

Coarse-graining in suspensions of charged nanoparticles*

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Abstract: A coarse-grain description of nanocolloidal suspensions in the presence of an added salt is presented here. It enables us to simulate trajectories of the nanoparticles from effective functions that depend on average densities of salt ions. In practice, the ion-averaged effective potential is used as input of a Brownian dynamics (BD) simulation. This potential may be derived by various methods, ranging from purely analytical to fully numerical ones. For the description of dynamical properties, this simulation also requires an effective diffusion coefficient that must be calculated or experimentally determined, and that accounts for the effects of microions on the mobility of the nanoparticles. The different versions of our coarse-graining procedure are applied to the case of a maghemite suspension, for which an explicit description of all ions would be very time-consuming.

Keywords: nanocolloidal suspensions; coarse-grain description; Brownian dynamics; microions; nanoparticles; coarse-graining; maghemite; maghemite suspension.

INTRODUCTION

Calculating the transport coefficients of charged nanocolloidal particles is not an easy task, not only because those interactions are intense and long-ranged, but also because the number of solvent molecules and salt ions (microions) which interact with the colloidal particles (macroions) is huge. Nevertheless, what simplifies the description of those suspensions is the gap of time scale on which the different kinds of particles reach equilibrium. On the time scale of macroions, the microions equilibrate instantaneously, and on the time scale of microions, the solvent molecules equilibrate instantaneously. It is therefore possible to use equilibrium densities of the fastest particles in nonequilibrium descriptions of the slowest ones. In particular, one may derive intermacroion potentials thanks to microion densities equilibrated for a given intermacroion distance. Such reduction of the degrees of freedom of the system is often referred to as coarse-graining [1–3]. Those multiscale descriptions are especially interesting to carry out simulations: longer scales and/or bigger systems can then be explored because the number of particles is considerably reduced.

The derived intermacroion potential is called potential of mean force (PMF). Ion-averaged PMF may be derived from various theoretical [4–9] or experimental methodologies [10–12].

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Furthermore, in order to derive the transport coefficient of the macroions, the role of the microions on the *dynamics* of macroions should also be rigorously included. A number of works have treated this problem [13–17]. So far, no simple and fast simulation procedure was available to study the influence of salt on the dynamical properties of colloidal systems. Nevertheless, as far as charged particles are studied in the framework of the continuous solvent model, the so-called electrostatic relaxation effect (which is due to the forces that tend to restore the local electroneutrality when charged particles move) is known to lower the mobility of particles, and thus should be carefully included in a coarse-grained description. The actual methodologies are not sufficient to study this effect both with a reasonable computing time and with the same level of approximation as the works devoted to static properties.

In a previous paper, we presented a new rigorous coarse-graining procedure, based on the Brownian dynamics (BD) simulation method [18]. This simulation only describes the motions of nanoparticles but takes into account the influence of the smaller solutes on both their static and dynamic properties. The first scale of description is based on the continuous solvent model, and requires the knowledge of the radii, the bare charges, and the infinite dilution diffusion coefficients of all the solute species. The procedure enables us to link those parameters to the effective properties of the macroions. It is easy to implement: It only requires the calculation of the PMF and of the self-diffusion coefficient of a unique macroion in the presence of small ions (or “effective diffusion coefficient”).

In the present paper, we compare different coarse-graining procedures to obtain the PMF between iron oxide (maghemite) nanoparticles, and we calculate the effective diffusion coefficient of those particles. Those suspensions, also named ferrofluids, exhibit interesting magnetic properties used in an increasing number of applications [19–22]. Several dynamical quantities are available for those suspensions, but not for all of them: One can easily access the electrical conductivity [12] and the diffusion coefficient of a diluted suspension. Since maghemite nanoparticles are highly charged (around +400 in our sample), their study by standard BD simulations [23] with the full number of counterions and coions is almost impossible. The use of a coarse-grained scheme is thus the unique way to understand the dynamics of those nanoparticles without drastic simplifications, and to compute the diffusion coefficient of maghemite particles in concentrated suspensions. The paper is organized as follows: in the first part, we present various ways to obtain a potential between charged nanoparticles, and we compare these methods in the case of a maghemite suspension. Then, we present the methods used to simulate the motion of the nanoparticles and to compute their diffusion coefficient.

