

Computer Simulation of Electrokinetics in Colloidal Systems

R. Schmitz¹, V. Starchenko¹, and B. Dünweg^{1,2,a}

¹ Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

² Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

Abstract. The contribution gives a brief overview outlining how our theoretical understanding of the phenomenon of colloidal electrophoresis has improved over the decades. Particular emphasis is put on numerical calculations and computer simulation models, which have become more and more important as the level of description became more detailed and refined. Due to computational limitations, it has so far not been possible to study “perfect” models. Different complementary models have hence been developed, and their various strengths and deficiencies are briefly discussed. This is contrasted with the experimental situation, where there are still observations waiting for theoretical explanation. The contribution then outlines our recent development of a numerical method to solve the electrokinetic equations for a finite volume in three dimensions, and describes some new results that could be obtained by the approach.

1 Introduction

The electrophoretic motion of charged colloids in an external electric field is a more than hundred years old classical problem [1–3]. To introduce the notation, let us consider a system of colloidal spheres with volume fraction Φ , each of which has a radius R and a charge Ze , where e denotes the absolute value of the elementary charge. The system is at absolute temperature T (or thermal energy $k_B T$, where k_B is Boltzmann’s constant), and the surrounding fluid is characterized by the shear viscosity η and the dielectric constant ε . The colloidal particles are surrounded by ions of different species i . For each species, the corresponding concentration (particle number per unit volume) is c_i , and the ionic charge is $z_i e$. Additional important ionic properties are the ion radii a_i and the collective diffusion coefficient of species i , D_i . Finally, an external electric field \mathbf{E}_{ext} is applied. In the linear-response regime (weak driving field) the average drift velocity of the colloidal particles \mathbf{u} is then given by

$$\mathbf{u} = \mu e \mathbf{E}, \quad (1)$$

where μ is the electrophoretic mobility. It should be noticed that this definition is tailored to the needs of experiments: The charge in Eq. 1 is e and not Ze , because

^a e-mail: duenweg@mpip-mainz.mpg.de

the actual charge of the sphere may be difficult to measure, and the driving is characterized by the electric field and not the local force — the latter is difficult if not impossible to be measured directly.

An important length scale in electrostatic problems is the so-called Bjerrum length l_B ,

$$l_B = \frac{e^2}{4\pi\epsilon k_B T}, \quad (2)$$

and hence we can define the so-called reduced (dimensionless) mobility via a Stokes law based on the length scale l_B :

$$\mu_{red} = \mu 6\pi\eta l_B. \quad (3)$$

The electrophoretic motion is therefore, in general, the result of a complicated interplay of electrostatics (effective colloid-colloid interactions, with possible importance of multibody and charge-charge correlation effects), solvent dynamics (which may however be safely described by low Reynolds number hydrodynamics), and the dynamics of the charge clouds, which constitute important non-trivial degrees of freedom in their own right. In its full generality, the problem has therefore not yet been solved, neither analytically nor numerically, where in the latter case the reason is the computational complexity that is still a challenge even for today's computers. On the other hand, there is great experimental interest to understand the dependence of μ on the various system parameters, since this can help to estimate important colloid parameters like Z or R . Some understanding can however be obtained from simple limiting situations.

The conceptually simplest case is a single colloidal sphere at infinite dilution in a salt-free environment. Since all counterions are infinitely far away, one may apply Stokes' law to obtain

$$\mu_{red} = Z \frac{l_B}{R} =: \hat{Z}. \quad (4)$$

In this situation ("Hückel limit"), we may also introduce the concept of a zeta potential ζ , which is the electrostatic potential between the surface of the colloid and infinity, in the absence of driving:

$$\zeta = \frac{Ze}{4\pi\epsilon R} = Z \frac{l_B}{R} \frac{k_B T}{e} \quad (5)$$

or

$$\zeta_{red} := \frac{e\zeta}{k_B T} = Z \frac{l_B}{R} = \mu_{red}. \quad (6)$$

We now study the opposite limit, where we assume that the salt concentration is rather large. From the point of view of electrostatics, it is clear that this implies strong electrostatic screening, with a Debye screening length [3] $l_D = \kappa^{-1/2}$ and screening parameter κ

$$\kappa^2 = 4\pi l_B \sum_i z_i^2 c_i. \quad (7)$$

In the limit of high salt concentration, it does not matter if the small concentration of counterions is included in this definition or not. However, when considering Poisson-Boltzmann theory in a finite volume, and its linearization (which assumes that the concentrations c_i differ not much from their volume-averaged values), it becomes clear that in the general case the definition of κ^2 should comprise all ionic species, including the counterions.

