbol{T}$ denotes the Oseen tensor,[6]

$$\boldsymbol{T}(\mathbf{r})=\frac{1}{8\pi\eta r}(\mathbf{I}+\hat{\mathbf{r}}\hat{\mathbf{r}}). \tag{8}$$

Now let us choose a particle i and consider Eq. (7) at its surface S_i. Taking into account the boundary conditions (6), one can write Eq. (7) in terms of integral operators as

$$\mathbf{w}_i=\mathbf{Z}_0^{-1}(i)\,\mathbf{f_i}+\sum_{j\neq i}\mathbf{G}(ij)\,\mathbf{f}_j. \tag{9}$$

In the above equation we decomposed the integral operator at the r.h.s. of Eq. (7) into two parts. The first one[64] describes the contribution to the velocity of particle i from the induced forces located on the same particle i. The second part involves Green operators[65,66] $\mathbf{G}(ij)$, where $j=1,\ldots,N$, but $j\neq i$, which account for the contributions to $\mathbf{w_i}$ coming from other particles than i. The operator $\mathbf{G}(ij)$ it is not symmetric with respect to the interchange of i and j.

To solve the integral Eq. (9), the multipole expansion is introduced. In this way the problem is reduced to an infinite system of linear algebraic equations for matrix elements, which are labeled by the particle number and by three multipole indices l, m, σ, where $l=1,2,\ldots$, while $m=-l,\ldots,+l$, and $\sigma=0,1,2$. The details on the integral operators $\mathbf{G}$, $\mathbf{Z}_0$ may be found, e.g., in Ref. 53; their multipole matrix elements are given explicitly in the Appendix.

The system of equations, which follow from the multipole matrix representation of Eq. (9) allows to solve the friction and mobility problems. In the mobility problem,[6] $\mathbf{U}$ and $\boldsymbol{\Omega}$ are evaluated in terms of $\boldsymbol{\mathcal{F}}$ and $\boldsymbol{\mathcal{T}}$. In the absence of an external ambient fluid flow this relation has the form,

$$\begin{pmatrix}\mathbf{U}\\ \boldsymbol{\Omega}\end{pmatrix}=\begin{pmatrix}\boldsymbol{\mu}^{tt} & \boldsymbol{\mu}^{tr}\\ \boldsymbol{\mu}^{rt} & \boldsymbol{\mu}^{rr}\end{pmatrix}\begin{pmatrix}\boldsymbol{\mathcal{F}}\\ \boldsymbol{\mathcal{T}}\end{pmatrix}, \tag{10}$$

where $\boldsymbol{\mu}^{\mathbf{pq}}$ $(p,q=t$ or $r)$ are the $3N\times3N$ Cartesian tensors, and the superscripts t and r correspond to the translational and the rotational components, respectively. The $6N\times6N$ matrix, which appears at the r.h.s. of Eq. (10) is called the N-particle mobility matrix,[59,67] and denoted in short as $\boldsymbol{\mu}$. Its inverse is called the friction matrix.

The analysis of Eq. (7) allows to express the mobility (10) as the multiple scattering series[67] (equivalent to superposition of all the reflections[68] for the mobility problem[6]). The sum of this series is given as[50]

$$\boldsymbol{\mu}=\boldsymbol{\mu}_0+\boldsymbol{\mu}_0\mathbf{Z}_0\frac{1}{\mathbf{1}+\mathbf{G}\hat{\mathbf{Z}}_0}\mathbf{G}\mathbf{Z}_0\boldsymbol{\mu}_0. \tag{11}$$

Here $\boldsymbol{\mu}_0$ is the one-particle mobility. The operator $\hat{\mathbf{Z}}_0=\mathbf{Z}_0-\mathbf{Z}_0\boldsymbol{\mu}_0\mathbf{Z}_0$ differs from $\mathbf{Z}_0$ for $l=1$ only[50,67] (see Appendix for its matrix elements). The operator $\mathbf{G}\hat{\mathbf{Z}}_0$ produces subsequent scattered (reflected) velocity fields, which are force-free and torque-free.[6]

Now let us consider the cluster expansion of the mobility matrix. That is, let us decompose $\boldsymbol{\mu}$ into the M-particle cluster matrices $\boldsymbol{\mu}_{jk}^{(M)}(1\cdots M)$ $(M=1,\ldots,N)$. For $j=k$ the M-particle cluster matrices were defined, e.g., in Ref. 52, and for $j\neq k$ they are given as

$$\boldsymbol{\mu}_{12}(1\cdots M)=\boldsymbol{\mu}_{12}^{(2)}(12)+\sum_{i\neq1,2}^{M}\boldsymbol{\mu}_{12}^{(3)}(12i)+\cdots+\boldsymbol{\mu}_{12}^{(M)}(1\cdots M). \tag{12}$$

In particular, $\boldsymbol{\mu}_{12}^{(2)}(12)=\boldsymbol{\mu}_{12}(12)$ and $\boldsymbol{\mu}_{12}^{(3)}(123)=\boldsymbol{\mu}_{12}(123)-\boldsymbol{\mu}_{12}(12)$. Here we consider a semidilute dispersion, and clusters of more than three particles will not be taken into account.

The cluster expansion of the mobility (12) is evaluated by splitting the multiple scattering series (11) into terms, which describe the interactions within the corresponding clusters. The three-particle cluster mobility,

$$\boldsymbol{\mu}_{12}^{(3)}(123)=\left[\boldsymbol{\mu}_0\mathbf{Z}_0\frac{1}{\mathbf{1}+\mathbf{G}\hat{\mathbf{Z}}_0}\mathbf{G}\mathbf{Z}_0\boldsymbol{\mu}_0\right]'_{12}(123) \tag{13}$$

is the sum of scatterings, which start from particle 1, finish at particle 2, and involve *all* three particles: (123). The last property is denoted by prime. For example, the lowest order scattering in $\boldsymbol{\mu}_{12}^{(3)}(123)$ has the form,

$$-\boldsymbol{\mu}_0(1)\mathbf{Z}_0(1)\mathbf{G}(13)\hat{\mathbf{Z}}_0(3)\mathbf{G}(32)\mathbf{Z}_0(2)\boldsymbol{\mu}_0(2). \tag{14}$$

In the following we assume that there is no applied torques, $\boldsymbol{\mathcal{T}}=0$, and we are interested only in the translational motion of all the spheres, $\mathbf{U}$. Therefore we evaluate $\boldsymbol{\mu}^{tt}$ only; so as we simplify the notation: from now on $\boldsymbol{\mu}$ will stand for $\boldsymbol{\mu}^{tt}$.

