

Direct numerical simulation of charged colloids in an oscillating electric field

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2015

Contents

1	General introduction	1
1.1	Introductory remarks	1
1.2	Electrophoresis	2
1.3	Smoothed Profile Method	3
1.3.A	Newton-Euler equations of motion	4
1.3.B	The Navier-Stokes equation	4
1.3.C	Advection-diffusion equation	5
1.4	Dynamic motion	6
1.5	Thesis objectives	6
2	Dynamic Electrophoresis of Charged Colloids in an Oscillating Electric Field	9
2.1	Introduction	9
2.2	Simulation Parameters	13
2.3	Validation	15
2.3.A	Zeta potential	15
2.3.B	External electric field	16
2.4	Results	16
2.4.A	Electrophoretic mobility in DC and AC fields	16
2.4.B	Complex mobility of a single charged particle	18
2.4.C	Effect of ionic diffusion	20
2.4.D	Complex mobility of a dense colloidal dispersion	22
2.5	Conclusions	24
3	Dynamic Polarizability of Charged Colloids in an Oscillating Electric Field	27
3.1	Introduction	27
3.2	Definitions	29
3.2.A	Dipole moment	29
3.2.B	Polarizability	30

3.3	Method	30
3.3.A	Approximate theories	30
3.4	Simulation	32
3.5	Validation	34
3.5.A	Zeta potential and charge distributions	34
3.5.B	Linear dependence on external electric field	34
3.6	Results	35
3.6.A	Influence of zeta potential ζ	35
3.6.B	Influence of ion diffusion constants D_α	36
3.6.C	Influence of the Debye length κa	37
3.6.D	Frequency dependency of polarizability	38
3.7	Conclusions	42
4	Inter-particle force between two colloidal particles in an oscillating electric field	45
4.1	Introduction	45
4.2	Definitions	46
4.2.A	Inter-particle interaction force	46
4.3	Method	47
4.4	Simulation	49
4.5	Results	51
4.5.A	Influence of the electric field E_0	51
4.5.B	Influence of zeta potential ζ	53
4.5.C	Influence of the Debye length κa	54
4.5.D	Frequency dependency of inter-particle force	55
4.5.E	Inter-particle force between particles that are not aligned parallel to the electric field	56
4.5.F	Multiple unfixed particles simulation	57
4.6	Conclusions	59
5	General conclusion	63
	Acknowledgements	67

Chapter 1

General introduction

1.1 Introductory remarks

A colloidal dispersion is a system in which small colloidal particles (disperse phase) are dispersed in a continuous phase (i.e. when the particle Knudsen number is large enough) of a different composition (dispersion medium). The size of colloidal particles is between approximately 1 nm (10^{-9} m) and $1\text{ }\mu\text{m}$ (10^{-6} m). Colloidal dispersions are very common in daily life and widely used in industry, such as cosmetics, emulsions, pharmaceuticals, food, and paints. [1] The disperse phase and the dispersion medium can be gases, liquids, or solids. Excluding the case in which both are gas, eight kinds of patterns can be formed, as shown in Table 1.1 [2]. Among them, sols and emulsions are the most important and most widely used colloidal dispersions.

Table 1.1: The various types of colloidal dispersion with some common examples [2].

Disperse phase	Dispersion medium	name	example
solid	gas	aerosol	Smoke
liquid	gas	aerosol	Mist, Fog
solid	liquid	sol	Paint
liquid	liquid	emulsion	Milk
gas	liquid	foam	Beer foam
solid	solid	solid dispersion	Alloy
liquid	solid	solid emulsion	Ice cream
gas	solid	solid foam	Insulating foam

For colloidal dispersions, their surface properties strongly determine the stability of the system, a property which is very important in the industrial application. The stability of the colloidal system is influenced by the particle interaction, such as Van der Waals attraction between the particles, electric repulsive interaction, and the particle-solvent affinity. In a stable dispersion the particle interactions do not lead to aggregation because of inter-particle repulsion, which the overlap of the ionic clouds gives rise to a repulsion that pushes the particles apart. In an unstable dispersion, the collisions lead to aggregate formation. This is generally undesirable and colloid scientists aim to prevent it from occurring. If we want to increase the stability of the colloidal system, we usually add some electrolyte or polymer material. The former allows the colloidal particles absorb or dissociate

the ions and acquire an electric charge and surrounded by a cloud of counter-ions that repel each other, the latter allows the polymer material adsorbed on the colloid surface to increase the surface charges and repel each other more strongly or to increase the affinity between the particles and solvent.

Therefore, understanding the surface properties of colloidal dispersions is an important problem in many fields of science and engineering, such as statistical physics, soft matter physics, chemical engineering, and mechanical engineering. Thus, this system is currently being actively investigated. However, surface properties are very difficult to observe directly through optical measurements. Electrophoresis is recognized as a good method to probe the surface properties of the charged colloid. For example, as particles move under the influence of an external electric field, the electric double layer [1] (EDL, the cloud of counterions around charged particles) tends to be deformed and its distribution becomes anisotropic because due to the applied external field and also of the friction between ions and fluid. The electrophoretic mobility is then determined by the balance between the electrostatic driving force and the hydrodynamic frictional force acting on the particle. Assuming a suitable model of electrophoresis, the relationship between the electrophoretic mobility and the surface properties can be clearly defined. In this dissertation, I develop the direct numerical simulation method to study charged dispersions with a electrolyte solution, and reveal the polarization effects of the ion distribution.

1.2 Electrophoresis

The first successful theories for this phenomena can be found in the pioneering works of Helmholtz [3] and Smoluchowski [4]. By solving the one-dimensional Navier-Stokes and Poisson equations, Smoluchowski [4] derived an expression for the electrophoretic mobility μ of a single colloidal particle of:

$$\mu \equiv \frac{V}{E} = \frac{\epsilon \zeta}{\eta} \quad (1.1)$$

where V is the velocity of the colloid; E is the amplitude of the constant (direct current, DC) electric field; ϵ and η are the permittivity and the viscosity of the solvent, respectively; and ζ is the zeta potential (the electric potential of the slipping plane near the colloidal surface). This expression is correct for dilute dispersions of colloidal particles with an infinitely thin electrical double layer (EDL, a cloud of counterions that surrounds the colloidal particles). Later, Hückel [5]

derived a similar expression but in the opposite limit, where the double layer is infinitely thick:

$$\mu = \frac{2}{3} \frac{\epsilon \zeta}{\eta} \quad (1.2)$$

These theoretical results for opposite limits were combined by Henry [6], with the introduction of the Henry factor $f(\kappa a)$ ($f = 2/3$ for $\kappa a \ll 1$ and $f = 1$ for $\kappa a \gg 1$, where κ^{-1} is the thickness of the double layer and a is the radius of the colloidal particle). The expression

$$\mu = f(\kappa a) \epsilon \zeta / \eta \quad (1.3)$$

holds for colloidal particles with arbitrary double-layer thickness κ^{-1} but is still only applicable for low ζ , where the double-layer polarization (which deforms the EDL and causes its distribution to become anisotropic) is negligible.

The effect of double-layer polarization was first analyzed theoretically by Overbeek [7] and Booth [8]. Then Wiersema et al. [9] solve the full set of differential equations using numerical methods. They found that the electrophoretic mobility deviates from the Smoluchowski result at high ζ . However, their method was cumbersome to use and not easy to generalize. A more wieldy approach was provided by O'Brien and White [10], through a linearization of the differential equations. In this way, they were able to apply an arbitrary ζ potential and electric double-layer thickness κ^{-1} .

1.3 Smoothed Profile Method

Let us consider charged colloidal particles that are immersed in an electrolyte solution subject to an external electric field $\mathbf{E}(t)$. The charged colloidal particles, and the surrounding ions, will tend to move towards either the positive or negative pole, according to their charges. This relative motion of the particles with respect to the fluid will result in a drag force, which strongly determines their mobility. Additionally, the fluid flow will also affect the diffusion of the ions, thus disturbing the EDL and inducing an internal electric field which tends to slow down the colloidal particles. The complete dynamics of the system is therefore obtained by solving for the coupled time evolution of the Newton-Euler, Navier-Stokes, and advection-diffusion equations. In what follows, I briefly review the relevant form of these three equations within the SP method used in our simulations. Further details regarding the solution method can be found in our previous publications [11, 12], and references therein.

1.3.A Newton-Euler equations of motion

Consider monodisperse spherical colloids with mass M_p and tensor of inertia $\mathbf{I}_p$. The motion of the colloidal particles is given by

$$\dot{\mathbf{R}}_i = \mathbf{V}_i \quad (1.4)$$

$$M_p \dot{\mathbf{V}}_i = \mathbf{F}_i^H + \mathbf{F}_i^c + \mathbf{F}_i^{ext} \quad (1.5)$$

$$\mathbf{I}_p \cdot \dot{\mathbf{\Omega}}_i = \mathbf{N}_i^H + \mathbf{N}_i^{ext} \quad (1.6)$$

The quantities $\mathbf{V}_i$ and $\mathbf{\Omega}_i$ are the velocity and angular velocity of the i -th particle, respectively, and $\mathbf{F}_i^H$ and $\mathbf{N}_i^H$ are the hydrodynamic force and torque, respectively. $\mathbf{F}_i^{ext}$ and $\mathbf{N}_i^{ext}$ are the external force and torque, respectively, and $\mathbf{F}_i^c$ is the force that arises from the excluded volume of particles and prevents the colloids from overlapping. A soft-core truncated Lennard-Jones potential is adopted for $\mathbf{F}_i^c$.

1.3.B The Navier-Stokes equation

Within the (SP) method, the sharp interface at the colloid-fluid boundary is replaced with a diffuse interfacial region of finite thickness ξ . This is done by introducing a smooth profile function $0 \leq \phi_i \leq 1$ to represent the region of the i -th particle, where $\phi_i = 1$ in the particle domain and $\phi_i = 0$ in the fluid domain. This ϕ function allows us to define a continuous particle density field

$$\phi(\mathbf{r}, t) = \sum_i \phi_i(\mathbf{r}, t) \quad (1.7)$$

For notational simplicity, I will drop explicit reference to the spatial and time dependence of all field variables in what follows. Since this profile function has a compact support over the interfacial region, I use it to define the surface charge density of the particles as

$$eq = Ze|\nabla\phi|/4\pi a^2 \quad (1.8)$$

where Ze is the charge of a single colloid (Z the valency and e the elementary charge). With this colloid charge density field, the total charge field is defined as

$$\rho_e = \sum_{\alpha} Z_{\alpha} e C_{\alpha} + eq \quad (1.9)$$

with C_{α} and Z_{α} the concentration field and valency of type α ion species.

Finally, I can define a total velocity field, which includes both the host fluid $\mathbf{v}_f$ and particle velocity $\mathbf{v}_p$ fields as

$$\mathbf{v} = (1 - \phi) \mathbf{v}_f + \phi \mathbf{v}_p \quad (1.10)$$

$$\phi \mathbf{v}_p = \sum_i \phi_i [\mathbf{V}_i + \boldsymbol{\Omega}_i \times (\mathbf{r} - \mathbf{R}_i)] \quad (1.11)$$

This velocity field satisfies a modified Navier-Stokes equation given by

$$\rho (\partial_t + \mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v} - \rho_e \nabla (\Psi + \Psi_{ex}) + \phi \mathbf{f}_p \quad (1.12)$$

with the incompressibility condition

$$\nabla \cdot \mathbf{v} = 0 \quad (1.13)$$

where ρ , η , and p are the density, viscosity and pressure of the host fluid, respectively, Ψ is the electrostatic potential due to the charges in the system (obtained by solving the Poisson equation $\epsilon \nabla^2 \Psi = -\rho_e$), Ψ_{ex} is the potential due to the external field ($\Psi_{ex}(\mathbf{r}) = -\mathbf{E}_{ex} \cdot \mathbf{r}$ for a uniform electric field), and $\phi \mathbf{f}_p$ acts as a constraint force to maintain the rigidity of the particles.

1.3.C Advection-diffusion equation

The law of mass conservation for each of the α ionic species is given by

$$\partial_t C_\alpha^* = -\nabla \cdot C_\alpha^* \mathbf{v} + D_\alpha \nabla \cdot [(\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot C_\alpha^* \nabla \mu_\alpha] \quad (1.14)$$

where D_α is the diffusion constant of the α ions, $\mathbf{I}$ is the unit tensor, and $\mathbf{n}$ is a unit-vector field that is defined by $\mathbf{n} = -\nabla \phi / |\nabla \phi|$. In our method, C_α^* is an auxiliary density field, used to avoid the penetration of ions into colloids without the use of artificial potentials, which would require significantly smaller time steps. The actual ionic density is defined as $C_\alpha = (1 - \phi) C_\alpha^*$. The operator $(\mathbf{I} - \mathbf{n}\mathbf{n})$, appearing in the second term on the right hand side of Eq. (1.14), ensures that C_α is conserved because the no-penetration condition $\mathbf{n} \cdot \nabla \mu_\alpha = 0$ is directly assigned at the diffuse interface. Thus, charge neutrality $\int \rho_e d\mathbf{r} = 0$ of the total system is automatically guaranteed. Using density functional theory [13, 14], and considering only the ideal contributions to the free energy, the chemical potential can be defined as

$$\mu_\alpha = k_B T \ln C_\alpha^* + Z_\alpha e (\Psi + \Psi_{ex}) \quad (1.15)$$

where k_B is the Boltzmann constant and T is the absolute temperature. I note that Eq. (1.14) reduces to the Boltzmann distribution, in the absence fluid flow $\mathbf{v} = 0$ at the steady state.

$$C_\alpha^* = \bar{C}_\alpha \exp \left[-\frac{Z_\alpha e (\Psi - \Psi_{ex})}{k_B T} \right] \quad (1.16)$$

where the $\bar{C}_\alpha$ is the bulk salt concentration.

1.4 Dynamic motion

An electric field $\mathbf{E}(t) = (E(t), 0, 0)$ is applied, where

$$E(t) = E_0 \exp(-i\omega t) \quad (1.17)$$

and E_0 and ω are the magnitude and frequency, respectively, of the oscillating electric field. I measure the response of the system by analyzing the time dependence of the particle velocity

$$\mathbf{V}(t) = (V(t), 0, 0) \quad (1.18)$$

$$V(t) = V_0 \exp[-i\omega(t - \delta)], \quad (1.19)$$

where V_0 is the magnitude of the velocity, and δ is the phase lag (delay angle) with respect to the external driving force. I define the dimensionless complex mobility E_m^* , *i.e.*, the electrophoretic mobility normalized by Hückel's mobility $\mu_0 = 2\epsilon\zeta/3\eta$ (with $\zeta = k_B T/e$), as

$$E_m^* = \frac{3e\eta}{2\epsilon k_B T} \left\langle \frac{V(t)}{E(t)} \right\rangle_t = \frac{3e\eta V_0}{2\epsilon k_B T E_0} \exp(i\omega\delta) \quad (1.20)$$

$$= E_m' + iE_m'', \quad (1.21)$$

where

$$|E_m^*| = \frac{3e\eta V_0}{2\epsilon k_B T E_0} \quad (1.22)$$

is the magnitude of the dimensionless mobility and E_m' and E_m'' are the real and imaginary parts of E_m^* , respectively.

1.5 Thesis objectives

In order to elucidate the influence of the coupling between hydrodynamics and electrostatics, a few problems were investigated using direct numerical simulation. These problems are as follows:

- The problem of the dynamics of charged dispersion in an electric field
- The influence of the polarization effect
- The interaction between polarized particles

This dissertation is composed of five chapters as described below.

In **Chapter 2**, I present a direct numerical simulation method for investigating the dynamics of dispersed charged colloidal particles in an electric field. The validity of the simulation is examined by calculating the velocity of a dilute dispersion with a known analytical solution. The simulation also gives information about the fluid and ion motion, which provides some insight into the particle motion. I also extend our result into highly concentrated dispersions.

In **Chapter 3**, I focus on the response of the charged colloid and its surrounding ion cloud. In an electric field, both the colloidal particle and its surrounding electric double layer will be polarized, which acquires an electric dipole moment and influence the particle motion. Here, I quantify the effect of polarization phenomena and identify the factors that affect it.

In **Chapter 4**, the polarization effects between multiple particles is studied by direct numerical simulation. The interactions for a system of two particles in a fluid are estimated by the potential and force correlation of the particles. The validity of the simulation is examined by calculating the interaction force between two particles with a known analytical solution.

In **Chapter 5**, the thesis is summarized.

Chapter 2

Dynamic Electrophoresis of Charged Colloids in an Oscillating Electric Field

2.1 Introduction

Electrohydrodynamic phenomena are of great importance in the physical, chemical, and biological sciences as well as several engineering fields. Among these phenomena, electrophoresis, or the motion of suspended particles subject to an external electric field, has been an active area of research for over one hundred years. It is well known that particles in ionic solutions will almost always acquire a surface charge [15], and thus experience a Coulomb force in the presence of an external electric field. This external force, together with the drag exerted by the fluid, and the charge-charge interactions between the colloidal surface and any ionic species present in the fluid, determine the motion of the particle. The first successful theories for this phenomena can be found in the pioneering works of Helmholtz [3] and Smoluchowski [4]. By solving the one-dimensional Navier-Stokes and Poisson equations, Smoluchowski [4] derived an expression for the electrophoretic mobility of a single colloidal particle of the form $\mu \equiv V/E = \epsilon\zeta/\eta$, where V is the velocity of the colloid; E is the amplitude of the constant (direct current, DC) electric field; ϵ and η are the permittivity and the viscosity of the solvent, respectively; and ζ is the zeta potential (the electric potential of the slipping plane near the colloidal surface). This expression is correct for dilute dispersions of colloidal particles with an infinitely thin electrical double layer (EDL, a cloud of counterions that surrounds the colloidal particles). Later, Hückel [5] derived a similar expression but in the opposite limit, where the double layer is infinitely thick, of the form $\mu = 2\epsilon\zeta/3\eta$. These theoretical results for opposite limits were combined by Henry [6], with the introduction of the Henry factor $f(\kappa a)$ ($f = 2/3$ for $\kappa a \ll 1$ and $f = 1$ for $\kappa a \gg 1$, where κ^{-1} is the thickness of the double layer and a is the radius of the colloidal particle). The expression $\mu = f(\kappa a)\epsilon\zeta/\eta$ holds for colloidal particles with arbitrary double-layer thickness κ^{-1} but is still only applicable for low ζ , where the double-layer polarization (which deforms the EDL and causes its distribution to become anisotropic) is negligible.

The effect of double-layer polarization was first analyzed theoretically by Overbeek [7] and

Booth [8]. They found that the electrophoretic mobility deviates from the Smoluchowski result at high ζ . However, subsequent studies by Wiersema et al. [9], who were the first to solve the full set of differential equations using numerical methods, showed that the approximate solution of Overbeek and Booth [7, 8] overestimated the impact of polarization effects. While Wiersema et al. provided detailed tabulated results, their method was cumbersome to use and not easy to generalize. A more wieldy approach was provided by O'Brien and White [10], through a linearization of the differential equations. In this way, they were able to apply an arbitrary ζ potential and electric double-layer thickness κ^{-1} , while still taking into account the electric field, ion density, and fluid flow (provided the external field is sufficiently small). Lozada-Cassou et al. [16, 17] considered the surrounding counterions as hard spheres of finite size using the new primitive model electrophoresis (PME) theory. Their results support the occurrence of the charge inversion of a colloidal particle, which has been observed experimentally and also successfully reproduced by extensive molecular dynamics simulations [18, 19]. Lobaskin et al. [20, 21] used a coupling method of hydrodynamics with an explicit ions to study the electrophoretic behavior of salt-free systems. Zhou et al. [22, 23] used dissipative particle dynamics to study the response of a single colloid to oscillatory electric fields. More recent advances in the structure and the dynamics of charged colloidal particles are well summarized in a recent review article by Palberg et al. [24].

The theories mentioned above only address a single particle and are therefore only applicable to very dilute dispersions. However, in nature, and in engineering and industrial settings, concentrated dispersions are more common. For this reason, numerous attempts have been made to extend such solutions to dense dispersions, using a variety of models and boundary conditions. Levine and Neale [25] first accounted for the effects of particle interactions using Kuwabara's cell model [26] to describe concentrated dispersions at low ζ . They assumed that each colloidal particle is contained in a virtual spherical cell and that the particle distribution is perfectly homogeneous. Kozak [27] and Davis [28] developed a generalized theory that is applicable to arbitrary values of ζ but still ignores the effects of particle interactions, such as double-layer overlapping. Ohshima [29] derived a general equation that yields a simple analytical mobility formula for arbitrary double-layer thickness but is limited to low ζ . However, this equation exhibited unsatisfactory agreement with experimental results. Dukhin [30] suggested that this disagreement is due to the improper application of boundary conditions at the outer cell boundary, rather than the treatment of the cell model. He used the Shilov and Zhafkikh [31] outer boundary condition, which has been found to be more appropriate

than that used by Levine and Neale [25].