An important observation for electrophoresis is the notion of hydrodynamic screening [4]. The process is fundamentally different from sedimentation, which is the motion

of colloids driven by an external gravitational field, which in turn is directly related to the tracer diffusion of the particles, as a result of the fluctuation-dissipation theorem. In this latter case, the surrounding flow field decays like $1/r$, i. e. the hydrodynamic interaction is unscreened. This is a result of the fact that the force density (the “source” of the flow field) has a nonzero component at zero wavenumber. Conversely, in case of electrophoresis the force density vanishes at zero wavenumber, since the total force on the positive charges exactly compensates the force on the negative ones. In other words, the long-range flow field generated by the moving colloid is, in leading order, compensated by a counter-flow generated by the counterions. The angle-averaged flow field thus decays just like the charge cloud, with the same screening length.

This implies, in turn, that the electrophoresis problem is expected to reduce to a single-particle problem whenever the average colloid-colloid distance is substantially larger than the Debye screening length, and this happens for sufficiently large amounts of salt. This is the reason why most investigations have focused on the case of a single colloid surrounded by counterions and salt [1,5–7], where the theoretical analysis become more and more refined and generalized, and involved more and more numerics. The end point of this development was the seminal contribution by O’Brien and White [7], where the electrophoretic mobility was numerically calculated for this situation in its full generality. Apart from the restriction already mentioned, another important restriction is the fact that this theory treats the ionic atmospheres as structureless fields, i. e. in the static limit the theory is identical to (nonlinear) Poisson-Boltzmann theory, which is a standard example of a Mean Field theory. In the extreme limit, where the Debye length is even substantially smaller than the particle radius, the geometry becomes effectively planar, and the problem is amenable to a simple analytical solution (the Smoluchowski limit [1,3]):

$$\mu_{red} = \frac{3}{2}\zeta_{red}. \quad (8)$$

Starting from this background, theoreticians have mainly attempted to go beyond the simple Mean Field picture and to include ionic correlations (see, e. g., Refs. [8, 9]), while experiments deliberately have violated the high-salt condition, such that colloid-colloid interactions become important [10–15]. An observation that still is poorly understood is the fact that for very small Φ there is a regime where μ *decreases* upon decreasing Φ [10]. It was mainly this experimental background that prompted us to attempt to attack the problem by numerical simulation.

In what follows, we will first (in Sec. 2) briefly outline possible computational methods to deal with colloidal electrophoresis, and discuss their strengths and limitations. This will also imply a brief discussion of some older results of our group. In Sec. 3 we will then report on more recent results, which are the main focus of the present paper. Finally, in Sec. 4 we will provide a brief outlook.

2 Computational approaches, and dimensional analysis

Ideally, one would like to include effects of ion-ion correlations, and of hydrodynamic interactions. One possible model that takes all these effects into account is the so-called “raspberry model” [16–20], where a colloidal sphere is represented by a set of roughly 100 Molecular Dynamics particles arranged on the surface. These particles are coupled dissipatively to a Lattice Boltzmann (LB) background to represent the hydrodynamic interactions. Ions are represented by additional Molecular Dynamics particles, and electrostatic interactions are calculated directly via an efficient evaluation of Coulomb’s law. The system is kept at constant temperature by applying

Langevin thermostats to both the particles and the LB fluid, and the structure of the charge clouds arises from averaging over these fluctuations. This allows to evaluate the mobility either by applying an external electric field (where one needs to take care to extrapolate to the $E_{ext} = 0$ limit), or via a Green-Kubo relation [21] from simulations at zero driving.