III. SEDIMENTATION COEFFICIENT

In this section we outline the method,[35,37,38] which leads to the microscopic expression for the sedimentation coefficient K, defined in Eq. (1). Let us stress that although we start from analysis of the Fourier transforms, but the final expression for K has a form of a sum of the convergent integrals over particle configurations, with no $\boldsymbol{k}\to\mathbf{0}$ limit involved. To begin, let us consider the sedimentation phenomena when an external force field $\boldsymbol{E}(\mathbf{r})$ is applied to suspended particles, so that $\boldsymbol{E}(\mathbf{r}_i)$ is equal to the force $\boldsymbol{\mathcal{F}}_i$ acting on particle i. The external field induces a particle current, which can be described by the density

$$\boldsymbol{j}(\mathbf{r})=\sum_{i=1}^{N}\mathbf{U}_i\,\delta(\mathbf{r}-\mathbf{r}_i). \tag{15}$$

We assume that the distribution of particles is the equilibrium one. The respective averaging operation will be denoted by $\langle\cdot\rangle$. Relation between the average particle current and the force field is a linear one, as follows from Eq. (10). With the use of the Fourier transforms $\hat{\boldsymbol{j}}(\boldsymbol{k})$, $\hat{\boldsymbol{E}}(\boldsymbol{k})$ of the current and of the force field, respectively, one has

$$\langle\hat{\boldsymbol{j}}(\boldsymbol{k})\rangle=\hat{\boldsymbol{X}}(\boldsymbol{k})\,\hat{\boldsymbol{E}}(\boldsymbol{k}), \tag{16}$$

with the response kernel given by

$$\hat{\boldsymbol{X}}(\boldsymbol{k})=\frac{1}{V}\sum_{i,j=1}^{N}\langle\boldsymbol{\mu}_{ij}e^{i\boldsymbol{k}(\mathbf{r}_i-\mathbf{r}_j)}\rangle, \tag{17}$$

where V is volume of the system. It has to be stressed that, strictly speaking, Eqs. (16)–(17) (and also the corresponding expressions in this section) are valid in the thermodynamic limit, i.e., when $N\to\infty$, $V\to\infty$, but $N/V=\text{const}$.

The above kernel can be decomposed into two parts,

$$\hat{\boldsymbol{X}}(\boldsymbol{k})=\hat{\boldsymbol{X}}_{\text{self}}+\hat{\boldsymbol{X}}_o(\boldsymbol{k}). \tag{18}$$

The self-term corresponds to the sum over $i=j$ in Eq. (17) and can be written as

$$\hat{\boldsymbol{X}}_{\text{self}}=n\langle\boldsymbol{\mu}_{11}\rangle. \tag{19}$$

Its virial expansion has been analyzed in Ref. 52.

The kernel $\hat{\boldsymbol{X}}_o(\boldsymbol{k})$ in turn contains the off-diagonal terms with $i\neq j$ in Eq. (17). With the use of the cluster expansion (12), its structure can be expressed as

$$\hat{\boldsymbol{X}}_o(\boldsymbol{k})=\sum_{s=2}^{\infty}\frac{n^s}{(s-2)!}\times\int \mathrm{d}2\cdots\mathrm{d}s\;\; g(1\cdots s)\,\boldsymbol{\mu}_{12}^{(s)}(1\cdots s)\,e^{i\boldsymbol{k}(\mathbf{r}_1-\mathbf{r}_2)}, \tag{20}$$

where the integral is over positions of particles $2,3,\ldots,s$, while n is the number density, and $n^s g(1\cdots s)$ stands for the s-particle equilibrium distribution function. As far as the cluster expansions are considered, it is worthwile to mention Ref. 69.

The sedimentation coefficient K, introduced in Eq. (1), is related[2] to the element $\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{X}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}}$ (where $\hat{\boldsymbol{k}}=\boldsymbol{k}/|\boldsymbol{k}|$) by

$$K=\frac{1}{n\mu_0}\lim_{\boldsymbol{k}\to\mathbf{0}}[\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{X}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}}]. \tag{21}$$

In general it is a cumbersome task to compute K with the use of the above formula because of the long-wavelength limit involved. Moreover, due to long-range of hydrodynamic interactions the kernel $\hat{\boldsymbol{X}}(\boldsymbol{k})$ is not continuous at $\boldsymbol{k}=\mathbf{0}$, so that one cannot just put $\boldsymbol{k}=\mathbf{0}$ there. This problem can be resolved by the regularization procedure, the idea of which was first outlined by Felderhof[34] and then developed by Nozières,[37] Felderhof,[35] and Noetinger.[38] The rest of the chapter is devoted to a brief summary of those results.

As it has been pointed out by many authors (see, e.g., Refs. 12, 13, 33, 34), in general, the external force $\boldsymbol{E}$ gives rise not only to the particle current, but also to the nonzero flow of suspension as a whole. The idea behind regularization is to calculate the particle current relative to the average velocity of suspension $\langle\boldsymbol{v}(\mathbf{r})\rangle$, which incorporates all long-range terms of the r.h.s. of Eq. (16). The definition of $\boldsymbol{v}(\mathbf{r})$ is the following: for a given configuration of particles $\boldsymbol{v}(\mathbf{r})$ is equal to the fluid velocity wherever $\mathbf{r}$ is inside the fluid and coincides with the rigid body motion wherever $\mathbf{r}$ lies inside the particle. It has been proven in Refs. 35, 38 that in the long-wavelength limit Eq. (16) can be rewritten as

$$\langle\hat{\boldsymbol{j}}(\boldsymbol{k})\rangle-n\langle\hat{\boldsymbol{v}}(\boldsymbol{k})\rangle=\hat{\boldsymbol{X}}^{\text{irr}}(\boldsymbol{k})\,\hat{\boldsymbol{E}}(\boldsymbol{k}),\quad \boldsymbol{k}\to\mathbf{0}, \tag{22}$$

where the ''irreducible'' kernel $\hat{\boldsymbol{X}}^{\text{irr}}(\boldsymbol{k})$ is continuous at $\boldsymbol{k}=\mathbf{0}$. Moreover, the $\boldsymbol{k}\to\mathbf{0}$ limit of $\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{X}}^{\text{irr}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}}$ is the same as this of $\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{X}}(\boldsymbol{k})\cdot\hat{\boldsymbol{k}}$. Taking into account isotropy of the system, we therefore get for K the expression, which may be evaluated directly, without taking any Fourier transforms,

$$K=\frac{1}{3n\mu_0}\,\mathrm{Tr}\,\hat{\boldsymbol{X}}^{\text{irr}}(\boldsymbol{k}=\mathbf{0}). \tag{23}$$

The structure of the kernel $\hat{\boldsymbol{X}}^{\text{irr}}(\boldsymbol{k})$ is analogous to the structure of $\hat{\boldsymbol{X}}(\boldsymbol{k})$, given by Eq. (18). In the following we are going to concentrate on the ''off-diagonal'' term $\hat{\boldsymbol{X}}_o^{\text{irr}}(\boldsymbol{k}=\mathbf{0})$, as the ''self'' term $\hat{\boldsymbol{X}}_{\text{self}}=\hat{\boldsymbol{X}}_{\text{self}}^{\text{irr}}$ does not depend on $\boldsymbol{k}$. For $\hat{\boldsymbol{X}}_o^{\text{irr}}(\boldsymbol{k}=\mathbf{0})$ one gets

$$\hat{\boldsymbol{X}}_o^{\text{irr}}(\boldsymbol{k}=\mathbf{0})=\sum_{s=2}^{\infty}\frac{n^s}{(s-2)!}\times\int \mathrm{d}2\cdots\mathrm{d}s[g(1\cdots s)\boldsymbol{\mu}_{12}^{(s)}(1\cdots s)]^{\text{irr}}, \tag{24}$$

where the exact meaning of $[\;]^{\text{irr}}$ is to be elucidated.