Experimentally, electrophoretic mobility measurements are typically done using optical methods. However, this is only possible for transparent dispersions at low colloidal concentrations. For dense dispersions, a popular alternative is to use electro-acoustic phenomena, whereby an oscillating electric field produces an acoustic wave (or vice versa). In such cases, the particle mobility becomes frequency dependent, and is referred to as the dynamic electrophoretic mobility $\mu^*(\omega)$. The idea of generating oscillating (alternating current, AC) electric fields with the application of sound waves was first proposed by Debye [32] in 1933. He noted that the difference in the effective mass or friction coefficient between the anion and cation would result in different displacement amplitudes in a longitudinal wave. This difference can create an alternating electric potential in the dispersion. This technique was then considered a very promising tool for characterizing the electro-kinetic properties of colloidal dispersions. Prominent examples for such studies include the colloid vibration potential (CVP) and electric sonic amplitude (ESA) measurements which were actively performed from the 1950's up until the 1980's. It becomes widely used for characterizing zeta potential in dispersions and emulsions in nowadays. From a theoretical viewpoint, O'Brien [33] used the concept of dynamic electrophoretic mobility μ^* and demonstrated that the CVP and ESA data obtained from the measurements were well reproduced by his dynamic electrophoretic mobility theory. Ohshima [34] derived a simpler expression for the dynamic mobility of single particles that is applicable to an EDL of arbitrary thickness. Later [35], he derived a more generalized theory based on Kuwabara's cell model that is applicable to concentrated dispersions. However, above model is limited to the virtual boundary condition and is not very suitable for multi-particle simulations of electrophoretic phenomena.

In the present study, I performed direct numerical simulations (DNS) of charged colloidal dispersions in AC electric fields using the smoothed profile (SP) method [11, 12, 36, 37], in order to calculate the dynamic mobility. The SP method enables us to compute the time evolution of colloidal particles, the host fluid, and the ion density simultaneously, by solving the Newton, advection-diffusion, and Navier-Stokes equations, while fully accounting for the electrohydrodynamic couplings. Our DNS results exhibit quantitative agreement with approximate theories that use the cell model for dilute dispersions. However, our results systematically deviate from the predictions of the cell model as the density of the dispersion is increased.

Table 2.1: Comparison of the parameters used in the present simulations and those in the corresponding experiments for colloids in KCl solutions.

Parameters in physical units	Symbols	Corresponding experimental values (KCl solution)	Present simulation values
Radius of colloids	a	4.5×10^{-9} [m]	5 [Δ]
Diameter of colloids	d	9.0×10^{-9} [m]	10 [Δ]
Bjerrum length	λ_B	0.7×10^{-9} [m]	$1/4\pi$ [Δ]
Elementary charge	e	1.6×10^{-19} [A · s]	1 [e]
Thermal energy	$k_B T$	$298.15 k_B = 4.11 \times 10^{-21}$ [m ² · kg/s ²]	1 [$\eta^2 \Delta / \rho$]
Zeta potential (typical value)	ζ	2.57×10^{-2} [kg · m ² / A · s ³]	1 [$\eta^2 \Delta / \rho e$]
Electric field	E	2.84×10^5 [V/m]	0.1 [$\eta^2 / \rho e$]
Phoretic velocity (typical value)	V	2.5×10^{-6} [m/s]	5×10^{-3} [$\eta / \rho \Delta$]
Permittivity of solvent	ϵ	$78.5 \epsilon_0 = 6.95 \times 10^{-10}$ [A ² · s ⁴ / kg · m ³]	1 [$\rho e^2 / \Delta^2 \eta^2$]
Viscosity of solvent	η	8.90×10^{-4} [kg/m · s]	12.7 [η]
Density of solvent	ρ	997 [kg/m ³]	0.1 [ρ]
Diffusion constant of ions (typical value)	D	2×10^{-9} [m ² /s]	0.285 [η / ρ]
Frequency of AC field	ω	$10^5 - 10^9$ [1/s]	$5 \times 10^{-3} - 50$ [$\eta / \rho \Delta^2$]
Parameters in dimensionless units	Symbols	Corresponding experimental values (KCl solution)	Present simulation values
Zeta potential	$y = e\zeta / k_B T$	1	1
Friction constant of ions	$m_\alpha = 2\epsilon(k_B T)^2 / 3\eta e^2 D$	0.184	0.184
Reynolds number of colloids	$\text{Re} = \rho d V_0 / \eta$	1×10^{-3}	1×10^{-3}
Frequency of external electric field	$\omega^* = \omega \rho a^2 / \eta$	$10^{-3} - 10$	$10^{-3} - 10$
Frequency of momentum diffusion	$\omega_\nu^* = (\nu / d^2) \rho a^2 / \eta$	0.25	0.25
Frequency of ionic diffusion	$\omega_D^* = (D / d^2) \rho a^2 / \eta$	5.6×10^{-4}	5.6×10^{-4}

2.2 Simulation Parameters

In this study, we use a periodic cubic box of length $L = 64\Delta$, where the lattice spacing $\Delta = 4\pi\lambda_B$ is the unit of length, with $\lambda_B = e^2/4\pi\epsilon k_B T$ the Bjerrum length, which is approximately 0.72 nm in water at 298 K. The units of temperature and electrostatic potential are $1/k_B$ and $k_B T/e$, respectively. The latter corresponds to 2.57×10^{-2} V at 298 K. We define the unit of time as

$$\tau = \Delta^2/\nu \quad (2.1)$$

where $\nu = \eta/\rho$ is the kinematic viscosity. The simulation box contains a single spherical particle of radius $a = 5\Delta$ and interfacial thickness $\xi = 2\Delta$. The (negative) surface charge of the colloid is fixed in order to obtain a specified ζ potential ($0 < \zeta < 5$). Formally, ζ is defined as the potential at the slip plane, which we take to be the particle surface $\zeta = \Psi_{\text{surface}}$. However, within the SP method, the surface of the particle is diffuse. In order to uniquely define the ζ potential, we define an effective colloid radius a_{eff} , such that the simulated ζ potential matches Ohshima's non-linear Poisson-Boltzmann solution $\Psi(a_{\text{eff}}) = \zeta_{\text{theory}}$. A detailed description of this parametrization procedure can be found in the next section. The host fluid contains a dilute 1 : 1 electrolyte solution, with ionic diffusion constants D_α ($\alpha = +$ for the monovalent counterions and $\alpha = -$ for the coions). Unless stated otherwise, the salt concentration is fixed to recover an EDL thickness equal to the particle radius, i.e. $\kappa a = 1$, where this thickness is defined in terms of the Debye length κ^{-1}

$$\kappa^{-1} = \left(4\pi\lambda_B \sum_{\alpha} Z_{\alpha}^2 \bar{C}_{\alpha} \right)^{-\frac{1}{2}} \quad (2.2)$$

An electric field $\mathbf{E}(t) = (E(t), 0, 0)$ is applied, where

$$E(t) = E_0 \exp(-i\omega t) \quad (2.3)$$

and E_0 and ω are the magnitude and frequency, respectively, of the oscillating electric field. We measure the response of the system by analyzing the time dependence of the particle velocity

$$\mathbf{V}(t) = (V(t), 0, 0) \quad (2.4)$$

$$V(t) = V_0 \exp[-i\omega(t - \delta)], \quad (2.5)$$

where V_0 is the magnitude of the velocity, and δ is the phase lag (delay angle) with respect to the external driving force. We define the dimensionless complex mobility E_m^* , i.e., the electrophoretic

mobility normalized by Hückel's mobility $\mu_0 = 2\epsilon\zeta/3\eta$ (with $\zeta = k_B T/e$), as

$$E_m^* = \frac{3e\eta}{2\epsilon k_B T} \left\langle \frac{V(t)}{E(t)} \right\rangle_t = \frac{3e\eta V_0}{2\epsilon k_B T E_0} \exp(iw\delta) \quad (2.6)$$

$$= E_m' + iE_m'', \quad (2.7)$$

where

$$|E_m^*| = \frac{3e\eta V_0}{2\epsilon k_B T E_0} \quad (2.8)$$

is the magnitude of the dimensionless mobility and E_m' and E_m'' are the real and imaginary parts of E_m^* , respectively.

The values of all parameters used in the present simulations, and the corresponding value for experiments with KCl solutions, are summarized in Table I. To compare our simulations with earlier studies [34, 35], the following dimensionless numbers are used. These values are summarized in Table I and are set to be equal in the present simulations and the corresponding experimental case.

i) Dimensionless zeta potential:

$$y = \frac{e\zeta}{k_B T} \quad (2.9)$$

ii) Dimensionless ionic friction constant:

$$m_\alpha = \frac{2\epsilon(k_B T)^2}{3\eta e^2 D_\alpha} \quad (2.10)$$

iii) Reynolds number of colloids:

$$\text{Re} = \frac{dV_0}{\nu} \quad (2.11)$$

where $d = 2a$ is the diameter of the colloidal particle.

iv) Dimensionless frequencies of the external electric field, normalized by the momentum diffusion time (ν/a^2)

$$\omega^* = \omega \frac{a^2}{\nu} \quad (2.12)$$

This parameter is used to compare the experimental and simulation frequencies relative to the momentum diffusion time a^2/ν over the particle radius a . Other system intrinsic frequencies can also be defined in terms of the momentum diffusion time. These frequencies include the frequency of momentum diffusion over the particle diameter d

$$\omega_\nu^* = \frac{\nu}{d^2} \frac{a^2}{\nu} = \frac{1}{4} \quad (2.13)$$

and the frequency of ionic diffusion over the particle diameter d

$$\omega_D^* = \frac{D_\alpha}{d^2} \frac{a^2}{\nu}. \quad (2.14)$$

2.3 Validation

2.3.A Zeta potential

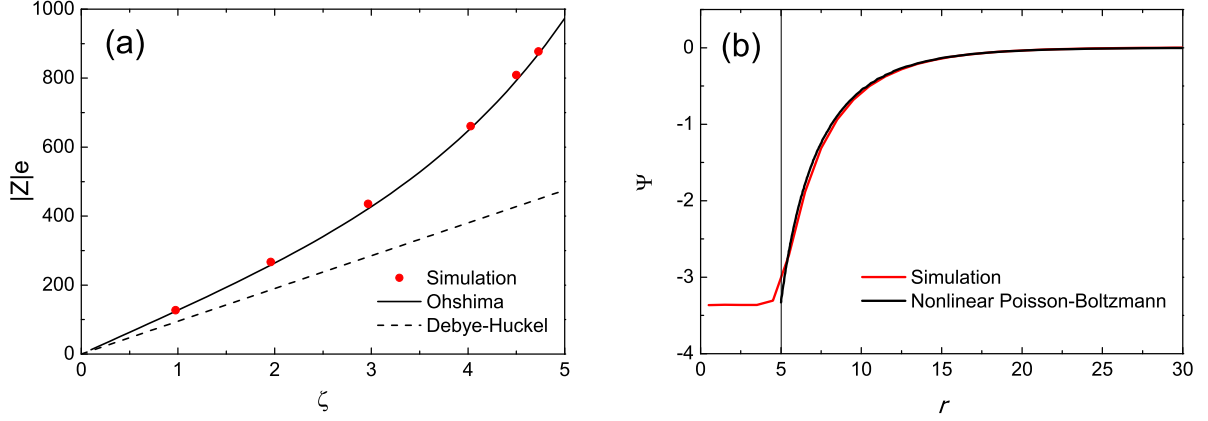


Figure 2.1: The relationship between the total charge $|Z|e$ carried by a single colloidal particle and the zeta potential ζ is shown in (a). Our simulation results (red points) are consistent with the analytical solution of the nonlinear Poisson-Boltzmann (PB) equation proposed by Ohshima [38] (solid line). The corresponding results obtained using the linearized Debye-Hückel theory is also plotted for comparison (dashed line). Our numerical results for the electrostatic potential Ψ around a single colloidal particle are plotted in (b), as a function of the radial distance r from the particle center (black solid line).

We start with a system that contains a single colloidal particle in an aqueous KCl solution. Because of the Coulomb interaction with the charged colloid, counterions will tend to accumulate close to the surface of the colloid, whereas coions will be depleted in this region. The distribution of the surface charge on the colloidal particle has been shown to be very relevant for the calculation of the zeta potential [16, 17, 39]. In the SP method, however, the surface of the particle and the corresponding charge density are smeared out over a finite thickness ξ . By fitting our numerical data to Ohshima's theory [38], we determined the effective radius $a_{\text{eff}} = 4.5 (= 0.9a)$ at which $\Psi(a_{\text{eff}}) = \zeta_{\text{theory}}$. With this definition, the relationship between Z , the total charge on a single colloidal particle, and ζ is well reproduced, as demonstrated in Fig. 2.1(a). In Fig. 2.1(b), we plot our numerical result for $\Psi(r)$ around a single charged colloid located at $r = 0$ together with the analytical solution of the nonlinear PB equation [38]. We confirmed that our numerical results are consistent with the nonlinear PB theory for $r > a$ when ζ is small ($\zeta \lesssim 5$) and the Debye length κ^{-1} is reasonably larger than Δ . This condition is not always satisfied in the cases of large ζ and/or

large salt concentration, where the SP method is less useful.

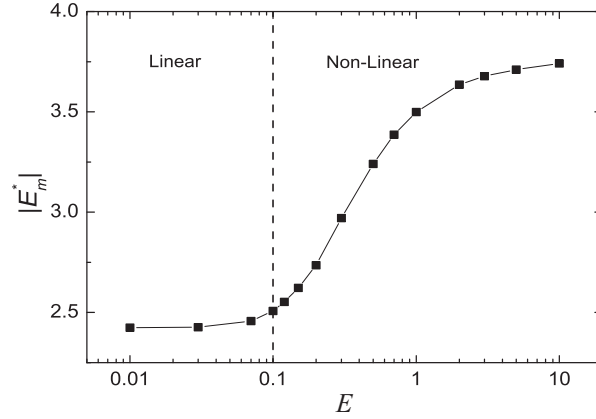


Figure 2.2: The dimensionless mobility $|E_m^*|$ in a DC electric field as a function of the magnitude of the electric field E . The mobility behaves linearly for $E \leq 0.1$ and decreases with increasing E for $E > 0.1$.

2.3.B External electric field

Most experimental and theoretical studies of electrophoresis have been performed in the linear-response regime, where the electrophoretic mobility is independent of the magnitude of the external electric field. To confirm that our simulations were also performed in the linear-response regime, we plot the amplitude of the dimensionless mobility $|E_m^*|$ as a function of the magnitude of the static (DC) electric field E in Fig 2.2. It is confirmed that $|E_m^*|$ remains constant in the low-field region $E \leq 0.1$, whereas $|E_m^*|$ starts to increase with increasing E in the high-field region $E > 0.1$. Hence, in the present study, we set the amplitude of the AC electric field as $E_0=0.1$, which is confirmed to be within the linear response regime.

2.4 Results

2.4.A Electrophoretic mobility in DC and AC fields

To check the consistency of our numerical results with the O'Brien-White theory [10], we first consider a single charged particle that moves in a DC electric field E . The dimensionless mobility $|E_m^*|$ is plotted as a function of the zeta potential ζ for $\kappa a = 1.0$ in Fig. 2.3(a). The figure indicates that the present method successfully reproduces the O'Brien-White theory within an error of a few percent, even within the non-linear regime $\zeta \geq 2$, where the deviations from Smoluchowski [4] and Hückel's [5] theories are significant because of the double-layer polarization.

We then apply an AC electric field, and we plot the resulting dimensionless mobility $|E_m^*|$ as a

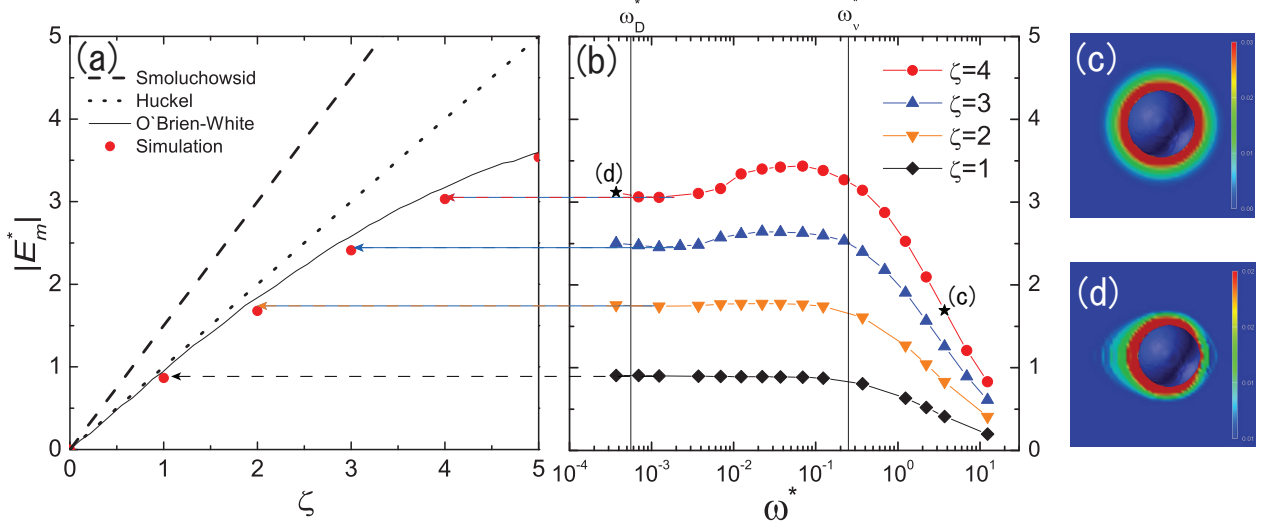


Figure 2.3: In (a), the dimensionless mobility $|E_m^*|$ of a single particle in a DC electric field is plotted as a function of the zeta potential ζ and compared with the results obtained using the Smoluchowski, Hückel, and O'Brien-White theories. In (b), $|E_m^*|$ is plotted for an AC electric field. The entire frequency range is divided into three sub-regions that are separated by two characteristic frequencies ω_ν^* and ω_D^* . The mobility is confirmed to be very close to the values in a DC field in the completely deformed region, where $\omega^* < \omega_D^*$, whereas it tends to decrease with increasing ω^* in the undeformed region, where $\omega^* > \omega_\nu^*$. In the intermediate region, where $\omega_D^* < \omega^* < \omega_\nu^*$, the mobility exhibits a shallow maximum for $\zeta \geq 3$. The shapes of the EDL at $\zeta = 4$ in the undeformed region and the completely deformed region are depicted in (c) and (d), respectively.

function of the dimensionless frequency ω^* in Fig. 2.3(b). We divide the entire frequency range into three regions, which are related to the deformation of the EDL, using two specific frequencies ω_ν^* and ω_D^* , the momentum diffusion and ionic diffusion frequencies, respectively. In the Undeformed Region (I), where the external electric field frequency ω^* is greater than the momentum diffusion frequency over the particle scale ω_ν^* , the particle and the fluid around it cannot immediately follow the alternating external field. Thus, the dimensionless mobility $|E_m^*|$ decreases with increasing dimensionless frequency ω^* . The low particle and fluid mobility lead to a negligible convection of the ion density, which results in a constant shape for the EDL. A snapshot of the EDL for $\zeta = 4$ is presented in Fig. 2.3(c); this snapshot indicates that the EDL is not deformed in this region ($\omega^* > \omega_\nu^*$). Thus, we call this the undeformed region. In the Intermediate Region (II), where ω^* is smaller than the momentum diffusion frequency ω_ν^* , but larger than the ionic diffusion frequency ω_D^* , $\omega_D^* \leq \omega^* \leq \omega_\nu^*$, the fluid motion around the particle reaches a quasi-steady state but the shape of the EDL is not yet fully developed with respect to the instantaneous electric field $\mathbf{E}(t)$. One can see that $|E_m^*|$ at $\zeta = 3$ and 4 exhibits a shallow maximum around $\omega^* \simeq 10^{-1}$ and tends to decrease with decreasing ω^* . This decrease in $|E_m^*|$ in Region II is attributable to the

polarization of the EDL, which occurs at small ω^* , as shown in Fig. 2.3(d). Here, the electric field induced by the polarization of the EDL, which is opposite to the external electric field, slows down the particle. Finally, in the Completely Deformed Region (III), where ω^* is less than the ionic diffusion frequency ω_D^* , the system becomes identical to the case of a DC electric field.

2.4.B Complex mobility of a single charged particle

As defined in Eq. (2.7), we decompose the complex mobility E_m^* into its real and imaginary components, E_m' and E_m'' , respectively, which represent the in-phase and out-of-phase components of the particle velocity and are plotted in Fig. 2.4(a) and (b). The phase angle defined in Eq. (2.5) is shown in Fig. 2.4(c). To elucidate the nature of the forces that act on the particle, we compute the hydrodynamic and electrostatic contributions to the total force. The former can be obtained by neglecting the charge terms $-\rho_e \nabla (\Psi + \Psi_{ex})$ in the Navier-Stokes equation. The amplitudes of these three oscillating forces are plotted in Fig. 2.4 (d).

