

The roles of surfactant and pair interactions in
leaky dielectric drop electrohydrodynamics

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Abstract

When a weakly conducting (leaky dielectric) drop is suspended in another fluid and exposed to a uniform DC electric field, a charge distribution develops on the interface of the drop due to the discontinuity of the electrical properties there. This charge distribution leads to electric stresses on the interface, which drive both fluid motion and deformation of the drop. This thesis explores two aspects of this challenging electrohydrodynamic problem, namely the effects of the presence of surfactant on the behaviour of a single drop and the effects of interactions on the behaviour of a pair of clean drops. We present semi-analytical theories built within the framework of the Taylor–Melcher leaky dielectric model assuming small drop deformations and large viscosity ratios. Specifically, we derive systems of coupled nonlinear ordinary differential equations which are solved numerically using a fourth-order Runge–Kutta time-stepping scheme and a pseudo-arclength continuation algorithm. The novelty of our theories lies in the retention of surface charge convection, which couples the interfacial charge to the flow fields in a nonlinear fashion and precludes closed-form solutions to the governing equations, but which it is necessary to include if one wishes to capture the transition to Quincke rotation, a symmetry-breaking instability in which the drop begins to rotate spontaneously when the electric field strength is greater than a critical value. We first briefly explore an isolated clean drop, for which we discuss the experimentally observed hysteresis at the onset of Quincke rotation, and derive an expression for the critical field strength for the onset of Quincke rotation of a spherical drop. For the problem of a surfactant-laden drop, we find that the presence of a weakly-diffusing surfactant on the drop interface can eliminate this hysteresis and significantly decrease the critical field strength, and we systemat-

ically explore the effects of varying the surfactant diffusivity and the sensitivity of the surface tension to the local surfactant concentration on the rotation of a drop. For the problem of a pair of interacting clean drops, we report qualitatively different types of trajectories followed by pairs of interacting drops undergoing Quincke rotation and explore the effects of interactions on the deformation, tilt angle, and angular velocity of pairs of fixed drops as the alignment of the drop pair relative to the electric field is varied. By exploring the behaviour of drops in these two new contexts, this thesis extends our understanding of droplet electrohydrodynamics, particularly with regard to Quincke rotation, and opens up several promising avenues for future research.

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Chapter 1

Introduction

1.1 History and applications of electrohydrodynamic flows

The field of electrohydrodynamics is concerned with the interactions between electric fields and charged or polarisable fluids. It is a field with broad scope and a rich history, dating back as far as 1600 to the publication of William Gilbert's *De Magnete*, which describes the first reported electrohydrodynamic experiment. In that work, Gilbert noted that a drop of water would be drawn up into a cone if a charged piece of amber were held above it. This phenomenon was later studied experimentally and explained theoretically by Taylor [1964]. Intriguing interactions also occur between electric fields and gases; in 1629, Niccolo Cabeo recorded another early observation of an electrohydrodynamic phenomenon (although he did not recognise it as such) when he noticed that sawdust was initially attracted to an electrified body, before making contact and subsequently being repelled by the body [Fylladitakis et al., 2014]. Subsequent investigation into this behaviour (by such figures as Newton, Faraday and Maxwell) identified it as an instance of ion wind, a phenomenon wherein charged particles produced via a corona discharge near a pointed electrode migrate in an electric field and collide with electrically neutral particles, imparting some of their momentum to the latter to give rise to bulk air flow. This principle has recently been employed

to generate thrust in the first ‘solid-state’ plane, which here means one whose propulsion system includes no moving parts [Xu et al., 2018].

Since the aforementioned early experiments, a wide range of electrohydrodynamic systems have been studied, which have attracted widespread attention not only due to their fundamental scientific importance but also because the unique phenomena associated with these systems find application in various industrial and commercial settings. For example, electrosprays rely on the formation of liquid cones as described by Taylor [1964]. At a sufficiently high voltage, a fine liquid jet is emitted from the tip of the cone, which breaks up into small charged droplets which repel one another to form a mist [Hayati et al., 1986, Fernández de La Mora, 2007, Collins et al., 2008, Smith, 2008]. This behaviour is commonly exploited in mass spectrometry [Fenn et al., 1989], as well as for developing ozone-free air purifiers [Tepper et al., 2007], inkjet printers [Park et al., 2007, Basaran et al., 2013], and even highly efficient and finely controllable propulsion mechanisms (known as colloid thrusters) for light spacecraft [Bailey, 1973]. Electrohydrodynamic principles are also employed in the development of novel types of pump [Seyed-Yagoobi, 2005, Bart et al., 1990]. In addition to electrohydrodynamic gas pumps [Robinson, 1961, Moreau and Touchard, 2008, June et al., 2011], there are three basic types of electrohydrodynamic liquid pump: ion-drag [Crowley et al., 2002, Feng and Seyed-Yagoobi, 2004], conduction [Feng and Seyed-Yagoobi, 2004, Kano and Nishina, 2013], and induction [Melcher, 1966, Bohinsky and Seyed-Yagoobi, 1990] pumps. These have variously been considered as a means of promoting mass transfer in microgravity environments [Yagoobi, 2019], used in the development of actuators for soft robotics [Cacucciolo et al., 2019, Peng et al., 2023, Bai et al., 2024], and used to enhance heat transfer in various settings [Wawzyniak and Seyed-Yagoobi, 2002, Selvakumar et al., 2022, Brand and Seyed-Yagoobi, 2003, Laohalertdecha et al., 2007]. In addition, electrocoalescence [Atten, 1993], whereby electric fields are used to induce coalescence of drops, is employed in the development of microfluidic devices [Chabert et al., 2005, Priest et al., 2006, Zagnoni et al., 2010] and for separating water from crude oil in petroleum processing [Ptasinski and Kerkhof, 1992, Eow et al., 2001, Eow

and Ghadiri, 2002], amongst other uses.

1.2 Modelling of electrohydrodynamics

To better understand the physics underlying the mentioned applications of electrohydrodynamic systems, theoretical studies have explored various paradigmatic systems, such as drops, thin films, and jets. These idealized systems capture important electrohydrodynamic phenomena and provide physical insight while remaining analytically and numerically tractable. Developing accurate models for such systems requires coupling the equations governing fluid motion with those governing electric fields and charge dynamics. In this section, we outline some of the fundamental equations on which these studies of electrohydrodynamics are based and highlight some commonly invoked assumptions and approximations.

1.2.1 Electrostatics

In macroscopic media, electromagnetic phenomena are described by Maxwell's equations, which in differential form are written

$$\nabla \cdot \mathbf{D} = \rho, \quad (1.1a)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (1.1b)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (1.1c)$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}. \quad (1.1d)$$

Eq. (1.1a) is Gauss's law, which relates the charge at a point to the resulting electric field. Here, $\mathbf{D}(\mathbf{r}, t)$ denotes the electric displacement field, $\rho(\mathbf{r}, t)$ denotes the electric charge density (charge per unit volume), $\mathbf{r}$ denotes a position vector and t denotes time. Eq. (1.1b) is Gauss's law for magnetism, which expresses the absence of magnetic monopoles. Here, $\mathbf{B}(\mathbf{r}, t)$ is the magnetic field. Eq. (1.1c) is the Maxwell–Faraday equation, which describes electromagnetic induction: a time-varying magnetic field generates a circulating electric field. Here, $\mathbf{E}(\mathbf{r}, t)$ is

the electric field. Finally, Eq. (1.1d) is the Ampère–Maxwell law, which describes the circulation of a magnetic field in the presence of electric and displacement currents. Here, $\mathbf{J}(\mathbf{r}, t)$ denotes the current density (charge per unit area per unit time) and $\mathbf{H}(\mathbf{r}, t)$ denotes the magnetising field.

In order to fully determine the electromagnetic fields, Maxwell’s equations must be supplemented with phenomenological constitutive equations that describe the response of the materials to the fields. First, an equation is required to determine the displacement field $\mathbf{D}$, a vector that generally contains the effects of both the electric field $\mathbf{E}$ and the permanent or induced polarisation vector of a dielectric material, $\mathbf{p}(\mathbf{r}, t)$. Specifically,

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{p}, \quad (1.2)$$

where ϵ_0 is the permittivity of free space. In a linear material, the polarisation is proportional to the local electric field, i.e.,

$$\mathbf{p} = \epsilon_0 \chi_E \mathbf{E} \quad (1.3)$$

where χ_E is the electric susceptibility of the material. In this case, one may use the simple linear constitutive equation

$$\mathbf{D} = \epsilon \mathbf{E}, \quad (1.4)$$

where $\epsilon = \epsilon_r \epsilon_0$ is the absolute permittivity of the material (hereafter referred to simply as the permittivity), and $\epsilon_r = 1 + \chi_E$ is the relative permittivity of the material. In the problems considered in this thesis, the permittivity of each material is taken to be spatially uniform and constant. A second equation is required to determine the magnetising field $\mathbf{H}$, which generally contains contributions from the external magnetic field $\mathbf{B}$ as well as the magnetisation vector of the material, $\mathbf{M}(\mathbf{r}, t)$. Specifically,

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M}, \quad (1.5)$$

where μ_0 is the magnetic permeability of free space. In a linear material, the

magnetisation is proportional to the magnetising field, i.e.,

$$\mathbf{M} = \chi_M \mathbf{H}, \quad (1.6)$$

where χ_M is the magnetic susceptibility of the material. In this case, one may use the simple linear constitutive equation

$$\mathbf{H} = \frac{1}{\mu_r \mu_0} \mathbf{B}, \quad (1.7)$$

where $\mu_r = 1 + \chi_M$ is the relative permeability of the material under consideration.

In cases where magnetic fields are constant in time or vary only very slowly, then the electrostatic approximation to Maxwell's equations can be invoked. In this case, Faraday's law (1.1c) simplifies to

$$\nabla \times \mathbf{E} = \mathbf{0}, \quad (1.8)$$

which implies that the electric field is conservative and may therefore be expressed in terms of a scalar potential $\varphi(\mathbf{r}, t)$, where

$$\mathbf{E} = -\nabla \varphi. \quad (1.9)$$

Substituting (1.9) into Gauss's law (1.1a) and using (1.4) then yields Poisson's equation, allowing one to relate the electric potential to the local charge density,

$$\nabla^2 \varphi = -\frac{\rho}{\epsilon}. \quad (1.10)$$

In many problems of interest, however, the charge density is not given *a priori*, but instead evolves dynamically due to the motion of charge carriers. The evolution of the charge density is constrained by the requirement that charge is conserved, and is determined by eliminating the magnetising field from (1.1d) by taking the divergence, and then combining the resulting equation with (1.1a), yielding

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0, \quad (1.11)$$

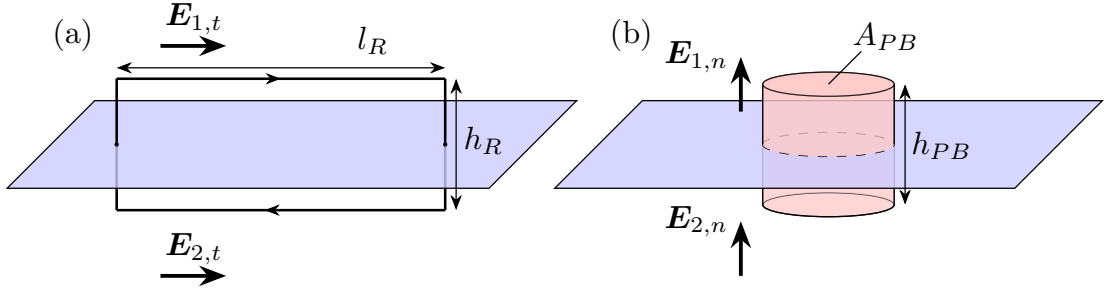


Figure 1.1: (a) A rectangle and (b) a cylindrical Gaussian pillbox straddling the interface between two different materials.

which requires that any local accumulation of charge be accounted for by net inward current flux, and vice versa. In general, $\mathbf{J}$ may take a complicated form arising from using the Nernst–Planck equation to model the transport of the various ionic species in the material, generally involving electromigration (electric field-induced motion of the ion relative to the material), diffusion, and, if the material is a fluid, convection. A source term may also appear in (1.11), accounting for the production of charge via recombination and disassociation reactions [Castellanos, 1998]. However, various approximations that greatly simplify $\mathbf{J}$ are commonly invoked in studies of electrohydrodynamics, as will be discussed in §1.3.2.

When solving problems involving electric fields in two or more materials with different electrical properties, it is essential to apply appropriate boundary conditions to the interface between the materials, which are derived from Maxwell’s equations. First, Faraday’s law in the electrostatic limit (1.8) implies that $\mathbf{E}$ is a conservative vector field; that is, the line integral of $\mathbf{E}$ over any closed loop is zero:

$$\oint \mathbf{E} \cdot d\boldsymbol{\ell} = 0, \quad (1.12)$$

where $d\boldsymbol{\ell}$ is a line element. Consider a small rectangle of length l_R and height h_R straddling the interface between two materials (Figure 1.1(a)). Now consider the limit as $h_R \rightarrow 0$, while l_R is kept fixed. As long as the electric field remains finite at the interface, the contributions to the line integral from the left and right sides of the rectangle vanish in this limit. Along the top and bottom of the rectangle, the line element may be written as $d\boldsymbol{\ell} = \hat{\mathbf{t}}d\ell$, where $\hat{\mathbf{t}}$ is a unit vector tangent to

the interface and parallel to the top and bottom of the rectangle. Then,

$$\int_{top} \mathbf{E}_{1,t} \cdot \hat{\mathbf{t}} d\ell + \int_{bottom} \mathbf{E}_{2,t} \cdot \hat{\mathbf{t}} d\ell = 0, \quad (1.13)$$

where $\mathbf{E}_{1,t}$ and $\mathbf{E}_{2,t}$ are the electric fields tangential to the interface in materials 1 and 2, respectively, i.e., $\mathbf{E}_{i,t} = \mathbf{E}_i \cdot (\mathbf{I} - \mathbf{n}\mathbf{n})$, where $\mathbf{E}_i$ is the electric field in the i th material, $\mathbf{I}$ is the identity tensor and $\mathbf{n}$ is the unit vector normal to the interface. If we next assume that l_R is sufficiently small that $\mathbf{E}_{1,t}$ and $\mathbf{E}_{2,t}$ are constant on the respective sides of the interface, we have

$$E_{1,t}l_R - E_{2,t}l_R = 0, \quad (1.14)$$

where $E_{1,t} = \mathbf{E}_{1,t} \cdot \hat{\mathbf{t}}$ and $E_{2,t} = \mathbf{E}_{2,t} \cdot \hat{\mathbf{t}}$, and thus $E_{1,t} = E_{2,t}$, i.e., the tangential components of the electric field are continuous across the interface.

Next, Gauss's law (1.1a) can be written in terms of integrals over a volume V bounded by surface ∂V using the divergence theorem,

$$\iint_{\partial V} \epsilon \mathbf{E} \cdot \mathbf{n}_{\partial V} dA = \iiint_V \rho dV, \quad (1.15)$$

where $\mathbf{n}_{\partial V}$ is the unit normal to the surface ∂V . We integrate over a cylindrical Gaussian pillbox of height h_{PB} and cross sectional area A_{PB} whose flat surfaces are parallel to the interface (Figure 1.1(b)). In the limit $h_{PB} \rightarrow 0$, the fluxes through the curved side of the pillbox vanish and the enclosed charge is simply the surface charge on the enclosed portion of the interface, i.e.,

$$\iint_{top} \epsilon_1 \mathbf{E}_1 \cdot \mathbf{n} dA - \iint_{bottom} \epsilon_2 \mathbf{E}_2 \cdot \mathbf{n} dA = \iint_S q dA, \quad (1.16)$$

where ϵ_1 and ϵ_2 are their permittivities, q is the surface charge density, S is the region of the interface contained in the pillbox and the unit normal $\mathbf{n}$ is defined to be pointing into material 1. Then, if A_{PB} is small enough that the normal field components $E_{1,n} = \mathbf{E}_1 \cdot \mathbf{n}$ and $E_{2,n} = \mathbf{E}_2 \cdot \mathbf{n}$ and the surface charge density

q can all be treated as constant within the pillbox, then (1.16) reduces to

$$\epsilon_1 E_{1,n} - \epsilon_2 E_{2,n} = q. \quad (1.17)$$

The normal component of the displacement field is thus discontinuous at the interface, and the discontinuity is equal to the enclosed surface charge density.

In addition, an electric field exerts stresses in a material as a result of forces acting on free or bound charges. In the electrostatic limit, the state of stress in a material due to the electric field is expressed by the electrostatic Maxwell stress tensor $\boldsymbol{\tau}^E(\mathbf{r}, t)$, defined as

$$\boldsymbol{\tau}^E = \epsilon_r \epsilon_0 \mathbf{E} \mathbf{E} - \frac{1}{2} \epsilon_r \epsilon_0 E^2 \mathbf{I}, \quad (1.18)$$

in which $E = |\mathbf{E}|$ is the magnitude of the electric field and $\mathbf{I}$ is the identity tensor. The net force per unit volume is given by the divergence of $\boldsymbol{\tau}^E$, so for a uniform electric field in a material with uniform permittivity, the force vanishes. However, non-uniform fields or spatially varying permittivities lead to non-zero forces. In particular, at the interface between two materials, a discontinuity in the permittivity or the presence of surface charge produces an interfacial electric stress given by $\boldsymbol{\tau}^E \cdot \mathbf{n}$. The net electric force $\mathbf{F}^E(\mathbf{r}, t)$ on the face of an element A of the interface is given by

$$\mathbf{F}^E = \iint_A (\boldsymbol{\tau}_1^E - \boldsymbol{\tau}_2^E) \cdot \mathbf{n} dA, \quad (1.19)$$

where $\boldsymbol{\tau}_1^E$ and $\boldsymbol{\tau}_2^E$ are the Maxwell stress tensors in the two materials. If the materials are fluids, the electric forces can drive both fluid flow and deformation of the interface.

1.2.2 Hydrodynamics

The flow of incompressible Newtonian fluids is governed by the incompressible Navier–Stokes equations, which are written

$$\nabla \cdot \mathbf{v} = 0, \quad (1.20a)$$

$$\varrho \frac{D\mathbf{v}}{Dt} = -\nabla p + \mu \nabla^2 \mathbf{v} + \mathbf{F}^B. \quad (1.20b)$$

Here, $\mathbf{v}(\mathbf{r}, t)$ is the fluid velocity and $p(\mathbf{r}, t)$ is the pressure, ϱ and μ are the density and the dynamic viscosity of the fluids, both of which we assume to be spatially uniform and constant, $D/Dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ is the material derivative, and $\mathbf{F}^B(\mathbf{r}, t)$ is some imposed body force, which may be due to gravity or an electromagnetic field, for example. Eq. (1.20a) represents conservation of mass, while (1.20b) is a balance of momentum. Together, they form a coupled, nonlinear set of PDEs for the fluid velocity and pressure that admits analytical solutions in only a very limited number of special cases. However, we can exploit certain features of the physical system under consideration to invoke simplifications of the equations, which can substantially increase the range of problems for which analytical solutions can be obtained. In particular, in this thesis we focus on problems for which we can exploit the disparity between viscous and inertial forces in the Navier–Stokes momentum equation (1.20b). This is quantified by the Reynolds number Re , which arises naturally when nondimensionalising the Navier–Stokes momentum equation and is defined as

$$\text{Re} = \frac{\varrho U \ell}{\mu}, \quad (1.21)$$

where U and ℓ are velocity and length scales characteristic of the problem under consideration. For small Reynolds numbers, i.e., $\text{Re} \ll 1$, inertia has little impact on the flow and it is acceptable to neglect the left hand side of (1.20b), including the nonlinear term. This yields the Stokes momentum equation, written

$$-\nabla p + \mu \nabla^2 \mathbf{v} + \mathbf{F}^B = \mathbf{0}. \quad (1.22)$$

The Stokes equations, composed of (1.22) and (1.20a), are especially relevant in systems with short characteristic lengths, such as microfluidic devices, the locomotion of microorganisms like bacteria, or the slow settling of particles in viscous fluids. In such systems, viscous effects play a greater role in determining the flow than do inertial ones. In electrohydrodynamic experiments of drops and the related practical applications, the drops are often small and the fluids are often oils with relatively large viscosities. For example, the experiments of Salipante and Vlahovska [2010] as well as those of Karp et al. [2024] examined castor oil drops suspended in corn oil, both with viscosities on the order of 1 Pa s and densities on the order of 10^3 kg/m^3 . The drop sizes were on the order of millimetres. Hence, assuming the characteristic fluid velocity is much smaller than 1 m/s, which is not restrictive for such small drop systems (Karp et al. [2024] use the electrohydrodynamic flow velocity U_{EHD} , as will be defined in §1.3.3, and state that $8 \times 10^{-5} \text{ m/s} \leq U_{\text{EHD}} \leq 4 \times 10^{-3} \text{ m/s}$ for their systems), the inertial terms in the Navier–Stokes equations can be discarded and the fluid flow is governed by the homogeneous Stokes equations (1.22) and (1.20a). The Stokes equations have several useful properties that do not extend to the full Navier–Stokes equations [Pozrikidis, 2011, Guazzelli and Morris, 2011]. Most importantly for our purposes, they are linear, so that any linear combination of solutions is itself a solution. This facilitates the use of powerful mathematical tools such as Green’s functions and fundamental solutions. Another property is instantaneity; there is no explicit time dependence in the Stokes equations, so the flow has no memory of its history and changes in forcing or boundary conditions are transmitted instantly to the whole domain. A consequence of the instantaneity of the equations is time-reversibility, meaning that the fluid motion is reversible if the forcing is reversed. This is demonstrated in the famous video clips featuring Taylor that show the insertion of coloured drops of dye into the annular gap between two concentric cylinders, which is filled with a clear fluid. After one cylinder is slowly rotated through several full revolutions, the coloured drops are sheared and seemingly mixed in with the surrounding fluid, but after the cylinder is turned back the other direction, the coloured drops are

recovered with only very slight blurring due to diffusion. Solutions to the Stokes equations with given driving forces and boundary conditions are also unique, and two solutions in the same domain but with different forcing or boundary conditions obey the Lorentz reciprocal theorem, which relates the forces and stresses of one solution to those of another solution and is widely used in low Reynolds number hydrodynamics. For example, it has been used to relate the swimming speed of microorganisms to the surface velocities produced by periodic coordinated motion of cilia or flagella [Stone and Samuel, 1996].

When solving problems involving two or more fluids with an interface between them, for example, problems featuring bubbles, drops, or stratified fluids, appropriate boundary conditions must be applied at the interface. Two types of condition are required; first, a kinematic condition which relates the velocity of the fluids at the interface to the motion of the interface itself, and a dynamic condition which enforces a balance of stresses at the interface. A mobile interface between two fluids can generally be expressed implicitly as $\xi(\mathbf{r}, t) = 0$. For example, the interface between two fluids stratified in the z direction might be expressed as

$$\xi = z - h(x, y, t) = 0, \quad (1.23)$$

where x, y, z are coordinates in a Cartesian coordinate system. An almost spherical interface might be expressed as

$$\xi = r - f(\theta, \phi, t) = 0, \quad (1.24)$$

where r, θ, ϕ are the radial distance and the polar and azimuthal angles in a spherical coordinate system, respectively. In either case, one can define a unit normal vector to the interface by

$$\mathbf{n} = \frac{\nabla \xi}{|\nabla \xi|}. \quad (1.25)$$

A fundamental characteristic of an interface between two fluids is that it moves and deforms with the fluid flow. This is captured by the kinematic boundary

condition, which is a consequence of the conservation of mass and is expressed as

$$\frac{D\xi}{Dt} = \frac{\partial\xi}{\partial t} + \mathbf{v} \cdot \nabla\xi = 0. \quad (1.26)$$

Eq. (1.26) ensures that any fluid particles located on the interface remain there for all time, and no fluid passes through the interface. This is equivalent to saying that the normal components of the fluid velocities either side of the interface are equal, and equal to the normal velocity of the interface itself, i.e.,

$$\mathbf{v}_1 \cdot \mathbf{n} = \mathbf{v}_2 \cdot \mathbf{n} = -\frac{1}{|\nabla\xi|} \frac{\partial\xi}{\partial t}, \quad (1.27)$$

where $\mathbf{v}_1(\mathbf{r}, t)$ and $\mathbf{v}_2(\mathbf{r}, t)$ are the fluid velocities in the two domains. Thus, at steady state, (1.27) enforces $\mathbf{v}_1 \cdot \mathbf{n} = \mathbf{v}_2 \cdot \mathbf{n} = 0$. The kinematic condition is often supplemented with the assumption that the tangential components of the velocities at the interface are also equal, known as the no-slip condition,

$$\mathbf{v}_1 \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}) = \mathbf{v}_2 \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}). \quad (1.28)$$

Unlike the kinematic condition, the no-slip condition is not based on any fundamental physical law, and in principle there may exist a discontinuity between the tangential components of the fluid velocities, known as slip. Nonetheless, the assumption of no-slip is widely accepted for clean interfaces between Newtonian fluids owing to compelling and repeated empirical evidence, and will be adopted in the problems discussed in this thesis.

In addition to the kinematic condition, a dynamic boundary condition is required at the interface, requiring that the sum of stresses acting on any portion of the interface is zero. The condition can be derived by considering the force balance on a small element A of the interface, as depicted in Figure 1.2. The element is generally affected by hydrodynamic forces exerted by the fluids on either side, as well as by surface tension, an attractive force between neighbouring surface elements arising due to molecular cohesion. The hydrodynamic force on

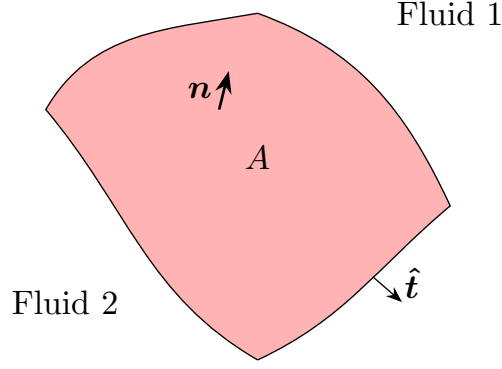


Figure 1.2: A surface element of the interface between two fluids

the face of the element is given by

$$\mathbf{F}^H = \iint_A (\boldsymbol{\tau}_1^H - \boldsymbol{\tau}_2^H) \cdot \mathbf{n} \, dA, \quad (1.29)$$

where

$$\boldsymbol{\tau}_i^H = -p_i \mathbf{l} + \mu_i (\nabla \mathbf{v}_i + (\nabla \mathbf{v}_i)^T) \quad (1.30)$$

Surface tension acts tangentially to the interface with magnitude given by the surface tension coefficient $\gamma(\mathbf{r}, t)$, which depends on various physical and chemical factors such as the temperature and the fluids involved and may vary in time or space. The net force due to surface tension is therefore written

$$\mathbf{F}^S = \int_{\partial A} \gamma \hat{\mathbf{t}} \, d\ell, \quad (1.31)$$

where ∂A is the boundary of the element and $\hat{\mathbf{t}}$ is a unit vector tangent to the interface and normal to the boundary ∂A . Eq. (1.31) can be transformed into a surface integral over A , leading to

$$\mathbf{F}^S = \iint_A \nabla_s \gamma - \gamma (\nabla_s \cdot \mathbf{n}) \mathbf{n} \, dA, \quad (1.32)$$

where $\nabla_s = (\mathbf{l} - \mathbf{n}\mathbf{n}) \cdot \nabla$ is the surface gradient operator, which projects the gradient of a variable onto the interface. Then, the balance of forces requires

$$\mathbf{F}^H + \mathbf{F}^S = \mathbf{0}, \text{ i.e.,}$$

$$\iint_A [(\boldsymbol{\tau}_1^H - \boldsymbol{\tau}_2^H) \cdot \mathbf{n} + \nabla_s \gamma - \gamma(\nabla_s \cdot \mathbf{n})\mathbf{n}] dA = \mathbf{0}, \quad (1.33)$$

and since (1.33) holds for any element of the interface, the integrand must itself vanish, leading to

$$(\boldsymbol{\tau}_1^H - \boldsymbol{\tau}_2^H) \cdot \mathbf{n} = \gamma(\nabla_s \cdot \mathbf{n})\mathbf{n} - \nabla_s \gamma, \quad (1.34)$$

which enforces a balance of stresses everywhere on the interface. In the first term on the right hand side, $(\nabla_s \cdot \mathbf{n})$ is the mean surface curvature of the element. Hence, if the interface is curved, it experiences a normal stress due to surface tension. The second term concerns gradients of surface tension and acts tangentially to the interface; this term is especially relevant if impurities like surfactants are present in the system, as will be explored in Chapter 3.

1.3 Electrohydrodynamics of drops

This thesis is concerned with the behaviour of viscous drops exposed to a direct current (DC) electric field. The types of behaviour observed in such systems depend strongly on the properties of the fluids. Early work on drop electrohydrodynamics generally focused on fluids assumed to be either perfect conductors or perfect insulators.

Probably the first theoretical investigation into the electrohydrodynamics of drops was that of Rayleigh [1882], who determined theoretically the maximum amount of charge a conducting spherical drop could sustain before becoming unstable. Above this amount, the drop would begin expelling fluid in fine jets, a phenomenon known as tip streaming. Zeleny [1917] conducted experiments to investigate tip streaming from drops hanging from the bottom of a capillary tube. A similar problem concerning the breakup of uncharged soap bubbles was studied by Wilson and Taylor [1925]. O’Konski and Thacher [1953] were the first to provide a theoretical prediction of the equilibrium shape of a slightly

deformed insulating drop suspended in a second insulating fluid. They calculated the electric and surface free energies, and minimised their sum to calculate the steady drop shape. Their calculations predicted that the drop would always assume a prolate shape, regardless of which fluid has the greater permittivity. Their theory is also applicable to a conducting drop in an insulating carrier fluid, in which case the drop permittivity is treated as infinite since charge redistribution inside the drop negates the applied electric field there. The theory was tested shortly afterwards against experimental results [O’Konski and Gunther, 1955], and described the observed deformation fairly well. In another work [O’Konski and Harris, 1957], a theoretical treatment was provided for drop–fluid systems in which the conductivity in both phases is sufficiently large to cause appreciable changes to the electrostatic free energy. This theory was the first to predict oblate drop deformation in some circumstances. A few years later, Allan and Mason [1962] conducted a theoretical analysis of the problem of a drop in an insulating fluid using a different approach. They computed the electric stresses to the drop surface due to the known potential distribution, and then enforced a balance between electric and capillary stresses at the drop surface to derive the drop shape. They arrived at results identical to those given in O’Konski and Thacher [1953]. Meanwhile, the theory and experiments of Garton and Krasucki [1964] also supported the conclusion that drop deformation was invariably prolate. It should be noted that in all of these models, the electric stress is normal to the drop surface and is balanced by surface tension, and both fluids remain at rest in the steady state.