First, the notion of articulation structure is introduced and assigned to the scattering expansion terms of $\boldsymbol{\mu}$ in Eq. (11). An operator $\mathbf{G}$ is called the articulation line if all the particles following it in the scattering sequence are different from those, which come before it. The scattering sequence with no articulation line is said to be $\mathbf{G}$-irreducible. On the other hand, the scattering sequence with at least one articulation line is said to be $\mathbf{G}$-reducible. For any such $\mathbf{G}$-reducible sequence of scatterings, which starts at particle 1 and ends at particle 2, the set of particle labels $1,2,\ldots,s$ is partitioned into a sequence of disjoint subsets

$C_1, C_2, \ldots, C_k$, such that $1 \in C_1$, $2 \in C_k$ and each subset is connected with the preceding subset by an articulation line. Such a partition is called the articulation structure and denoted as $(C_1|C_2|\cdots|C_k)$. For example, the term

$$\boldsymbol{\mu}_0(1)\,\mathbf{Z}_0(1)\,\mathbf{G}(12)\hat{\mathbf{Z}}_0(2)\mathbf{G}(23)\,\hat{\mathbf{Z}}_0(3)\,\mathbf{G}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2) \tag{25}$$

has the articulation structure of the form $(1|23)$, as particle 1 is connected with the group of particles 2 and 3 by one operator $\mathbf{G}(12)$ only. [Note that scattering sequences, which share the same articulation structure, may have different articulation lines. For example, the sequence $\boldsymbol{\mu}_0(1)\,\mathbf{Z}_0(1)\,\mathbf{G}(13)\,\hat{\mathbf{Z}}_0(3)\,\mathbf{G}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)$ has the articulation line $\mathbf{G}(13)$ and the same articulation structure $(1|23)$ as the expression (25), for which the articulation line is equal to $\mathbf{G}(12)$.]

Therefore each term $\boldsymbol{\mu}_{12}^{(s)}(1\cdots s)$ in the cluster expansion (12) may be written as

$$\boldsymbol{\mu}_{12}^{(s)}(1\cdots s)=\sum_{k=1}^{s}\sum_{\{C_1\cdots C_k\}}\tilde{\boldsymbol{\mu}}_{12}(C_1|\cdots|C_k), \tag{26}$$

where the second sum goes over different partitions of the set of the particle labels $(1,2,\cdots,s)$ into a sequence of k disjoint subsets $C_1, C_2, \ldots, C_k$ with $1 \in C_1$, $2 \in C_k$. The expression $\tilde{\boldsymbol{\mu}}_{12}(C_1|C_2|\cdots|C_k)$ stands for the sum of all the terms in the scattering expansion of $\boldsymbol{\mu}_{12}^{(s)}(12,\cdots s)$, which share the same articulation structure $(C_1|C_2|\cdots|C_k)$.

For example, for two particles,

$$\tilde{\boldsymbol{\mu}}_{12}(1|2)=\boldsymbol{\mu}_0(1)\mathbf{Z}_0(1)\mathbf{G}(12)\mathbf{Z}_0(2)\boldsymbol{\mu}_0(2), \tag{27}$$

$$\tilde{\boldsymbol{\mu}}_{12}(12)=\boldsymbol{\mu}_{12}^{(2)}(12)-\tilde{\boldsymbol{\mu}}_{12}(1|2), \tag{28}$$

where the scattering sequence in Eq. (28) is determined from Eq. (11).

For three particles,

$$\tilde{\boldsymbol{\mu}}_{12}(1|3|2)=-\boldsymbol{\mu}_0(1)\mathbf{Z}_0(1)\mathbf{G}(13)\hat{\mathbf{Z}}_0(3)\mathbf{G}(32)\times\mathbf{Z}_0(2)\boldsymbol{\mu}_0(2), \tag{29}$$

$$\tilde{\boldsymbol{\mu}}_{12}(13|2)=\mathbf{C}_{11}(13)\mathbf{G}(12)\mathbf{Z}_0(2)\boldsymbol{\mu}_0(2)+\mathbf{C}_{13}(13)\mathbf{G}(32)\mathbf{Z}_0(2)\boldsymbol{\mu}_0(2)-\tilde{\boldsymbol{\mu}}_{12}(1|3|2), \tag{30}$$

$$\tilde{\boldsymbol{\mu}}_{12}(1|32)=\boldsymbol{\mu}_0(1)\mathbf{Z}_0(1)\mathbf{G}(12)\mathbf{C}_{22}^{T}(23)+\boldsymbol{\mu}_0(1)\mathbf{Z}_0(1)\mathbf{G}(13)\mathbf{C}_{32}^{T}(23)-\tilde{\boldsymbol{\mu}}_{12}(1|3|2), \tag{31}$$

$$\tilde{\boldsymbol{\mu}}_{12}(123)=\boldsymbol{\mu}_{12}^{(3)}(123)-\tilde{\boldsymbol{\mu}}_{12}(13|2)-\tilde{\boldsymbol{\mu}}_{12}(1|32)-\tilde{\boldsymbol{\mu}}_{12}(1|3|2). \tag{32}$$

Here the operator $\mathbf{C}_{kl}(13)$ stands for the sum of those scatterings in Eq. (11), which contain only two particles (13), and which start from particle $k=1$ or 3, and finish at particle $l=1$ or 3,

$$\mathbf{C}_{kl}(13)=-\left[\boldsymbol{\mu}_0\mathbf{Z}_0\frac{1}{1+\mathbf{G}\hat{\mathbf{Z}}_0}\mathbf{G}\hat{\mathbf{Z}}_0\right]_{kl}(13). \tag{33}$$

Definition of $\mathbf{C}_{kl}(23)$ is a straightforward generalization of Eq. (33); $\mathbf{C}^T$ is the transposition of $\mathbf{C}$.

Next with each articulation structure $(C_1|\cdots|C_k)$ one associates an appropriate correlation function $h(C_1|\cdots|C_k)$, which is called the block distribution function. The block distribution function $h(C)$, which corresponds to a $\mathbf{G}$-irreducible term $\tilde{\boldsymbol{\mu}}(C)$ is just the usual particle distribution function,

$$h(C)=g(C). \tag{34}$$

The block distribution functions assigned to $\mathbf{G}$-reducible structures are defined by the following recursive relation:

$$h(C_1|\cdots|C_i|C_{i+1})=h(C_1|\cdots|C_i\,C_{i+1})-h(C_1|\cdots|C_i)h(C_{i+1}). \tag{35}$$

Finally, $[g(1\cdots s)\boldsymbol{\mu}_{12}(1\cdots s)]^{\mathrm{irr}}$ is defined in terms of articulation structures and block distribution functions as

$$[g(1\cdots s)\boldsymbol{\mu}_{12}^{(s)}(1\cdots s)]^{\mathrm{irr}}=\sum_{k=1}^{s}\sum_{\{C_1\cdots C_k\}}h(C_1|\cdots|C_k)\tilde{\boldsymbol{\mu}}_{12}(C_1|\cdots|C_k). \tag{36}$$

For two particles,

$$[g(12)\boldsymbol{\mu}_{12}^{(2)}(12)]^{\mathrm{irr}}=[g(12)-1]\tilde{\boldsymbol{\mu}}_{12}(1|2)+g(12)\tilde{\boldsymbol{\mu}}_{12}(12) \tag{37}$$

with $\tilde{\boldsymbol{\mu}}_{12}(1|2)$ and $\tilde{\boldsymbol{\mu}}_{12}(12)$ given by Eq. (28).