In the undeformed region, as previously described, the particle and the fluid around it cannot immediately follow the alternating external field. As shown in Fig. 2.4 (d), the Coulombic force is maintained at a constant value at high ω^* , but the hydrodynamic force exhibits a significant drop. This is because the frequency of the alternating external field is so high that the acceleration period $1/\omega^*$ of the charged particle tends to zero and the hydrodynamic force tends to decrease with increasing ω^* . Furthermore, the mobility is not completely in-phase with the external field, which results in an imaginary component as shown in Fig. 2.4 (b). The local maximum of E_m'' around $\omega \simeq 2$ in Fig. 2.4(b) indicates the interaction of two competing contributions: an increase in the out-of-phase component as ω^* increases and a decrease in the total mobility. In the intermediate region, the motion of the particle and that of the fluid around it are in quasi-steady states. The coulomb force and the hydrodynamic force balance each other, as shown in Fig. 2.4 (d). However, the shape of the EDL still cannot follow the alternating external field $\mathbf{E}(t)$. The shape of the EDL is fully developed only in the low-frequency limit of the intermediate region, where the magnitude of the effective electric field at the particle position is less than $E(t)$ because of the electric field induced by the polarized EDL. This reduction in the mobility is more significant when the EDL is highly deformed at high $\zeta = 4$, because of the strong concentration gradient, as shown in Figs. 2.3(b) and 2.4(a). This phenomenon can also be observed in the Coulomb force, as shown in Fig. 2.4 (d). The amplitude of the Coulomb force is maintained at a constant value in the undeformed region

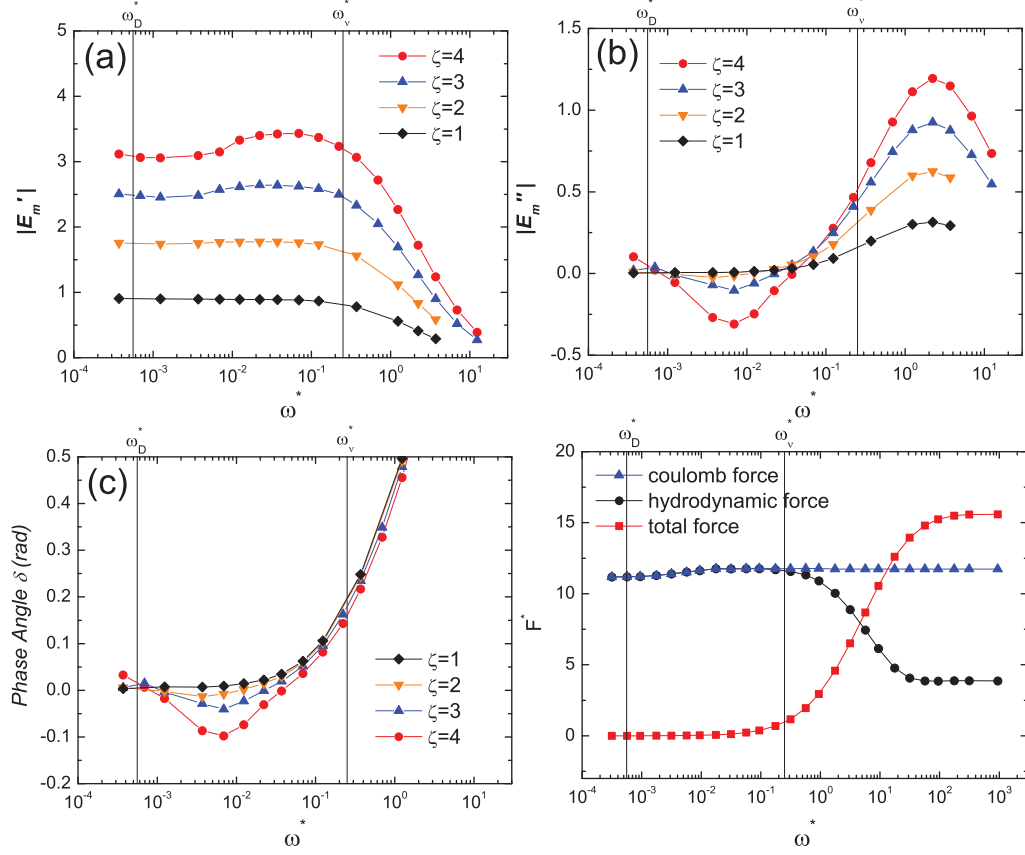


Figure 2.4: As defined by Eq. (2.7), we decompose the complex mobility E_m^* into its real and imaginary components, E'_m and E''_m , respectively, which are plotted in (a) and (b). The phase angle defined in Eq. (2.5) is shown in (c). (d) is the magnitudes of the Coulomb, hydrodynamic, and total forces are plotted as a function of frequency. The Coulomb force is almost constant because the amplitude of the AC electric field is constant. In the undeformed region, the acceleration period $1/\omega^*$ is very small, which leads to a decrease in the hydrodynamic force with increasing ω^* . In the intermediate region, the EDL induces an opposite electric field, which slightly reduces the Coulomb force.

and decreases slightly in the intermediate region. This decrease in the Coulomb force is attributable to the opposite electric field induced by the polarized EDL.

Figure 2.4(c) shows the phase angle between the external electric field and the particle velocity. In the undeformed region, the phase angle is positive, which indicates that the velocity is delayed relative to the alternating electric field. In the intermediate region, $\delta(\zeta = 1)$ decreases and converges to zero, which means that the hydrodynamic and Coulomb forces balance, as shown in Fig. 2.4 (d). However, some undershoots can be observed in the phase angle when ζ becomes large. According to the results shown in Fig. 2.4(a) and (b), the unknown force can be attributed to the EDL deformation. Because $\omega^* > \omega_D^*$, the ion distribution in this regime cannot follow the external electric field instantaneously. The change in the shape of the EDL induces an internal electric field with in-phase and out-of-phase components, which reduce the corresponding mobilities E'_m and

E_m'' . In the completely deformed region, the frequency is sufficiently low so that the EDL can fully develop and the phase angle converges to zero at all ζ .

2.4.C Effect of ionic diffusion

In this section, we discuss the effects of the ion diffusion constant and polarization in detail. The dimensionless mobility at $\zeta=3.0$ is plotted as a function of dimensionless frequency for three values of ionic diffusion coefficients $D = 2.85, 0.285$, and 0.09 in Fig. 2.5(a), (b), and (c), respectively. Snapshots of the charge density and fluid flow around a single colloidal particle taken at the lowest frequency $\omega^* = 3 \times 10^{-4}$ are shown in Fig. 2.5(d), (e), and (f). The color map represents the total ionic charge density $\sum_{\alpha} eZ_{\alpha}C_{\alpha}$ in the x - y plane at $z = 0$.

In the undeformed region, low particle and fluid mobility lead to a negligible convection of the ion density. Most of the ions surrounding the particle are firmly held by the surface charge and obey the Poisson-Boltzmann distribution, which results in a constant shape for the EDL, as shown in Fig. 2.3(c).

In the intermediate region, the mobility $|E_m^*|$ exhibits a shallow maximum for $D = 2.85$ and $D = 0.285$ and a significant maximum for $D = 0.09$ near $\omega^* \simeq \omega_{\nu}^*$. It then tends to gradual decrease near $\omega^* \simeq \omega_D^*$. This difference in the behavior occurs because of the development of the EDL, which is affected by the fluid field. We consider a high diffusion coefficient of $D = 2.85$. As defined by Eq. (1.14), when the influence of the fluid field on the concentration distribution is weak, the dominant contribution to the time evolution of the ion concentration is the diffusion term. The perturbation of the EDL is weak and the polarization effect in the intermediate region is not significant in Fig. 2.5(a).

Next, we consider the low diffusion coefficients of $D = 0.285$ and $D = 0.09$. Because the ion diffusion is much slower than the fluid, the ions that surround the particle are dragged away from the surface by the fluid and remain behind the particle, as shown in Fig. 2.5(e) and (f). According to Eq. (1.14), the convection term is the dominant component in the evolution of the ion concentration. Hence, the counterions behind the particle induce an opposite electric field with decreasing $|E_m^*|$, which is significant at $D = 0.09$. Figure 2.5(g) shows the phase angle δ as a function of the dimensionless frequency for the three ion diffusion constants mention above. In the undeformed region, there is almost no difference among the ion diffusion constants because the convection term in the advection-diffusion equation is small. In the intermediate region, different

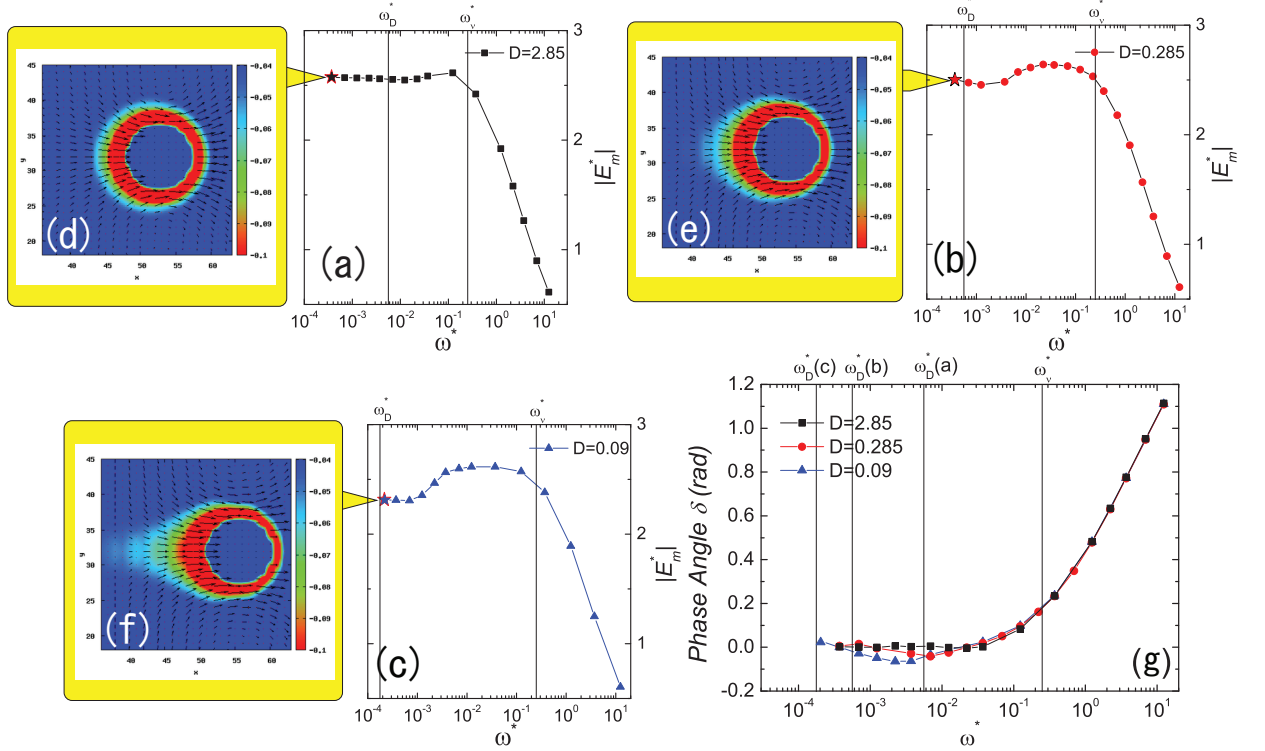


Figure 2.5: The dimensionless mobility at $\zeta=3.0$ is plotted as a function of dimensionless frequency for three values of the ionic diffusion coefficient $D = 2.85$, 0.285 , and 0.09 in (a), (b), and (c), respectively. The mobility in the low-frequency limit tends to decrease with decreasing frequency in the intermediate region, and this tendency is greatly enhanced for the smallest diffusion coefficient in (c). Snapshots of the charge density and fluid flow around a single colloidal particle taken at the lowest frequency $\omega^* = 3 \times 10^{-4}$ are shown in (d), (e), and (f). The external electric field was applied in the $+x$ direction, $\mathbf{E}(t) = (E(t), 0, 0)$, and the color map represents the total ionic charge density $\sum_{\alpha} eZ_{\alpha}C_{\alpha}$ in the $x-y$ plane at $z=0$. The phase angle is plotted in (g). One can see that an undershoot occurs for $D = 0.09$ near the frequency at which the mobility decreases in (c).

ion diffusion coefficients lead to different shapes of the EDL, as shown in Fig. 2.5(d), (e), and (f), thereby resulting in different field strengths being induced by this EDL polarization. Smaller ionic diffusion causes larger polarization, which results in a more significant undershoot of the phase angle, as seen in Fig. 2.5 (g).

2.4.D Complex mobility of a dense colloidal dispersion

While single particle models provide a good starting point to understand electrophoretic phenomena, experimental situations are usually concerned with concentrated particle dispersions. Fortunately, using direct numerical simulations, we can easily consider highly concentrated dispersions. Therefore, we examined the effects of the particle concentration on the electrophoretic mobility.

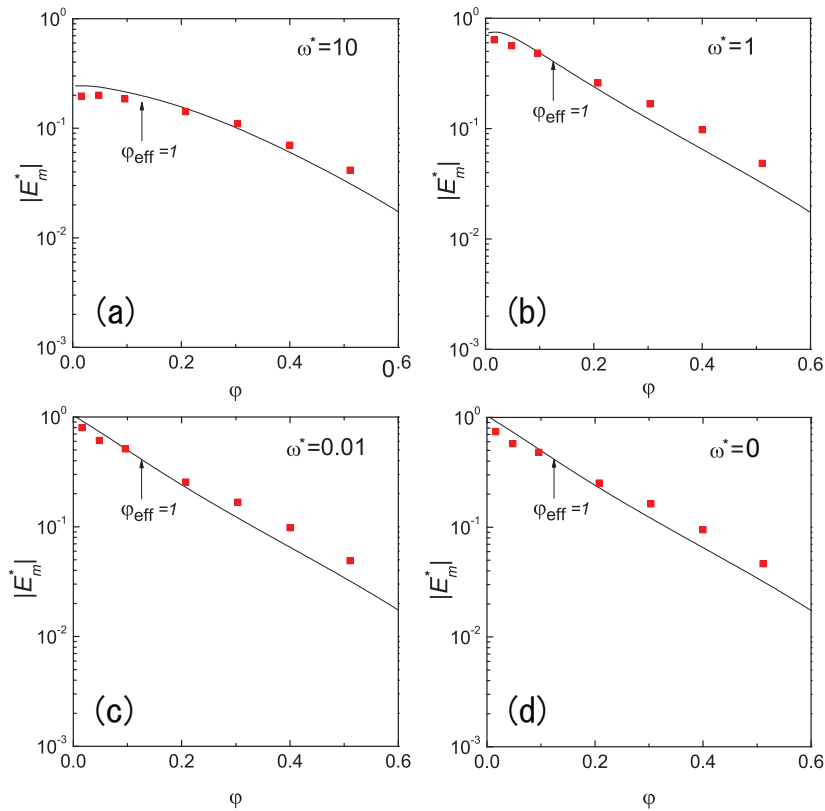


Figure 2.6: The dimensionless mobility $|E_m^*|$ as a function of the volume fraction ϕ at $\zeta=1.0$ and $\kappa a = 1.0$ for (a) $\omega^* = 10$, (b) $\omega^* = 1$, (c) $\omega^* = 0.01$, and (d) $\omega^* = 0$. The solid lines represent the approximation theory proposed by Ohshima [35]. This theory is confirmed to be accurate for $\phi_{\text{eff}} \leq 1$ and agrees well with our numerical results. However, it tends to deviate considerably from our results for $\phi_{\text{eff}} > 1$, where the overlapping of the EDLs of different particles becomes notable.

Here, we compare our result with the analytical solution proposed by Ohshima [35] for low ζ values, which ignores the double-layer overlap. We chose two different Debye lengths of $\kappa^{-1} = 5$ and $\kappa^{-1} = 10$, which corresponds to $\kappa a = 1$ and $\kappa a = 0.5$. Random initial particle configurations

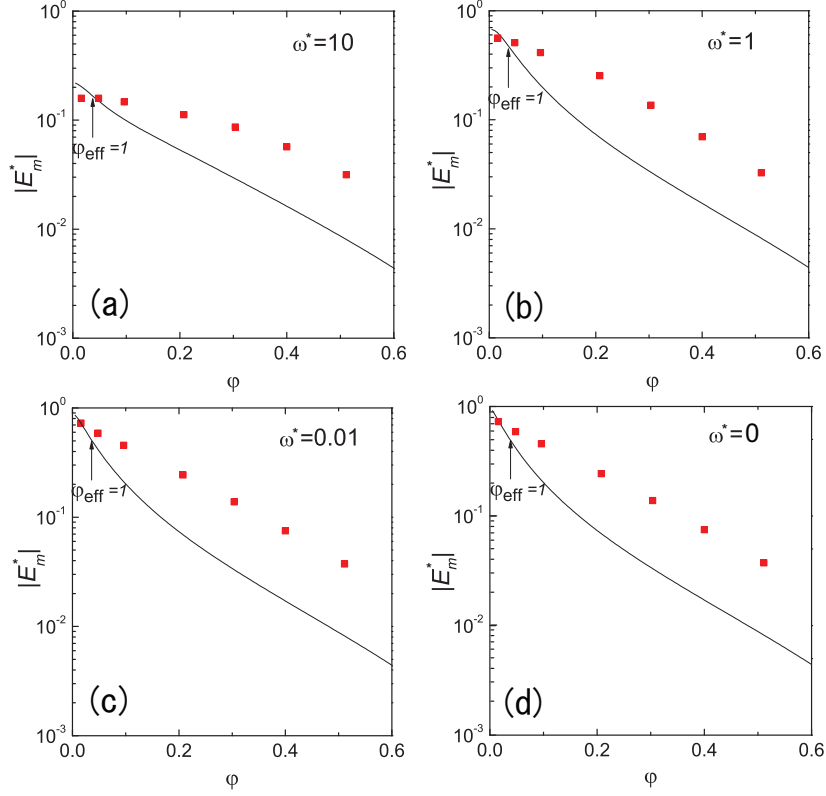


Figure 2.7: The same figures as shown in Fig. 2.6 but for $\kappa a = 0.5$

were used for $\varphi < 0.3$, whereas face-centered cubic (FCC) configurations were used for $\varphi \geq 0.3$. The dimensionless mobility $|E_m^*|$ for $\kappa a = 1$ and $\kappa a = 0.5$ are plotted as a function of volume fraction φ for different dimensionless frequencies $\omega^* = 10, 1, 0.01$, and 0 in Fig. 2.6 and Fig. 2.7. $|E_m^*|$ decreases rapidly with increasing φ for all frequencies. Our results agree well with Ohshima's theory at low φ for all ω^* , but they deviate as φ increases. In Fig. 2.7, which shows that $|E_m^*|$ exhibits more significant deviations at high φ in this case than in the case of $\kappa a = 1$.

This deviation is attributed to the overlap of the EDLs for larger φ , which is neglected in Ohshima's theory. A similar deviation is also observed by Manzanilla-Granados [40, 41]. They pointed out that the cell model neglects all colloid-colloid correlations and its description is simply that for a confined fluid. To this end, we estimate the effective radius $a + \kappa^{-1}$ of the ionically dressed particles and define the effective volume fraction $\varphi_{\text{eff}} \equiv 4\pi(a + \kappa^{-1})^3 N / 3L^3 = [1 + (\kappa a)^{-1}]^3 \varphi$. As clearly observed in Figs. 2.6 and Figs. 2.7, our results agree well with Ohshima's theory for $\varphi_{\text{eff}} \leq 1$, where the effect of EDL overlap is small. However, for $\varphi_{\text{eff}} > 1$, where the EDL overlap becomes significant, deviations between our simulation results and the theory become notable. Our results are consistent with recent studies that also account for the effects of EDL overlap [21, 42, 43].

We also investigate the high- ζ effect for different volume fractions φ . The dimensionless mobility

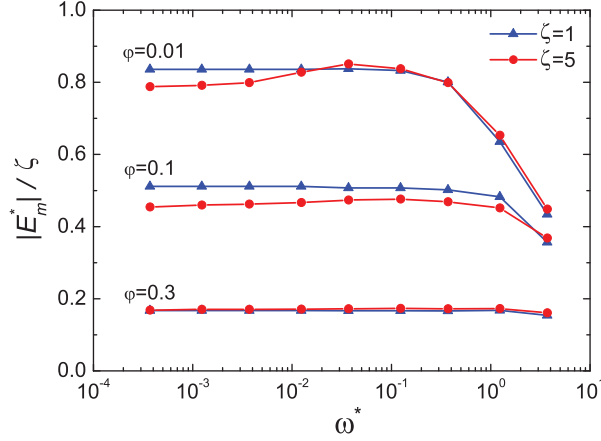


Figure 2.8: The dimensionless mobility $|E_m^*|$ is divided by the zeta potential and plotted as a function of ω^* for $\zeta = 1$ and 5 at three volume fractions $\varphi = 0.01, 0.1$, and 0.3 . The discrepancies between $\zeta = 1$ and 5 at small ω^* , which are noticeable at $\varphi = 0.01$ and 0.1 , represent the effect of the polarization of the EDL. At $\varphi = 0.3$, the effect of polarization becomes negligible because the EDLs tend to overlap considerably.

$|E_m^*|$ divided by ζ is plotted as a function of ω^* for $\zeta = 1$ and 5 for three volume fractions $\varphi = 0.01, 0.1$, and 0.3 in Fig. 2.8. When $\varphi = 0.01$ and $\varphi = 0.1$, the discrepancies between $\zeta = 1$ and 5 at small ω^* are noticeable because of the polarization of the EDL and are more significant at high $\zeta = 5$ than low $\zeta = 1$. When $\varphi = 0.3$, the effect of polarization is negligible, which is most likely because of the considerable overlap of the EDLs of neighboring particles.

2.5 Conclusions

We studied the electrophoresis of colloidal particles in AC electric fields using direct numerical simulations via the SP method. Previous studies of dynamic electrophoresis used the cell model with a virtual outer surface and fixed boundary conditions; examples include the studies of Levine and Neale [25] and Shilov and Zharkikh [31]. This study used the SP method, which is not limited to the virtual boundary condition and is more suitable for multi-particle simulations of electrophoretic phenomena.