1.3.1 Weakly conducting fluids

The theory of Allan and Mason [1962] was accompanied by a series of experiments, which again provided good agreement with the theory in most cases, but revealed anomalous drop behaviour in others. Most significantly, the authors reported that drops having a lower permittivity than the surrounding fluid could in fact deform into oblate spheroids, behaviour for which neither their theory nor that of [O’Konski and Thacher, 1953] could account. Although the theory

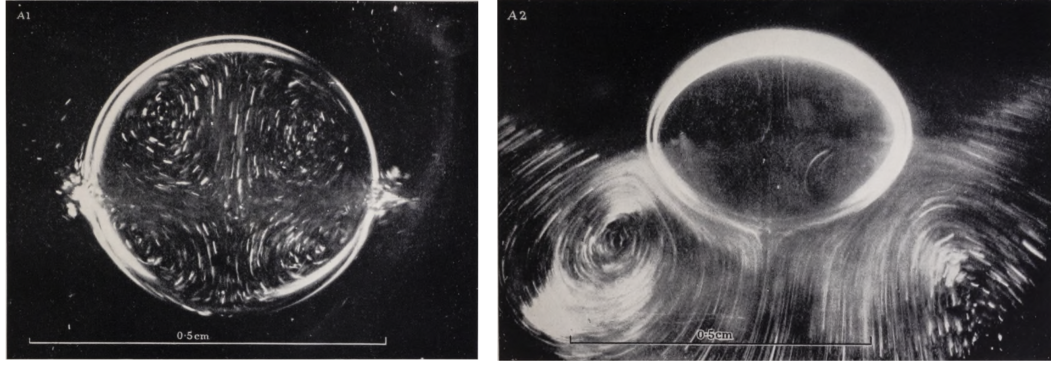


Figure 1.3: Circulatory fluid flow inside and outside a leaky dielectric drop. Reproduced from Taylor [1966].

for conducting media proposed by O’Konski and Harris [1957] anticipated oblate deformation under certain conditions on the material properties, those conditions were not satisfied by the materials used in the experiments.

It was pointed out by Taylor [1966] that modelling weak conductors as perfect insulators was inadmissible, because finite conductivities (even if very small) in the drop and surrounding fluid would substantially alter the response of the system to an applied field. Specifically, in the case of weakly conducting (leaky dielectric) fluids, free charges in both the drop and fluid migrate towards the drop interface upon application of the field, developing a surface charge distribution there as a result of the differing conductivities of the fluids. The interfacial charge interacts with the electric field to produce an electric stress tangential to the drop interface, which cannot be balanced by constant surface tension or a pressure jump across the drop interface. Taylor [1966] concluded that the only way the tangential electric stress could be supported was by shearing the fluid into motion both inside and outside the drop, thereby generating a counterbalancing tangential viscous stress. Taylor [1966] formulated a new small-deformation theory, linear in the electric capillary number Ca_E , defined as

$$Ca_E = \frac{\epsilon^+ E_0^2 a}{\gamma}, \quad (1.35)$$

which represents the ratio between electric and surface tension stresses; hence,

small values of Ca_E correspond to an almost spherical drop. Here, E_0 is the magnitude of the applied electric field, a is the radius of the undeformed spherical drop, and γ is the surface tension coefficient. The theory of Taylor [1966] showed that, at steady state, the drop would deform into an axisymmetric spheroid, which is either prolate or oblate depending on the sign of

$$\mathcal{F}_d = (S - 1)^2 + S(1 - SQ) \frac{16 + 19\lambda}{5(1 + \lambda)}, \quad (1.36)$$

where $\mathcal{F}_d$ is known as Taylor's discriminating function, and $\mathcal{F}_d > 0$, $\mathcal{F}_d = 0$, and $\mathcal{F}_d < 0$ correspond to a prolate, spherical, and oblate drop, respectively. Here, $S = \sigma^+/\sigma^-$, $Q = \epsilon^-/\epsilon^+$, and $\lambda = \mu^-/\mu^+$ represent the ratios of electrical conductivity, permittivity, and dynamic viscosity, respectively, and $\sigma^\pm$ denotes the conductivity, with the minus subscript here and henceforth referring to the properties of the drop and the plus subscript to those of the surrounding fluid. The conductivity of each phase is taken to be spatially uniform and constant in the problems considered in this thesis. Notice that the viscosity and permittivity ratios are defined as the property of the drop divided by that of the fluid, while the conductivity ratio is defined the other way round, following Das and Saintillan [2021]. The viscosity ratio λ plays a far smaller role than do S and Q in determining the nature of the deformation: specifically, the factor $(16 + 19\lambda)/5(1 + \lambda)$ in (1.36) varies only between 3.2 (for $\lambda = 0$) to 3.8 (for $\lambda = \infty$). The theory predicts that the deformed drop radius varies as $P_2(\cos \theta)$ along the polar angle, where P_2 is the second degree Legendre polynomial, i.e., the shape is symmetric around the equatorial plane.

The theory correctly predicts the oblate drop shapes seen in the experiments of Allan and Mason, and experiments by McEwan and de Jong [Taylor, 1966] verified the existence of the electrohydrodynamic flow fields (Figure 1.3). The

induced flow field around the drop is given by

$$\mathbf{v}^+ = \frac{9}{10} \frac{\epsilon^+ E_0^2 a}{\mu^+} \frac{S(SQ - 1)}{(1 + 2S)^2(1 + \lambda)} \left[\frac{a^2}{r^2} \hat{\mathbf{r}} - \frac{a^3}{r^4} \hat{\mathbf{r}} \right. \\ \left. - \frac{3a^2 \hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}}}{r^2} - \frac{a^4 \hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 \cdot \hat{\mathbf{r}}}{r^4} \cdot (2\mathbf{I} - 5\hat{\mathbf{r}} \hat{\mathbf{r}}) \right], \quad (1.37)$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$ is a unit vector in the radial direction, $\hat{\mathbf{E}}_0 = \mathbf{E}_0/E_0$ denotes the direction of the applied field and $:$ denotes the scalar product of two tensors, e.g. $\mathbf{A} : \mathbf{B} = A_{ij}B_{ji}$. The flow field defined by (1.37) consists of vortices which circulate fluid either from the poles to the equator or from the equator to the poles, if the product SQ is greater or less than unity, respectively. The product SQ can be interpreted as the ratio of the charge relaxation time of the drop, $\tau_c^- = \epsilon^-/\sigma^-$, to that of the surrounding fluid $\tau_c^+ = \epsilon^+/\sigma^+$. If $SQ > 1$, the surrounding fluid responds more quickly to the application of the electric field, in which case the polarisation of the drop is antiparallel to the field and fluid flows from the poles to the equator. Conversely, if $SQ < 1$, the polarisation of the drop is parallel to the field and fluid flows from the equator to the poles. This distinction, along with that expressed by the discriminating function (1.36), has led to the common classification of leaky dielectric drop–fluid systems as one of prolate A (with flow from equator to poles), prolate B (with flow from poles to equator) or oblate (in which case the flow is always from the poles to the equator) [Lac and Homsy, 2007]. These three drop classes are illustrated in Figure 1.4.

At this point, it is worth pre-empting some potential points of confusion. Throughout this thesis, frequent reference will be made to the dipole moment of the drop, denoted $\mathbf{P}$. First, this $\mathbf{P}$ should not be confused with the polarisation vector $\mathbf{p}$ appearing in the constitutive relation (1.2). Instead, it is the induced dipole moment associated with the disturbance to the electric potential and electric field due to the presence of the polarised drop. It is important to emphasise that $\mathbf{P}$ is not the dipole moment obtained by integration of the total surface charge distribution q . The surface charge is obtained via Gauss' law and depends on the total electric fields on either side of the interface. As a result, it contains

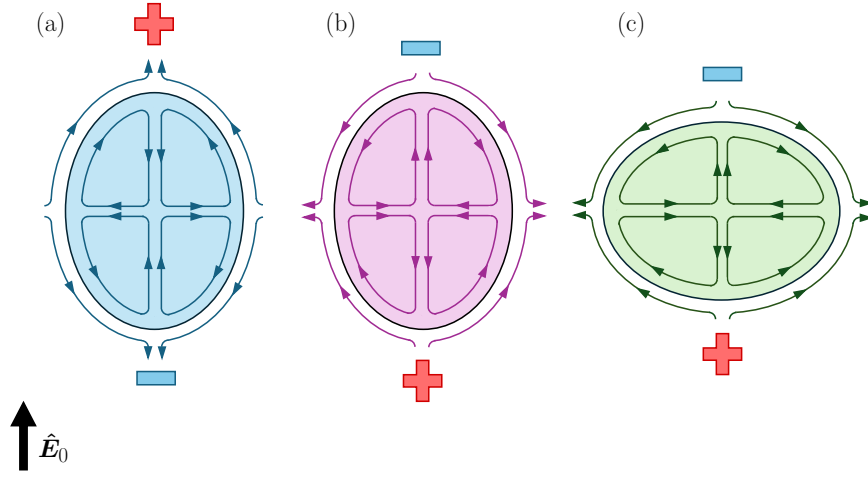


Figure 1.4: Leaky dielectric drops corresponding to (a) prolate A, (b) prolate B, and (c) oblate.

contributions from the applied field $\mathbf{E}_0$ as well as $\mathbf{P}$, and also depends explicitly on the permittivity ratio Q . Therefore, it is possible that the charge distribution is parallel to the applied field while $\mathbf{P}$ is antiparallel (or vice versa) and even if $\mathbf{P} = \mathbf{0}$, q need not be zero.

The oblate or prolate nature of the deformation results from contributions from the normal electric and hydrodynamic stresses in a manner which has been historically misconceived but recently clarified by Esmaeeli and Behjatian [2020]. Specifically, it has been stated by several authors [Ha and Yang, 1995, Feng and Scott, 1996, Lac and Homay, 2007] that electric stresses always promote prolate deformation, and that oblate deformation can thus only result from a hydrodynamic stress acting against, and outweighing, the electric stress. In fact, depending on the material ratios, both electric and hydrodynamic stresses can act cooperatively to produce oblate deformation, as can be shown by splitting the discriminating function (1.36) into the contributions from the two phenomena and examining them separately. These are

$$\mathcal{F}_E = 1 + S^2 - 2S^2Q, \quad (1.38)$$

$$\mathcal{F}_H = S(1 - SQ) \frac{3(2 + 3\lambda)}{5(1 + \lambda)}, \quad (1.39)$$

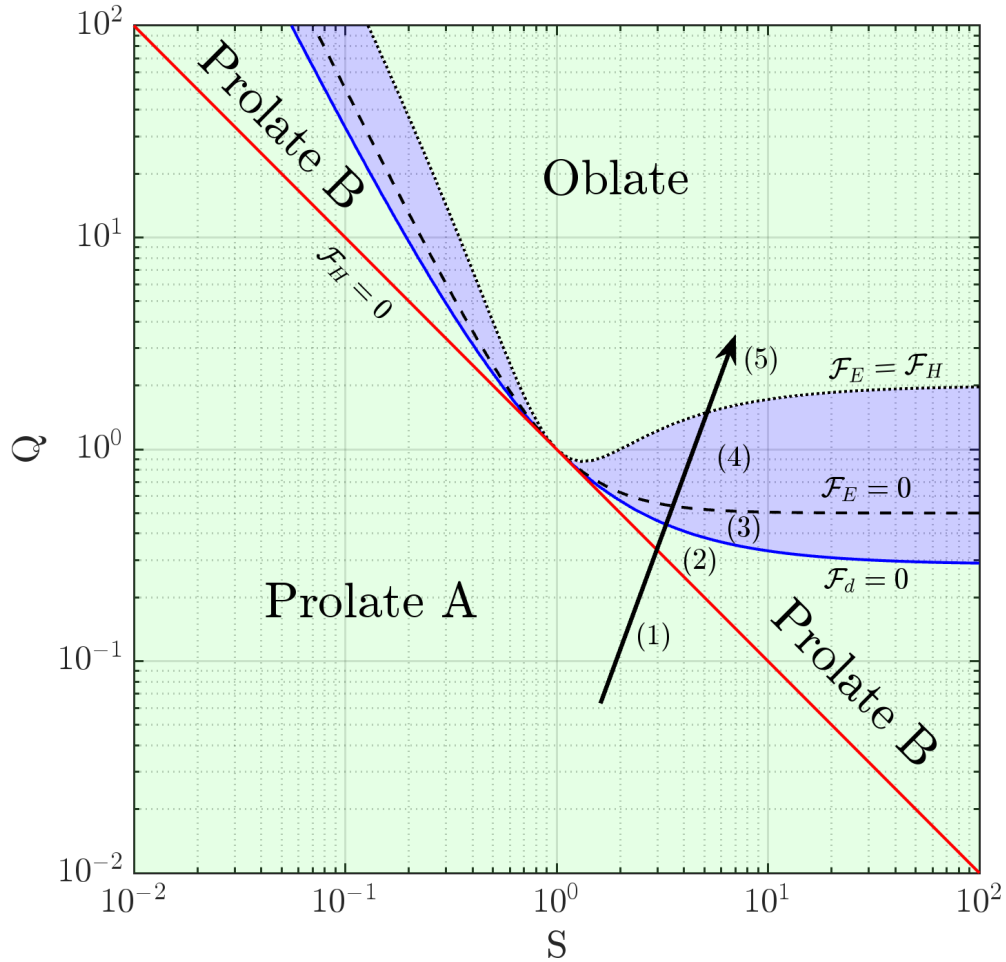


Figure 1.5: SQ diagram based on Esmaeeli and Behjatian [2020] showing the lines $\mathcal{F}_d = 0$ (blue solid line), $\mathcal{F}_E = 0$ (black dashed line), $\mathcal{F}_H = 0$ (red solid line) and $\mathcal{F}_E = \mathcal{F}_H$ (black dotted line). The lines $\mathcal{F}_d = 0$ and $\mathcal{F}_E = \mathcal{F}_H$ are evaluated for $\lambda = 1$. Pr B stands for Prolate B, and the green and blue shaded regions are those where the electric and hydrodynamic stress is the stronger of the two, respectively. $\mathcal{F}_d$, $\mathcal{F}_E$, and $\mathcal{F}_H$ are defined in (1.36), (1.38) and (1.39), respectively, and the regions labelled (1)–(5) denote regions in which the electric and hydrodynamic stresses play qualitatively different roles in determining the drop deformation.

where $\mathcal{F}_E$ is the contribution from the normal electrostatic stress and $\mathcal{F}_H$ is the contribution from the normal hydrodynamic stress, and $\mathcal{F}_E + \mathcal{F}_H = \mathcal{F}_d$. Figure 1.5 shows the lines $\mathcal{F}_d = 0$ (blue solid line), $\mathcal{F}_E = 0$ (black dashed line), $\mathcal{F}_H = 0$ (red solid line) and $\mathcal{F}_E = \mathcal{F}_H$ (black dotted line). The lines $\mathcal{F}_d = 0$ and $\mathcal{F}_E = \mathcal{F}_H$ are evaluated for $\lambda = 1$. The areas shaded green are those in which the electric stress dominates (i.e., $|\mathcal{F}_E| > |\mathcal{F}_H|$), while the areas shaded blue are those in which hydrodynamic stress dominates (i.e., $|\mathcal{F}_H| > |\mathcal{F}_E|$). More specifically, five distinct regions, labelled (1)–(5) in the figure, can be identified where the electric and hydrodynamic stresses play qualitatively different roles in determining the drop deformation. Moving along the direction of the arrow, these are

- (1) Prolate A deformation. The electric and hydrodynamic stresses work cooperatively. The electric stress is the stronger of the two in this region.
- (2) Prolate B deformation. The electric stress promotes prolate deformation, while the hydrodynamic stress promotes oblate deformation. The electric stress is the stronger of the two in this region.
- (3) Oblate deformation. The electric stress promotes prolate deformation, while the hydrodynamic stress promotes oblate deformation. The hydrodynamic stress is the stronger of the two in this region.
- (4) Oblate deformation. The electric and hydrodynamic stresses work cooperatively. The hydrodynamic stress is the stronger of the two in this region.
- (5) Oblate deformation. The electric and hydrodynamic stresses work cooperatively. The electric stress is the stronger of the two in this region.

In particular, Figure 1.5 shows that prolate deformation is always dominated by the electric stress, and the hydrodynamic stress may either oppose (in the case of prolate B drops) or promote it (in the case of prolate A drops). On the other hand, oblate deformation may be dominated by either the electric or the hydrodynamic stress, and the electric stress may either oppose or contribute to it.

1.3.2 Leaky dielectric model

The introduction of the surface charge distribution by Taylor [1966] led to a paradigm shift in the study of multiphase electrohydrodynamics. In particular, it spawned the much celebrated Taylor–Melcher leaky dielectric model [Melcher and Taylor, 1969, Saville, 1997], which invokes various approximations and simplifications to the general theory described in §1.2 in order to greatly facilitate theoretical modelling of leaky dielectric fluids. Perhaps the most fundamental assumption is that free charge resides only at the interface between the fluids, while the bulk fluids themselves are electrically neutral; i.e., $\rho = 0$ away from the interface. A highly convenient result of this assumption is that the electrostatic and hydrodynamic problems become decoupled in the bulk fluids, so that the electrical body force vanishes from the Stokes momentum equation (1.22). Moreover, Poisson’s equation (1.10) for the electric potential simplifies to Laplace’s equation,

$$\nabla^2 \varphi = 0. \quad (1.40)$$

Thus, the potential can immediately be easily expressed as a linear sum of harmonic functions.

To justify the assumption of electroneutral bulk fluids, we must briefly discuss the dynamics of the ionic species present in the fluids. For simplicity, consider a monovalent binary electrolyte. In this case, the volumetric charge density is given by

$$\rho = F(c_+ - c_-), \quad (1.41)$$

[Levich, 1962, Chen et al., 2005, Chen, 2011] where F is Faraday’s constant and c_+ and c_- are the concentrations of cations and anions (in mol m^{-3}), respectively. Clearly, a negligible bulk charge requires that the local concentrations of the two species are approximately equal. If the timescale for charge relaxation in the electrolyte is much faster than those for other relevant processes like drop deformation or fluid flow, then any accumulated bulk charge can be considered to dissipate quasi-instantaneously [Melcher and Taylor, 1969, Chen et al., 2005, Chen, 2011], and then $c_+ \approx c_-$ is reasonable. However, charge relaxation is often

not fast in leaky dielectrics with small conductivities. Alternatively, if relaxation is not fast, electroneutrality can still be justified if the length scale over which any bulk charge is screened, known as the Debye length, is much shorter than the characteristic length scale of the problem under consideration. Screening refers to the process by which the electric field produced by a charged body is damped when the body is placed among mobile charge carriers. Particles with opposite charge migrate towards the body, shielding the rest of the electrolyte from the electrostatic effects of the body. Therefore, the fluid can be considered electroneutral on length scales significantly larger than the Debye length, which generally holds for drop sizes on the order of millimetres [Saville, 1997, Schnitzer and Yariv, 2015, Mori and Young, 2018].

A second powerful assumption of the leaky dielectric model is that the current density in the fluids may be assumed to follow Ohm's law; that is,

$$\mathbf{J} = \sigma \mathbf{E}. \quad (1.42)$$

The justification for this requires analysis of the ionic transport in leaky dielectric fluids. As mentioned in §1.2.1, this is modelled in general by the Nernst–Planck equation, accounting for diffusion, convection, migration and dissociation and recombination reactions of the various ionic species present in the fluid. In particular, for the binary electrolyte, the fluxes of the cationic and anionic species are given by

$$\mathbf{N}_+ = c_+ \mathbf{v} - D_+ \nabla c_+ + m_+ F c_+ \mathbf{E} \quad (1.43)$$

and

$$\mathbf{N}_- = c_- \mathbf{v} - D_- \nabla c_- - m_- F c_- \mathbf{E}, \quad (1.44)$$

respectively, [Levich, 1962] where $D_{\pm}$ denotes the ionic diffusivity of either species, which are assumed to be uniform. The terms on the right hand side of (1.43) and (1.44) represent the fluxes associated with convection, diffusion and electromigration, respectively. Note that recombination and dissociation reactions do not constitute part of the ionic flux but appear as a source term in the transport

equation for $c_{\pm}$. The current density is given by a charge-weighted sum of (1.43) and (1.44), i.e.,

$$\mathbf{J} = F(\mathbf{N}_+ - \mathbf{N}_-) = \rho \mathbf{v} - F(D_+ \nabla c_+ - D_- \nabla c_-) + F^2(m_+ c_+ + m_- c_-) \mathbf{E}, \quad (1.45)$$

where we have used (1.41). Since the bulk is assumed electroneutral, $\rho = 0$ and the convective contribution vanishes. The diffusivities are related to the mobilities according to the Einstein-Smoluchowski relation for a monovalent species,

$$D_{\pm} = RTm_{\pm}, \quad (1.46)$$

Levich [1962] where R is the gas constant and T is the absolute temperature. Then, if E is a typical strength of the applied electric field, the ratio of the diffusive to electromigration currents in (1.45) scales as

$$V_r = \frac{RT}{\ell FE}, \quad (1.47)$$

which can be interpreted as the ratio of the thermal voltage driving the diffusive current to the applied voltage. The former, given by RT/F , is only around 25 mV at room temperature, which is greatly exceeded by the applied voltage in most electrohydrodynamic drop systems [Chen, 2011]. Therefore, the diffusive current can be neglected, and the coefficient of $\mathbf{E}$ is identified as the bulk conductivity,

$$\sigma = F^2(c_+ m_+ + c_- m_-), \quad (1.48)$$

yielding (1.42). The full ionic transport equations can be combined to yield the charge conservation equation (1.11). Including the reaction terms,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = F(r_+ - r_-). \quad (1.49)$$

Since dissociation and recombination reactions transform a neutral species into a cation–anion pair, or vice versa, they produce or deplete cations and anions in equal numbers regardless of the specific reaction kinetics, so that $r_+ = r_-$

identically. Furthermore, since the bulk fluids are assumed electroneutral, $\rho = 0$, and using (1.42) gives

$$\nabla \cdot (\sigma \mathbf{E}) = 0. \quad (1.50)$$

The leaky dielectric model further assumes that the conductivities of the fluids are constant and spatially uniform, in which case

$$\nabla \cdot \mathbf{E} = 0, \quad (1.51)$$

which is the governing equation for the electric field in the bulk.

The coupling between the hydrodynamic and electrostatic problems has thus been eliminated in the bulk, where we assume no charge resides. However, at the interface between the two fluids, there exists a surface charge distribution. In the leaky dielectric model, the coupling occurs only through boundary conditions at the interface, where we require a balance of electric, hydrodynamic and capillary stresses, as well as an equation describing the transport of surface charge (which generally cannot be simplified as readily as the transport equation for charge in the bulk). First, the electrohydrodynamic force balance requires that

$$\mathbf{F}^E + \mathbf{F}^H + \mathbf{F}^S = \mathbf{0}, \quad (1.52)$$

with $\mathbf{F}^E$, $\mathbf{F}^H$ and $\mathbf{F}^S$ given by (1.19), (1.29) and (1.32), respectively. Substituting those expressions into (1.52) yields the force balance

$$\iint_A [(\boldsymbol{\tau}^{E,+} - \boldsymbol{\tau}^{E,-}) \cdot \mathbf{n} + (\boldsymbol{\tau}^{H,+} - \boldsymbol{\tau}^{H,-}) \cdot \mathbf{n} + \nabla_s \gamma - \gamma(\nabla_s \cdot \mathbf{n})\mathbf{n}] dA = \mathbf{0} \quad (1.53)$$

on the surface element A . Here, the plus superscripts indicate the stress tensors of the surrounding fluid, the minus superscripts indicate the stress tensors of the drop, and the normal vector $\mathbf{n}$ is defined to point into the surrounding fluid. As for the hydrodynamic force balance (1.33), the integrand itself must be zero in (1.53) due to the arbitrariness of the element, yielding the electrohydrodynamic

stress balance:

$$(\boldsymbol{\tau}^{E,+} - \boldsymbol{\tau}^{E,-}) \cdot \mathbf{n} + (\boldsymbol{\tau}^{H,+} - \boldsymbol{\tau}^{H,-}) \cdot \mathbf{n} = \gamma(\nabla_s \cdot \mathbf{n})\mathbf{n} - \nabla_s \gamma. \quad (1.54)$$

The simplicity of the interfacial charge distribution assumed by the leaky dielectric model has come under considerable scrutiny. Most notably, it is considered to be confined to a mathematical surface having zero thickness; in particular, the model does not account for the possibility of an electric double layer. This refers to a thin structure in which the interfacial charge is distributed over a finite thickness and accompanied by a diffuse cloud of ions of opposite charge, which screens the interfacial charge. This point has received attention from a few authors who have attempted to recover the interfacial charge of the leaky dielectric model starting from primitive electrokinetic equations [Baygents and Saville, 1990, Zholkovskij et al., 2002, Schnitzer and Yariv, 2015, Mori and Young, 2018]. These studies will be discussed in more detail in §1.3.3. For now, we will introduce the classic transport equation for the surface charge of the leaky dielectric model, which is ubiquitous in macroscale electrohydrodynamics and will be the one used in this thesis. It includes Ohmic current from the bulk fluids and convection by the fluid velocity at the interface, but neglects diffusion. This warrants examination because it is not obvious that the neglect of diffusion in the bulk can be extended to the double layer, the characteristic thickness of which is much shorter than the drop radius. However, the simplified transport equation without diffusion is usually adequate to accurately model electrohydrodynamic systems [Saville, 1997, Chen, 2011]. Although the bulk fluids are assumed to be electroneutral in the leaky dielectric model, since the interface carries charge it is useful first to consider the charge conservation equation that retains both convection and the Ohmic current,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\sigma \mathbf{E} + \rho \mathbf{v}) = 0. \quad (1.55)$$

We integrate (1.55) over a Gaussian pillbox with height h_{PB} straddling the interface, like that depicted in Figure 1.1(b). If the area of the planar surfaces of the pillbox, A_{PN} , is again assumed small enough that $\mathbf{v}$ and $\mathbf{E}$ are approximately

constant on those surfaces, then in the limit $h_{PB} \rightarrow 0$ we obtain the transport equation for the surface charge,

$$\frac{\partial q}{\partial t} + (\sigma^+ \mathbf{E}^+ - \sigma^- \mathbf{E}^-) \cdot \mathbf{n} + \nabla_s \cdot (q\mathbf{v}) = 0. \quad (1.56)$$

As in the derivation of the boundary condition (1.17), the volumetric charge ρ reduces to the surface charge q in the limit $h_{PB} \rightarrow 0$. Note that Ohmic currents through the curved face of the pillbox are absent; the tangential currents in the two fluid domains vanish in the limit, while current on the interface itself (known as surface conduction) is neglected. Surface conduction is tacitly omitted in most models developed in accordance with the leaky dielectric model, likely because of the difficulty of assigning a surface conductivity to the idealised sheet of charge posited by the model. In contrast, there exist established constitutive frameworks to determine the conductivity in a finite-thickness electric double layer [Lyklema, 2005]. Also neglected from (1.56) are effects associated with surface electrochemistry like ion adsorption, desorption, and other reactions, which could provide additional sources or sinks of interfacial charge but are rarely accounted for in problems of the sort considered in this thesis.

1.3.3 Recent work on drop electrohydrodynamics

Although Taylor's theory was successful in predicting the nature of the drop deformation and the circulatory flow fields, it failed to accurately quantify the degree of deformation observed in experiments by Torza et al. [1971]. In particular, the observed deformation was significantly larger than that predicted by the theory in all cases. The agreement was especially poor for prolate drops, the observed deformations of which were generally two to four times larger than predicted. The observed deformations of oblate drops were one to two times larger than predicted. Furthermore, in no case was the deformation smaller than that predicted by the theory. Torza et al. [1971] considered and promptly discounted the possibility that the neglect of surface charge conduction or convection were responsible for the discrepancy, since the observed deformation varied linearly with increases

in Ca_E , while those effects would lead to a nonlinear relationship. In another attempt to resolve the discrepancy between the theoretical predictions of Taylor [1966] and the experimental findings of Torza et al. [1971], Ajayi [1978] extended the linear theory of Taylor to second order in the electric capillary number. While the experimental agreement was slightly improved in some systems, the higher order terms were generally insufficient to explain the significant disparities.

Torza et al. [1971] suggested that the discrepancy might be partly explained by the assumption of electrically neutral bulk fluids or the absence of an electrical double layer. To determine whether these effects could explain the poor experimental agreement, Baygents and Saville [1990] revisited the problem while forgoing the leaky dielectric model in favour of a more general electrokinetic model that includes the diffusion and convection of each ionic species. They decomposed the fluid domain into an inner region near the interface (in which diffuse charge accumulates and electrokinetic effects are considered) and an outer region away from the interface (in which the fluids are treated as classic leaky dielectrics with constant conductivities) and attempted an asymptotic matching procedure to obtain a uniformly valid solution. After directly matching the solutions for the inner and outer domains proved unachievable, the authors introduced an intermediate layer in which convection, diffusion, and electromigration are all relevant to charge transport, and succeeded in matching the intermediate solution with both the inner and outer solutions. Remarkably, this procedure yielded identical expressions for the drop deformation and fluid velocity to those found by Taylor [1966], suggesting that the interfacial charge assumed by the leaky dielectric model is a valid lumped-parameter evaluation of the ‘true’ interfacial charge including any screening effects of diffuse charge layers. Later, Zholkovskij et al. [2002] built on the work of Baygents and Saville [1990] and found that the result of Taylor [1966] arises when the drop radius is much larger than the Debye length of both fluids, while a small drop radius relative to the Debye lengths leads to the result of O’Konski and Thacher [1953], Allan and Mason [1962] for perfect dielectric fluids. Starting from the same set of basic electrokinetic equations as used by Baygents and Saville [1990], Schnitzer and Yariv [2015] derived

a macroscale model valid in the limits of strong applied fields and short Debye lengths, which very closely resembled the leaky dielectric model with only a few differences. Namely, the model suggested that charge convection is asymptotically small in the mentioned regime, that the conductivity of the drop depends on charge adsorption at the interface (and thus should not be treated as a bulk material parameter), and that net charge associated with the diffuse charge layers can give rise to electrophoretic translation of the drop (although this translation is much slower than the induced circulatory flow predicted by the leaky dielectric model). Yet another attempt at deriving the leaky dielectric model from electrokinetic theory was made by Mori and Young [2018], who concluded that charge convection may be non-negligible depending on the Péclet number for ion transport. Furthermore, their more general treatment of the electrokinetic interfacial boundary conditions allows for different ionic concentrations on either side of the interface. If the cation-to-anion concentration ratio is the same in both phases, the electric potential is continuous across the interface and the leaky dielectric model is recovered. If not, an equilibrium voltage jump known as the Galvani potential is present across the interface, which gives rise to translational drop motion [Girault and Schiffrin, 1989].

Considering that the works of Ajayi [1978] and Baygents and Saville [1990] had not meaningfully explained the discrepancy between theory [Taylor, 1966] and experiments [Torza et al., 1971], Vizika and Saville [1992] questioned whether shortcomings in the experimental method had a role to play, and conducted a new set of experiments. They focused in particular on accurate measurements of all relevant physical properties, and their results were in much better agreement with the theory of Taylor [1966] than were those of the previous experiments [Torza et al., 1971]. Nonetheless, discrepancies remained in some cases, and the authors suggested nonuniformities in the electric field, electric field-induced surface tension variations, and charge convection or surface conduction as possible explanations. More recent experiments have been conducted by Ha and Yang [2000a,b], Krause and Chandratreya [1998], Sato et al. [2006], and Karp et al. [2024].

