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Accurate method for the Brownian dynamics simulation of spherical particles with hard-body interactions

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In Brownian Dynamics simulations, the diffusive motion of the particles is simulated by adding random displacements, proportional to the square root of the chosen time step. When computing average quantities, these Brownian contributions usually average out, and the overall simulation error becomes proportional to the time step. A special situation arises if the particles undergo hard-body interactions that instantaneously change their properties, as in absorption or association processes, chemical reactions, etc. The common “naïve simulation method” accounts for these interactions by checking for hard-body overlaps after every time step. Due to the simplification of the diffusive motion, a substantial part of the actual hard-body interactions is not detected by this method, resulting in an overall simulation error proportional to the square root of the time step. In this paper we take the hard-body interactions during the time step interval into account, using the relative positions of the particles at the beginning and at the end of the time step, as provided by the naïve method, and the analytical solution for the diffusion of a point particle around an absorbing sphere. Öttinger used a similar approach for the one-dimensional case [Stochastic Processes in Polymeric Fluids (Springer, Berlin, 1996), p. 270]. We applied the “corrected simulation method” to the case of a simple, second-order chemical reaction. The results agree with recent theoretical predictions [K. Hyojoon and Joe S. Kook, Phys. Rev. E 61, 3426 (2000)]. The obtained simulation error is proportional to the time step, instead of its square root. The new method needs substantially less simulation time to obtain the same accuracy. Finally, we briefly discuss a straightforward way to extend the method for simulations of systems with additional (deterministic) forces. © 2002 American Institute of Physics. [DOI: 10.1063/1.1515775]

I. INTRODUCTION

Coarse graining of simulation models is still needed. With present computer power, particularly by large-scale parallel computing methods, it has become possible to simulate the behavior of relatively large molecular systems in detail. Still, full simulations of the long-time evolution of complex systems containing large numbers of large (polymer) molecules, in which all single atoms and their interactions are explicitly incorporated, are not feasible. In this context one could think of nanoscale systems, for instance biopolymers like proteins and DNA, interacting with other (bio-) polymers in the copying and transcription processes; biopolymers incorporated in complex membrane structures, performing various “pump”-activities, etc. For this kind of simulation one still has to resort to simplifications, mostly by omitting as many less relevant degrees of freedom of the system as possible. This “coarse graining” procedure is performed in different steps. For instance by the grouping of supposedly less important (parts of) molecules together into so-called “simulation atoms,” by the introduction of effective interactions between these particle collections and, if possible, also by setting limits to the range of these interactions. For this approach one often uses the information from more detailed Molecular Dynamics (MD) simulations of subsets of the system under consideration. After these simplifications, one is still in the MD regime; the—Newtonian—equations to be solved are still those of interacting atoms and consequently span very small time scales.

The Brownian Dynamics (BD) method has limited information. Here an effective friction with the solvent, which is, via the fluctuation-dissipation theorem, connected to their diffusive motion, replaces the explicit interactions between the molecules of interest and the solvent particles. This method is built on two important assumptions.

The first is a separation of time scales, in which the actual deterministic motion of Brownian particle plus solvent is replaced by a diffusive, random walklike, “fuzzy” path of the particles. This causes the time scale of BD simulations to

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be orders of magnitudes larger than that of MD. The magnitude of the Brownian displacement, \( \sim \sqrt{\Delta t} \), per time step, \( \Delta t \), is chosen from a symmetric probability distribution, having mean zero. Its second moment is dictated by the well known random walklike result for diffusive motion in an isotropic medium,

\[
\langle (\Delta R)^2 \rangle = 6D\Delta t, \tag{1}
\]

where \( D \) is the diffusion constant, so that the mean square root of the displacement is proportional to the root of the time step. In this way one assures that the average behavior of the diffusing particle is correctly described on the BD time scale. For the probability distribution of the Brownian displacements one might choose a uniform distribution instead of the full Gaussian. Indeed, for weak convergence the precise choice of this distribution is not relevant—provided its 1st and 2nd moments are correct—since in the limit of many time steps all distributions converge to the Gaussian distribution, and the simulation algorithms are usually only correct up to order \( \Delta t \). We return to this point later.

The second assumption is that of zero inertia, e.g., one assumes that on the BD time scale the forces on the particles always balance each other,

\[
F_{\text{other}} + F_{\text{friction}} + F_{\text{Brownian}} = 0, \tag{2}
\]

where \( F_{\text{other}} \) is the sum of all except the Brownian and friction forces. This effectively means that at every time step the friction must compensate the other forces present. This condition determines the friction and thus the particle’s velocity,

\[
F_{\text{friction}} = -\zeta (v - v_{\text{solvent}}), \tag{3}
\]

Here \( v \) is the particle’s velocity and \( v_{\text{solvent}} \) the solvent velocity at the position of the particle. The particle’s velocity then determines its displacement, \( \Delta r \), over the time step. Adding the different contributions, one obtains

\[
\Delta r = v_{\text{solvent}} \Delta t + \frac{1}{\zeta} F_{\text{other}} \Delta t + \sqrt{2D\Delta t} \Delta \chi, \tag{4}
\]

where \( \Delta \chi \) is a random vector, whose three components are independently chosen from a symmetric probability distribution with average zero and unit width, to represent the particle’s Brownian motion, as explained above. Note that the last contribution, the one from the Brownian ("stochastic") force, is proportional to the root of the time step, while that of the deterministic forces is proportional to the time step itself.

The fluctuation-dissipation theorem directly links the diffusion constant \( D \) of the particle to its friction coefficient \( \zeta \). Einstein \( ^3 \) obtained the well-known result

\[
D = \frac{kT}{\zeta}, \tag{5}
\]

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

For the friction coefficient of a sphere Stokes derived, \( ^4 \)

\[
\zeta = \frac{1}{6\pi \eta a}, \tag{6}
\]

where \( \eta \) is the solvent viscosity and \( a \) is the radius of the spherical particle. For nonspherical particles or a nonisotropic medium the constants \( D \) and \( \zeta \) are to be replaced by the appropriate tensors. This is not relevant for this work.