We compared our results with the O'Brien-White [10] analytical solution. First, we validated that the surface potential [38] and nonlinear PB solution around the colloidal particle were calculated correctly. Our results exhibit good agreement with the O'Brien-White theory for a single particle in a DC field. We extended our results to AC fields and found that they exhibited continuity from low-frequency AC fields to DC fields. Furthermore, we proposed two meaningful time scales, the momentum diffusion frequency ω_ν and ionic diffusion frequency ω_D , which divide the

frequency into three regions , which are clearly correlated with the deformation of the EDL. When $\omega^* > \omega_\nu$, the alternating external field is so fast that the fluid motion around the particle cannot immediately follow it. The fact that the fluid motion around the particle is slow makes the convection contribution to the ion disturbance negligible. Most of the ions surrounding the particle are firmly held by the surface charge and obey the Poisson-Boltzmann distribution. We refer to this as the undeformed region. When $\omega_\nu > \omega^*$, the fluid motion around the particle reaches a quasi-steady state but the shape of the EDL is not yet fully developed with respect to the instantaneous electric field $\mathbf{E}(t)$. When $\omega_D > \omega^*$, the fluid motion is slow enough that the ion distribution is fully developed, and the EDL is completely deformed. We refer to this as the completely deformed region. We also varied the diffusion coefficient to effectively study different electrolytes, as D_α is the only salt-specific parameter in our model . We changed the diffusion constant of the ions and found that the EDL presents different degrees of deformation, with a considerable polarization effect for lower values of the diffusion constant. Finally, we expanded our simulation to dense dispersions and compared our results with a theoretical analysis based on the cell model [35]. We found that the cell model is reliable when the EDL overlap is small and less reliable as the overlap becomes more significant.

Chapter 3

Dynamic Polarizability of Charged Colloids in an Oscillating Electric Field

3.1 Introduction

Many theoretical studies have been carried out for the electrophoresis of charged colloidal particles, however, many important problems still remain unsolved. In particular, when the zeta-potential ζ of the colloidal particles is high and the thickness κ^{-1} of the electric double layer (EDL, the cloud of counter-ions that surrounds the colloidal surface) is comparable to the colloidal radius a , current theoretical approaches remain insufficient.

Early theories of electrophoresis can be traced back to Smoluchowski [4] and Hückel [5]. Smoluchowski considered the limiting case of an extremely thin EDL, ($\kappa a \gg 1$) and low ζ , where the ion distribution inside the EDL can be ignored. Hückel considered the opposite limiting case, of a thick EDL ($\kappa a \ll 1$) and low ζ , where the ion concentration near the colloidal surface is low enough that the effects of the EDL can be neglected. However, the theoretical treatment becomes much more difficult at high ζ , where the complicated deformation of the EDL must be considered explicitly.

In the 1950's, Overbeek [7] and Booth [8] analyzed the EDL polarization effect theoretically, and found that the electrophoretic mobility deviates from the Smoluchowski result at high ζ . According to the subsequent studies of Wiersema et al. [9], who solved the full non-linear differential equations numerically, the approximate solution of Overbeek and Booth [7, 8] tends to overestimate the effect of the EDL polarization. In 1978, a very widely used theoretical model was proposed by O'Brien and White [10] for arbitrary ζ and κa .

For dense dispersions, further modifications are necessary. Levine and Neale [25] took into account the effects of colloid-colloid interaction using Kuwabara's cell model [26] at low ζ . Ohshima [29] proposed a general equation that yields a simple analytical mobility formula for arbitrary values of κa and ζ . This equation, however, exhibits poor agreement with experimental results due to a poor choice of boundary conditions. Dukhin [30] proposed an alternative, more successful theory, by using the more appropriate boundary conditions proposed by Shilov and Zhafkikh [31].

In comparison to the present problem of electrophoresis, which deals with charged particles

in an electrolyte solvent, dielectrophoresis is a phenomena which considers uncharged particles made of polarizable dielectric materials [44, 45] in a dielectric media. Dielectrophoresis is a widely used technique which can be used to separate colloidal [46, 47] and biological (DNA, viruses, cells, etc) [48–50] particles. Here, the dielectrophoretic force is governed by the particle’s polarizability, which can be evaluated theoretically from the permittivities ϵ_β and the conductivities K_β of the particle ($\beta = p$) and the medium ($\beta = m$), by using the Maxwell-Wagner (MW) theory [51, 52].

While the MW theory is not immediately applicable to charged colloidal particles with an EDL, several theoretical extensions have been proposed to approximately take into account the effect of the EDL as a single polarizable particle. O’Konski [53, 54] introduced the concept of surface conductivity to account for the effects of EDL polarization. For spherical particles, Hill and Saville [55–57] used the standard electro-kinetic model which includes the relevant electrical and hydrodynamic phenomena. Zhou et al. [58] presented the calculation of the dipole strength using the full electro-kinetic theory for both DC and AC electric fields.

Because it is extremely difficult to measure the polarizability of the EDL experimentally, the use of computer simulations has become essential to critically check the reliability of the extended theories. Zhou et al. [22, 23, 59, 60] used dissipative particle dynamics to study the response of a single colloid to oscillatory electric fields. I have developed the smoothed profile (SP) method [11, 12, 36, 37], which enables us to perform direct numerical simulations (DNS) for dispersions of charged colloidal particles in electrolyte solvents under external electric fields, while fully taking into account the complicated hydrodynamic and electrostatic coupling in the system.

In **Chapter 2**, the complex electrophoretic mobility under an AC electric field was studied using the SP method, and it was confirmed to depend on the polarization of the EDL. The purpose of the present chapter is to quantify the polarization of a charged particle with an EDL, and to establish a set of parameters that can quantify the induced dipole effects.

In this chapter, I first review the classic theories for the polarizability of a colloidal particle in an AC electric field. I then summarize our simulation results, which have been performed using the SP method, and finally, the DNS results are compared with the predictions of the MWO theory.

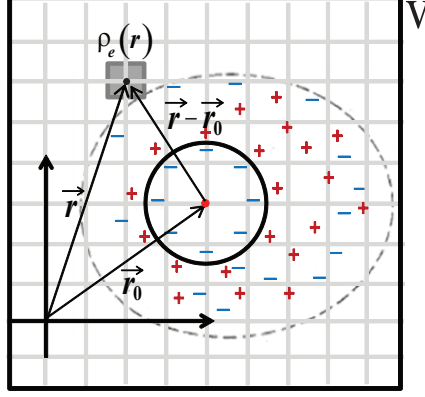


Figure 3.1: A schematic illustration of the calculation of the dipole moment $\mathbf{p}$. $\rho_e(\mathbf{r})$ is the charge density at $\mathbf{r}$ and $\mathbf{r}_0$ is the central position of the colloidal particle around which the dipole moment is calculated.

3.2 Definitions

3.2.A Dipole moment

In order to quantify the polarization effects under external fields, the dipole moment of the system must be calculated. The electric dipole moment is a measure of the charge distribution in a system of electric charges, that is, a measure of the charged system's overall polarity. More generally, for a continuous distribution of charge confined to a volume V , the corresponding expression for the dipole moment is

$$\mathbf{p}(\mathbf{r}_0) = \int_V \rho_e(\mathbf{r})(\mathbf{r} - \mathbf{r}_0)d\mathbf{r}, \quad (3.1)$$

where $\mathbf{p}(\mathbf{r}_0)$ is the dipole moment, $\rho_e(\mathbf{r})$ is the charge density field at $\mathbf{r}$, $\mathbf{r}_0$ locates the point of observation and $d\mathbf{r}$ denotes an elementary volume in V . A schematic illustration is shown in Fig. 3.1. In a charged colloidal system, the observation point r_0 is usually chosen as the center of the particle. When no external fields are present, theoretically, the EDL of a charged colloid is spherically symmetric and follows the Poisson-Boltzmann distribution. The center of the counter-ion cloud and the colloid center coincide, resulting in a zero net dipole moment. When an external electric field is applied, however, the charged colloid and counter-ion cloud move in opposite directions. At the same time, the charged colloid, through the strong Coulomb interaction, makes the counter-ion accumulate close to the colloid surface, such that the EDL assumes a dynamically stable ellipsoidal shape and results in a net dipole moment, which is parallel to the external electric field.

3.2.B Polarizability

In view of our research purpose, I first define the effective dipole moment. When an external electric field $\mathbf{E}(t)$ is applied to the suspension, the system becomes polarized. I assume an electric field of the form

$$\mathbf{E}(t) = (E(t), 0, 0) \quad \text{with} \quad E(t) = E_0 \exp(-i\omega t), \quad (3.2)$$

where E_0 and ω are the magnitude and frequency of the oscillating field, respectively. I measure the polarization of the system by analyzing the time dependence of the dipole moment

$$\mathbf{p}(t) = (p(t), 0, 0) \quad \text{with} \quad p(t) = p_0 \exp[-i\omega(t - \delta)], \quad (3.3)$$

where p_0 is the magnitude of the dipole moment and δ is the phase lag (delay angle) with respect to the external driving force. For weak electric fields, the magnitude of the dipole moment p_0 is proportional to the magnitude of the external field E_0

$$p(t) = \alpha^*(\omega)E(t). \quad (3.4)$$

where the constant of proportionality defines the complex polarizability α^* , which is an intrinsic property of the system. For strong electric fields, the system is no longer in the linear-response regime, and the dipole moment will show nonlinear behaviors.

I define the dimensionless complex polarizability $\mathcal{K}^*$, by normalizing the polarizability α^* with the value given by the Maxwell-Wagner theory, such that

$$\mathcal{K}^* = \frac{\alpha^*}{4\pi\epsilon_m R^3} = \mathcal{K}' + i\mathcal{K}'', \quad (3.5)$$

where $\mathcal{K}'$ and $\mathcal{K}''$ represent the real and imaginary parts of $\mathcal{K}^*$, respectively. A detailed description on the parametrization can be found in the next section.

3.3 Method

Here, I introduce the theoretical and numerical methods used to calculate the dipole moment.

3.3.A Approximate theories

Various approaches have been proposed to calculate the induced dipole moment of a particle immersed in a conductive medium. The Maxwell-Wagner theory [51, 52] is one of the most widely used method to estimate the dielectric dispersion, which only depends on the bulk properties of the solution and the colloids.

1 Maxwell-Wagner theory

This theory considers a single dielectric particle with permittivity ϵ_p and conductivity K_p , which is immersed in a conductive medium with permittivity ϵ_m and conductivity K_m . The dielectric response of the particle will exhibit a phase lag with respect to an external AC field. The complex effective polarizability $\alpha^*(\omega)$ can then be written as

$$\alpha^*(\omega) = 4\pi\epsilon_m R^3 \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*}, \quad (3.6)$$

where R is the radius of the particle and ϵ_p^* is the complex dielectric constant of the particle, which can be expressed as a function of its real part ϵ_p , and the corresponding volume conductivity K_p of the particle as

$$\epsilon_p^* = \epsilon_p + \frac{K_p}{i\omega}. \quad (3.7)$$

Similarly, ϵ_m^* is the complex dielectric constant of the medium, which can be expressed as a function of its real part ϵ_m , and the conductivity of the electrolyte solution K_m as

$$\epsilon_m^* = \epsilon_m + \frac{K_m}{i\omega} \quad (3.8)$$

with

$$K_m = \sum_{\alpha} \frac{n_{\alpha}^{\infty} z_{\alpha}^2 e^2 D_{\alpha}}{k_B T}, \quad (3.9)$$

where n_{α}^{∞} is the bulk ion concentration, e is the elementary charge, k_B is Boltzmann's constant, T is the absolute temperature, and z_{α} and D_{α} are the valency and diffusion constant of type α ion species, respectively. In the classical Maxwell-Wagner theory, the polarizability only depends on the bulk properties of the solution and the colloid, thus it can only be applied to dielectric particles. For charged particles, an appropriate method to include the EDL effect is required.

2 Maxwell-Wagner-O'Konski theory

O'Konski [53, 54] introduced a surface conductivity term to account for the contribution of the EDL. He considered that when the colloidal particles carry a highly charged thin EDL, the electrokinetic features of the polarizability can be included using an asymptotic theory which employs an appropriate surface conductivity, K_p^s

$$K_p = \frac{2K_p^s}{R}. \quad (3.10)$$

The idea is to encapsulate the contribution of the ion cloud around the colloid into one single parameter (the surface conductance), as shown in Fig. 3.2. To relate the surface conductance to

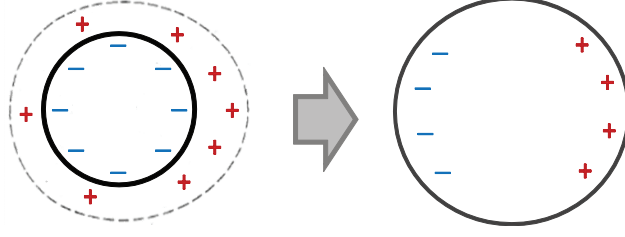


Figure 3.2: An illustration of a colloidal particle with its corresponding EDL. The contributions from the anisotropic distributions of ions around the colloidal particle (left) can be taken into account by assuming the total system (colloid+EDL) as a single dielectric particle (right) with surface conductivity K_p^s .

the particle surface charge, Bikerman's [61] expression is used for the surface conductivity near a highly charged flat surface in a 1:1 electrolyte, where the contribution from the co-ions has been neglected

$$K_p^s = \kappa^{-1} \left[\exp \left(\frac{e\zeta}{2k_B T} \right) - 1 \right] (1 + 3m_\alpha) K_m, \quad (3.11)$$

where κ^{-1} is the Debye screening length, ζ is the zeta potential, and m_α is a dimensionless ionic drag constant [61, 62]. The ionic drag constant is related to the viscosity η and ion diffusion constant D_α ,

$$m_\alpha = \frac{2\epsilon_m (k_B T)^2}{3\eta e^2 D_\alpha}. \quad (3.12)$$

Here, in the low frequency limit, the polarizability $\lim_{\omega \rightarrow 0} \alpha(\omega) = 4\pi\epsilon_m R^3 (K_p - K_m) / (K_p + 2K_m)$, such that the response is dominated by the conducting properties of the system. In contrast, in the high frequency limit, the polarizability $\alpha(\omega \rightarrow \infty) = 4\pi\epsilon_m R^3 (\epsilon_p - \epsilon_m) / (\epsilon_p + 2\epsilon_m)$, indicating that the dielectric properties determine the behavior.

3.4 Simulation

Numerical simulations are performed in three dimensions under periodic boundary conditions. I use a periodic cubic box of length $L = 64\Delta$, where the lattice spacing $\Delta = 4\pi\lambda_B$ is the unit of length, with $\lambda_B = e^2/4\pi\epsilon k_B T$ the Bjerrum length, which is approximately 0.72 nm in water at 298 K. The units of temperature and electrostatic potential are $1/k_B$ and $k_B T/e$, respectively. The latter corresponds to 2.57×10^{-2} V at 298 K. I define the unit of time as $\tau = \Delta^2/\nu$, where $\nu = \eta/\rho$ is the kinematic viscosity. The simulation box contains a single spherical particle of radius $a = 5\Delta$ and interfacial thickness $\xi = 2\Delta$. The surface charge, which is negative in the present simulations, of the colloid is fixed in order to obtain a specified ζ potential covering from very low to moderately high ($0.004 \leq \zeta \leq 4$). Formally, ζ is defined as the potential at the slip plane, which

I take to be the particle surface $\zeta = \Psi_{\text{surface}}$. However, within the SP method, the surface of the particle is diffuse. In order to uniquely define the ζ potential, I define an effective colloid radius a_{eff} , such that the simulated ζ potential matches Ohshima's non-linear Poisson-Boltzmann solution $\Psi(a_{\text{eff}}) = \zeta_{\text{theory}}$ [38]. A detailed description of this parametrization procedure can be found in the next section. The host fluid contains a dilute 1 : 1 electrolyte solution, with ionic diffusion constants D_α ($\alpha = +$ for the mono-valent counter-ions and $\alpha = -$ for the co-ions). Unless stated otherwise, the salt concentration is fixed to recover an EDL thickness equal to the particle radius, i.e. $\kappa a = 1$, where this thickness is defined in terms of the Debye length

$$\kappa^{-1} = \left(4\pi\lambda_B \sum_{\alpha} Z_{\alpha}^2 \bar{C}_{\alpha} \right)^{-\frac{1}{2}}. \quad (3.13)$$

The values of all parameters used in this chapter are summarized in Table 3.1.

Table 3.1: The parameters used in the present simulations. Comparisons of these values in simulation units and the corresponding experimental units are summarized in **Chapter 2**.

Parameters	Symbol	Simulation value	Units
Radius of colloids	a	5	Δ
Diameter of colloids	d	10	Δ
Bjerrum length	λ_B	$1/4\pi$	Δ
Elementary charge	e	1	e
Thermal energy	$k_B T$	1	$\eta^2 \Delta / \rho$
Surface charge	σ	$1 \sim 100$	e
Permittivity of particle	ϵ_p	1	$\rho e^2 / \Delta^2 \eta^2$
Permittivity of solvent	ϵ_m	1	$\rho e^2 / \Delta^2 \eta^2$
Viscosity of solvent	η	0.5	η
Density of solvent	ρ	0.1	ρ
Diffusion constant of ions	D_α	$0.1 \sim 7.24$	η / ρ
Magnitude of electric field	E_0	0.01	$\eta^2 / \rho e$
Frequency of AC field	ω	$0.002 \sim 100$	$\eta / \rho \Delta^2$
Dimensionless parameters	Symbol	Simulation value	
Zeta potential	$y = e\zeta / k_B T$	1	
Friction constant of ions	$m_\alpha = 2\epsilon(k_B T)^2 / 3\eta e^2 D_\alpha$	0.184	
Reynolds number	$\text{Re} = \rho d V_0 / \eta$	$10^{-3} \sim 10^{-2}$	
Frequency of external electric field	$\omega^* = \omega \rho a^2 / \eta$	$0.01 \sim 500$	
Frequency of ionic diffusion	$\omega_D^* = (D_\alpha / d^2) \rho a^2 / \eta$	0.362	

3.5 Validation

3.5.A Zeta potential and charge distributions

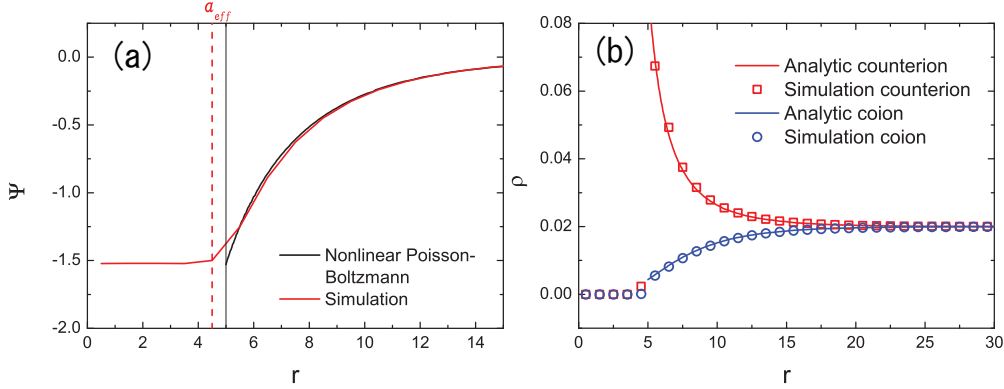


Figure 3.3: The electrostatic potential Ψ and the density ρ of counter-ions and co-ions are plotted in (a) and (b), respectively, as a function of the radial distance r from the center of the colloid. Our simulation results show quantitative agreements with the solutions of the nonlinear Poisson–Boltzmann equation.

Before attempting to study the response of the system to any external field, I first validate that the charged distribution obtained in our simulations is correct. I start with a system that contains a single colloidal particle in an aqueous KCl solution. Because of the Coulomb interaction with the charged colloid, counter-ions will tend to accumulate close to the surface of the colloid, whereas co-ions will be depleted in this region. The distribution of the surface charge on the colloidal particle has been shown to be very relevant for the calculation of the zeta potential [16, 17, 39]. In the SP method, however, the surface of the particle and the corresponding charge density are smeared out over a finite thickness ξ . By comparing our numerical data to the nonlinear PB equation [38], I determined the effective radius $a_{\text{eff}} = 4.5 (= 0.9a)$ at which $\Psi(a_{\text{eff}}) = \zeta_{\text{theory}}$, as demonstrated in Fig. 3.3(a). In Fig. 3.3(b), I plot our numerical result for the time-averaged charge distribution $\rho(r)$ $\Psi(r)$ around a single charged colloid located at $r = 0$, together with the analytical solution of the nonlinear PB equation [38]. I confirmed that our numerical results are consistent with the nonlinear PB theory for $r \geq a$ at least up to moderately high zeta potential $\zeta \leq 4$ provided the Debye length κ^{-1} is reasonably larger than Δ .

3.5.B Linear dependence on external electric field

Most experimental and theoretical studies of electrophoresis have been performed in the linear-response regime, where the polarizability is independent of the magnitude of the external electric field. To confirm that our simulations were also performed in the linear-response regime, I plot the

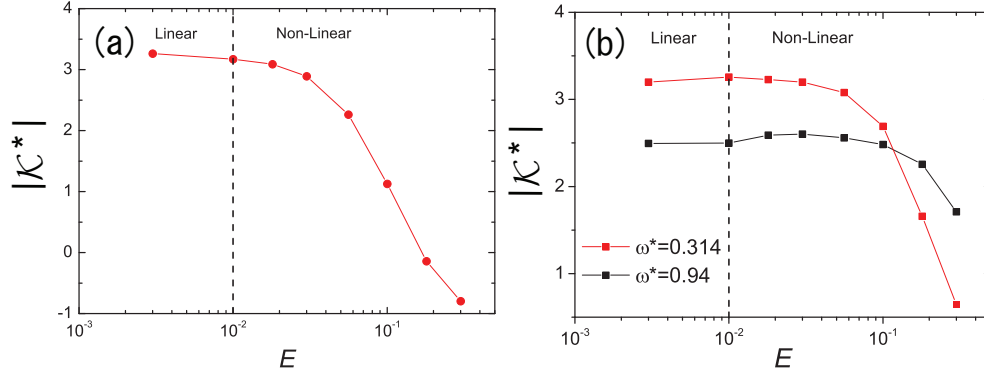


Figure 3.4: The magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ under (a) DC (b) AC electric fields is plotted as a function of the magnitude of the electric field E_0 . The polarizability shows a linear behavior for $E_0 \leq 0.01$, while it decreases with increasing E_0 for $E_0 > 0.01$.

magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ as a function of the magnitude of the static (DC) electric field E_0 in Fig. 3.4 (a). It is confirmed that $|\mathcal{K}^*|$ remains constant in the low-field region $E_0 \leq 0.01$, whereas $|\mathcal{K}^*|$ starts to decrease with increasing E_0 in the high-field region $E_0 > 0.01$. Hence, in the present study, I set the amplitude of the DC electric field as $E_0 = 0.01$, which is confirmed to be within the linear-response regime. For AC electric fields, the linear regime depends on the frequency of the external field ω^* , increasing with decreasing ω^* , as shown in Fig. 3.4 (b) (a detailed description of this phenomenon can be found in the next section). In the limiting case when $\omega^* \rightarrow 0$, the AC system have the most stringent linear response regime. Therefore, I also set the amplitude of the AC electric field to be $E_0 = 0.01$.