Surface conduction has received very scant attention, likely due in no small

part to the aforementioned difficulty of establishing a surface conductivity for an interface of zero thickness. Only quite recently was surface conduction included in a theory by Tyatyushkin [2017], who introduced the surface conductivity as a given material property with no constitutive relation or other discussion of its physical origin. Charge convection has attracted more attention, but it is difficult to include in theoretical studies because it introduces a nonlinear coupling between the interfacial charge and the flow fields, often eliminating the possibility of finding closed-form solutions for either. Theoretical studies have mostly been limited to asymptotic solutions valid for low values of the electric Reynolds number Re_E , defined as

$$\text{Re}_E = \frac{\epsilon^+ U}{\sigma^+ a}, \quad (1.57)$$

which can be interpreted as the ratio between the charge relaxation time, $\tau_c = \epsilon^+/\sigma^+$, and the convective flow time, $\tau_U = a/U$, where U is a characteristic velocity. Typically, the electrohydrodynamic flow velocity

$$U_{\text{EHD}} = \frac{\epsilon^+ E_0^2 a}{\mu^+} \quad (1.58)$$

is used, in which case $\tau_U = \tau_{\text{EHD}}$, where

$$\tau_{\text{EHD}} = \frac{\mu^+}{\epsilon^+ E_0^2} \quad (1.59)$$

is known as the electrohydrodynamic flow time. The first attempt to retain charge convection in a theoretical study was made by Spertell and Saville [1976], who studied the effect of convection on the settling velocity of a sedimenting drop exposed to an electric field. They found that when the electric field is in the opposite direction to gravity, the symmetry of the drop shape is lost due to charge convection, by which the interfacial charge is swept to the rear of the drop. Depending on the properties of the fluids, the effect of convection can either increase or decrease the settling velocity of the drop. The first theoretical study to consider the effect of convection on the deformation of neutrally buoyant drops was that of Feng [1999], closely followed by those of Shutov [2002]

and Shkadov and Shutov [2002]. All three studies predicted that the inclusion of charge convection leads to increased deformation for prolate drops, but decreased deformation for oblate drops. As discussed in §1.3.1, prolate deformation is primarily due to the normal electric stresses on the surface, while viscous stresses associated with the electrohydrodynamic flow are less significant. The convection of charge from the equator to the poles tends to strengthen the dipole moment of the interfacial charge distribution, leading to greater deformation. Oblate deformation, on the other hand, may be dominated by either viscous or electric stresses. Charge convection in this case weakens both the dipole moment and the pole-to-equator electrohydrodynamic flow, leading to smaller deformation. In addition, both the theory and experiments of Shkadov and Shutov [2002] showed that if the convective charge transport is sufficiently strong, oblate drop deformations can slow down and even reverse, such that drops that initially deform into an oblate shape can adopt a prolate shape at later times. Given the nonlinearities associated with convection, many of the existing works that retain the effect are based on computational techniques including finite element [Feng, 1999, Supeene et al., 2008], volume-of-fluid [López-Herrera et al., 2011, Dong and Sau, 2023], boundary element [Lanauze et al., 2015, Das and Saintillan, 2017a], level-set [Naz, 2025], front-tracking/finite-volume [Fernández, 2013, Esmaeeli and Behjatian, 2020], and hybrid methods [Basu et al., 2024]. However, difficulties also arise when using these approaches; several authors have noted the formation of steep charge gradients (shocks) at the drop equator due to convection which often lead to failure of the numerical method [Lanauze et al., 2015, Das and Saintillan, 2017a, Firouznia et al., 2023, Peng et al., 2024, Peng and Schnitzer, 2025].

Several other attempts have been made to extend the theory of Taylor [1966] to include various additional effects. For example, the transient dynamics of a drop in a weak field have been considered in a number of studies. The first of these was that of Sozou [1973], who derived a semi-analytical model that retains the local fluid acceleration term in the Stokes equations in order to study the evolution of the induced electrohydrodynamic flow. Esmaeeli and Sharifi [2011] retained the

derivatives of the drop shape in the kinematic condition to study the transient drop deformation and found that the shape relaxed monotonically to the steady shape predicted by Taylor [1966]. However, numerical simulations based on finite-element [Supeene et al., 2008] or finite-volume [Fernández et al., 2005] methods exhibited non-monotonic deformation dynamics, including overshoots in the deformation in many cases, as well as transitions from an initially prolate shape to an oblate one at later times. This discrepancy was explained by Lanauze et al. [2013], who developed a small deformation theory retaining linear fluid inertia and transient charge relaxation, and revealed that the non-monotonic behaviour could be captured when one of these effects is retained alongside the transient shape derivatives. Other studies concerning the transient drop dynamics include those by Das and Saintillan [2017a], Esmaeeli and Behjatian [2020], Esmaeeli [2022].

Another well explored aspect of leaky dielectric drop electrohydrodynamics is the coupling between the electric field and gravity-induced drop sedimentation. The first attempt to study this problem theoretically was that of Spertell and Saville [1976]. Xu and Homsy [2006] then built on the analysis of Spertell and Saville [1976] by considering also the effect of the deformation on the settling velocity. They found that prolate deformation increases the settling velocity, while oblate deformation decreases it due to the increased drag associated with the greater cross sectional area in the flow direction. Bandopadhyay et al. [2016] later generalised the work of Spertell and Saville [1976] and Xu and Homsy [2006] to analyse arbitrary alignments between gravity and the electric field and predicted lateral migration of the drop, which they also observed experimentally. Yariv and Almog [2016] considered the case where the electrohydrodynamic flow is weak compared to the settling velocity, in which case solutions could be obtained for arbitrary values of the electric Reynolds number. More recently, Boruah [2025] considered the effects of deformation and convection on the settling of a compound drop.

There is also a substantial body of work examining the drop deformation or breakup at large values of Ca_E . Most of this research uses experimental or compu-

tational techniques [Sherwood, 1988, Basaran et al., 1995, Feng and Scott, 1996, Feng, 1999, Lac and Homsy, 2007, Deshmukh and Thaokar, 2013, Karyappa et al., 2014, Sengupta et al., 2017, Dong and Sau, 2019], although theoretical models have also been proposed. For example, Benteitis and Krause [2005] developed a spheroidal theory, which assumes the drop takes a spheroidal shape, rather than an almost spherical one, and the aspect ratio of the drop is obtained as part of the solution. This theory, referred to as the extended leaky dielectric model, greatly outperformed the leaky dielectric model in measuring large prolate deformations, but, surprisingly, it generally performed worse for large oblate deformations. Similar spheroidal models have also been used by Zabaranin [2013], Zhang et al. [2013] and Zabaranin [2016]. A slender-body theory that assumes a highly elongated drop shape has been used by Yariv and Rhodes [2013]. In the case of prolate drops, there are two main modes of breakup. First is the emission of thin jets from pointed ends as discussed earlier in this chapter [Fernández de La Mora, 2007, Collins et al., 2008], and second is the elongation of the drop into a thread with bulbous ends which ultimately detach [Torza et al., 1971, Sherwood, 1988]. Which mode occurs depends on the viscosity ratio between the fluids and the electric capillary number. Sengupta et al. [2017] have also reported that charge convection can give rise to a transition between the two modes. In the case of oblate drops, two other breakup modes have been reported. One of these sees the drop compress in its centre to form a biconcave disc before taking a toroidal shape and ultimately breaking into several smaller drops [Ghazian et al., 2013]. Analytical theories assuming a toroidal drop shape have been proposed by Zabaranin [2017a] and Zabaranin [2017b]. The other breakup mode for oblate drops is called equatorial streaming and occurs when the drop develops a sharp edge around its equator, from which a thin fluid sheet protrudes. The sheet emits fluid rings, sometimes termed ‘Saturn rings’ that ultimately break up into fine drops [Brosseau and Vlahovska, 2017].

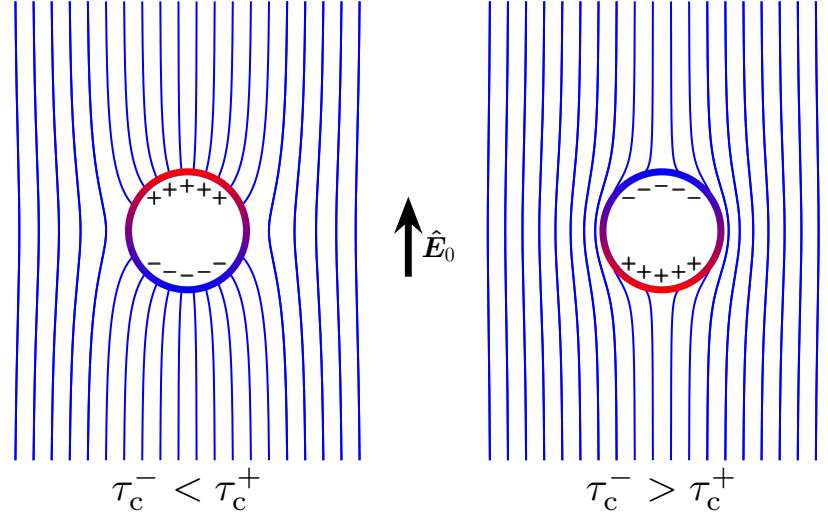


Figure 1.6: A solid sphere immersed in a viscous fluid for which (a) $\tau_c^- < \tau_c^+$ and (b) $\tau_c^- > \tau_c^+$. The blue lines are the corresponding electric field lines.

1.3.4 Quincke rotation

In the late 19th century, studies by Weiler [1893] and Quincke [1896] reported the spontaneous rotation of solid spheres and cylinders in sufficiently strong electric fields, a phenomenon that has become known as Quincke rotation. Jones [1984] and Turcu [1987] later described the mechanism behind this behaviour in spheres. In a uniform electric field $\mathbf{E}$, the charge distribution on the sphere can be approximated by a dipole moment $\mathbf{P}$. The dipole moment aligns with the field if the charge relaxation time $\tau_c^\pm = \epsilon^\pm / \sigma^\pm$ of the sphere material is shorter than that of the surrounding fluid [Lampa, 1906]. Conversely, if the relaxation time is shorter in the surrounding fluid, the dipole is antiparallel to the field (Figure 1.6). In the former case, corresponding to systems for which $SQ < 1$, any small rotational displacement of the dipole is quickly corrected by an electric torque of the form $\mathbf{P} \times \mathbf{E}$. However, in the latter case, corresponding to $SQ > 1$, the configuration becomes unstable above a critical electric field strength $E_{c,s}$, given by:

$$E_{c,s} = \sqrt{\frac{2\mu^+(2+Q)(1+2S)}{3\epsilon^+\tau_{MW}(SQ-1)}}, \quad (1.60)$$

where

$$\tau_{MW} = \frac{\epsilon^- + 2\epsilon^+}{\sigma^- + 2\sigma^+} \quad (1.61)$$

is the Maxwell–Wagner relaxation time [Jones, 1995], representing the time scale for polarisation of the sphere surface upon application of the electric field. In this scenario, if the dipole is perturbed, the induced electric torque $\mathbf{P} \times \mathbf{E}$ rotates the sphere until it reaches a steady angular velocity with the dipole moment tilted away from the axis of the applied field. The direction of the rotational axis, determined by the initial perturbation, is always perpendicular to the applied field. In steady state, the charge convected around the sphere by its rotation is balanced by the recharging of the interface due to the current discontinuity between the solid and fluid phases. Significant attention has been devoted to studying the dynamics of solid spheres undergoing Quincke rotation [Jones, 1984, Dolinsky and Elperin, 2012, Das and Saintillan, 2013]. In particular, Quincke rotation has recently featured prominently in studies of synthetic active matter. A spherical particle undergoing rotation near a substrate (a so-called ‘Quincke roller’) can convert its rotational velocity into self-propelled translational motion [Bricard et al., 2013, 2015]. Similarly, self propulsion can be achieved using pairs of counterrotating spheres [Das and Saintillan, 2013] or an isolated particle of anisotropic shape such as a helix [Das and Lauga, 2019] or biflagellated sphere [Han et al., 2021]. Moreover, experiments have demonstrated the emergence of coherent macroscopic motion of confined suspensions of Quincke rollers if the volume fraction of dispersed matter is sufficiently high [Bricard et al., 2013, 2015].

Viscous drops have also been observed experimentally to undergo Quincke rotation [Krause and Chandratreya, 1998, Sato et al., 2006]. Further experiments by Salipante and Vlahovska [2010, 2013] have revealed the existence of hysteresis in the onset of Quincke rotation in drops, as well as chaotic dynamics at higher field strengths. However, a theoretical analysis of Quincke rotation of drops is considerably more challenging than one for spheres due to the deformed interface and the straining component of the induced flow field, which introduce additional nonlinearities in the interfacial charge convection. Some theoretical models retain charge convection but are restricted to axisymmetric drops, so are unable to capture Quincke rotation [Shutov, 2002, Shkadov and Shutov, 2002, Das and

Saintillan, 2017b]. The first effort to capture Quincke rotation in a theoretical model was made by Feng [2002], who developed a 2D model valid for small values of the electric Reynolds number Re_E . He et al. [2013] developed a small deformation theory capable of capturing the transition to Quincke rotation, but included only the rotational component of the flow in the charge convection, and so obtained the same critical field as for a solid sphere. Yariv and Frankel [2016] considered large electric Reynolds numbers and found that Taylor’s fore-aft symmetric solution no longer exists in this limit, necessitating drop rotation. Das and Saintillan [2021] extended the theory of He et al. [2013] to develop a phenomenological model that includes the straining flow in the convection, and predicted that the critical electric field is greater for drops than for spheres. Recently, Peng and Schnitzer [2025] developed a 2D theory which captured the hysteretic onset of Quincke rotation observed by Salipante and Vlahovska [2010], and explained the phenomenon as a result of charge shocks at the equator.

1.4 Interactions between spheres or drops

Understanding the electrohydrodynamic interactions between two or more drops is important for modelling the microstructure of suspensions or emulsions such as electrorheological (ER) fluids, which can exhibit a range of non-Newtonian behaviours when exposed to sufficiently strong electric fields (typically a few kilovolts per millimetre) [Stangroom, 1983, Halsey, 1992, Conrad and Sprecher, 1991]. These fluids have garnered significant attention due to their applications in designing various mechanical devices, including shock absorbers [Maemori and Saito, 1998] and clutches and brakes [Papadopoulos, 1998]. Most studies on the bulk rheology of ER fluids have focused on suspensions of solid spheres rather than viscous drops, and typically involve AC electric fields, but similar effects have also been reported in DC fields. Winslow [1949] conducted a series of experiments on such suspensions and observed that particles formed chain structures aligned with the applied field as a result of their polarisation. This positive electrorheological effect increases resistance to shearing through tension in the chains,

leading to an increase in the apparent viscosity of the suspension of several orders of magnitude [Gast and Zukoski, 1989, Larson, 1999], the development of a field-strength-dependent yield stress [Klass and Martinek, 1967, Marshall et al., 1989], and shear thinning [Halsey et al., 1992]. In AC fields, the effect is possible only when the permittivity of the sphere is greater than that of the surrounding fluid. Conversely, in DC fields, the conductivity of the sphere must be larger than that of the fluid. Negative ER effects, whereby the apparent viscosity of a suspension decreases in an electric field, have also been observed. Boissy et al. [1995] and Wu and Conrad [1997] report one such effect when the spheres are charged, in which case the suspension is separated by the electrophoretic migration of the spheres towards the electrodes. Lobry and Lemaire [1999] discovered a different negative ER effect, which results from Quincke rotation of the spheres. Although the rotational axis of Quincke rotation is usually in a random direction perpendicular to the field, if a simple shear flow is applied to the suspension then the rotational axes of the spheres tend to align with the flow vorticity direction. The resulting motion of the particles gives rise to a force in the direction of the flow, which is equivalent to a reduction of the viscosity of the suspension. If the field strength is sufficiently strong, the effect can even lead to zero or negative effective viscosity, by which is meant that the rotation of the particles contributes so strongly to sustaining the applied shearing flow that it equals or exceeds the viscous resistance of the fluid to the flow [Cebers et al., 2002, Pannacci et al., 2007, Lemaire et al., 2008]. ER effects are also present in oil-in-oil emulsions, but are generally weaker and are more complicated given the possibilities of drop breakup or coalescence. Early experimental investigations by Pan and McKinley [1997], Tajiri et al. [1997], Kimura et al. [1998], and Ha and Yang [2000c] as well as the numerical simulations of Fernández [2008a,b] revealed both positive and negative ER effects, with complex dependence on the strain rate, field strength, and the conductivity and viscosity ratios between the two fluids. In some cases, the chaining effect seen in suspensions of solid particles leads to coalescence in the case of emulsions of drops, giving rise to fluid columns connecting the electrodes. Theoretical studies of dilute emulsions of almost spherical drops

in various linear flows [Vlahovska, 2011, Mandal and Chakraborty, 2017a,c, Mandal et al., 2018] have demonstrated that charge convection and drop deformation can have pronounced effects on the emulsion rheology, noting the emergence of normal stress differences and either shear-thickening or shear-thinning behaviour. In shear flows, the type of response depends on whether the drops become prolate or oblate; in extensional flows, it depends on the sign of $SQ - 1$. Kach et al. [2023] simulated emulsions of 1000 drops in two and three dimensions and observed a wide range of collective behaviours, including sheet and chain formation and clustering.

Interactions between pairs of uncharged but polarised drops or solid spheres in electric fields generally involves dielectrophoresis (DEP), an electrostatic effect which arises when a dielectric body is exposed to a nonuniform electric field, leading to translational motion of the body. DEP interactions have been studied between pairs of conducting or perfectly dielectric spheres [Jones, 1979, Washizu and Jones, 2002, Saintillan, 2008] and drops [Atten, 1993, Eow and Ghadiri, 2003]. These studies revealed that the DEP force between two spheres or drops is attractive if the angle between the applied field and the vector connecting the centres of the spheres or drops is smaller than 54.7° , and is repulsive otherwise. In the case of drops, this is often exploited to induce or inhibit coalescence of water drops in oil [Mhatre et al., 2015]. However, interactions between pairs of leaky dielectric drops generally include electrohydrodynamic effects in addition to DEP. The shape, interfacial charge and induced electrohydrodynamic flow of each drop are all affected by the presence of the other drop, and each drop is advected by the induced flow of the other drop. The first attempt to model the interactions between a pair of leaky dielectric drops was made by Sozou [1975], who used a bispherical coordinate system to calculate the induced flow fields of a pair of stationary, identical, spherical drops aligned with the applied field. Later, Baygents et al. [1998] investigated translating drops aligned with the field using a boundary integral method, which allowed them to include the effects of drop deformation. Their simulations revealed that dielectrophoretic forces, which are attractive in this configuration, cause the drops to move together, while the deformation of the

drops can be oblate or prolate depending on the value of $\mathcal{F}_d$. However, if $SQ < 1$ and the initial separation of the drops is sufficiently large, electrohydrodynamic flows (which scale as $\mathcal{O}(R^{-2})$ in the limit of widely-separated drops, $R \rightarrow \infty$, where R is the distance between the drops) can overcome the attraction of the DEP forces (which scale as $\mathcal{O}(R^{-4})$) and cause the drops to repel. In this situation, $\mathcal{F}_d$ is positive, and the drops deform into prolate spheroids. Lin et al. [2012] studied the same problem using a phase field model and found that varying the viscosity ratio and surface tension leads to qualitatively different drop dynamics before and during coalescence. More recently, Zabarankin [2020] explored the case of dissimilar drops using a spherical harmonic re-expansion technique, and was able to obtain solutions of arbitrary asymptotic accuracy in R^{-1} . These calculations showed that dissimilar drops can become oblate and repel one another if they are both much more viscous than the surrounding fluid (i.e., in the limit $\lambda_1, \lambda_2 \rightarrow \infty$, where λ_1 and λ_2 are the viscosity ratios of the two drops) and one drop (but not both) is more conductive than the surrounding fluid (i.e., if $(S_1 - 1)(S_2 - 1) < 0$, where S_1 and S_2 are the conductivity ratios of the two drops). Note that these works on drop interactions were restricted to axisymmetric configurations with the drops aligned with the applied field. Mhatre et al. [2015] were the first to investigate the interactions between identical drops with arbitrary alignment to the applied field. Their experiments revealed that leaky dielectric drops would attract or repel one another depending on whether the angle between the applied field and the vector connecting the centres of the drops is larger or smaller than the same critical angle (54.7°) as that for spheres or drops interacting through DEP alone. Next, Dong and Sau [2018] used a lattice Boltzmann method to study the interactions of a pair of two dimensional drops with a wide range of electrical properties while retaining fluid inertia and found that the attractive or repulsive nature of the interactions could be controlled by adjusting the conductivity and permittivity ratios. The three dimensional boundary element simulations of Sorgentone et al. [2021] revealed that the combined electrohydrodynamic and DEP interactions do not necessarily lead to monotonic attraction or repulsion; depending on the initial relative positions of the drops

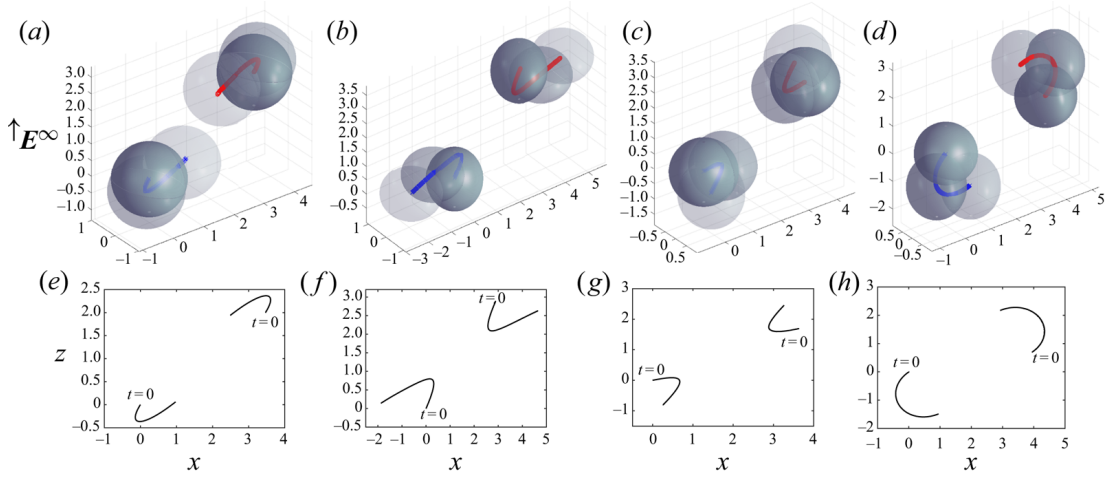


Figure 1.7: Two dimensional trajectories of a pair of drops reproduced from Sorgentone et al. [2021]. In each case, $\lambda = 1$ and $\text{Ca}_E = 0.1$, and the centres of the drops are initially separated by a distance of 4 drop radii. Other parameter values are as follows: (a) $S = 10$, $Q = 1$, $\theta_R(t = 0) = 60^\circ$; (b) $S = 1$, $Q = 10$, $\theta_R(t = 0) = 45^\circ$; (c) $S = 1$, $Q = 0.1$, $\theta_R(t = 0) = 65^\circ$; (d) $S = 0.01$, $Q = 1$, $\theta_R(t = 0) = 80^\circ$, where θ_R is the angle between the applied field and the vector connecting the centres of the drops.

and the electrical properties of the fluids, the drops may initially repel before ultimately coming into contact, or may initially attract before ultimately repelling one another (Figure 1.7). Sorgentone et al. [2021] also developed an analytical model, valid in the limits of large drop separation and small drop deformation, which qualitatively captured the drop interactions predicted by their numerical simulations for sufficiently widely separated drops. A quasi-steady version of their analysis assuming spherical drops was further validated by comparison with the experimental results of Kach et al. [2022], who found that the theory described the qualitative features of their observed drop trajectories well, despite the fairly small drop separations occurring in their experiments. In the same study, Kach et al. [2022] extended the quasi-steady theory of Sorgentone et al. [2021] to drops with different sizes and/or material properties and to systems of three or more drops. Subsequently, Sorgentone and Vlahovska [2022] studied dissimilar drops using boundary element simulations and identified conditions under which a pair of dissimilar drops can undergo self-sustained propulsion. However, almost all of the studies on drop interactions neglect charge convection, precluding the prediction of Quincke rotation. The only work to have retained the effect is that

of Dong et al. [2024], who conducted numerical simulations to explore the possibility of self-sustained propulsion of pairs of identical counter-rotating drops, as found previously for solid spheres by Das and Saintillan [2013]. They found that the motion of the pair of drops varied nonlinearly with the viscosity ratio of the drops, changing direction as it increased. However, these simulations were limited to two dimensional drops.

1.5 Surfactants

Although the classical leaky dielectric model assumes a clean fluid interface, many practical systems contain surfactants (surface active agents), which are either deliberately added or naturally present as impurities. Surfactants are a class of chemical compounds that reduce the surface tension between a liquid and a second medium, and are commonly employed in a diverse range of industries owing to their unique properties. Among their uses are emulsification, often exploited for food processing [Kralova and Sjöblom, 2009]; wetting, used to develop improved agricultural chemicals like pesticides and fertilisers [Kovalchuk and Simmons, 2021]; foaming, used to develop a range of personal care products [Bureiko et al., 2015] as well as aqueous film-forming foams for firefighting [Moody and Field, 2000, Kovalchuk and Simmons, 2021]; and dispersion, preventing particle agglomeration in suspensions [Vaisman et al., 2006, Lotya et al., 2010]. However, the effects of surfactants on drop hydrodynamics are fascinating in their own right, and many experimental, theoretical and computational studies have sought to elucidate the impact on drop deformation, breakup and motion, amongst other phenomena. In many cases, a quantitative understanding of surfactant effects is especially desirable because these effects often contribute to discrepancies between theoretical predictions and observations in experiments, where drop systems are rarely truly clean. A classic example is that of a small drop sedimenting in an unbounded fluid, which has been repeatedly shown to obey Stokes' law for translating spheres rather than the Hadamard-Rybczynski equation [Savic, 1953, Griffith, 1962]. This is explained by the presence of small amounts of surfactant

which are convected to the trailing tip of the sedimenting drop, where they give rise to a stagnant cap, a region of the interface which is immobilised by the dense packing of surfactant molecules. The gradient in surfactant coverage leads to a gradient in surface tension, in turn leading to Marangoni stresses which impede the surface flow and thereby decrease the terminal velocity of the drop [Levich, 1962, Davis and Acrivos, 1966, Sadhal and Johnson, 1983].

Surfactants also play a complex role in the deformation of drops in various paradigmatic settings. Investigations into these effects began after the equations initially derived by Taylor [1932, 1934] (and later generalised or extended by other workers [Cox, 1969, Chaffey and Brenner, 1967, Barthès-Biesel and Acrivos, 1973]) failed to adequately describe experimental observations [Nawab and Mason, 1958, Bartok and Mason, 1959, Rumscheidt and Mason, 1961] of the circulation inside drops in shear flows. The theory of Taylor [1932, 1934] assumed that tangential viscous stresses exerted on the drop surface were unimpeded in their transmission to the interior of the drop, but the experimentalists noted that the circulation was absent (or significantly weaker than predicted) in several cases, and suggested that the discrepancy could be due to the development of an interfacial layer of surfactant. A framework for computing the shape and flow fields of an almost spherical drop in an arbitrary flow field accounting for surfactant was presented by Haber and Hetsroni [1972]. Greenspan [1977] calculated the small deformations of a drop in a quiescent fluid with a prescribed deposition of surfactant to the interface and applied his model to cell division. Flumerfelt [1980] developed a small-deformation theory accounting for dynamic interfacial effects like surface shear and dilational viscosities and spatially nonuniform surface tension due to nonuniform surfactant distributions, as well as surfactant transport between the interface and the bulk fluids. The experiments of Phillips et al. [1980] tested the theory of Flumerfelt [1980] against that of Cox [1969], who had extended the theory of Taylor [1932, 1934] to arbitrary flow fields, while still neglecting dynamic interfacial effects. Both theories accurately described the experimental observations only when the viscosities of both the drop and surrounding fluid were very large, but only the theory of Flumerfelt [1980] suc-

ceeded in explaining the behaviour of less viscous systems, which proved highly susceptible to surface viscous effects. Sadhal and Johnson [1986] calculated the deformation of a sedimenting drop with an arbitrary prescribed surfactant distribution, and in the case of a stagnant cap distribution found that the drop would deform into a prolate spheroid. Stone and Leal [1990] studied the deformation and breakup of a surfactant-laden drop in an extensional flow using a boundary integral method accompanied by a small-deformation theory. This work was later generalised by Milliken et al. [1993] to capture transient breakup dynamics and to treat drop–fluid systems with nonidentical viscosities as well as interactions between surfactant molecules.

The results of these studies highlighted two competing effects of variable surface tension, the balance of which determines the ultimate effect of the surfactant on the drop deformation. The first of these, known as tip stretching, occurs when surfactant is convected from the equator of an elongated drop towards the tips. The surface tension is decreased at the tips, requiring the interface to assume a greater degree of curvature in order to satisfy the normal stress balance, leading to increased deformation when compared to a drop with uniform surface tension. The second effect, known as surface dilution, occurs due to the increasing surface area of the drop that accompanies deformation. The surfactant concentration is globally diluted, leading to a global increase in the surface tension and hence reduced deformation when compared to a drop with constant surface tension. Generally, strong surface convection relative to diffusion (large surface Péclet number) is found to promote tip stretching due to the accumulation of surfactant at the tips of the drop, leading to larger deformations at a given strain rate. On the other hand, increasing the sensitivity of the surface tension to the local surfactant concentration leads to increased Marangoni stresses that impede the convective flux and allow more uniform surfactant distributions. This promotes the surface dilution effect and thus smaller deformations at a given strain rate, and increases the critical strain rate at which drop breakup occurs.

It is important to note that the work of Stone and Leal [1990] assumes that the surfactant was insoluble in the bulk fluids and was present in dilute quantities

only on the interface. Surfactant solubility was considered by Milliken and Leal [1994], who found that adsorption and desorption fluxes between the interface and bulk fluids mitigated both of the mentioned effects of varying surface tension by reducing surfactant concentration gradients (in fact, the limit of rapid adsorption and desorption corresponds to a clean drop, after rescaling the small deformation parameter to account for the uniform surfactant coating). Pawar and Stebe [1996] considered the effects of nondilute quantities of surfactant as well as interactions between the surfactant molecules. This study showed that compression of the surfactant layer due to strong cohesive interactions can lead to a phase transition between an expanded phase and a condensed phase, requiring a piecewise equation of state. Eggleton and Stebe [1998] and Eggleton et al. [1999] focused on using physically realistic material parameters to study nondilute surfactant concentrations approaching saturation. The studies on nondilute concentrations showed that Marangoni stresses are strong even for small gradients in the surfactant concentration, significantly impeding the fluid flow and leading to a correspondingly uniform surfactant distribution, emphasising the surface dilation behaviour. Vlahovska et al. [2005] extended the theory of Stone and Leal [1990] to third order in the deformation, with the goal of capturing nonlinear rheological effects. They reported normal stress differences and shear thinning in equiviscous drop–fluid systems, in qualitative agreement with their boundary element simulations. Some other related investigations include those on compound droplets [Mandal et al., 2016b] and the effect of Marangoni stresses on the rheology of emulsions of surfactant-laden drops in linear flow fields [Mandal et al., 2017].