It turns out that this needs a lot of sampling, since the charge clouds comprise only a few particles, such that fluctuations are big. Furthermore, the number of ions per colloidal particle is typically substantially smaller than in experiment. Similarly, the colloid radius is typically only one order of magnitude larger than the ion radius (or even less), while in typical experiments it is much larger. Therefore the model strongly overestimates the effects of ion packing at the colloid surface. Furthermore, the computational effort of the method is so big that so far we have not been able to study a multi-colloid system. This would however be highly desirable, since one must expect that such a system will be qualitatively different from a single-colloid system. A single colloid in a cubic box with periodic boundary conditions is best viewed as an infinitely stiff simple-cubic colloidal crystal, whose lattice spacing is identical to the linear box dimension. This picture allows us to assign a well-defined colloid volume fraction and well-defined ionic concentrations to the system. Nevertheless, a colloid system in the fluid phase, even at the same volume fraction and ion concentrations, is expected to behave somewhat differently. The most important difference is that in the stiff crystal all colloidal spheres move with the same velocity, while in the fluid there is no reason why this should happen. In other words, the single-colloid case allows us to apply a Galilei transform in order to study the system in the particle's rest frame. In the multi-colloid case, such a global rest frame does not exist, and the drift velocity is obtained from an average over both time and particles. It is also expected that the velocity fluctuations between the particles introduce complex hydrodynamic interactions that are important for the overall phenomenon.

Although being confined to single-colloid studies, the raspberry model nevertheless allowed us to gain important insights into the process, and, in particular, to achieve a favorable match with experiments [18]. One question that arose was the identification of a suitable set of independent dimensionless parameters that govern the problem. This was answered by dimensional analysis [18,21], and a possible set that we found are κR , \hat{Z} , the rescaled diffusion coefficients $\tilde{D}_i = D_i 6\pi l_B \eta / (k_B T)$, the fractions of the various ionic species

$$f_i = \frac{c_i}{\sum_j z_j^2 c_j}, \quad (9)$$

and the ratio l_B/R . Interestingly enough, this last parameter drops out when one describes the system on the level of Mean Field theory, i. e. within the framework of the electrokinetic equations.

Given the outlined limitations of the raspberry model in terms of both computational efficiency and physical realism, we continued to study the system numerically via solving the electrokinetic equations on a lattice, which is computationally easier but still challenging. We thus gained computational speed by discarding some ion correlation effects, which are however apparently fairly weak for many systems. Furthermore, we now no longer overestimate ion packing effects; however, they may now be somewhat underrepresented. It turns out that the method is subject to fairly strong discretization effects, and therefore we often needed to study several lattice spacings, and to extrapolate to the continuum limit. However, we did not use the gain in efficiency in order to study many colloids (which turned out to still be challenging), but rather to vary parameters over a broad range, and to obtain results with much-improved numerical accuracy, which was necessary to answer some more subtle questions. In contrast to previous work [22] that solved the full nonlinear equations,

we improved the accuracy by taking a perturbative approach from the outset, starting from a system at zero driving (which means to solve the nonlinear Poisson-Boltzmann equation), and linearizing the equations with respect to the driving field around that state. A first important step in that program was the development of a highly stable Poisson-Boltzmann solver [23], building upon Maggs' field-based formulation of electrostatics. This solver was also very useful for the studies of J. Zhou and F. Schmid [24], which are reported in their contribution in this volume. Most results that are the focus of the present report (i. e. the following section) have been published in a long paper [25], and hence we will be fairly brief here.

3 Numerical solution of the electrokinetic equations

Since we study the single-colloid system in the stationary state, the equations need to be studied only in their time-independent formulation (in the colloid's rest frame):

$$0 = \nabla^2 \psi + \frac{1}{\epsilon} e \sum_i z_i c_i, \quad (10)$$

$$0 = \nabla \cdot \left(D_i \nabla c_i + \frac{D_i}{k_B T} e z_i (\nabla \psi) c_i - \mathbf{v} c_i \right), \quad (11)$$

$$0 = -\nabla p + \eta \nabla^2 \mathbf{v} - e (\nabla \psi) \sum_i z_i c_i, \quad (12)$$

$$0 = \nabla \cdot \mathbf{v}. \quad (13)$$

The first equation is the Poisson equation for the electrostatic potential ψ , the second the convection-diffusion equation for the ionic concentration c_i , the third the Stokes equation for the velocity flow field \mathbf{v} where p is the pressure enforcing the incompressibility condition (the fourth equation). Linearization involves an expansion

$$c_i = c_i^{(0)} + \epsilon c_i^{(1)} + \mathcal{O}(\epsilon^2), \quad (14)$$

$$\psi = \psi^{(0)} + \epsilon \psi^{(1)} + \mathcal{O}(\epsilon^2), \quad (15)$$