The nature of the interactions between the particles determines the simulation error. If the interactions in a BD simulation are soft, several time steps are needed to substantially affect the state of the particles. In that case, the random Brownian contributions average out and, for additive noise, the simulation error becomes the same as without the Brownian forces, e.g., proportional to \( \Delta t \). A completely different situation arises if the particles interact via hard-body potentials, with each other and/or with other entities, like hard walls. Most commonly, one identifies the hard-body interactions by searching for hard-body overlaps after every time step. Using this "naive" method one seriously underestimates the number of hard body interactions. This is because the trajectory is fractal, and the Brownian particle travels great distances between the endpoints of its trajectory. The simulation tells us nothing about this detailed trajectory, other than where the particle begins and ends. In some cases this naive approach leads to convergence problems. If an interaction (a "contact") between the particles or between a particle and the wall does not lead to a "special event" but just to the transfer of momentum via the collision or the reflection, the error made is not important. Because of the zero inertia condition, inherent in the BD method, any transferred momentum is instantaneously dissipated via the friction with the solvent anyway. Therefore the overall error remains the same as without the Brownian forces. In contrast, if the hard body contact leads to a completely new "state" of the particle, as in absorption or association processes, chemical reactions, etc., the number of such special events is seriously underestimated if one uses the naive approach to account for interactions. As a result, such simulations suffer from a very slow convergence behavior; the overall simulation error being proportional to the square root of the time step. \( ^1 \) This means that one should take such small time steps that the substantial gain in simulation time by using a more coarse grained (BD) method could easily be lost again, as a consequence of the slow convergence of the naive simulation method.

Previous approaches to treat this problem are tedious and not generally applicable. Some authors before Ottinger already ran into the same problem. \( ^5-8 \) However, in most of these papers (1) the seriousness of the convergence problem is not clearly stated; (2) the solution chosen is not general. The authors attempt to solve the full Fokker–Planck equation. This is (of course) only analytically doable for some special cases of the deterministic forces. For application to a simulation, the displacement probability distribution obtained must be inverted, which gives even more complicated expressions. These are completely different for every choice of the force. These expressions are then in a more or less trial-and-error fashion \( ^3 \) approximated by more treatable functions. As a result of this approach, one appears to end up with series approximations, the overall error of which \( ^4 \) gradually shifts from order \( \sqrt{\Delta t} \) to order \( \Delta t \) behavior while decreasing the time step. This makes error handling also
quite complicated. However, as the different force contributions are additive—at least in a first-order approximation—there is no need to solve the full diffusion equation for the particle. Instead, the deterministic contributions can be separated from the diffusion equation. This simplifies matters a lot.

The slow convergence of naïve simulations with hard interactions is to be expected. The replacement of the real, diffusive path of Brownian particles by random displacements \( \sim \sqrt{D\Delta t} \), leads to a relative error of order one in the number of interactions with the wall. Of course, this error only occurs for those particles that are close enough to the wall to possibly interact, e.g., in a region of width \( \sim \sqrt{D\Delta t} \), while the other dimensions of this region do not depend on \( \Delta t \). Clearly, the number of particles contributing to the error is in a first approximation proportional to this width. Therefore the overall simulation error, equal to the number of particles that contribute to the error times the magnitude of these error contributions should scale as \( \sim \sqrt{\Delta t} \).

Contents of this paper. In the next section we present a way to correct for this relatively large error in quite a general way, recapitulating a method described by Öttinger for the case of a point particle near a wall, in one dimension.\(^1\) We then extend this method to the three-dimensional case of two spherical particles with hard-body interaction. In the third section we apply our method to a simple but very common case, that of hard spherical particles, undergoing a second-order diffusion-controlled chemical (annihilation) reaction. This means that the encounter of the reactive particles itself is, of course, dependent on their diffusion toward each other. If they interact, they react instantaneously, without additional conditions, while the reaction product is assumed to be completely inert. The simulation results are presented in Sec. IV, where one can see the effectiveness of the proposed correction method. In our simulation we assume no other forces than the random Brownian force and the associated friction. Section V contains a discussion of the results, a brief prescription of the application of our method to more complex simulations, c.q. those including more (deterministic) interactions, and ends with our conclusions.

II. THEORY

First we explain the method in 1D; a diffusing particle near a flat, absorbing wall. Consider a “small part” of the Brownian motion of a freely diffusing particle, close to a wall \( (x=0) \), sketched in Fig. 1. At some instant in time (“initially”), the particle is positioned in \( x \). Its Brownian displacement in the next time step \( \Delta t \) is simulated by randomly picking a number from a Gaussian distribution, \( \psi_1 \), having symmetry axis, \( x=x_0 \), and width \( \sqrt{2D\Delta t} \). Two possible outcomes of this operation are indicated; the (“final”) positions \( x_1 \) and \( x_2 \).

Clearly, if the final position found for the particle is behind the wall (like \( x_2 \)), the particle must have “touched” the wall somewhere during this time step. This is the assumption used in the naïve approach. However, also positions on the positive, right side of the wall (like \( x_1 \)) may have been reached after a contact with the wall. This implies that also a part of the final positions at the “allowed” side of the wall are actually “forbidden.” Using the moment of first contact with the wall as the start of this distribution and the fact that the diffusion process is symmetric, the probability distribution of the forbidden positions is given by the area under curve \( \psi_2 \), found by reflecting the forbidden part of \( \psi_1 \). The correct probability distribution for the possible diffusion paths not involving a wall contact is therefore given by \( \psi_3 (=\psi_1-\psi_2) \). This is the solution for diffusion near an absorbing wall; all diffusion paths that involve a wall contact do not contribute to the probability distribution of final positions. The solution \( \psi_3 \) has the expected properties. It is a linear combination of solutions of the diffusion equation, and thus a solution itself. Its value is zero at the absorbing wall. Far from the wall it converges to the undisturbed Gaussian \( (\psi_1) \) and the area under \( \psi_3 \) is smaller than that under the Gaussian (equal to one), to account for the probability of absorption.