STATIC COARSE-GRAINING

Some of the most frequently used methods to derive effective pair potentials between macroions are recalled in this section and applied to the case of maghemite particles in aqueous suspension. These methods may be split into two classes. The first class of methods requires the introduction of adjustable parameters that may be obtained by a comparison of analytical theories and experiments: the theory gives a formula whose parameters are fitted to recover the experimental data. Those methods are particularly suited for highly charged macroions, when the microions may be easily separated into bound and free ones. The second class of treatment is fully numerical, which enables us to avoid approximations but reduces the range of applications to systems containing a moderate number of counterions (i.e., for a macroion charge smaller than a few hundred). In all cases, the particles are described in the framework of the continuous solvent model.

Effective potentials at the mean field level

Simple analytical expressions for the ion-averaged potentials can be obtained provided the mean field Poisson–Boltzman (PB) equation is linearized, which implies that the electrostatic potential between the ionic particles is less intense than thermal energy. This leads to two successive coarse-graining

steps: first, the macroion and the microions that are strongly bounded to its surface are grouped within a *renormalized* macroion [24]. The charge of the resulting particle (the effective charge Z_{eff}) is then smaller than the bare charge of the macroion, and its effective radius a_{eff} is bigger than the bare radius. Second, the microions that weakly interact with the macroion are coarse-grained by integrating the linearized PB equation. The electrostatic potential around the macroion is then expressed as

$$\frac{\phi(r)}{k_{\text{B}}T} = L_{\text{B}} Z_{\text{eff}} \frac{\exp(\kappa a_{\text{eff}}) \exp(-\kappa r)}{1 + \kappa a_{\text{eff}}} \frac{1}{r} \quad (1)$$

where r is the distance to the center of the macroion, L_{B} is the Bjerrum length ($L_{\text{B}} = \frac{e^2}{4 \epsilon_0 \epsilon_r k_{\text{B}}T}$) and κ^{-1} is the Debye length. In order to get the intermacroion potential, the electrostatic potentials around the two macroions are linearly superimposed. The integration of the stress tensor (electrostatic and kinetic contributions) leads to the Derjaguin–Landau–Verwey–Overbeek (DLVO) PMF between two macroions [5,25]

$$\frac{U_{\text{DLVO}}(r)}{k_{\text{B}}T} = L_{\text{B}} Z_{\text{eff}}^2 \frac{\exp(2\kappa a_{\text{eff}}) \exp(-\kappa r)}{(1 + \kappa a_{\text{eff}})^2} \frac{1}{r} \quad (2)$$

where r is the intermacroion distance. The knowledge of an effective potential reduces then to the knowledge of the effective charge and of the effective radius of the macroion.

From the experimental point of view, those effective parameters can be adjusted to recover the macroion/macroion density autocorrelation functions, obtained from scattering data, or they may be linked to the osmotic pressure or other static quantities [11]. Interestingly, they may also be deduced from the measurement of transport coefficient, with electrophoresis, dielectric spectroscopy, acoustophoresis, or electrical conductivity [11,26]. Among these quantities, the electrical conductivity is the one for which experimental determinations are the oldest and the most precise. Moreover, the ideal value of the electrical mobility of the solutes is directly proportional to the square of their charge, and the effective charge is closely linked to the mobility of the colloidal particle. In our group, a robust method has been developed to determine the effective parameters of charged nanoparticles from conductivity measurements, by using an analytical transport theory based on the mean spherical approximation (MSA) to interpret the data [27–31]. Contrary to the DLVO treatment, this theory accounts for the size of microions. As shown in previous papers from Durand-Vidal et al., it allows the determination of the effective charge and the effective radius of charged nanoparticles with a good accuracy. This methodology has been carefully compared to other experimental tools and to BD simulations [17,27,32].

