Computer Simulation of Nanometer Colloid in Salt Solution under Alternating Electric Field

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Abstract: We study the response of nanoscopic spherical colloid in salt solution by computer simulation, accounting in full for hydrodynamic and electrostatic interactions. Specifically, we systematically investigate the effect of frequency and amplitude of the AC-fields, the ionic strength of the solution, and the bare charge of the colloids. A coarse-grained molecular dynamics approach is taken to model the fluids, in which the solvent particles are simulated using Dissipative Particle Dynamics (DPD). The electrostatic interaction between all charges are calculated explicitly using Particle-Particle-Particle Mesh (P3M) method.

Introduction

Characterization of the dynamic and dielectric response:

* external electric field $\mathbf{E}\exp(i\omega t)$ with amplitude $\mathbf{E}$ and frequency ω

* velocity of the colloidal particle: $\mathbf{v}\exp(i\omega t)$

* dipole moment of the system: $\mathbf{p}\exp(i\omega t)$

* the crucial quantities to characterize the response of colloidal particles to external field are the mobility $\mu(\omega)$: $\qquad \mathbf{v} = \mu(\omega)\mathbf{E}$

and the polarizability $\alpha(\omega)$: $\qquad \mathbf{p} = \alpha(\omega)\mathbf{E}$

Important length scales:

* Debye screening length $\quad l_D = \left[\dfrac{\sum_i z_i^2 e^2 n_i(\infty)}{\epsilon_m k_B T}\right]^{-\frac{1}{2}}$
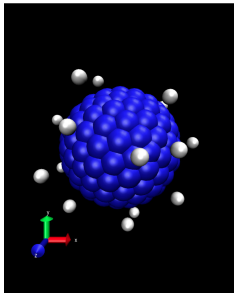
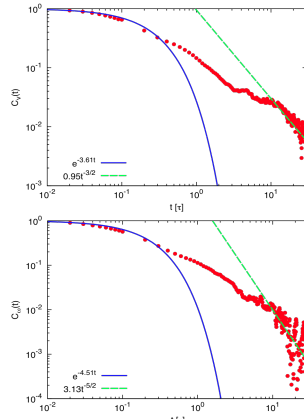* colloid diameter $2R$

Important time scales:

* Maxwell-Wagner relaxation time $\quad \tau_{\mathrm{mw}} = \dfrac{\epsilon_p + 2\epsilon_m}{K_p + K_m} = \dfrac{3}{2}\dfrac{l_D^2}{D_I}$

* time required for concentration gradient to build up $\quad \tau_c = (2R)^2/D_I$

Simulation Model

Top: snapshot of a colloidal particle and couterions.
Right: translational and rotational velocity autocorrelation functions.

* solvents: Dissipative Particle Dynamics (DPD) [1]. The DPD beads have a density of $3.0\sigma^{-3}$, friction coefficient $5.0\sqrt{m\epsilon}/\sigma$, cutoff 1.0σ.

* colloid: a large sphere with interacting sites on its surface. Short-range repulsive interaction is modeled as WCA-potential. The hydrodynamic interaction is modeled through the DPD interaction between the surface sites and solvent beads.
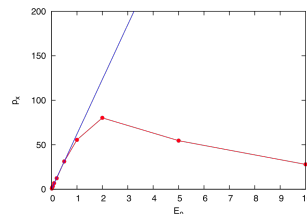
* ions: particles with unit charge and WCA-potential. The electrostatic interaction is calculated using Partile-Particle-Partile Mesh (P3M) [2] method.

* all simulations are carried out using open source package ESPResSo [3].