3.6 Results

In this chapter, I investigate the polarization phenomena of a spherical colloidal particle in both a uniform and an oscillating electric field. According to previous research [22, 23, 58], the polarization is affected by the zeta potential ζ , ion diffusion constant D_α , and the thickness of the EDL κa . Therefore, I will separately discuss the influence of ζ , κa and D_α . Then I will compare to the Maxwell-Wagner-O’Konski theoretical solution, which is valid for thin EDL, highly charged colloids and high frequency.

3.6.A Influence of zeta potential ζ

I start with a system that contains a single colloidal particle in a KCl solution, with a diffusion constant $D_\alpha = 7.24(m_\alpha = 0.184)$, in a DC electric field. Figure 3.5(a) shows $|\mathcal{K}^*|$ as a function of ζ . One can see that $|\mathcal{K}^*|$ tends to increase with increasing ζ . This is because when ζ is increased,

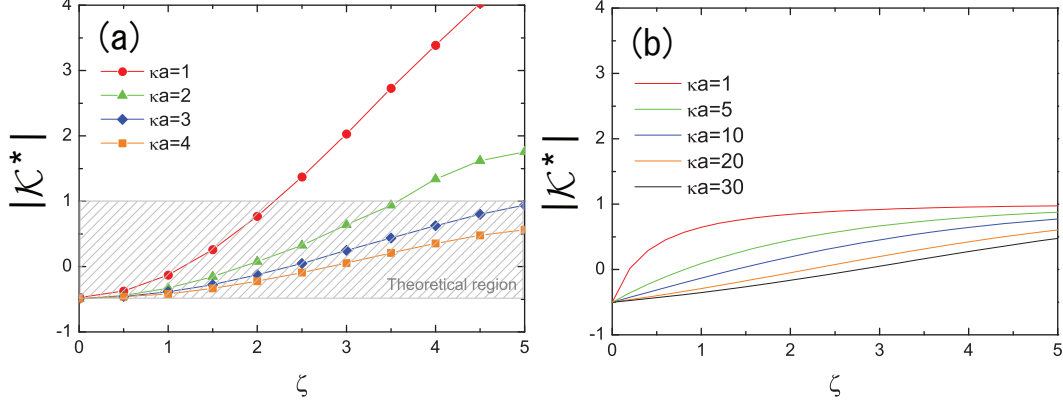


Figure 3.5: In (a), the magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ of a single colloidal particle in a DC electric field is plotted as a function of ζ for $\kappa a = 1, 2, 3$, and 4 . In (b), the predictions of the MWO theory for $\omega \rightarrow 0$ are plotted as a function of ζ for $\kappa a = 1, 5, 10, 20$, and 30 . Our simulation results tend to show better agreements with the MWO theory for large κa . The deviations become significant for smaller κa because the MWO theory is only valid for large κa and low ζ .

more counter-ions are attracted to the charged particle surface to form the EDL. So, the charge density surrounding the particle becomes larger, which in turn increases the strength of the dipole.

Figure 3.5(b) shows the results of the Maxwell-Wagner-O’Konski (MWO) theory, where $|\mathcal{K}^*|$ is plotted as a function of ζ . The MWO theory is often used to calculate the induced dipole moment of a particle immersed in an electrolyte. As one can see, the prediction of MWO theory for $|\mathcal{K}^*|$ is limited only within $-1/2$ and 1 .

This is because of the following reasons. At low ζ , the surface conductivity K_p^s tends to be zero (Eq. (3.11)), and the conductivity of the particle $K_p \approx 0$. Therefore, $|\mathcal{K}^*| = (K_p - K_m)/(K_p + 2K_m) \approx -1/2$. At high ζ in contrast, the particle conductivity K_p becomes much larger than the medium conductivity K_m because of the large surface conductivity K_p^s . Therefore, $\mathcal{K}^* = (K_p - K_m)/(K_p + 2K_m) \approx 1$.

I compared our results with the predictions of the MWO theory. Our simulation results tend to show better agreements with the MWO theory for large κa . The deviations become significant for smaller κa because the MWO theory is only valid for large κa and low ζ .

3.6.B Influence of ion diffusion constants D_α

In this sub-section, I discuss the effects of the ion diffusion constant on the polarization in detail. The magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ for $\kappa a = 3.0$ is plotted as a function of ζ for four values of ionic diffusion constant $D_\alpha = 0.1, 0.5, 1.0, 4.0$ and 7.24 in Fig. 3.6 (a). The

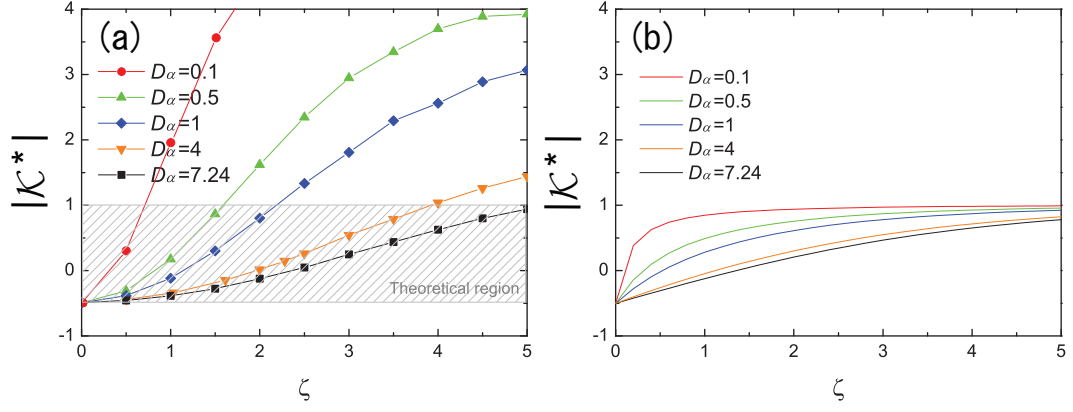


Figure 3.6: In (a), the magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ is plotted as a function of ζ for $D_\alpha = 0.1, 0.5, 1, 4$, and 7.24 . In (b), the predictions of the MWO theory for $\omega \rightarrow 0$ are plotted as a function of ζ for $D_\alpha = 0.1, 0.5, 1, 4$, and 7.24 . Our simulation results tend to show better agreements with the MWO theory for larger D_α .

predictions of the MWO theory are also plotted as a function of ζ in Fig. 3.6 (b).

I found that with small diffusion constants such as $D_\alpha = 0.5$ and $D_\alpha = 0.1$, the polarizability is considerably larger than that with large diffusion constants. This is because the motion of the counter-ions that surround the particle becomes slow. Therefore, when the external electric field is applied, counter-ions cannot catch up with the particle being pushed in the opposite direction. They are thus dragged away from the surface and remain behind the particle. Hence, the counter-ions behind the particle induce a dipole moment which increases as a function of ζ , which is significant at $D_\alpha = 0.5$ and $D_\alpha = 0.1$.

3.6.C Influence of the Debye length κa

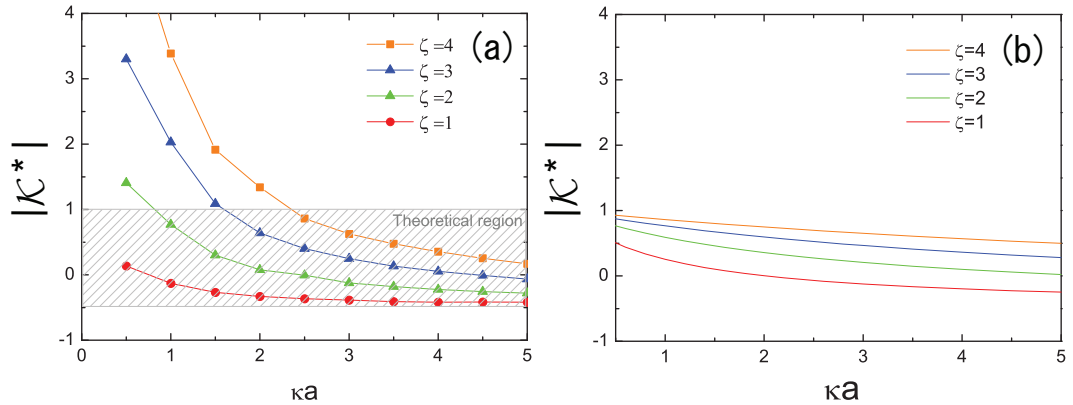


Figure 3.7: In (a), the magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ is plotted as a function of κa for $\zeta = 1, 2, 3$, and 4 . In (b), the predictions of the MWO theory for $\omega \rightarrow 0$ are plotted as a function of κa for $\zeta = 1, 2, 3$, and 4 . Our simulation results tend to show better agreements with the MWO theory for larger κa and lower ζ . The deviations become more significant for smaller κa and higher ζ because the MWO theory is only applicable for large κa and low ζ .

The magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ is plotted as a function of κa for $\zeta = 1, 2, 3$, and 4 in Fig. 3.7(a). It is shown that $|\mathcal{K}^*|$ becomes larger when κa becomes smaller. This is because a large κa corresponds to a thin EDL, which is difficult to polarize since most counter-ions are strongly attracted to the particle surface.

Here I also compare our results with the MWO theory. Figure 3.7(b) shows $|\mathcal{K}^*|$ as a function of κa for $\zeta = 1, 2, 3, 4$ and $D_\alpha = 7.24$ in a DC electric field $\omega \rightarrow 0$. The deviations become more significant for smaller κa and higher ζ because the MWO theory is only applicable for large κa and low ζ .

3.6.D Frequency dependency of polarizability

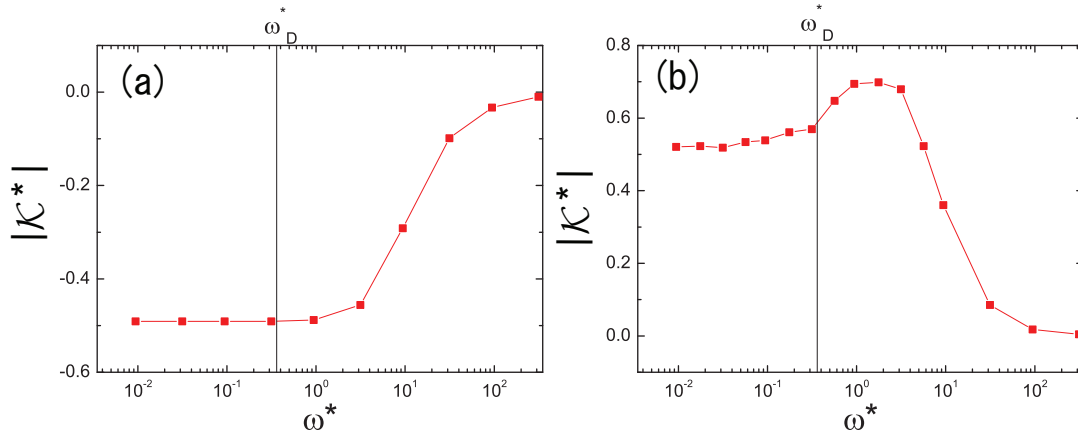


Figure 3.8: The magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ with $\kappa a = 3$ is plotted as a function of ω^* for $\zeta = 0.004$ and 3 in (a) and (b), respectively. In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore the system behaves almost identical to the case of a DC electric field. In the high frequency regime $\omega^* \gg \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$. With increasing ω^* , the variation of the external field is too fast for the motions of ions and solvent around the colloidal particle to follow, the polarizability of the EDL tends to zero. In the intermediate regime $\omega^* \sim 1$, the polarization of the EDL tends to show an overshoot behavior when ζ is large.

In this section, I focus on the effect of varying the frequency of the external AC electric field. According to the results under a DC electric field, I chose $\kappa a = 3.0$, $D_\alpha = 4.0$, and $E_0 = 0.01$.

I here consider two different cases of particles placed in an AC electric field of strength E_0 and frequency ω : first, with a weakly charged particle ($\zeta = 0.004$), and second, with a highly charged particle ($\zeta = 3$). The magnitude of the dimensionless polarizability $|\mathcal{K}^*|$ is plotted as a function of dimensionless frequency ω^* for $\zeta = 0.004$ and $\zeta = 3$ in Fig. 3.8 (a) and (b), respectively.

I divide the entire frequency range into three regimes, which are related to the deformation of

the EDL, using as characteristic frequency the ionic diffusion frequency ω_D^* . In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore the system behaves almost identical to the case of a DC electric field. In the high frequency regime $\omega^* \gg \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$. At the high ω^* limit in this regime, the fluid and ions around the particle cannot immediately follow the alternating external field. The fact that the fluid motion around the particle is slow makes the convection contribution to the ion distribution negligible. Most of the ions surrounding the particle are firmly held by the surface charge and obey the Poisson-Boltzmann distribution, such that the system shows almost no polarization (indeed, $|\mathcal{K}^*|$ is effectively zero). In the intermediate regime $\omega^* \sim 1$, the polarization of the EDL becomes significant and thus the polarizability tends to show an overshoot behavior when ζ is large.

1 Weakly charged particle

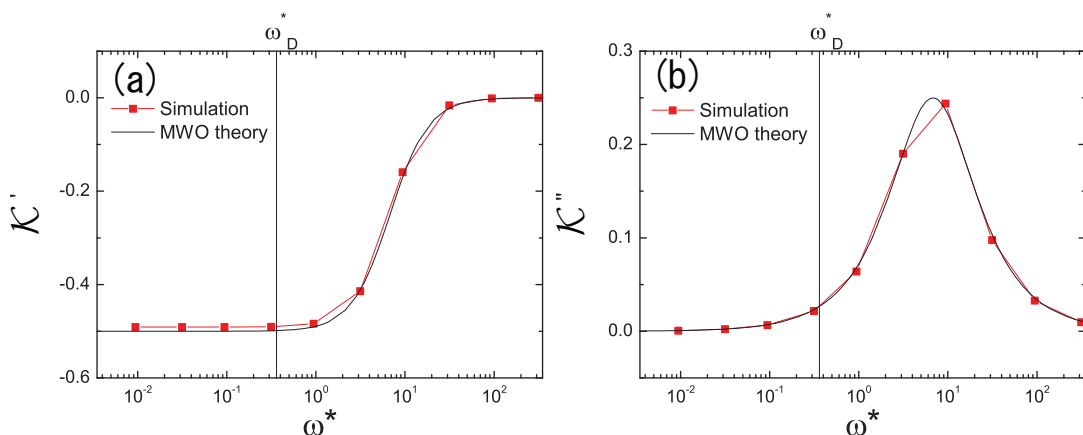


Figure 3.9: The real $\mathcal{K}'$ and the imaginary $\mathcal{K}''$ parts of the complex dimensionless polarizability $\mathcal{K}^*$ are plotted as a function of ω^* for a low $\zeta = 0.004$ and a thin EDL $\kappa a = 3$. The solid lines indicate the predictions of the MWO theory, which show quantitative agreements with the present simulation results for the entire frequency range.

In the case of a weakly charged colloidal particle ($\zeta = 0.004$), the charge density around the particle is very low. As defined in Eq. (3.5), I decompose the complex polarizability $\mathcal{K}^*$ into its real and imaginary components, $\mathcal{K}'$ and $\mathcal{K}''$, respectively, which represent the in-phase and out-of-phase components of the particle polarizability. The corresponding results are plotted in Figs. 3.9 (a) and (b).

In the low frequency regime, the real component of the polarizability $\mathcal{K}'$ shows a negative value. This means that the dipole moment is anti-parallel to the external electric field, as shown in the

snapshot in Fig. 3.10(a). This is a phenomenon called the *volume polarization* [63]. The positive and negative ions are rapidly migrating under the influence of the external field, however, since the ions cannot penetrate inside the core of the colloid, the volume of the particle acts as a physical obstacle, which hinders the migration. A schematic representation of this volume polarization effect is given in Fig. 3.10(b). This leads to an accumulation of negative (positive) ions on one side of the colloid with negative (positive) surface charge, while positive (negative) ions are depleted in this region. For similar reasons, there is an excess of positive (negative) charge on the another side of the colloid. Therefore, an induced dipole moment pointing from the front side toward the back side will be formed, which is anti-parallel to the external electric field.

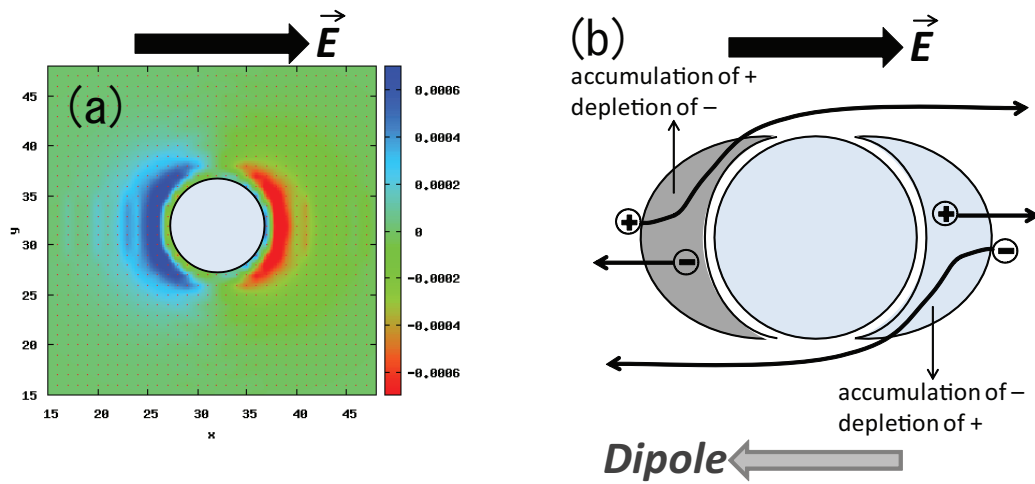


Figure 3.10: A snapshot (a) and a schematic illustration (b) of the *volume polarization*.

In the high frequency regime, the ions around the particle cannot immediately follow the alternating external field. Thus, I observed almost no accumulation or depletion of ions in the front or back of the particle, and no net dipole moment is obtained. The dimensionless polarizabilities $\mathcal{K}'$ and $\mathcal{K}''$ converge to zero upon further increasing the frequency.

In Fig. 3.9 (a) and (b), the solid lines indicate the predictions of the MWO theory, which show quantitative agreements with the present simulation results for the entire frequency range including the intermediate regime.

2 Highly charged particle

In the case of highly charged colloidal particles ($\zeta = 3$), for which the existence of the EDL around the particle cannot be ignored. Figure 3.11(a) and (b) shows the real and imaginary dimensionless

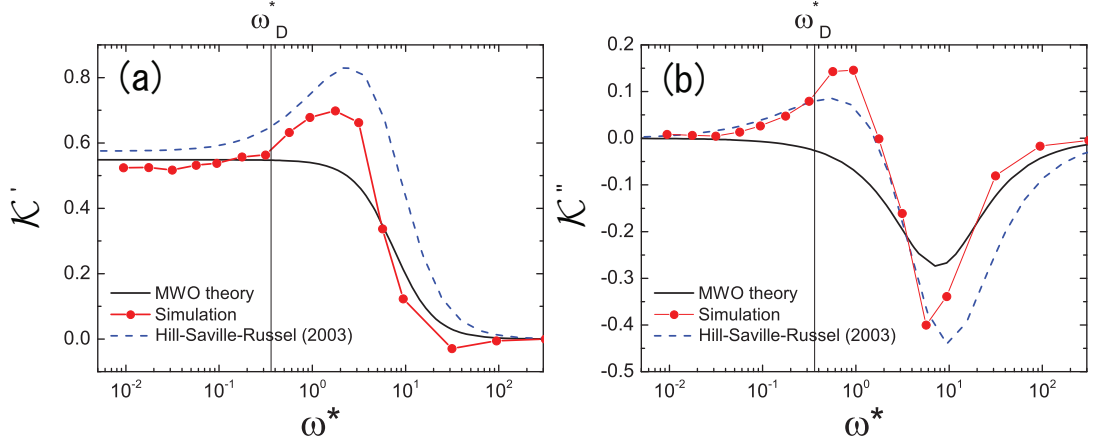


Figure 3.11: The real $\mathcal{K}'$ and the imaginary $\mathcal{K}''$ parts of the complex dimensionless polarizability $\mathcal{K}^*$ are plotted as a function of ω^* for high $\zeta = 3$ and a thin EDL $\kappa a = 3$. The solid lines indicate the predictions of the MWO theory, which show good agreements with the present simulation results only in low and high frequency regimes, but not for the intermediate regime where the deformation of the EDL becomes important.

polarizability $\mathcal{K}'$ and $\mathcal{K}''$, respectively.