When the systems are not easy to study experimentally, an alternative approach is to derive numerically the effective charge and radius. When it is not linearized, the PB equation provides a reasonable estimate of the electrostatic potential close to the macroions surface. This potential is related to the microion density profile around the macroion. From this distribution, one can link the effective charge to the effective radius. Generally, the procedure used to obtain the couple of values ($Z_{\text{eff}}, a_{\text{eff}}$) is to fit the nonlinearized PB electrostatic potential to the linearized PB potential. It is also possible to solve the PB equation in bispherical coordinates, considering the volume of the two interacting macroions [33], and to fit the resulting PMF to the DLVO one. These strategies are valid as long as ionic correlations lead to negligible deviations from the PB theory, which may not be the case in systems containing nanoparticles [34,35].

Effective potentials from simulations

Computer simulations present a helpful alternative tool to extract “exact” results for a given model. Monte Carlo (MC) simulations are particularly suited for systems containing hard spheres, and they may be used either to derive the effective parameters, or to calculate directly the effective potential. When the structural charge of the macroions is moderate, it is possible to derive directly the PMF between the particles without using any adjustable parameters but the size and the bare charge of ions. The configurations of the microions are equilibrated according to the Metropolis algorithm [36], so that they

are canonically distributed. The ions interact through the pair potential: $V_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r} \frac{1}{r_{ij}}$, where ϵ_0

is the permittivity of the vacuum, ϵ_r is the relative permittivity of water (taken equal to 78.25), e is the elementary charge, Z_i is the charge of particle i , and r_{ij} is the distance between particles i and j . When the primitive model of electrolyte is assumed, a hard potential $V_H(r_{ij})$ is added, which is infinite in the particles and zero outside. The forces are averaged over the ion configurations for a set of intermacroion distances. The computed mean force includes two contributions in addition to the direct Coulombic interaction between the macroions: the electrostatic interactions of the macroions with the surrounding ions, plus an osmotic term or collision force. The later term arises from the compression of the ionic cloud in between the macroions, and corresponds to the kinetic contribution to the DLVO potential. The mean force is then integrated over distances to get the PMF. A complete description of the procedure may be found elsewhere (see, e.g., [35,37]).

Comparison of the different procedures in the case of a maghemite suspension

The previous methodologies are applied to determine the effective charge and the effective radius of maghemite nanoparticles ($\gamma - \text{Fe}_2\text{O}_3$) in solution. The synthesis protocol is described in ref. [38]. These colloidal particles are suspended in water in the presence of nitric acid HNO_3 , at $\text{pH} = 3.0$ and $T = 298 \text{ K}$. The packing fraction is 1.5 %. Under those conditions, the bare surface charge of these particles is experimentally estimated at $0.14 \text{ C}\cdot\text{m}^{-2}$ by proton titrimetry [39], and the mean radius of the particles has been estimated at 6.0 nm by atomic force microscopy. High-precision conductivity measurements are conducted thanks to a homemade conductivity cell with platinum electrodes [32]. The temperature of the experimental cell is precisely controlled, so that the electrical conductivity is measured with a relative precision lower than 0.1 %. The conductivity computed from the MSA treatment corresponds to the experimental value for an effective charge of 169 and for an effective radius of 7.1 nm.

PB calculations and MC simulations have been carried out to determine a theoretical value of those effective parameters. The PB equation was solved in spherical symmetry to obtain the radial distribution function of microions. The macroion is infinitely diluted in a solution whose Debye length corresponds to the experimental one (7.6 nm). Consistently, the simulation box for MC contains one macroion. The box length and the number of counterions are chosen to reproduce the experimental conditions of pH and volume fraction. As shown in Fig. 1, the PB and MC numerical methods lead to very close structures of the ionic double layer around the colloids, which means that the PB treatment is valid for this system. The DLVO potential fits well the PB potential for high distances for an effective charge of +104 and for an effective radius of 7.9 nm.