For three particles,

$$\begin{aligned}[g(123)\boldsymbol{\mu}_{12}^{(3)}(123)]^{\mathrm{irr}}&=g(123)\tilde{\boldsymbol{\mu}}_{12}(123)+[g(123)-g(13)]\tilde{\boldsymbol{\mu}}_{12}(13|2)\\&\quad+[g(123)-g(23)]\tilde{\boldsymbol{\mu}}_{12}(1|32)\\&\quad+[g(123)-g(13)-g(23)+1]\tilde{\boldsymbol{\mu}}_{12}(1|3|2),\end{aligned} \tag{38}$$

with the articulation structures $\tilde{\boldsymbol{\mu}}$ given in Eqs. (29)–(32).

IV. VIRIAL EXPANSION OF THE SEDIMENTATION COEFFICIENT

In this section we expand Eq. (23) in powers of volume fraction to evaluate the sedimentation coefficient up to $\mathcal{O}(\phi^2)$, as indicated in Eq. (4). We quote known results for the linear term in Eq. (4), $\lambda_c\phi$, and for the quadratic terms in the self-contributions, defined by Eq. (19). We use Eq. (24) to evaluate the remaining part of $b_c\phi^2$.

First, we perform virial expansion of the hard sphere equilibrium correlation functions in powers of volume fraction ϕ,

$$g(1\cdots s)=W(1\cdots s)[1+\phi g^{(1)}(1\cdots s)+\cdots], \tag{39}$$

where

$$W(1\cdots s)=\prod_{i>j=1}^{s}W(ij), \tag{40}$$

and $W(ij)$ are given as

$$W(ij)=\begin{cases}0 & \text{for } |\mathbf{r}_i-\mathbf{r}_j|\leqslant 2a,\\ 1 & \text{elsewhere.}\end{cases} \tag{41}$$

In particular,[70]

$$g^{(1)}(12)=\begin{cases} 8-6R_{12}+\dfrac{R_{12}^3}{2} & \text{for } 1\leqslant R_{12}\leqslant 2, \\ 0 & \text{elsewhere.} \end{cases} \tag{42}$$

From now on we use dimensionless distances, normalized by the particle diameter $2a$: $\mathbf{R}_i=\mathbf{r}_i/(2a)$, $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ and $R_{ij}=|\mathbf{R}_{ij}|$.

Next we perform virial expansion of the sedimentation coefficient K, defined in Eq. (1), i.e. we specify the coefficients λ_c and b_c in Eq. (4). Coefficient λ_c comes from two-particle hydrodynamic interactions. It consists of two parts,

$$\lambda_c=\lambda_{\text{self}}+\lambda_o. \tag{43}$$

In Eq. (43), λ_{self} accounts for chains of two-particle scattering processes, which start and end at particle 1. Such self-contributions were calculated by Batchelor,[13] and next recalculated with higher accuracy by Cichocki and Felderhof,[45,71]

$$\lambda_{\text{self}}=-1.8315. \tag{44}$$

In Eq. (43) λ_o accounts for chains of two-particle scattering processes, which start at particle 1 and end at particle 2. Equations (37) and (41) allow us to write λ_o as a sum of two parts: with virtually overlapping and with nonoverlapping particles 1 and 2,

$$\lambda_o=-\frac{2}{\pi\mu_0}\int_{\mathbf{R}_{12}\leqslant 1} d^3\mathbf{R}_{12}\,\mathrm{Tr}\,\tilde{\boldsymbol{\mu}}_{12}(1|2) + \frac{2}{\pi\mu_0}\int_{\mathbf{R}_{12}\geqslant 1} d^3\mathbf{R}_{12}\,\mathrm{Tr}\,\tilde{\boldsymbol{\mu}}_{12}(12). \tag{45}$$

The virtually overlapping part is equal to -5 (see Refs. 12, 42–44, 46). The nonoverlapping integral was calculated approximately in Refs. 12, 43, 44, 46, and recalculated with higher accuracy in Ref. 45 to be equal to 0.285. Combination of those results with Eq. (44) gives[45]

$$\lambda_c=-6.546. \tag{46}$$

To describe the structure of the coefficient b_c, we decompose it into seven parts of a different type,

$$b_c=\sum_{i=1}^{7} b_i. \tag{47}$$

The first term, b_1, is the contribution coming from X_{self}, given in Eq. (19). That is, b_1 is the ϕ^2 coefficient in the virial expansion of the self-diffusion coefficient. It has been already calculated in Ref. 52,

$$b_1=-0.219\pm 0.004. \tag{48}$$

The second term, b_2, accounts for the two-particle contribution, $[g(12)\boldsymbol{\mu}_{12}^{(2)}(12)]^{\text{irr}}$, given in Eq. (37). Due to virial expansion of the two-particle equilibrium correlation function $g(12)$, displayed in Eq. (42), this term has the following form:

$$b_2=\frac{2}{\pi\mu_0}\int_{1\leqslant R_{12}\leqslant 2} d^3\mathbf{R}_{12}\left(8-6R_{12}+\frac{R_{12}^3}{2}\right) \times \mathrm{Tr}[\boldsymbol{\mu}_{12}^{(2)}(12)]. \tag{49}$$

To calculate this term, we perform the scattering expansion of the two-particle mobility in inverse powers of the interparticle distance, R, up to $1/R^{500}$, and we get

$$b_2=13.6386. \tag{50}$$

The result agrees with the value $b_2=13.64$ given in Ref. 32.

The other parts in Eq. (47) correspond to contributions from the three-particle term $[g(123)\boldsymbol{\mu}_{12}^{(3)}(123)]^{\text{irr}}$, which is specified in Eq. (38). To calculate those contributions, we have to expand the block distribution functions up to $\mathcal{O}(\phi)$. To simplify this procedure, we make use of the corresponding symmetry of the response kernel, and we perform permutations of the particles in the expression (30), to get the same articulation line $\mathbf{G}(23)$ for each term [by analogy, we get the same articulation line $\mathbf{G}(13)$ for all the terms in the expression (31)].