The error in the naïve method is corrected by means of the absorption probability. Using the above picture, one can deduce the probability that the particle, although it started in \( x_0 \) and its end point is \( x_1 \), has still touched the wall somewhere during the time step \( \Delta t \). This probability is equal to the ratio \( \psi_2/\psi_1 \) in \( x_1 \),

\[
P_{\text{abs}}(x_0,x_1,D,\Delta t) = \frac{\psi_2(x_0,x_1,D,\Delta t)}{\psi_1(x_0,x_1,D,\Delta t)} = \frac{\psi_1(x_0,-x_1,D,\Delta t)}{\psi_1(x_0,x_1,D,\Delta t)} = \exp\left[\frac{-(x_0+x_1)^2}{4D\Delta t}\right] \exp\left[\frac{(x_0-x_1)^2}{4D\Delta t}\right] = \exp\left[\frac{-x_0x_1}{D\Delta t}\right]. \tag{7}
\]

Note that normalization factors cancel. Öttinger\(^1\) used this expression to study the one-dimensional Brownian motion of...
a polymer segment in its “reptation tube,” by simulating a diffusing point on a line element. If this diffusive point particle crosses the boundary of the line element, it is interpreted as the polymer segment leaving its confining tube. Upon leaving its tube the polymer segment must start from a completely new, random, relaxed configuration. In this particular simulation this “renewal process” is the “special event,” upon the hard-body contact, as discussed above.

Öttinger used expression (7) in a probabilistic way, to decide whether a particle has touched the wall during its last time step or not. Such a probabilistic approach is the “best one can do” in this type of simulations, as one has no desire to resolve the particle’s precise motion during the time step (which would be equivalent to an undesired reduction of the time scale of the simulation by several orders of magnitude).

The probability that the particle survives a diffusion step is central to the algorithm. For later use we note that this probability is equal to

$$P_{\text{surv}} = 1 - \frac{\psi_2(x_0, x_1, D, \Delta t)}{\psi_1(x_0, x_1, D, \Delta t)} = \frac{\psi_1(x_0, x_1, D, \Delta t) - \psi_2(x_0, x_1, D, \Delta t)}{\psi_1(x_0, x_1, D, \Delta t)}$$

and we summarize that the survival probability (the probability of not having touched the wall during the time step) is equal to the correct probability (density) of ending up at $x_1$, in the presence of the absorbing wall, divided by the probability (density) of ending up at $x_1$, in absence of the wall. The latter is given by the Gaussian distribution for free diffusion.

Extension to the three dimensional case is straightforward, albeit more complicated. One can do the same for diffusing spherical particles with hard body interactions in three dimensions. We calculate the probability that during a certain time interval two diffusing particles have approached each other at or closer than their interaction distance (= the sum of their radii), given their relative positions at the start and the end of that time interval.

This problem can be approached more or less in the same way as above. First, since the only relevant parameter for the interaction is the relative distance between the two particles, this problem can be simplified to the problem of the diffusion of a single point particle around a fixed, absorbing sphere, during a certain time interval (see Fig. 2). The starting position of the particle is determined by the initial relative position of the two original particles. The radius of the sphere is taken equal to the sum of the interaction radii of the original particles. As the absorbing sphere is fixed in the origin, the point particle is given a diffusion constant equal to the sum of those of the original particles, so that their relative diffusion is correctly taken into account.

Comparing this problem to the one-dimensional case, the probability distribution for the position of the diffusing point particle somewhere around the absorbing sphere is equivalent to distribution $\psi_3$. The distribution $\psi_4$ for the diffusion of a free particle is a three-dimensional Gaussian distribution. First we present the analytical result for $\psi_3$ and discuss some of its properties. Then we return to the precise algorithm for the case of spherical particles with hard-body interactions.

The analytical solution for the diffusion of a point particle around an absorbing sphere is known and, scaled by the parameters of the problem, given by

$$\psi_3(R_0, R_1, A) = \frac{1}{4 \pi a^3 \sqrt{R_2}} \sum_{n=0}^{\infty} (2n+1)P_n(\cos(\theta)) \times \int_0^{\infty} \frac{c_{n+1/2}(x, xR_0)c_{n+1/2}(x, xR_1)}{J_{n+1/2}(x) + Y_{n+1/2}(x)} x^2 \exp(-Ax^2) dx,$$

where $A$ is the interaction distance and $d$ the distance of separation.

FIG. 2. Sketch of the parameters used to describe the behavior of two diffusing, reactive particles, (1) and (2), about each other during a certain time interval. Since only the relative position of the two particles is relevant, this problem can be simplified to a single, diffusing point particle near an absorbing sphere. $\mathbf{R}_0$ and $\mathbf{R}_1$ are the relative position vectors of the original particles before and after the time step, respectively. These become the position vectors of the single particle with respect to the absorbing sphere, before and after the time step. The radius of the sphere is equal to the “interaction distance,” of the original particles (e.g., the sum of their radii). The value of the diffusion constant of the point particle is taken equal to the effective diffusion constant of the original particles with respect to each other (e.g., the sum of those of the original particles).
where the indices 0 and 1 are used for comparison with the above discussion for a flat wall, \( R_0 \) and \( R_1 \) are thus the relative position vectors of the particles before and after the time step (normalized by the interaction distance, the sphere radius \( a \)), and where \( \theta \) is the angle between them. \( P_n \) are the Legendre functions of order \( n \). The functions \( c_{n+1/2} \) are defined by

\[
c_{n+1/2}(x,y) = J_{n+1/2}(y) \cdot Y_{n+1/2}(x) - J_{n+1/2}(x) \cdot Y_{n+1/2}(y),
\]

where the \( J_r \) and \( Y_r \) are Bessel functions of the first and second kind, respectively. \( A \) is the scaled time step of the problem, \( A = D' \Delta t / a^2 \), where \( D' \) is the relative diffusion constant of the reacting particles (here equal to twice that of a single particle; the prime is added to keep this in mind). Although expression (9) seems quite complicated at first sight, it is possible to calculate some of its properties analytically. Generally, however, one has to approximate its value numerically.

