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Brownian dynamics: divergence of mobility tensor

E. Wajnryb[a], P. Szymczak[b,*], B. Cichocki[b]

[a] *Institute of Fundamental Technological Research, Polish Academy of Sciences, Świętokrzyska 21, Warsaw, 00-049, Poland*

[b] *Institute of Theoretical Physics, Warsaw University, Hoża 69, Warsaw, 00-618, Poland*

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Abstract

The mobility tensor for many spheres suspended in a viscous fluid is considered. An analytical formula for the divergence of this tensor is derived. It is then applied in calculations of long-time collective diffusion coefficient of hard-sphere suspension by means of Brownian dynamics method.

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1. Introduction

The Brownian dynamics method is a powerful numerical tool for exploring the evolution and properties of interacting Brownian particle systems. In the simplest case, such a system consists of N identical spherical particles performing Brownian motion in an incompressible viscous fluid at temperature T. On the time-scale characteristic for light scattering experiments the evolution of the configuration space distribution function $P(\boldsymbol{X},t)$ is described by the generalized Smoluchowski equation [1]

$$\frac{\partial}{\partial t}P(\boldsymbol{X},t)=\sum_{i,j=1}^{N}\nabla_j\cdot\boldsymbol{\mu}_{ji}^{tt}(\boldsymbol{X})\cdot[k_BT\nabla_i+\mathscr{F}_i]P(\boldsymbol{X},t)\,, \tag{1.1}$$

* Corresponding author.
E-mail address: piotrek@fuw.edu.pl (P. Szymczak).

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where $\boldsymbol{X}=(\boldsymbol{R}_1,\boldsymbol{R}_2\ldots,\boldsymbol{R}_N)$, with $\boldsymbol{R}_i$ being the position of ith particle and $\mathscr{F}_i$ the force acting on it. Next, ∇_i denotes the gradient with respect to the position of particle i and $\boldsymbol{\mu}^{tt}$ is the translational mobility matrix. The latter is obtained by solving the hydrodynamic problem of finding the velocities of the particles, $\boldsymbol{U}_i, i=1,\ldots,N$, in terms of the forces acting on them (in the absence of torques)

$$\boldsymbol{U}_i=\sum_j \boldsymbol{\mu}^{tt}_{ij}\mathscr{F}_j\ . \tag{1.2}$$

In general, due to hydrodynamic interactions, the mobility matrix depends on configuration $\boldsymbol{X}$ and is nondiagonal in particle indices.

The numerical algorithm to calculate the mobility matrix using multipole expansion method is well established [2–7] and has been tested extensively in a number of studies. This algorithm has been extended in the present work to incorporate a scheme of calculating divergence of mobility matrix. Although in principle this can be done by numerical differentiation of $\boldsymbol{\mu}^{tt}$, such a scheme is not only numerically expensive but also inaccurate. Instead, we calculate the divergence of mobility matrix analytically with use of the multipole expansion method.

Divergence of mobility matrix is an important object for studying the dynamics of interacting Brownian particles. In particular, it is needed in Brownian dynamics simulations of a system governed by the Smoluchowski equation. It can be shown [8] that a fixed time-step (coarse) realization of the stochastic process described by the Smoluchowski equation is constructed by advancing the particles according to

$$\boldsymbol{R}_i(t+\Delta t)=\boldsymbol{R}_i(t)+k_BT\sum_j \nabla_j\cdot\boldsymbol{\mu}^{tt}_{ji}(t)\Delta t+\sum_j \boldsymbol{\mu}^{tt}_{ij}(t)\cdot\mathscr{F}_j(t)\Delta t+\boldsymbol{\gamma}_i(\Delta t)\ . \tag{1.3}$$

The vector $\boldsymbol{\gamma}_i(\Delta t)$ is a random displacement with Gaussian distribution of zero mean and covariance given by

$$\langle\boldsymbol{\gamma}_i(\Delta t)\boldsymbol{\gamma}_j(\Delta t)\rangle=2k_BT\boldsymbol{\mu}^{tt}_{ij}(t)\Delta t\ . \tag{1.4}$$

As can be seen from the above, key quantities needed to compute the trajectories are the mobility matrix and its divergence summed over all particles

$$\mathbf{d}_i=\sum_j \nabla_j\cdot\boldsymbol{\mu}^{tt}_{ji}\ . \tag{1.5}$$

As the mobility matrix depends in a nontrivial way on positions of all particles in the system, its computation is highly time and memory consuming. Thus various approximations are usually resorted to in order to reduce the complexity. The crudest approximation is to write $\boldsymbol{\mu}^{tt}$ as the sum of terms describing two-body interactions given by Oseen or Rotne–Prager tensors [8–15]. However, in any two-body approximation the vector $\mathbf{d}_i$ vanishes. Even if more sophisticated schemes of calculating mobility matrix are used in Brownian dynamics simulations, the divergence term is often either neglected or calculated by a 'brute-force' numerical differentiation. The latter is both inaccurate and extremely slow since one needs to calculate $\boldsymbol{\mu}^{tt}$ at least $3N$ times to obtain $\mathbf{d}_i$ for a given configuration.

Another problem in which the divergence of mobility matrix plays a central role is calculation of long-time collective diffusion coefficient, D_c^l. This coefficient is defined in terms of intermediate scattering function $F(k,t)$ by

$$D_c^l = \lim_{k\to 0} \frac{1}{k^2} \lim_{t\to\infty} \frac{\mathrm{d}\log F}{\mathrm{d}t} \,. \tag{1.6}$$

In the system of interacting Brownian particles there is a nonzero difference between the value of the long-time diffusion coefficient and that of the short-time one given by

$$D_c^s = \lim_{k\to 0} \frac{1}{k^2} \lim_{t\to 0} \frac{\mathrm{d}\log F}{\mathrm{d}t} \,. \tag{1.7}$$

This difference is due to the memory effects in the system which are associated with the relaxation of the particle distribution function [16]. The strength of these effects is measured by a dimensionless factor Δ [17]

$$\Delta = \frac{D_c^s - D_c^l}{D_c^s} \,. \tag{1.8}$$

The explicit expression for this factor reads

$$\Delta = \lim_{k\to 0} \int_{t=0}^{\infty} M(k,t) \,, \tag{1.9}$$

where the memory function $M(k,t)$ is closely related to the autocorrelation function of the divergence of mobility tensor. For example, for hard-sphere suspensions $M(k,t)$ reads [18,16]

$$M(k,t) = \frac{k_B T \left\langle \sum_{i,j=1}^{N} \mathbf{d}_i(0)\cdot\mathbf{d}_j(t)\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{R}_j(t)-\boldsymbol{R}_i(0))} \right\rangle}{\left\langle \sum_{i,j=1}^{N} \mathrm{Tr}\, \boldsymbol{\mu}_{ij}^{tt}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{ji}} \right\rangle} \,, \tag{1.10}$$

where Tr stands for trace and angular brackets denote equilibrium average. Again, in crude approximations for $\boldsymbol{\mu}^{tt}$ the vector $\mathbf{d}_i$ vanishes and the information about memory effects is lost as $M(k,t)=0$. Hence an accurate and efficient algorithm of calculating $\mathbf{d}_i$ is essential for investigation of memory effects. Efficiency of the algorithm is particularly important since the numerical complexity is usually a key issue when computing the properties of interacting Brownian particle system.