So we will need only the following three-particle hard-sphere block distribution functions (35):

$$g(123)-g(13)-g(23)+1=f(12)W(13)W(23) + f(13)f(23)+\mathcal{O}(\phi), \tag{51}$$

$$g(123)-g(13)=f(12)W(13)W(23) + W(13)f(23)+\mathcal{O}(\phi), \tag{52}$$

$$g(123)=W(123)+\mathcal{O}(\phi), \tag{53}$$

where $f(ij)=W(ij)-1$ is the Mayer function.[70]

Evaluation of the response kernel (24) may be further simplified. To this goal, the Green operator $\mathbf{G}(ij)$ is decomposed into a long-range part, $\overline{\mathbf{G}}(ij)$, and a short-range part, $\mathbf{G}^s(ij)$ (the details are given in the Appendix),

$$\mathbf{G}(ij)=\overline{\mathbf{G}}(ij)+\mathbf{G}^s(ij). \tag{54}$$

By definition, $\overline{\mathbf{G}}(ij)$ consists of all the terms, which scale as R_{ij}^{-n}, where $n\leqslant 3$, for $R_{ij}\to\infty$. Taking into account transformation properties of the part $\mathbf{G}^s(ij)$ under rotations of the reference system, one obtains the following relation (see Appendix),

$$\int d^3\mathbf{R}_{ij}\mathbf{G}^s(ij)W(ij)=0, \quad i\neq j. \tag{55}$$

Now we use expansion of the block distribution functions from Eqs. (51) to (53) and the scattering sequences from Eqs. (29) to (32) to write down explicitly the contribution to sedimentation coefficient from the three-particle term $[g(123)\boldsymbol{\mu}_{12}^{(3)}(123)]^{\text{irr}}$. With the simplification introduced by Eq. (55), this contribution may be written as a sum of the following expressions:

$$b_3=-\frac{12}{\pi^2\mu_0}\int_{R_{13}\leqslant 1,R_{23}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23} \times \mathrm{Tr}[\boldsymbol{\mu}_0(1)\,\mathbf{Z}_0(1)\,\mathbf{G}(13)\,\hat{\mathbf{Z}}_0(3)\,\mathbf{G}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)], \tag{56}$$

$$b_4=\frac{12}{\pi^2\mu_0}\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23} \times \mathrm{Tr}[\boldsymbol{\mu}_0(1)\,\mathbf{Z}_0(1)\,\overline{\mathbf{G}}(13)\,\hat{\mathbf{Z}}_0(3)\,\overline{\mathbf{G}}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)], \tag{57}$$

$$b_5=-\frac{24}{\pi^2\mu_0}\int_{R_{13}\geqslant 1,R_{23}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23} \times \mathrm{Tr}[\mathbf{B}(13)\,\mathbf{G}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)], \tag{58}$$

$$b_6=-\frac{24}{\pi^2\mu_0}\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23} \times \mathrm{Tr}[\mathbf{B}(13)\,\overline{\mathbf{G}}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)], \tag{59}$$

$$b_7=\frac{12}{\pi^2\mu_0}\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\geqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23}\,\mathrm{Tr}[\tilde{\bar{\boldsymbol{\mu}}}_{12}(123)], \tag{60}$$

where $\tilde{\bar{\boldsymbol{\mu}}}$ are defined by the equations, which follow from Eqs. (29) to (32) under the replacement: $\mathbf{G}\rightarrow\overline{\mathbf{G}}$, $\tilde{\boldsymbol{\mu}}\rightarrow\tilde{\bar{\boldsymbol{\mu}}}$, with the unchanged Eq. (33) for $\mathbf{C}$. The operator $\mathbf{B}(13)$ is given as

$$\mathbf{B}(13)=\mathbf{C}_{33}(13)+\mathbf{C}_{13}(13) + \boldsymbol{\mu}_0(1)\,\mathbf{Z}_0(1)\,\overline{\mathbf{G}}(13)\,\hat{\mathbf{Z}}_0(3). \tag{61}$$

The integrals b_3-b_7 will be calculated in the next section.

V. EVALUATION OF ϕ^2 CONTRIBUTIONS TO SEDIMENTATION COEFFICIENT

Equations (57)–(60) contain traces of certain operators. We evaluate them from the multipole matrix elements (without transformation to Cartesian representation). We use the multipoles defined in Ref. 53, and in this case Eqs. (B7)–(B8) from Appendix B in Ref. 53 lead to the following formula:

$$\mathrm{Tr}[\cdots]=\frac{3}{4\pi}\sum_{m=-1,0,1}(1m0|\cdots|1m0). \tag{62}$$

To evaluate matrix elements of operators $\mathbf{G}(13)$ and $\mathbf{G}(32)$ in Eqs. (57)–(59), we use the displacement theorems,[72] which contain spherical harmonics $Y_{LM}(\hat{\mathbf{R}})$ with two different arguments, $\hat{\mathbf{R}}=\hat{\mathbf{R}}_{13}$ or $\hat{\mathbf{R}}_{32}$. To simplify calculations, we choose the system of spherical coordinates, in which $\hat{\mathbf{z}}=\hat{\mathbf{R}}_{31}$, the unit vectors $(\hat{\mathbf{R}}_{13},\ \hat{\mathbf{R}}_{23})$ span the plane $\phi=0$, and $\cos\theta=\hat{\mathbf{R}}_{13}\cdot\hat{\mathbf{R}}_{23}$. In this way, for example, the multipole matrix elements of the operator $\mathbf{B}(13)$ are diagonal in (m,m'), and they depend only on the interparticle distance R_{13}. In the following, we will need only the elements $(1m0|\mathbf{B}(13)|lm\sigma)$, with $m=-1,0,1$, which can be written as

$$(1m0|\mathbf{B}(13)|lm\sigma)=(2a)^{l+\sigma-1}B_{lm\sigma}(R_{13}), \tag{63}$$

where $B_{lm\sigma}$ has been made dimensionless. To determine $B_{lm\sigma}(R_{13})$, an algorithm for the calculation of two-sphere hydrodynamic functions is needed. Following, e.g., Refs. 49, 52, we represent $B_{lm\sigma}(R_{13})$ as a series expansion in inverse powers of the interparticle distance,

$$B_{lm\sigma}(R_{13})=\sum_{n=4}^{\infty}c_n^{(lm\sigma)}\frac{1}{R_{13}^n}. \tag{64}$$

Let us stress that, according to the structure of Eq. (61), the long-range parts do not appear in the above equation, therefore the series starts from the fourth power. We calculated the coefficients with $n\leqslant 500$, what leads to the desired accuracy.

In our system of coordinates, matrix elements of the operator $\mathbf{G}(32)$ depend on interparticle distance R_{23} and on the angle θ. Since both operators $\mathbf{B}(13)$ and $\hat{\mathbf{Z}}_0$ are diagonal in (m,m'), then Eq. (62) selects only the matrix elements of $\mathbf{G}(32)$ diagonal in (m,m'). Therefore to evaluate the terms b_i, $i=3,\ldots,6$, we will need only the elements $(lm\sigma|\mathbf{G}(32)|1m0)$, where $m=-1,0,1$. With the use of Eq. (A9) and of the explicit form of S^{+-} from Ref. 72, those matrix elements can be written as

$$(lm\sigma|\mathbf{G}(32)|1m0)=\frac{1}{\eta(2a)^{l+\sigma}}w_{lm\sigma}(\cos\theta)\frac{1}{R_{23}^{l+\sigma}}, \tag{65}$$

where $w_{lm\sigma}(\cos\theta)$ are dimensionless combinations of the Legendre polynomials $P_L(\cos\theta)$, with $L=1,2,3,4$ [see Appendix for the explicit form of $w_{lm\sigma}(\cos\theta)$].

After these preliminaries, we are ready to calculate the subsequent integrals b_i. Essentially, we use three different procedures: first for b_3 and b_5, second for b_4 and b_6, and third for b_7. In Sec. V A we outline the first and the second method, and we apply them to the simplest case: analytical evaluation of b_3 and b_4. In Sec. V B we use the first and the second procedures to simplify and calculate the integrals b_5 and b_6. In Sec. V C we apply the Monte Carlo method to integrate the last part, and we get b_7.

