Dynamic and Dielectric Response of Charged Colloids in Electrolyte Solutions to External Electric Fields

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Computer simulations are used to investigate the response of a charged colloid and its surrounding microion cloud to an external electric field. Both static fields (DC) and alternating fields (AC) are considered. A mesoscopic simulation method is implemented to account in full for hydrodynamic and electrostatic interactions. The response of the system can be characterized by two quantities: the mobility and the polarizability. Due to the interplay of the electrostatic attraction and hydrodynamic drag, the response of the microions close to the colloid surface is different from that of the microions far away from the colloid. Both the mobility and polarizability exhibit a dependency on the frequency of the external fields, which can be attributed to the concentration polarization, the mobility of the microions, and the inertia of microions. The effects of the colloidal charge, the salt concentration, and the frequency of the external fields are investigated systematically.

I. INTRODUCTION

Colloidal suspensions have numerous applications in different fields such as chemistry, biology, medicine, and engineering. In an aqueous solution, colloidal particles are often charged, either by ionization or dissociation of a surface group, or preferential adsorption of ions from the solution. Therefore, they can be efficiently controlled or manipulated by electric fields. Electric fields can be applied in two different ways. One is to use static (DC) fields which induce electrophoresis, i.e., the migration of individual colloids [1, 2]. Electrophoresis is commonly used to measure the surface charge density of colloidal particles. The other possibility is alternating electric field (AC field). The time-dependent perturbation allows one to selectively probe dynamic phenomena at different time scales and produces substantially more information than just probing the response to a static field [1, 2].

The colloids respond to external fields on relatively short time scales and in an often fully reversible way. One important quantity characterizing the dynamic response of the colloid is the electrophoretic mobility. If an external electric field of the form \( E = E_0 \exp(i\omega t) \hat{x} \) is applied in the \( x \)-direction, the \( x \)-component of the colloid velocity exhibits an oscillation of the form \( v_x = v_0 \exp(i\omega t) \), where \( v_0 \) can be a complex number. For weak fields, the frequency of the colloid motion is the same as the external field, and the response depends linearly on the strength of the perturbation. The amplitude of the colloid velocity then can be written as

\[
v_0 = \mu(\omega)E_0. \tag{1}\n\]

The mobility \( \mu(\omega) \) is in general a complex number, whose magnitude characterizes the sensitivity of the response, i.e., how fast the colloid moves under fixed external field, and the phase describes the synchronization between the response and perturbation, i.e., whether the colloid motion is in phase with the external field. We explicitly include the argument \( \omega \) to emphasize that the mobility is a function of the driving frequency.

The microions, which include the counterions from the surface charge and the dissolved salt molecules in the solution, play an important role in determining the colloidal response to the external field. Counterions accumulate around the colloid surface due to the electrostatic attraction between opposite charges and form an electric double layer (EDL). In close vicinity of the colloid, the counterions stick to the surface and move together with the colloid. Further away, microions are relatively mobile and experience thermal motion. The thickness of the electric double layer is characterized by the Debye screening length

\[
l_D = \kappa^{-1} = \left[ 4\pi\rho B \sum_i z_i^2 \rho_i(\infty) \right]^{-\frac{1}{2}}, \tag{2}\n\]

where the summation runs over different ion types. In Eq. (2), \( l_B = e^2/(4\pi\epsilon_m k_B T) \) is the Bjerrum length which depends on the medium permittivity \( \epsilon_m \) and the temperature of the solution \( T \), and \( z_i \) and \( \rho_i(\infty) \) are the valence and bulk concentration for type \( i \) ion, respectively. When an external electric field is applied to the suspension, both the colloidal particle and its surrounding electric double layer will be polarized. The colloid acquires a dipole moment of the form \( p_0 \exp(i\omega t) \) in the direction of the applied field, and the amplitude the dipole moment can be written as

\[
p_0 = \alpha(\omega)E_0. \tag{3}\n\]

The polarizability \( \alpha(\omega) \) is used to characterize the colloid’s dielectric response to the external fields, and it is a complex function of the frequency and the amplitude of the external field. In the linear response region, the
The dipole moment is proportional to the magnitude of the external field; thus the polarizability does not depend on the field strength for weak external fields.

The response of the colloid to the external field, be it dynamic or dielectric, is a combined effect of hydrodynamic and electrostatic interactions. We can control the response by adjusting various factors such as the surface charge density of the colloid and the salt concentration. Fischer et al. observed a salt-dependent change of sign in the mobility of the condensed counterions in poly electrolyte solutions. Similar phenomena are observed in our colloidal system, and the mobility change can also be induced by varying the colloid charges. Furthermore, we explore the response to alternating electric fields, and systematically study the frequency-dependence of mobility and polarizability.

Various theories have been proposed to understand the frequency-dependent response of colloid dispersions. Already for uncharged colloids, this response is far from trivial. On the MHz scale, the main contribution to the induced dipole moment stems from the conductivity mismatch between the particle and the solvent due to the presence of the free microions in the solvent. The so-called Maxwell-Wagner relaxation only depends on the bulk properties of the solution and the colloid, and has been widely used to interpret experimental results. For charged colloids, the electric double layer plays an important role, and its contribution can be included in the Maxwell-Wagner theory as a surface conductivity term, which was first introduced by O’Konski. The Maxwell-Wagner-O’Konski theory has also been extended to ellipsoidal colloids. On long time scales up to 100 MHz, a salt concentration gradient builds up along the colloid and the thickness of the double layer varies accordingly, leading to an additional source of polarization (α-polarization). Theories for the low-frequency response have been developed in the Ukraine school based on the standard electrokinetic model. Their analytic results rely on the assumption that the electric double layer is much thinner than the radius of the colloid. This is justified for micrometer-sized colloids, but becomes questionable for particles of nanometer radius. For situations that involve thick electrical double layers and the whole frequency spectrum, one can solve the full electrokinetic equations using various numerical methods.