The outline of the paper is as follows. Section 2 reviews the numerical scheme for calculating hydrodynamic interactions between spheres in Stokes flow. In particular, we recall the method of obtaining the mobility matrix using multipole expansion technique. Next, in Section 3, this formalism is applied to derive an expression for divergence of mobility matrix. It turns out that it is possible to represent $\mathbf{d}_i$ in terms of the same functions as those that appear in multipole representation of mobility matrix. Finally, in Section 4 the memory factor Δ (1.8) is calculated numerically using Brownian dynamics simulations. In the calculation the divergence of mobility tensor is used twice: in the expression for memory function as well as in Brownian dynamics algorithm (1.3) itself.

2. Hydrodynamic interactions between many spheres: mobility problem

Consider N spheres of equal radii a, which undergo external forces $\mathscr{F}_1,\ldots,\mathscr{F}_N$ and external torques $\mathscr{T}_1,\ldots,\mathscr{T}_N$ (in the following abbreviated as $\mathscr{F}$ and $\mathscr{T}$), 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 [19]

$$\eta\boldsymbol{\nabla}^2\boldsymbol{v}(\mathbf{r}) - \boldsymbol{\nabla}\, p(\mathbf{r}) = \mathbf{0}, \quad \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0\,, \tag{2.1}$$

with the stick boundary conditions at the particle surfaces S_i:

$$\boldsymbol{v}(\mathbf{r}) = \mathbf{w}_i(\mathbf{r}) \equiv \mathbf{U}_i + \boldsymbol{\Omega}_i \times (\mathbf{r} - \boldsymbol{R}_i) \quad \text{for } \mathbf{r}\in S_i, \quad i = 1,\ldots,N\,, \tag{2.2}$$

where $\mathbf{U}_1,\ldots,\mathbf{U}_N$ 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. (2.1)–(2.2), the density $\mathbf{f}_i(\mathbf{r})$ of induced forces [20–22] 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 (2.2). The rigid body motion of the particles may be now interpreted as a fictitious fluid flow for $|\mathbf{r} - \boldsymbol{R}_i| \leqslant a$, which obeys the Stokes equations (2.1). In this way Eqs. (2.1), 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 [20–22]. Their solution for an unbounded fluid, which is at rest at infinity, $\boldsymbol{v}(\mathbf{r})$, can be written as:

$$\boldsymbol{v}(\mathbf{r}) = \sum_{j=1}^{N}\int \mathbf{T}(\mathbf{r}-\mathbf{r}')\,\mathbf{f}_j(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\,, \tag{2.3}$$

where $\mathbf{T}$ denotes the Oseen tensor [19]:

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta r}(\mathbf{I} + \hat{\mathbf{r}}\hat{\mathbf{r}})\,. \tag{2.4}$$

Now let us choose a particle i and consider Eq. (2.3) at its surface S_i. Taking into account the boundary conditions (2.2), one can write Eq. (2.3) in terms of integral operators as

$$\mathbf{w}_i = \mathbf{Z}_0^{-1}(i)\,\mathbf{f}_i + \sum_{j\neq i}\mathbf{G}(ij)\,\mathbf{f}_j\,. \tag{2.5}$$

In the above equation we decomposed the integral operator at the r.h.s. of Eq. (2.3) into two parts. The first part, given in terms of the one-particle friction operator $\boldsymbol{Z}_0(i)$ [23], describes the contribution to the velocity of particle i from the induced forces located on the same particle (i)

$$[\boldsymbol{Z}_0^{-1}(i)\boldsymbol{f}_i](\boldsymbol{r}) \equiv \int \mathbf{T}(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{f}_i(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}', \quad \boldsymbol{r}\in S_i\,. \tag{2.6}$$

The second part involves Green operators [24,25] $\mathbf{G}(ij)$, where $j = 1,\ldots,N$, but $j \neq i$, which account for the contributions to $\mathbf{w}_i$ coming from the particles other than i

$$[\boldsymbol{G}(ij)\boldsymbol{f}_j](\boldsymbol{r}) \equiv \int \mathbf{T}(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{f}_j(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}', \quad i\neq j, \quad \boldsymbol{r}\in S_i\,. \tag{2.7}$$

To solve the integral equation (2.5), the multipole expansion is applied [4,5,7]. The induced forces as well as velocity fields are then represented by infinite set of multipoles. The multipoles are labeled by three multipole indices l, m, σ, where $l = 1,2,\ldots,$

while $m=-l,\ldots,+l$, and $\sigma=0,1,2$. The first two multipoles ($l=1$; $\sigma=0,1$) of the induced force $\boldsymbol{f}_i$ are: the total force $\mathscr{F}_i$ and the total torque $\mathscr{T}_i$ acting on sphere i. On a level of velocity field the multipoles $l=1$; $\sigma=0,1$ correspond to particle translational and rotational velocities, respectively. Within this framework the integral operators $\mathbf{G}$, $\mathbf{Z}_0$ become matrices and Eq. (2.5) is reduced to an infinite system of linear algebraic equations. The details on the integral operators $\mathbf{G}$, $\mathbf{Z}_0$ may be found, e.g. in Ref. [7]; their multipole matrix elements are given explicitly in Appendix A.

The system of equations which follows from the multipole matrix representation of Eq. (2.5) allows us to solve the friction problem [19], where $\mathscr{F}$ and $\mathscr{T}$ are evaluated in terms of $\mathbf{U}$ and $\boldsymbol{\Omega}$. In the absence of an external ambient fluid flow this relation has the form

$$\begin{pmatrix}\mathscr{F}\\ \mathscr{T}\end{pmatrix}=\zeta\begin{pmatrix}\mathbf{U}\\ \boldsymbol{\Omega}\end{pmatrix}, \tag{2.8}$$

with

$$\zeta=\begin{pmatrix}\zeta^{tt} & \zeta^{tr}\\ \zeta^{rt} & \zeta^{rr}\end{pmatrix},$$

where ζ^{pq} ($p,q=t$ or r) are the $3N\times 3N$ Cartesian tensors, and the superscripts ^{t} and ^{r} correspond to the translational and the rotational components, respectively. The $6N\times 6N$ matrix, which appears at the r.h.s. of Eq. (2.8) is called the N-particle friction matrix [26,27].

The analysis of Eq. (2.5) allows to express the friction matrix (2.8) in the following form:

$$\zeta=\mathscr{P}\left(\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}\right)\mathscr{P}, \tag{2.9}$$

where $\mathscr{P}$ is the projection operator on the subspace $l=1;\sigma=(0,1)$. Note that in the abbreviated notation used above, the product of two operators involves the sum over particle indices.

