Mesoscopic simulations of electrokinetic phenomena

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Mesoscopic simulations of electrokinetic phenomena can provide valuable information in parameter ranges where theoretical understanding is poor, experiments are difficult, and atomistic simulations too expensive. This poster presents a lattice-Boltzmann-based framework to simulate binary electrolyte solutions with charged particles. We show exemplary cases of neutral and charged drops deformation, particle electrophoresis, and particle–coated droplets.

Model

Solvents and ions are considered at the continuum level. The solvents are described by the continuity and Navier–Stokes equations,

$$\frac{\partial \rho^\sigma}{\partial t} + \nabla \cdot (\rho^\sigma \vec{u}) = 0,$$
$$\frac{\partial (\rho^\sigma \vec{u})}{\partial t} + \nabla \cdot (\rho^\sigma \vec{u} \otimes \vec{u}) = -\nabla \cdot (p\mathbb{I}) + \nabla \cdot \vec{s}^\sigma + \vec{F}^\sigma$$

These are recovered via a Boltzmann equation with a BGK collisional operator, solved in a D3Q19 lattice,

$$f_d^\sigma(\vec{r}_i + \vec{c}_d, t+1) - f_d^\sigma(\vec{r}_i, t) = \frac{1}{\tau}\left(\tilde{f}_d^\sigma(\vec{r}_i, t) - f_d^\sigma(\vec{r}_i, t)\right)$$

Solvent-solvent interactions are implemented using the Shan–Chen method [1]. The ions' kinetics are modeled by the Nernst-Planck equation:

$$\frac{\partial n^\pm}{\partial t} + \vec{u} \cdot \nabla n^\pm = \nabla \cdot \left(-D^\pm \nabla n^\pm + D^\pm \beta n^\pm \vec{f}^\pm\right)$$

with an external conservative force

$$\vec{f}^\pm = -\nabla U = -\nabla(z^\pm e\phi + \mu^\pm_{\text{solv}})$$

The solvation potential is taken to be proportional to the concentration

$$\mu^\pm_{\text{sol}}(c) = \Delta\mu^\pm \left(\frac{2c - c_b - c_a}{c_b - c_a}\right) \quad \text{with} \quad c(\vec{r}) = \frac{\rho^b(\vec{r}) - \rho^a(\vec{r})}{\rho^a(\vec{r}) + \rho^b(\vec{r})}$$

The Nernst–Planck equation is solved using a finite-volume scheme, inspired by the link-flux method [2]. The electric potential is given by Poisson's equation,

$$\nabla \cdot (\varepsilon \nabla \phi_I) = -e(z^+ n^+(\vec{r}) + z^- n^-(\vec{r})) + q_p(\vec{r})$$

and is solved using a Fourier spectral method.

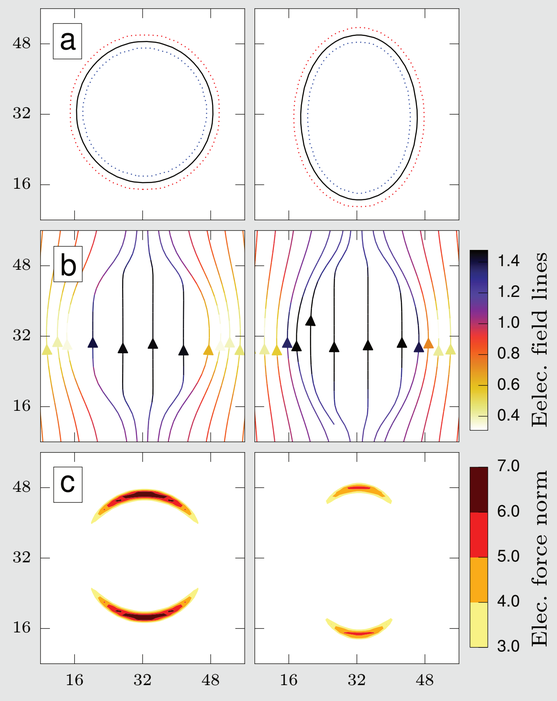
The total external force is given by a contribution from the Shan-Chen model, and an electric contribution through a friction coupling of the ions and the solvent:

$$\vec{F}_e = -k_B T \nabla n - \sum_\pm n^\pm \nabla \mu^\pm_{\text{solv}} + q\vec{E} - \frac{(\varepsilon - \bar{\varepsilon})}{2}\nabla \vec{E}^2 \qquad (1)$$

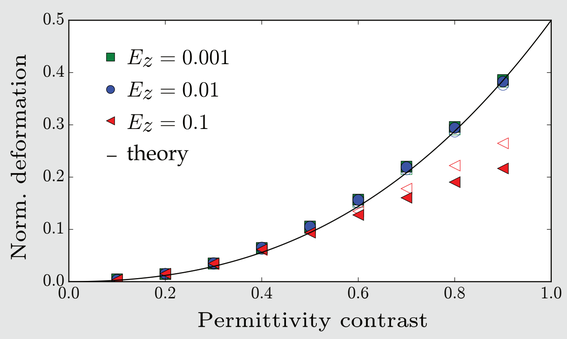
The interaction between solvents and particles is implemented using Ladd's methodology, with corrections for mixtures [3]. To avoid large fluctuations in the electric field, the particle solid fraction is computed at each boundary site, and the flux of ions is modified accordingly, as proposed by Kuron et al. [4].