We return to the numerical approximation later, and first use Eq. (9) to calculate the probability that a diffusing particle with diffusion constant \( D \) and released at a (scaled) distance \( R_0 \) from an absorbing sphere of radius \( a \), is still not absorbed after a time step \( \Delta t \). This is just the zeroth order moment of \( \psi_0 \), e.g., the integral of \( \psi_0 \) taken over \( R_1 \). Using that \( d R_1 = R_1^2 dR_1 d \cos(\theta) d\varphi \), the symmetry of the problem gives for the integration over \( \varphi \) a factor 2 \( \pi \), the integration over \( \cos(\theta) \) only involves \( P_n(\cos(\theta)) \). This gives a contribution of a factor of 2 for \( n = 0 \) only,

\[
\int_{-1}^{1} \cos \theta \sum_{n=0}^{\infty} (2n+1)P_n(\cos(\theta)) = \left\{ \begin{array}{ll}
2 & \text{for } n = 0 \\
0 & \text{for all other } n
\end{array} \right.
\]

The summation over \( n \) therefore disappears, and the survival probability of the particle becomes

\[
P_{\text{surv}}(R_0, A) = \int dR_1 \psi_0(R_0, R_1, \cos(\theta), A)
= \frac{1}{a^3 \sqrt{R_0}} \int_{0}^{\infty} R_1^2 dR_1 \frac{1}{\sqrt{R_1}}
\times \sum_{n=0}^{\infty} c_{1/2}(x,xR_0)c_{1/2}(x,xR_1)
\times J_{1/2}(x) + Y_{1/2}(x)
\times \exp[-A x^2] x dx.
\]

Substituting the known exact forms for \( J_{1/2} \) and \( Y_{1/2} \),

\[
J_{1/2}(x) = \sqrt{\frac{2}{\pi x}} \sin(x),
\]

\[
Y_{1/2}(x) = -\sqrt{\frac{2}{\pi x}} \cos(x),
\]

and using the well-known formulas for addition and subtraction of arguments of sine and cosine functions, this integral can be calculated. One obtains

\[
P_{\text{surv}}(R_0, A) = 1 - \frac{1}{R_0} \text{erfc} \left( \frac{R_0 - 1}{2 \sqrt{A}} \right),
\]

where \( \text{erfc} \) is the complementary error function.

To limit calculation time, a cutoff to the interaction distance is needed. Clearly, to save simulation time, one wants to check only neighboring particles for possible interactions, i.e., only those having non-negligible interaction probability. One can use expression (15) to determine a “cutoff distance” \( d \), beyond which the interaction probability between particles (in one time step) is neglected. Of course, every finite choice for \( d \) leads to an underestimation of the number of interactions between the particles, so that error accumulate. The magnitude of these error contributions can, however, be set as small as desired, by increasing \( d \). We fixed this allowed error by setting it (much) smaller than the order of magnitude of the inherent fluctuations in the system, which is proportional to the inverse square root of the number of simulation particles.

Another approach to decrease this particular error source is to decrease the magnitude of the time step. As the space explored by every particle in one time step decreases, also this cutoff error decreases (for fixed cutoff distance). As the time step and the cutoff distance are thus connected, one would expect that there is an optimum value (in terms of the overall simulation time) for their combination. Indeed we found this to be the case, albeit for combinations of very small values of \( \Delta t \) and \( d \), which are only appropriate for systems with very small inherent fluctuations, i.e., very large systems. We therefore did not investigate this point any further.

The analytical solution can easily be approximated numerically. For numerical approximation of \( \psi_0 \), Eq. (9), we use well-known iteration formulas. For \( P_n \) (in a numerically appropriate form\(^{10}\)),

\[
P_{n+1}(x) = 2xP_n(x) - P_{n-1}(x) = \frac{xP_n(x) - P_{n-1}(x)}{n+1},
\]

where \( P_0 = 1 \) and \( P_1(x) = x \), and for \( J_n \) and \( Y_n \),

\[
J_{\nu}(x) = \frac{2(\nu+1)}{x}J_{\nu+1}(x) - J_{\nu+2}(x),
\]

\[
Y_{\nu+2}(x) = \frac{2(\nu+1)}{x}Y_{\nu+1}(x) - Y_{\nu}(x),
\]

both for \( \nu \) real and \( \nu \geq 0 \). The presentation of the first iterative expression (17), indicates that to accurately calculate \( J_{n+1/2}(x) \) for use in Eq. (9) one has to start from an arbitrary but high value \( \nu_{\text{start}} \) of the index [we took \( \nu_{\text{start}} = \text{round}(3/2\max(n,x)) + 1/2 \), where \( \max(x,y) \) gives the larger of \( x \) and \( y \) and \( \text{round}(x) \) rounds \( x \) to the nearest integer value], then set \( \nu_{\text{start}}(x) = 0 \) and \( \nu_{\text{start}}(1) = 10^{-100} \), and iterate down to \( n = 0 \). In this way one obtains, up to a constant proportionality factor, the whole series of values for \( J_{n+1/2}(x) \) (\( n \) an integer), with relative errors smaller than \( 10^{-8} \) for the needed \( n \) and \( x \) values. The correction factor for the whole series follows from the known form of the lowest order member of the series, \( J_{1/2}(x) \), Eq. (13).
Originally, this method was devised to calculate values of Bessel functions of integer order, and is as such implemented in most standard numerical routines. For half-order Bessel functions it gives perfect results as well.

To calculate $Y_{n+1/2}(x)$ one has to iterate up to the desired $n$ value, using Eq. (18), and starting from the two known lowest order members of the series, $Y_{1/2}(x)$, Eq. (14), and

$$Y_{1/2}(x) = -\sqrt{\frac{2}{\pi x}} \sin(x) + \frac{\cos(x)}{x}.$$  

The integrand of Eq. (9) contains a quadratic exponential. This feature strongly limits the range of $x$ values for which its value is non-negligible. We found that for an interaction distance $a=1$, diffusion constant $D=1$, and time step $\Delta t = 1$ (note that this gives $D'=2$ and thus $A=2$), $x \in [0,10]$ is a sufficient range over which to integrate; for time step $\Delta t = 0.1$ one obtains the range $x \in [0,25]$; for $\Delta t = 0.01$, $x \in [0,60]$, and for $\Delta t = 0.001$, $x \in [0,145]$.

To efficiently approximate (9) we perform the integration after summing over $n$. Truncating the $n$-series at $n_{\text{max}} = 50$ gives sufficiently accurate results. The integrand is sampled for equidistant values of the integration variable, $x$. To calculate the value of the full integrand (i.e., including the summation over $n$) for a certain $x$ value, we employ the iteration expressions (17) and (18), to quickly generate all members of the series in the integran $x$ value, up to $n_{\text{max}}$.

For the integration procedure itself we chose an iterative Simpson method, in which every three consecutive values of the integrand are approximated by a second-order polynomial, and then integrated. The first approximation of the integral is calculated using a distance between the sampling points of $\Delta x = 1$. Then, for every next iteration step, the $\Delta x$ intervals are cut in two equal parts. The values of the integrand at the new, intermediate $x$ values are calculated, and used together with the "old ones" in the next iteration step.