A. Analytical result for b_3 and b_4

From the structure of Eq. (56) it follows that calculation of b_3 can be reduced to evaluation of products of two integrals of the operator $\mathbf{G}$: over $\mathbf{R}_{13}$ and over $\mathbf{R}_{23}$. The integral of $\mathbf{G}(ij)$ over the virtual overlap of particles i and j have been carried out analytically in Ref. 42. Taking into account Eq. (5.3) from Ref. 42, we write

$$(lm\sigma|\left[\int_{R_{ij}\leqslant 1}\mathbf{G}(ij)\,d^3\mathbf{R}_{ij}\right]|l'm'\sigma') = \frac{\delta_{ll'}\ \ \delta_{mm'}}{\eta(2a)^{2l+\sigma+\sigma'-1}}\kappa_{l,\sigma\sigma'}, \tag{66}$$

where the only nonvanishing dimensionless matrix elements $\kappa_{l,\sigma\sigma'}$ are listed below,

$$\kappa_{1,02}=\kappa_{1,20}=-\frac{4\pi}{135},\quad \kappa_{1,00}=\frac{4\pi}{9}, \tag{67}$$

$$\kappa_{1,11}=\frac{2\pi}{9}, \quad \kappa_{2,00}=\frac{2\pi}{75}. \tag{68}$$

Taking into account that $\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)$ is diagonal in (l,l'), applying Eqs. (A6) for $\hat{\mathbf{Z}}_0$, and using Eqs. (66)–(68), we are left only with $\kappa_{1,02}=\kappa_{1,20}$ in Eq. (56),

$$b_3=-\frac{9^2}{\pi^2}\kappa_{1,02}^2\hat{z}_{1,22}. \tag{69}$$

The dimensionless elements $\hat{z}_{l,\sigma\sigma'}$, where $l=1,2,\ldots$ and $\sigma,\sigma'=0,1,2$, are evaluated from the multipole matrix elements of $\hat{\mathbf{Z}}_0$ in Eqs. (A1)–(A6). Making use of Eqs. (68) and (A6), we finally get the analytic result,

$$b_3=-\tfrac{1}{5}. \tag{70}$$

The integrand of b_4 depends on the long-range Green operator $\overline{\mathbf{G}}(32)$, and therefore it may be simplified, if the following relation and its transposition are applied:

$$(lm\sigma|\hat{\mathbf{Z}}_0(3)\,\overline{\mathbf{G}}(32)\,\mathbf{Z}_0(2)\,\boldsymbol{\mu}_0(2)|1m0)$$
$$=(lm\sigma|\hat{\mathbf{Z}}_0(3)\,\overline{\mathbf{G}}(32)|1m0). \tag{71}$$

[Equation (71) may be proved with the use of multipole formulas from the Appendix.] As a result, in evaluation of b_4 there appear only the multipoles $(lm\sigma|\mathbf{G}(32)|1m0)$ with $(l\sigma)\in A$, where

$$A=\{(12),(20),(21),(30)\}. \tag{72}$$

[There is no $(l\sigma)=(10),(11)$, because for such $(l\sigma)$ matrix elements of $\hat{\mathbf{Z}}_0$ vanish.]

Equations (57), (62), (65), (A6), and symmetry property (A11) give

$$b_4=\frac{27}{\pi^2}\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23}$$
$$\times\sum_{(l\sigma)\in A}\sum_{m=-1,0,1} w_{lm\sigma}(1)\,\hat{z}_{l,\sigma\sigma}\,w_{lm\sigma}(\cos\theta)$$
$$\times\left(\frac{1}{R_{23}\;\;R_{13}}\right)^{l+\sigma}, \tag{73}$$

where $w_{lm\sigma}(\cos\theta)$ are polynomials in $\cos\theta$, given explicitly in the Appendix.

In our system of coordinates, b_4 may be reduced to a triple integral, parameterized by $(R_{13},\,R_{23},\,\theta)$. In this parameterization, the integral from Eq. (73) has the form,

$$\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23}[\cdots]$$
$$=8\pi^2\left(\int_1^2 dR_{13}\int_1^{R_{13}+1} dR_{23}\int_{\frac{R_{13}^2+R_{23}^2-1}{2R_{13}R_{23}}}^1 d(\cos\theta)\right.$$
$$\left.+\int_2^\infty dR_{13}\int_{R_{13}-1}^{R_{13}+1} dR_{23}\int_{\frac{R_{13}^2+R_{23}^2-1}{2R_{13}R_{23}}}^1 d(\cos\theta)\right)$$
$$\times R_{23}^2R_{13}^2[\cdots]. \tag{74}$$

We carry out analytically the integrals of expression (73) over the range specified in Eq. (74), and we get the exact result,

$$b_4=\frac{233343}{20480}\approx 11.3937. \tag{75}$$

B. Evaluation of b_5 and b_6 by series expansion

From Eq. (58) it follows that b_5, similarly as b_3, is a product of two integrals. With the use of Eqs. (62), (66)–(68), expression (58) for b_5 is reduced to the following nonoverlap integral over $\mathbf{R}_{13}$:

$$b_5=-\frac{6^3}{\pi}\sum_{m=-1,0,1}\left[\int_{R_{13}\geqslant 1} dR_{13}\,R_{13}^2\,B_{1m2}(R_{13})\right]\kappa_{1,20}. \tag{76}$$

We evaluate numerically the coefficients in the series expansion (64) of $B_{1m2}(R_{13})$, and we carry out the integral (76) analytically for each of the terms in Eq. (64). Taking 500 terms in the series, we finally get

$$b_5=-0.0647. \tag{77}$$

The integral in b_6 does not reduce to a product of two integrals, as b_5 does. To write b_6 in a form similar to expression (73) for b_4, we apply Eqs. (62)–(63) and (65),

$$b_6=-\frac{54}{\pi^2}\int_{R_{13}\geqslant 1,R_{23}\geqslant 1,R_{12}\leqslant 1} d^3\mathbf{R}_{13}\,d^3\mathbf{R}_{23}$$
$$\times\sum_{(l\sigma)\in A}\frac{1}{R_{23}^{l+\sigma}}\sum_{m=-1,0,1} B_{lm\sigma}(R_{13})\,w_{lm\sigma}(\cos\theta). \tag{78}$$

To evaluate b_6, we use essentially the same method of integration as for b_4, i.e., the parameterization (R_{13},R_{23},θ) and the range (74). As in Eq. (76), we take 500 terms in the series expansion (64) of $B_{lm\sigma}(R_{13})$, and we perform analytically the integrals in Eq. (78) for each term. The sum results in

$$b_6=-2.8001. \tag{79}$$

C. Calculation of b_7 by the Monte Carlo method

To evaluate b_7, we calculate the mobility matrix according to the scheme presented in Ref. 52. In this algorithm the multipole expansion is performed and the short range lubrication effects are taken into account. That is, we add a pairwise lubrication correction to the friction matrix, and we invert the result to get the corrected mobility matrix. To get the corrected articulation structure $\bar{\bar{\boldsymbol{\mu}}}_{ij}(123)$, the regularization procedure described in Sec. III is repeated for the corrected three-particle mobility.