$$\mathbf{v} = \epsilon \mathbf{v}^{(1)} + \mathcal{O}(\epsilon^2), \quad (16)$$

$$p = p^{(0)} + \epsilon p^{(1)} + \mathcal{O}(\epsilon^2), \quad (17)$$

where the dimensionless parameter ϵ is a measure for the strength of the external driving. At zeroth order, one just obtains the Poisson-Boltzmann system (the solution of which is obtained by the method discussed in Ref. [23]), and the zeroth-order concentrations and potential then show up as coefficients of the linear first-order equations. The first-order convection-diffusion equation then acquires source and sink terms. Each of the first-order equations is solved by its own specialized method, and the whole procedure is coupled by a big iteration that finally brings the system into the stationary solution, from which μ can be read off. While the Poisson equation is solved by Fast Fourier Transform, the convection-diffusion equation is handled by a finite-volume solver that moves the concentrations from one lattice site to another along the links, and modifies them locally according to the sources and sinks. Finally, the Stokes equation is solved by a surface element method, which is based upon the lattice Green's function, and a self-consistent determination of reaction forces at the particle surface, such that the no-slip boundary condition is satisfied. As outlined in more detail in Ref. [25], we find good agreement with previous raspberry and experimental results, and we find also good agreement with the results of O'Brien

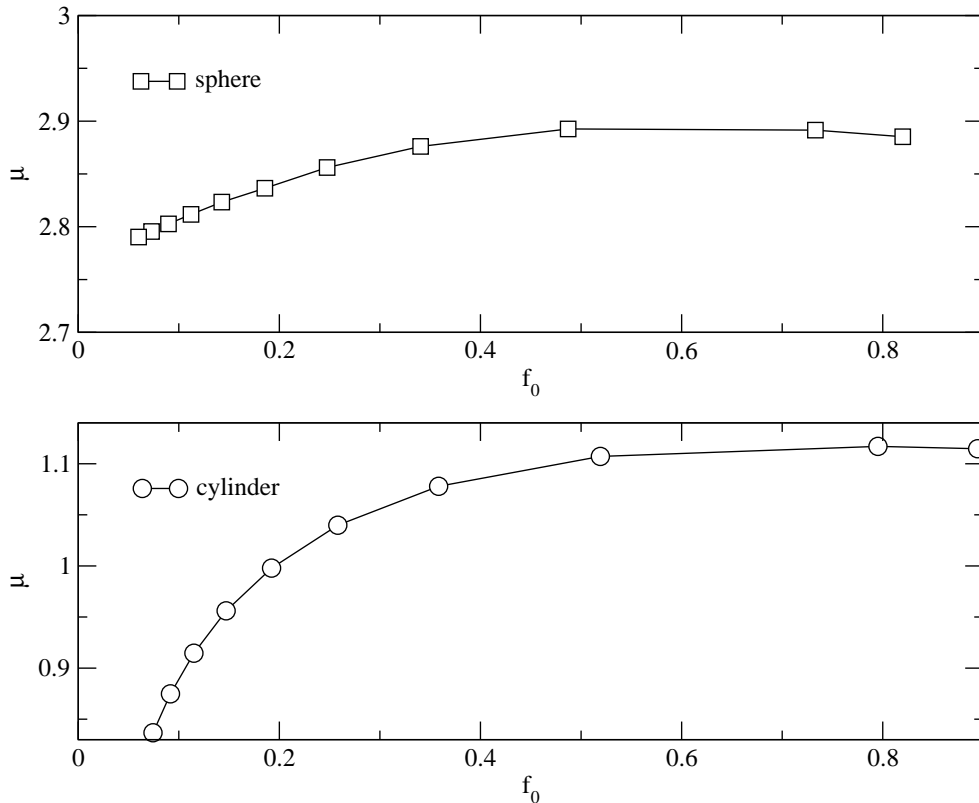


Fig. 1. Dependence of the reduced electrophoretic mobility μ_{red} on f_0 , the fraction of counterions relative to the salt ions.

and White [7] in the limit of strong salt screening, in which case the charge clouds of the colloids in the crystal do not overlap, and the two theories must coincide.