In every iteration step, $\phi_3$ is calculated [using Eqs. (9) and (16)] and compared to its previous value. If the relative difference between the last three results remains smaller than $10^{-5}$, the result for $\phi_3$ is considered sufficiently accurate and the iteration is stopped.

In Fig. 3 we plot a typical result; the probability distribution obtained for a diffusing point particle around an absorbing sphere, fixed in the origin. For the parameters we chose $D = 1/2$, $\Delta t = 1$, and $a = 1$, so that the scaled time step $A = 1$. The particle is released from $(x,y) = (2,0)$, so at scaled distance $R = 2$ from the sphere center. For symmetry reasons only half of the distribution is shown.

The numerical result is checked by means of a naive simulation. To check this result we simulated the same process in the "naive way," by releasing $10^8$ Brownian particles from the same distance from the sphere. To obtain sufficient accuracy, the time step $\Delta t = 1$ used for Fig. 3 is cut in $10^4$ equal parts. The particles thus are allowed to diffuse for $10^5$ "sub time steps," randomly taken from a Gaussian distribution with root mean square value $\sqrt{10^{-4} \cdot 6D \Delta t}$. Every "sub time step" the (naive) algorithm checks whether the point particle has entered the sphere. In that case it is considered absorbed; otherwise, after $10^4$ Brownian steps, its final position is recorded, and the next particle is released from $(x,y) = (2,0)$. At the end of the simulation the recorded three-dimensional frequency distribution of final coordinates $(x',y',z')$ is rescaled into new, two-dimensional coordinates, $(x,y)$,

$$x = x', \quad y = \sqrt{(y')^2 + (z')^2}.$$  

Then, for every value of $y$, the frequency was rescaled by $(2\pi y)^{-1}$, to enable comparison to Fig. 3. The resulting probability density is not shown, as the eye cannot distinguish any difference with Fig. 3.

If one carefully inspects the data one can see that the analytical approximation is still more “smooth” than the naive result, although the former took just a couple of hours to calculate on a PC, the latter about a week. For comparison we plotted, in Fig. 4, the relative difference between the numerical approximation of the exact distribution, Eq. (9) and the result from the naive simulation, both appropriately normalized. Note that the $x$ and $y$ ranges in Figs. 3 and 4 are chosen to be identical. As one can observe, in the range where the probability density is not too small, the relative error is small, in some percent. In the range where the probability density distribution is small, only a few particles arrive.

Therefore fluctuations are large in those regions, leading to large relative errors, as can be seen close to the sphere. Of course, the same is true far away from the point of release, $(x,y) = (2,0)$. Although this is not shown very explicitly, one sees that near the domain boundaries the fluctuations become larger.

Another way one might suggest circumventing the slow convergence of BD simulations with hard interactions between the particles, would be to take large time steps for particles without close neighbors, while selectively taking

FIG. 3. Numerical approximation of the analytical result for the probability density distribution of the position of a diffusing point particle, in the horizontal plane. The diffusion constant $D=0.5$, i.e., $D'=1$. The particle is released from $(x,y)=(2,0)$, i.e., at a scaled distance $R=2$ from an absorbing sphere of radius 1, positioned in the origin. The diffusion time $\Delta t = 1$. As the probability density is zero at the sphere boundary, its contour can be distinguished (between $x=-1$ and $x=1$).
much smaller time steps for particles that are close to others. Apart from the “administrative” difficulties that accompany such an approach, the outcome will still not be very satisfactory, due to the large relative errors that still occur close to the sphere, just in the region where all relevant processes take place.

The correction for the three-dimensional case can now be calculated. Using the numerical approximation method for the distribution of Eq. (9), we proceed in the same manner as for the one-dimensional case, given in Eq. (8). Every time step our algorithm checks whether pairs of particles end up at a distance smaller than the interaction distance. If this is the case, they have undergone an interaction. If their distance before and after the time step is larger than the interaction distance, the algorithm calculates the survival probability, using the relative positions before \((\mathbf{R}_0)\) and after \((\mathbf{R}_1)\) the time step, to calculate on the one hand, \(R_0\), \(R_1\) and the cosine of the angle \(\vartheta\) between them, for determination of \(\psi_1(\mathbf{R}_0, \mathbf{R}_1, A)\), on the other hand the distance traveled in the time step, \(|\mathbf{R}_1 - \mathbf{R}_0|\), to determine \(\psi_1\), via

\[
\psi_1(\mathbf{R}_0, \mathbf{R}_1, D' \Delta t) = \frac{1}{4 \pi D' \Delta t} \exp\left(\frac{|\mathbf{R}_1 - \mathbf{R}_0|^2}{4 D' \Delta t}\right) \tag{21}
\]

After the calculation of the survival probability \(P_{\text{surv}}\), using Eq. (8), a random number \(s\), drawn from a uniform probability distribution on \([0,1]\), is then used to determine whether the reaction has taken place (if \(s > P_{\text{surv}}\)), in the same way as described for the one-dimensional case. If this turns out to be the case, the algorithm acts accordingly.

The effectiveness of the corrected method is checked by simulating a chemical reaction. To apply the proposed correction method and study its effectiveness, we simulated the irreversible, diffusion-controlled, second-order chemical (annihilation) reaction of hard spherical particles,

\[
2A \rightarrow B. \tag{22}
\]

The rate of this reaction is commonly described by

\[
\frac{dc}{dt} = -2kc^2, \tag{23}
\]

where \(c\) is the concentration of \(A\) particles, \(k\) is called the “reaction constant,” and \(t\) the time (since the beginning of the reaction). Essentially this equation states that the decrease of the number of \(A\) particles is proportional to their probability of encounter, which is (assumed to be) proportional to the square of their average concentration. It is also common to define the reaction constant \(k\) such that it counts the number of reactions (per unit of volume and of time). The factor of 2 corrects for the fact that at every reaction of an \(A\) particle with another one, two \(A\) particles “disappear” at once. Assuming \(k\) is constant in time, Eq. (23) can readily be integrated,

\[
c(t) = \frac{1}{2kt + c_0}, \tag{24}
\]

where \(c_0\) is the initial concentration of \(A\) particles. Therefore, a plot of \(\frac{1}{2}(c(t)^{-1} - c_0^{-1})t^{-1}\) versus \(t\) should be constant and equal to \(k\). The classical approach by von Smoluchowski (see Appendix A) predicts the rate constant, \(k = 4 \pi Da\).