In the low frequency regime, $\mathcal{K}'$ shows positive values. This means that the dipole moment is parallel to the external electric field, as shown in the snapshot in Fig. 3.2(a). This is a phenomenon called the *field polarization* [63], which is due to the Coulombic interactions between the charged colloidal particle and the surrounding ions. For a negatively (positively) charged colloid, the induced dipole moment due to field-polarization of the two oppositely charged ion species is parallel to the electric field, since the positive (negative) ion is drawn from the bulk towards the colloid, while the negative (positive) ions are repelled, as sketched in Fig. 3.12(b). This leads to the positive (negative) ions being accumulating at the back side of the particle, while the negative (positive) ions are depleted in this region. Therefore, an induced dipole moment pointing from the back side toward the front side will be formed, which is parallel to the external electric field.

In the high frequency regime, the fluid and ions around the particle cannot immediately follow the alternating external field. Thus, I observed almost no polarization in the high frequency region: $\mathcal{K}'$ and $\mathcal{K}''$ are both effectively zero in this regime.

In Fig. 3.11 (a) and (b), the solid lines indicate the predictions of the MWO theory, which show good agreements with the present simulation results only in the low and high frequency regimes, but not for the intermediate regime, where the deformation of the EDL becomes important. To take into account the contribution of the EDL, Hill[57] solved the full electrokinetic equations using numerical methods. These numerical solutions are shown in dashed lines and show good agreement

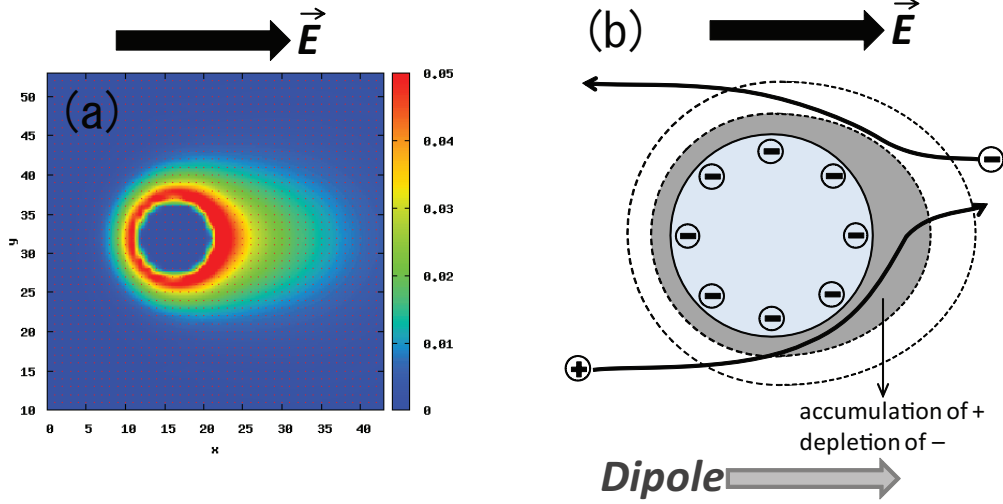


Figure 3.12: A snapshot (a) and a schematic illustration (b) of *the field polarization*.

with the present simulation for all frequency regimes.

3.7 Conclusions

In **Chapter 2**, I showed that the effect of polarization of the EDL under the influence of external fields plays an important role in determining the electrophoretic motions of colloidal particles. However, very little work has been performed so far to systematically study the polarization of the EDL. This includes theoretical works, particularly in situations where the Debye length is comparable to the colloidal size, ζ is moderately high, and/or the applied frequency of the external electric field is of the same order as the rate of ionic diffusion over the colloidal size. In all such cases, the effect of the EDL polarization becomes important and cannot be ignored.

In the present chapter, I studied the dynamic polarization of a charged colloidal particle in AC electric fields by performing systematic DNS via the SP method which fully resolves the coupled equations of hydrodynamics and electrostatics. I calculated the polarizability of a single colloidal particle with a EDL for ranges of the Debye length $1 \leq \kappa a \leq 5$, zeta potential $1 \leq \zeta \leq 5$, and applied frequency $\omega^* = 0$ (DC) or $1 \times 10^{-2} \leq \omega^* \leq 500$ (AC).

When a DC electric field is applied, I found that the polarization is affected by ζ , κa , and D_α . The present DNS results agree fairly well with the MWO theory [51–54] in the case of thin Debye length $\kappa a \gg 1$, low zeta potential $\zeta \leq 1$, and fast ionic diffusion $D_\alpha \gg 1$. The MWO theory, however, tends to disagree with the present DNS results when the Debye length becomes comparable to the colloidal size, ζ is moderately high, and/or the ionic diffusion is slow, for which

the system is highly polarized due to large deformations of the EDL.

When an AC electric field is applied, the dynamic response of the colloid and ions depends on the applied frequency ω^* . For small ω^* , I found two distinct pictures of polarization depending on whether ζ is low or high. For a weakly charged particle with low ζ , $|\mathcal{K}^*|$ has a negative value, which means that the dipole moment is anti-parallel to the external electric field. This phenomenon is called the *volume polarization* and is due to the presence of the colloid, which hinders the ionic flux. The accumulations of ions near the colloidal surface induce a dipole moment anti-parallel to the external electric field. For highly charged particles with high ζ , the induced dipole moment is proportional to the external electric field. This phenomenon is called the *field polarization* and is due to the Coulombic attraction/repulsion between the charged colloidal particle and the clouds of surrounding ions. Counter-ions/co-ions tend to accumulate in the back/rear side of the particle as those ions pass around the colloidal particle, resulting in a dipole moment proportional to the external electric field.

Upon increasing ω^* , I observed two dynamically distinct regimes, which depend specifically on whether ω^* is faster or slower than the ionic diffusion rate ω_D^* over the colloidal size. In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore the system behaves almost identical to the case of a DC electric field. In the high frequency regime $\omega^* > \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$. With a further increase in ω^* , where the oscillations in the external field take place so fast that the motions of ions and solvent around the colloidal particle cannot follow, the polarization of the EDL is completely suppressed. In the intermediate regime $\omega^* \sim 1$, the polarization of the EDL tends to show an overshoot behavior when ζ is large.

While the MWO theory is confirmed to work fine for all frequency regimes provided the zeta-potential is low, the predictions of the MWO theory tend to deviate from the present DNS results for highly charged particles with high zeta-potentials at intermediate frequencies, where the deformation of the EDL becomes significant.

Chapter 4

Inter-particle force between two colloidal particles in an oscillating electric field

4.1 Introduction

It is important to control the degree of dispersion and coagulation of charged particles in various media. For example, coagulation is a key part of many industrial processes such as paper production, extraction of proteins or other macro-ions from solution, or in the treatment of waste waters. On the other hand, there are many other cases where coagulation should be avoided, such as to prevent coagulation of paint resin, and to determine the physical properties of particle dispersions (size or ζ potential measurements). Therefore, it is important to understand the behaviour of dispersion and coagulation of charged particles in the medium.

In an aqueous colloidal dispersion system, under a sufficiently large electric field (ac or dc), these charged particles will align themselves to form linear structures (chains) [64, 65], this phenomenon is called pearl chain formation. This phenomenon arises because when the electric fields are applied to charged particles, counter-ions in the electric double layer (EDL) around the particles accumulate on one side of the EDL and are depleted on the other side. This is referred to as ion concentration polarization of the EDL [66]. The induced charged dipole moments arising from the ion concentration polarization of the EDL cause the formation of linear arrays of colloidal particles under AC electric fields [67–69]. Because it is extremely difficult to measure the induced electrical dipole moments of the EDL experimentally, the use of computer simulations has become essential to critically check the reliability of the extended theories. However, this phenomenon cannot be explained by the previous models that assume the EDL has an isotropic distribution. Additionally, these kinds of models are usually not suitable for evaluating the coagulation of particles at high concentration. In order to explain the mechanisms responsible for the formation of these arrays of colloidal particles, I performed direct numerical simulations (DNS) of charged colloidal dispersions in AC electric fields using the smoothed profile (SP) method [11, 12, 36, 37], which accurately takes into account the polarization effect of the EDL, as shown in **Chapter 2** and **Chapter 3**.

In **Chapter 2**, I simulated the complex electrophoretic mobility for both single particle and

multi-particle (dense dispersion) systems under an AC electric field using the SP method. The mobility was confirmed to depend on the polarization of the EDL. In **Chapter 3**, I quantified the polarization of a single charged particle with an EDL, and established a set of parameters that can quantify the induced dipole effects.

In this chapter, I first consider two identical particles aligned parallel to the external electric field and investigate the inter-particle force between them. I then consider the cases for two particles which are not aligned parallel to the external electric field, and investigate the inter-particle force, and its dependence at the particle configuration.

4.2 Definitions

4.2.A Inter-particle interaction force

The inter-particle interactions are forces of attraction or repulsion which act between other particles (atoms, molecules or ions). They are weak compared to the intramolecular forces (covalent bonds or metallic bonds) which keep a molecule together. For example, the covalent bond, involving the sharing of electron pairs between atoms is much stronger than the forces present between neighbouring molecules. They are an essential part of force fields used in molecular mechanics. Attractive inter-particle force are summarized in Table 4.1. The strengths of the inter-particle

Table 4.1: The various types of interaction with some common examples

Type of solid	Type of particle	Inter-particle force	Example
Ionic	Ions	Ionic-ionic attraction	NaCl, KBr
Polar molecular	Polar molecules	Hydrogen bond	H ₂ O
Polar molecular	Polar molecules	Dipole-dipole attraction	HCl
Instantaneous polar molecular	Instantaneous polar molecules	London dispersion force	CO ₂

forces are in this order: Ionic-ionic attraction > Hydrogen bond > Dipole-dipole attraction > London dispersion force

In this chapter, I consider two instantaneous dipole colloidal particles in an AC electric field. According to the conclusions of the previous chapters, the colloidal particles in an electric field will experience a polarization, which produces partial positive and negative charges on either side of the colloid. Figure 4.1 shows the schematic illustration of the dipole-dipole interaction between two colloid particles. In Fig. 4.1 (a), the dipoles are aligned parallel to the field and arranged in an end to end configuration. The partial positive charge on one particle is attracted to the partial negative

charge on the neighbouring particle. In contrast, when the particles are aligned perpendicular to the electric field, as shown in Fig. 4.1 (b), the particle charges on the neighbouring sides of the colloids lead to a repulsion. These interactions tend to align the colloidal particles to increase their attraction (reducing potential energy), and thus form hierarchical arrays of colloidal particles.

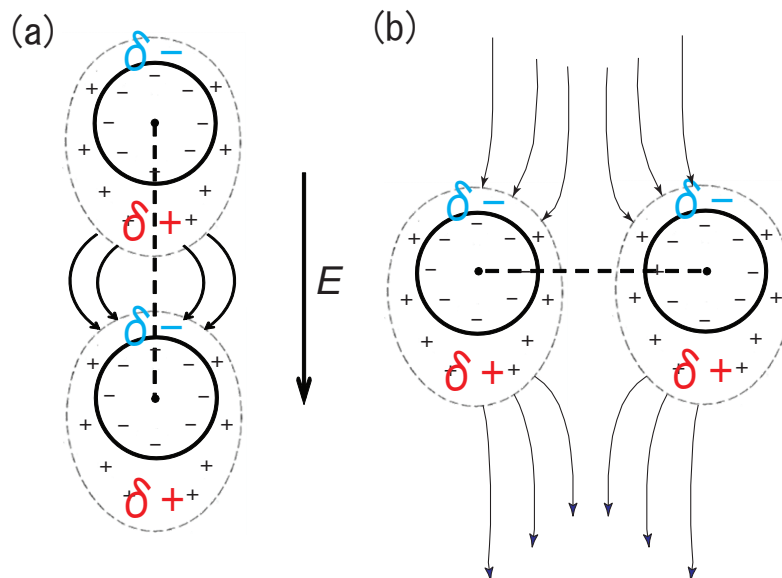


Figure 4.1: A schematic illustration of the dipole moment between two particles aligned (a) parallel and (b) perpendicular to the external electric field. The former induces an attractive inter-particle force and the latter a repulsive one.

4.3 Method

Here, I introduce the theoretical and numerical methods used to calculate the inter-particle force.

1 Debye-Hückel approximation

In order to calculate the inter-particle force under external fields, the electrostatic potential of the system must be calculated. This is a very complex problem, because the potential will have contributions not only from the particle, but also the ions around it. The contribution of Debye and Hückel was to reduce this complex problem to a simple model that could be solved analytically.

When a colloidal particle is immersed in an electrolyte solution, the particle surface absorbs or dissociates the ions and acquires an electric charge. The layer of surface charges and counter-ions is the so-called electric double layer (EDL). With the appropriate approximations (ignoring solvation and specific ion-ion effects), the ion distribution within this region can be described by the Poisson and Boltzmann equations, as described below. The Poisson equation provides a

relationship between the electrostatic potential Ψ and the charge density ρ_e :

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon}, \quad (4.1)$$

where ε is the electrical permittivity. The Boltzmann equation gives a relationship between the ion distributions and the potential:

$$\rho_e = \sum_{\alpha} z_{\alpha} e n_{\alpha}^{\infty} \exp\left(-\frac{z_{\alpha} e}{k_B T} \Psi\right), \quad (4.2)$$

where n_{α}^{∞} and z_{α} are the bulk ion concentration and valency of type α ions, respectively, e is the elementary charge, k_B is Boltzmann's constant, and T is the absolute temperature. Combining the Poisson and Boltzmann equations, I obtain:

$$\nabla^2 \Psi = -\sum_{\alpha} \frac{z_{\alpha} e n_{\alpha}^{\infty}}{\varepsilon} \exp\left(-\frac{z_{\alpha} e}{k_B T} \Psi\right), \quad (4.3)$$

This is known as the Poisson-Boltzmann equation, which describes the dependence of the charge density ρ_e on the electrostatic potential at electrochemical equilibrium.

However, the Poisson-Boltzmann equation is a non-linear partial differential equation and is hard to solve since Ψ is on both sides of the equation. To simplify this equation, Debye and Hückel obtained an approximate analytic solution under the assumption of a sufficiently low potential such that

$$\frac{z_{\alpha} e}{k_B T} \Psi \ll 1, \quad (4.4)$$

and expanded the exponential in a Taylor's series, $e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots$,

which leads to

$$e^{-z_{\alpha} e \Psi / k_B T} \simeq 1 - \frac{z_{\alpha} e}{k_B T} \Psi. \quad (4.5)$$

This is the so-called the Debye-Hückel approximation and the resulting Poisson-Boltzmann equation is called the linear Poisson-Boltzmann equation.

$$\nabla^2 \Psi = -\frac{1}{\varepsilon} \left[\sum_{\alpha} z_{\alpha} e n_{\alpha}^{\infty} - \sum_{\alpha} \frac{z_{\alpha}^2 e^2 n_{\alpha}^{\infty}}{k_B T} \Psi \right] \quad (4.6)$$

$$= \sum_{\alpha} \frac{z_{\alpha}^2 e^2 n_{\alpha}^{\infty}}{\varepsilon k_B T} \Psi \quad (4.7)$$

$$= \kappa^2 \Psi \quad (4.8)$$

$$\kappa^{-1} \equiv \left(\sum_{\alpha} \frac{\varepsilon k_B T}{z_{\alpha}^2 e^2 n_{\alpha}^{\infty}} \right)^{\frac{1}{2}} \quad (4.9)$$

The first sum, $\sum_{\alpha} z_{\alpha} e n_{\alpha}^{\infty}$, vanishes because the solution is electrically neutral. κ^{-1} is called the Debye length, which is the characteristic thickness of the electric double layer. Here, the linear Poisson-Boltzmann equation (4.8) has a general solution

$$\Psi(r) = \frac{eZ'}{4\pi\epsilon} \frac{\exp(-\kappa r)}{r} \quad (4.10)$$

$$Z' = \frac{z \exp(\kappa a)}{1 + \kappa a} \quad (4.11)$$

Comparing Eqs (4.1) and (4.8), I find $\rho = -\kappa^2 \epsilon \Psi$ and using Ψ from (4.10)

$$\rho_e = -\frac{\kappa^2 Z' e}{4\pi} \frac{\exp(-\kappa r)}{r} \quad (4.12)$$

The total charge of the particle is equal in magnitude to the total charge in the cloud.

$$q = - \int_{\text{volume}} \rho_e(r) dv = - \int_a^{\infty} \rho_e(r) 4\pi r^2 dr \quad (4.13)$$

$$= Z' e (\kappa a + 1) \exp(-\kappa a) \quad (4.14)$$

for a point charge ($a = 0$), $q = Z' e$.

I assume one point charge q at position r in the presence of an electrostatic potential $\Psi(r)$, the electrostatic potential energy $U(r)$ is defined as:

$$U(r) = q\Psi(r) = \frac{e^2 Z'^2}{4\pi\epsilon} \frac{\exp(-\kappa r)}{r} \quad (4.15)$$

the electrostatic force $F(r)$ is then obtained from the electrostatic potential energy as:

$$F(r) = -\nabla U(r) = \frac{e^2 Z'^2 \kappa^2}{4\pi\epsilon} \exp(-\kappa r) \left(\frac{1}{\kappa r} + \frac{1}{(\kappa r)^2} \right) \quad (4.16)$$

By reduction to dimensionless form, I define $F^*(r) = (4\pi\epsilon/e^2 \kappa^2 Z'^2) F(r)$, and $r^* = \kappa r$,

$$F^*(r^*) = \exp(-r^*) \left(\frac{1}{r^*} + \frac{1}{r^{*2}} \right) \quad (4.17)$$

As the results obtained within this approximation do not take into account the influence of the polarization of the EDL, they can be used to perform qualitative comparisons with our simulation results, and gauge the relative importance of this polarization.

4.4 Simulation

Numerical simulations are performed in three dimensions under periodic boundary conditions. The system size is $L_x \times L_y \times L_z = 128 \times 64 \times 64$, where the lattice spacing $\Delta = 4\pi\lambda_B$ is the unit of

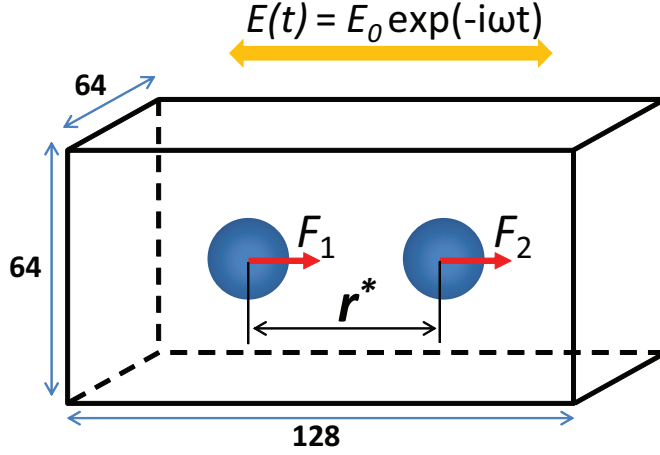


Figure 4.2: The geometry of the simulation setup. Two fixed identical spherical particles are arranged parallel to the external oscillating electric field in an electrolyte solution. The particle radius is a , and the center-to-center distance between the two particles is r^* . The system is placed in a simulation box of size $L_x \times L_y \times L_z = 64 \times 64 \times 128$.

length, with $\lambda_B = e^2/4\pi\epsilon k_B T$ the Bjerrum length, which is approximately 0.72 nm in water at 298 K. The units of temperature and electrostatic potential are $1/k_B$ and $k_B T/e$, respectively. The latter corresponds to 2.57×10^{-2} V at 298 K. I define the unit of time as $\tau = \Delta^2/\nu$, where $\nu = \eta/\rho$ is the kinematic viscosity.

I consider a system in which two **fixed** identical spherical particles of radius $a = 5\Delta$, with interfacial thickness $\xi = 2\Delta$ and particle surface potential $\zeta = \Psi_{\text{surface}}$, are aligned parallel to the external oscillating electric field, with a center-to-center distance of $r^* = \kappa r$. The geometry is described in Fig. 4.2. When an external electric field $\mathbf{E}(t)$ is applied to the suspension,

$$\mathbf{E}(t) = (E(t), 0, 0) \quad \text{with} \quad E(t) = E_0 \exp(-i\omega t), \quad (4.18)$$

where E_0 and ω are the magnitude and frequency of the oscillating field, respectively, the system becomes polarized. I denote the left-hand side particle as particle 1 and right-hand side particle as particle 2, the total force acting on each particle is $\mathbf{F}_1(t)$ and $\mathbf{F}_2(t)$, which can be written as:

$$\mathbf{F}_1(t) = \mathbf{F}_E(t) + \mathbf{F}_{12}(t) = \mathbf{F}_E(t) - \mathbf{F}_{21}(t) \quad (4.19)$$

$$\mathbf{F}_2(t) = \mathbf{F}_E(t) + \mathbf{F}_{21}(t) \quad (4.20)$$

where $\mathbf{F}_E$ is the external force due to the electric field $\mathbf{E}$, $\mathbf{F}_{21}$ is the inter-particle force on particle 2 due to the presence of particle 1. Combining equation (4.19) and (4.20), the inter-particle force

can be expressed as

$$\mathbf{F}_{21}(t) = \frac{\mathbf{F}_2(t) - \mathbf{F}_1(t)}{2} \quad (4.21)$$

$$= \mathbf{F}_{21}^{\parallel}(t) + \mathbf{F}_{21}^{\perp}(t) \quad (4.22)$$

where

$$\mathbf{F}_{21}^{\parallel}(t) = (\mathbf{F}_{21}(t) \cdot \mathbf{r}_{21})\mathbf{r}_{21} \quad (4.23)$$

$$\mathbf{F}_{21}^{\perp}(t) = (\mathbb{I} - \mathbf{r}_{21}\mathbf{r}_{21}) \cdot \mathbf{F}_{21}(t). \quad (4.24)$$

$\mathbf{F}_{21}^{\parallel}$ and $\mathbf{F}_{21}^{\perp}$ are the parallel and perpendicular components of the force, $\mathbb{I}$ is the unit tensor, and $\mathbf{r}_{21}$ is a unit vector pointing from 2 to 1. As before, I define the dimensionless force as $\mathbf{F}_{21}^{\parallel *} (t) = (4\pi\varepsilon/e^2\kappa^2Z'^2)\mathbf{F}_{21}^{\parallel}(t)$, with $r^* = \kappa r$. The time averaged inter-particle force can be then expressed as

$$\overline{F}_{21}^{\parallel *} = \frac{\int_0^T F_{21}^{\parallel *} dt}{T}. \quad (4.25)$$

Where $\overline{F}_{21}^{\parallel *} > 0$ is a repulsive force and $\overline{F}_{21}^{\parallel *} < 0$ is a attractive force. The values of all parameters used in this study are summarized in Table 4.2.