Using molecular dynamic simulations to study macroion solutions under alternating electric fields is a relatively new approach; only a few works in the literature have tackled this subject. Most studies have focused on the conformation change of a single polyelectrolyte (PE) chain. Liu et al. studied the unfolding and collapse of a flexible PE chain under a sinusoidal electric field. Hsiao et al. examined a similar system, but in trivalent salt solutions under a square-wave electric field. Zhang et al. investigated the dynamics of an anchored PE chain, for both flexible and semiflexible cases. The detection of DNA sequences using an AC-field in a nanopore was discussed in Ref. 24. A Langevin thermostat was used in most studies, because the hydrodynamic interactions were taken to be screened for long PE chains in solutions with high salt concentration. For the system of nanometer-sized colloids, hydrodynamic interactions are important, and we include coarse-grained solvent particles.

Simulations with explicit solvents and microions are numerically challenging, because both the hydrodynamic and the electrostatic interactions are long-ranged. In recent years, a number of coarse-grained simulation methods have been developed to address this class of problem. The general idea is to couple the explicit charges with a mesoscopic model for Navier-Stokes fluids. There are a few choices of the fluid model in the literature, such as the Lattice Boltzmann (LB) method, Multi-Particle Collision Dynamics (MPCD), and Dissipative Particle Dynamics (DPD). In this paper, we use the particle-based DPD approach. DPD is a coarse-grained simulation method which is Galilean invariant and conserves momentum. Since it is a particle-based method, microions can be introduced in a straightforward manner. A recent comparative study indicated that the electrostatic interaction is the most expensive part in terms of the computational cost. Therefore, for intermediate or high salt concentrations, different methods for modelling the fluid becomes comparable.

In this work, we study the response of the charged colloidal particle and its surrounding ionic clouds under external electric fields. In a recent publication, we have presented first results on the frequency-dependent dielectric response of a colloid in solutions of high ionic strength. In that case, the results were in qualitative agreement with the prediction of the Maxwell-Wagner theory. Here, we systematically vary the salt concentration down to the low-salt regime where the Maxwell-Wagner theory no longer applies, and analyze the contributions of microions to the dynamic and dielectric response. We use DPD simulations, including in full the hydrodynamic and electrostatic interactions. The remainder of this article is organized as follows: In section II, we give a brief introduction to the simulation model and describe important parameters for the system. We present the simulation results on the mobility and polarizability in section III and IV respectively. Finally, we conclude in section V with a brief summary.

II. SIMULATION MODEL

In this section, we briefly review our simulation model for a colloidal particle in a salt solution and describe some important physical quantities (see also Ref. 37). In the following, physical quantities will be reported in a model unit system of \( \sigma \) (length), \( m \) (mass), \( \varepsilon \) (energy), \( e \) (charge) and a derived time unit \( \tau = \sigma \sqrt{m/\varepsilon} \).

Our simulation system has three components: the solvent, the microions, and the colloidal particle. The sol-
vent is modelled as a fluid of DPD beads, where DPD is used as a canonical thermostat (i.e. including the dissipative and stochastic part) without conservative forces \[38\]. Some important parameters in the simulation are listed in Table I. Our DPD fluid has a density $\rho = 3.0 \sigma^{-3}$ and a shear viscosity $\eta_s = 1.23 \pm 0.01 m/\sigma \tau$. Counterions and salt microions are introduced as the same DPD beads as the fluid particle, but carry charges and have exclusive interactions. We only consider the monovalent case where microions carry a single elementary charge $\pm e$. The exclusive interaction is necessary to prevent the collapse of charged system. A short-range repulsive Weeks-Chandler-Andersen interaction is used \[39\],

\[
V(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma}{r-r_0} \right)^6 - \left( \frac{\sigma}{r-r_0} \right)^{12} + \frac{1}{4} & \text{for } r < r_c \\
0 & \text{otherwise}
\end{cases}
\]

(4)

The cutoff radius is set at the potential minimum $r_c = r_0 + \sqrt{2}\sigma$. The microions have a size of $1.0\sigma$ ($r_0 = 0$).

One useful quantity for later discussions is the diffusion constant of the microion $D_I$, which can be determined by measuring the mean-square displacement

\[
\lim_{t \to \infty} \langle (r(t) - r(0))^2 \rangle = 6D_I t.
\]

(5)

The diffusion constant is a function of the salt concentration. We performed simulations with different salt concentrations, $\rho_s = 0.003125 \sigma^{-3} - 0.2 \sigma^{-3}$. The simulation results are compared with the empirical Kohlrausch law \[40\], which states that microion diffusion constant depends linearly on the square root of the salt concentration $\sqrt{\rho_s}$.

\[
D_I = A - B\sqrt{\rho_s},
\]

(6)

where $A$ and $B$ are fitting parameters. Fig. I shows the simulation results and a fit to Kohlrausch law.