In reality, the situation is much more complex. Assuming that the reaction starts from a random, homogeneous distribution of particles, instead of from the semistationary distribution used by von Smoluchowski, the reaction rate at the start will be faster than his theory predicts. Second, the process of approaching the semistationary state is driven by the same diffusion process as the reaction itself, so that their time scales are at least not fully decoupled. Third, the particle concentration will show fluctuations. These aspects and their effect on the reaction rate have recently been studied in detail.\(^2\) For the case of infinite reactivity (i.e., the reaction between particles is only diffusion limited, and not hindered by energetic or geometric barriers), the limiting case of very small reaction times can be solved analytically,
where $D'$ is again the relative diffusion constant of the reacting particles, equal to $2D$, and $t$ is the time since the start of the reaction of the particles, that are assumed to initially be randomly distributed.

III. SIMULATION

The simulation setup is straightforward. For the simulation of the diffusion-controlled second-order chemical reaction, $2A \rightarrow B$, a number of $10^5$ spheres of radius 0.5 are placed randomly in a cubic simulation box with periodic boundary conditions. We chose the linear dimensions of the box equal to 215.44, so that the starting value of the number concentration of the particles is 1/100 per cubic length unit (their volume fraction 0.52%). The diffusive behavior of the particles is simulated by the standard Brownian Dynamics algorithm (see Sec. I). Only Brownian forces and friction are taken into account. The three-dimensional displacements of the particles per time step are determined by three random numbers, one for each of the dimensions ($x$, $y$, $z$), taken from a Gaussian distribution\textsuperscript{12} of width 1, and multiplied by $\sqrt{2D\Delta t}$. For the diffusion constant $D$ of the particles we chose $D=1$, and the time step was varied between 1 and $10^{-4}$, by factors of 10. The spheres (A particles) are assumed to interact instantaneously upon contact. Their reaction product, B, is assumed to be inert. For simplicity, reacted A particles are removed from the simulation box, so that effectively we simulate the second order annihilation reaction studied in Ref. 2.

The results of the naïve and corrected simulation methods are compared to check the effectiveness of our correction method. In the naïve method, every time step of all particles are given a random Brownian displacement, and the algorithm then checks whether two A particles have approached each other within the interaction distance $a$ (we took $a=1$, equal to twice the particle radius). In that case they react instantaneously. In the corrected method the same is done. However, if the particles show no overlap after the time step, they still may have interacted somewhere within the time step. This algorithm calculates this probability [see Eqs. (10), (11), and (22)] for all pairs of particles with a distance smaller than the cutoff distance $d$ (which was chosen such that interaction probabilities smaller than $10^{-3}$ were neglected). For this calculation the relative positions of the particles before and after the last time step, as provided by the naïve method, are used, as explained in Sec. II. Of course, particles can only react once; reacted particles cannot react anymore with another nearby particle.

IV. RESULTS

The number of particles strongly decreases over time. In Fig. 5 we plotted the simulation results for the number of A particles versus time, for four different values of the time step, $\Delta t$, in the naïve simulations ($1, 10^{-1}, 10^{-2}, 10^{-3}$) and for three different values of $\Delta t$ for the corrected simulation method ($1, 10^{-1}, 10^{-2}$). The most time-consuming naïve calculations could not be performed for the entire simulation period, but the results obtained are sufficient to draw conclusions. All simulations started with $10^5$ particles and all but one for the smallest time step continued until the number of A particles had become $<10^3$ (i.e., 1% of the starting value).

The effective initial particle number is lower than the starting value. Although the volume fraction of particles is small, about 4% of the initially randomly placed particles already overlap before the start of the simulation of their

![Graph showing simulation results](image-url)
reaction (see Appendix B). This causes the number of particles to decrease very fast at the first time step. Therefore one would introduce a large error in the calculation of \( k \) [see text near Eq. (24)], if one would take \( 10^2 \) as the initial number of particles. As the time steps are relatively small, we corrected for the fast initial decay of particles by using the second time step as the initial one. In Fig. 6, the resulting (apparent) reaction rate \( k \) is plotted, as a function of time.

*The reaction rate constant depends on time, in particular for short times.* This time dependence of \( k \), shown in Fig. 6, is no surprise, as the diffusion process responsible for the attainment of the "semistationary state" (see Appendix A) is at the same time responsible for the reaction itself. Von Smoluchowski’s separation of these processes in a fast and a slow one, which leads to a constant value for \( k \), is therefore (somewhat) artificial. For sufficiently small time steps (which means 0.1 for the corrected method and \( 10^{-2} \) for the naïve method) and shortly after the reaction start, the observed \( k \) values are higher than the von Smoluchowski value, albeit decreasing with time, in agreement with recent theory. ² Further down the reaction one sees, as expected, that all methods underestimate the number of interactions per time step and therefore the value of \( k \). In particular this is the case for the naïve method, in combination with large time steps.

The most accurate results for long reaction times (corrected, time step 0.1 and 0.01) still lie somewhat below the von Smoluchowski value. But for the decreasing time step the curves indeed seem to approach this value for long times, which are also in agreement with the prediction of recent theory. ²

*For very small simulation times, theory and simulations agree well.* As the starting configuration of spheres is chosen at random, the reaction proceeds very fast at the start, as described by Eq. (25). This prediction has been checked by means of simulations on a lattice, ² but never by BD simulations. Therefore we also performed a number of naïve simulations of the start of the reaction, using very small time steps (\( \Delta t = 10^{-6} \)), to simulate the behavior of the system near \( t = 0 \). The results for 16 simulations, repeated for different particle starting configurations, were averaged and corrected for the observed average initial number of overlapping particles (≈4053, which lies within the predicted boundaries for this number, see Appendix B). The results are plotted in Fig. 7. The agreement between simulations and theory is quite good.

*Convergence of the corrected method has improved substantially.* In Fig. 8 we present, in a log–log plot, the (absolute) error in the halflife time of the particles versus the chosen time step, according to the different simulation methods. We defined the halflife time as the moment at which 50 000 of the 100 000 particles have reacted. Both dashed lines have the indicated slope. Indeed the error in the results of the naïve method is proportional to the square root of the time step, while that in the corrected method is linear in the time step.

Irrespective of the chosen simulation method, and for any choice of the time step, one finds too high simulation outcomes for the halflife time. This is in agreement with the underestimation of the number of interactions in both methods, which is, of course, much more serious in the case of the naïve method.