The combined effect of surfactant and an electric field on drop dynamics has been studied to a limited extent. The first attempts to study the combined effects were those of Ha and Yang [1995, 1998], who conducted experiments and used a second order small deformation theory to conclude that the deformation of an oblate drop was more strongly affected by the presence of surfactant than was that of a prolate one due to weak convective flow in the latter case, and that the surfactant led to increased deformation in both cases. Later, Teigen and

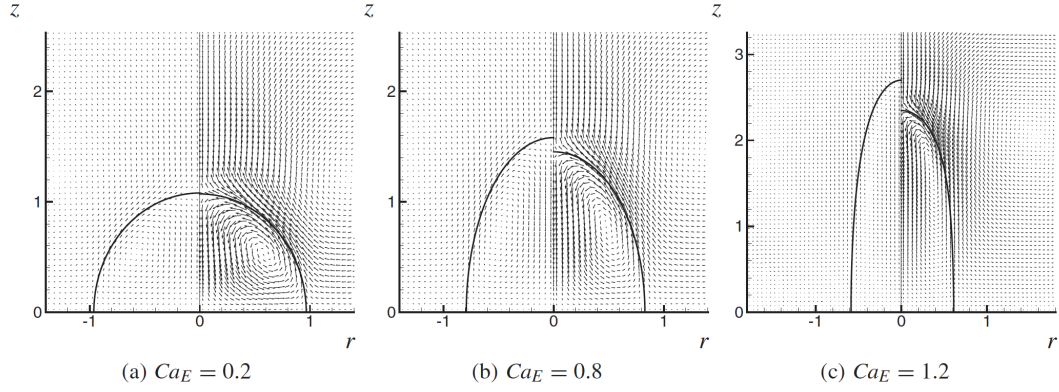


Figure 1.8: A prolate A drop at (a) $Ca_E = 0.2$, (b) $Ca_E = 0.8$, and (c) $Ca_E = 1.2$, reproduced from Teigen and Munkejord [2010]. The left hand side of each subfigure corresponds to a surfactant coated drop, while the right hand side corresponds to a clean drop.

Munkejord [2010] used a level set method to investigate the effect of surfactant on drops of each of the three classes described by Lac and Homsy [2007]. Their findings clarified that while the presence of surfactant does indeed augment the deformation of prolate A or oblate drops, it instead decreases the deformation of prolate B drops, because in this case the surface tension is greatest at the tips and smallest around the equator. They also found that the induced electrohydrodynamic flow could be significantly suppressed by Marangoni stresses. Nganguia et al. [2013] studied the effect of nondiffusing surfactant using both a second-order small deformation theory as well as a spheroidal theory, which is able to capture larger drop deformations. In the spheroidal theory, a nonlinear equation of state is used which allows for greater surfactant concentrations than does the small-deformation theory. As the concentration is varied, the varying relative strengths of tip stretching and surface dilution give rise to a non-monotonic trend between the concentration and the deformation. Mandal et al. [2016a] considered the effect of surfactant on the dielectrophoretic motion of drops in a nonuniform field. Nganguia et al. [2019] generalised their earlier work [Nganguia et al., 2013] to include surface diffusion of surfactant and found that increasing surfactant concentration increases the deformation of prolate A drops and decreases the deformation of prolate B drops only when convection is strong compared to diffusion. When diffusion is the stronger effect, the trend reverses and the deformation

of prolate A drops decreases with increasing concentration, while the deformation of prolate B drops increases. Poddar et al. [2018] used an asymptotic analysis to conclude that surfactants can reduce the settling velocity of a drop sedimenting in an electric field. Ervik et al. [2018] studied the effect of surfactants on the deformation experimentally, and found that surfactants can damp transient oscillations of the deformation around its equilibrium value. Poddar et al. [2019a] studied theoretically the effect of surfactant and electric fields on the cross-stream motion of a drop in Poiseuille flow, and shortly afterwards, the rheology of an emulsion of surfactant coated drops in a unbounded shear flow [Poddar et al., 2019b]. A few other recent related studies include those of Sorgentone et al. [2019], who used a boundary integral method to study electrohydrodynamic interactions between surfactant-laden drops; Han et al. [2022], who also used a boundary integral method and considered the combined effects of surfactant and dilational viscosity on electrohydrodynamic drop deformation; and Zhang et al. [2021], who studied the combined effects of surfactant, an imposed shear flow and an electric field using a hybrid lattice Boltzmann/finite difference method.

1.6 Numerical schemes

Nonlinearities arising through the charge convection and kinematic boundary conditions will generally exclude the possibility of closed-form solutions to the problems discussed in this thesis. Instead, we present semi-analytical solutions to the problems, reducing the governing equations to systems of coupled nonlinear ordinary differential equations (ODEs) which will be solved with numerical techniques. The first of these techniques is a time-stepping algorithm, by which we can obtain transient and steady stable solutions to the problems. The second is a numerical continuation algorithm which captures steady unstable solutions, giving more insight into the bifurcation structure of the onset of Quincke rotation.

1.6.1 Runge–Kutta methods

Runge–Kutta methods are commonly used for numerical integration of ODEs due to their good accuracy and stability and easy implementation. In this thesis, we use the most well known of these, an explicit fourth-order method generally known as RK4. It is used to solve initial value problems of the form

$$\frac{\partial \mathbf{X}}{\partial t} = \mathbf{F}(\mathbf{X}, t), \quad \mathbf{X}(t = 0) = \mathbf{X}_0. \quad (1.62)$$

Time is discretised into steps of suitably short duration δt , and temporal derivatives at the n th time step are approximated by

$$\frac{\partial \mathbf{X}}{\partial t} \approx \frac{\mathbf{X}_{n+1} - \mathbf{X}_n}{\delta t} = \frac{1}{6} (\mathbf{k}_1 + 2\mathbf{k}_2 + 2\mathbf{k}_3 + \mathbf{k}_4), \quad (1.63)$$

where $\mathbf{X}_n$ and $\mathbf{X}_{n+1}$ are the approximations to the solution vector at the current and following time steps, and

$$\mathbf{k}_1 = \mathbf{F}(\mathbf{X}_n, t_n), \quad (1.64)$$

$$\mathbf{k}_2 = \mathbf{F}\left(\mathbf{X}_n + \frac{1}{2}\delta t \mathbf{k}_1, t_n + \frac{1}{2}\delta t\right), \quad (1.65)$$

$$\mathbf{k}_3 = \mathbf{F}\left(\mathbf{X}_n + \frac{1}{2}\delta t \mathbf{k}_2, t_n + \frac{1}{2}\delta t\right), \quad (1.66)$$

$$\mathbf{k}_4 = \mathbf{F}(\mathbf{X}_n + \delta t \mathbf{k}_3, t_n + \delta t), \quad (1.67)$$

are increments contributing to the approximate solution at $\mathbf{X}_{n+1}$, which is determined from the weighted sum of the four on the right hand side of (1.63).

1.6.2 Numerical continuation

Numerical continuation refers to a range of algorithms used to find solutions to parameterised nonlinear systems of the form

$$\mathbf{F}(\mathbf{X}, \lambda) = \mathbf{0}, \quad (1.68)$$

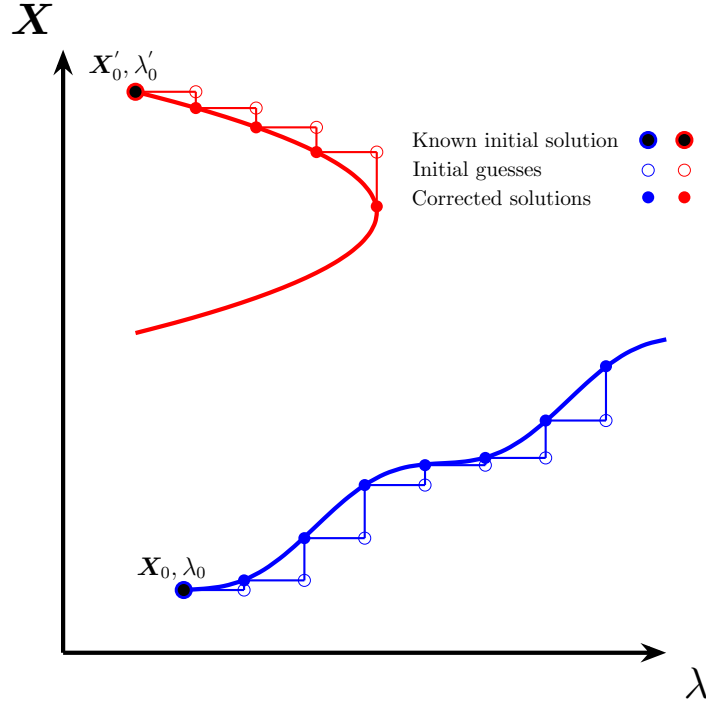


Figure 1.9: Natural parameter continuation along two solution branches in extended solution space. $\mathbf{X} = \mathbf{X}_0$ and $\mathbf{X} = \mathbf{X}'_0$ denote initial solutions on two distinct solution branches starting from $\lambda = \lambda_0$ and $\lambda = \lambda'_0$, respectively.

where $\mathbf{X} \in \mathbb{R}^N$ is a vector of state variables and $\lambda \in \mathbb{R}$ is a scalar parameter. By varying the value of λ , one can trace out branches of solutions in the extended solution space $\mathbb{R}^{N+1}$, which comprises the N state variables together with the parameter λ . The most simple continuation algorithm is natural parameter continuation, in which a known initial solution $(\mathbf{X}_0, \lambda_0)$ is supplied, and then λ is advanced by constant increments of $d\lambda$ and the solution $\mathbf{X}_n$ at a given value λ_n is taken as an initial guess of the solution at the following value $\lambda_{n+1} = \lambda_n + d\lambda$. The solution itself is obtained at each λ_n to the required tolerance using some corrector scheme which may be Newton's method or a more sophisticated algorithm. Figure 1.9 displays the application of natural parameter continuation to two solution branches. Assuming the increments $d\lambda$ are suitably small, it is adequate to capture solutions along the blue branch. However, it often fails at bifurcation points or folds, where the $N \times N$ Jacobian matrix $\mathbf{J}_{\mathbf{X}} = \partial \mathbf{F} / \partial \mathbf{X}$ becomes singular [Keller, 1987]. Such a point occurs on the red branch in Figure 1.9, which features a fold that cannot be followed by natural parameter continuation

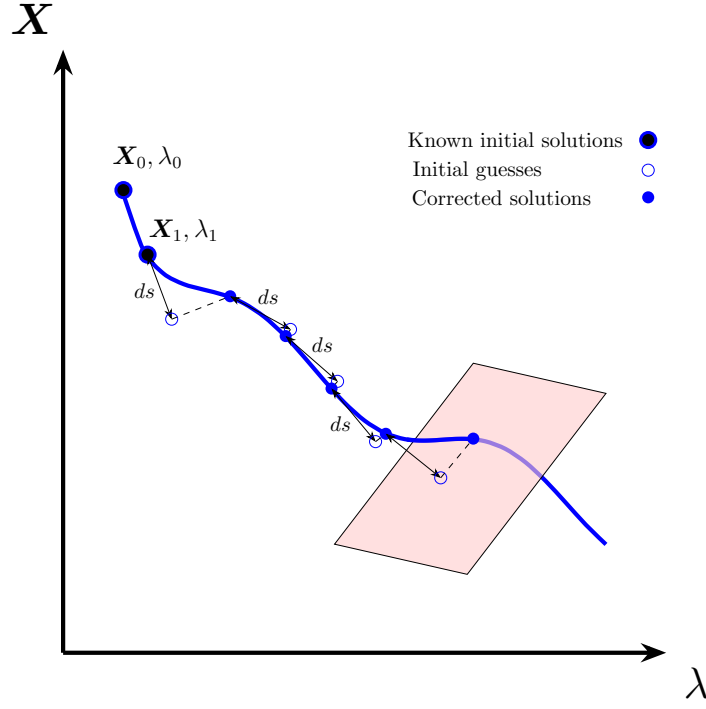


Figure 1.10: Pseudo-arclength continuation along a solution branch in extended solution space. $\mathbf{X} = \mathbf{X}_0$ and $\mathbf{X} = \mathbf{X}_1$ are two solutions on a solution branch at $\lambda = \lambda_0$ and $\lambda = \lambda_1$, respectively.

no matter the size of the increments. Such solutions must be tracked using another algorithm. Pseudo-arclength continuation, as illustrated in Figure 1.10 is an adaptation to natural parameter continuation which is better suited to problems with bifurcations and folds. Instead of parameterising the solution branch in steady increments of λ , λ is instead treated as a state variable and allowed to increase or decrease as required while the algorithm proceeds a fixed distance ds along the solution branch at each iteration [Dahlke and Bettinger, 2024]. Explicitly, λ is appended to $\mathbf{X}$ to create the augmented solution vector

$$\mathbf{Z} = (\mathbf{X}, \lambda) \in \mathbb{R}^{N+1}, \quad (1.69)$$

and to proceed along the solution branch we require the tangent vector $\mathbf{T} = \partial \mathbf{Z} / \partial s \in \mathbb{R}^{N+1}$. After discretising the solution branch into segments of arclength ds , we approximate the tangent vector at the n th iteration, $\mathbf{T}_n$, using finite dif-

ferences between the current and previous solution points [Aruliah et al., 2012],

$$\mathbf{T}_n = \frac{\mathbf{Z}_n - \mathbf{Z}_{n-1}}{|\mathbf{Z}_n - \mathbf{Z}_{n-1}|}. \quad (1.70)$$

At each iteration an augmented system of equations $\mathbf{G}(\mathbf{Z}_n)$ is solved. The augmented system includes (1.68) supplemented with an arclength constraint and can be written

$$\mathbf{G}(\mathbf{Z}_n) = \begin{bmatrix} \mathbf{F}(\mathbf{Z}_n) \\ (\mathbf{Z}_n - \mathbf{Z}_{n-1}) \cdot \mathbf{T}_{n-1} - ds \end{bmatrix} = \mathbf{0}. \quad (1.71)$$

The arclength constraint ensures that the solution lies the correct distance ds from the previous solution; or more precisely, that it lies in the hyperplane which is normal to $\mathbf{T}_{n-1}$ and a distance ds from $\mathbf{Z}_{n-1}$. A solution of the full system $\mathbf{G}$ therefore corresponds to a point of intersection of the solution branch and the hyperplane.

1.6.3 Bifurcation detection and branch switching

Pseudo-arclength continuation, as outlined in the previous subsection, is a valuable tool for tracing out a solution branch given two initial solutions. Two initial solutions are required because the algorithm requires an approximation of the tangent vector to the solution branch, calculated according to (1.70). The next problems to address are those of locating bifurcation points along the known branch and tracking any new branches emanating from the bifurcation point. Generally, bifurcations are detected using some test function $\tau(\mathbf{Z})$, defined such that $\tau(\mathbf{Z}^*) = 0$ at a bifurcation point $\mathbf{Z}^*$. Therefore, a change of sign of τ between consecutive solution points $\mathbf{Z}_{n-1}$ and $\mathbf{Z}_n$, i.e., satisfaction of

$$\tau(\mathbf{Z}_{n-1})\tau(\mathbf{Z}_n) < 0, \quad (1.72)$$

indicates that a bifurcation point has been passed between the two solutions. A common choice for τ , and that which will be used in this thesis, is simply the

greatest of the real parts of the eigenvalues of $\mathbf{J}_{\mathbf{X}}$.

If ds is very small, then $\mathbf{Z}_{n-1}$ or $\mathbf{Z}_n$ may provide an adequate approximation of $\mathbf{Z}^*$ for many purposes. However, several techniques exist to improve the approximation. The simplest is to perform a linear interpolation of the test function between $\mathbf{Z}_{n-1}$ and $\mathbf{Z}_n$ and to identify the zero of the straight line. The corresponding approximation $\bar{\mathbf{Z}}^* = (\bar{\mathbf{X}}^*, \bar{\lambda}^*)$ to $\mathbf{Z}^*$ is then given by

$$\bar{\mathbf{Z}}^* = \mathbf{Z}_{n-1} - \tau(\mathbf{Z}_{n-1}) \frac{\mathbf{Z}_n - \mathbf{Z}_{n-1}}{\tau(\mathbf{Z}_n) - \tau(\mathbf{Z}_{n-1})} \approx \mathbf{Z}^*, \quad (1.73)$$

which is likely to be accurate enough for most purposes. If further accuracy is desired, $\bar{\mathbf{X}}^*$ can be used as an initial guess to solve $\mathbf{F}(\mathbf{X}, \lambda) = \mathbf{0}$ with $\lambda = \bar{\lambda}^*$. In addition, the solution of this equation, $\hat{\mathbf{Z}}^*$, yields a third value of τ which may be then used to perform a quadratic interpolation between $\mathbf{Z}_{n-1}$, $\mathbf{Z}_n$, and $\hat{\mathbf{Z}}^*$, if desired.

Another type of method of bifurcation detection, which is often more robust than performing an interpolation alone, involves setting up a new system of equations whose only solutions are bifurcation points. This can be achieved by supplementing the system of equations $\mathbf{F}(\mathbf{Z}) = \mathbf{0}$ with further equations which exclude regular solution points of $\mathbf{F}(\mathbf{Z}) = \mathbf{0}$ as solutions of the whole system. One such approach relies on the fact that the Jacobian $\mathbf{J}_{\mathbf{X}}$ is singular at a steady-state bifurcation point. Note that steady-state bifurcations are those associated with a simple zero eigenvalue such as saddle node, transcritical and pitchfork bifurcations. This excludes Hopf bifurcations, which are characterised by a conjugate pair of purely imaginary eigenvalues. A different approach is required to detect them, and they are not considered in this thesis. However, at steady-state bifurcation points,

$$\mathbf{J}_{\mathbf{X}}(\mathbf{Z}^*)\mathbf{h} = \mathbf{0} \quad (1.74)$$

has a nontrivial solution. At regular points, the only solution is the trivial vector $\mathbf{h} = \mathbf{0}$, but at steady-state bifurcation points $\mathbf{h}$ is the nonzero eigenvector corresponding to the zero eigenvalue. Thus, only bifurcation points satisfy (1.74) if $\mathbf{h} \neq \mathbf{0}$ is enforced. This may be achieved by introducing another equation which

requires that the scalar product between $\mathbf{h}$ and another vector (usually $\mathbf{h}$ itself or a unit vector $\hat{\mathbf{e}}_k$) take a nonzero value, which, without loss of generality, can be taken to be 1. For example, using the unit vector $\hat{\mathbf{e}}_k$,

$$\mathbf{h} \cdot \hat{\mathbf{e}}_k - 1 = h_k - 1 = 0. \quad (1.75)$$

Then, $\mathbf{F}(\mathbf{Z}) = \mathbf{0}$, (1.74) and (1.75) can be combined into a larger system of $(2N + 1)$ equations. This system, known as a Moore–Spence system [Moore and Spence, 1980] (although first proposed by Seydel [1979]), may be written

$$\begin{pmatrix} \mathbf{F}(\mathbf{Z}) \\ \mathbf{J}_X(\mathbf{Z})\mathbf{h} \\ h_k - 1 \end{pmatrix} = \mathbf{0}. \quad (1.76)$$

Eq. (1.76) can be solved only at steady-state bifurcation points, given reasonable initial guesses of $\mathbf{Z}^*$ and $\mathbf{h}$. A good initial guess for $\mathbf{Z}^*$ could be one of the points straddling the bifurcation, $\mathbf{Z}_n$ or $\mathbf{Z}_{n-1}$, or, preferably, $\bar{\mathbf{Z}}^*$ or $\hat{\mathbf{Z}}^*$ if an interpolation procedure has been followed. It is slightly more difficult to find an initial guess for $\mathbf{h}$, because the Jacobian $\mathbf{J}_X$ is nonsingular when evaluated at the approximation ($\bar{\mathbf{Z}}^*$ or $\hat{\mathbf{Z}}^*$) rather than at the true bifurcation point $\mathbf{Z}^*$. Therefore, no nonzero eigenvector exists to satisfy (1.74). However, one can obtain a solvable system if one row of the Jacobian is eliminated and replaced with the unit vector $\hat{\mathbf{e}}_k$. Explicitly, we define

$$\mathbf{J}'_X = (\mathbf{I} - \hat{\mathbf{e}}_l \hat{\mathbf{e}}_l) \mathbf{J}_X + \hat{\mathbf{e}}_l \hat{\mathbf{e}}_k, \quad (1.77)$$

and then seek solutions to

$$\mathbf{J}'_X(\bar{\mathbf{Z}}^*)\mathbf{h} = \hat{\mathbf{e}}_l. \quad (1.78)$$

The modified system (1.78) excludes the trivial solution $\mathbf{h} = \mathbf{0}$ by incorporating the normalisation constraint $h_k = 1$, and since $\bar{\mathbf{Z}}^*$ is close to the true bifurcation point $\mathbf{Z}^*$, (1.78) yields a good initial guess for the true null vector $\mathbf{h}$.

Once a bifurcation has been detected and the corresponding solution vector $\mathbf{Z}^*$ and null vector $\mathbf{h}$ have been approximated, a point on the bifurcating branch may

be located by perturbing the solution at the bifurcation point a small distance in the direction of $\mathbf{h}$. That is, if the approximations are given by $\tilde{\mathbf{Z}}^*$ and $\tilde{\mathbf{h}}$, then an initial guess for a solution on the bifurcating branch, $\mathbf{Y}_0$, is given by

$$\mathbf{Y}_0 = \tilde{\mathbf{Z}}^* + \delta \tilde{\mathbf{h}}, \quad (1.79)$$

where δ is the size of the perturbation. A true solution on the bifurcating branch, $\mathbf{Y}$, can be computed from (1.79) using a given corrector scheme as long as the guess $\mathbf{Y}_0$ is suitably close to $\mathbf{Y}$. Since $\tilde{\mathbf{Z}}^*$ and $\tilde{\mathbf{h}}$ have been approximated rather well by the Moore–Spence system, it remains to choose the appropriate value for δ . If δ is too large, the solver may fail to converge to any solution, and if δ is too small, the solver may miss the bifurcating branch and simply converge to a solution back on the initial branch. Unfortunately, it is prohibitively difficult to compute the correct value of δ for a given $\tilde{\mathbf{Z}}^*$ and $\tilde{\mathbf{h}}$ [Seydel, 2009]. A common solution to this problem is to instead prescribe a value to δ , and to seek a pair of solutions $\mathbf{Z}$ and $\mathbf{Y}$ which fit the chosen δ . Specifically, another augmented system of equations is formed, given by

$$\begin{pmatrix} \mathbf{F}(\mathbf{Z}) \\ \mathbf{F}(\mathbf{Y}) \\ Y_k - Z_k - \delta \end{pmatrix} = \mathbf{0}, \quad (1.80)$$

where $Y_k = \mathbf{Y} \cdot \hat{\mathbf{e}}_k$ and $Z_k = \mathbf{Z} \cdot \hat{\mathbf{e}}_k$ are the k th components of the solutions $\mathbf{Y}$ and $\mathbf{Z}$. Hence, (1.80) returns two solutions, one on each branch, with the two solutions differing by δ in their k th components. A new tangent vector can then be computed between the solution on the emanating branch and the bifurcation point in order to proceed with the continuation on the emanating branch.

1.7 Overview of thesis

The remainder of this thesis is structured as follows. In Chapter 2, we discuss in detail the three-dimensional phenomenological model proposed by Das and

Saintillan [2021] for an isolated, clean, almost spherical drop and present some important novel results, focusing particularly on the presence of hysteresis at the onset of Quincke rotation. This model retains transient shape deformations and charge relaxation and convection, and forms the basis of the theories developed in the following chapters. In Chapter 3, we build on the model by assuming the drop is coated with a monolayer of insoluble apolar surfactant, and delineate the combined effects of charge convection and surface tension gradients on the drop dynamics. We perform a linear stability analysis to highlight the effects of the Marangoni stresses and variable surface tension on the onset of Quincke rotation. In Chapter 4, we consider the pair interactions between two clean drops. We explore the trajectories of the drops under the combined electrohydrodynamic and dielectrophoretic interactions with a particular focus on the impact of Quincke rotation, and then discuss the effect of the interactions on the drop dynamics when the drops are fixed in place. Finally, in Chapter 5, we summarise the findings of the previous chapters and propose some directions for future work. A table of nomenclature defining all the variables used in this thesis is presented in Appendix A. An account of the work contained in Chapters 2 and 4 has been accepted for publication in *Physical Review Fluids* [McDougall et al., 2026a], and an account of the work contained in Chapter 3 is under review for publication [McDougall et al., 2026b].

Chapter 2

An Isolated Clean Drop

In this chapter, we describe the three-dimensional phenomenological model for an isolated, clean, almost spherical, leaky dielectric drop introduced by Das and Saintillan [2021] that accounts for transient charge convection and relaxation. This model forms the basis for the subsequent chapters concerning surfactant effects and drop pair interactions, and therefore is reproduced here using the notation and scaling employed in this thesis in order to establish the general framework on which the subsequent theories are based. Furthermore, we present novel results concerning the effects of charge convection on drops in both the Taylor regime (when the electric field strength is smaller than the critical field for rotation and the drop shape and flow field are axisymmetric) and the Quincke regime (when the electric field strength is greater than the critical field for rotation and the drop shape is tilted) that were not reported in Das and Saintillan [2021]. In §2.1, we outline the problem under consideration, recapitulating the governing equations and boundary conditions. In §2.2, we present our approach to solving the problem. In §2.3, we present the results of the model, first for a drop in the Taylor regime and then for one in the Quincke regime. In §2.4, we derive the critical field strength for Quincke rotation of a spherical drop. Finally, in §2.5, we summarize the key findings of the present model.

2.1 Problem formulation

First, we briefly restate the relevant governing equations and boundary conditions as set out in §1.2 and §1.3.2. Consider an uncharged leaky dielectric drop, immersed in a second leaky dielectric fluid. We use a spherical coordinate system (radial distance r , polar angle θ , azimuthal angle ϕ) with origin at the centre of the drop. The fluids are assumed to be immiscible and to have the same density. The electric permittivities of the fluids are denoted by $\epsilon^\pm$, the conductivities $\sigma^\pm$, and the viscosities $\mu^\pm$, where, as before, the plus subscript refers to the properties of the surrounding fluid, and the minus subscript refers to the properties of the drop. The drop domain is denoted by V^- , the surrounding fluid domain is denoted by V^+ , and the interface between the two is denoted by ∂V . The drop is initially spherical with radius a , but deforms upon the application of a uniform DC electric field $\mathbf{E}_0 = E_0 \hat{\mathbf{E}}_0$, which we take to be pointing in the z direction. Upon the application of the field, free charge from both fluids accumulates at the drop interface, developing an interfacial charge distribution. Assuming that both of the fluids are electrically neutral, the electric field in each fluid domain, $\mathbf{E}^\pm(\mathbf{r}, t)$, is divergence free. Further, in the electrostatic limit, the electric field is irrotational, which as discussed in §1.2.1 allows the introduction of an electric potential $\varphi^\pm(\mathbf{r}, t)$, such that $\mathbf{E}^\pm = -\nabla\varphi^\pm$. The electric potential is governed by Laplace's equation (1.40) in both the drop and the surrounding fluid,

$$\nabla^2\varphi^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm. \quad (2.1)$$

The tangential components of the electric field are continuous over the interface, and consequently so is the potential,

$$[\![\mathbf{E} \cdot (\mathbf{I} - \mathbf{n}\mathbf{n})]\!] = \mathbf{0}, \quad [\![\varphi]\!] = 0, \quad \text{for } \mathbf{r} \in \partial V, \quad (2.2)$$

where $\mathbf{I}$ is the identity tensor, $\mathbf{n}(\mathbf{r}, t)$ is a unit vector normal to the drop surface, pointing into the surrounding fluid, and the double bracket notation denotes the jump across the interface of any field variable defined in both the drop and

surrounding fluid, i.e., $\llbracket f \rrbracket = f^+(\mathbf{r}) - f^-(\mathbf{r})$ for $\mathbf{r} \in \partial V$. Conversely, the normal component of the electric field is discontinuous, and the interfacial charge density $q(\theta, \phi, t)$ is given by Gauss' law,

$$q = \llbracket \epsilon \mathbf{E} \rrbracket \cdot \mathbf{n} \quad \text{for } \mathbf{r} \in \partial V. \quad (2.3)$$

Two mechanisms contribute to the evolution of q . The first is the Ohmic current jump across the interface, and the second is surface charge convection by the fluid flow. These are represented by the second and third terms, respectively, in the transport equation

$$\frac{\partial q}{\partial t} + \llbracket \sigma \mathbf{E} \cdot \mathbf{n} \rrbracket + \nabla_s \cdot (q \mathbf{v}) = 0 \quad \text{for } \mathbf{r} \in \partial V. \quad (2.4)$$

Here, $\nabla_s = (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \nabla$ is the surface gradient operator and $\mathbf{v}(\mathbf{r}, t)$ is the fluid velocity. The presence of the convective term renders (2.4) nonlinear, which makes analytical progress difficult. However, it is still amenable to numerical solution. In most of the relevant experiments and industrial applications, the drops are typically small (on the order of millimetres) and the fluids are rather viscous, so we assume the Reynolds number of the flow to be small and hence inertia is neglected, as discussed in §1.2.2. The fluid velocity $\mathbf{v}^\pm$ and dynamic pressure $p^\pm(\mathbf{r}, t)$ then satisfy the Stokes equations in both domains,

$$\mu^\pm \nabla^2 \mathbf{v}^\pm = \nabla p^\pm, \quad \nabla \cdot \mathbf{v}^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm, \quad (2.5)$$

and the velocity is continuous across the interface,

$$\llbracket \mathbf{v} \rrbracket = \mathbf{0} \quad \text{for } \mathbf{r} \in \partial V. \quad (2.6)$$

The interface is defined implicitly as

$$\xi(\mathbf{r}, t) = 0 \quad \text{for } \mathbf{r} \in V^\pm, \quad (2.7)$$

and is advected with the flow, so the kinematic boundary condition (1.26) applies:

$$\frac{\partial \xi}{\partial t} + \mathbf{v} \cdot \nabla \xi = 0 \quad \text{for } \mathbf{r} \in \partial V. \quad (2.8)$$

The discontinuity of the material parameters between the drop and surrounding fluid gives rise to electric stresses on the interface, which are balanced by hydrodynamic and capillary stresses. Given that no surfactant is present on the drop surface, we assume the surface tension is constant in time and space, and thus Marangoni stresses are absent from the dynamic boundary condition (1.54). Thus,

$$[\![\mathbf{f}^E]\!] + [\![\mathbf{f}^H]\!] = 2\gamma\kappa\mathbf{n} \quad \text{for } \mathbf{r} \in \partial V, \quad (2.9)$$

where $\kappa(\mathbf{r}, t) = \frac{1}{2}(\nabla_s \cdot \mathbf{n})$ is the mean surface curvature, γ is the surface tension, and $[\![\mathbf{f}^E]\!] = [\![\boldsymbol{\tau}^E]\!] \cdot \mathbf{n}$ and $[\![\mathbf{f}^H]\!] = [\![\boldsymbol{\tau}^H]\!] \cdot \mathbf{n}$ are the electric and hydrodynamic traction jumps across the interface, where

$$\boldsymbol{\tau}^{E\pm} = \epsilon^\pm \left(\mathbf{E}^\pm \mathbf{E}^\pm - \frac{1}{2} E^{\pm 2} \mathbf{I} \right) \quad (2.10)$$

and

$$\boldsymbol{\tau}^{H\pm} = -p^\pm \mathbf{I} + \mu^\pm (\nabla \mathbf{v}^\pm + \nabla \mathbf{v}^{\pm T}) \quad (2.11)$$

are the electric and hydrodynamic stress tensors, respectively.