In the numerical implementation the infinite matrices $\boldsymbol{G}$ and $\boldsymbol{Z}_0$ are truncated at finite multipole order L [5,28] (such that only elements with $l\leqslant L$ are taken into account) which leads to the approximation for the friction matrix denoted by ζ_L

$$\zeta_L=\mathscr{P}\left(\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}\right)_L\mathscr{P}. \tag{2.10}$$

However, we know from the solution of the two-sphere problem that multipole components of very high order are required for an accurate description of the lubrication effects which dominate the friction between two near spheres in relative motion. To account for it, one makes use of the notion that lubrication effects are well described by the following two-body object:

$$\boldsymbol{s}=\sum_{i<j}\boldsymbol{s}(i,j)\equiv\sum_{i<j}\boldsymbol{q}^{\mathrm{T}}\cdot\zeta(i,j)\cdot\boldsymbol{q}, \tag{2.11}$$

where $\boldsymbol{q}$ is a 12×12 matrix, which projects out the collective motion of a given pair of particles, leaving only the relative motion. The explicit form of $\boldsymbol{q}$ can be found in Ref. [28]. The two-body friction matrices $\boldsymbol{\zeta}(i,j)$ are known with a very high accuracy [19,20]. Then, the results of multipole expansion and lubrication contributions are combined to yield

$$\boldsymbol{\zeta}_L^{corrected} = \mathscr{P}\left(\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}\right)_L \mathscr{P} + \boldsymbol{s} - \boldsymbol{s}_L \,, \tag{2.12}$$

with

$$\boldsymbol{s}_L = \sum_{i<j} \boldsymbol{s}_L(i,j) \,, \tag{2.13}$$

where $\boldsymbol{s}_L(i,j)$ is obtained from the corresponding $\boldsymbol{s}(i,j)$ matrix by removing the multipoles with $l > L$.

The inverse of the friction matrix, the mobility matrix $\boldsymbol{\mu}$, allows us to find translational and rotational velocities of particles for given forces and torques

$$\begin{pmatrix} \mathbf{U} \\ \boldsymbol{\Omega} \end{pmatrix} = \boldsymbol{\mu} \begin{pmatrix} \mathscr{F} \\ \mathscr{T} \end{pmatrix} \,, \tag{2.14}$$

$$\boldsymbol{\mu} = \begin{pmatrix} \boldsymbol{\mu}^{tt} & \boldsymbol{\mu}^{tr} \\ \boldsymbol{\mu}^{rt} & \boldsymbol{\mu}^{rr} \end{pmatrix} \,.$$

In the approximation described above the mobility matrix is given by

$$\boldsymbol{\mu} = \left[\mathscr{P}\left(\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}\right)_L \mathscr{P} + \boldsymbol{s} - \boldsymbol{s}_L\right]^{-1} \,, \tag{2.15}$$

where we have used Eq. (2.12).

3. Divergence of mobility matrix in an unbounded fluid

The goal of this section is to find an analytical expression for the divergence of mobility matrix suitable for numerical implementation in frames of multipole expansion formalism.

Starting from the matrix identity

$$\partial(\mathbf{A}\mathbf{A}^{-1}) = 0, \quad \partial(\mathbf{A})\mathbf{A}^{-1} + \mathbf{A}\partial(\mathbf{A}^{-1}) = 0 \tag{3.1}$$

one gets the following expression for the derivative of the inverse of a matrix:

$$\partial\mathbf{A}^{-1} = -\mathbf{A}^{-1}\partial(\mathbf{A})\mathbf{A}^{-1} \,. \tag{3.2}$$

This, together with Eq. (2.15), allows us to rewrite $\nabla_i\boldsymbol{\mu}$ as

$$\nabla_i \boldsymbol{\mu} = \boldsymbol{\mu}\left[\mathscr{P}\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}(\nabla_i\mathbf{G})\frac{1}{\mathbf{Z}_0^{-1}+\mathbf{G}}\mathscr{P} - \nabla_i(\boldsymbol{s}-\boldsymbol{s}_L)\right]\boldsymbol{\mu} \,. \tag{3.3}$$

Thus, in order to calculate the gradient (or divergence) of $\boldsymbol{\mu}$ we need to evaluate the gradient of the matrix $\mathbf{G}$ as well as the gradient of lubrication correction $\boldsymbol{s}-\boldsymbol{s}_L$. The latter task, according to Eq. (2.11), requires the evaluation of the gradient of two-body friction matrices $\boldsymbol{\zeta}(i,j)$. This can be easily performed using the expressions for $\boldsymbol{\zeta}(i,j)$ in form of series in $\boldsymbol{R}_{ij}$, as given in Refs. [19,29].

The differentiation of Green operator is more complicated. The matrix elements $(l_1m_1\sigma_1|\boldsymbol{G}(ij)|l_2m_2\sigma_2)$ follow from the displacement theorems for the solutions of the Stokes equation [30]. With the normalization of Ref. [7] they are given by

$$(l_1m_1\sigma_1|\mathbf{G}(ij)|l_2m_2\sigma_2)=\frac{n_{l_1m_1}}{\eta\, n_{l_2m_2}}\,S^{+-}(\boldsymbol{R}_{ij};l_1m_1\sigma_1,l_2m_2\sigma_2)\,, \tag{3.4}$$

with normalization factors n_{lm}

$$n_{lm}=\left[\frac{4\pi}{2l+1}\,\frac{(l+m)!}{(l-m)!}\right]^{1/2}\,. \tag{3.5}$$

The coefficients S^{+-} are linear combinations of spherical harmonics $Y_{LM}(\hat{\boldsymbol{R}}_{ij})$ and can be written as [30]

$$\begin{aligned}S^{+-}(\boldsymbol{R}_{ij};l_1m_1\sigma_1,l_2m_2\sigma_2)&=A(l_1m_1\sigma_1,l_2m_2\sigma_2)\hat{C}_{L'M}(\mathbf{R}_{ij})\\&\quad+B(l_1m_1\sigma_1,l_2m_2\sigma_2)\hat{H}_{LM}(\mathbf{R}_{ij})\,,\end{aligned} \tag{3.6}$$

with

$$L=l_1+l_2+\sigma_1+\sigma_2,\quad L'=L-2,\ M=m_2-m_1$$

and the functions

$$\hat{C}_{LM}(\mathbf{r})=\frac{\hat{Y}_{LM}(\hat{\mathbf{r}})}{r^{L+1}}\,, \tag{3.7}$$

$$\hat{H}_{LM}(\mathbf{r})=\frac{\hat{Y}_{LM}(\hat{\mathbf{r}})}{r^{L-1}}\,. \tag{3.8}$$

The scalar coefficients $A(l_1m_1\sigma_1,l_2m_2\sigma_2)$ and $B(l_1m_1\sigma_1,l_2m_2\sigma_2)$ are given in Appendix A.

Above, $\hat{Y}_{lm}(\hat{\mathbf{r}})$ is an unnormalized spherical harmonic related to the usual $Y_{lm}(\hat{\mathbf{r}})$ by

$$\hat{Y}_{lm}(\hat{\mathbf{r}})=n_{lm}Y_{lm}(\hat{\mathbf{r}})=(-1)^mP_{lm}(\cos\theta)\mathrm{e}^{\mathrm{i}m\varphi}\,. \tag{3.9}$$

In this paper we use hat to denote the quantity related to the unnormalized spherical harmonics.