Experimental investigations often interpret their μ_{red} data in terms of the O’Brien-White theory, even in the low-salt limit, although that theory was clearly not developed for that case. This means, implicitly, that one does not only assume the validity of a Mean Field description (which seems more or less reasonable), but also ignores the dependence of μ_{red} on all of the discussed scaling parameters except κR and Zl_B/R . In other words, it assumes that the non-dimensionalized diffusion coefficients take the value unity (which seems to be the value used in Ref. [7], and is also physically reasonable), and that the dependence on the ion species fractions f_i does not exist or at least is weak (at fixed κR and Zl_B/R). This latter assumption means that one can replace a system with counterion-dominated screening by an “equivalent” system whose screening is salt-dominated, and for which Ref. [7] is valid. In physical terms, this means that one has to envision a thought experiment where more and more salt is added to the system, while at the same time the simulation box size is systematically increased in order to keep κR constant. Our investigations then showed clearly that indeed μ_{red} does depend on the f_i , as predicted by scaling theory, but that on the other hand the dependence is fairly moderate and is typically of order five to ten percent (which is comparable to the accuracy of the experiments). Furthermore, the dependence of μ_{red} on the rescaled diffusion coefficients was also found to be fairly weak.

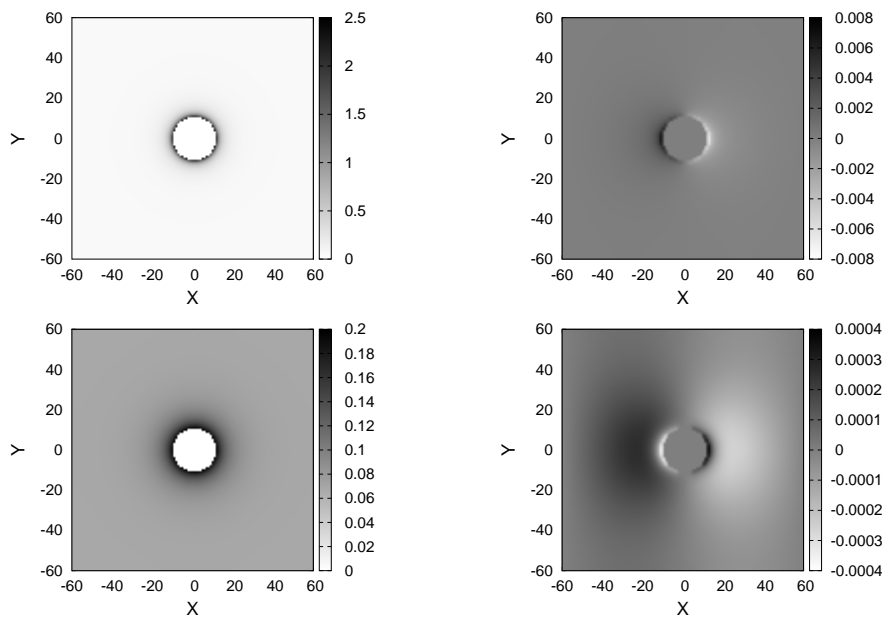


Fig. 2. Concentration profile of negative salt ions for a sphere (upper panel) and a cylinder (lower panel), where the zeroth-order contribution (left) and the first-order contribution (right) are shown separately.

An interesting effect was found when studying the orientation of the charge cloud (e. g. in terms of the first-order dipole moment). The picture of a static polarizability implies that one should expect the dipole moment to be aligned *with* the driving field. On the other hand, the picture of ionic currents that result in an accumulation of charges at the surface of the colloid (which can be viewed as an “obstacle”) leads to the prediction of a dipole moment aligned *in the opposite direction*. This means that there is a competition between electrostatic and hydrodynamic effects. We found that there is no universal answer to the question which effect wins. Rather, the hydrodynamic prediction is correct only in the limit of weak colloid charges (the special case $Z = 0$ is amenable to analytic treatment [26], and that theory could be nicely confirmed). Upon increasing Z , the absolute value of the dipole moment decreases, and at a critical Z value the charge cloud changes its orientation. It should be noted that this “flipping” has no direct influence on the behavior of the electrophoretic mobility, which is a perfectly smooth function of Z .

Fairly recent (and so far unpublished) studies have generalized these investigations to the two-dimensional case, which means the electrophoresis of infinitely long cylinders with a driving field perpendicular to the cylinder axis. Figure 1 studies μ_{red} for $\kappa R = 1$, $\hat{Z} = 10$, $\tilde{D}_i = 1.5$ for the two ionic species $i = 1, 2$ ($z_1 = -z_2 = 1$), where we varied the fraction of counterions f_0 . This is done for both a sphere as well as for a cylinder, and one sees that the dependence is clearly stronger in the two-dimensional case. On the other hand, when comparing the ionic profiles of both zeroth and first order, one sees that the two-dimensional case is substantially flatter (Fig. 2).