2.1.1 Nondimensionalisation and scaling assumptions

We rescale the problem taking the initial drop radius a as the characteristic length and the electrohydrodynamic flow time

$$\tau_{\text{EHD}} = \frac{\mu^+}{\epsilon^+ E_0^2} \quad (2.12)$$

as the characteristic time. Other choices for the time scale which are sometimes used in studies of drop electrohydrodynamics include the Maxwell–Wagner relaxation time (1.61), which characterizes the timescale of dipole moment polarization and the angular velocity associated with Quincke rotation [Das and Saintillan,

2017a,b, 2021], the charge relaxation time of the outer fluid τ_c^+ [Lanauze et al., 2015, Peng and Schnitzer, 2025], and the capillary relaxation time $\tau_\gamma = \mu^+ a / \gamma$, which is the timescale for the drop to return to a spherical shape [Esmaeeli and Sharifi, 2011, Esmaeeli and Behjatian, 2020]. After scaling electric fields, surface tension and velocities by E_0 , γ and a/τ_{EHD} , respectively, the stress balance (2.9) can be written in nondimensional form as

$$[\![\mathbf{f}^E]\!] + [\![\mathbf{f}^H]\!] = \frac{1}{\text{Ca}_E} (\nabla_s \cdot \mathbf{n}) \mathbf{n} \quad \text{for } \mathbf{r} \in \partial V. \quad (2.13)$$

The dimensionless number appearing in (2.13) is the electric capillary number Ca_E , defined as

$$\text{Ca}_E = \frac{\epsilon^+ E_0^2 a}{\gamma}, \quad (2.14)$$

which represents the ratio of electric to capillary stresses. It can also be interpreted as the ratio of τ_γ and τ_{EHD} . We assume that the drop is almost spherical, in which case it is appropriate to follow the classical domain perturbation approach in which the flow fields are calculated assuming that the drop remains perfectly spherical (see, for example, Taylor [1934], Cox [1969], Barthès-Biesel and Acrivos [1973]). These flow fields are then used in the normal stress balance at the drop interface to determine the drop shape to first order in δ , a small parameter quantifying the deviation of the drop shape from sphericity. It will be shown in §2.2.5 that $\delta \propto \text{Ca}_E$, hence we require $\text{Ca}_E \ll 1$ in order for the drop to remain approximately spherical. If desired, the $\mathcal{O}(\delta)$ drop shape can be used to obtain the corrections to the flow fields at the next order in δ , but in the present work we describe only the leading order solution.

The charge conservation equation (2.4) in nondimensional form is written

$$\frac{\partial q}{\partial t} + \frac{1}{\text{Re}_E} [\![\mathbf{j} \cdot \mathbf{n}]\!] + \nabla_s \cdot (q\mathbf{v}) = 0, \quad (2.15)$$

where $\mathbf{j}$ is the nondimensional Ohmic current and where

$$\text{Re}_E = \frac{\epsilon^{+2} E_0^2}{\sigma^+ \mu^+} \quad (2.16)$$

is the electric Reynolds number, which quantifies the rates of charge convection and relaxation relative to the rate of charging of the interface by Ohmic currents from the bulk fluids.

In general, the convective term in the charge transport equation introduces nonlinearities that prevent closed-form analytical solutions, as will be explained in more detail in §2.2.2. One possible approach is to linearize the equations and perform double asymptotic expansions in Re_E and Ca_E , but this can be cumbersome. Here we instead retain the nonlinear term and solve the resulting equations numerically. The numerical solution of the charge transport equation is accurate in parameter regimes where either charge convection is weak, which corresponds to $\text{Re}_E \ll 1$, or where the straining component of the induced flow is weak, which corresponds to $\lambda \gg 1$ (recall that $\lambda = \mu^-/\mu^+$ is the viscosity ratio). In this thesis, we take the latter approach, and assume $\lambda \gg 1$ and $\text{Re}_E = \mathcal{O}(1)$.

2.2 Problem solution

We now describe the solution to the problem formulated in the previous section. In §2.2.1, we describe the parameterisation of the drop shape. In §2.2.2, we present the solution to Laplace's equation (2.1) based on a multipole expansion. In §2.2.3, we present the solution to the Stokes equations (2.5) for the fluid velocity and pressure. In §2.2.4, we apply the kinematic boundary condition to relate the flow fields inside and outside the drop to one another and to the motion of the interface. In §2.2.5, we apply the stress boundary condition to relate the electric, hydrodynamic, and capillary stresses at the interface. In §2.2.6, we use the charge transport equation (2.15) to derive ODEs governing the evolution of the interfacial charge distribution.

2.2.1 Parameterisation of interface

We parameterise the interface of the drop as

$$\xi = r - (1 + \delta f) = 0, \tag{2.17}$$

where $\delta \ll 1$ will be defined in §2.2.5. Deviations of the interface from sphericity are captured by the function $f = f(\theta, \phi, t)$ which is expanded as a series of surface spherical harmonics. In a uniform electric field, the leading order (in both δ and λ^{-1}) component of the polarisation of the drop is a dipole, and it will be shown in §2.2.2 that under these circumstances the leading order normal electric traction on the spherical drop surface contains isotropic and quadrupolar components, due to the fact that the electric stress is quadratic in the electric field (see (2.10)). The quadrupolar traction generates quadrupolar fluid flow and drop deformation, corresponding to the second order harmonic. Higher order harmonics arise only through nonlinear couplings between the deformed shape, induced charge, and flow field, and are asymptotically small under the assumptions of $\delta \ll 1$ and $\lambda \gg 1$ and not considered here. With this in mind, the shape function f can be written

$$f = \sum_{m=0}^2 P_2^m(\cos \theta) \left[f_2^m \cos m\phi + \tilde{f}_2^m \sin m\phi \right], \quad (2.18)$$

where $f_2^m(t)$ and $\tilde{f}_2^m(t)$ are coefficients to be determined via the boundary conditions and P_2^m is the associated Legendre function of degree 2 and order m . Any surface spherical harmonic of order n can be expressed as the contraction of an irreducible symmetric tensor of order n and the tensor product of n unit position vectors $\hat{\mathbf{r}}$,

$$T_{i_1 i_2 i_3 \dots i_n}^{(n)} \hat{r}_{i_1} \hat{r}_{i_2} \hat{r}_{i_3} \dots \hat{r}_{i_n} = \sum_{m=0}^n P_n^m(\cos \theta) [a_n^m \cos m\phi + b_n^m \sin m\phi], \quad (2.19)$$

with summation implied over $i_1, i_2, i_3, \dots, i_n$, and where $T^{(n)}$ is an irreducible symmetric tensor of order n [Applequist, 1989]. Thus, for $n = 2$,

$$f = \mathbf{Q}^f : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad (2.20)$$

where $\mathbf{Q}^f$ is a symmetric, traceless, second-order tensor that contains five independent coefficients. From (2.20), the coefficients in $\mathbf{Q}^f$, which we refer to as the shape coefficients, are related to the coefficients f_2^m and $\tilde{f}_2^m$ in (2.18) according

to

$$\mathbf{Q}^f = \begin{bmatrix} \frac{6f_2^2 - f_2^0}{2} & 3\tilde{f}_2^2 & -\frac{3}{2}f_2^1 \\ 3\tilde{f}_2^2 & -\frac{6f_2^2 + f_2^0}{2} & -\frac{3}{2}\tilde{f}_2^1 \\ -\frac{3}{2}f_2^1 & -\frac{3}{2}\tilde{f}_2^1 & f_2^0 \end{bmatrix} \equiv \begin{bmatrix} Q_{xx}^f & Q_{xy}^f & Q_{xz}^f \\ Q_{yx}^f & Q_{yy}^f & Q_{yz}^f \\ Q_{zx}^f & Q_{zy}^f & Q_{zz}^f \end{bmatrix}. \quad (2.21)$$

In the following sections, ODEs governing the evolution of the components of $\mathbf{Q}^f$ will be derived. Using the definition in (2.17), the surface normal $\mathbf{n}$ and the mean surface curvature κ of the interface are given by

$$\mathbf{n} = \frac{\nabla \xi}{|\nabla \xi|} = \hat{\mathbf{r}} - 2\delta(\mathbf{Q}^f \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}), \quad \kappa = \frac{1}{2}\nabla_s \cdot \mathbf{n} = 1 + 2\delta\mathbf{Q}^f : \hat{\mathbf{r}}\hat{\mathbf{r}}, \quad (2.22)$$

respectively.

2.2.2 Electrostatics

In spherical coordinates (r, θ, ϕ) , Laplace's equation for the electric potential (2.1) can be separated to yield the general real solution

$$\varphi^\pm = \sum_{n=0}^{\infty} \sum_{m=0}^n (A_n r^n + B_n r^{-(n+1)}) P_n^m(\cos \theta) [C_n^m \cos m\phi + D_n^m \sin m\phi], \quad (2.23)$$

where P_n^m is the associated Legendre function of degree n and order m , and $A_n(t), B_n(t), C_n^m(t)$ and $D_n^m(t)$ are unknown coefficients determined by application of boundary conditions. Each value of n corresponds to a different charge multipole, with increasing angular complexity with increasing n . $n = 0$ corresponds to a monopole (the net charge on the drop), $n = 1$ a dipole moment, $n = 2$ a quadrupole moment, and so on. The potentials inside and outside the drop include both a contribution from the externally applied field, denoted by φ_0 , and a contribution from the charge distribution on the drop interface, referred to as the disturbance potential. To enforce regularity at $r = 0$ we retain only growing harmonics in the disturbance potential inside the drop,

$$\varphi^- = \varphi_0 + \sum_{n=0}^{\infty} r^n \sum_{m=0}^n P_n^m(\cos \theta) [a_n^m \cos m\phi + b_n^m \sin m\phi], \quad (2.24)$$

where $a_n^m(t) = A_n C_n^m$ and $b_n^m(t) = A_n D_n^m$. To ensure that $\varphi^+ \rightarrow \varphi_0$ as $r \rightarrow \infty$, we retain only decaying harmonics in the disturbance potential outside the drop,

$$\varphi^+ = \varphi_0 + \sum_{n=0}^{\infty} r^{-(n+1)} \sum_{m=0}^n P_n^m(\cos \theta) [c_n^m \cos m\phi + d_n^m \sin m\phi], \quad (2.25)$$

where $c_n^m(t) = B_n C_n^m$ and $d_n^m(t) = B_n D_n^m$. For an electric field applied in the z direction, the potential associated with the applied field is simply $\varphi_0 = -r \cos \theta$. In general, any number of harmonics may be required to accurately describe the disturbance potential. However, since the applied field is uniform, the leading order polarisation of the drop includes only a dipole moment; that is, the $n = 1$ terms in (2.24) and (2.25). This gives

$$\varphi^- = -r \cos \theta + r [a_1^0 P_1^0(\cos \theta) + P_1^1 (a_1^1 \cos \phi + b_1^1 \sin \phi)] \quad (2.26)$$

and

$$\varphi^+ = -r \cos \theta + r^{-2} [c_1^0 P_1^0(\cos \theta) + P_1^1 (a_1^1 \cos \phi + b_1^1 \sin \phi)]. \quad (2.27)$$

In light of (2.19), we can rewrite (2.26) and (2.27) compactly as

$$\varphi^- = -\hat{\mathbf{E}}_0 \cdot \mathbf{r} + \mathbf{P} \cdot \mathbf{r} \quad (2.28)$$

and

$$\varphi^+ = -\hat{\mathbf{E}}_0 \cdot \mathbf{r} + \frac{\mathbf{P} \cdot \mathbf{r}}{r^3}, \quad (2.29)$$

where $\mathbf{P}(t) = (a_1^1, b_1^1, a_1^0)$ is a dipole moment vector (this is the $\mathbf{P}$ whose role was clarified in §1.3.1). A system of ODEs governing the evolution of the components of $\mathbf{P}$ will be derived in the following sections. Note that continuity of the potential across the interface has been satisfied by setting $c_1^0 = a_1^0$, $c_1^1 = a_1^1$ and $d_1^1 = b_1^1$. Higher order charge multipoles arise due to charge convection by the induced straining flow, which scales as λ^{-1} and gives rise to an octupole moment ($n = 3$ terms in (2.24) and (2.25)). The octupole moment then leads to electric stresses which drive fluid flow, which scales as λ^{-2} , which in turn induces addi-

tional higher order charge multipoles via charge convection. Given that λ^{-1} is an asymptotically small quantity, the effects of the octupole on the drop shape and flow fields can be neglected, and hence we do not include it in (2.28) and (2.29).

The electric fields associated with the potentials (2.28) and (2.29) are

$$\mathbf{E}^- = \hat{\mathbf{E}}_0 - \mathbf{P}, \quad \mathbf{E}^+ = \hat{\mathbf{E}}_0 - r^{-3} \mathbf{P} \cdot (\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}), \quad (2.30)$$

respectively, which are used to calculate the Maxwell stress tensor in each domain,

$$\boldsymbol{\tau}^{E\pm} = \epsilon^\pm \mathbf{E}^\pm \mathbf{E}^\pm - \frac{1}{2} \epsilon^\pm (E^\pm)^2 \mathbf{I}. \quad (2.31)$$

Then, the traction jump across the drop interface can be written as

$$[\![\mathbf{f}^E]\!] = [\![\boldsymbol{\tau}^E]\!] \cdot \hat{\mathbf{r}} = p^E \hat{\mathbf{r}} + \mathbf{Q}_{\hat{\mathbf{r}}}^E : \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} + (\mathbf{Q}_{\hat{\mathbf{t}}}^E \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}) + \mathbf{T}^E \times \hat{\mathbf{r}}, \quad (2.32)$$

where

$$p^E = -\frac{1-Q}{6} + \frac{4-Q}{3} (\hat{\mathbf{E}}_0 \cdot \mathbf{P}) + \frac{Q+2}{6} P^2, \quad (2.33a)$$

$$\begin{aligned} \mathbf{Q}_{\hat{\mathbf{r}}}^E &= (1-Q) \hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 + \frac{1+2Q}{2} (\hat{\mathbf{E}}_0 \mathbf{P} + \mathbf{P} \hat{\mathbf{E}}_0) + \frac{5-2Q}{2} \mathbf{P} \mathbf{P} \\ &\quad + \left[-\frac{1-Q}{3} - \frac{1+2Q}{3} (\hat{\mathbf{E}}_0 \cdot \mathbf{P}) - \frac{5-2Q}{6} P^2 \right] \mathbf{I}, \end{aligned} \quad (2.33b)$$

$$\begin{aligned} \mathbf{Q}_{\hat{\mathbf{t}}}^E &= (1-Q) \hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 + \frac{1+2Q}{2} (\hat{\mathbf{E}}_0 \mathbf{P} + \mathbf{P} \hat{\mathbf{E}}_0) - (2+Q) \mathbf{P} \mathbf{P} \\ &\quad + \left[-\frac{1-Q}{3} - \frac{1+2Q}{3} (\hat{\mathbf{E}}_0 \cdot \mathbf{P}) + \frac{2+Q}{3} P_1^2 \right] \mathbf{I}, \end{aligned} \quad (2.33c)$$

$$\mathbf{T}^E = \frac{3}{2} \mathbf{P} \times \hat{\mathbf{E}}_0, \quad (2.33d)$$

where $P = |\mathbf{P}|$ is the magnitude of the dipole moment. In (2.33), $p^E(t)$ is a scalar representing an isotropic electric pressure, $\mathbf{Q}_{\hat{\mathbf{r}}}^E(t)$ and $\mathbf{Q}_{\hat{\mathbf{t}}}^E(t)$ are symmetric, traceless second-order tensors representing the radial and tangential electric stresses driving drop deformation and straining flows, and $\mathbf{T}^E(t)$ is a vector representing the net electric torque on the drop. Furthermore, the discontinuity of the normal

current across the interface is given in nondimensional form by

$$\llbracket \mathbf{j} \cdot \mathbf{n} \rrbracket = \mathbf{E}^+ \cdot \mathbf{n} - \frac{1}{S} \mathbf{E}^- \cdot \hat{\mathbf{r}}, \quad (2.34)$$

while the charge distribution q introduced in (2.3) is

$$q = (1 - Q) \hat{\mathbf{E}}_0 \cdot \hat{\mathbf{r}} + (2 + Q) \mathbf{P} \cdot \hat{\mathbf{r}}. \quad (2.35)$$

Recall that $Q = \epsilon^-/\epsilon^+$ and $S = \sigma^+/\sigma^-$ are the permittivity and conductivity ratios, respectively.

2.2.3 Hydrodynamics

The fluid flow inside and outside the drop is governed by the Stokes equations (2.5). The general solution in spherical coordinates was derived by Lamb [1932]. First, taking the divergence of (2.5) reveals that in Stokes flow the pressure is harmonic in both domains,

$$\nabla^2 p^\pm = 0. \quad (2.36)$$

As for the electric potential in (2.24) and (2.25), the general solutions for the pressure involve growing harmonics inside the drop, and decaying harmonics outside the drop,

$$p^- = \sum_{n=0}^{\infty} p_n, \quad (2.37)$$

$$p^+ = \sum_{n=0}^{\infty} p_{-(n+1)}, \quad (2.38)$$

where p_n and $p_{-(n+1)}$ are solid spherical harmonics of degree n and $-(n+1)$, respectively, and are defined as

$$p_n = r^n \sum_{m=0}^n P_n^m(\cos \theta) (a_n^m \cos m\phi + b_n^m \sin m\phi), \quad (2.39)$$

$$p_{-(n+1)} = r^{-(n+1)} \sum_{m=0}^n P_n^m(\cos \theta) (c_n^m \cos m\phi + d_n^m \sin m\phi), \quad (2.40)$$

where $a_n^m(t)$, $b_n^m(t)$, $c_n^m(t)$ and $d_n^m(t)$ are again coefficients to be determined [Kim and Karrila, 2013, Happel and Brenner, 1965]. Again making use of (2.19), constant or growing harmonics (non-negative n) can be expressed as the contraction of an irreducible symmetric tensor of order n and the tensor product of n unit position vectors $\hat{\mathbf{r}}$,

$$p_n = r^n T_{i_1 i_2 i_3 \dots i_n}^{(n)} \hat{r}_{i_1} \hat{r}_{i_2} \hat{r}_{i_3} \dots \hat{r}_{i_n}, \quad (2.41)$$

and the decaying harmonics (negative n) are similarly given by

$$p_{-(n+1)} = r^{-(n+1)} T_{i_1 i_2 i_3 \dots i_n}^{(n)} \hat{r}_{i_1} \hat{r}_{i_2} \hat{r}_{i_3} \dots \hat{r}_{i_n}. \quad (2.42)$$

In particular, the first few modes, corresponding to $n = 0, 1, 2, -1, -2, -3$, are

$$\begin{aligned} p_0(t) &= m^p, & p_1 &= r \mathbf{d}^p \cdot \hat{\mathbf{r}}, & p_2 &= r^2 \mathbf{q}^p : \hat{\mathbf{r}} \hat{\mathbf{r}}, \\ p_{-1}(t) &= r^{-1} M^p & p_{-2} &= r^{-2} \mathbf{D}^p \cdot \hat{\mathbf{r}}, & p_{-3} &= r^{-3} \mathbf{Q}^p : \hat{\mathbf{r}} \hat{\mathbf{r}}. \end{aligned} \quad (2.43)$$

Here, $m^p(t)$ and $M^p(t)$ are scalars, $\mathbf{d}^p(t)$ and $\mathbf{D}^p(t)$ are vectors, and $\mathbf{q}^p(t)$ and $\mathbf{Q}^p(t)$ are traceless symmetric second order tensors. The solution for the velocity is sought as the sum of a homogeneous and particular solution. To obtain the homogeneous solution, $\mathbf{v}^{H\pm}$, we note that any smooth vector field can be written via the Helmholtz decomposition as the sum of a curl-free vector field $\nabla \phi^\pm$ and a divergence-free vector field $\nabla \times \mathbf{A}^\pm$. The incompressibility constraint $\nabla \cdot \mathbf{v}^{H\pm} = 0$ demands that $\phi^\pm$ be harmonic. In spherical geometry, it is convenient and general when working with spherical harmonics to take $\mathbf{A}^\pm = \chi^\pm \mathbf{r}$, in which case the homogeneous equation $\nabla^2 \mathbf{v}^{H\pm} = \mathbf{0}$ requires that $\chi^\pm$ also be harmonic. The homogeneous solution is then given by

$$\mathbf{v}^{H\pm} = \sum_{n=-\infty}^{\infty} \nabla \phi_n + \nabla \times (\chi_n \mathbf{r}), \quad (2.44)$$

where ϕ_n and χ_n are also solid spherical harmonics. These are defined in the same way as p_n , i.e.,

$$\phi_1 = r \mathbf{d}^\phi \cdot \hat{\mathbf{r}}, \quad \phi_2 = r^2 \mathbf{q}^\phi : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad \phi_{-2} = r^{-2} \mathbf{D}^\phi \cdot \hat{\mathbf{r}}, \quad \phi_{-3} = r^{-3} \mathbf{Q}^\phi : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad (2.45)$$

$$\chi_1 = r \mathbf{d}^\chi \cdot \hat{\mathbf{r}}, \quad \chi_2 = r^2 \mathbf{q}^\chi : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad \chi_{-2} = r^{-2} \mathbf{D}^\chi \cdot \hat{\mathbf{r}}, \quad \chi_{-3} = r^{-3} \mathbf{Q}^\chi : \hat{\mathbf{r}} \hat{\mathbf{r}}. \quad (2.46)$$

The ϕ_n terms represent a potential flow, while the χ_n terms represent a toroidal flow. The same solution can alternatively be obtained by writing $\mathbf{v}^{H\pm}$ as a general sum of vector spherical harmonics and eliminating terms by enforcing $\nabla \cdot \mathbf{v}^{H\pm} = 0$ and $\nabla^2 \mathbf{v}^{H\pm} = \mathbf{0}$. For the particular solution, $\mathbf{v}^{P\pm}$, an appropriate ansatz is

$$\mathbf{v}^{P\pm} = \sum_{n=-\infty}^{\infty} \alpha_n r^2 \nabla p_n + \beta_n \mathbf{r} p_n. \quad (2.47)$$

Enforcing the incompressibility constraint gives $2n\alpha_n + (n+3)\beta_n = 0$, and $\mu^\pm \nabla^2 \mathbf{v}^{P\pm} = \nabla p^\pm$ is satisfied when $2\mu^\pm(2n+1)\alpha_n + 2\mu^\pm\beta_n = 1$. Solving these linear equations for α_n and β_n gives

$$\alpha_n = \frac{n+3}{2\mu^\pm(2n+3)(n+1)}, \quad (2.48a)$$

$$\beta_n = -\frac{n}{\mu^\pm(2n+3)(n+1)}, \quad (2.48b)$$

which leads to the final solution

$$\begin{aligned} \mathbf{v}^\pm = \mathbf{v}^{H\pm} + \mathbf{v}^{P\pm} &= \sum_{n=-\infty}^{\infty} [\nabla \phi_n + \nabla \times (\chi_n \mathbf{r})] \\ &+ \sum_{n=-\infty, n \neq -1}^{\infty} \left[\frac{(n+3)r^2 \nabla p_n}{2\mu^\pm(2n+3)(n+1)} - \frac{n \mathbf{r} p_n}{\mu^\pm(2n+3)(n+1)} \right], \end{aligned} \quad (2.49)$$

as first obtained by Lamb [1932].

As for the pressure and potential, the fluid velocity involves growing harmonics

inside the drop and decaying harmonics outside the drop,

$$\mathbf{v}^- = \sum_{n=0}^{\infty} \nabla \phi_n + \nabla \times (\chi_n \mathbf{r}) + \frac{(n+3)r^2 \nabla p_n}{2\lambda(2n+3)(n+1)} - \frac{n \mathbf{r} p_n}{\lambda(2n+3)(n+1)}, \quad (2.50)$$

$$\begin{aligned} \mathbf{v}^+ = & \sum_{n=0}^{\infty} \nabla \phi_{-(n+1)} + \nabla \times (\chi_{-(n+1)} \mathbf{r}) \\ & + \sum_{n=1}^{\infty} \frac{(2-n)r^2 \nabla p_{-(n+1)}}{2n(2n-1)} + \frac{(n+1) \mathbf{r} p_{-(n+1)}}{n(2n-1)}. \end{aligned} \quad (2.51)$$

To determine which harmonics must be retained in (2.50) and (2.51), we construct the general hydrodynamic traction jump associated with Lamb's solution (2.49) and retain only those harmonics whose traction jumps are of the same form as the electric traction jumps in (2.32). The hydrodynamic stress tensor in each domain is

$$\boldsymbol{\tau}^{H\pm} = -p^{\pm} \mathbf{I} + \mu^{\pm} (\nabla \mathbf{v}^{\pm} + (\nabla \mathbf{v}^{\pm})^T), \quad (2.52)$$

and after substituting the pressures in (2.37) and (2.38) and the velocities in (2.50) and (2.51), the terms in the traction jump of the same form as (2.32) are

$$\begin{aligned} \mathbf{f}^H = & (m^p - M^p) \hat{\mathbf{r}} + \left(24\mathbf{Q}^{\phi} - 3\mathbf{Q}^p - 4\lambda\mathbf{q}^{\phi} + \frac{\mathbf{q}^p}{7} \right) : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}} \\ & + \left[\left(-16\mathbf{Q}^{\phi} + \mathbf{Q}^p - \frac{16\mathbf{q}^p}{21} - 4\lambda\mathbf{q}^{\phi} \right) \cdot \hat{\mathbf{r}} \right] \cdot (\mathbf{I} - \hat{\mathbf{r}} \hat{\mathbf{r}}) - 3\mathbf{D}^x \times \hat{\mathbf{r}}. \end{aligned} \quad (2.53)$$

Then, keeping only these harmonics, the pressures inside and outside the drop are

$$p^- = m^p + r^2 \mathbf{q}^p : \hat{\mathbf{r}} \hat{\mathbf{r}} \quad (2.54)$$

and

$$p^+ = r^{-1} M^p + r^{-3} \mathbf{Q}^p : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad (2.55)$$

respectively, while the associated velocities are

$$\mathbf{v}^- = r \mathbf{d}^x \times \hat{\mathbf{r}} + \mathbf{d}^{\phi} + 2r \mathbf{q}^{\phi} \cdot \hat{\mathbf{r}} + \frac{r^3 \mathbf{q}^p \cdot \hat{\mathbf{r}}}{21\lambda} \cdot (5\mathbf{I} - 2\hat{\mathbf{r}} \hat{\mathbf{r}}) \quad (2.56)$$

and

$$\mathbf{v}^+ = r^{-2} \mathbf{D}^\chi \times \hat{\mathbf{r}} + r^{-2} \frac{\mathbf{Q}^p : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}}}{2} + r^{-4} (\mathbf{Q}^\phi \cdot \hat{\mathbf{r}}) \cdot (2\mathbf{I} - 5\hat{\mathbf{r}} \hat{\mathbf{r}}). \quad (2.57)$$

Here, $\mathbf{d}^\phi$ is a uniform velocity field inside the drop and so exerts no hydrodynamic stress. Since an isolated drop does not experience translational motion, $\mathbf{d}^\phi$ vanishes when applying the kinematic boundary condition, but is retained in (2.56) for completeness. $\mathbf{d}^\chi$ and $\mathbf{D}^\chi$ are associated with solid body rotation, and are zero in the Taylor regime but become the leading-order components of the fluid velocity in the Quincke regime, since the solid body rotation is independent of $\lambda \gg 1$, while the straining flow scales as λ^{-1} . The terms involving $\mathbf{q}^p$, $\mathbf{q}^\phi$, $\mathbf{Q}^p$ and $\mathbf{Q}^\phi$ give rise to the straining flow, which is present in both the Taylor and Quincke regimes.