Calculation of the gradient of $\mathbf{G}$ now reduces to evaluating the gradients of the functions $\hat{C}_{LM}$ and $\hat{H}_{LM}$. To proceed we introduce the following irreducible tensors of the lth rank, $l=0,1,\ldots$,

$$\hat{\mathbf{Y}}_{lm}=\frac{1}{l!}\,\boldsymbol{\nabla}^l\left(r^l\hat{Y}_{lm}(\hat{\mathbf{r}})\right)=\frac{1}{l!}\underbrace{\boldsymbol{\nabla}\boldsymbol{\nabla}\ldots\boldsymbol{\nabla}}_{l\ \text{times}}\left(r^l\hat{Y}_{lm}(\hat{\mathbf{r}})\right), \tag{3.10}$$

which obey the orthogonality relation

$$\hat{\mathbf{Y}}^*_{lm}\overset{l}{\odot}\hat{\mathbf{Y}}_{lm'}=\delta_{mm'}n_{lm}^2\gamma_l^2\,, \tag{3.11}$$

with

$$\gamma_l = \sqrt{\frac{(2l+1)!!}{4\pi l!}} \ . \tag{3.12}$$

The symbol $\overset{l}{\odot}$ denotes the full, *l-fold*, contraction of two tensors of the lth rank

$$\mathbf{A}\overset{l}{\odot}\mathbf{B} = A_{i_1 i_2 \ldots i_l} B_{i_1 i_2 \ldots i_l} \ . \tag{3.13}$$

The above introduced irreducible tensors $\hat{\mathbf{Y}}_{lm}$ are related to the spherical harmonics (3.9) by

$$\hat{Y}_{lm}(\hat{\mathbf{r}}) = \hat{\mathbf{Y}}_{lm}\overset{l}{\odot}\hat{\mathbf{r}}^l = \hat{\mathbf{Y}}_{lm}\overset{l}{\odot}\overline{\hat{\mathbf{r}}^l} \ . \tag{3.14}$$

Here we have used the symbol $\bar{\mathbf{A}}$ to denote the irreducible (i.e. symmetric and traceless) part of the tensor $\mathbf{A}$. In addition, the following expressions for the irreducible tensor $\overline{\hat{\mathbf{r}}^l}$ will be used

$$\overline{\hat{\mathbf{r}}^l} = (-1)^l \frac{r^{l+1}}{(2l-1)!!} \boldsymbol{\nabla}^l \frac{1}{r} \tag{3.15}$$

and

$$\overline{\hat{\mathbf{r}}^l} = (-1)^{l+1} \frac{r^{l-1}}{(2l-3)!!} \overline{\boldsymbol{\nabla}^l r} \ . \tag{3.16}$$

Note that the multiple gradient in the r.h.s. of Eq. (3.15) is irreducible by itself.

Now we are ready to calculate the gradients of the functions $\hat{C}_{LM}$ and $\hat{H}_{LM}$ in Eq. (3.6). First, for $l = 1$ definition (3.10) gives three linearly independent vectors $\hat{\mathbf{Y}}_{1m}, (m = -1, 0, 1)$ which constitute the basis in the 3D space. We use them to define the spherical components $f_{;m}$ of the gradient of an arbitrary function $f(\mathbf{r})$ as

$$f_{;m}(\mathbf{r}) = \hat{\mathbf{Y}}^*_{1m} \cdot \boldsymbol{\nabla} f(\mathbf{r}), \quad m = -1, 0, 1 \ . \tag{3.17}$$

Applying (3.14), (3.15) and (3.16) we can write the functions $\hat{C}_{LM}$ and $\hat{H}_{LM}$ in the following form:

$$\hat{C}_{LM}(\mathbf{r}) = \frac{(-1)^L}{(2L-1)!!} \hat{\mathbf{Y}}_{LM}\overset{L}{\odot}\boldsymbol{\nabla}^L \frac{1}{r} \ , \tag{3.18}$$

$$\hat{H}_{LM}(\mathbf{r}) = \frac{(-1)^{L+1}}{(2L-3)!!} \hat{\mathbf{Y}}_{LM}\overset{L}{\odot}\boldsymbol{\nabla}^L r \ . \tag{3.19}$$

Next, with use of formula (3.18) the spherical components of the gradient of $\hat{C}_{LM}(\mathbf{r})$ can be written as

$$\hat{C}_{LM;m}(\mathbf{r}) = \frac{(-1)^L}{(2L-1)!!} \overline{\hat{\mathbf{Y}}^*_{1m}\hat{\mathbf{Y}}_{LM}}\overset{L+1}{\odot}\boldsymbol{\nabla}^{L+1} \frac{1}{r} \ . \tag{3.20}$$

The r.h.s. of the above formula can be calculated using the identity

$$\overline{\hat{\mathbf{Y}}^*_{l_1 m_1}\hat{\mathbf{Y}}_{l_2 m_2}} = \widehat{\mathscr{H}}(l_1 m_1, l_2 m_2)\hat{\mathbf{Y}}_{l_1+l_2, m_2-m_1} \ , \tag{3.21}$$

where

$$\widehat{\mathscr{H}}(l_1m_1,l_2m_2)=\frac{1}{n_{lm}}\oint \hat{Y}^*_{l_1m_1}(\hat{\mathbf{r}})\hat{Y}_{l_2m_2}(\hat{\mathbf{r}})\hat{Y}^*_{lm}(\hat{\mathbf{r}})\,\mathrm{d}\hat{\mathbf{r}}$$
$$=(-1)^{m_1}\frac{(2l_1-1)!!(2l_2-1)!!(l-m)!}{(2l-1)!!(l_1-m_1)!(l_2-m_2)!} \tag{3.22}$$

and

$$l=l_1+l_2,\quad m=m_2-m_1\ . \tag{3.23}$$

This, together with Eqs. (3.7) and (3.15), leads to the following relation between the components of the gradient of $\hat{C}_{LM}$ and the function itself

$$\hat{C}_{LM;m}(\mathbf{r})=(-1)^{m+1}\frac{(L-M+m+1)!}{(L-M)!(1-m)!}\,\hat{C}_{L+1,M-m}(\mathbf{r})\ . \tag{3.24}$$

In a similar way the spherical components of the gradient of the function $\hat{H}_{LM}(\mathbf{r})$ can be expressed as

$$\hat{H}_{LM;m}(\mathbf{r})=\frac{(-1)^{L+1}}{(2L-3)!!}\,\hat{\mathbf{Y}}^*_{1m}\hat{\mathbf{Y}}_{LM}\overset{L+1}{\odot}\boldsymbol{\nabla}^{L+1}r\ . \tag{3.25}$$

Next, we use the explicit expression for the irreducible part of an arbitrary symmetric tensor [31]

$$\overline{\boldsymbol{\nabla}^{L+1}r}=\boldsymbol{\nabla}^{L+1}r-\frac{2L}{2L+1}[\mathbf{I}\,\boldsymbol{\nabla}^{L-1}r]_{S'}+\cdots\ , \tag{3.26}$$

where the brackets $[.]_{S'}$ denote the symmetric part of a tensor over the last L indices. The ellipsis denotes finite number of tensors containing at least one unit tensor with both indices other than the first index. Further quite simple but tedious calculations with the use of formulas (3.18), (3.19) and (3.16) lead to the relation linking the gradient of $\hat{H}$ to the functions $\hat{H}$ and $\hat{C}$ itself

$$\hat{H}_{LM;m}(\mathbf{r})=\frac{2(L+M)!}{(2L+1)(L+M-m-1)!(1-m)!}\hat{C}_{L-1,M-m}(\mathbf{r})$$
$$+(-1)^{m+1}\frac{(2L-1)(L-M+m+1)!}{(2L+1)(L-M)!(1-m)!}\hat{H}_{L+1,M-m}(\mathbf{r})\ . \tag{3.27}$$

Relations (3.24) and (3.27) together with Eqs. (3.4) and (3.6) allow us to calculate the spherical components of the gradient of the operator $\boldsymbol{G}$ in terms of the functions $\hat{H}$ and $\hat{C}$, so that the calculation of $\nabla\boldsymbol{G}$ has the same complexity as that of $\boldsymbol{G}$ itself.