The results of both methods converge to the same value for the halflife time, \( t_{1/2} = 2.324 \), as they should. Using this value and Eq. (24), we find \( k = 21.6 \), almost twice as high as the long-time, limiting value for \( k \). This is a consequence of the high initial reaction rate. We return to this point in the Discussion.

*Due to the incorporation of the full diffusion behavior, one can use large time steps.* In Fig. 8, we observe that for \( \Delta t = 0.1 \) the relative error in the corrected method is about 5%. This is very small, concerning that the average displacement is about as large as the interaction distance itself;
\sqrt{6D \Delta t} = 0.8a. The reason for this high accuracy is the incorporation of the full analytic solution (9) in combination with a sufficiently large cutoff distance \( d \). In particular for simulations that involve many operations per time step or large equilibration times it is imperative to be able to take as large time steps as possible, without sacrificing too much accuracy. In our method the discretization error of the finite step length compared to the particle dimensions is brought down to zero by using Eq. (9), provided the displacements are sufficiently smaller than the cutoff distance. Regarding the other fundamental length scale, the average distance between the particles, there is no essential problem, as the algorithm keeps track of all interparticle distances and the associated non-negligible interaction probabilities.

V. DISCUSSION AND CONCLUSIONS

"Naive simulation method" introduces slow convergence. Depending on the precise simulation conditions, Brownian Dynamics simulations of systems with hard interactions might bring about a very slow convergence behavior as a function of the chosen time step. This is the case for simulations in which the "state" of particles abruptly changes upon an interaction; chemical reactions, association
and absorption processes, and similar “events” resulting from a contact interaction between particles. In these simulations interactions are often identified in a naïve way, by searching for hard-body overlaps at discrete moments, e.g., after every time step. However, the actual motion of the Brownian particle is of a diffusive, “fuzzy” nature, of which the random linear displacement, taken proportional to the root of the time step, is a strong simplification. All possible interactions taking place in the intervals between the discrete time steps are neglected and consequently the number of “events” is seriously underestimated. For these cases the overall simulation error is proportional to the square root of the chosen time step.1

Corrected method is an extension of the existing one-dimensional approach. To correct for this slow convergence, we extended a method for the one-dimensional case, introduced by Öttinger,3 in which essentially the probability of the interaction—within the period of the previous time step—of nearby particles is calculated, using their positions at the beginning and at the end of that time step, as provided by the naïve algorithm. This probability is used to determine, also in a probabilistic way [see Eq. (8)], whether during the last time step an interaction has taken place. Since for the interaction of the particles only their relative position is relevant, the method to calculate this probability is based on the analytical solution for the diffusion of a single particle around an absorbing sphere, Eq. (9); survival of the particle during the period of a time step is equivalent to the conclusion that no interaction has taken place.

Corrected method converges much better. We used this correction for the BD simulation of the simplest second order chemical reaction between two equal particles, and showed that the results are quite satisfactory (see Fig. 8). The overall error of the corrected algorithm becomes proportional to the time step, instead of its square root, and, taking this dependence into account properly, the “prefactor” of the error is also much smaller. The incorporation of the full analytical solution (9) in the corrected method allows for taking large time steps and still obtaining relatively high accuracy. In particular for simulations with many operations per time step or large equilibration times this is an important advantage.13

Some authors use the large errors in the naïve method to arrive at desired outcomes. The results for the (apparent) k value and its associated half-life time \( t_{1/2} \) (see Figs. 6 and 8) explain to a large extent why some BD simulations with hard-body interactions have given outcomes very close to von Smoluchowski’s limiting prediction. On the one hand, using the naïve method, many interactions are not detected, which leads to an underestimate for \( k \) (Fig. 6, bold curves, long times). On the other hand, systems with hard-body interactions that govern reversible association reactions are far from the semistationary state, described by the von Smoluchowski limit (see Appendix A), and therefore show higher (apparent) \( k \) values (Fig. 6, bold curves, short times). Depending on the precise choice of the combination of parameters of the problem, both effects can be set to largely compensate each other, which is the reason for the “very good agreement” between most of the simulations of associating dumbbells presented in Ref. 14 and the limiting theory of von Smoluchowski. Concerning the large errors one should thus be very careful drawing quantitative conclusions from this and comparable work.

The method is easily adapted for additional forces. Extension of our method to simulations with other (deterministic) forces than the friction and the Brownian force can be done in a straightforward way. In this case, the displacement [see Eq. (4)] of the particle must be separated into two parts. The part caused by the effect of the deterministic forces, is, over the period of the time step, a straight line. This part of the displacement does not contain diffusive behavior. Only the Brownian part of the displacement should be corrected for “unnoticed interactions,” as described in this work. In every time step the simulation algorithm should therefore do the following. One starts by calculating the sum of the deterministic forces on the particles. The particles are then displaced according to these forces. Then one must check for interactions (= particle overlaps). The particles that have not interacted after this first move are given a Brownian displacement. Then one must again check for interactions. For the particles that still have not interacted, but which are close enough (a criterion governed by the cutoff distance), one must use the above correction (N.B.: only using the positions before and after the Brownian part of the displacement!), to finally determine, in the mentioned probabilistic way, which additional particle pairs must be considered to have interacted during the Brownian displacement. Performing these steps one must carefully keep track of all interactions, as, of course, every particle can react only once. Finally, one performs the appropriate action on all interacted particles, and the algorithm is ready for the next time step.

Uniform distribution suffices for Brownian displacements. In our simulations we used random numbers taken from a Gaussian distribution of the appropriate width to simulate the Brownian motion of the particles. Indeed this is not necessary, and one can gain some simulation time by taking the Brownian displacements from the uniform probability distribution \([-\sqrt{6D\Delta t}, \sqrt{6D\Delta t}]\). The correction for unnoticed interactions must of course be calculated in the prescribed way, using the Gaussian probability distribution for \(\psi_1\) in Eq. (8). For some simulations we tried this approach. It did not give essentially different results.