- ρ^σ: density of fluid $\sigma \in \{a, b\}$
- $\vec{u}$: hydrodynamic velocity
- p: pressure
- $\vec{s} = \lambda^\sigma(\nabla \cdot \vec{u})\mathbb{I} + \eta^\sigma(\nabla\vec{u} + \nabla\vec{u}^T)$
- $F^\sigma = F_i^\sigma + F_e^\sigma$: external force
- f_d^σ: distribution function
- $\tau = 1$: relaxation time
- $\vec{c}_d$: lattice vectors in D3Q19
- $n^\pm$: ions number density
- $n = n^+ + n^-$
- $D^\pm$: ion diffusivity
- $\beta = (k_B T)^{-1}$
- e: proton charge
- $z^\pm$: ion valence (signed)
- $\phi = \phi_I + \phi_E$: electric potential
- $E = -\nabla\phi$: electric field
- ε: electric permittivity

Dielectric drop deformations

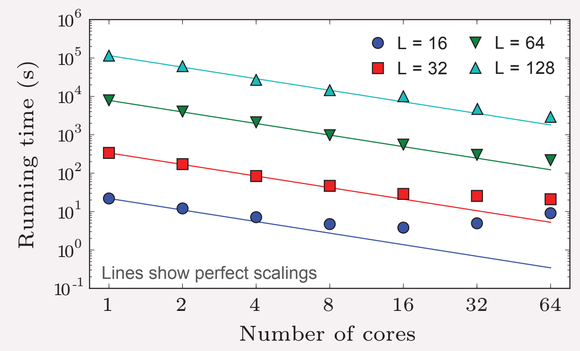


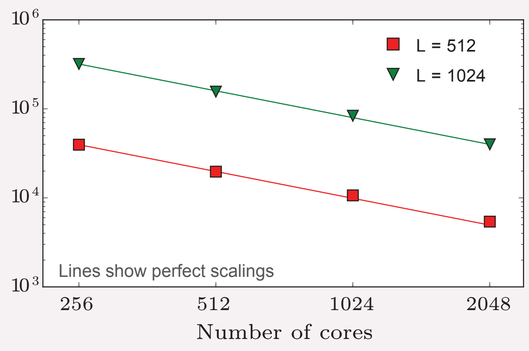
An oil drop in a water medium with no ions, deformed only by the dielectric forces exherted by an electric field. Drop contours initially (left) and at equilibrium (right) are shown in the left figure (a), together with the electric field lines (b), and the modulus of the electric force (c). The deformation agrees with the analytics for small deformations (down).



Algorithm benchmark

In order to test the scaling of the algorithm, we performed benchmark simulations in the JURECA supercomputer. As test case we consider the electro-osmotic flow of a single fluid driven by an external electrical field parallel to two walls. Test cases were run for cubes of size L in two limits, L ≤ 128 and large L ≥ 512.



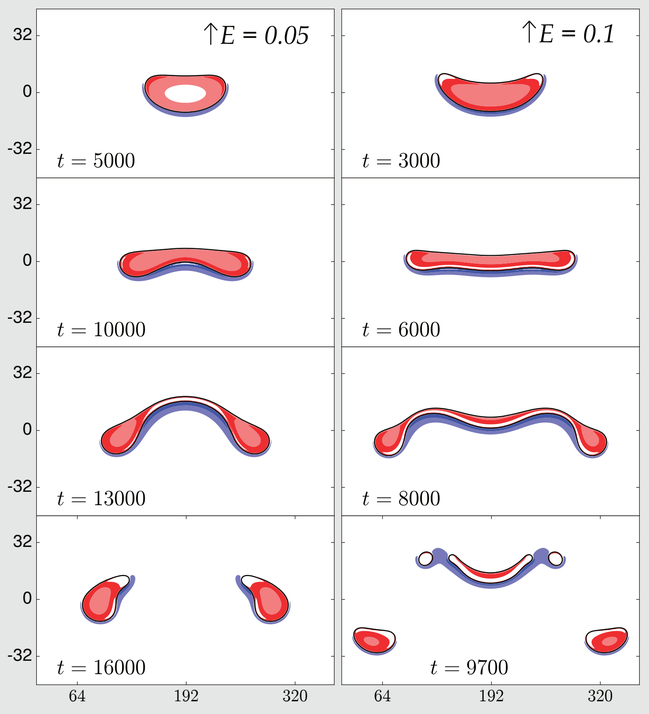


The top plots show that finite size effects quickly dominate in small systems, while for larger systems there is an adequate scaling until the maximum number of cores considered (2048). We have recently implemented new Poisson solvers based on the Fourier and Conjugated Gradient methods, in order to solve the general equation with variable permittivities and arbitrary boundary conditions.