Next, with use of Eq. (3.3) we find the spherical components of the gradient of mobility matrix. The last step is to use them to calculate the divergence of $\boldsymbol{\mu}$. One should be careful here as it is easy to overlook the normalization factors in the final expressions for $\mathbf{d}_i$. Since the vectors $\hat{\mathbf{Y}}_{1m}, m=-1,0,1$ constitute the orthogonal basis in the 3D space we can write the identity operator as

$$\mathbf{I}=\frac{1}{\gamma_1^2}\sum_{m=-1,0,1}\frac{1}{n_{1m}^2}\,\hat{\mathbf{Y}}_{1m}\hat{\mathbf{Y}}^*_{1m}\ , \tag{3.28}$$

see Eq. (3.11). Thus the product of an arbitrary vector $\boldsymbol{A}$ with $\nabla f(\mathbf{r})$ can be expressed in terms of spherical components as

$$\mathbf{A}\cdot\nabla f(\mathbf{r}) = \sum_{m=-1,0,1} \frac{1}{n_{1m}} A_m f_{;m} \,, \tag{3.29}$$

where the spherical components of $\boldsymbol{A}$ are

$$A_m = \frac{1}{n_{1m}\gamma_1^2}\,\mathbf{A}\cdot\hat{\mathbf{Y}}_{1m} \,, \tag{3.30}$$

so that

$$\mathbf{A} = \sum_{m=-1,0,1} \frac{1}{n_{1m}} A_m \hat{\mathbf{Y}}^*_{1m} \,. \tag{3.31}$$

Analogously, the translational mobility matrix is written in terms of its spherical components as

$$\boldsymbol{\mu}^{tt}_{ij} = \sum_{m_1=-1,0,1}\ \sum_{m_2=-1,0,1} \frac{1}{n_{1m_1}n_{1m_2}} \hat{\mathbf{Y}}_{1m_1}\mu^{tt}_{ij,m_1m_2}\hat{\mathbf{Y}}^*_{1m_2} \,, \tag{3.32}$$

where

$$\begin{aligned}&\mu^{tt}_{ij,m_1m_2}(\mathbf{R}_1,\ldots,\mathbf{R}_N)\\ &\quad=(l=1,m_1,\sigma=0|\boldsymbol{\mu}_{ij}(\mathbf{R}_1,\ldots,\mathbf{R}_N)|l=1,m_2,\sigma=0) \,,\end{aligned} \tag{3.33}$$

so that the divergence of the mobility matrix is given by

$$\mathbf{d}_i(\mathbf{R}_1,\ldots,\mathbf{R}_N) = \sum_j \sum_{m_1=-1,0,1}\ \sum_{m_2=-1,0,1} \frac{1}{n_{1m_1}n_{1m_2}}\,\hat{\mathbf{Y}}_{1m_1}\mu^{tt}_{ij,m_1m_2;m_2}(\mathbf{R}_1,\ldots,\mathbf{R}_N) \,. \tag{3.34}$$

In the above formula the symbol; m_2 denotes spherical components of the gradient with respect to $\mathbf{R}_j$ (see Eq. (3.17)).

The above procedure of calculating the divergence of the mobility tensor is well suited for numerical implementation and is only about three times slower that the calculation of $\boldsymbol{\mu}$ itself. In Appendix B this algorithm is extended to the case of periodic boundary conditions. It is conceptually similar to the present case since the elements of $\boldsymbol{G}$ matrix for periodic boundary conditions involve lattice sums of the functions $\hat{C}_{LM}$ and $\hat{H}_{LM}$ which we already know how to differentiate.

4. Numerical results for the collective diffusion memory function

The above-presented scheme of computing the divergence of the mobility tensor has been used in Brownian dynamics calculations of the memory factor Δ (defined by Eq. (1.8)), for hard-sphere suspension. The simulations have been performed with periodic boundary conditions for three values of volume fraction: $\phi = 0.2, 0.3$ and 0.4, and for different numbers of spheres in a periodic cell (up to 100). Use of periodic

boundary conditions simplifies considerably the expression for the memory function, as it can be shown [16] that

$$\lim_{k\to 0} M(k,t) = M(t)\,, \tag{4.1}$$

where the function $M(t)$ reads (for hard-sphere system)

$$M(t) = \frac{\langle \sum_{i,j=1}^{N} \mathbf{d}_i(0)\cdot\mathbf{d}_i(t)\rangle_{per}}{\beta\langle \sum_{i,j=1}^{N} \mathrm{Tr}\ \boldsymbol{\mu}_{ij}^{tt}\rangle_{per}}\,, \tag{4.2}$$

where $\langle\ \rangle_{per}$ stands for the equilibrium average over hard-sphere configurations with periodic boundary conditions.

The formal justification of equality (4.1) is not trivial. Namely, due to the presence of hydrodynamic interactions in the system, the mobility matrix $\boldsymbol{\mu}_{ij}^{tt}$ has nonzero nondiagonal ($i\neq j$) elements, which decay with interparticle distance R_{ij} as $R_{ij}^{-\gamma}$ with $\gamma = 1,2,3$. Such long-ranged interactions can cause discontinuity in memory function at $k=0$ [32], so that in general it is not possible to identify $\lim_{k\to 0} M(k,t)$ with $M(0,t)$. In fact, $k=0$ value of the memory function picks up a contribution from the motion of a system as a whole. This contribution depends on the shape of the container and is given by integrals which diverge with the size of the system. However, when deriving the mobility matrix for periodic system one adds the constrain that the net suspension velocity in whole sample vanishes [33,34]. This removes the discontinuity at $k=0$ and allows to write $\lim_{k\to 0} M(k,t)$ in the form of Eq. (4.2).

For a number of reasons it is advantageous to calculate $M(t)$ in two steps: first calculating the initial value of the memory function $M(0)$ and then estimating its mean relaxation time $\tau_M = M(0)^{-1}\int_0^\infty M(t)\,\mathrm{d}t$. The initial value of the memory function can be obtained by means of equilibrium averaging which gives much greater accuracy than the calculations of τ_M that require Brownian dynamic simulations. Hence, as it was noted by Zwanzig and Ailawadi [35], such a two-step procedure increases considerably an accuracy of the numerically obtained memory function.

Additionally, even without Brownian dynamics simulations, the value of the memory factor Δ can be estimated based on the assumption that the mean relaxation time τ_M is similar to characteristic times of other relaxation processes in the system.

4.1. Calculations of initial value of memory function

For small particle concentrations the value of $M(0)$ can be assessed by means of the virial expansion. As it was mentioned in Introduction, the two-body contributions to the vector $\mathbf{d}_i$ vanish. Hence the first nonvanishing term in the virial expansion of $M(0)$ corresponds to the three-particle contribution. For hard-sphere system one gets

$$\frac{a^2}{D_o} M(0) = m_3\phi^2 + O(\phi^3)\,, \tag{4.3}$$

with

$$m_3 = \frac{9\eta^2}{8a^2}\int \mathrm{d}\boldsymbol{R}_2\,\mathrm{d}\boldsymbol{R}_3 \left(\sum_{i=1}^{3}\mathbf{d}_i(1,2,3)\right)^2 W(1,2,3)\,. \tag{4.4}$$

In the above equations ϕ is the volume fraction, a the sphere radius and $D_o = k_BT(6\pi\eta a)^{-1}$, with η standing for the fluid viscosity. The initial value of the memory function is rescaled by a^2/D_o in order to make it dimensionless. Finally, $\mathbf{d}_i(1,2,3) = \sum_{j=1}^{3} \nabla_j \cdot \boldsymbol{\mu}_{ji}^{tt}$, and the function $W(1,2,3)$ is unity for nonoverlapping configurations of the spheres and vanishes otherwise. Numerical integration in the three-body configuration space (analogous to the calculations presented in Ref. [28]) yields $m_3 = 1.42 \pm 0.02$.