We model the large colloidal particle as a sphere with many interacting sites on its surface. The interaction between these surface sites and the solvent beads is modelled using DPD dissipative interactions. To prevent solvent particles from penetrating the colloid, a similar repulsive interaction as Eq. (4) acts between the colloid and fluid/microion particles, but with the colloid radius $R = r_0 + \sigma = 3.0\sigma$. The colloid carries a positive charge $Q$, and the mass of the colloidal particle is $M = 100m$.

The moment of inertia is $I = 360m\sigma^2$, corresponding to a sphere with constant volume density. The diffusion constant of an uncharged colloid is measured by a linear regression of the mean-squared displacement, similar to the case of microions. For a colloid with radius $R = 3.0\sigma$, the diffusion constant is measured to be $D = 0.010 \pm 0.002 \sigma^2/\tau$ in a simulation box with linear dimension $L = 30\sigma$. This result compares well to the diffusion constant of a Stokes sphere of radius $3.0\sigma$ in a simple cubic lattice \[41\].

We carried out simulations using the open source package ESPResSo \[42\]. Modifications have been made to incorporate an external time-dependent electric field. The temperature of the system is kept at $k_BT = 1.0\varepsilon$. Electrostatic interactions are calculated using the Particle-Particle-Particle Mesh (P3M) method \[43\,44\], with the Bjerrum length $l_B$ set to $1.0\sigma$. The Velocity-Verlet algorithm is used to integrate the equation of motion \[45\,46\] with a time step of $\Delta t = 0.01\tau$. We use a cubic simula-

| Parameter | Value |
|-----------------|--------|
| Fluid density $\rho$ | 3.0 $\sigma^{-3}$ |
| Friction coefficient for fluid DPD interaction $\gamma_{DPD}$ | 5.0 $m/\tau$ |
| Cutoff for fluid DPD interaction | 1.0 $\sigma$ |
| Shear viscosity $\eta_s$ | $1.23 \pm 0.01 m/(\sigma \tau)$ |
| Friction coefficient for colloid DPD interaction | 10.0 $m/\tau$ |
| Cutoff for colloid DPD interaction | 1.0 $\sigma$ |
| Size of fluid particle, microion, and colloid | 1.0, 1.0, 3.0 $\sigma$ |
| Mass of fluid particle, microion, and colloid | 1.0, 1.0, 100 $m$ |
| Bjerrum length $l_B$ | 1.0 $\sigma$ |
| Simulation box | 30 $\sigma$ |

TABLE I: Parameters used in the DPD simulations.
tion box with linear dimension $L = 30\sigma$, with periodic boundary conditions in all three directions. We note that the application of periodic boundary conditions makes the measurement in our system somewhat different from the experimental situation. The periodic images of the colloids are coupled both hydrodynamically and electrostatically. Therefore, we measure in fact the mobility and polarizability of a particle in a simple cubic lattice.

In simulations, various time-series of the velocity or dipole moment are obtained, but the data is noisy due to the thermal fluctuations. For example, in Fig. 4 we show the external electric field and the colloid velocity as a function of the time for one set of parameters ($Q = 50e$ and $\rho_s = 0.0125\sigma^{-3}$). In order to extract the amplitude and the phase of the velocity oscillation, we apply a Fourier transform to the time-series of the velocity. The real and imaginary parts of the Fourier spectrum exhibit peaks at the frequency of the external electric field, and the peak values correspond to the real and imaginary part of the complex velocity amplitude.

To map the simulation units to real physical numbers, we use an aqueous solution of KCl as a reference system. For an aqueous solution ($\rho_s = 0.0125\sigma^{-3}$) under the influence of an AC field with frequency $f = 0.01\tau^{-1}$ and amplitude $E_0 = 0.5e/(\sigma \varepsilon)$. Top: instantaneous electric field. Bottom: translational velocity along the field direction.

![FIG. 2: Dynamics of a charged colloidal particle with charge $Q = +50e$ and radius $R = 3.0\sigma$ in a salt solution ($\rho_s = 0.0125\sigma^{-3}$) under the influence of an AC field with frequency $f = 0.01\tau^{-1}$ and amplitude $E_0 = 0.5e/(\sigma \varepsilon)$. Top: instantaneous electric field. Bottom: translational velocity along the field direction.](image)

The mobility for counterions at different distances $r$ away from the colloid center are plotted in solid curves. The mobility of the colloid depends only weakly on the salt concentration, but is negligible at intermediate and high salt concentrations. For the parameter range considered here ($0.003125\sigma^{-3} \leq \rho_s \leq 0.2\sigma^{-3}$), the electrophoretic mobility of the colloid depends only weakly on the salt concentration. The number of counterions to neutralize the colloid charge is comparable to the number of salt at the lowest salt concentration, but is negligible at intermediate and high salt concentrations. We systematically vary some important parameters, such as the salt concentration, the colloid charge, and the frequency of the external fields.

III. DYNAMIC RESPONSE

In the following sections, we report simulation results for a single charged colloid of radius $R = 3.0\sigma$ in an electrolyte solution. We focus on the dynamic response of the colloid and microions, characterized by the mobility $\mu$, and the dielectric response, represented by the polarizability $\alpha$. We systematically vary some important parameters, such as the salt concentration, the colloid charge, and the frequency of the external fields.

A. Effect of salt concentration

To study the effect of the salt concentration and the colloid charge, we will focus on the case of static electric fields. For static fields, the motion of the colloid and its surrounding microions can be characterized by a scalar mobility $\mu$, which represents the ratio between the velocity of the particle and the magnitude of the applied field. For the microions, the mobility also depends on their position with respect to the colloid. In the simulation, we average over the velocities of microions which have a distance $r$ from the colloid center.