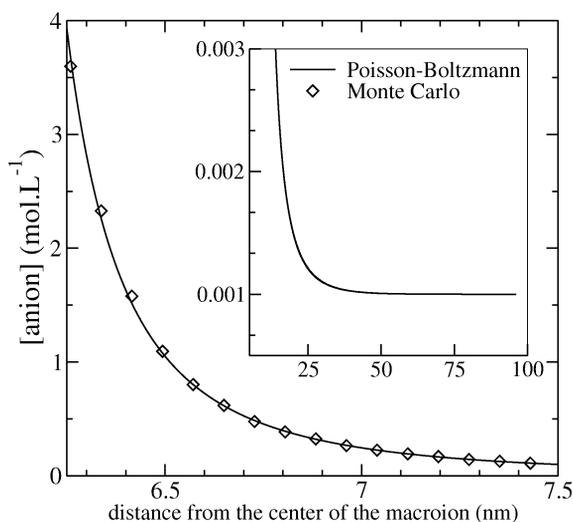


Fig. 1 Concentration profile of the HNO_3 anion around an isolated macroion as a function of the distance between the anion and the center of the macroion. The line is the PB results, and is obtained up to 40 nm, while the diamonds are the MC results, computed up to 7.5 nm only.

We finally used the fully numerical methodology to derive the ion-averaged potential between two maghemite nanoparticles. All the simulations are carried out in the canonical (NVT) ensemble with the temperature set to 298 K. The macroions are symmetrically placed along the room diagonal of a cubic simulation box with periodic boundaries. Their concentration is sufficiently low so that the ion distributions are not influenced by the periodic images of the macroions [18,35]. In such conditions, a cut-off of electrostatic interactions is justified, yielding identical results with bigger box lengths. The force is averaged over 10^9 steps, so that the uncertainty of the calculations does not exceed 3 %. The PMFs obtained by the three methods are depicted in Fig. 2.

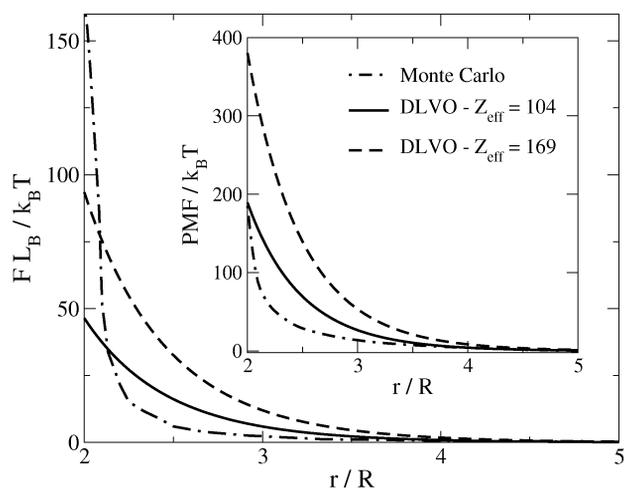


Fig. 2 Microion-averaged potentials of mean force between two maghemite particles at $\text{pH} = 3$. The straight line and the dashed line are the DLVO potential for values of the effective charge of 104 and 169, respectively, and the dot/dash line is the exact MC potential. R is the radius of the maghemite particle, equal to 6 nm.

Discussion

The mean forces obtained by the different methodologies are different, which is often the case with nanoparticles for which the condensation is not as clear as with micrometric particles. The limitation of the results may have three reasons: (i) the model misses non-negligible interactions; (ii) the approximations of the theory are not valid; and (iii) the results contain experimental or numerical systematic errors. The direct MC derivation avoids the errors ii and iii. It provides then the target PMF if the model is correct. The shape of this potential is indeed not very close to a DLVO potential for short distances, which indicates that the approximations of this theory are not valid in that range. Nevertheless, the primitive model may be not sufficient in treating the interactions at the surface of the nanoparticles, and neglects both image charge effects [40] and dispersion interactions [41], which can be important. The PB theory misses correlations between ions, but the later does not seem to be important, as mentioned earlier. Nevertheless, while correlations are negligible around isolated colloid, when two macroions get close to each other, the strength of the electrostatic field becomes so intense that the ions are very concentrated and thus very correlated. The superposition approximation is also critical when the nanoparticles are close. This may explain the difference of behavior for short intermacroion distances. It should be added that this difference happens for potentials that are much more repulsive than thermal energy, and thus that it should have little impact on the dynamical properties of the particles. Furthermore, it should be noticed that the method based on the conductivity measurements is sensitive to another weakness of the model: it is possible that a part of the electrostatically condensed counterions participates to the electric current, which would lead to an overestimation of the effective charge by this method.

