

## The marriage of electrostatics and hydrodynamics: simulating the dynamics of charged colloids

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## VIEWPOINT

## The marriage of electrostatics and hydrodynamics: simulating the dynamics of charged colloids

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Charged colloidal particles dispersed in a fluid solvent are omnipresent in nature: inks, paints and many other complex fluids known from everyday life typically consist of highly charged mesoscopic solutes. On the nanoscale, biomaterials such as proteins and DNA solutions represent further prominent candidates for exhibiting charged macromolecules. Furthermore, well-characterized suspensions of polystyrene microspheres are important model systems for studying the principles of phase transformations. A full calculation of the dynamical properties of charged suspensions is therefore important both for fundamental purposes and for many practical applications, e.g. in the rheology of paints.

However, a realistic computer simulation of the dynamics of charged colloids is not straightforward since one has to tackle *two* problems simultaneously:

- The strong Coulomb coupling between the highly charged colloidal particles ('macroions' or 'polyions') and their microscopic counterions left in the solution, which in turn screen the effective interactions between the macroions. This is mainly a problem of *electrostatics* together with appropriate thermostatics.
- The presence of *hydrodynamic* interactions mediated via the solvent when the macroions are moving.

While the first problem arises from statics, the second is inherent to dynamics. Both interactions are long ranged.

Significant progress has been made in the last decade by solving just one of the two problems. For the *statics*, such as the structural correlations and phase transitions, hydrodynamic interactions are irrelevant and one is just left with the strong Coulomb coupling. On the other hand, the dynamics of *neutral* colloids in the flow of the solvent has been studied by different mesoscale methods for the solvent.

Computer simulation codes for the structure of charged colloids are mainly based on the Poisson–Boltzmann equations for the microions for any given configuration of the macroions [1–3] or on the full strongly asymmetric primitive model [4] of electrolytes, which includes a hard core and the Coulomb interactions between the charged components (macroions and microions) reduced by the dielectric constant of the solvent. Simulations of the latter have been performed by using a classical analogue of the celebrated Car–Parrinello

method [5] and by direct Monte Carlo and molecular dynamics methods [6–8]. Although these methods are efficient for sampling the configuration space, none of them contains the real physical colloidal dynamics which includes hydrodynamic interactions.

On the other hand, the hydrodynamics of many neutral colloids can now be studied by discrete lattice Boltzmann methods, continuum solvent models or dissipative particle dynamics [9]. There are even whole packages for solving for the hydrodynamic interactions between spherical colloids based on the linearized Navier–Stokes equation with the appropriate stick boundary conditions for the solvent flow field at the colloidal particle surfaces. Another ingenious alternative was proposed by Tanaka and Araki [10]: in a way that is quite complementary to lattice Boltzmann methods, where the fluid solvent is put on a ‘solid’ grid, in the Tanaka–Araki method the solid particle is modelled as a highly viscous fluid. This ‘fluidization method’ avoids the numerically costly non-slip boundary condition at the colloidal surfaces and provides an efficient computation of dynamical phenomena, such as phase separation kinetics.

The hard problem is how to include both explicit ions and hydrodynamics on the same level, combining electrostatics (for the microions) and hydrodynamics (for the solvent). One obvious ‘escape route’ is to simulate macroions, microions and explicit solvent (e.g. water within the simple point charge-extended (SPC/E) model) by means of molecular dynamics. Recent progress has been made by Dzubiella and Hansen [11] but certainly only small macroparticle size (appropriate for proteins) can be treated on present-day computers. A complementary strategy (more appropriate for microsized colloids) is to stick to a mesoscale treatment of the solvent flow and couple this dynamically to the ion density field. One of the recent attempts based on lattice Boltzmann approaches was proposed by He and Li [12], assuming local charge neutrality. A different lattice Boltzmann approach with an additional charge density field was introduced by Warren [13] and later technically improved by Horbach and Frenkel [14].

In a recent letter, Kodama *et al* [15] propose a new approach which is based on the ‘fluidization method’ [10] applied to solid colloidal particles. The electrostatics of the microions is described on the level of Poisson–Boltzmann theory. Kodama *et al* then consistently couple the diffusive dynamics of the microion density field (including added salt) to the hydrodynamics of the solvent flow. They were able to solve a *full dynamical problem* of electro-deposition of charged colloids near a charged planar substrate. The method is immediately applicable to many other interesting problems of charged colloidal dynamics such as those of electrophoresis [16], electrolyte friction [17], conductivity in suspensions driven by an electric field [18, 19] and crystal nucleation and growth [20].

It is too early to give the ultimate judgment of the practical advantages and disadvantages of the different methods which solve electrokinetic problems for charged colloids. It will certainly take almost a generation of upcoming physicists to test the various schemes for different problems. However, it is already fair to say that the method of Kodama and co-workers has the advantage of being conceptually and numerically simple and physically intriguing. It has the potential to bring a breath of fresh air into the realm of simulation of electrokinetic processes of charged colloids. A fundamental understanding of charged colloidal dynamics with important implications for the fabrication of microfluidic devices [21], where the adsorption of charged particles on charged substrates plays a key role, lies ahead.

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