In Fig. 6, we plot the mobility of the colloid and microions as a function of the salt concentration $\rho_s$. The colloid carries a total charge of $Q = +50e$. The number of counterions to neutralize the colloid charge is comparable to the number of salt at the lowest salt concentration, but is negligible at intermediate and high salt concentrations. For the parameter range considered here ($0.003125\sigma^{-3} \leq \rho_s \leq 0.2\sigma^{-3}$), the electrophoretic mobility of the colloid depends only weakly on the salt concentration. When the salt concentration increases, the Debye length becomes shorter, and the electrostatic interaction becomes more screened. This reduces the effective charge of the colloid, which includes the bare colloid charge and the contribution from condensed counterions, resulting in a slight reduction of the electrophoretic mobility of the colloid.

The mobilities for counterions at different distances $r$ away from the colloid center are plotted in solid curves. Due to the strong electrostatic attraction towards the colloid, counterions overcome the entropic repulsion and accumulate in the vicinity of the colloidal surface. Their mobility is a result of the interplay between two conflicting interactions. On the one hand, counterions have the opposite charge as the colloid, thus the external electric field drives counterions away from the colloid. Similarly, the entropic force also tends to separate counterions and the colloid and pushes counterions towards regions where the ionic concentration is lower. On the other hand, the Coulomb attraction from the colloid charge and the hydrodynamic interaction from the colloid surface drag counterions along with the colloid. The mobility of the...
counterion is a result from these two competing effects. At low salt concentration, counterions close to the colloid experience strong attraction from the colloid, and they can be considered as attached to the colloid surface. Therefore, the counterion mobility has the same sign as that of the colloid. Note that both the hydrodynamic and the Coulomb interaction depend on the distance between the counterion and the colloid. When the distance is increased, both interactions become weaker, resulting in a reduction of the counterion mobility.

The counterion mobility also depends on the salt concentration. When the salt concentration increases, the Debye length decreases and the electrostatic interaction becomes screened, resulting in a reduction of the attractive force from the colloid. In Fig. 3, all curves of counterion mobility exhibit an initial reduction as the salt concentration increases. For counterions close to the colloid surface, there exists a salt concentration at which the electrostatic interaction is screened so much that the external electric field dominates, resulting in a change of the sign of the mobility. In this case, the external field is strong enough to overcome the attraction, and drives even the closest counterions to move in the opposite direction of the colloid. A similar phenomenon has been discussed in Ref. [4] for condensed counterions in poly-electrolyte solutions.

The situation is different for coions, as shown in Fig. 3 (dash-dotted lines). The coions have the same charge as the colloid, thus the external fields and the hydrodynamic interactions both drive the coions to move along with the colloid. The mobility for the coions always has the same sign as the colloid, and its dependence on the salt concentration shows the opposite trend, compared to that of the counterions.

At high salt concentration and far away from the colloid, the electrostatic and hydrodynamic interactions are fully screened, and the forces exerted by the colloid on the microions are negligible. In this case, the mobilities for counterions and coions are both proportional to the diffusion constant of the microion $D_I$, but with the opposite sign. The mobility for microions in solution without the colloid is shown as the dashed lines in Fig. 3. The decrease of the mobility value at high salt concentration is the result of the reduction in the diffusion constant of the microion.

B. Effect of colloid charge

The response of the colloid and microions can also be tuned by varying the bare charge on the colloid. Compared to the previous situation of adjusting the salt concentration, where the range of the electrostatic interaction (the Debye screen length) is varied, the change of the colloid charge directly alters the strength of the electrostatic interaction with the microions. Fig. 4 shows the mobility of the colloid and its surrounding microions as a function of the colloid charge $Q$. The salt concentration is kept constant $\rho_s = 0.05 \sigma^{-3}$. The electrophoretic mobility of the colloid increases as the colloid charge increases, but the increase is less than linear.

The counterions are negatively charged, thus their mobility is in general negative. The mobility depends strongly on the distance between the counterions and the colloid. Far away from the colloid, the electrostatic interaction is sufficiently screened for the salt concentration $\rho_s = 0.05 \sigma^{-3}$. It can be seen in Fig. 4 for the counterion curve $r = 6.0 \sigma$; the mobility is insensitive to the colloid charge and almost coincides with the mobility value for free negative ions (dashed grey line). Close to the colloid surface, the attraction from the colloid charge and the hydrodynamic drag dominate, and the difference between mobilities of the counterion and the colloid becomes smaller. For highly charged colloid $Q > 60 e$, the attraction is strong enough for the closest counterions to be dragged along with the colloid, resulting in a positive counterion mobility.

The mobility of coions (Fig. 4, dash-dotted lines) has the opposite sign from that of the counterions. Coions close to the colloid are slowed down by the slower colloid. The mobility of coions far from the colloid approaches...
that of free microions.

C. Effect of frequency

In this section, we investigate the frequency-dependent response of the colloid in electrolyte solutions. We apply a sinusoidal external field to probe the colloidal suspension, and measure the mobility of the colloid and its surrounding counterions. The motion is in general not in phase with the external field. Thus, the mobility becomes a complex number, where the real part of the mobility characterizes the in-phase component of the motion, and the imaginary part is the out-phase contribution. In Fig. 5, we show the complex mobility $\mu(\omega)$ for a system with salt concentration $\rho_s = 0.0125 \sigma^{-3}$ and colloid charge $Q = +50 e$.