Corrected method consumes much less time. Clearly, the method described above gives a much better convergence of the simulation, even for relatively large time steps; at a time step of 0.1 our corrected simulation has already reached full convergence (within the error dictated by the inherent fluctuations in the system). Of course, the corrected simulations need (for the same value of the time step) more simulation time, as a major part of the CPU time is sacrificed to calculate the correction. To compare time consumption we compared simulations giving about the same accuracy; the corrected method with a time step of 0.01 and a “cutoff distance” of 1.63 (corresponding to a cutoff probability of \(10^{-3}\)), and the naïve case with time step \(10^{-3}\) (cf. Fig. 8). We found that our method is at least 25 times faster than the naïve method. Using a uniform probability distribution would still increase the calculation speed somewhat (see above). Besides, we expect that our correction algorithm
could still be "fine tuned" for efficiency. Most important, the speed-up factor increases with the desired accuracy; as for smaller time steps the cutoff distance can be taken smaller, so that the amount of particle combinations to be checked for "unnoticed interactions" decreases significantly. This part consumes most of the CPU time. Of course, while decreasing the time step to increase the accuracy, one has to set the cutoff error accordingly. Still, as one can check by means of Eq. (15), the cutoff distance decreases with decreasing time step. In the simulation presented here, the fluctuations in the particle concentration are of the order of percent (square root of the order of $10^4$ particles or less), which means that simulating more accurately would not give better results.

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APPENDIX A: VON SMOLUCHOWSKI'S CALCULATION OF THE REACTION CONSTANT $K$

A well-known way to calculate an approximate value for the reaction constant $k$ of the diffusion controlled chemical reaction, Eq. (22), the reaction rate of which is customarily described by Eq. (23), is by a simplified version of the approach of von Smoluchowski, who studied the association reaction of spherical gold particles. Von Smoluchowski assumed that during the reaction process the particles establish, relatively quickly, a smooth, more or less stationary concentration profile around each other. For this to be true, the time scale of reaching this "(semi)stationary state" is assumed much shorter than the time scale of the reaction itself. Von Smoluchowski therefore set this time scale to zero. To then calculate the semistationary concentration profile around an arbitrarily chosen central particle, fixed in the origin, he solved the diffusion equation in spherical coordinates using a mean field approximation,

$$0 = \frac{\partial c}{\partial t} = D \Delta c = \frac{D'}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right). \quad \text{(A1)}$$

According to the above assumption, the left-hand term is set to zero. $D'$ is the diffusion constant of the mobile, other particles, relative to the fixed, central particle. As the particles react upon contact, the concentration of the neighboring particles is zero at the interaction distance $a$. Far away from the central particle the concentration must be equal to the bulk concentration $c_\infty$. Using these boundary conditions, the remaining Laplace equation can readily be solved, to give

$$c(r) = c_\infty \left[ 1 - \frac{a}{r} \right]. \quad \text{(A2)}$$

The total flux, $j$, of particles that reach the boundary of the central particle, is

$$j(r) = -D' \frac{\partial c}{\partial r} \bigg|_{r=a} \cdot [4 \pi r^2]_{r=a} = c_\infty D' \left( \frac{a}{r^2} \right)_{r=a} \cdot 4 \pi a^2 = 4 \pi a D' c_\infty. \quad \text{(A3)}$$

This flux is equal to the number of particles per second that reacts with the central particle. Note that, due to continuity, the number of particles per unit of time that passes any spherical shell around the central particle is the same.

This result must be adapted to describe a chemical reaction. We use that the concentration $c_\infty$ is established by the presence of the total number of $A$ particles, $N$, in the volume $V$. All particles contribute equally to the reaction rate. A factor $1/2$ is needed to correct for double counting. The diffusion constant, $D'$, to be used for the mean field approach, is the effective diffusion constant of two particles diffusing with respect to each other. This is given by twice the diffusion constant $D$ of an $A$ particle. Then the total number of reactions (per unit of volume per unit of time) is given by

$$r = \frac{1}{2} \cdot 4 \pi a (2D) c_\infty \frac{N}{V} = 4 \pi a D c_\infty = k c^2, \quad \text{(A4)}$$

leading to a value for the rate constant, $k = 4 \pi D a \approx 12.56$, for the chosen values of the parameters.

APPENDIX B: INITIAL OVERLAP OF RANDOMLY PLACED A PARTICLES

In a random distribution of $N = 10^5$ particles with excluded volume $a = 4 \pi a^3$, between them, placed in a volume $V = 10^7$ the probability that none of them overlaps with one of the other, is given by

$$\prod_{k=0}^{N-1} \left( 1 - \frac{k}{V} \right)^2 < 10^{-300}. \quad \text{(B1)}$$

Therefore, even at the low (1%) particle concentration used in our simulations, we may certainly not neglect the number of particles that overlap after the random placement in the simulation domain, before the actual simulation has started. We study the interacting particle pairs, and neglect the (much lower) number of higher order overlaps. If $p$ denotes the probability that two randomly chosen particles with interaction distance $a$ overlap,

$$p = \frac{1}{V} \approx 4.189 \times 10^{-7} \quad \text{(B2)}$$

and neglecting the loss of excluded volume caused by the overlap of some of the particles, the probability that a chosen particle does not overlap with any of the $N-1$ others is

$$1 - p = 0.9590. \quad \text{(B3)}$$

Therefore the probability $P$ that a chosen particle does overlap with one of the others, is given by

$$P = (1 - p)^{N-1} \approx 0.04102. \quad \text{(B4)}$$

The average number of particles overlapping with one of the others is therefore

$$N \cdot P = N \cdot (1 - ((1 - p)^{N-1})) \approx 4.102 \times 10^3, \quad \text{(B5)}$$

and the estimated standard deviation in this number is equal to

$$\sqrt{N \cdot P \cdot (1 - P)} \approx 63. \quad \text{(B6)}$$
Using 95% confidence intervals, the number of particles in our simulation having no initial overlap should lie between 95,772 and 96,024.


4 For elaborate comments on the applicability of this expression see also Ref. 3.


11 In Ref. 10, pp. 623–627.


14 B. H. A. A. van den Brule and P. J. Hoogerbrugge, J. Non-Newtonian Fluid Mech. 60, 303 (1995). The parameters in this work seem at first sight to be chosen more or less arbitrarily. In fact they are chosen such that the scaled time step is 0.082, leading (see Fig. 8) to $t_{1/2} = 4.14$. This is far away from the converged value, 2.32, but gives $k = 12.1$ [see Eq. (24)], rather close to the von Smoluchowski limit of 12.6, to which the authors their result compared and which was obviously considered the “desired outcome.”