Virial expansion results can be used for very dilute suspensions only. For larger concentrations the initial value of memory function $M(0)$ can be assessed by means of Monte Carlo averaging over different configurations of the spheres in periodic boundary conditions. To account for finite-size effects one analyzes the dependence of $M(t=0,N)$ on the number of spheres in the periodic cell, N. It turns out that the dependence of the data on N can be described by the function $A + BN^{-1/3}$. By fitting the data for $N = 30, 50, 60, 70$ and 100 to the above dependence the asymptotic values $M(t=0, N=\infty)$ were obtained for wide range of volume fractions (see Table 2).

4.2. Calculation of mean memory relaxation time

To estimate the mean relaxation time, τ_M, Brownian dynamics simulations have been performed. The trajectories of particles were constructed according to Eq. (1.3). Since we consider the hard-sphere suspension, the forces $\mathscr{F}_j$ in (1.3) are put to zero. However, to account for the fact that the particles cannot overlap, the scheme should be supplemented with the condition of vanishing normal component of the probability current on the surfaces of the spheres

$$\boldsymbol{R}_{ij} \cdot (\boldsymbol{\mathscr{J}}_i - \boldsymbol{\mathscr{J}}_j)|_{R_{ij}=2a} = 0, \quad i \neq j\,, \tag{4.5}$$

with

$$\boldsymbol{\mathscr{J}}(\boldsymbol{X};t) = k_BT\boldsymbol{\mu}^{tt}(\boldsymbol{X}) \cdot \nabla P(\boldsymbol{X};t)\,. \tag{4.6}$$

We implement the above condition by assigning in each step auxiliary velocities $\boldsymbol{u}_i = \Delta\boldsymbol{R}_i/\Delta t$ to all particles and then solving a classical molecular dynamics problem of finding the evolution of N hard spheres with the velocities $\boldsymbol{u}_i$ over the time period Δt [36–38]. The numerical procedure applied here locates time, collision partners and impact parameters for every collision occurring in the system in chronological order. The hard-sphere dynamics applied over the time interval Δt assures that the probability current through the surface $R_{ij} = 2a$ vanishes. Note that the component of $\boldsymbol{u}_{ij}$ perpendicular to $\boldsymbol{R}_{ij}$ remains unchanged as it should, since the boundary condition (4.5) affects only the parallel component.

The simulations have been performed for three values of the volume fraction: $\phi = 0.2, 0.3$ and 0.4 and different numbers of spheres in a periodic cell (30, 50 and 100) with the time step $\Delta t = 4 \times 10^{-4} a^2/D_o$.

In each step a quantity

$$\boldsymbol{U}_{tot}(t) = \sum_{i=1}^{N} \mathbf{d}_i(t) \tag{4.7}$$

has been calculated using the method presented in Section 3. The correlation function $T(t) = \langle \boldsymbol{U}_{tot}(0)\boldsymbol{U}_{tot}(t)\rangle$ can then be used to calculate τ_M because

$$\frac{1}{M(0)}\int_{t=0}^{\infty} M(t')\,\mathrm{d}t' = \frac{1}{T(0)}\int_{t=0}^{\infty} T(t')\,\mathrm{d}t' \,. \tag{4.8}$$

The correlation function $T(t)$ is obtained from the simulation data with use of the formula [38,39]

$$T(\tau) = \frac{1}{K_{\max}(\tau)}\sum_{K=1}^{K_{\max}(\tau)} \boldsymbol{U}_{tot}(K\Delta t)\boldsymbol{U}_{tot}(\tau + K\Delta t), \quad \tau = m\Delta t, \quad m = 1,2,3\ldots \,. \tag{4.9}$$

Here $K_{\max}$ is given by the condition that $K_{\max}(\tau)\Delta t + \tau$ must not exceed the total time of a given trajectory, i.e.,

$$K_{\max}(\tau) + \frac{\tau}{\Delta t} = K_{traj} \,, \tag{4.10}$$

where K_{traj} is the total number of time steps in a given trajectory. From Eq. (4.9) one sees that the statistics for longer times τ gets worse. The last step is to average $T(\tau)$ over all the trajectories obtained for the given volume fraction ϕ and number of particles N.

4.3. The long-time tail fitting

To get the time integral of the memory function, one needs to know the behavior of $M(t)/M(0)$ for long times. Some indications can be found in theoretical studies on the memory function of the self diffusion problem in suspensions [17,40–43]. It was namely predicted that the self-diffusion memory function have an algebraic long-time tail, $t^{-5/2}$, and the amplitude of the tail was calculated for a number of limiting cases (e.g. the dilute suspension, lack of hydrodynamic interactions, etc.). This behavior is connected with the fact that the Fourier transform of the memory function $\hat{M}(\omega)$ is a meromorphic function of the square root of ω. Therefore, one gets the following expansion [42,43]:

$$\hat{M}(\alpha) = \hat{M}(0) + \hat{M}_1\alpha + \hat{M}_2\alpha^2 + \hat{M}_3\alpha^3 + \cdots \,, \tag{4.11}$$

with

$$\alpha = \sqrt{\omega} \,.$$

The first coefficient in the above expansion is closely connected to the relaxation time, since

$$\tau_M = \frac{\hat{M}(\alpha = 0)}{M(0)} \,, \tag{4.12}$$

whereas the second gives the amplitude of the long-time tail, $t^{-3/2}$, of the function $M(t)$. If, however, M_1 vanishes then $M(t)$ has a long-time tail of the form $t^{-5/2}$ with the amplitude determined by M_3.

Table 1
The values of the factor Δ and the mean relaxation time τ_M for the hard-sphere suspension of volume fraction ϕ obtained from the equilibrium Monte Carlo averaging and Brownian dynamics simulations

ϕ	$D_o a^{-2}\tau_M$	Δ
0.2	0.126 ± 0.025	0.01 ± 0.003
0.3	0.120 ± 0.015	0.03 ± 0.01
0.4	0.09 ± 0.02	0.05 ± 0.015

It is not unreasonable to expect that such an algebraic long-time tail will also be present in our case. However, because of the complicated form of the memory function in our case and particularly the fact that the two-body contributions to $M(t)$ vanish, the techniques applied in the above-cited papers to determine the coefficients in (4.11) are not directly applicable here.

Therefore, we decided on semi-empirical way of accounting for the long-time behavior of the memory function: by fitting to the data a tail of the form $At^{-(2n+1)/2}$ with $n = 1, 2, 3...$. In all cases the best fit was obtained for the tail of the form $t^{-3/2}$. The fitting cannot serve as a proof that the collective diffusion memory function has indeed the $t^{-3/2}$ long-time tail. Nevertheless, fitting of the $t^{-3/2}$ tail to the data gives the upper bound of the value of τ_M, as the tails of the form $At^{-(2n+1)/2}$ with $n > 1$ decay faster.