Let us focus on the counterions far away from the colloid first. For those counterions, the influence from the colloid is small; thus they can be approximated as free microions in a salt solution. The only important time scale is determined by the microion’s inertia. The equation of motion for a charged particle with mass $m$ and charge $-e$ in a viscous fluid is

$$m \ddot{x} = -\gamma \dot{x} - e E_0 e^{i\omega t},$$

where $\gamma = k_B T / D_I$ is the Langevin friction coefficient. The equation can be solved using Fourier transform, and one obtains the complex mobility

$$\mu(\omega) = \frac{v_0}{E_0} = -e \frac{1 - i \left( \frac{m \omega}{\gamma} \right)}{\gamma + (\frac{m \omega}{\gamma})^2}.$$  (8)

From the diffusion constant $D_I = 0.60 \sigma^2 / \tau$ for the solution of salt concentration $\rho_s = 0.0125 \sigma^{-3}$, one obtains $\gamma = 1.67 m / \tau$. Eq. (8) is plotted as dashed grey curves in Fig. 5. The complex mobility of the counterions far away from the colloid ($r = 8.0 \sigma$) resembles that of free microions. The variation of mobility is characterized by a time scale set by

$$\tau_m = \frac{2 \pi m}{\gamma} \quad \text{or} \quad f_m = \frac{\gamma}{2 \pi m}.$$  (9)

Using the friction coefficient $\gamma = 1.67 m / \tau$, one obtains a frequency $f_m = 0.27 \tau^{-1}$. This is roughly the position of...
the maximum peak in the imaginary component of mobility for \( r = 8.0 \sigma \). At frequencies higher than \( f_m \), the finite mass of the counterions limits ions from responding to the external field, resulting in a reduction of the mobility.

For counterions close to the colloid surface, their motion is strongly influenced by the motion of the colloid. We shall examine the mobility of counterions at distances \( r = 3.0 \sigma \), starting from low to high frequencies. At low frequency, one important contribution comes from the enhanced salt concentration building up near the colloid surface. The situation is depicted for a positively charged colloid in Fig. 6. At the back side of the colloid, a wake of negative counterions builds up which are dragged away from the surface by the external field. These counterions, combined with the coions coming in from the bulk solution, create an increase of the salt concentration on the left-hand side of the colloid – a salt source. A similar process occurs on the right-hand side of the colloid, where depletion of the counterions and coions results in a reduction of the salt concentration – a salt sink. Therefore, a salt concentration gradient is established along the colloid surface, which drives the microions in the direction of the external field. For counterions close to the surface, the effect due to the concentration gradient, combined with the hydrodynamic drag from the colloid, partially cancels out the effect of the external field, which drives the counterions in the direction opposite to the field. The result is an increase of the in-phase component of the mobility at low frequency for counterions that are close to the colloid surface.

For our system, this time scale, \( \tau_c = 60 \tau \), sets a frequency scale, \( f_c = 1/\tau_c = 0.017 \tau^{-1} \). Above the crossover frequency \( f_c \), the variation of the external field is too fast for the concentration gradient to build up, and the motion of the counterions is mainly driven by the external field. Thus, the response of the counterions reverts to that of free microions under oscillating external field. At even higher frequency around \( f_m \), the inertia effect sets in and the mobility of the counterions is reduced to zero.

![Diagram](https://example.com/diagram.png)

**FIG. 6:** Scheme of the buildup of concentration gradient around a positive colloid. The salt concentration increases on the left-hand side of the colloid, and decreases on the right-hand side. As a consequence, a concentration-induced diffusion flux is formed in the direction of the external field.

The accumulation of the salt concentration cannot be accomplished instantaneously, and the associated time scale is the time required for microions to diffuse over the diameter of the colloid,

\[
\tau_c = \frac{(2R)^2}{D_I}.
\]

### IV. DIELECTRIC RESPONSE

In this section, we study the dielectric response of the charged colloid in salt solution. The main quantity calculated from the simulation is the complex polarizability \( \alpha(\omega) \), which characterizes the ratio between the dipole moment and the external field. We focus on the effect of varying the frequency of the external field. The amplitude of the field is chosen in the linear region, \( E_0 = 0.5 \varepsilon/(\sigma e) \), and frequency range from \( f = 0.001 \) to \( 2.0 \tau^{-1} \) is considered. Fig. 7 shows the real and imaginary parts of the polarizability \( \alpha(\omega) \) for a colloid particle with bare charge \( Q = +50 e \). The solution has a salt concentration \( 0.125 \sigma^{-3} \), corresponding to the Debye length \( l_D = 1.72 \sigma \) including 50 counterions. The Debye length is smaller than, but comparable to the colloidal radius \( (R = 3.0 \sigma) \).

In the low-frequency region, the external perturbation is slow enough that the system can follow, and the change of the polarizability is connected to the polarization of the ionic cloud surrounding the colloid. Two opposite effects take place at the same time at low frequencies. One is due to the external field, which drives the negative counterion cloud in the opposite direction of the colloid movement. The resulting dipole moment points in the same direction as the external field. The other effect is induced by the salt concentration gradient near the colloid surface (see Fig. 6), where counterions diffuse in the direction of the external field. The concentration-induced effect results in a dipole moment in the opposite direction of the field. The time required for the concentration gradient to be established is \( \tau_c = 60 \tau \) (or \( f_c = 0.017 \tau^{-1} \)). At frequencies higher than \( f_c \), the concentration-induced effect diminishes, resulting in an increase of the in-phase component of the polarizability.