Having the corrected expression for $\bar{\bar{\boldsymbol{\mu}}}_{ij}(123)$, we apply to Eq. (60) the method of integration introduced in Ref. 52. The integrand depends on the relative positions only, therefore b_7 may be reduced to a triple integral. To carry it out, we use the parameterization $(R_{12},\,\alpha,\,\beta)$, displayed in Fig. 1, where R_{12} is the smallest of the interparticle separations in the triplet (123), and we perform symmetrization with respect to the particle labels.

We write Eq. (60) as

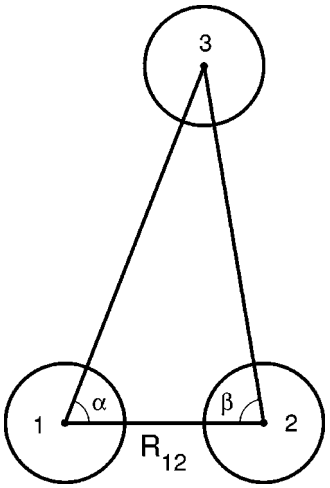

FIG. 1. For nonoverlap of particles 1 and 2, the relative configuration of a triplet is parameterized by (R_{12}, α, β).

$$b_7=\frac{96}{\mu_0}\int_{\pi-\beta\geqslant\alpha\geqslant\beta\geqslant\pi-(\alpha+\beta)} d\alpha\, d\beta \frac{\sin^2\alpha \sin^2\beta}{\sin^4(\alpha+\beta)} \times \int_1^\infty dR_{12} R_{12}^5 \sum_{i=1}^{3}\sum_{j\neq i}^{3} \mathrm{Tr}\tilde{\boldsymbol{\mu}}_{ij}(123). \quad (80)$$

First, we perform integration over R_{12}, applying the Simpson method. To get better accuracy we split the interval $[1,\infty]$ into five unequal parts, matching smaller size to more steep integrand. In the last interval $[5,\infty]$, it is sufficient to approximate the three-particle mobility by the leading term, which scales as $(R_{12})^{-8}$. The Monte Carlo technique is applied to carry out the integration over angles in each part separately. We perform 30 000 Monte Carlo trials for $R_{12} \in (1,1.005)$, 150 000 trials for $R_{12}\in(1.005,1.1)$, 550 000 trials for $R_{12}\in(1.1,1.9)$, 158 000 trials for $R_{12}\in(1.9,5)$, and 100 000 trials for $R_{12}\in(5,\infty)$. Finally, we obtain

$$b_7=0.169\pm0.005, \quad (81)$$

where the error bars correspond to the standard deviation due to all the Monte Carlo trials.

VI. FINAL RESULTS AND CONCLUSIONS

We evaluate b_c, the ϕ^2 coefficient in the virial expansion of the sedimentation coefficient given by Eq. (4). The sum of all the three-particle contributions from Sec V is given as

$$\sum_{i=3}^{7} b_i=8.498\pm0.005. \quad (82)$$

By combination of Eqs. (48), (50), and (82), we finally get the ϕ^2 contribution to the sedimentation coefficient as $b_c=21.918\pm0.006$. Therefore virial expansion of K has the form,

$$K=1-6.546\,\phi+21.918\,\phi^2+\cdots. \quad (83)$$

Discussion of the above results consists of two parts. First, we compare the derivation of ϕ^2 contributions to the sedimentation coefficient, presented in this work, with the previous papers on this subject. Second, we point out the dominant contributions in our calculations, and therefore we suggest a scheme of approximation, which goes beyond the context of this paper.

The method applied here takes into account lubrication effects and avoids uncertainty due to numerical evaluation of the limit $k\to0$. These two reasons, in our opinion, account for the differences between values obtained in this paper and the previous results,[32,48] and allow to control the uncertainty. The total ϕ^2 contribution to the sedimentation coefficient is evaluated here as 21.918 ± 0.006. To relate this result to the previous papers,[32,46,48] we concentrate on comparison with Ref. 32, which contains the most complete calculation. Our value is larger by about 5% than 20.8, the number following from Ref. 32 after correction of a misprint in their Eq. (5.24). The three-particle contribution to the sedimentation coefficient from such chains of scattering processes, which start and end at two different particles, i.e., 8.498 ± 0.005, given in Eq. (82), is larger by about 15% than 7.4, the corresponding number evaluated in Ref. 32.

If one would like to approximate the three-particle mobility matrix by a finite sum of expressions, which are proportional to inverse powers of the interparticle distances, then within the method presented here one is able to evaluate the corresponding contribution to the sedimentation coefficient analytically. For example, let us consider the long-interparticle-distance asymptotics, introduced by Mazur and van Saarloos.[59,73,74] By definition, this approximation is constructed as a sum of all the terms in the three particle mobility matrix, which decrease as $1/R^n$, with $n\leqslant7$, when all the distances within the triplet are increased by a factor R. The contribution to the second order virial term of the sedimentation coefficient from the scattering sequences, which start and end at different particles, that is, the sum of the terms b_i with $i=3,\ldots,7$, in this asymptotic approximation is equal to $163973/20480\approx8.0065$. This exact value agrees well with 8.0, the corresponding numerical estimation performed by Clercx and Schram.[32]

The advantage of the method presented in this paper is that it allows to identify the terms, which give the dominant contribution to the ϕ^2 term in the sedimentation coefficient. The significant effect of the self-diffusion term b_1 and the term b_2 following from virial expansion of the two-particle correlation function $g(12)$, has been already known. Here we analyze how large are $b_3,\ldots,b_7$, the contributions to the sedimentation coefficient from the scattering sequences, which involve exactly three particles, and which start and end at different spheres. We conclude that all such contributions may be approximated by b_4+b_6, which is easy to be accurately calculated. Indeed, $b_4+b_6=8.5936$, while the remaining terms are equal to $b_3+b_5+b_7=-0.096$, that is, to only about 1% of the three-particle term $\Sigma_{i=3}^{7}b_i$, given in Eq. (82). Therefore from all the scattering sequences, which involve exactly three spheres, and which start and end at different particles, the largest contribution to the sedimentation coefficient comes from the configurations with virtual overlap of two particles, which are not directly connected by neither **G** nor its long-distance part, as schematically drawn in Fig. 2. This suggests how to approximately evaluate the

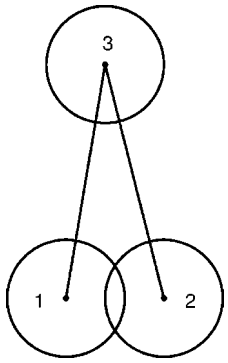

FIG. 2. Relative configuration of a triplet with virtual overlap of spheres 1 and 2, as in the integrals b_4 and b_6. Solid lines connect the particles (ij), which are joined by at least one $\mathbf{G}(ij)$ (or its long-distance part) in the scattering expansion of the integrands of b_4 and b_6.

corresponding part of the sedimentation coefficient for concentrated suspensions. That is, in higher order terms of the virial expansion, one should sum up the contributions from similar configurations, that is with virtual overlap of those particles, which are not connected by any operator G in the scattering expansion of the mobility matrix.