4.4. Final results

By combining the results for τ_M with the values of $M(0)$, we calculate the values of the memory factor Δ as given in Table 1. As it can be seen the memory contribution to the collective diffusion coefficient is relatively small but increases with the volume fraction.

As it was mentioned before, an estimation of the mean relaxation time, τ_M, can be obtained by assuming that it is similar to other relaxation times for collective processes in a suspension which are expected to be of the order $\tau_c^o = a^2 S(0)/D_s^s$ [44]. Here D_s^s is the short-time self-diffusion coefficient, whereas $S(0)$ is the value of static structure factor at $k = 0$. Taking the values of D_s^s from the numerical simulations of Ladd [45] we get an estimate of Δ, given in Table 2. These estimates are in reasonable agreement with the results obtained using Brownian dynamics simulation.

5. Summary

We have derived the multipole expansion formulas for the divergence of mobility tensor in an N-body system of spherical particles in an incompressible viscous fluid. Both the case of an unbounded fluid and that of periodic boundary conditions have been considered. The use of an analytical formula in calculations of the divergence of mobility tensor is a substantial improvement over a brute-force finite-difference

Table 2
The estimates of the factor Δ for hard-sphere suspension of volume fraction ϕ obtained from initial values of the memory function $M(0)$ calculated by Monte Carlo averaging and the relaxation time $\tau_c = a^2 S(0)/D_s^s$

ϕ	$D_o^{-1} a^2 M(0)$	$D_o a^{-2} \tau_c$	Δ_{est} (%)
0.01	$(1.55 \pm 0.05) \times 10^{-4}$	0.94	0.01
0.1	$(1.7 \pm 0.1) \times 10^{-2}$	0.55	1
0.2	$(9.2 \pm 0.3) \times 10^{-2}$	0.32	3
0.3	0.24 ± 0.015	0.20	5
0.4	0.54 ± 0.03	0.13	7
0.45	0.67 ± 0.02	0.10	7

algorithm of determining derivatives and allows to improve the accuracy of Brownian dynamics simulations. The method has been applied to calculations of memory contribution to long-time collective diffusion coefficient of a Brownian suspension.

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Appendix A. Multipole expansion

In the multipole expansion we use two complete sets of vector functions [46], which are fitted to the spherical symmetry of the Stokes equations (2.1): $\boldsymbol{v}^+_{lm\sigma}(\mathbf{r})$, regular at $\mathbf{r} = \mathbf{0}$, 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 $m = 0, \pm 1, \ldots, \pm l$. These multipole vectors were introduced in Ref. [23]; here we use the modified definition from Ref. [7]. 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 and m indices.

The matrix elements of the operator $\mathbf{Z}_0$ have the form [7]

$$(l_1 m_1 \sigma | \mathbf{Z}_0 | l_2 m_2 \sigma_2) = \delta_{l_1 l_2} \delta_{m_1 m_2} \eta (2a)^{2l_1 + \sigma_1 + \sigma_2 - 1} z_{l_1, \sigma_1 \sigma_2} \,, \tag{A.1}$$

where the elements $z_{l,\sigma_1\sigma_2}$ are dimensionless and the only nonzero ones are given below

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

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

$$z_{l,11} = \frac{l(l+1)(2l+1)}{2^{2l+1}} \,, \tag{A.4}$$

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

The only nonzero matrix elements of the one-body mobility matrix $\boldsymbol{\mu}_0$ are

$$(1m0|\boldsymbol{\mu}_0|1m0) = (1m0|\mathbf{Z}_0|1m0)^{-1} = \frac{2}{9\eta a}\ , \tag{A.6}$$

$$(1m1|\boldsymbol{\mu}_0|1m1) = (1m1|\mathbf{Z}_0|1m1)^{-1} = \frac{1}{6\eta a^3}\ . \tag{A.7}$$

Let us finally give the formulas for the coefficients $A(l_1m_1\sigma_1, l_2m_2\sigma_2)$ and $B(l_1m_1\sigma_1, l_2m_2\sigma_2)$ in Eq. (3.6) for the matrix element of operator $\boldsymbol{G}$. They read

$$\begin{aligned}
B(l_1m_10, l_2m_20) &= \frac{1}{2}\,\frac{(l_1+1)(l_2+1)}{2l_1+2l_2+1}\,A(l_1m_11, l_2m_21)\ ,\\
A(l_1m_10, l_2m_20) &= \frac{1}{(l_1+l_2-m_2+m_1)(l_1+l_2-m_2+m_1-1)}\,(-l_1l_2(l_1+l_2)\\
&\quad + 2m_2^2l_1^2 + 2m_1^2l_2^2 + (4m_1m_2+1)l_1l_2\\
&\quad - m_2(2m_1+m_2)l_1 - m_1(2m_2+m_1)l_2 + m_1m_2)\\
&\quad \times\frac{(l_1+1)(l_2+1)(l_1l_2-2l_1-2l_2+1)}{l_1l_2(2l_1-1)(2l_2-1)(2l_1+2l_2-1)}A(l_1m_11, l_2m_21)\ ,\\
A(l_1m_10, l_2m_21) &= \frac{(m_2l_1+m_1l_2)(l_1+1)}{l_1l_2(l_1+l_2+m_1-m_2)}\,A(l_1m_11, l_2m_21)\ ,\\
A(l_1m_10, l_2m_22) &= -\frac{l_2(l_1+1)}{(2l_2+1)(2l_2+3)}\,A(l_1m_11, l_2m_21)\ ,\\
A(l_1m_11, l_2m_20) &= -\frac{(m_2l_1+m_1l_2)(l_2+1)}{l_1l_2(l_1+l_2+m_1-m_2)}A(l_1\,m_11, l_2m_21)\ ,\\
A(l_1m_12, l_2m_20) &= -\frac{l_1(l_2+1)}{(2l_1+1)(2l_1+3)}A(l_1m_11, l_2m_21)\ ,
\end{aligned} \tag{A.8}$$

with

$$A(l_1m_11, l_2m_21) = (-1)^{l_1+m_1+1}\,\frac{1}{(l_2+1)(2l_2+1)(l_1+1)}\,\frac{(l_1+l_2-m_1+m_2)!}{(l_1+m_1)!(l_2-m_2)!}\ .$$

All coefficients not listed in (A.8) vanish.

