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.

Characterization of the dynamic and dielectric response:
- external electric field $E_\omega = |E| \exp(i\omega t)$ with amplitude $|E|$ and frequency $\omega$.
- velocity of the colloidal particle $\mathbf{v} = \mu(\omega) \mathbf{E}$ and the polarizability $\alpha(\omega)$:
- dipole moment of the system: $p = \alpha(\omega) |E|$
- the crucial quantities to characterize the response of colloidal particles to external field are the mobility $\mu(\omega)$:
- time required for concentration gradient to build up $t_{dp} = \frac{t_D}{3} \frac{\rho_c}{|E|}$ and the relaxation time $t_{MW}$.

Important length scales:
- Debye screening length $l_D = \frac{\sqrt{\epsilon}}{\lambda_D}$
- colloid diameter $2R$

Important time scales:
- Maxwell-Wagner relaxation time $t_{MW} = \frac{t_D}{3} \frac{\rho_c}{|E|}$
- time required for concentration gradient to build up $t_{dp} = \frac{t_D}{3} \frac{\rho_c}{|E|}$

Simulation Model

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

- solvents: Dissipative Particle Dynamics (DPD) [1]. The DPD beads have a density of $3.0 \times 10^{-2}$ frictions coefficient $5.0 \times 10^{-5} \text{ s}^{-1}$, cut-off $1.0 \text{ nm}$.
- colloid: a large sphere with interacting sites on its surface. Short-range repulsive interaction is modelled as WCA-potential. The hydrodynamic interaction is modelled through the DPD interaction between surface sites and solvent beads.
- ions: particles with unit charge and WCA-potential. The electrostatic interaction is calculated using Partile-Particle-Particle 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]

* Linear dependence breaks down at about $E_\text{p} \approx 1.0e/(\text{nm})$.
* The amplitudes of the colloid velocity and the dipole moment reduces as the field strength increases.

Amplitude of the dipole moment as a function of field strength

Uncharged Colloid

- Real and Imaginary part of $\alpha(\omega)$ for an uncharged colloid [5]
- Transition frequency as a function of the conductivity

Charged Colloid

- Complex mobility of the counterion cloud for $Q = +5e$ and $\rho_c = 0.0125 \sigma$ [6]
- Complex polarizability $\alpha(\omega)$ for a charged colloid $Q = +5e$ and $\rho_c = 0.0125 \sigma$.

- Far away from the colloid, the counterions behave like free micrions.
- The inertia of the micrion determines a time scale: $t_{MW} \sim \frac{2 \tau_{\text{mic}}}{\gamma}$
- 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, the counterions are co-moving with the colloid.

- 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 micrions to respond.
- 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 $K_w$), Maxwell-Wagner theory is good. Deviation is possibly due to the layering effect.
- At low salt concentration (large $l_D$, small $K_w$), the distribution of microions is important. Dhont-Kang theory gives better agreement.

References:

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