Effect of Field Strength
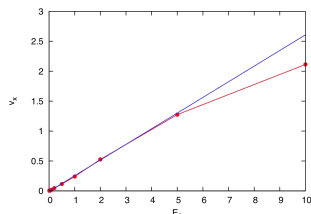
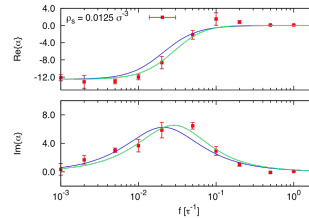Amplitude of colloid velocity as a function of field strength [4]

Amplitude of the dipole moment as a function of field strength

* Linear dependence breaks down at about $E_0 = 1.0\varepsilon/(\sigma e)$

* The amplitudes of the colloid velocity and the dipole moment reduces as the field strength increases.
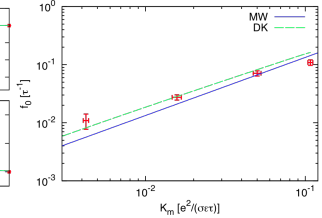
Uncharged Colloid

Real and Imaginary part of $\alpha(\omega)$ for an uncharged colloid [5]

Transition frequency as a function of the conductivity

* At low frequency, coions accumulate on the front side of the colloid and cations on the back side, resulting a negative dipole moment.

* At high frequency, the field varies too fast for the microions to response.

* Blue curves: Maxwell-Wagner theory. Only bulk properties are taken into account.

* Green curves: Dhont-Kang theory [5], which considers the microion distribution.

* The spatial distribution of microions around the colloid is on the order of Debye screening length.

* At high salt concentration (small l_D, large K_m), Maxwell-Wagner theory is good. Deviation is possibly due to the layering effect.

* At low salt concentration (large l_D, small K_m), the distribution of microions is important. Dhont-Kang theory gives better agreement.

Charged Colloid
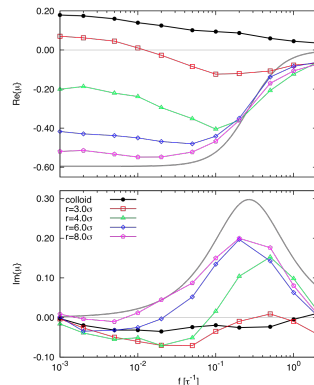
Complex mobility of the counterion cloud for $Q = +50e$ and $\rho_s = 0.0125\sigma^{-3}$ [6]
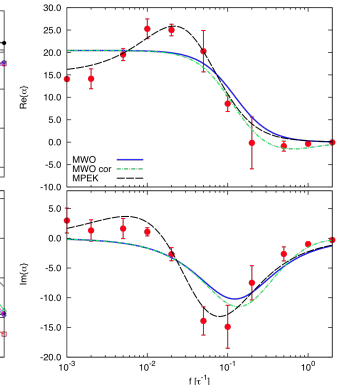
Complex polarizability $\alpha(\omega)$ for a charged colloid $Q = +50e$ and $\rho_s = 0.0125\sigma^{-3}$

* Far away from the colloid, the counterions behave like free micrions.

* The inertia of the microion determines a time scale:
$$\tau_m = \frac{2\pi m}{\gamma} \sim \frac{1}{0.27}$$

* Close to the colloid, the motion of the counterions is strongly influenced by the motion of the colloid.

* At low frequency and close to the colloid (red line), counterions are co-moving with the colloid.

* At high frequency, Maxwell-Wagner relaxation time:
$$\tau_{\mathrm{mw}} = \frac{3}{2}\frac{l_D^2}{D_I} \sim \frac{1}{0.12}$$

* At low frequency, a gradient of salt concentration builds up near the colloid surface.

* The related time scale for the concentration polarization is the time for microions to diffuse over $2R$:
$$\tau_c = \frac{(2R)^2}{D_I} \sim \frac{1}{0.017}$$

References: [1] Hoogerbrugge and Koelman, Europhys. Lett. **19**, 155 (1992); Espanol and Warren, Europhys. Lett. **30**, 191 (1995); Groot and Warren, J. Chem. Phys. **107**, 4423 (1997)
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[3] Limbach, Arnold, Mann and Holm, Comp. Phys. Comm. **174**, 704 (2006); http://espressomd.org
[4] Zhou and Schmid, J. Phys.: Condens. Matter **24**, 464112 (2012)
[5] Zhou and Schmid, Eur. Phys. J. E **36**, 33 (2013); Dhont and Kang, Eur. Phys. J. E **33**, 51 (2010)
[6] Zhou, Schmitz, Dünweg and Schmid, J. Chem. Phys. **139**, 024901 (2013)
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