Appendix B. Divergence of mobility matrix in periodic boundary conditions

When periodic boundary conditions are applied, the solution of the flow equations is given by a relation analogous to Eq. (2.3)

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

where the Oseen tensor (2.4) was replaced by the Hasimoto tensor $\boldsymbol{T}_{\boldsymbol{H}}$ [47,34,48]. The decomposition similar to Eq. (2.5) can still be performed, this time leading to [34]

$$\mathbf{w}_i = \mathbf{Z}_0^{-1}(i)\mathbf{f}_i + \sum_{j\neq i} \mathbf{G}_{\mathbf{H}}(ij)\mathbf{f}_j + \mathbf{G}'_{\mathbf{H}}(i)\mathbf{f}_i \,, \tag{B.2}$$

where

$$[\mathbf{G}_{\mathbf{H}}(ij)\boldsymbol{f}_j](\boldsymbol{r}) \equiv \int \boldsymbol{T}_H(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{f}_j(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}', \quad i\neq j,\ \ \boldsymbol{r}\in S_i \,, \tag{B.3}$$

whereas the additional self-term $\mathbf{G}'_{\mathbf{H}}(i)$ gives the contribution due to the induced force density on the periodic images of particle i:

$$[\mathbf{G}'_{\mathbf{H}}(i)\boldsymbol{f}_i](\boldsymbol{r}) \equiv \int (\boldsymbol{T}_H(\boldsymbol{r},\boldsymbol{r}') - \mathbf{T}(\boldsymbol{r},\boldsymbol{r}'))\cdot\boldsymbol{f}_i(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}', \ \ \boldsymbol{r}\in S_i \,. \tag{B.4}$$

The matrix elements of $\mathbf{G}_{\mathbf{H}}(ij)$ are expressed by the relationship similar to (3.4)

$$(l_1m_1\sigma_1|\mathbf{G}_{\mathbf{H}}(ij)|l_2m_2\sigma_2) = \frac{n_{l_1m_1}}{\eta n_{l_2m_2}} S_H^{+-}(\boldsymbol{R}_{ij}; l_1m_1\sigma_1, l_2m_2\sigma_2) \,, \tag{B.5}$$

with

$$\begin{aligned} &S_H^{+-}(\mathbf{R}_{ij}; l_1m_1\sigma_1, l_2m_2\sigma_2) \\ &\quad = A(l_1m_1\sigma_1, l_2m_2\sigma_2)\hat{\Psi}_{L'M}(\mathbf{R}_{ij}) + B(l_1m_1\sigma_1, l_2m_2\sigma_2)\hat{W}_{LM}(\mathbf{R}_{ij}) \\ &\qquad + E(l_1m_1\sigma_1, l_2m_2\sigma_2) \,. \end{aligned} \tag{B.6}$$

As it is seen, the functions $\hat{C}_{L'M}$ and $\hat{H}_{LM}$ in Eq. (3.6) were replaced here by functions $\hat{\boldsymbol{\Psi}}_{L'M}$ and $\hat{W}_{LM}$, the explicit form of which will be given below. Additionally, a constant term independent of $\boldsymbol{R}_{ij}$ has been added. This term reads explicitly

$$E(l_1m_1\sigma_1, l_2m_2\sigma_2) = \frac{1}{\eta}\,\delta_{l_1l_2}\delta_{l_{m1m_2}}[\delta_{l_11}M^{(1)}_{\sigma_1\sigma_1} + \delta_{l_12}M^{(2)}_{\sigma_1\sigma_1}] \,, \tag{B.7}$$

where the nonzero elements of M matrices are given by

$$M^{(1)}_{1,3} = M^{(1)}_{3,1} = \frac{4\pi}{135} \,, \tag{B.8}$$

$$M^{(1)}_{2,2} = -\frac{4\pi}{9} \,, \tag{B.9}$$

$$M^{(2)}_{1,1} = -\frac{2\pi}{75} \,. \tag{B.10}$$

The functions $\hat{\Psi}$ and $\hat{W}$ are essentially lattice sums of $\hat{C}$ and $\hat{H}$:

$$\hat{\Psi}_{00}(\mathbf{R}) = \lim_{\mathcal{N}\to\infty}\left[\sum_{|\mathbf{n}|\leqslant\mathcal{N}} \hat{C}_{00}(\mathbf{R}-\mathbf{n}) + \frac{2\pi}{3}R^2 - 2\pi\mathcal{N}^2\right] \,, \tag{B.11}$$

$$\hat{\Psi}_{1m}(\mathbf{R}) = \lim_{\mathcal{N}\to\infty}\left[\sum_{|\mathbf{n}|\leqslant\mathcal{N}} \hat{C}_{1m}(\mathbf{R}-\mathbf{n}) - \frac{4\pi}{3}R\hat{Y}_{1m}(\hat{\mathbf{R}})\right] \,, \tag{B.12}$$

$$\hat{\Psi}_{lm}(\mathbf{R}) = \lim_{\mathcal{N}\to\infty} \sum_{|\mathbf{n}|\leqslant\mathcal{N}} \hat{C}_{lm}(\mathbf{R}-\mathbf{n}), \quad l=2,3,\dots \ , \tag{B.13}$$

$$\hat{W}_{2m}(\mathbf{R}) = \lim_{\mathcal{N}\to\infty} \left[\sum_{|\mathbf{n}|\leqslant\mathcal{N}} \hat{H}_{2m}(\mathbf{R}-\mathbf{n}) - \frac{8\pi}{15} R^2 \hat{Y}_{2m}(\hat{\mathbf{R}}) \right] , \tag{B.14}$$

$$\hat{W}_{lm}(\mathbf{R}) = \lim_{\mathcal{N}\to\infty} \sum_{|\mathbf{n}|\leqslant\mathcal{N}} \hat{H}_{lm}(\mathbf{R}-\mathbf{n}), \quad l=3,4,\dots \ , \tag{B.15}$$

where $\mathbf{n}$, with integer components n_x, n_y, n_z, denotes a lattice point.

Finally, the matrix elements of $\mathbf{G}'_{\mathbf{H}}(ij)$ are given by

$$(l_1m_1\sigma_1|\mathbf{G}'_{\mathbf{H}}(ij)|l_2m_2\sigma_2) = \frac{n_{l_1m_1}}{\eta\, n_{l_2m_2}} \Bigg(A(l_1m_1\sigma_1, l_2m_2\sigma_2)\hat{\psi}_{L'M} + B(l_1m_1\sigma_1, l_2m_2\sigma_2)\hat{w}_{LM} + E(l_1m_1\sigma_1, l_2m_2\sigma_2) \Bigg) , \tag{B.16}$$

where the coefficients $\hat{\psi}$ and $\hat{w}$ can be expressed as

$$\hat{\psi}_{LM} = \hat{\Psi}'_{LM}(0) , \tag{B.17}$$

$$\hat{w}_{LM} = \hat{W}'_{LM}(0) , \tag{B.18}$$

with the prime indicating that in the sums in Eqs. (B.11)–(B.15) the $\mathbf{n}=0$ term is to be omitted.

Since we have already derived the spherical gradient rules for functions $\hat{C}$ and $\hat{H}$ in Eqs. (3.24) and (3.27), now we can apply these rules to the lattice sums (B.11), (B.12), (B.13) and (B.14), (B.15), and finally obtain the gradient formulas for $\hat{\Psi}$ and $\hat{W}$

$$\hat{\Psi}_{LM;m}(\mathbf{R}) = (-1)^{m+1} \frac{(L-M+m+1)!}{(L-M)!(1-m)!} \hat{\Psi}_{L+1,M-m}(\mathbf{R}) - \frac{4\pi}{3} 2^m \delta_{L1}\delta_{Mm} , \tag{B.19}$$

$$\hat{W}_{LM;m}(\mathbf{R}) = \frac{2(L+M)!}{(2L+1)(L+M-m-1)!(1-m)!} \hat{\Psi}_{L-1,M-m}(\mathbf{R}) + (-1)^{m+1} \frac{(2L-1)(L-M+m+1)!}{(2L+1)(L-M)!(1-m)!} \hat{W}_{L+1,M-m}(\mathbf{R}) , \tag{B.20}$$

which allows us to find the gradient of $\boldsymbol{G}_H$ and then the divergence of mobility matrix in a complete analogy with the infinite space case.

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