The choice of the method used to calculate the PMF between nanoparticles must be guided by the aim of the study: If the goal is to test whether the model (in this case, the primitive model) well describes the system, then the fully numerical method seems the more appropriate. If the potential leads to the right transport coefficient, then this primitive model is sufficient. Conversely, the use of experimental data to adjust a parameter may enable one to erase the lacks of details of a model. Even though the physics of the system is not well described, the obtained potential is the one that should lead to the more trustable transport coefficients.

DYNAMIC COARSE-GRAINING

Once the intermacroion potential is known, the trajectories of the macroions can be simulated with the appropriate equation of motion. One must then “coarse-grain” the dynamical effects of microions.

Principle of Brownian dynamics simulations

In BD simulation, the trajectories of the particles are obtained by the iterative use of a stochastic equation of motion. When hydrodynamic interactions are neglected, the displacement of N particles included in the simulation box from time t to time $t + \delta t$ is then [42]

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \frac{D^\circ}{kT} \mathbf{F}(t) \delta t + \mathbf{R} \quad (3)$$

where T is the temperature, k is the Boltzmann constant, D° is the self-diffusion coefficient of the particles at infinite dilution, δt is the time increment, \mathbf{r} is the $3N$ -dimensional configuration vector, and \mathbf{F} is the total force acting on the particles at the beginning of the step. \mathbf{R} is a random displacement, chosen from a Gaussian distribution with zero mean, $\langle \mathbf{R} \rangle = 0$, and variance $\langle \mathbf{R} \mathbf{R}^T \rangle = 2D^\circ \delta t$.

Once the trajectories of particles are computed, their self-diffusion coefficient D may be obtained from the following expression, which depends on the autocorrelation function of the forces [23]

$$D = D^\circ - \frac{1}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{F}(t) \mathbf{F}(0) \rangle dt \quad (4)$$

Coarse-grained Brownian dynamics

To simulate the dynamical behavior of solutions containing nanoparticles interacting with smaller solutes, we propose a coarse-grained procedure, based on the separation between the time scales relative to the two types of particles. The goal of this method is to simulate the trajectory of the macroions that interact through the effective potential averaged on the microion configurations. In particular, the macroions are submitted to a friction from the microions that must be included in the equation of motion. The passage between the “microscopic” level—which takes into account the microions explicitly—and the coarse-grained level must be done with a special care.

To perform a BD simulation *at the coarse-grained level of description*, one can use the Ermak algorithm (3) given above with the effective force \mathbf{F}_{eff} and a new effective parameter D_{eff}°

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \beta D_{\text{eff}}^\circ \mathbf{F}_{\text{eff}}(t) \delta t + \mathbf{R}_{\text{eff}} \quad (5)$$

with $\langle \mathbf{R}_{\text{eff}} \mathbf{R}_{\text{eff}}^T \rangle = 2D_{\text{eff}}^\circ \delta t$. Then, the self-diffusion coefficient D of the macroion can be determined by using eq. 4. At the coarse-grained level of description, this equation reads

$$D = D_{\text{eff}}^\circ - \frac{1}{3} \int_0^\infty \left(\frac{D_{\text{eff}}^\circ}{kT} \right)^2 \langle \mathbf{F}_{\text{eff}}(t) \mathbf{F}_{\text{eff}}(0) \rangle dt \quad (6)$$