4 Outlook

The numerical solution of the electrokinetic equations is a viable route to study electrokinetic phenomena, and in many cases the involved Mean Field approximation is reasonably accurate. The description of the Poisson-Boltzmann theory in terms of the positive-definite Maggs functional [23] allows us to straightforwardly construct a well-defined equilibrium thermodynamics and statistical mechanics of the system. To accurately study many-colloid systems under the influence of a driving electric field is still demanding but possible. In this case the absence of a colloidal rest frame prohibits the application of the perturbative approach that we have taken so far; rather it will be necessary to solve the full nonlinear equations.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) within the framework of the collaborative research center (SFB) TR-6 “Physics of Colloidal Dispersions in External Fields”, subproject B4 (“Computer Simulation of Electrokinetics in Colloidal Systems”) is gratefully acknowledged.

References

1. M. von Smoluchowski, Bull. Intern. Acad. Sci. Cracovie **1903**, (1903) 184
2. E. Hückel, Phys. Z. **25**, (1924) 204
3. W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989)
4. D. Long and A. Ajdari, Europ. Phys. J. E **4(1)**, (2001) 29
5. D. C. Henry, Proc. R. Soc. A **133(821)**, (1931) 106
6. P. H. Wiersema, A. L. Loeb, and J. T. G. Overbeek, J. Colloid Interface Sci. **22**, (1966) 78
7. R. W. O’Brien and L. R. White, J. Chem. Soc., Faraday Trans. 2 **74**, (1978) 1607
8. H. M. Manzanilla-Granados, F. Jiménez-Ángeles, and M. Lozada-Cassou, Colloids and Surfaces A: Physicochem. Eng. Aspects **376(1)**, (2011) 59
9. H. M. Manzanilla-Granados, F. Jimenez-Angeles, and M. Lozada-Cassou, J. Phys. Chem. B **115**, (2011) 12094
10. M. Evers, N. Garbow, D. Hessinger, and T. Palberg, Phys. Rev. E **57(6)**, (1998) 6774
11. P. Wette, H. J. Schöpe, and T. Palberg, J. Chem. Phys. **116(24)**, (2002) 10981
12. M. Medebach and T. Palberg, J. Chem. Phys. **119(6)**, (2003) 3360
13. M. Medebach and T. Palberg, J. Phys. Condens. Matter **16**, (2004) 5653
14. N. Garbow, M. Evers, T. Palberg, and T. Okubo, J. Phys. Condens. Matter **16**, (2004) 3835
15. T. Palberg, M. Medebach, N. Garbow, M. Evers, A. B. Fontecha, H. Reiber, and E. Bartsch, J. Phys. Condens. Matter **16**, (2004) S4039
16. V. Lobaskin and B. Dünweg, New J. Phys. **6**, (2004) 54
17. V. Lobaskin, B. Dünweg, and C. Holm, J. Phys. Condens. Matter **16(38)**, (2004) S4063
18. V. Lobaskin, B. Dünweg, M. Medebach, T. Palberg, and C. Holm, Phys. Rev. Lett. **98(17)**, (2007) 176105
19. A. Chatterji and J. Horbach, J. Chem. Phys. **122**, (2005) 184903
20. A. Chatterji and J. Horbach, J. Chem. Phys. **126**, (2007) 064907
21. B. Dünweg, V. Lobaskin, K. Seethalakshmy-Hariharan, and C. Holm, J. Phys. Condens. Matter **20**, (2008) 404214
22. F. Capuani, I. Pagonabarraga, and D. Frenkel, J. Chem. Phys. **121(16)**, (2004) 973
23. M. Baptista, R. Schmitz, and B. Dünweg, Phys. Rev. E **80(1)**, (2009) 016705
24. J. Zhou, R. Schmitz, B. Dünweg, and F. Schmid, J. Chem. Phys. **139**, (2013) 024901
25. R. Schmitz and B. Dünweg, J. Phys. Condens. Matter **24(46)**, (2012) 464111
26. J. K. G. Dhont and K. Kang, Eur. Phys. J. E **33**, (2010) 51