In the opposite limit of high frequency, the colloid and the ion cloud can no longer follow the field; thus both \( \text{Re}\{\alpha\} \) and \( \text{Im}\{\alpha\} \) converge to zero. At intermediate frequencies \( f \sim 10^{-1} \tau^{-1} \), the real part \( \text{Re}\{\alpha\} \) crosses over from positive to zero with an overshoot below the transition frequency and a slight undershoot to negative values after the transition frequency. The imaginary part \( \text{Im}\{\alpha\} \) drops to large negative values, indicating that the response is out of phase and that there is high dissipation. At high frequencies, the main contribution to the dipole moment stems from the conductivity mismatch between the colloid and the solvent due to the presence of free...
counterions in the solvent. The finite time required for the formation of the free charges is responsible for the well-known Maxwell-Wagner dispersion, and this relaxation time is given by

$$\tau_{mw} = \frac{\epsilon_p + 2\epsilon_m}{K_p + 2K_m},$$

where $\epsilon$ and $K$ are the permittivity and conductivity of the colloidal particle ($p$) and medium ($m$). For our simulation model, $\epsilon_p = \epsilon_m$ and $K_p = 0$. Using the relation between the conductivity and the diffusion constant of the microion (for 1-1 electrolytes), $K_m = 2p_s e^2 D_l / k_B T$, the Maxwell-Wagner relaxation time can be rewritten as

$$\tau_{mw} = \frac{3\epsilon_m}{2K_m} = \frac{3}{2} \frac{r^2_D}{D_l}.$$  

Thus, $\tau_{mw}$ is on the same order of the time required for the microion to diffuse over the distance of Debye length. The related frequency $f_{mw} = 1/\tau_{mw} \approx 0.12 \tau^{-1}$. This is roughly the frequency at which $\text{Im}\{\alpha\}$ reaches a minimum.

We compare our simulation results with the predictions from two theoretical models. One is the Maxwell-Wagner-O’Konski (MWO) theory, which was originally developed for micrometer colloids where the electric double layer is much thinner than the colloid size ($\kappa R \gg 1$). We shall see that it still captures some high-frequency features of the polarizability. We briefly sketch the MWO theory in Appendix A. Another theory is based on the standard electrokinetic model, which can be applied to arbitrary salt concentrations. We summarize the governing equations of electrokinetic model in Appendix B. In general, analytic solutions only exist for large and small $\kappa R$ limits. For intermediate value of $\kappa R$, one need to rely on numerical methods to solve the electrokinetic equations. We compute the complex polarizability using the software MPEK.

One important quantity required as an input for the theory is the zeta potential, defined as the electric potential at the shear plane, an imaginary plane separating the hydrodynamically mobile and immobile fluid. The exact position of the shear plane is difficult to determine, and it is also possible that there is no sharp boundary at all. Since the interacting sites of the colloid are set at $R = 3.0 \sigma$, and in our model, they are responsible for the hydrodynamical coupling to the fluid, it is reasonable to use $R = 3.0 \sigma$ for the position of the shear plane. The zeta-potential can be obtained by solving the Poisson-Boltzmann equation. For a spherical particle, numerical tables for the solution to Poisson-Boltzmann equation were given by Loeb et al. \cite{Loeb1970}. An analytic expression for the relationship between the $\zeta$-potential and the surface charge density $\sigma$ was derived by Ohshima et al. \cite{Ohshima1987, Ohshima1988}

$$\sigma = \frac{2\epsilon_m \kappa k_B T}{e} \sinh \left( \frac{e\zeta}{2k_B T} \right) \left[ 1 + \frac{1}{\kappa R \cosh^2(e\zeta/4k_B T)} \right]^{1/2} \left( 1 + \frac{1}{(\kappa R)^2} \frac{8 \ln[\cosh(e\zeta/4k_B T)]}{\sinh^2(e\zeta/2k_B T)} \right)^{1/2}.$$  

For our system, we obtain a scaled zeta potential $\zeta = 4.12 \epsilon/e$. We also measure the charge density as a function of the distance to the colloid center. The simulation results are shown in Fig. 5. Also shown are the numerical solutions from solving the Poisson-Boltzmann equation by a variational approach \cite{Ohshima1987, Ohshima1988}. The simulation and numerical results show good agreement. By integrating the charge density from the simulation, we obtain the zeta potential $\zeta = 4.26 \epsilon/e$, close to the value computed using Ohshima’s formula \cite{Ohshima1987}. We use the simulation value in the following calculation.

According to the Maxwell-Wagner-O’Konski theory, the effect of the electric double layer can be taken into account by introducing a surface conductance in the Maxwell-Wagner theory. We estimate the surface conductance, $K_\sigma = 0.23 e^2/(\sigma \varepsilon \tau)$, based on Bikerman’s ex-
In the Maxwell-Wagner theory, the colloid and its surrounding medium are treated as homogeneous substances, and only the bulk properties of the components are taken into account. The induced charges due to the external field only appear at the colloid-fluid interface, and the effect of the spatial distribution of the polarization charges is neglected. This simplification is valid for large colloids, but for small particles \((\kappa R \sim 1)\), the distribution of the polarization charges near the interface may become important. The theory taking into consideration of the effect of space charge variation is based on standard electrokinetic equations. One important result from the electrokinetic theory is the low-frequency dielectric dispersion \([13]\). We use the program MPEK to calculate the complex polarizability, and the results are shown as dashed lines in Fig. 7. The prediction from the electrokinetic theory is in good agreement with the simulation, and correctly captures the overshoot at low frequency.