4.5 Results

In this study, I investigate the polarization phenomena between two spherical colloidal particles in both a uniform and an oscillating electric field. According to previous research [22, 23, 58], the polarization is affected by the magnitude of electric field E_0 , the zeta potential ζ , and the thickness of the EDL κa . Therefore, I will separately discuss the influence of E_0 , ζ , and κa . Then, I will compare our results for the inter-particle force with the Debye-Hückel approximate solution, which is valid for a thick EDL, weakly charged colloids and low frequency.

4.5.A Influence of the electric field E_0

In this section, I start with a system that contains two colloidal particles in a KCl solution, with a diffusion constant $D_\alpha = 7.24$ ($m_\alpha = 0.184$), in (a) no electric field (b) an AC electric field. First, I discuss the effects of the electric field on the inter-particle force in detail. The magnitude of the dimensionless inter-particle force $\overline{F}_{21}^{\parallel *}$ for $\kappa a = 2.5$ is plotted as a function of r^* for three values of oscillating electric field $E_0 = 0.1, 0.2$ and 0.3 in Fig. 4.3 (a), (b) and (c).

I found that with a large oscillating electric field such as $E_0 = 0.2$ and $E_0 = 0.3$, the inter-particle force is attractive ($\overline{F}_{21}^{\parallel *} < 0$). This is due to the Coulomb force between the polarized

Table 4.2: The parameters used in the present simulations. Comparisons of these values in simulation units and the corresponding experimental units are summarized in chapter 2.

Parameters	Symbol	Simulation value	Units
Radius of colloids	a	5	Δ
Diameter of colloids	d	10	Δ
Bjerrum length	λ_B	$1/4\pi$	Δ
Elementary charge	e	1	e
Thermal energy	$k_B T$	1	$\eta^2 \Delta / \rho$
Zeta potential (typical value)	ζ	$0.5 \sim 4$	$\eta^2 \Delta / \rho e$
Permittivity of particle	ϵ_p	1	$\rho e^2 / \Delta^2 \eta^2$
Permittivity of solvent	ϵ_m	1	$\rho e^2 / \Delta^2 \eta^2$
Viscosity of solvent	η	0.5	η
Density of solvent	ρ	0.1	ρ
Diffusion constant of ions	D_α	7.24	η / ρ
Magnitude of electric field	E_0	$0.01 \sim 3$	$\eta^2 / \rho e$
Frequency of AC field	ω	$0.002 \sim 20$	$\eta / \rho \Delta^2$
Dimensionless parameters	Symbol	Simulation value	
Zeta potential	$y = e\zeta / k_B T$	$0.5 \sim 4$	
Friction constant of ions	$m_\alpha = 2\epsilon(k_B T)^2 / 3\eta e^2 D_\alpha$	0.184	
Reynolds number	$Re = \rho d V_0 / \eta$	$10^{-3} \sim 10^{-2}$	
Frequency of external electric field	$\omega^* = \omega \rho a^2 / \eta$	$0.01 \sim 100$	
Frequency of ionic diffusion	$\omega_D^* = (D_\alpha / d^2) \rho a^2 / \eta$	0.362	

colloids. When the external electric field is applied, the particle and surrounding counter-ions become strongly polarized and develop a partial positive and negative charge on opposite sides of the particle, as shown in Fig. 4.1 (a). A larger electric field E_0 creates a stronger polarization, which increases the intensity of the partial charge distribution, and hence induces a stronger inter-particle force. Here, I selected a specific center-to-center distance $r^* = 8$, and plotted the magnitude of the dimensionless force $\bar{F}_{21}^{\parallel *}$ as a function of the magnitude of the oscillating external field E_0 in Fig. 4.3 (d). It is confirmed that $\bar{F}_{21}^{\parallel *}$ remains constant in the low-field region $E_0 \leq 0.1$, whereas $\bar{F}_{21}^{\parallel *}$ starts to decrease with increasing E_0 in the high-field region $E_0 \geq 0.1$.

I also found that different dimensionless frequencies have different effects on the inter-particle force $\bar{F}_{21}^{\parallel *}$. For high ω^* , the results for the inter-particle forces are consistent with the Debye-Hückel approximate results. This is because the motion of the counter-ions that surround the

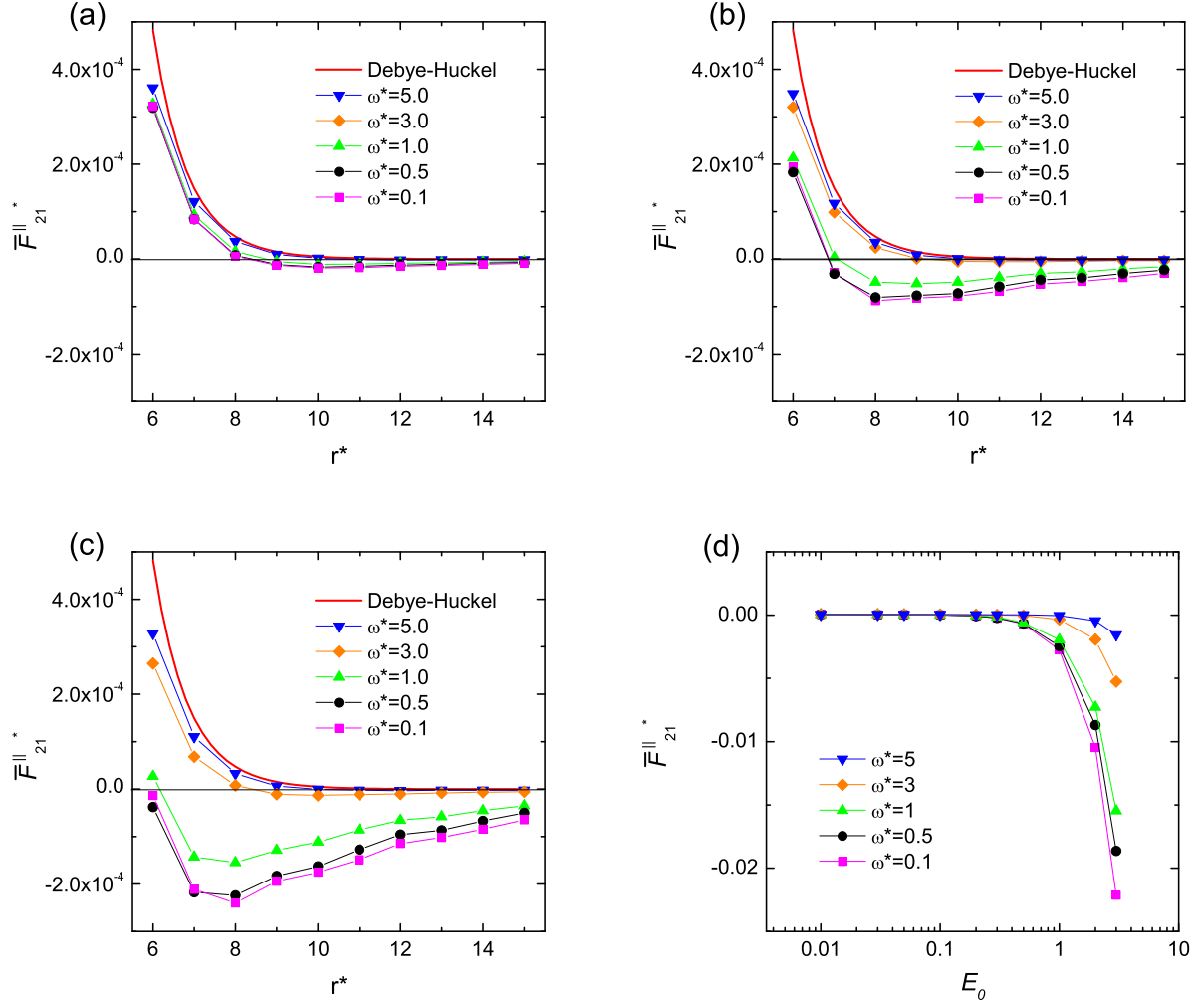


Figure 4.3: The magnitude of the dimensionless inter-particle force $\overline{F}_{21}^{||*}$ is plotted as a function of the center-to-center distance between the two particles r^* at various dimensionless frequencies ω^* for three magnitudes of the oscillating electric field (a) $E_0 = 0.1$, (b) $E_0 = 0.2$ and (c) $E_0 = 0.3$. In (d), the dimensionless inter-particle force $\overline{F}_{21}^{||*}$ is plotted as a function of the magnitude of the oscillating field E_0 for a specific center-to-center distance $r^* = 8$. Our simulation results show larger electric field E_0 creates a stronger polarization, which increases the intensity of the partial charge distribution, and hence induces a stronger inter-particle force.

particle cannot immediately follow the oscillating external field at high ω^* , and the perturbation of the EDL can then be neglected. However, when ω^* decreases, the colloid particles start to polarize, and the forces considerably deviate from the Debye-Hückel approximate results. A detailed description of this phenomenon can be found in the next section.

4.5.B Influence of zeta potential ζ

I now discuss the effects of the ζ on the inter-particle force in detail. Figure 4.4 shows $\overline{F}_{21}^{||*}$ as a function of r^* for $\zeta = 0.5, 1.0, 2.0, 3.0$, and 4.0 in (a) no electric field and (b) in an AC electric

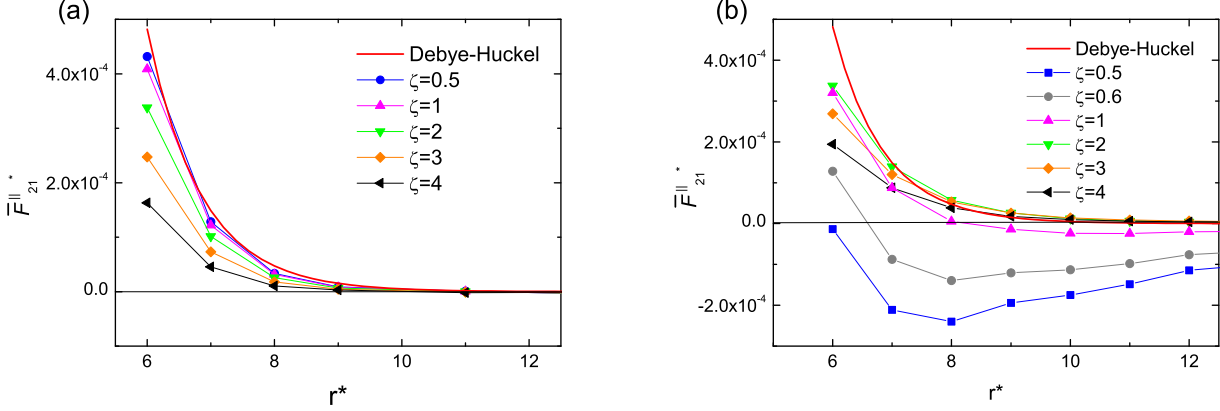


Figure 4.4: The magnitude of the dimensionless inter-particle force $\overline{F}_{21}^{||*}$ is plotted as a function of r^* for $\zeta = 0.5, 1.0, 2.0, 3.0$, and 4.0 in (a) no electric field (b) an AC electric field $E_0 = 0.3$. In (a), our simulation results tend to show better agreements with the Debye-Hückel approximate results for smaller ζ . The deviations become significant for larger ζ because the Debye-Hückel approximation is only valid for small κa and low ζ . In (b), the results show $\overline{F}_{21}^{||*}$ undergoes a significant decline at $\zeta < 2$, but is almost unchanged at $\zeta > 2$, compared to the results for no external field (a). This is because when ζ is increased, more counter-ions are attracted to the charged particle surface to form the EDL, which makes it more difficult to be perturbed by other particles.

field. In Fig. 4.4 (a), One can see that $\overline{F}_{21}^{||*}$ tends to deviate from the Debye-Hückel approximate inter-particle force at high ζ . This deviation is because the Debye-Hückel approximation (4.4) assumes a low electric potential, so the deviation becomes notable when ζ increase.

Figure 4.4 (b) shows the influence of ζ for an oscillating electric field of magnitude $E_0 = 0.3$. One can see that the inter-particle force $\overline{F}_{21}^{||*}$ significantly declines at $\zeta < 2$, but is almost unchanged at $\zeta > 2$ compared to the results in (a). This is because when ζ is increased, more counter-ions are attracted to the charged particle surface to form the EDL. Therefore, the charge density surrounding the particle becomes larger, which makes it more difficult to be perturbed by other particles.

4.5.C Influence of the Debye length κa

The magnitude of the dimensionless inter-particle force $\overline{F}_{21}^{||*}$ is plotted as a function of r^* for $\kappa a = 2.0, 2.5, 2.7, 2.9$, and 3.0 in Fig. 4.5. in (a) no electric field (b) an AC electric field. In Fig. 4.5 (a), it is shown that $\overline{F}_{21}^{||*}$ is in good agreement with the theoretical results at small κa but deviates considerably at larger κa . This is due to the fact that a large κa corresponds to a thin EDL, which is not accurately represented by the linearized Poisson-Boltzmann equation together with the Debye-Hückel approximation.

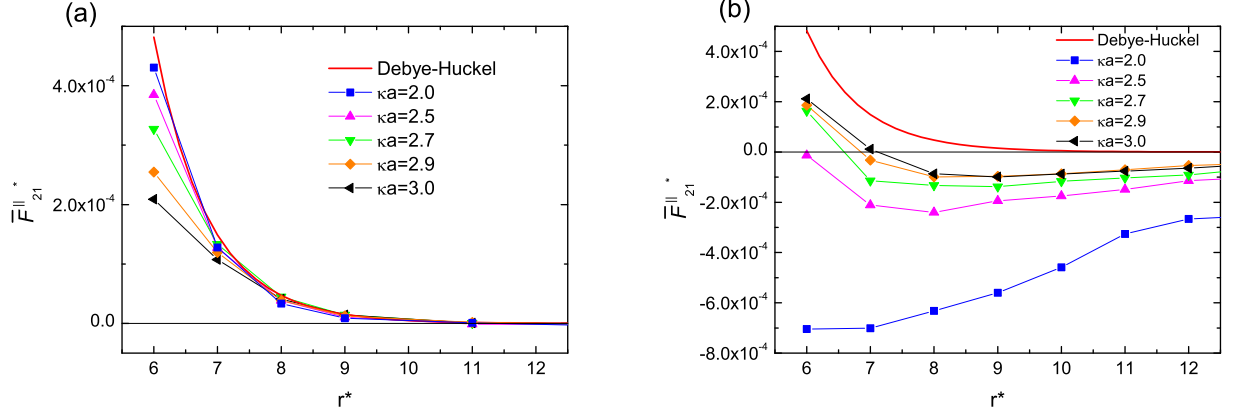


Figure 4.5: The magnitude of the dimensionless inter-particle force $\overline{F}_{21}^{||*}$ is plotted as a function of r^* for $\zeta = 0.5, 1.0, 2.0, 3.0$, and 4.0 in (a) no electric field (b) an AC electric field $E_0 = 0.3$. In (a), our simulation results tend to show better agreements with the Debye-Hückel approximate results for smaller κa . The deviations become significant for larger κa because the Debye-Hückel approximate is only valid for small κa and low ζ . In (b), the results show $\overline{F}_{21}^{||*}$ declines significantly at small κa , but only slightly at larger κa . This is because a large κa corresponds to a thin EDL, which is difficult to polarize since most counter-ions are strongly attracted to the particle surface. For low polarization, the induced dipole-dipole force becomes small.

Figure 4.5 (b) shows the influence of κa for an oscillating electric field with $E_0 = 0.3$. One can see that the inter-particle force $\overline{F}_{21}^{||*}$ decline significantly at small κa , but only slightly at larger κa . This is because a large κa corresponds to a thin EDL, which is difficult to polarize since most counter-ions are strongly attracted to the particle surface. For low polarization, the induced dipole-dipole force becomes small.

4.5.D Frequency dependency of inter-particle force

In this section, I focus on the effect of varying the frequency of the external AC electric field. Based on our results for an AC electric field, I chose a specific center-to-center distance $r^* = 8$, and investigate the relationship between frequency and the magnitude of the external AC electric field E_0 .

Figure 4.6 (a) shows $\overline{F}_{21}^{||*}$ as a function of the dimensionless frequency ω^* for $E_0 = 0.1, 0.2$ and 0.3 at $r^* = 8$. Fig. 4.6 (b) shows in more detail the interaction between frequency, external electric field and inter-particle force. Here, I divide the entire frequency range into three regimes, which are related to the deformation of the EDL of the colloid particles, using as characteristic frequency the ionic diffusion frequency ω_D^* . In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$. The colloidal system becomes

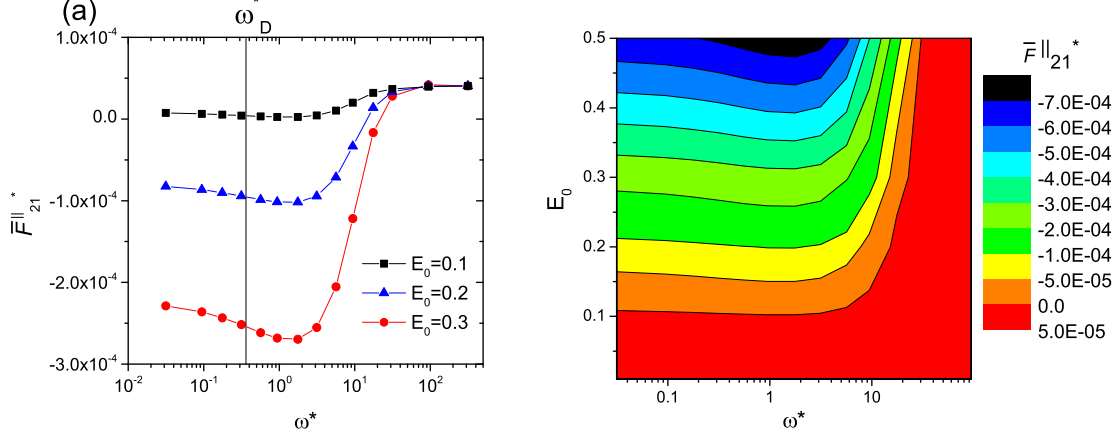


Figure 4.6: The magnitude of the dimensionless inter-particle force $\bar{F}_{21}^{\parallel*}$ is plotted as a function of ω^* for $E_0 = 0.1, 0.2$ and 0.3 in (a), and various E_0 in (b). In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore the system behaves almost identical to the case of a DC electric field. In the high frequency regime $\omega^* \gg \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$. With increasing ω^* , the variation of the external field is too fast for the motions of ions and solvent around the colloidal particle to follow, and therefore the system behaves almost identical to the case of no electric field.

polarized and induces an attractive inter-particle force. In the high frequency regime $\omega^* \gg \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$. The polarization of the colloid particle becomes weak, and the attractive force between the two particles is decreased. At the high ω^* limit in this regime, the ions around the particle cannot immediately follow the alternating external field, and therefore the system behaves almost identical to the case of no electric field. Most of the ions surrounding the particle are firmly held by the surface charge and obey the Poisson-Boltzmann distribution, such that the system shows almost no polarization.

4.5.E Inter-particle force between particles that are not aligned parallel to the electric field

In the previous section, I found that a strong external electric field E_0 with a low frequency ω induces an attractive force when the particles are aligned parallel to the external electric field. In this section, I investigate the inter-particle force between particles that are not aligned parallel to the electric field. The geometrical setup is described in Fig. 4.7. I consider a system in which two **fixed** identical spherical particles of radius $a = 5\Delta$, whose distance vector $\mathbf{r}^*$ makes an θ angle with the direction of the oscillating electric field. According to the results in previous section, I chose $\kappa a = 2.5$, $D_\alpha = 7.24$, $\omega^* = 0.1$, and $E_0 = 0.3$. The magnitude of the dimensionless inter-particle force $\bar{F}_{21}^{\parallel*}$ is plotted as a function of the offset angle θ for $r^* = 7, 9, 11$, and 13 .