2.2.4 Kinematic boundary condition

In this section, we apply the kinematic boundary condition (2.8) and the no-slip condition (1.28) to find relations between the flow coefficients inside and outside the drop given in (2.56) and (2.57). Firstly, the no-slip condition (1.28) states that the velocity is continuous across the drop interface. In particular, applying continuity of velocity tangential to the interface and using orthogonality of spherical harmonics gives the relations

$$\mathbf{D}^\chi = \mathbf{d}^\chi, \quad \mathbf{0} = \mathbf{d}^\phi, \quad 2\mathbf{Q}^\phi = 2\mathbf{q}^\phi + \frac{5\mathbf{q}^p}{21\lambda}. \quad (2.58)$$

Secondly, substituting the expression for ξ given in (2.17) into the kinematic condition (2.8) yields

$$\mathbf{v}^- \cdot \hat{\mathbf{r}} - \delta \mathbf{v}^- \cdot \nabla f = \mathbf{v}^+ \cdot \hat{\mathbf{r}} - \delta \mathbf{v}^+ \cdot \nabla f = \delta \frac{\partial f}{\partial t}. \quad (2.59)$$

Since the solid body rotational flows $\mathbf{D}^\chi$ and $\mathbf{d}^\chi$ are independent of λ while the straining flow is assumed to be comparatively weak (scaling as λ^{-1}), the velocities $\mathbf{v}^\pm$ appearing in the nonlinear convective products $\mathbf{v}^\pm \cdot \nabla f$ include only $\mathbf{D}^\chi$ and

$\mathbf{d}^\chi$. According to (2.58), $\mathbf{d}^\chi = \mathbf{D}^\chi$, and hence $\delta \mathbf{v}^+ \cdot \nabla f = \delta \mathbf{v}^- \cdot \nabla f \equiv \delta \mathbf{v} \cdot \nabla f$. The kinematic condition (2.59) thus reads

$$\mathbf{v}^- \cdot \hat{\mathbf{r}} = \mathbf{v}^+ \cdot \hat{\mathbf{r}} = \delta \left(\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f \right), \quad (2.60)$$

where, using Einstein notation, the final term on the right hand side can be written as

$$\mathbf{v} \cdot \nabla f = \left(\varepsilon_{lkj} Q_{li}^f D_k^\chi + \varepsilon_{lki} Q_{lj}^f D_k^\chi \right) \hat{r}_i \hat{r}_j = \mathbf{Q}^{\chi f} : \hat{\mathbf{r}} \hat{\mathbf{r}}. \quad (2.61)$$

Here, ε_{lkj} and ε_{lki} are Levi-Civita tensors, and

$$Q_{ij}^{\chi f} = \varepsilon_{lkj} Q_{li}^f D_k^\chi + \varepsilon_{lki} Q_{lj}^f D_k^\chi. \quad (2.62)$$

In the Taylor regime, this term has no effect since there is no rotational flow. In the Quincke regime, it acts to reduce the drop deformation by convecting away the shape distortions caused by the electric stresses and the straining flow. Substituting the fluid velocities given in (2.56) and (2.57), the drop shape given in (2.17), and $\mathbf{v} \cdot \nabla f$ given in (2.61) into the kinematic condition (2.60) yields

$$2\mathbf{q}^\phi + \frac{1}{7\lambda} \mathbf{q}^p = \frac{1}{2} \mathbf{Q}^p - 3\mathbf{Q}^\phi = \delta \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right). \quad (2.63)$$

Combining (2.63) with the relations given in (2.58) allows us to express the flow coefficients $\mathbf{Q}^\phi$, $\mathbf{q}^\phi$ and $\mathbf{q}^p$ in terms of $\mathbf{Q}^p$ and $\partial \mathbf{Q}^f / \partial t + \mathbf{Q}^{\chi f}$:

$$\mathbf{Q}^\phi = \frac{1}{6} \mathbf{Q}^p - \frac{\delta}{3} \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right), \quad (2.64a)$$

$$\mathbf{q}^p = \frac{7\lambda}{2} \mathbf{Q}^p - \frac{35\lambda\delta}{2} \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right), \quad (2.64b)$$

$$\mathbf{q}^\phi = -\frac{1}{4} \mathbf{Q}^p + \frac{7\delta}{4} \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right). \quad (2.64c)$$

With these relations, we can rewrite the hydrodynamic traction (2.53) as

$$\llbracket \mathbf{f}^H \rrbracket = \llbracket \boldsymbol{\tau}^H \rrbracket \cdot \hat{\mathbf{r}} = p^H \hat{\mathbf{r}} + \mathbf{Q}_{\hat{\mathbf{r}}}^H : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}} + (\mathbf{Q}_{\hat{\mathbf{t}}}^H \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}} \hat{\mathbf{r}}) + \mathbf{T}^H \times \hat{\mathbf{r}}, \quad (2.65)$$

where

$$p^H = m^p - M^p, \quad (2.66a)$$

$$\mathbf{Q}_{\hat{\mathbf{r}}}^H = \frac{2+3\lambda}{2}\mathbf{Q}^p - \frac{16+19\lambda}{2}\delta\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (2.66b)$$

$$\mathbf{Q}_{\hat{\mathbf{t}}}^H = -\frac{5(1+\lambda)}{3}\mathbf{Q}^p + \frac{16+19\lambda}{3}\delta\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (2.66c)$$

$$\mathbf{T}^H = -3\mathbf{D}^\chi. \quad (2.66d)$$

2.2.5 Stress balance

We now apply the dynamic boundary condition (2.13), enforcing a balance between the electric, hydrodynamic and capillary stresses (2.32) and (2.65). Substituting the expressions for the normal vector and curvature of the interface given in (2.22) into the right-hand side of (2.13) yields

$$\llbracket \mathbf{f}^E \rrbracket + \llbracket \mathbf{f}^H \rrbracket = \frac{2}{\text{Ca}_E}\hat{\mathbf{r}} - \frac{4}{\text{Ca}_E}\delta(\mathbf{Q}^f \cdot \mathbf{r}) \cdot (\mathbf{I} - 2\hat{\mathbf{r}}\hat{\mathbf{r}}). \quad (2.67)$$

In the radial direction, we retain $\mathcal{O}(\delta)$ terms to capture the perturbation of the drop shape associated with the electric and hydrodynamic stresses calculated in the preceding subsections. Considering the radial component of (2.67), we obtain a balance of isotropic pressures and quadrupolar stresses, which via the orthogonality of spherical harmonics yields two equations; one for the pressures,

$$p^H = -p^E + \frac{2}{\text{Ca}_E}, \quad (2.68)$$

and one for the quadrupolar stresses,

$$\mathbf{Q}_{\hat{\mathbf{r}}}^H = \frac{4\delta}{\text{Ca}_E}\mathbf{Q}^f - \mathbf{Q}_{\hat{\mathbf{r}}}^E. \quad (2.69)$$

In order for the capillary stresses to balance the $\mathcal{O}(1)$ electric and hydrodynamic stresses, we require $\delta \propto \text{Ca}_E$, and for consistency with previous works on the

subject, including that of Taylor [1966], we choose

$$\delta = \frac{3\text{Ca}_E}{4(1+2S)^2}. \quad (2.70)$$

Next, examining the tangential components of (2.67) we have a balance of quadrupolar stresses and torques, which again yields two equations; one for the quadrupolar stresses,

$$\mathbf{Q}_{\hat{\mathbf{t}}}^H = -\mathbf{Q}_{\hat{\mathbf{t}}}^E, \quad (2.71)$$

and one for the torques,

$$\mathbf{T}^H = -\mathbf{T}^E. \quad (2.72)$$

Substituting the expressions for the quadrupolar hydrodynamic stresses (2.66b) and (2.66c) into (2.69) and (2.71) gives an expression for the flow coefficients in $\mathbf{Q}^p$ and a system of ODEs for the shape coefficients $\mathbf{Q}^f$, given by

$$\mathbf{Q}^p = \frac{2}{3+2\lambda} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}^f + \mathbf{Q}_{\hat{\mathbf{r}}}^E + \frac{3}{2} \mathbf{Q}_{\hat{\mathbf{t}}}^E \right] \quad (2.73)$$

and

$$\frac{\partial \mathbf{Q}^f}{\partial t} = \frac{10(1+\lambda)}{\delta(16+19\lambda)(3+2\lambda)} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}^f + \mathbf{Q}_{\hat{\mathbf{r}}}^E + \frac{6+9\lambda}{10(1+\lambda)} \mathbf{Q}_{\hat{\mathbf{t}}}^E \right] - \mathbf{Q}^{\chi f}. \quad (2.74)$$

Note that the shape coefficients in $\mathbf{Q}^f$ are coupled to one another through $\mathbf{Q}^{\chi f}$. Substituting the electric and hydrodynamic torques given in (2.33d) and (2.66d) into (2.72), we find

$$\mathbf{D}^\chi = \frac{1}{2} \mathbf{P} \times \hat{\mathbf{E}}_0. \quad (2.75)$$

At this point, the flow fields and drop shape are known in terms of the dipole moment $\mathbf{P}$, which will be determined in the following section via application of the transport equation (2.15).

2.2.6 Charge transport

The dipole moment evolves according to the dimensionless charge transport equation (2.15) at the interface of the drop. Substituting the fluid velocity from either (2.56) or (2.57), the charge density (2.35) and the radial current jump (2.34) into (2.15) yields an evolution equation for the dipole moment $\mathbf{P}$,

$$\begin{aligned} \frac{d\mathbf{P}}{dt} = & -\frac{1+2S}{S(2+Q)\text{Re}_E}\mathbf{P} - \frac{S-1}{S(2+Q)\text{Re}_E}\hat{\mathbf{E}}_0 + \mathbf{D}^\chi \times \left(\frac{1-Q}{2+Q}\hat{\mathbf{E}}_0 + \mathbf{P} \right) \\ & + \left(\frac{1-Q}{2+Q}\hat{\mathbf{E}}_0 + \mathbf{P} \right) \cdot \left[\frac{1}{5}\mathbf{Q}^p - \frac{6}{5}\delta \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right) \right]. \end{aligned} \quad (2.76)$$

In the limit $\text{Re}_E \rightarrow 0$, charge convection and relaxation are much slower than the interfacial charging by Ohmic currents. Under these circumstances, the dipole moment does not evolve according to (2.76) and instead adjusts instantaneously to its equilibrium value, given by

$$\mathbf{P} = \frac{1-S}{1+2S}\hat{\mathbf{E}}_0. \quad (2.77)$$

In this case, Quincke rotation is not possible since the electric torque is zero, as is evident from (2.75).

2.2.7 Model summary

We have thus derived a system of nonlinear coupled ODEs consisting of (2.74) and (2.76), which we summarise as

$$\frac{d}{dt} \begin{bmatrix} \mathbf{P} \\ \mathbf{Q}^f \end{bmatrix} = \mathcal{F}(\mathbf{P}, \mathbf{Q}^f; \text{Ca}_E, \text{Re}_E, Q, S, \lambda). \quad (2.78)$$

The nonlinearities associated with charge convection and the convective product $\mathbf{v} \cdot \nabla f$ make it unfeasible to find closed-form solutions to (2.78). It may be possible to obtain series solutions valid for early times, but this is not attempted in this thesis. Instead, we solve the system numerically with the methods introduced in §1.6. Transient solutions are obtained using the RK4 scheme described in §1.6.1

with initial conditions corresponding to a spherical drop,

$$\mathbf{Q}^f(0) = \mathbf{0}, \quad (2.79)$$

and zero charge density, i.e.,

$$q(\mathbf{r}, 0) = (1 - Q)\hat{\mathbf{E}}_0 \cdot \hat{\mathbf{r}} + (2 + Q)\mathbf{P}(0) \cdot \hat{\mathbf{r}} = 0, \quad (2.80)$$

which gives

$$\mathbf{P}(0) = \frac{Q - 1}{2 + Q}\hat{\mathbf{E}}_0. \quad (2.81)$$

To induce Quincke rotation, it is necessary to apply an infinitesimal perturbation to the initial condition for the dipole moment in a direction perpendicular to $\hat{\mathbf{E}}_0$. With no loss of generality, we perturb the dipole moment in the x direction, and analyse the ensuing behaviour of the drop in the xz plane. Steady solutions are obtained using both the RK4 scheme as well as the pseudo-arclength continuation algorithm described in §1.6.2, which uses the MATLAB solver `fsolve` as a corrector algorithm at each step [The MathWorks, Inc., 2024] and is able to capture unstable steady solutions.

In both the Taylor and Quincke regimes, the dynamics are governed by the system of ODEs (2.78). However, in the Taylor regime, the dipole moment is parallel to the applied field. Therefore, $\mathbf{T}^E = \mathbf{T}^H = \mathbf{D}^\chi = \mathbf{0}$ and $\mathbf{Q}^{\chi f} = \mathbf{0}$. Furthermore, due to the axisymmetry of the drop, $\mathbf{Q}^f$, $\mathbf{Q}^p$, $\mathbf{q}^p$, $\mathbf{Q}^\phi$, $\mathbf{q}^\phi$, $\mathbf{Q}_\mathbf{f}^E$ and $\mathbf{Q}_\mathbf{t}^E$ are all diagonal traceless tensors. Given that, for example, $Q_{xx}^f = Q_{yy}^f = -1/2Q_{zz}^f$ for an electric field applied in the z direction (the other mentioned tensors exhibit the same symmetry), each tensor has only one independent component. Therefore, $\mathbf{Q}^f$ can be fully described by just Q_{zz}^f , for example, and the system (2.78) could be reduced to a pair of scalar ODEs for P_z and Q_{zz}^f .

2.3 Results

In this section, we present results obtained from the model described in §2.2. First, we discuss the effect of charge convection on the deformation of drops of each of the three classes (prolate A, prolate B, and oblate) in the Taylor regime. Second, we discuss the Quincke regime, focusing in particular on the hysteretic onset of Quincke rotation in drops.

2.3.1 Charge convection

As discussed in §1.3.3, previous authors [Feng, 1999, Fernández, 2013, Das and Saintillan, 2017b] have shown that retaining charge convection increases the deformation of prolate drops and decreases the deformation of oblate drops in the Taylor regime. Here we show that the model described in the previous sections is consistent with these findings, and we delineate the differences between the effects of convection on prolate A and prolate B drops. In this thesis, we quantify drop deformation using the parameter D_Q , defined as

$$D_Q = \frac{L - B}{L + B}, \quad (2.82)$$

where L and B are the longest and shortest axes of the drop [Das and Saintillan, 2021]. In the Taylor regime, where the drop assumes a spheroidal shape, L and B are parallel and perpendicular to the applied field, respectively, or vice versa. In the Quincke regime, the drop adopts a steady tilted shape with its longest axis misaligned with the z axis (in the case of a prolate B drop) or the x axis (in the case of an oblate drop) by an angle which we denote θ_T . The deformation parameter D_Q can be written as

$$D_Q = \frac{1}{2}\delta |Q_{xx}^f - Q_{zz}^f| \sqrt{1 + \left(\frac{2Q_{xz}^f}{Q_{xx}^f - Q_{zz}^f} \right)^2} + \mathcal{O}(\delta^2). \quad (2.83)$$

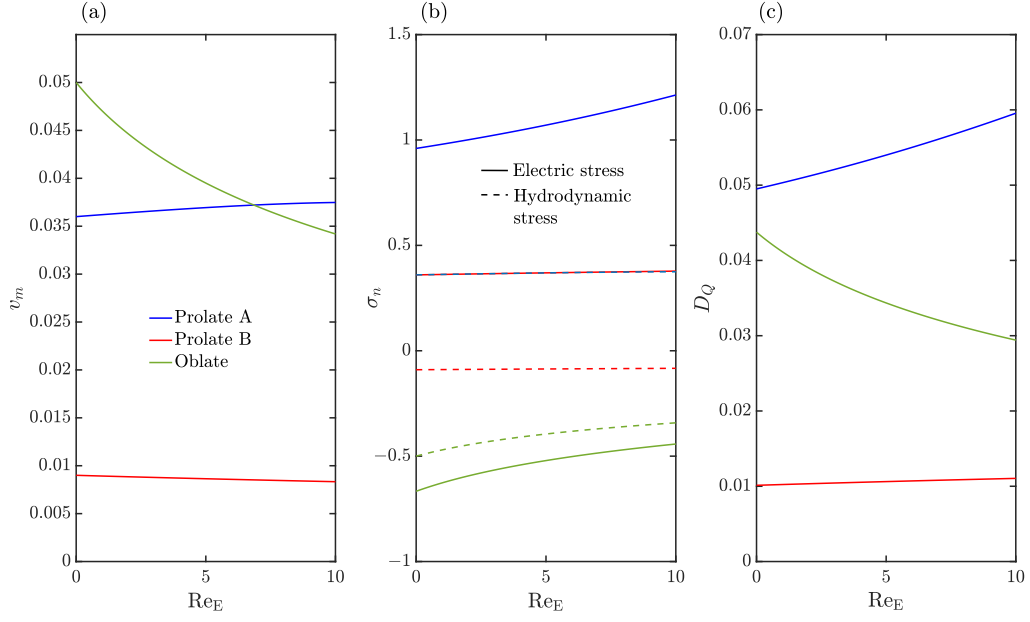


Figure 2.1: (a) The maximum fluid velocity at the drop surface v_m , (b) the normal electric and hydrodynamic stresses, and (c) the deformation of a prolate A drop with $S = 1/3$, $Q = 1$ (blue lines), a prolate B drop with $S = 1/3$, $Q = 7/2$ (red lines), and an oblate drop with $S = 1$, $Q = 2$ (green lines). The other relevant parameters are $Ca_E = 0.2$ and $\lambda = 1$. In (b), the solid lines correspond to the electric stresses while the dashed lines correspond to the hydrodynamic stresses. Note that the line representing the hydrodynamic stress on the prolate A drop and the line representing the electric stress on the prolate B drop lie almost on top of one another.

Note that D_Q is always positive, unlike the more commonly used parameter

$$D = (l_{\parallel} - l_{\perp}) / (l_{\parallel} + l_{\perp}), \quad (2.84)$$

where $l_{\parallel}$ and $l_{\perp}$ are the lengths of the axes of the drop parallel and perpendicular to the applied field, respectively. In the Taylor regime, $Q_{xz}^f = 0$ so $D_Q = \frac{1}{2}\delta|Q_{xx}^f - Q_{zz}^f|$, in which case $D_Q = |D|$. First, Figure 2.1 shows (a) the maximum fluid velocity at the drop surface, (b) the normal electric and hydrodynamic stresses, and (c) the deformation of a prolate A drop with $S = 1/3$, $Q = 1$ (blue lines), a prolate B drop with $S = 1/3$, $Q = 7/2$ (red lines), and an oblate drop with $S = 1$, $Q = 2$ (green lines) as functions of Re_E . The other relevant parameters are $Ca_E = 0.2$ and $\lambda = 1$. In Figure 2.1(b), the solid lines correspond to the electric stresses while the dashed lines correspond to the hydrodynamic stresses.

The maximum fluid velocity shown in Figure 2.1(a) is given by

$$v_m = \frac{1}{4}|Q_{zz}^p|, \quad (2.85)$$

and the normal electric and hydrodynamic stresses shown in Figure 2.1(b) are given by $Q_{\hat{r},zz}^E$ and $Q_{\hat{r},zz}^H$, respectively. Consistent with the results of previous work [Feng, 1999, Fernández, 2013, Das and Saintillan, 2017b], the present model predicts that in the case of prolate A drops, the polarisation of the drop is increased as Re_E is increased because the flow convects charge from the equator to the poles (refer back to Figure 1.4 for a qualitative illustration of the flow fields and shapes of each of the three drop classes). This, in turn, increases the strength of the induced flow field and both the electric and hydrodynamic normal stresses, resulting in greater deformation. Conversely, in the case of oblate drops, the polarisation of the drop (i.e., the maximum magnitude of q) is weakened as Re_E is increased because charge is convected from the poles to the equator. The induced fluid flow and the electric and hydrodynamic stresses are weakened accordingly, and the deformation is decreased. The effect of convection on the behaviour of prolate B drops is much smaller than it is on the other two classes of drop. Charge is again convected from the poles to the equator, weakening the polarisation. The fluid flow and hydrodynamic stress are slightly weakened, but the electric stress is slightly strengthened. The increase in the electric stress is larger than the decrease in the hydrodynamic stress, so the deformation increases, but again, the effect is small compared to the other two classes of drop. Figure 2.2 shows the transient deformation of (a) a prolate A, (b) a prolate B drop, and (c) an oblate drop, with the same values of S and Q as in Figure 2.1. Black solid lines correspond to zero charge convection ($\text{Re}_E = 0$), while the green dash-dotted lines, red dashed lines and blue dotted lines correspond to $\text{Re}_E = 0.5$, $\text{Re}_E = 1$, and $\text{Re}_E = 2$, respectively. In each case, $\text{Ca}_E = 0.2$ and $\lambda = 10$. Insets show an enlarged view of the steady state deformation in each case, while the lower inset in Figure 2.2(c) shows an enlarged view of the deformation at the beginning of the simulation. For each class of drops, the present model pre-

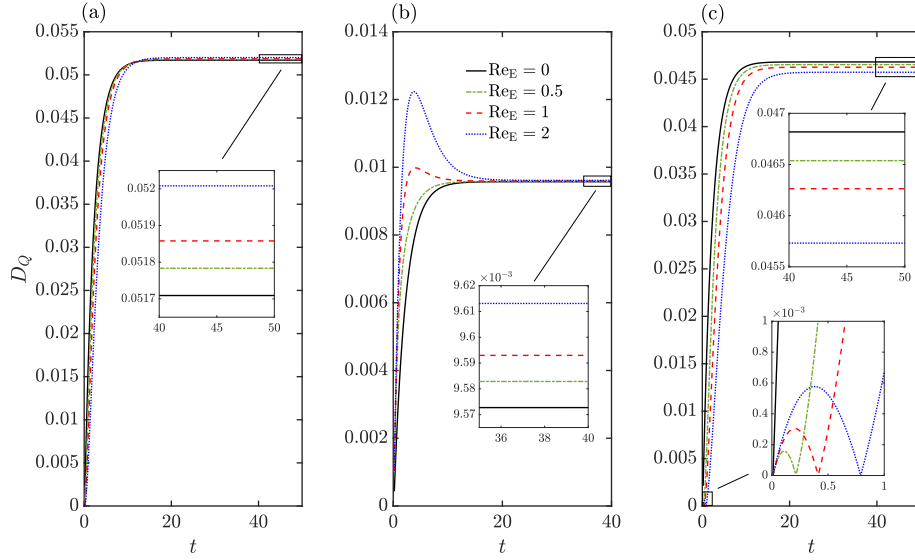


Figure 2.2: Transient deformation of (a) a prolate A drop with $S = 1/3$, $Q = 1$, (b) a prolate B drop with $S = 1/3$, $Q = 7/2$, and (c) an oblate drop with $S = 1$, $Q = 2$. Black solid lines correspond to zero charge convection ($\text{Re}_E = 0$), while the green dash-dotted lines, red dashed lines and blue dotted lines correspond to $\text{Re}_E = 0.5$, $\text{Re}_E = 1$, and $\text{Re}_E = 2$, respectively. In each case, $\text{Ca}_E = 0.2$ and $\lambda = 10$. Insets show an enlarged view of the steady state deformation in each case.

dicts that the deformation approaches its steady value monotonically with no overshoot when charge convection is absent. When convection is included, the deformation of prolate A drops still increases monotonically, but the time it takes for the steady deformation to be reached increases. When convection is relatively weak ($\text{Re}_E = 0.5$), the deformation of prolate B drops is again monotonic, and the time it takes for the steady deformation to be reached decreases. However, when convection is stronger ($\text{Re}_E = 1$ and $\text{Re}_E = 2$), there is an overshoot in the deformation of prolate B drops. The deformation of oblate drops is non-monotonic when convection is included. The inset shows an initial increase in the deformation, before it decreases again to zero, before finally increasing again towards its steady value. In fact, during this early stage of the deformation, the drop briefly adopts a prolate shape, before the deformation reverses and the drop returns to the spherical shape before ultimately becoming oblate, consistent with the experimental findings of Lanauze et al. [2015]. As explained by Das and Saittilan [2017b], this behaviour occurs when, in addition to charge convection, both

ϵ^+/ϵ_0	ϵ^-/ϵ_0	σ^+	σ^-	μ^+	μ^-	γ	a
5.3	3	4.5×10^{-11} S/m	1.23×10^{-12} S/m	0.69 Pa/s	9.73 Pa/s	4.5×10^{-3} N/m	0.9×10^{-3} m

Table 2.1: Parameter values of Salipante and Vlahovska [2010]. $\epsilon_0 = 8.8542 \times 10^{-12}$ F/m is the permittivity of free space.

transient charge relaxation and transient deformation are retained in the charge transport equation (2.76) and the kinematic condition (2.59), respectively. Alternatively, the work of Lanauze et al. [2013] showed that the behaviour may also occur when transient fluid inertia is retained, which may be important for large drops or relatively inviscid fluids.

2.3.2 Hysteresis

It is well known that the onset of Quincke rotation of an isolated solid sphere corresponds to a supercritical pitchfork bifurcation [Turcu, 1987, Jones, 1984] at a critical electric field strength. For an isolated deforming drop, the behavior is slightly more complicated. Experiments by Salipante and Vlahovska [2010] revealed the existence of hysteresis in the onset of rotation for a drop, which becomes more prominent as the viscosity ratio is decreased or drop size is increased. Hysteresis has also recently been captured in the theoretical model of Peng and Schnitzer [2025]. This behaviour corresponds to the supercritical pitchfork bifurcation seen in solid spheres being replaced by a subcritical pitchfork bifurcation followed by two saddle node bifurcations in the case of drops. Figure 2.3(a) displays a bifurcation diagram in which solid blue lines denote stable solutions, while red dashed lines denote unstable solutions. Figure 2.3(b) displays the corresponding hysteresis loop, in which the green solid and pink dashed lines mark the angular velocity of the drop in increasing and decreasing electric fields, respectively. We use the parameter values of Salipante and Vlahovska [2010], given in Table 2.1. For the electric field strengths used in Figure 2.3, Ca_E ranges between 0.79 and 0.8, and Re_E ranges between 5.9 and 6.

In particular, Figure 2.3 shows that increasing the electric field strength gradually from zero eventually causes the angular velocity of the drop, $\Omega = |\mathbf{D}^\chi|$, to jump discontinuously from the stable zero-rotation solution branch to a stable

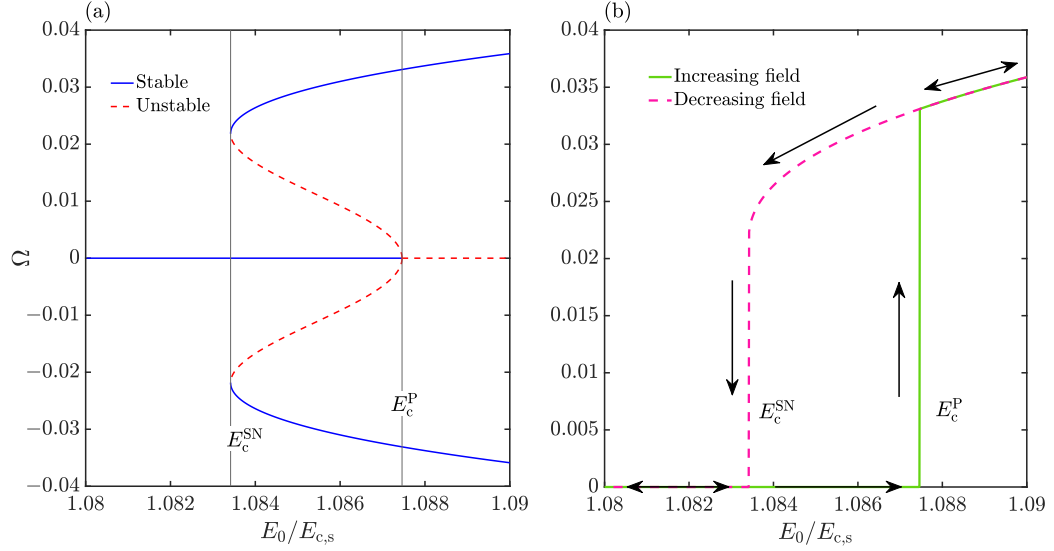


Figure 2.3: (a) Bifurcation diagram and (b) corresponding hysteresis loop for the onset of rotation in an isolated drop. In (a), the blue solid lines denote stable solutions, while the red dashed lines denote unstable ones. In (b), the green solid line marks the angular velocity of the drop when the field is increased, and the pink dashed line marks the angular velocity of the drop when the field is subsequently decreased.

nonzero rotation solution branch at the critical electric field strength of the pitchfork bifurcation (denoted by E_c^P , and indicated with a vertical line). However, if the electric field strength is then decreased, the rotation persists until the critical electric field strength of the saddle node bifurcations is reached (denoted by E_c^{SN} , and indicated with another vertical line), causing the angular velocity to discontinuously jump back to the stable zero rotation solution branch [Strogatz, 2015]. Figure 2.4 shows the streamlines in and around the drop on (a) the axisymmetric zero-rotation branch, (b) on the unstable rotation branch, and (c) on the stable rotation branch. Figure 2.4(d) shows the charge distribution on the drop as a function of the scaled polar angle θ/π in each case. Close to the stagnation points in Figure 2.4(b), streamlines can be seen to pass through the interface. However, note that in the present model the steady fluid flow is that produced by a spherical drop, and so does indeed penetrate the perturbed interface displayed in the figure.

Figure 2.5 displays the scaled critical field strengths for the pitchfork bifurcation E_c^P and saddle node bifurcations E_c^{SN} as functions of the viscosity ratio for

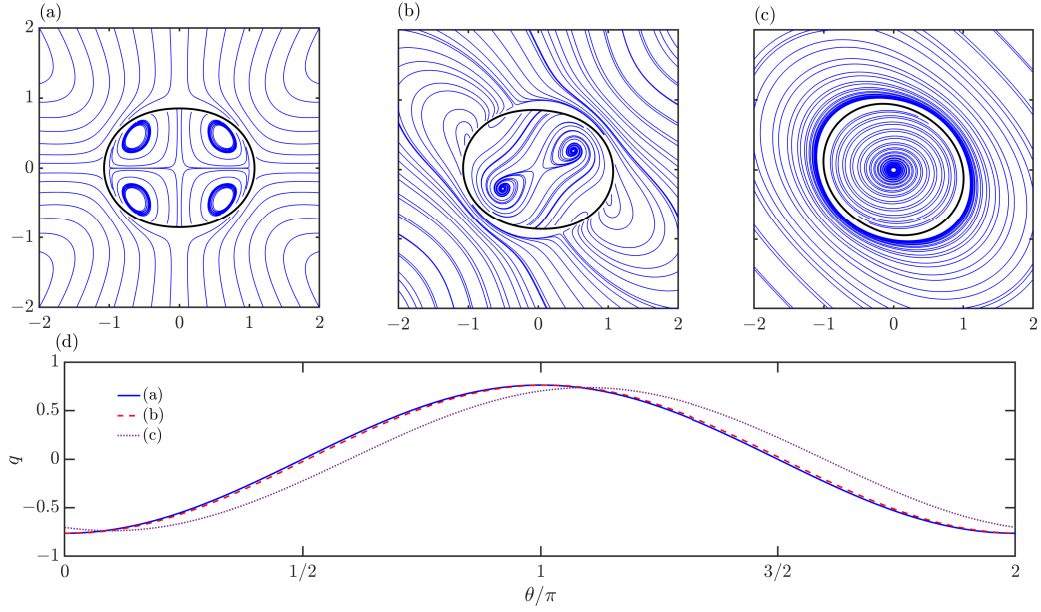


Figure 2.4: Streamlines in and around a drop on (a) the axisymmetric zero-rotation branch, (b) on the unstable rotation branch, and (c) on the stable rotation branch. (d) shows the charge distribution on the drop as a function of the scaled polar angle θ/π in each case.

two different drop sizes. The other material parameters are those in Table 2.1. Dotted and solid lines of the same color correspond to E_c^{SN} and E_c^{P} , respectively, for the same drop-fluid system. The model of Das and Saintillan [2021] correctly predicts that the hysteresis becomes more prominent (i.e., the hysteresis window between the pitchfork and saddle node bifurcations widens) as the drop size is increased. A large drop, $a = 2.3 \text{ mm}$ (red lines), exhibits hysteresis across the entire range of viscosity ratios. Further, the hysteresis becomes slightly more prominent as the viscosity ratio is decreased, in agreement with the experimental findings of Salipante and Vlahovska [2010]. However, for the smaller drop, the model incorrectly predicts that the hysteresis should appear only for more viscous drops. Note that below $\lambda \approx 10$, no hysteresis is seen for the $a = 0.9 \text{ mm}$ drop. This discrepancy is likely a result of the limitations of the assumptions of large λ and small Ca_{E} (using the other parameters given in Table 2.1, Ca_{E} is around 1.1 for a drop of radius $a = 0.9 \text{ mm}$ in a field strength of $E_0 = 1.5E_{\text{c,s}}$). It is remarkable then, but likely coincidental, that the model captures the correct trend for the larger drops (Ca_{E} is close to 7 for a drop of radius $a = 2.3 \text{ mm}$ in a field strength

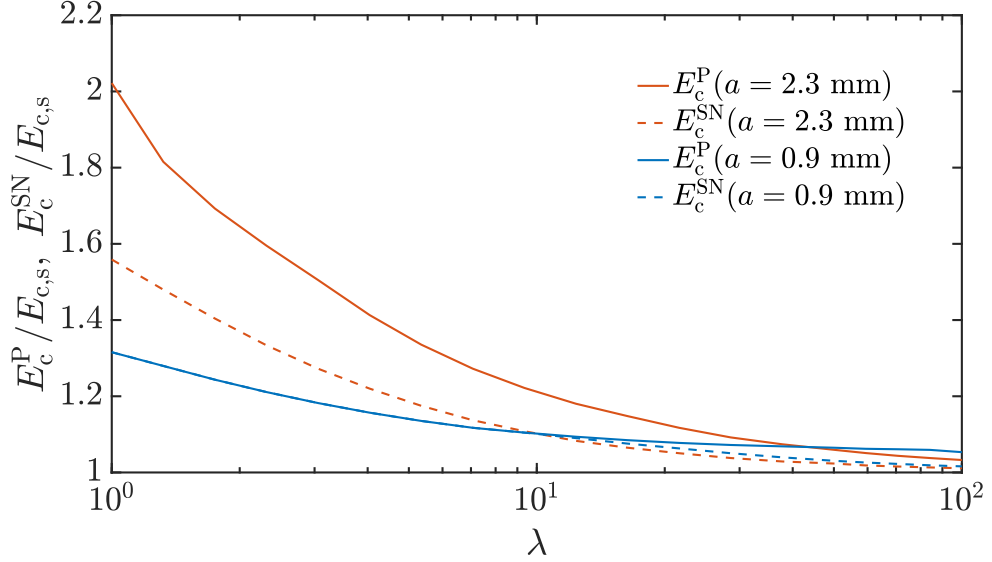


Figure 2.5: Scaled critical field strengths for the pitchfork bifurcation E_c^P and saddle node bifurcations E_c^{SN} of an isolated drop as functions of the viscosity ratios, for two different drop sizes. Dotted lines denote the critical field strength of the saddle node bifurcations E_c^{SN} and solid lines denote the critical field strength of the subcritical pitchfork bifurcation E_c^P .

of $E_0 = 2E_{c,s}$). We note that the hysteresis is found to occur only for deforming drops, and more specifically as a result of the convective product $\mathbf{Q}^{xf}$ as defined in (2.61). The recent theoretical work of Peng and Schnitzer [2025] also captured hysteresis, but in that work it is explained by the presence of charge shocks at the equator. However, the model of Das and Saintillan [2021] does not account for such shocks, while the model of Peng and Schnitzer [2025] does not account for deformation, suggesting that there are at least two distinct physical mechanisms that can lead to hysteresis. Given that the role of $\mathbf{Q}^{xf}$ is to reduce deformation after rotation begins, we hypothesise that the hysteresis in the present model occurs because the drop deformation is greater on the axisymmetric zero-rotation solution branch than on the rotational solution branch. An axisymmetric drop requires a stronger applied field to induce rotation than that required to sustain the rotation of a drop which is less deformed than the axisymmetric drop.