In the Maxwell-Wagner theory, the dis-tribution of the polarization charges near the interface may become important. The theory taking into consid-

![Diagram](image-url)

**FIG. 8:** The densities for the negative counterions \((\rho_{-})\) and positive coions \((\rho_{+})\) as a function of the distance to the colloid center. The parameters are the same as in Fig. 7. The lines are results by solving the Poisson-Boltzmann equation \([54, 55]\).

Pression (see Appendix A for details). Using this value, we can calculate the theoretical polarizability as a function of frequency without any fitting parameters. The resulting curves are shown in Figure 7 with solid lines. The result of the MWO theory is only in qualitative agreement with the simulation. The theory captures the main qualitative features, and roughly the correct crossover frequency, but it misses most of the details around the transition frequency.

The simulation results feature a slight undershoot at the high frequency region. This can be explained by considering the inertia effect of the microions, which are not entirely negligible in our simulations. (In real systems, they are negligible.) The inertia effect can be incorporated into the theory by a frequency-dependent conductivity (see Appendix A) and the theory can be revised accordingly, giving the dash-dotted lines in Figure 7. It predicts small undershoots in both the real and the imaginary part of the polarizability, which are consistent with the simulation. However, both results from the MWO theory, the original one and the one with the inertia correction, miss the overshoot of the \(\text{Re}\{\alpha}\) at the low-frequency regime.

When an alternating electric field is applied, the dynamic response of the colloid and microions depends on the frequency. The frequency-dependence of the microion mobility is controlled by two different processes. On the one hand, the oscillating field drives the microions directly. At low frequency, the movement of the microion is in phase with the perturbation. At high frequency, the inertia effect prevents the microion from following the external field. The frequency that separates these two different regions is related to the time scale \(\tau_m\). On the other hand, a concentration gradient can build up around the colloid surface at low frequency, which drives a diffusive motion of the microions from the region of high concentration to that of low concentration. The time required for the gradient to develop is \(\tau_c\). The motion of the microion is determined by the interplay between the field-induced and concentration-induced effects. For microions away from the colloid surface, the interaction to the colloid is weak, and the field-induced effect dominates. For microions close to the surface, the microions follow the colloid’s motion at low frequency, but recover.
to the free-ion case at high frequency.

The dielectric response of the charged colloid is characterized by the polarizability. For our colloid model \( \epsilon_p = \epsilon_m \) and \( K_p = 0 \), the main contribution to the dipole moment comes from the electric double layer. For microions, there are two important length scales: one is the Debye screening length \( l_D \), and the other one is the diameter of the colloid \( 2R \). Associated with these two length scales, are the two time scales \( \tau_{miw} \) and \( \tau_c \), which correspond to the time required for the microion to diffuse over the distance \( l_D \) and \( 2R \), respectively. For the parameters considered in this work, \( 2R > l_D \), thus the frequency \( f_{miw} \) is larger than \( f_c \). The competition of these two time scales results in a maximum of \( \text{Re}\{\alpha\} \) at the intermediate frequency \( f_c = f < f_{miw} \). We compare the simulation results to the predictions from the Maxwell-Wagner-O’Konski theory and standard electrokinetic model. The MWO theory only captures the dielectric response in the high-frequency region, while the electrokinetic theory performs well over the whole frequency range.

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**Appendix A: Maxwell-Wagner-O’Konski theory**

In this appendix, we give a short introduction to the Maxwell-Wagner-O’Konski theory. More detailed information can be found in Refs. [7, 8, 11, 12].

Assume an external electric field with a form \( \mathbf{E} = E_0 e^{i \omega t} \hat{x} \) is applied to a colloidal solution. The external field induces a dipole moment to the colloidal particle. The amplitude of the dipole moment can be written as \( p_0 = 4 \pi \epsilon_m K(\omega) R^3 E_0 \) (cf. Equation (3)), where the Clausius-Mossotti factor \( K(\omega) \) is a complex number containing both the magnitude and the phase information. In the Maxwell-Wagner theory, it has the form

\[
K(\epsilon_p^*, \epsilon_m^*) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*}, \tag{A1}
\]

where \( \epsilon_p^* \) and \( \epsilon_m^* \) are the complex dielectric constants of the particle and the medium, respectively. They are defined as

\[
\epsilon_p = \epsilon_p^* + \frac{K_p}{i \omega}, \quad \epsilon_m = \epsilon_m^* + \frac{K_m}{i \omega}, \tag{A2}
\]

where \( \epsilon \) (without the star) and \( K \) are the permittivity and conductivity, respectively. For \( \epsilon_m = \epsilon_p = \epsilon \), the Clausius-Mossotti factor can be rewritten as

\[
K = K_0 \frac{1 - i \omega}{1 + \omega^2} \tag{A3}
\]

with

\[
K_0 = \frac{K_p - K_m}{K_p + 2K_m} \quad \text{and} \quad \omega = \frac{3 \epsilon}{K_p + 2K_m} \omega. \tag{A4}
\]

The conductivity of the medium \( K_m \) is related to the microion diffusion constant \( D_I \) via \( K_m = 2 \rho_s \epsilon_0^2 D_I / (k_B T) \) for 1-electrolytes.

The classical Maxwell-Wagner theory fails to explain the dielectrophoretic properties of latex particles. Latex has a low intrinsic conductivity, but the measurement indicated that the particle conductivity is high. It was concluded that the electric double layer surface significantly contributes to the particle conductivity. This was first demonstrated by O’Konski [11] where \( K_{C} \) is the surface conductance (unit S instead of S m\(^{-1}\)) due to the electric double layer.