APPENDIX: MULTIPOLE EXPANSION

In the multipole expansion we use two complete sets of vector functions,[75] which are fitted to the spherical symmetry of the Stokes equations (5): $\boldsymbol{v}^{+}_{lm\sigma}(\mathbf{r})$, regular at $\mathbf{r}=0$, and $\boldsymbol{v}^{-}_{lm\sigma}(\mathbf{r})$, regular at $|\mathbf{r}|\to\infty$, where $\sigma=0,1,2$, while $l=1,2,3,\ldots$ and $m=0,\pm1,\ldots\pm l$. These multipole vectors were introduced in Ref. 64; here we use the modified definition from Ref. 53. The corresponding matrix elements of the operators $\mathbf{Z}_0$, $\hat{\mathbf{Z}}_0$, and $\boldsymbol{\mu}_0$ between the multipole vectors at the sphere surface are diagonal in (l,l') and in (m,m').

The matrix elements of the operator $\mathbf{Z}_0$ have the form,[53]

$$(lm\sigma|\mathbf{Z}_0|l'm'\sigma')=\delta_{ll'}\,\delta_{mm'}\,\eta(2a)^{2l+\sigma+\sigma'-1}\;z_{l,\sigma\sigma'}, \tag{A1}$$

where the elements $z_{l,\sigma\sigma'}$ are dimensionless, and the only nonzero ones are given below:

$$z_{l,00}=\frac{l(2l-1)(2l+1)^2}{2^{2l-1}(l+1)}, \tag{A2}$$

$$z_{l,02}=z_{l,20}=\frac{(2l-1)(2l+1)^2(2l+3)}{2^{2l+2}}, \tag{A3}$$

$$z_{l,11}=\frac{l(l+1)(2l+1)}{2^{2l+1}}, \tag{A4}$$

$$z_{l,22}=\frac{(l+1)(2l+1)^4(2l+3)}{2^{2l+5}\,l}. \tag{A5}$$

The matrix elements of the operator $\hat{\mathbf{Z}}_0$ are equal to those of the operator $\mathbf{Z}_0$ (i.e., $\hat{z}_{l,\sigma\sigma'}=z_{l,\sigma\sigma'}$), if $l\neq1$. For $l=1$ the only nonvanishing matrix element of $\hat{\mathbf{Z}}_0$ is

$$(1m2|\hat{\mathbf{Z}}_0|1m2)=\eta(2a)^5\hat{z}_{1,22}=\eta(2a)^5\frac{45}{16}. \tag{A6}$$

The only nonzero matrix elements of $\boldsymbol{\mu}_0$ are

$$(1m0|\boldsymbol{\mu}_0|1m0)=(1m0|\mathbf{Z}_0|1m0)^{-1}=\frac{2}{9\eta a}, \tag{A7}$$

$$(1m1|\boldsymbol{\mu}_0|1m1)=(1m1|\mathbf{Z}_0|1m1)^{-1}=\frac{1}{6\eta a^3}. \tag{A8}$$

For nonoverlapping particles, that is for $r_{ij}>2a$, evaluation of $(lm\sigma|\mathbf{G}(ij)|l'm'\sigma')$ is based on the displacement theorems for $\boldsymbol{v}^{\pm}_{lm\sigma}$, the solutions of the Stokes equations.[72] These theorems give

$$(lm\sigma|\mathbf{G}(ij)|l'm'\sigma')=\frac{n_{lm}}{\eta\,n_{l'm'}}S^{+-}(\mathbf{r}_{ij};lm\sigma,l'm'\sigma')$$
$$\sim\frac{1}{r_{ij}^{l+l'+\sigma+\sigma'-1}},\quad r_{ij}>2a, \tag{A9}$$

where the coefficients S^{+-} are given in Ref. 72. They are linear combinations of spherical harmonics $Y_{LM}(\hat{\mathbf{r}}_{ij})$ and are proportional to inverse powers of r_{ij}. The normalization factors n_{lm} are

$$n_{lm}=\left[\frac{4\pi}{2l+1}\frac{(l+m)!}{(l-m)!}\right]^{1/2}. \tag{A10}$$

Note that the Green operator $\mathbf{G}(ij)$ is not equal to $\mathbf{G}(ji)$, and that its matrix elements, given by Eq. (A9), satisfy the Lorentz symmetry,

$$(lm\sigma|\mathbf{G}(ij)|l'm'\sigma')=(l'm'\sigma'|\mathbf{G}(ji)|lm\sigma). \tag{A11}$$

The matrix elements of $\mathbf{G}(ij)$ are now decomposed into two groups, according to the rate of their decay at $r_{ij}\to\infty$, specified by Eq. (A9) as r_{ij}^{-n}, where n is a positive integer. According to the definitions from Sec. III, matrix elements, for which $n>3$, correspond to the short-range Green operator $\mathbf{G}^{\mathbf{s}}$, and matrix elements, for which $n\leqslant3$, correspond to the long-range Green operator $\overline{\mathbf{G}}$. From Eq. (A9) it follows that the only matrix elements of $\overline{\mathbf{G}}$, which appear in Eqs. (38), correspond to $(l'\sigma')=(10)$ and $(l\sigma)\in A=\{(12),(20),(21),(30)\}$, or the interchange of $(l\sigma)$ and $(l'\sigma')$.

The key point is that the integral of $\mathbf{G}^s(ij)\,W(ij)$ over $\mathbf{r}_{ij}$ vanishes. Indeed, the integral over r_{ij} is absolutely convergent [unlike the integral of $\overline{\mathbf{G}}(ij)\,W(ij)$]. Moreover, the matrix elements of $\mathbf{G}^s$ are linear combinations of spherical harmonics Y_{LM} with $L>0$, which are orthogonal to the constant Y_{00}. Therefore the integral over angles vanishes, and Eq. (55) is proved.

Finally, we evaluate explicitly those matrix elements of the long-range Green operator, which have been used in the calculations. That is, we use Eq. (A9) with the formulas for S^{+-}, taken from Ref. 72, to express $w_{lm\sigma}$ in terms of Leg-

endre polynomials, and to determine explicitly the dependence of $w_{lm\sigma}$ on $\cos\theta$,

$$w_{102} = -\frac{1}{30}\left(\cos^2\theta - \frac{1}{3}\right), \tag{A12}$$

$$w_{112} = w_{1-12} = \frac{1}{60}\left(\cos^2\theta - \frac{1}{3}\right), \tag{A13}$$

$$w_{200} = -\frac{1}{4}\sqrt{\frac{3}{5}}\cos\theta\left(\cos^2\theta - \frac{1}{3}\right), \tag{A14}$$

$$w_{210} = w_{2-10} = \frac{1}{4\sqrt{5}}\cos\theta\,(\cos^2\theta - 1), \tag{A15}$$

$$w_{201} = 0, \tag{A16}$$

$$w_{211} = -w_{2-11} = -\frac{1}{4\sqrt{5}}\left(\cos^2\theta - \frac{1}{3}\right), \tag{A17}$$

$$w_{300} = \frac{5}{4\sqrt{21}}\left(\cos^4\theta - \frac{18}{25}\cos^2\theta + \frac{1}{25}\right), \tag{A18}$$

$$w_{310} = w_{3-10} = -\frac{5}{8\sqrt{14}}\left(\cos^4\theta - \frac{26}{25}\cos^2\theta + \frac{11}{75}\right). \tag{A19}$$

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