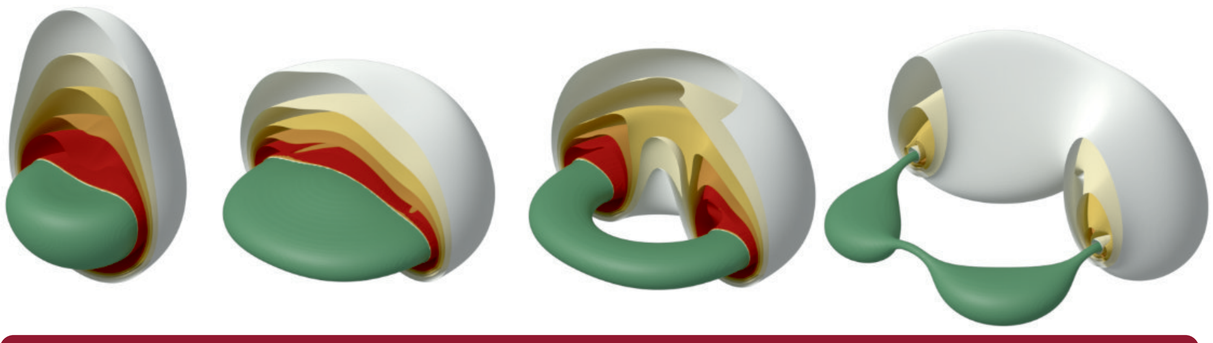
Charged drop deformations

A conducting oil drop in a less conducting water medium. An electric field is applied in the vertical direction. On the right the time evolution is shown for two different field strengths. The concentration of charge is shown from negative (**red**) to positive (**blue**) regions. Electrostatic and drag forces deform the drop. The morphology and the relevant dimensionless numbers, Ohnesorge and Weber, are consistent with the bag-breakup scenario observed in experiments of drops and bubbles:

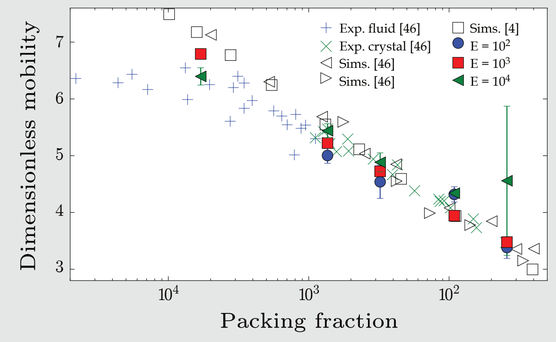
$$\text{We} = \rho^a u_d^2 r_d/\gamma \in (10, 30)$$
$$\text{Oh} = \eta^a/\sqrt{\rho^a r_d \gamma} \in (0.1, 1.0)$$



Charged drop deformation in 3D. **Green**: drop contour. **Red**/**Yellow**: positive charge.



Electrophoresis

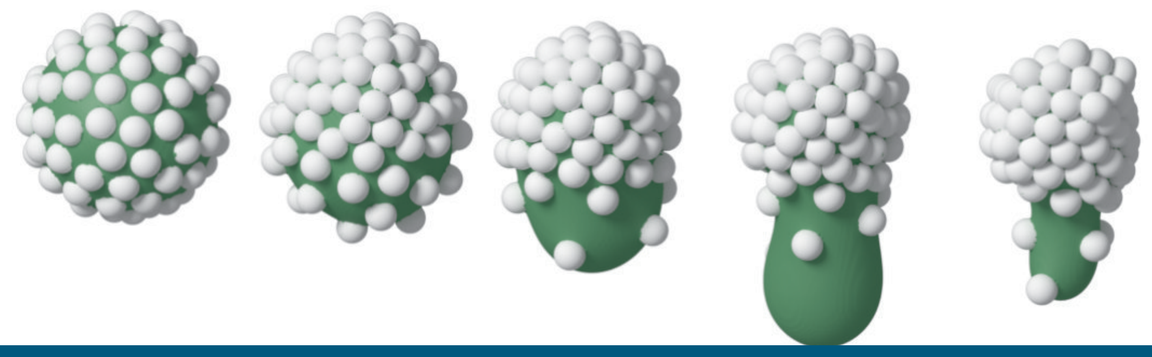


A single particle moves in an electrolyte solution under the effect of an electric field. The mobility of the particle,

$$\mu = v/E$$

is proportional to the packing fraction (the size of a periodic box), in agreement with previous experiments and other simulations, as shown on the left figure.

Conducting drop coated by neutral particles, deformed by an electric field.



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