Once again, the problem reduces thus to the determination of an effective parameter, here the effective diffusion coefficient D_{eff}° . An implicit equation of the effective diffusion coefficient is obtained if the motions of macroions and microions are assumed not to be correlated. In that case, *at the microscopic level of description*, the total force \mathbf{F} acting between macroions may be written as the sum of two contributions

$$\mathbf{F} = \mathbf{F}_{\text{eff}} + \mathbf{f} \quad (7)$$

with \mathbf{f} being a small fluctuating force that corresponds to the fast motion of the microions and that varies on the time scale of the microions. \mathbf{F} and \mathbf{f} are not correlated ($\langle \mathbf{F}_{\text{eff}}(t) \mathbf{f}(t') \rangle = \langle \mathbf{F}_{\text{eff}}(t) \rangle \langle \mathbf{f}(t') \rangle = 0$), in the limit where the time scales relative to microions and macroions are separated. The self-diffusion coefficient of the macroion given by eq. 4 becomes

$$D = D^\circ - \frac{1}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{F}_{\text{eff}}(t) \mathbf{F}_{\text{eff}}(0) \rangle dt - \frac{1}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{f}(t) \mathbf{f}(0) \rangle dt \quad (8)$$

Then, by identifying eq. 6 with eq. 8, the following equation is obtained

$$D_{\text{eff}}^\circ = D^\circ - \frac{1}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{f}(t) \mathbf{f}(0) \rangle dt - \frac{1}{3} \int_0^\infty \frac{D^{\circ 2} - D_{\text{eff}}^{\circ 2}}{(kT)^2} \langle \mathbf{F}_{\text{eff}}(t) \mathbf{F}_{\text{eff}}(0) \rangle dt \quad (9)$$

This implicit definition of D_{eff}° may be used to derive D_{eff}° as explained in the next section. All the details of the procedure may be found in ref. [18].

Determination of the effective diffusion coefficients

In practice, a first set of BD simulations should be performed with a single macroion in the simulation box and the appropriate number of microions. The main characteristic of those simulations is to avoid all fluctuations on the time scale of the macroions because $\mathbf{F}_{\text{eff}} = \mathbf{0}$ and $\mathbf{F} = \mathbf{f}$. Consequently, the self-diffusion coefficient D computed from those simulations by using eq. 4 is equal to

$$D = D_{\text{eff}}^* = D^\circ - \frac{1}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{F}(t) \mathbf{F}(0) \rangle dt \quad (10)$$

where $\mathbf{F}(t)$ is the sum of all forces exerted on the macroion at time t .

The effective coefficient D_{eff}^* may also be measured by dynamic light scattering [10]. The spectra are indeed usually obtained at a low volume fraction in colloid (typically below 0.2 %), at a given ionic strength. Nevertheless, those measurements are very sensitive to the polydispersity of the suspensions, and the signals of the smallest nanoparticles are frequently hidden by the signal of the biggest ones.

Then, the PMF and the effective diffusion coefficient D_{eff}^* are used as input data of a BD simulation code. The autocorrelation function of the effective force is calculated, and D_{eff}° is obtained from

$$D_{\text{eff}}^\circ = \frac{1}{2} \left(\alpha + \left\{ \alpha \left[\alpha - \frac{4}{3} \int_0^\infty \left(\frac{D^\circ}{kT} \right)^2 \langle \mathbf{F}_{\text{eff}}(t) \mathbf{F}_{\text{eff}}(0) \rangle_{D=D_{\text{eff}}^*} dt \right] \right\}^{0.5} \right) \quad (11)$$

with

$$\alpha = D_{\text{eff}}^* \left[1 - \frac{1}{3} \int_0^\infty \frac{D_{\text{eff}}^*}{(kT)^2} \langle \mathbf{F}_{\text{eff}}(t) \mathbf{F}_{\text{eff}}(0) \rangle_{D=D_{\text{eff}}^*} dt \right]^{-1} \quad (12)$$

In principle, the modeling of the macroions can be as sophisticated as needed at the microscopic level of description (including van der Waals dispersion forces or charge distributions for instance). In particular, our procedure provides a fast tool to test the effects of ion specificity on transport properties.