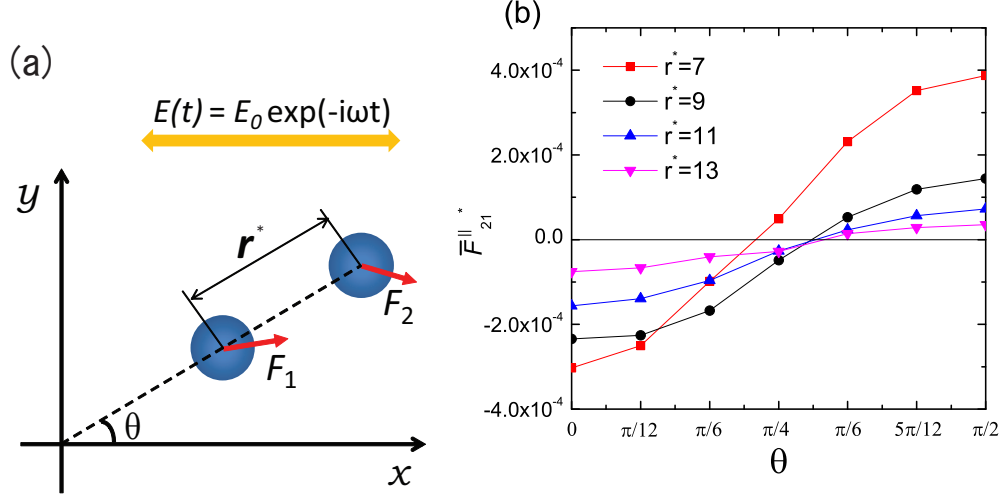


Figure 4.7: (a) Geometrical setup of the model system. Two spherical particles of equal radius a , with a center to center distance vector $\mathbf{r}^*$, which forms an angle θ with the x -axis (direction along which the electric field is applied). The magnitude of the dimensionless inter-particle force $\bar{F}_{21}^*$ is plotted as a function of θ for $r^* = 7, 9, 11$ and 13 in (b). The configuration of the two particles strongly affects the interaction, which shows an attractive force at near parallel configurations (low θ) and a repulsive force at near perpendicular configurations (high θ).

I divide the entire angular range into three regimes, which are related to the relative position of the two particles. In the low angle regime $0 < \theta < \pi/6$, the particles are almost parallel to the external electric field, and the dipoles are oriented in an end-to-end fashion. The partial positive charge on one particle is attracted to the partial negative charge on another particle, as shown in Fig. 4.1 (a), and this induces an attractive force ($\bar{F}_{21}^{\parallel *} < 0$). In the high angle regime $\pi/3 < \theta < \pi/2$, the particle alignment is nearly perpendicular to the external electric field. The partial charge on one particle is repulsed by the same partial charge on the other particle, as shown in Fig. 4.1 (b), and this induces a repulsive force ($\bar{F}_{21}^{\parallel *} > 0$).

4.5.F Multiple unfixed particles simulation

In this section, I consider particles which can move freely, and investigate the effect of inter-particle forces on the particle arrangement. I first consider a system in which six **free** particles are aligned parallel to the oscillating electric field, with an **initial** center-to-center distance of $r^* = 8$ for each adjacent particle. The initial state is described in Fig. 4.8 (a). When an oscillating electric field $E(t) = 0.3$ is applied, the middle particles are attracted by the neighbouring particles on the both sides. However, the outermost particles are attracted by the neighbouring particles in only one direction, so the outermost particles are preferentially attracted by the neighbouring particles, as

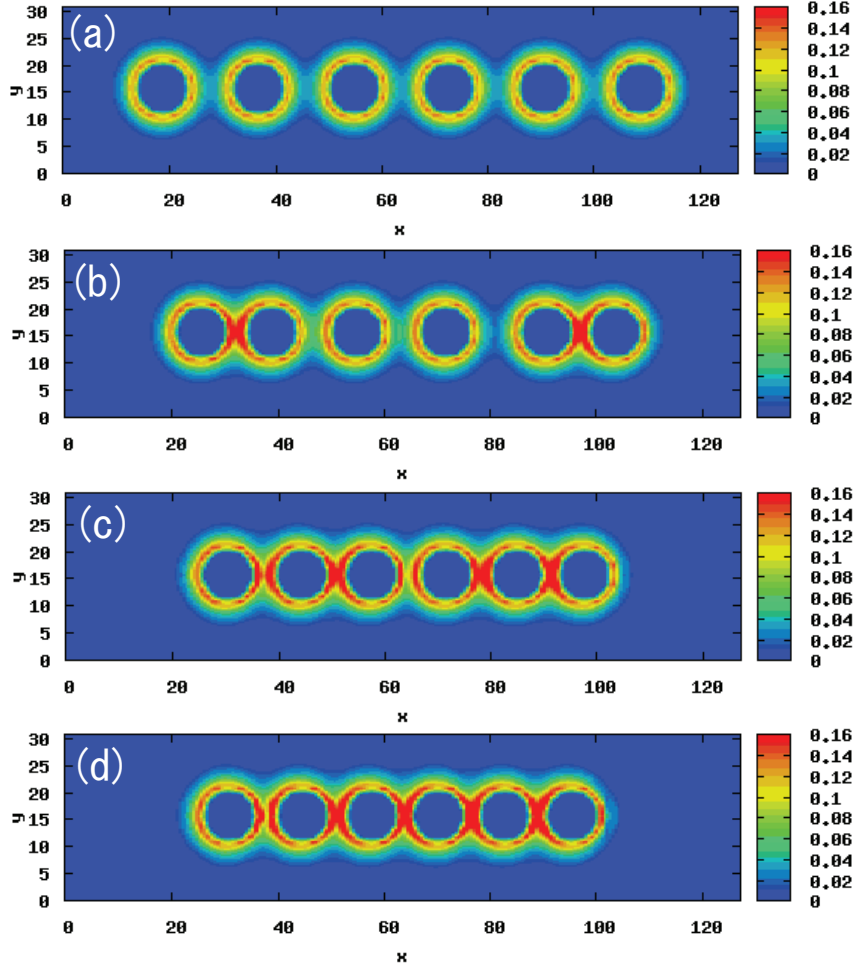


Figure 4.8: Geometrical setup of six unfixed particles are aligned parallel to the oscillating electric field, Snapshots of the charge density around the particles taken at $\zeta = 0.5$, $\kappa a = 2.5$, $E = 0.3$, and $\omega^* = 0.001$ for 550000 step simulation, which corresponds to 0.1 seconds. (a) Time step=1000 (b) Time step=140000 (c) Time step=348000 (d) Time step=550000.

shown in Fig. 4.8 (b). Next, for the same reason, the outermost particle pairs are attracted by the middle particle, as shown in Fig. 4.8 (c). Finally, after a sufficient time, the inter-particle interaction makes the particles closer together and form linear arrays.

Then, I consider a system in which twelve **free** particles, which are arranged in two rows parallel to the oscillating electric field, with an **initial** center-to-center distance of $r^* = 8$ for each adjacent particle. The initial state is described in Fig. 4.9 (a). When an oscillating electric field $\mathbf{E}(t) = 0.3$ is applied, the particles aligned parallel to the electric field induce an attractive inter-particle force, that leads to particle aggregation. Furthermore, the repulsive inter-particle force between the particles aligned perpendicular to the electric field cause the particles to move away. The coupling between attractive and repulsive inter-particle forces causes the formation of the hierarchical arrays which have already reported experimentally [70].

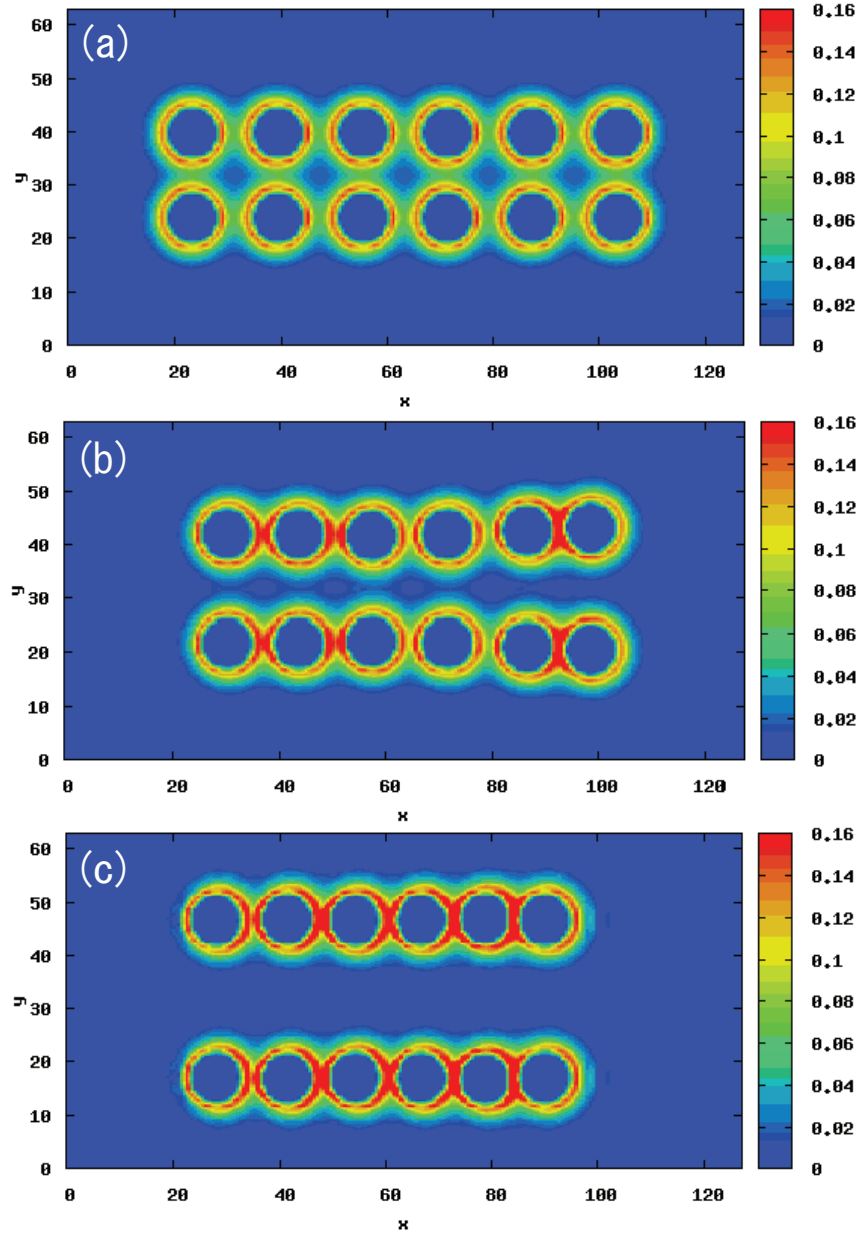


Figure 4.9: Geometrical setup of six unfixed particles, which are aligned in two line parallel to the oscillating electric field. Snapshots of the charge density around the particles taken at $\zeta = 0.5$, $\kappa a = 2.5$, $E = 0.3$, and $\omega^* = 0.001$ for 700000 step simulation, which corresponds to 0.073 seconds. (a) Time step=1000 (b) Time step=65000 (c) Time step=400000.

4.6 Conclusions

In **Chapter 2** and **Chapter 3**, I showed that the effect of the polarization of the EDL under the influence of external fields plays an important role in determining the electrophoretic motions of colloidal particles. However, very little work has been performed so far to systematically study the polarization of the EDL. This includes theoretical works, particularly in situations where the Debye length is comparable to the colloidal size, ζ is moderately high, and/or the applied frequency of

the external electric field is of the same order as the rate of ionic diffusion over the colloidal size. In all such cases, the effect of the EDL polarization becomes important and cannot be ignored.

In the present chapter, I first derived a simple model for two identical charged particles in AC electric fields, which are aligned parallel to the electric field. The dynamic interactions of this system are investigated by performing systematic DNS via the SP method which fully resolves the coupled equations of hydrodynamics and electrostatics.

When no electric field is applied, the overlap of the ionic clouds gives rise to a repulsive inter-particle force that pushes the particles apart. The present DNS results of repulsive forces agree fairly well with the linearized Poisson-Boltzmann solution.

I extended our results to AC fields, and found that the interaction is affected by E_0 , ζ , and κa . For large oscillating electric fields E_0 , the inter-particle force becomes attractive. This is because the particle and surrounding counter-ions becomes strongly polarized, which induces an attractive force. For large surface potentials (large ζ), more counter-ions are attracted to the charged particles surface to form the EDL, the charge density surrounding the particle becomes large, making it more difficult to perturb it. For thin double layers (large κa), it is more difficult to polarize since most counter-ions are strongly attracted to the particle surface, which leads to a decrease of the EDL thickness.

Furthermore, I found that the dynamic response of the colloids and ions depends on the applied frequency ω^* . For small ω^* , the inter-particle force $\overline{F}_{21}^{\parallel *}$ is an attractive force. This is due to the dipole moment of the particles. When particles are aligned parallel to the AC electric field, the induced dipoles of the two particles are aligned in an end-to-end fashion, and the partial positive charge on one particle is attracted to the partial negative charge on the neighboring particle.

Upon increasing ω^* , I observed two dynamically distinct regimes, which depend specifically on whether ω^* is faster or slower than the ionic diffusion rate ω_D^* over the colloidal size. In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore induces a strong inter-particle force. In the high frequency regime $\omega^* > \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$, and the inter-particle force decrease with increasing ω^* . With a further increase in ω^* , where the oscillations in the external field take place so fast that the motions of ions and solvent around the colloidal particle cannot follow instantaneously, the polarization of the EDL is completely suppressed, and inter-particle force behaves almost identical to the case of no

electric field.

The configuration of the particles is also an important factor in determining the inter-particle forces. When particles are aligned in a near parallel or near perpendicular configuration to the external field, the inter-particle force is attractive and repulsive, respectively. This is because the particle charge on one particle is attracted/repulsed to the partial charge on the other particle, depending on the relative configuration.

Furthermore, I consider more concentrated suspensions, where hierarchical arrays have already been observed experimentally. For particles that are aligned parallel to the oscillating electric field, I found that the inter-particle interaction make the particles closet together and form linear arrays. For particle aligned in two line parallel to the oscillating electric field, I found that particles are aggregated in parallel direction but segregated in perpendicular direction, and thus form the hierarchical arrays seen in experiments.

Chapter 5

General conclusion

This dissertation is devoted to the study of the dynamics of charged particle dispersions in electrolyte solutions. In particular, I have focused on the coupling between electrostatics and hydrodynamics, to determine their relative importance. For this purpose, we have presented a direct numerical simulation (DNS) method for dispersed charged particles under external direct or alternating electric field (**Chapter 2**). Using this simulation method, we have studied the polarization effects and investigated the effective interaction between particles in **Chapter 3** and **Chapter 4**.

In **Chapter 2**, we have presented the detailed formulation of the DNS method we have used to study the dynamics of particles in external fields. The validity of the method was confirmed by comparing our results for a single particle to the analytic solution of the nonlinear Poisson-Boltzmann equation proposed by O'Brien-White. Our results exhibit good agreement for a single particle in a DC field, as shown in Fig. 2.3. I then extended our study to AC fields and found that they exhibited continuity from low-frequency AC fields to DC fields. Furthermore, I proposed two meaningful time scales, the momentum diffusion frequency ω_ν^* and the ionic diffusion frequency ω_D^* , which divide the frequency into three regions (see Fig. 2.4) that are clearly correlated with the deformation of the electric double layer around the particles (EDL). I also investigated the role of the diffusion coefficient, to effectively study different electrolytes, as D_α is the only salt-specific parameter in our model. I varied the diffusion constant of the ions and found that the EDL presents different degrees of deformation, with a considerable polarization effect for lower values of the diffusion constant, as shown in Fig. 2.6. Finally, I extended our study to dense dispersions, and compared our results with a theoretical analysis based on the cell model. I found that the cell model is reliable when the EDL overlap is small and less reliable as the overlap becomes more significant. Our results clearly show that the polarization effects due to the deformation of the EDL, under the influence of an external field, plays an important role in determining the electrophoretic motion of colloidal particles.

In **Chapter 3**, I studied the dynamic polarization effect of a charged colloidal particle in AC electric fields, and found that the polarization is affected by the zeta potential ζ , the ion diffusion

constant D_α , and the thickness of the EDL κa . The present DNS results agree fairly well with the Maxwell-Wagner-O’Konski (MWO) theory in the case of a thin Debye length $\kappa a \gg 1$, low zeta potential $\zeta \leq 1$, and fast ionic diffusion $D_\alpha \gg 1$. In such cases, the effect of the EDL polarization is small and can be ignored. However, the MWO theory tends to disagree with the present DNS results when the Debye length becomes comparable to the colloidal size, ζ is moderately high, and/or the ionic diffusion is slow. In such cases, the system becomes highly polarized due to large deformations of the EDL.

I have also found that the dynamic response of the colloids and ions depends strongly on the applied frequency ω^* . For small ω^* , I found two distinct polarization regimes, depending on whether ζ is low or high. For a weakly charged particle, with low ζ , the dipole moment is anti-parallel to the external electric field. This is due to the presence of the colloid, which hinders the ionic flux, as shown in Fig. 3.10 (a). The accumulation of ions near the colloidal surface induces a dipole moment anti-parallel to the external electric field. For highly charged particles, with high ζ , the induced dipole moment is proportional to the external electric field. This is due to the Coulombic attraction/repulsion between the charged colloidal particle and the cloud of surrounding ions, as shown in Fig. 3-12 (a). Counter-ions (co-ions) tend to accumulate in the back (rear) side of the particle, as the ions move past the colloidal particle, resulting in a dipole moment proportional to the external electric field. Finally, I observed two dynamically distinct regimes, which depend specifically on whether ω^* is faster or slower than the ionic diffusion rate ω_D^* over the colloidal size. The two regimes are clearly correlated with the deformation of the EDL, as I reported in **Chapter 2**. These results show that the magnitude of the polarization is affected by the properties of the particle (ζ) and ions (κa , D_α), and the frequency of applied field ω^* .

In **Chapter 4**, I considered the polarization effects on the effective interaction between a pair of charged colloidal particles. I first derived a simple model, using the linearized Poisson-Boltzmann equation, that describes the force between two identical charged particles aligned parallel to an applied external field. In the absence of a field, the overlap of the ionic clouds gives rise to a repulsive inter-particle force that pushes the particles apart. Our DNS results agree fairly well with the simple model. I then extended our simulations to consider AC fields, and found that the pair interaction is affected by E_0 , ζ , and κa . For strong amplitudes of the oscillating electric fields E_0 , I found that the inter-particle force can become attractive. This is because the particle and surrounding counter-ions become strongly polarized, leading to a partial accumulation of positive

and negative charges on either side of the colloid, and inducing an attractive force when the particles are aligned parallel to the electric field, as shown in Fig. 4.1 (a). However, when the particles are aligned perpendicular to the electric field, as shown in Fig. 4.1 (b), the particle charges on the neighboring sides of the colloids lead to a repulsive interaction. These pair interactions tend to align the colloidal particles, in order to increase their attraction (reducing their potential energy), and thus lead to the formation of hierarchical arrays of colloidal particles. Furthermore, I also found two dynamically distinct regimes, which depend specifically on whether ω^* is faster or slower than the ionic diffusion rate ω_D^* over the colloidal size. In the low frequency regime $\omega^* < \omega_D^*$, the polarization of the EDL is fully developed with respect to the instantaneous electric field $E(t)$, and therefore induces a strong inter-particle force. In the high frequency regime $\omega^* > \omega_D^*$, the polarization of the EDL cannot be fully developed with respect to the instantaneous $E(t)$, and the inter-particle force decreases with increasing ω^* . Moreover, I consider more concentrated suspensions and observed the movement of multiple particles under oscillating electric field. I found that the inter-particle interaction make the particles become hierarchical arrays, which have already been observed in the experiments.

In this dissertation, I have studied the dynamics of charged colloidal particles in AC electric fields using a DNS method that takes into account the many-body hydrodynamic interactions. By considering the full electro-hydrodynamic coupling between the colloids, the ions, and the fluid, I was able to gain a deeper understanding of the nature of electrophoresis. In particular, I have identified the regimes in which the commonly used analytic theories breakdown. Based on these results, I now understand that polarization effects are very important and cannot be ignored when $\kappa^{-1} \simeq a$, $\zeta \gg 1$, or $D_\alpha \ll 1$. I have seen that the complex nature of the electro-hydrodynamic coupling can give rise to non-trivial interactions just between pairs of particles. In future work, the application of electroacoustics on a colloidal dispersion involves the effect of electrokinetic sonic amplitude is popular in recent years, which is useful to measure the surface potential to a concentrated dispersion directly. One remaining problem, which I have yet to solve, is how to partition the overlapping ionic distribution among many particles, to evaluate the polarizability of such dense suspensions. Work along these lines is now in progress.

Acknowledgements

I would like to express my deep gratitude to my supervisor Professor Ryoichi Yamamoto for his encouragement, support and guidance throughout my PhD course. I also acknowledge Professor Minoru Miyahara and Professor Shuji Matsusaka for their insightful review on this thesis. I would like to express their gratitude to Assistant Professor John J. Molina for useful discussions and suggestions. I would like to appreciate Dr. Hideki Kobayashi, Dr. Hideyuki Mizuno, Dr. Rei Tatsumi, and Dr. Adnan Hamid for all their precious comments and discussions.

I acknowledge Associate Professor Takashi Taniguchi and Professor Hiroyuki Shinto for their helpful suggestions and useful discussions. I would like to thank Assistant Professor Takahiro Murashima, Dr. Masayuki Uranagase, and Dr. Yukitaka Ishimoto for their showing of excitement of academic life. I am indebted to the laboratory secretary, Ms. Kana Ishida for her various supports. I would like to give special thanks to all the members of Transport Phenomena Laboratory including the past members.

List of Publications

Chapter 2

C. Shih and R. Yamamoto, “ Dynamic electrophoresis of charged colloids in an oscillating electric field ”, Phys. Rev. E, **89** 062317, (2014).

Chapter 3

C. Shih, John J. Molina and R. Yamamoto, “ Dynamic polarization of a charged colloid in an oscillating electric field ”, Mol. Phys., **accepted for publication**.

Chapter 4

C. Shih, John J. Molina and R. Yamamoto, “ Inter-particle force between two colloidal particles in an oscillating electric field ”, **in preparation**.

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