Figure 2.6 displays the dependence of the angular velocity of a drop on the scaled electric field strength for two different pairs of λ and a that correspond to those studied by Salipante and Vlahovska [2010]. The viscosity ratio is adjusted

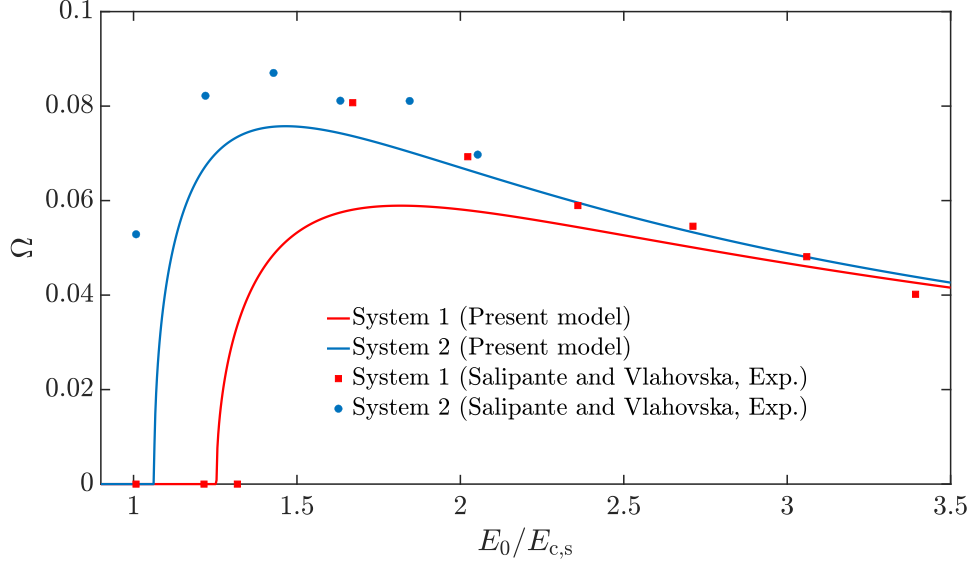


Figure 2.6: Angular velocity of an isolated drop as a function of the scaled electric field strength for two sets of material parameters: System 1, for which $\lambda = 1.4$ and $a = 0.76$ mm (red line and red squares); and System 2, for which $\lambda = 14$ and $a = 0.565$ mm (blue line and blue dots).

by varying μ^- , and the other material parameters are those in Table 2.1. For System 1 ($\lambda = 1.4$ and $a = 0.76$ mm), indicated by the red line and squares, the model underestimates the experimentally observed angular velocities in most instances. The sharp jump between the third and fourth experimental data points suggests possible hysteresis, but this is not captured by the model. The agreement with the experimental results is better for System 2 ($\lambda = 14$ and $a = 0.565$ mm), indicated by the blue line and dots, which has a higher viscosity ratio and lower electric capillary number. However, it should be noted that the assumptions that $\text{Re}_E = \mathcal{O}(1)$ and $\text{Ca}_E \ll 1$ fail as the electric field strength is increased through the range used in Figure 2.6. In particular, between $E_0/E_{c,s} = 0.9$ and at $E_0/E_{c,s} = 3.5$, Re_E varies between 4.1 and 62.3, and Ca_E ranges between 0.5 and 7 for System 1, and between 0.3 and 5.2 for System 2. Given this, the agreement with the experimental results is better than might be expected, but should be interpreted with caution. The experimental results suggest that a high-viscosity drop has a critical electric field strength which is less than that of a solid sphere, which is corroborated by the numerical simulations of Das and Saintillan

[2017c] and Firouznia et al. [2023], but is not captured by the present model. We speculate that retaining higher order charge multipoles may help to resolve this discrepancy.

2.4 Critical field for rotation of a spherical drop

As already discussed, it is impractical to solve the system of ODEs (2.78) analytically, but steady solutions may be obtained after invoking certain simplifications. At steady state, the charge transport equation reduces to

$$\begin{aligned} \mathbf{0} = & -\frac{S-1}{1+2S}\hat{\mathbf{E}}_0 - \mathbf{P} + \mathbf{D}^\times \times \left(\frac{1-Q}{2+Q}\hat{\mathbf{E}}_0 + \mathbf{P} \right) \\ & + \frac{1}{5} \left(\frac{1-Q}{2+Q}\hat{\mathbf{E}}_0 + \mathbf{P} \right) \cdot (\mathbf{Q}^p - 6\delta\mathbf{Q}^{\chi f}). \end{aligned} \quad (2.86)$$

The term involving $\mathbf{Q}^{\chi f}$ couples the dipole moment to the drop shape and generally precludes a closed form solution. However, if the drop is assumed to remain spherical, then $\mathbf{Q}^{\chi f} = \mathbf{0}$ and the straining flow $\mathbf{Q}^p$ is known in terms of the dipole moment. Under these circumstances, two ODEs for the two components of the dipole moment can be decoupled and steady solutions can be obtained. Specifically, by combining the x and z components of the transport equation we arrive at the relatively simple result

$$P_z = \frac{Q-1}{2+Q} - \beta \frac{1+2S}{S(2+Q)\text{Re}_E}, \quad (2.87)$$

where

$$\beta = \frac{2 + \frac{118}{25}\lambda^{-1} + \frac{68}{25}\lambda^{-2} + \frac{24}{25}(\lambda^{-1} + \lambda^{-2})\frac{SQ-1}{1+2S}}{1 + \frac{56}{25}\lambda^{-1} + \frac{748}{625}\lambda^{-2}}. \quad (2.88)$$

In addition,

$$P_x = \pm \sqrt{\frac{(SQ-1) \left(6 + \frac{282}{25}\lambda^{-1} + \frac{132}{25}\lambda^{-2} \right)}{S(2+Q)^2\text{Re}_E \left(1 + \frac{56}{25}\lambda^{-1} + \frac{748}{625}\lambda^{-2} \right)} - \left(\frac{1+2S}{S(2+Q)\text{Re}_E} \beta \right)^2}, \quad (2.89)$$

and using that $D^\chi = -P_x/2$, the angular velocity can be written as

$$D^\chi = \mp \frac{\beta(1+2S)}{2S(2+Q)\text{Re}_E} \sqrt{\left(\frac{E_0}{E_{c,d}^*}\right)^2 - 1}, \quad (2.90)$$

where $E_{c,d}^*$ is the critical field for rotation of an isolated spherical drop, given by

$$E_{c,d}^* = \sqrt{\frac{\mu^+(2+Q)(1+2S)\beta^2\left(\frac{1}{6} + \frac{28}{75}\lambda^{-1} + \frac{374}{1875}\lambda^{-2}\right)}{\epsilon^+\tau_{MW}(SQ-1)\left(1 + \frac{47}{25}\lambda^{-1} + \frac{22}{25}\lambda^{-2}\right)}}, \quad (2.91)$$

which, in the limit $\lambda \rightarrow \infty$, reduces to the classic solution derived by Jones [1984] for a solid sphere (1.60), and was not derived in Das and Saintillan [2021]. Figure 2.7 shows the scaled critical field strengths for Quincke rotation of a deforming drop (specifically E_c^{SN} , denoted by the solid line) and a spherical drop (denoted by the dotted line) as functions of λ using the material parameters in Table 2.1. The line for the spherical drop is obtained using (2.91), while that for the deforming drop is obtained using the linear stability analysis described by Das and Saintillan [2021]. The details of the linear stability analysis are given in §3.3.1, in which an extended version applicable to a surfactant-laden drop will be introduced. As expected, the curves for both the deforming and the spherical drop converge to $E_0/E_{c,s} = 1$ as λ grows large. At lower values of λ , the critical field for rotation of a spherical drop is lower than that of a deformed drop across the whole range of λ shown. Curiously, the critical field for the deforming drop increases substantially more quickly than does that for the spherical drop as λ is decreased from around $\lambda = 10^3$ to $\lambda = 10^2$, but further decreases in λ have a similar effect on the critical fields for rotation of both drops.

2.5 Conclusions

In this chapter, we have described the phenomenological model of Das and Saintillan [2021] for an isolated leaky dielectric drop exposed to a uniform DC electric field. We have derived and numerically solved a system of ODEs governing the dipole moment and shape of the drops, and have reported results on the be-

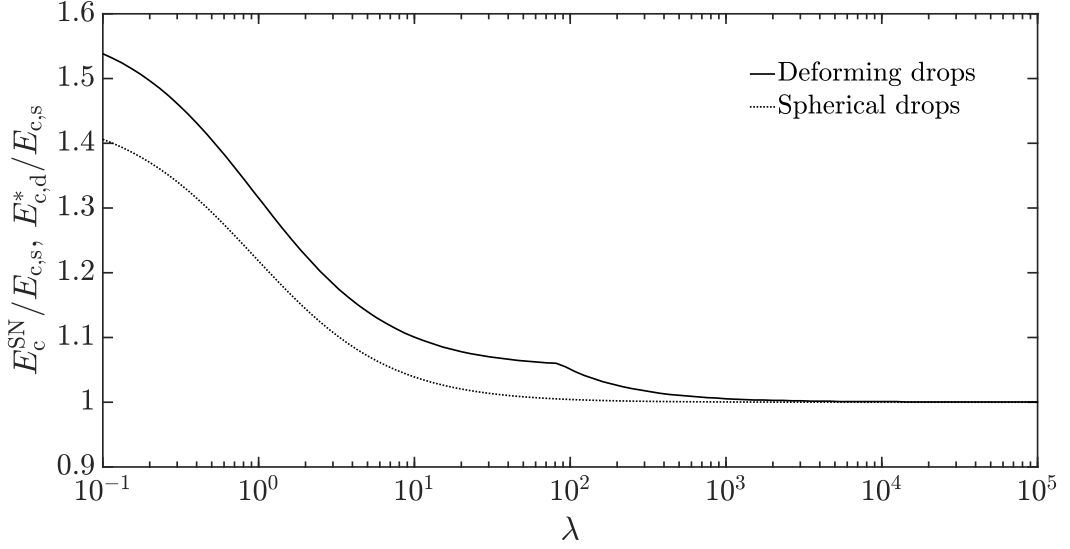


Figure 2.7: Scaled critical field strengths for Quincke rotation for a deforming drop (solid line) and a spherical drop (dotted line) as functions of λ using the material parameters in Table 2.1.

haviour of a drop in both the Taylor and Quincke regimes. We have verified that the predictions of the model of the effects of charge convection on the steady and transient drop dynamics in the Taylor regime are in agreement with those of earlier work, and report for the first time that the inclusion of charge convection can lead to an overshoot in the deformation of prolate B drops. We have demonstrated that the present model captures hysteresis in the angular velocity of drops (as has been observed experimentally by Salipante and Vlahovska [2010]), which was not reported by Das and Saintillan [2021]. We hypothesise that the deformation of the drop is the cause of the hysteresis in the present model, in contrast to the recent work of Peng and Schnitzer [2025], who captured hysteresis by accounting for charge shocks at the drop equator. Finally, by neglecting drop deformation, we have derived a novel expression for the critical field for rotation of a spherical drop, accounting for its straining flow, and find that the critical field for a spherical drop is consistently lower than that of a deformed drop.

Chapter 3

An Isolated Surfactant-Laden Drop

As discussed in §1.5, the combined effects of surfactants and electric fields on drop dynamics have been explored theoretically [Nganguia et al., 2013, Mandal et al., 2016a, Poddar et al., 2018, Nganguia et al., 2019, Poddar et al., 2019a,b], computationally [Teigen and Munkejord, 2010, Sorgentone et al., 2019, Zhang et al., 2021, Han et al., 2022], and experimentally [Ha and Yang, 1995, Ervik et al., 2018]. However, with the exception of the works of Poddar et al. [2018, 2019a,b], most of the previous theoretical and computational studies concerning surfactants and electric fields have neglected charge convection, and no results have been reported pertaining to the effect of surfactant on a drop undergoing Quincke rotation. On the one hand, in the Taylor regime the flow is impeded by Marangoni stresses when diffusion is weak and thus, in this case, one would expect charge convection to be insignificant in the steady state. On the other hand, the flow can be remobilised by diffusion, and, in addition, the transient impact of charge convection remains unexplored in either the diffusion-dominated or convection-dominated surfactant transport regimes. Furthermore, although Marangoni stresses are able to balance the quadrupolar stresses accompanying the axisymmetric deformation, they are unable to balance an external electric torque such as that driving Quincke rotation, so it appears unlikely that the rotational component of the flow could be similarly impeded. Hence, in this

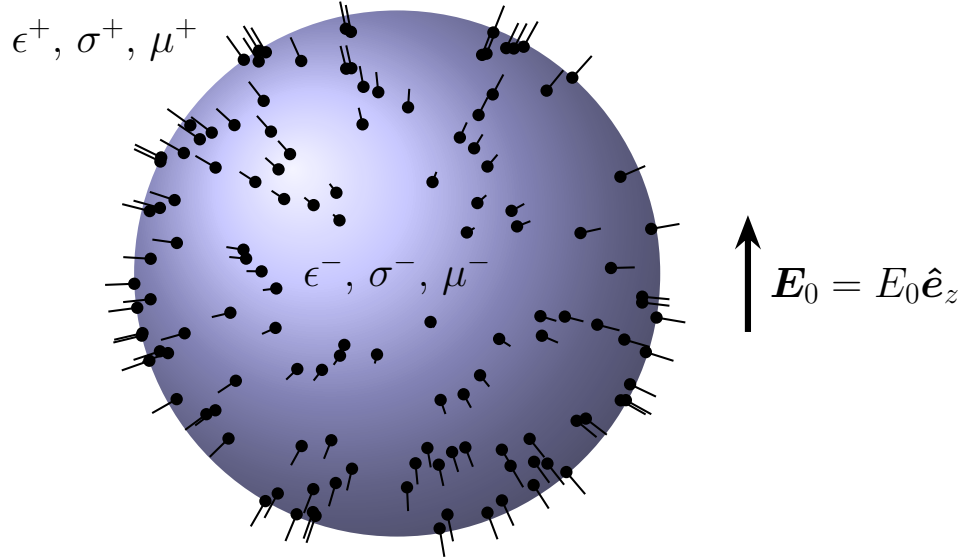


Figure 3.1: An uncharged, neutrally buoyant, leaky dielectric drop coated with a dilute monolayer of insoluble, apolar surfactant immersed in an immiscible leaky dielectric fluid. A uniform DC electric field is applied in the z direction, $\mathbf{E}_0 = E_0 \hat{\mathbf{e}}_z$.

chapter, we describe a novel phenomenological model for an almost spherical, surfactant-laden drop that retains the effect of charge convection, and so is able to capture the transition to Quincke rotation. This chapter is organised as follows. In §3.1, we outline the problem under consideration, recapitulating the governing equations and boundary conditions. In §3.2, we present our approach to solving the problem, focusing in particular on the necessary additions to the equations for a clean drop presented in Chapter 2. In §3.3, we present the results of our model, first focusing on the combined effects of surfactant and charge convection on a drop in the Taylor regime and then on a drop in the Quincke regime. Finally, in §3.4, we summarise the key findings of the present model.

3.1 Problem formulation

We consider an uncharged leaky dielectric drop immersed in another leaky dielectric fluid and coated with a dilute monolayer of insoluble, apolar surfactant as shown in Figure 3.1. As in Chapter 2, the initial drop radius is denoted by a , the two fluids are assumed to be immiscible and to have the same density,

and the electric permittivities of the fluids are denoted by $\epsilon^\pm$, the conductivities $\sigma^\pm$, and the viscosities $\mu^\pm$, where the plus subscript refers to the properties of the surrounding fluid, and the minus subscript refers to the properties of the drop. Similarly, the drop domain is denoted by V^- , the surrounding fluid domain is denoted by V^+ , and the interface between the two is denoted by ∂V . The drop polarises upon application of a uniform DC electric field $\mathbf{E}_0$ and the electric potential $\varphi(\mathbf{r}, t)$ is governed by Laplace's equation in both the drop and the surrounding fluid,

$$\nabla^2 \varphi^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm, \quad (3.1)$$

and the electric field in each domain is given by $\mathbf{E}^\pm(\mathbf{r}, t) = -\nabla \varphi^\pm$. The interfacial charge distribution $q(\theta, \phi, t)$ is again given by

$$q = \llbracket \epsilon \mathbf{E} \rrbracket \cdot \mathbf{n} \quad \text{for } \mathbf{r} \in \partial V, \quad (3.2)$$

and its evolution is governed by the transport equation (2.4):

$$\frac{\partial q}{\partial t} + \llbracket \sigma \mathbf{E} \cdot \mathbf{n} \rrbracket + \nabla_s \cdot (q \mathbf{v}) = 0 \quad \text{for } \mathbf{r} \in \partial V. \quad (3.3)$$

The fluid velocity $\mathbf{v}^\pm(\mathbf{r}, t)$ and the pressure $p^\pm(\mathbf{r}, t)$ are governed by the Stokes equations in both domains,

$$\mu^\pm \nabla^2 \mathbf{v}^\pm = \nabla p^\pm, \quad \nabla \cdot \mathbf{v}^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm. \quad (3.4)$$

As for a clean drop, the fluid velocity is continuous across the interface,

$$\llbracket \mathbf{v} \rrbracket = \mathbf{0} \quad \text{for } \mathbf{r} \in \partial V, \quad (3.5)$$

and the interface is defined as

$$\xi(\mathbf{r}, t) = 0 \quad \text{for } \mathbf{r} \in V^\pm. \quad (3.6)$$

The kinematic boundary condition (1.26) again holds:

$$\frac{\partial \xi}{\partial t} + \mathbf{v} \cdot \nabla \xi = 0 \quad \text{for } \mathbf{r} \in \partial V. \quad (3.7)$$

In contrast to the case of a clean drop, in the presence of surfactant the surface tension $\gamma(\theta, \phi, t)$ varies around the drop surface depending on the local surfactant concentration $\Gamma(\theta, \phi, t)$. Gradients in γ give rise to tangential Marangoni stresses, expressed by the second term on the right hand side of the electrohydrodynamic stress balance (1.54):

$$[\mathbf{f}^E] + [\mathbf{f}^H] = 2\gamma\kappa\mathbf{n} - \nabla_s \gamma \quad \text{for } \mathbf{r} \in \partial V. \quad (3.8)$$

The precise relationship between γ and Γ is not straightforward, and several equations of state have been proposed to capture various physical effects relevant in different regimes [Rosen and Kunjappu, 2012, Manikantan and Squires, 2020]. Most commonly used is the Langmuir equation,

$$\gamma = \gamma_0 + RT\Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right), \quad (3.9)$$

where R is the gas constant, T is the absolute temperature, Γ_∞ is the maximum (i.e., the fully saturated) surfactant concentration, and γ_0 is the surface tension of the drop in the absence of surfactant.

The Langmuir equation is generally valid for a wide range of surfactant concentrations, including those approaching Γ_∞ . However, for dilute concentrations of surfactant like those considered in this thesis, it is appropriate to linearise it about $\Gamma = 0$, in which case the surface tension is given by

$$\gamma = \gamma_0 - RT\Gamma. \quad (3.10)$$

Gradients in Γ arise from convection by the fluid flow and are counteracted by surface diffusion. The evolution of Γ is therefore governed by the surface convec-

tion–diffusion equation,

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v}_s \Gamma) + (\nabla_s \cdot \mathbf{n})(\mathbf{v} \cdot \mathbf{n})\Gamma - D_s \nabla_s^2 \Gamma = 0 \quad \text{for } \mathbf{r} \in \partial V, \quad (3.11)$$

where D_s is the surface diffusivity of the surfactant and $\mathbf{v}_s = (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \mathbf{v}$ is the tangential surface velocity [Stone, 1990]. The second and third terms correspond to surfactant convection, while the last term corresponds to diffusion. In the absence of external forcing, or in the limit of rapid diffusion, the surfactant concentration is uniform around the drop and is given by the equilibrium concentration Γ_{eq} . The corresponding surface tension at $\Gamma = \Gamma_{\text{eq}}$ is $\gamma = \gamma_{\text{eq}} (< \gamma_0)$.

3.1.1 Nondimensionalisation and scaling assumptions

As in Chapter 2, the initial drop radius a and the electrohydrodynamic flow time τ_{EHD} are taken to be the characteristic length and time scales of the problem, respectively. In addition, Γ_{eq} and γ_{eq} are taken to be the characteristic surfactant concentration and surface tension, respectively. The nondimensional form of the stress balance retaining Marangoni stresses (3.8) is

$$\llbracket \mathbf{f}^E \rrbracket + \llbracket \mathbf{f}^H \rrbracket = \frac{1}{\text{Ca}_E} (2\gamma\kappa\mathbf{n} - \nabla_s \gamma) \quad \text{for } \mathbf{r} \in \partial V, \quad (3.12)$$

in which electric capillary number Ca_E for a surfactant covered drop is defined as

$$\text{Ca}_E = \frac{\epsilon^+ E_0^2 a}{\gamma_{\text{eq}}}. \quad (3.13)$$

Note that the uniform reduction of surface tension from that of the clean drop γ_0 to that of the uniformly-coated drop γ_{eq} is implicitly accounted for by using γ_{eq} to define Ca_E . Defining the capillary number this way allows one to focus only on the effects of Marangoni stresses and spatial variations in the surface tension. As before, we assume that the drop is almost spherical, so we require $\text{Ca}_E \ll 1$.

The charge conservation equation (3.3) in nondimensional form is the same

as that for the clean drop (2.15):

$$\frac{\partial q}{\partial t} + \frac{1}{\text{Re}_E} [\mathbf{j} \cdot \mathbf{n}] + \nabla_s \cdot (q\mathbf{v}) = 0. \quad (3.14)$$

The surfactant transport equation (3.11) in nondimensional form is written

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v}_s \Gamma) + (\nabla_s \cdot \mathbf{n})(\mathbf{v} \cdot \mathbf{n})\Gamma - \frac{1}{\text{Pe}_s} \nabla_s^2 \Gamma = 0 \quad \text{for } \mathbf{r} \in \partial V, \quad (3.15)$$

where

$$\text{Pe}_s = \frac{\epsilon^+ E_0^2 a^2}{D_s \mu^+} \quad (3.16)$$

is the surface Péclet number, which is the ratio of the advective and diffusive surfactant transport rates. However, instead of treating Pe_s as an independent parameter, we instead define

$$\zeta = \frac{\text{Pe}_s}{\text{Re}_E}, \quad (3.17)$$

which is analogous to the parameter γ used in studies of drops in extensional flows [Stone and Leal, 1990, Milliken et al., 1993], and is convenient because it characterises the strength of the diffusion of the surfactant while remaining independent of the electric field strength. Finally, the equation of state (3.10) in nondimensional form is written

$$\gamma = 1 + \text{El} (1 - \Gamma). \quad (3.18)$$

Here, El denotes the elasticity number, defined as

$$\text{El} = \frac{RT\Gamma_{\text{eq}}}{\gamma_{\text{eq}}} = \frac{\gamma_0 - \gamma_{\text{eq}}}{\gamma_{\text{eq}}}, \quad (3.19)$$

which quantifies the variation of the surface tension as a function of the surfactant concentration. Changing El alters the sensitivity of the surface tension to variations in surfactant concentration, thereby modifying the strength of the Marangoni stresses.

As for the convective term in the charge transport equation, the convective

term in the surfactant transport equation introduces nonlinearities that preclude analytical solutions. Again, we retain the nonlinear terms in both equations and solve the resulting system of equations numerically, and assume $\text{Re}_E = \mathcal{O}(1)$ and $\lambda \gg 1$ in order to ensure the solution of the charge transport equation is accurate. The solution of the surfactant transport remains accurate when the surfactant distribution remains almost uniform, which occurs either when $\zeta \ll 1$ or when $\text{Ca}_E/\text{El} \ll 1$. In the present work, we adopt the latter assumption, and make no assumption about the magnitude of ζ . In fact, it is worth noting that in real systems, ζ is typically large. However, we retain it as a free parameter in order to study the transition between the diffusion-dominated and convection-dominated surfactant transport regimes, which exhibit qualitatively different dynamics. Thus, given that $\text{Ca}_E \ll 1$, we therefore require $\text{El} = \mathcal{O}(1)$, consistent with Vlahovska et al. [2005].

3.2 Problem solution

We now describe the solution to the problem set out in the previous section. In §3.2.1, we show the parameterisations of the drop shape and surfactant distributions. In §3.2.2, we present the solution to Laplace’s equation (3.1) based on a multipole expansion. In §3.2.3, we present the solution to the Stokes equations (3.4) for the fluid velocity and pressure. In §3.2.4, we apply the kinematic boundary condition to relate the flow fields inside and outside the drop to one another and to the motion of the interface. In §3.2.5, we apply the stress boundary condition to relate the electric, hydrodynamic, capillary and Marangoni stresses at the interface. In §3.2.6 and §3.2.7, we use the charge and surfactant transport equations (3.14) and (3.2.7) to derive ODEs governing the evolutions of the dipole moment and surfactant distribution.

3.2.1 Definitions of drop shape and surfactant distribution

Both the drop shape f and the surfactant distribution Γ are expanded in series of surface spherical harmonics. As mentioned previously, we assume the deviations of f and Γ from the spherical drop and the uniform surfactant concentration, respectively, are small. Then, in anticipation of the form of the electric stress and the resulting flow fields, we retain only the second order harmonics,

$$f(\theta, \phi, t) = 1 + \delta \mathbf{Q}^f : \hat{\mathbf{r}} \hat{\mathbf{r}}, \quad (3.20a)$$

$$\Gamma(\theta, \phi, t) = 1 + \epsilon \mathbf{Q}^\Gamma : \hat{\mathbf{r}} \hat{\mathbf{r}}. \quad (3.20b)$$

$\mathbf{Q}^f$ and $\mathbf{Q}^\Gamma$ are symmetric irreducible second-order tensors each containing five independent coefficients, referred to as the shape coefficients and the surfactant coefficients, respectively. In addition, $\delta \ll 1$ and $\epsilon \ll 1$ are small parameters which quantify the deviations of the drop shape from sphericity and the deviations of the surfactant distribution from the uniform coverage Γ_{eq} , respectively, both of which will be defined in §3.2.5. Throughout the analysis we assume $\delta \sim \epsilon$.

As in Chapter 2, the surface normal $\mathbf{n}$ and the mean surface curvature κ of the interface are given by

$$\mathbf{n} = \hat{\mathbf{r}} - 2\delta(\mathbf{Q}^f \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}} \hat{\mathbf{r}}), \quad \kappa = 1 + 2\delta \mathbf{Q}^f : \hat{\mathbf{r}} \hat{\mathbf{r}}. \quad (3.21)$$

3.2.2 Electrostatics

Given that the surfactant is apolar, it does not directly interact with the charge distribution on the interface of the drop. It generally affects the charge distribution only indirectly, specifically by modifying the flow field in which charge is convected. Hence, the solution to the electrostatic problem is of the same form as that in Chapter 2, and we briefly recapitulate it here for convenience. The

electric potentials inside and outside the drop are

$$\varphi^- = \varphi_0 + \mathbf{P} \cdot \mathbf{r}, \quad \varphi^+ = \varphi_0 + r^{-3} \mathbf{P} \cdot \mathbf{r}, \quad (3.22)$$

respectively, and the corresponding electric fields are

$$\mathbf{E}^- = \hat{\mathbf{E}}_0 - \mathbf{P}, \quad \mathbf{E}^+ = \hat{\mathbf{E}}_0 - r^{-3} \mathbf{P} \cdot (\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}), \quad (3.23)$$

respectively. After calculating the electric stress tensors in both domains according to (2.10), the traction jump across the drop interface is given by

$$[\![\mathbf{f}^E]\!] = [\![\boldsymbol{\tau}^E]\!] \cdot \hat{\mathbf{r}} = p^E \hat{\mathbf{r}} + \mathbf{Q}_{\hat{\mathbf{r}}}^E : \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} + (\mathbf{Q}_{\hat{\mathbf{t}}}^E \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}) + \mathbf{T}^E \times \hat{\mathbf{r}}, \quad (3.24)$$

where $p^E(t)$, $\mathbf{Q}_{\hat{\mathbf{r}}}^E(t)$, $\mathbf{Q}_{\hat{\mathbf{t}}}^E(t)$ and $\mathbf{T}^E(t)$ again capture the isotropic electric pressure, radial and tangential quadrupolar electric stresses, and the electric torque, respectively, and are defined as in (2.33).