DIFFUSION COEFFICIENT OF A MAGHEMITE NANOPARTICLE

First, the diffusion coefficient D_{eff}^* is calculated thanks to BD simulations with a single macroion in a salt, in the same conditions of temperature and concentrations as for the MC simulations described in the section “Static coarse-graining”. The infinite dilution self-diffusion coefficient of the maghemite nanoparticle is computed thanks to the Stokes–Einstein law with non-slipping boundary conditions, for a radius of 6 nm

$$D^\circ = \frac{kT}{6\pi\eta R} \quad (13)$$

The total simulation time is of 10 ns. We obtain a value of $\frac{D_{\text{eff}}^*}{D^\circ} = 0.79$ with an uncertainty of 0.02.

Second, the effect of the PMF on the diffusion coefficient is studied with the three potentials obtained in the section “Static coarse-graining”: The PMF obtained from MC simulations, the DLVO PMFs obtained first from the electrical conductivity ($Z_{\text{eff}} = 169$ and $a_{\text{eff}} = 7.1$ nm), and second by solving the nonlinearized PB equation ($Z_{\text{eff}} = 104$ and $a_{\text{eff}} = 7.9$ nm). Two volume fractions are considered, that correspond to average intermacroion distances of 4.71R (4 %) and 3.74R (8 %), where R is the ra-

dus of the macroions. The simulation box contains 100 maghemite nanoparticles. The total simulation time is of 100 ns for each PMF and each volume fraction. The results are presented in Table 1.

Table 1 $\frac{D}{D_{\text{eff}}^{\circ}}$ for the different PMFs obtained in the section “Static coarse-graining” for two volume fractions ϕ .

PMF	MC		DLVO ($Z_{\text{eff}} = 104$)		DLVO ($Z_{\text{eff}} = 169$)	
ϕ	4 %	8 %	4 %	8 %	4 %	8 %
$\frac{D}{D_{\text{eff}}^{\circ}}$	0.88	0.81	0.86	0.74	0.62	0.37

For a volume fraction of 4 %, the diffusion coefficients obtained from the coarse-grained simulations are of the same order of magnitude in the three cases, even if the three PMFs are different (see Fig. 2). In particular, the two PMFs obtained by fully numerical methods lead to the same value of

$\frac{D}{D_{\text{eff}}^{\circ}}$ within the statistical error of the results. This shows that the limitations of the PB treatment do

not lead to inadequate dynamical properties for this moderate volume fraction. This result can be explained by considering that the particles only explore parts of the PMF for which the PB treatment is valid. However, for a volume fraction of 8 %, the influence of the mean forces on the diffusion properties is more pronounced. Indeed, the nanoparticles are more likely to explore short intermacroion distances, for which the values of the mean forces are much more different.

CONCLUDING REMARKS

We have presented a new coarse-graining approach leading to a one-component description of suspensions of charged nanoparticles in a salt. This method relies on the assumption that the suspension can be well described with pair potentials between the nanoparticles and an adequate diffusion coefficient. Two steps are required: (i) the derivation of the PMFs between the nanoparticles, averaged on the configurations of the smaller solutes; and (ii) the derivation of an effective diffusion coefficient. For each step, the effective quantities may be determined either by a simulation that directly links a given model to a value of the transport coefficient, or by an experimental approach if the model is not accurate or if a simulation is not possible. We applied such methodology for the study of maghemite particles, in order to understand the role of electrostatic interactions on the dynamics of the particles. There are several hundred counterions per maghemite particle, and thus the use of a simulation of all the ions of the system would not be possible in sufficiently long time scales. The computed diffusion coefficients depend on the method used to determine the PMF. The experimental observation of the diffusion coefficient should enable one to test whether this difference comes from a lack of the primitive model that is used to describe the solutes, or if it comes from a limitation in the interpretation of the experimental electrical conductivity. In order to answer this question, the dynamical coarse-graining step should rigorously include a treatment of hydrodynamic interactions in order to compute the electrical conductivity of the suspension. Indeed, hydrodynamic interactions have a stronger influence on the electrophoretic mobility than on the diffusion coefficient, and neglecting those interactions leads to nonrealistic values of the conductivity. A rigorous coarse-graining of those interactions would then lead to a fast but realistic methodology to study all kinds of charge-mediated phenomena in nanocolloidal suspensions.

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