The surface conductance then can be related to the \( \zeta \)-potential by Bikerman’s expression

\[
K_{C} = l_D \left( \exp\left(\frac{e \zeta}{2 k_B T}\right) - 1 \right) (1 + 3m) K_m, \tag{A6}
\]

where \( m \) is a dimensionless ionic drag coefficient [56, 57]. Bikerman’s expression is applicable for 1-electrolytes, and the contribution from coions has been neglected. The ionic drag coefficient is related to the viscosity \( \eta_s \) and ion diffusion constant \( D_I \),

\[
m = \frac{2 \epsilon_m (k_B T)^2}{3 \eta_s \epsilon_0^2 D_I}, \tag{A7}
\]

\((m = 0.072 \text{ for salt density } \rho_s = 0.0125 \text{g cm}^{-3}, \text{ and } m = 0.18 \text{ for KCl}). \) With \( Q = 50e \) and \( R = 3.0a \), we obtain the surface conductance \( K_{C} = 0.23 \epsilon^2 / (\sigma \sqrt{m \rho_s}) \).

The inertia effect of ions can be taken into account by considering a charged particle with charge \( e \), mass \( m \) immersed in a viscous fluid. The equation of motion for the particle under an AC field \( E_0 e^{i \omega t} \hat{x} \)

\[
\dot{m} \ddot{x} = -\gamma \dot{x} + eE_0 e^{i \omega t} \hat{x}, \tag{A8}
\]

where \( \gamma = k_B T / D_I \) is the friction constant. After solving the equation of motion, one finds that the velocity of the particle has the form

\[
\dot{x} \propto \frac{1 - i(m \omega)}{1 + (m \omega)^2}. \tag{A9}
\]
Since the conductivity of salt solutions is proportional to the ion’s velocity, it is reasonable to assume that the conductivity has the same frequency dependency

\[ K_m \rightarrow K_m \frac{1 - i \left( \frac{\omega \zeta}{\sigma_c} \right)}{1 + \left( \frac{\omega \zeta}{\sigma_c} \right)^2}. \quad (A10) \]

The corrected MWO results in Fig. 7 are obtained by substituting (A10) into the Clausius-Mossoti factor (A3).

**Appendix B: Electrokinetic equations**

Consider a colloidal particle immersed in an electrolyte solution. The solution consists of \( \sum \) ionic species of charge \( z_k e \) and bulk concentration \( c_k(\infty) \). The spherical colloid has a hydrodynamic radius of \( R \). The external electric field is \( \mathbf{E} \).

The system is described in terms of the electrostatic potential \( \phi(r) \), the ion concentration field \( c_k(r) \), the flow velocity field \( \mathbf{u}(r) \) and the pressure \( p(r) \). The governing laws of the system are the Poisson equation, the Nernst-Planck equation and the Navier-Stokes equations.

**Poisson Equation**

The electrostatic potential \( \psi \) outside the colloid is related to the ion concentration by the Poisson equation

\[ \nabla^2 \psi = -\frac{1}{\epsilon_m} \sum_k z_k e c_k, \quad (B1) \]

where \( \epsilon_m \) is the solvent permittivity. The boundary conditions for the potential are

\[ \phi = \zeta, \quad r = R, \]
\[ \phi = -\mathbf{E} \cdot \mathbf{r}, \quad r \to \infty. \quad (B2) \]

**Nernst-Planck Equation**

The flux of type-\( k \) ion can be written as

\[ \mathbf{j}_k = -D_k \nabla c_k - z_k D_k \left( \frac{e \psi}{k_B T} \right) c_k + \mathbf{u} c_k. \quad (B4) \]

The first term is the contribution from the ion’s diffusion due to the concentration gradient. The second term represents the effect of electric field. The last term expresses the flow-induced hydrodynamic drag force.

The conservation of ion number is described by a continuity equation,

\[ \frac{\partial c_k}{\partial t} + \nabla \cdot \mathbf{j}_k = 0, \quad (B5) \]

After substituting Eq. (B4) and omitting the subscript \( k \) for simplicity, Eq. (B5) takes the form

\[ \frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) - \nabla \cdot \left( zD \left( \frac{e \psi}{k_B T} \right) c \right) + \nabla \cdot (\mathbf{u} c) = 0. \quad (B6) \]

The boundary condition at the colloid surface is

\[ \mathbf{j} \cdot \mathbf{n} = 0, \quad r = R, \quad (B7) \]

where \( \mathbf{n} \) is the normal to the surface. Far away from the colloid, the concentration reaches to the bulk value

\[ c = c(\infty), \quad r \to \infty. \quad (B8) \]

**Navier-Stokes Equation**

The Navier-Stokes equation with an external body force is

\[ \rho_0 \frac{\partial \mathbf{u}}{\partial t} + \rho_0 \mathbf{u} \cdot \nabla \mathbf{u} = \eta_0 \nabla^2 \mathbf{u} - \nabla p - \nabla \psi \sum_k z_k e c_k, \quad (B9) \]

where \( \rho_0 \) is the solvent density and the last term on the right-hand side is due to the electric field. The second term on the left-hand side can be dropped for incompressible fluid, \( \nabla \cdot \mathbf{u} = 0 \). No-slip boundary condition at the colloid surface requires

\[ \mathbf{u} = \mathbf{V}, \quad r = R, \quad (B10) \]

where \( \mathbf{V} \) is the velocity of the colloid.

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