3.2.3 Hydrodynamics

The presence of surfactant affects the flow fields around the drop as a result of Marangoni stresses, which can generally excite new flow modes in addition to those excited by the electric stresses alone (i.e., those retained in (2.53)). However, in the present model, it was assumed in (3.20b) (and will be justified in §3.2.7) that the surfactant distribution remains almost uniform, with a small quadrupolar correction given by $\epsilon \mathbf{Q}^\Gamma : \hat{\mathbf{r}}\hat{\mathbf{r}}$. In this case, the Marangoni stresses take the same form as the quadrupolar stresses in (3.24), and thus no new flow modes are required in the hydrodynamic problem. The fluid velocities inside and outside the drop then take the same form as those for a clean drop in (2.50) and (2.51):

$$\mathbf{v}^- = \mathbf{d}^\chi \times \mathbf{r} + \mathbf{d}^\phi + 2\mathbf{q}^\phi \cdot \mathbf{r} + \frac{r^2 \mathbf{q}^p \cdot \mathbf{r}}{21\lambda} \cdot (5\mathbf{I} - 2\hat{\mathbf{r}}\hat{\mathbf{r}}), \quad (3.25)$$

$$\mathbf{v}^+ = r^{-3} \mathbf{D}^\chi \times \mathbf{r} + r^{-5} \frac{\mathbf{Q}^p : \mathbf{r}\mathbf{r}\mathbf{r}}{2} + r^{-5} (\mathbf{Q}^\phi \cdot \mathbf{r}) \cdot (2\mathbf{I} - 5\hat{\mathbf{r}}\hat{\mathbf{r}}). \quad (3.26)$$

As before, $\mathbf{d}^\chi(t)$ and $\mathbf{D}^\chi(t)$ are vectors which correspond to the solid body rotational flow, $\mathbf{d}^\phi(t)$ is a vector which corresponds to the uniform flow field inside the drop, and $\mathbf{q}^p(t)$, $\mathbf{Q}^p(t)$, $\mathbf{q}^\phi(t)$, and $\mathbf{Q}^\phi(t)$ are second-order irreducible symmetric tensors which correspond to the straining flows. The hydrodynamic traction jump associated with (3.25) and (3.26) is

$$\begin{aligned} \llbracket \mathbf{f}^H \rrbracket = & (m^p - M^p) \hat{\mathbf{r}} + \left(24\mathbf{Q}^\phi - 3\mathbf{Q}^p - 4\lambda\mathbf{q}^\phi + \frac{\mathbf{q}^p}{7} \right) : \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} \\ & + \left[\left(-16\mathbf{Q}^\phi + \mathbf{Q}^p - \frac{16\mathbf{q}^p}{21} - 4\lambda\mathbf{q}^\phi \right) \cdot \hat{\mathbf{r}} \right] \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}) - 3\mathbf{D}^\chi \times \hat{\mathbf{r}}, \end{aligned} \quad (3.27)$$

where m^p and M^p are the isotropic pressures inside and outside the drop, respectively.

3.2.4 Kinematic boundary condition

In this section, we apply the kinematic boundary condition (3.7). The presence of surfactant affects neither the kinematic boundary condition – which only enforces that the interface deforms as a material surface – nor the no-slip condition. Hence, we briefly restate the main points of §2.2.4. First, the no-slip condition gives that

$$\mathbf{D}^\chi = \mathbf{d}^\chi, \quad \mathbf{0} = \mathbf{d}^\phi, \quad 2\mathbf{Q}^\phi = 2\mathbf{q}^\phi + \frac{5\mathbf{q}^p}{21\lambda}. \quad (3.28)$$

Second, the kinematic condition gives that

$$2\mathbf{q}^\phi + \frac{1}{7\lambda}\mathbf{q}^p = \frac{1}{2}\mathbf{Q}^p - 3\mathbf{Q}^\phi = \delta \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right), \quad (3.29)$$

where

$$Q_{ij}^{\chi f} = \varepsilon_{lkj} Q_{li}^f D_k^\chi + \varepsilon_{lki} Q_{lj}^f D_k^\chi. \quad (3.30)$$

Combining (3.28) and (3.29) leads to the relations

$$\mathbf{Q}^\phi = \frac{1}{6}\mathbf{Q}^p - \frac{\delta}{3}\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (3.31a)$$

$$\mathbf{q}^p = \frac{7\lambda}{2}\mathbf{Q}^p - \frac{35\lambda\delta}{2}\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (3.31b)$$

$$\mathbf{q}^\phi = -\frac{1}{4}\mathbf{Q}^p + \frac{7\delta}{4}\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right). \quad (3.31c)$$

Eq. (3.31) allows the hydrodynamic traction (3.27) to be rewritten as

$$\llbracket \mathbf{f}^H \rrbracket = \llbracket \boldsymbol{\tau}^H \rrbracket \cdot \hat{\mathbf{r}} = p^H \hat{\mathbf{r}} + \mathbf{Q}_{\hat{\mathbf{r}}}^H : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}} + (\mathbf{Q}_{\hat{\mathbf{t}}}^H \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}} \hat{\mathbf{r}}) + \mathbf{T}^H \times \hat{\mathbf{r}}, \quad (3.32)$$

where

$$p^H = m^p - M^p, \quad (3.33a)$$

$$\mathbf{Q}_{\hat{\mathbf{r}}}^H = \frac{2+3\lambda}{2}\mathbf{Q}^p - \frac{16+19\lambda}{2}\delta\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (3.33b)$$

$$\mathbf{Q}_{\hat{\mathbf{t}}}^H = -\frac{5(1+\lambda)}{3}\mathbf{Q}^p + \frac{16+19\lambda}{3}\delta\left(\frac{\partial\mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f}\right), \quad (3.33c)$$

$$\mathbf{T}^H = -3\mathbf{D}^\chi. \quad (3.33d)$$

3.2.5 Stress balance

We next apply the dynamic boundary condition (3.12), which for a surfactant-laden drop must account for Marangoni stresses arising from nonuniform surface tension in addition to the usual capillary stresses and the electric and hydrodynamic stresses (3.24) and (3.32). Expanding the right hand side of (3.12) yields

$$\llbracket \mathbf{f}^E \rrbracket + \llbracket \mathbf{f}^H \rrbracket = \frac{2}{\text{Ca}_E} \hat{\mathbf{r}} - \frac{4}{\text{Ca}_E} \delta (\mathbf{Q}^f \cdot \mathbf{r}) \cdot (\mathbf{I} - 2\hat{\mathbf{r}} \hat{\mathbf{r}}) + \frac{2\text{El}}{\text{Ca}_E} \epsilon (\mathbf{Q}^\Gamma \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - 2\hat{\mathbf{r}} \hat{\mathbf{r}}). \quad (3.34)$$

Considering the radial component of (3.34), we obtain a balance of isotropic pressures,

$$p^H = -p^E + \frac{2}{\text{Ca}_E}, \quad (3.35)$$

and a balance of quadrupolar stresses,

$$\mathbf{Q}_{\hat{\mathbf{r}}}^H = \frac{2}{\text{Ca}_E} (-\text{El}\epsilon \mathbf{Q}^\Gamma + 2\delta \mathbf{Q}^f) - \mathbf{Q}_{\hat{\mathbf{r}}}^E. \quad (3.36)$$

As before, we choose

$$\delta = \frac{3\text{Ca}_E}{4(1+2S)^2}, \quad (3.37)$$

so that the capillary stresses balance the $\mathcal{O}(1)$ electrostatic and hydrodynamic stresses. Analogously, for the Marangoni stresses to balance the electrostatic and hydrodynamic stresses, we require $\epsilon \propto \text{Ca}_E/\text{El}$, and so define

$$\epsilon = \frac{\text{Ca}_E}{\text{El}}, \quad (3.38)$$

which is the reciprocal of the usual Marangoni number. Next, the tangential component of (3.34) yields a tensor equation relating the quadrupolar stresses,

$$\mathbf{Q}_{\hat{\mathbf{t}}}^H = 2\mathbf{Q}^\Gamma - \mathbf{Q}_{\hat{\mathbf{t}}}^E, \quad (3.39)$$

and a vector equation relating the torques,

$$\mathbf{T}^H = -\mathbf{T}^E. \quad (3.40)$$

Then, combining (3.36) and (3.39) gives equations for the flow coefficients $\mathbf{Q}^p$ and the shape evolution $\partial \mathbf{Q}^f / \partial t$, which are similar to (2.73) and (2.74) but now also involve $\mathbf{Q}^\Gamma$:

$$\mathbf{Q}^p = \frac{2}{3+2\lambda} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}^f + \mathbf{Q}_{\hat{\mathbf{r}}}^E + \frac{3}{2} \mathbf{Q}_{\hat{\mathbf{t}}}^E - \mathbf{Q}^\Gamma \right], \quad (3.41)$$

$$\begin{aligned} \frac{\partial \mathbf{Q}^f}{\partial t} = & \frac{10(1+\lambda)}{\delta(16+19\lambda)(3+2\lambda)} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}^f + \mathbf{Q}_{\hat{\mathbf{r}}}^E \right. \\ & \left. + \frac{6+9\lambda}{10(1+\lambda)} \mathbf{Q}_{\hat{\mathbf{t}}}^E + \frac{4+\lambda}{5(1+\lambda)} \mathbf{Q}^\Gamma \right] - \mathbf{Q}^{\chi f}. \end{aligned} \quad (3.42)$$

Meanwhile, the torque balance is unchanged from that for a clean drop, and reads

$$\mathbf{D}^\chi = \frac{1}{2} \mathbf{P} \times \hat{\mathbf{E}}_0. \quad (3.43)$$

To close the problem, the dipole moment $\mathbf{P}$ and surfactant distribution $\mathbf{Q}^\Gamma$ must be determined. The following two sections detail the transport equations used to do so.

3.2.6 Charge transport

As discussed in §3.2.2, the surfactant interacts with the interfacial charge only by modifying the flow field in which charge is convected. In particular, in the Taylor regime, the fluid flow may be partially or entirely suppressed by Marangoni stresses. However, given that the general form of the fluid velocities (3.25) and (3.26) are unchanged from those of the clean drop, the same evolution equation exists for the dipole moment $\mathbf{P}$:

$$\begin{aligned} \frac{d\mathbf{P}}{dt} = & -\frac{1+2S}{S(2+Q)\text{Re}_E} \mathbf{P} - \frac{S-1}{S(2+Q)\text{Re}_E} \hat{\mathbf{E}}_0 + \mathbf{D}^\chi \times \left(\frac{1-Q}{2+Q} \hat{\mathbf{E}}_0 + \mathbf{P} \right) \\ & + \left(\frac{1-Q}{2+Q} \hat{\mathbf{E}}_0 + \mathbf{P} \right) \cdot \left[\frac{1}{5} \mathbf{Q}^p - \frac{6}{5} \delta \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right) \right]. \end{aligned} \quad (3.44)$$

3.2.7 Surfactant transport

The surfactant concentration evolves according to the dimensionless transport equation (3.15). Substituting in Γ from (3.20b), $\mathbf{v}$ from (3.25) or (3.26), $\mathbf{n}$ and κ from (3.21), and retaining leading-order terms, we obtain a system of ODEs for the quadrupole $\mathbf{Q}^\Gamma$,

$$\frac{\partial \mathbf{Q}^\Gamma}{\partial t} = \frac{1}{\epsilon} \mathbf{Q}^p - 4 \frac{\delta}{\epsilon} \left(\frac{\partial \mathbf{Q}^f}{\partial t} + \mathbf{Q}^{\chi f} \right) - \mathbf{Q}^{\chi \Gamma} - \frac{6}{\zeta \text{Re}_E} \mathbf{Q}^\Gamma, \quad (3.45)$$

where

$$Q_{ij}^{\chi \Gamma} = Q_{il}^\Gamma \epsilon_{lkj} D_k^\chi + Q_{jl}^\Gamma \epsilon_{lki} D_k^\chi. \quad (3.46)$$

Analogously to $\mathbf{Q}^{\chi f}$ as defined in (3.30), $\mathbf{Q}^{\chi \Gamma}$ acts to restore a uniform surfactant coverage after rotation begins. As can be seen from the first two terms on the right hand side of (3.45), the leading order quadrupolar correction to the surfactant distribution arises due to the quadrupolar straining flow. Any higher order corrections must then arise due to interactions between the small ($\mathcal{O}(\epsilon)$) quadrupole mode and the weak ($\mathcal{O}(\lambda^{-1})$) straining flow, and are therefore asymptotically small, so are not retained in the present model.

3.2.8 Model summary

Hence, the full system of nonlinear ODEs governing the system is written compactly as

$$\frac{d}{dt} \begin{bmatrix} \mathbf{P} \\ \mathbf{Q}^f \\ \mathbf{Q}^\Gamma \end{bmatrix} = \mathcal{F}(\mathbf{P}, \mathbf{Q}^f, \mathbf{Q}^\Gamma; \text{Ca}_E, \text{Re}_E, \zeta, \text{El}, Q, S, \lambda). \quad (3.47)$$

As before, we proceed by solving the above system of equations numerically using the methods introduced in §1.6. The initial conditions for the RK4 scheme are again those of a spherical drop with zero interfacial charge (2.79) and (2.81), and now also with an initially uniform surfactant concentration:

$$\mathbf{Q}^\Gamma(0) = \mathbf{0}. \quad (3.48)$$

3.3 Results

In this section, we present results obtained from the model described in the previous sections. In §3.3.1, we describe the linearisation of the differential equations derived in the previous section, which is used to examine the stability of the system. In §3.3.2, we demonstrate that the predictions of the present model are in agreement with those of earlier models. In §3.3.3, we investigate the combined effects of surfactant and charge convection on the drop dynamics in the Taylor regime. In §3.3.4, we explore how surfactant effects impact the stability and angular velocity of a drop in the Quincke regime.

3.3.1 Linear stability analysis

To investigate the onset of Quincke rotation, we linearly perturb the system around a steady, axisymmetric base state corresponding to a drop in the Taylor regime which allows us to perform the analysis in the xz plane without loss of generality. We denote the base state variables with a zero subscript, and in the base state we have that

$$P_{0,x} = Q_{0,xz}^\Gamma = Q_{0,xz}^f = 0, \quad Q_{0,xx}^\Gamma = Q_{0,yy}^\Gamma, \quad Q_{0,xx}^f = Q_{0,yy}^f. \quad (3.49)$$

Therefore, $\mathbf{D}_0^\chi = \mathbf{0}$ and so $\mathbf{Q}_0^{\chi f} = \mathbf{Q}_0^{\chi \Gamma} = \mathbf{0}$. Explicitly, we perturb the variables as

$$\begin{pmatrix} P_x \\ P_z \\ Q_{xx}^f \\ Q_{zz}^f \\ Q_{xz}^f \\ Q_{xx}^\Gamma \\ Q_{zz}^\Gamma \\ Q_{xz}^\Gamma \end{pmatrix} = \begin{pmatrix} 0 \\ P_{0,z} \\ Q_{0,xx}^f \\ Q_{0,zz}^f \\ 0 \\ Q_{0,xx}^\Gamma \\ Q_{0,zz}^\Gamma \\ 0 \end{pmatrix} + \Delta \begin{pmatrix} P_{\Delta,x} \\ P_{\Delta,z} \\ Q_{\Delta,xx}^f \\ Q_{\Delta,zz}^f \\ Q_{\Delta,xz}^f \\ Q_{\Delta,xx}^\Gamma \\ Q_{\Delta,zz}^\Gamma \\ Q_{\Delta,xz}^\Gamma \end{pmatrix}, \quad (3.50)$$

where the small parameter $\Delta \ll 1$ is a measure of the size of the perturbations to the variables, and the Δ subscript denotes the perturbed variables. The z component of the base state dipole moment, $P_{0,z}$, is computed from a cubic equation derived from the charge transport equation (3.14), namely

$$\mathcal{A}P_{0,z}^3 + \mathcal{B}P_{0,z}^2 + \mathcal{C}P_{0,z} + \mathcal{D} = 0, \quad (3.51)$$

where

$$\mathcal{A} = -\frac{2(2+Q)}{25(1+\lambda) + 5\frac{\text{El}}{\text{CaE}}\zeta\text{ReE}}, \quad (3.52a)$$

$$\mathcal{B} = \frac{6Q}{25(1+\lambda) + 5\frac{\text{El}}{\text{CaE}}\zeta\text{ReE}}, \quad (3.52b)$$

$$\mathcal{C} = -\frac{1+2S}{S(2+Q)\text{ReE}} + \frac{6(1-Q^2)}{25(2+Q)(1+\lambda) + 5(2+Q)\frac{\text{El}}{\text{CaE}}\zeta\text{ReE}}, \quad (3.52c)$$

$$\mathcal{D} = \frac{1-S}{S(2+Q)\text{ReE}} + \frac{2(1-Q)^2}{25(2+Q)(1+\lambda) + 5(2+Q)\frac{\text{El}}{\text{CaE}}\zeta\text{ReE}}, \quad (3.52d)$$

which we solve numerically. (3.51) generally admits three solutions. In the parameter regime in which our model remains valid (weak charge convection by the straining flow, i.e., high λ and moderate ReE), there is one real solution and one complex conjugate pair of solutions, and only the real solution corresponds to a physically admissible steady state. However, if charge convection by the straining flow is strong, then saddle node bifurcations may occur in the solution space of (3.51) as ReE is increased to large values, depending on the value of SQ . If SQ is small, only one real solution exists, which increases monotonically for all ReE . For SQ slightly smaller than unity, the solution curve bends into an S-shape. Two saddle node bifurcations occur, between which two stable solutions and one unstable solution exist and the solution exhibits hysteresis. For $SQ > 1$, one monotonically increasing real solution again exists for all ReE , but a saddle node bifurcation occurs away from this branch, giving rise to two new solutions, one stable and one unstable. In this case, all three real solutions exist in the limit $\text{ReE} \rightarrow \infty$. The scaling assumptions underlying the model are substantially violated when charge convection by the straining flow is strong enough to give rise to multiple real solutions for $P_{0,z}$. Moreover, in cases where $SQ > 1$, the axisymmetric base state generally becomes unstable at electric field strengths corresponding to such high values of ReE . These considerations raise doubts as to whether these additional solutions are physically realised or are instead artefacts of the reduced equations. Hence, at the parameter values considered in this thesis, to select the correct root of (3.51) it generally suffices to choose whichever one is purely real.

Nonetheless, as an additional safeguard in the numerical implementation in case more than one real solution does exist, we choose the smallest real solution, which in all cases lies on the physical solution branch (i.e., the one branch that exists at small and moderate values of Re_E).

The base-state surfactant coefficients are given by

$$Q_{0,xx}^\Gamma = -\frac{1 - Q + (1 + 2Q)P_{0,z} - (2 + Q)P_{0,z}^2}{30(1 + \lambda)\frac{1}{\zeta\text{Re}_E}\frac{\text{Ca}_E}{\text{El}} + 6}, \quad (3.53a)$$

$$Q_{0,zz}^\Gamma = -2Q_{0,xx}^\Gamma, \quad (3.53b)$$

and the base-state shape coefficients are

$$Q_{0,xx}^f = \frac{(1 + 2S)^2}{3} \left[-\frac{3}{2}P_{0,z}^2 - \frac{(16 + 19\lambda)\frac{1}{\zeta\text{Re}_E}\frac{\text{Ca}_E}{\text{El}} + 4}{30(1 + \lambda)\frac{1}{\zeta\text{Re}_E}\frac{\text{Ca}_E}{\text{El}} + 6} \right. \\ \left. \times (1 - Q + (1 + 2Q)P_{0,z} - (2 + Q)P_{0,z}^2) \right], \quad (3.54a)$$

$$Q_{0,zz}^f = -2Q_{0,xx}^f. \quad (3.54b)$$

Ultimately, the resulting linear system can be written as

$$\frac{d}{dt} \begin{pmatrix} P_{\Delta,x} \\ P_{\Delta,z} \\ Q_{\Delta,xx}^f \\ Q_{\Delta,zz}^f \\ Q_{\Delta,xz}^f \\ Q_{\Delta,xx}^\Gamma \\ Q_{\Delta,zz}^\Gamma \\ Q_{\Delta,xz}^\Gamma \end{pmatrix} = \begin{bmatrix} J_{11} & 0 & 0 & 0 & J_{15} & 0 & 0 & J_{18} \\ 0 & J_{22} & 0 & J_{24} & 0 & 0 & J_{27} & 0 \\ 0 & J_{32} & J_{33} & 0 & 0 & J_{36} & 0 & 0 \\ 0 & J_{42} & 0 & J_{44} & 0 & 0 & J_{47} & 0 \\ J_{51} & 0 & 0 & 0 & J_{55} & 0 & 0 & J_{58} \\ 0 & J_{62} & J_{63} & 0 & 0 & J_{66} & 0 & 0 \\ 0 & J_{72} & 0 & J_{74} & 0 & 0 & J_{77} & 0 \\ J_{81} & 0 & 0 & 0 & J_{85} & 0 & 0 & J_{88} \end{bmatrix} \begin{pmatrix} P_{\Delta,x} \\ P_{\Delta,z} \\ Q_{\Delta,xx}^f \\ Q_{\Delta,zz}^f \\ Q_{\Delta,xz}^f \\ Q_{\Delta,xx}^\Gamma \\ Q_{\Delta,zz}^\Gamma \\ Q_{\Delta,xz}^\Gamma \end{pmatrix}, \quad (3.55)$$

where, for brevity, the elements of the Jacobian matrix are given in Appendix B. The electric field strength is increased until one of the eigenvalues of the Jacobian has a positive real part, indicating instability.

The linear stability analysis described here is an extension of that presented

by Das and Saintillan [2021] for a clean drop. The latter can be recovered by setting either $\text{El} = 0$ or $\zeta = 0$ in (3.52)–(3.54) and removing the last three rows and columns from (3.55).

3.3.2 Validation

In this section, we demonstrate that the present model recovers the linear term of the second-order small-deformation theory of Nganguia et al. [2013] in the limits of zero electric Reynolds number, $\text{Re}_E \rightarrow 0$, and zero surfactant diffusion, $\text{Pe}_s \rightarrow \infty$ or equivalently $\zeta \rightarrow \infty$. Our model also reduces to that of Stone and Leal [1990] if the electric field is switched off and the drop is instead exposed to an extensional flow.

First, we consider the behaviour of a drop in the Taylor regime in the limit of zero surfactant diffusion, as studied by Nganguia et al. [2013]. In this limit, the flow is completely arrested once the surfactant has been redistributed such that the Marangoni stresses balance the electric stresses. Therefore, charge convection can have no impact on the steady drop shape or surfactant distribution, although it can have a transient impact while the surfactant is being redistributed. At steady state, in the absence of charge convection, the charge transport equation (3.14) simplifies to

$$[\![\mathbf{j} \cdot \mathbf{n}]\!] = 0, \quad (3.56)$$

which yields a simple expression for the dipole moment,

$$\mathbf{P} = \frac{1 - S}{1 + 2S} \hat{\mathbf{E}}_0. \quad (3.57)$$

Hence, if charge convection is absent, then the dipole moment is either parallel or anti-parallel to the applied field and Quincke rotation is impossible, as is clear from (3.43). Then, the terms associated with rotation ($\mathbf{Q}^{xf}$ and $\mathbf{Q}^{x\Gamma}$) may be removed from the ODE for the surfactant quadrupole (3.45), which in the limit $\zeta \rightarrow \infty$ becomes

$$\frac{\partial \mathbf{Q}^\Gamma}{\partial t} = \frac{1}{\epsilon} \mathbf{Q}^p + 4 \frac{\delta}{\epsilon} \frac{\partial \mathbf{Q}^f}{\partial t}. \quad (3.58)$$

Evidently, at steady state we have $\mathbf{Q}^p = \mathbf{0}$. Using this result together with (3.57) allows us to obtain algebraic solutions of (3.41) and (3.42), yielding

$$\mathbf{Q}^f = \frac{3}{2} (4S(1 - SQ) + (1 - S)^2) \left(\hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 - \frac{1}{3} \mathbf{I} \right) \quad (3.59a)$$

and

$$\mathbf{Q}^\Gamma = \frac{9S(1 - SQ)}{2(1 + 2S)^2} \left(\hat{\mathbf{E}}_0 \hat{\mathbf{E}}_0 - \frac{1}{3} \mathbf{I} \right). \quad (3.59b)$$

Thus, the sign of the discriminating function $4S(1 - SQ) + (1 - S)^2$ determines the prolate (positive) or oblate (negative) nature of the deformation, as found by Nganguia et al. [2013].

Using this expression, the steady drop shape (3.59a) corresponds to a deformation of

$$D_Q = \frac{9\text{Ca}_E}{16(1 + 2S)^2} |4S(1 - SQ) + (1 - S)^2|, \quad (3.60)$$

which is equivalent to the linear term of Eq. (18) of Nganguia et al. [2013], up to the sign convention for oblate deformations.

Next, to demonstrate consistency with the results of the model of Stone and Leal [1990], we consider the case in which diffusion is strong, and replace the electric field with an imposed straining flow of the form

$$\mathbf{v}^\infty = \mathbf{S}_e \cdot \mathbf{r} = \pm k \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \mathbf{r}, \quad (3.61)$$

where k is the shear rate. Equation (3.61) corresponds to a uniaxial extensional flow for positive k , and a biaxial extensional flow for negative k . These flow fields have been studied by Stone and Leal [1990] for low Pe_s and involve qualitatively similar convective fluxes at the drop surface to those induced by a prolate A drop (uniaxial extension) or an oblate or prolate B drop (biaxial extension) exposed an electric field. In either case, the surfactant transport equation (3.45) becomes

$$\frac{\partial \mathbf{Q}^\Gamma}{\partial t} = \frac{1}{\epsilon} \mathbf{Q}^p - 4 \frac{\text{Ca}}{\epsilon} \frac{\partial \mathbf{Q}^f}{\partial t} + \frac{5}{\epsilon} \mathbf{S}_e - \frac{6}{\text{Pe}_s} \mathbf{Q}^\Gamma, \quad (3.62)$$

where

$$\text{Ca} = \frac{\mu^+ ka}{\gamma_{\text{eq}}} \ll 1 \quad (3.63)$$

is the capillary number, which represents the ratio of viscous to capillary stresses.

Also, the Péclet number for the extensional flow is

$$\text{Pe}_s = \frac{ka^2}{D_s}, \quad (3.64)$$

and the flow coefficients in $\mathbf{Q}^p$ are given by

$$\mathbf{Q}^p = \frac{2}{3+2\lambda} \left(-4\mathbf{Q}^f - \frac{\text{El}}{\text{Ca}} \epsilon \mathbf{Q}^\Gamma + 5(1-\lambda) \mathbf{S}_e \right). \quad (3.65)$$

In addition, the drop shape evolves according to

$$\frac{\partial \mathbf{Q}^f}{\partial t} = \frac{1}{\text{Ca}(3+2\lambda)} \left(-\frac{40(1+\lambda)}{(16+19\lambda)} \mathbf{Q}^f + \frac{2(4+\lambda)}{(16+19\lambda)} \frac{\text{El}}{\text{Ca}} \epsilon \mathbf{Q}^\Gamma + 5\mathbf{S}_e \right). \quad (3.66)$$

Then, $\mathbf{Q}^\Gamma$ can be eliminated between (3.62) and (3.66) to form an equation for $\partial \mathbf{Q}^\Gamma / \partial t$ in terms of $\partial \mathbf{Q}^f / \partial t$, $\mathbf{Q}^f$ and $\mathbf{S}_e$. Differentiating (3.66) and substituting in this equation gives a second order ODE for $\mathbf{Q}^f$ which is decoupled from $\mathbf{Q}^\Gamma$,

$$\begin{aligned} & \frac{(3+2\lambda)(16+19\lambda)}{2} \frac{\text{Ca}^2}{\text{El}} \frac{\partial^2 \mathbf{Q}^f}{\partial t^2} \\ & + \left[(32+23\lambda)\text{Ca} + 20(1+\lambda) \frac{\text{Ca}}{\text{El}} + 3(3+2\lambda)(16+19\lambda) \frac{\text{Ca}^2}{\text{ElPe}_s} \right] \frac{\partial \mathbf{Q}^f}{\partial t} \\ & + 24 \left[1 + 5(1+\lambda) \frac{\text{Ca}}{\text{Pe}_s} \right] \mathbf{Q}^f = 15 \left[4 + (16+19\lambda) \frac{\text{Ca}}{\text{ElPe}_s} \right] \mathbf{S}_e, \end{aligned} \quad (3.67)$$

which is equivalent to Eq. (22) of Stone and Leal [1990]. A similar decoupled ODE can be written for $\mathbf{Q}^\Gamma$.

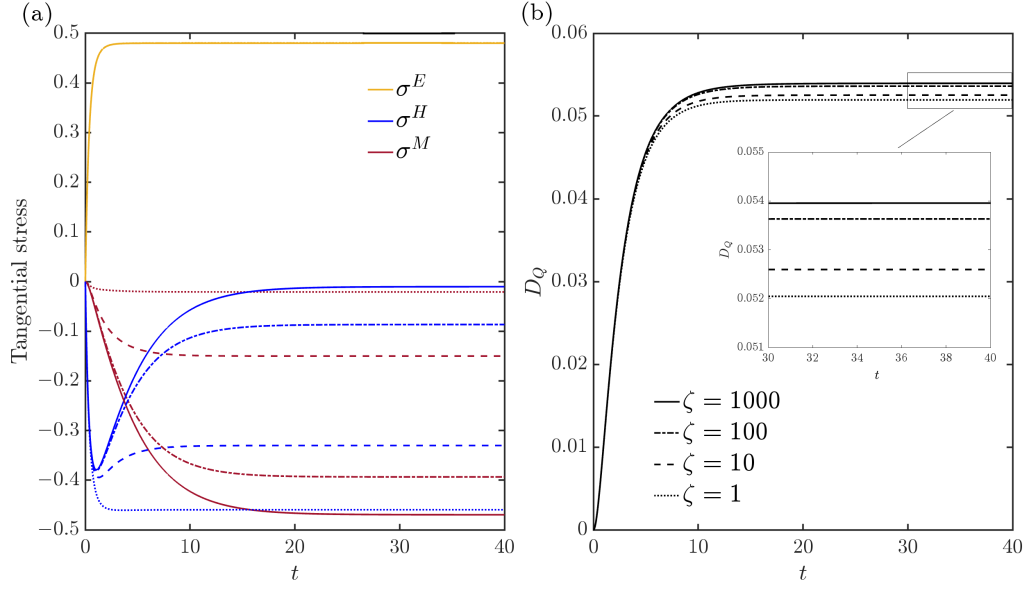


Figure 3.2: Evolution of (a) the tangential electric (yellow lines), hydrodynamic (blue lines) and Marangoni (dark red lines) stresses and (b) the deformation D_Q (defined in (2.83)) of a prolate A drop, for $\zeta = 1$ (dotted lines), $\zeta = 10$ (dashed lines), $\zeta = 100$ (dash-dotted lines) and $\zeta = 1000$ (solid lines). In these figures, $S = 1/3$, $Q = 1$, $\lambda = 10$, $\text{El} = 0.5$, $\text{Re}_E = 1$, and $\text{Ca}_E = 0.2$.

3.3.3 Taylor regime

In this section, we study the combined effects of surfactant and charge convection on the drop dynamics in the Taylor regime. First, Figure 3.2(a) shows the evolution of the tangential electric (yellow lines), hydrodynamic (blue lines) and Marangoni (dark red lines) stresses on the surface of a prolate A drop for which $S = 1/3$, $Q = 1$, $\lambda = 10$. Specifically, we plot σ^E , σ^H and σ^M , defined as

$$\sigma^E = Q_{\mathbf{t},zz}^E, \quad \sigma^H = Q_{\mathbf{t},zz}^H, \quad \sigma^M = -2Q_{zz}^\Gamma. \quad (3.68)$$

In Figure 3.2, $\text{El} = 0.5$, $\text{Re}_E = 1$, $\text{Ca}_E = 0.2$, and results are shown for $\zeta = 1$ (dotted lines), $\zeta = 10$ (dashed lines), $\zeta = 100$ (dash-dotted lines), and $\zeta = 1000$ (solid lines). The electric stress remains almost unchanged between these values of ζ , suggesting that charge convection does not impact the steady state dipole moment values from (3.44) significantly and so the four yellow lines are indistinguishable. When $\zeta = 1$, the electric stress shears the fluid into motion and is largely balanced by the resulting hydrodynamic stress, while the Marangoni

stress remains relatively weak due to relatively strong surfactant diffusion. Each of σ^E , σ^H , and σ^M monotonically approaches its steady value with no overshoot as time increases. When $\zeta = 10$, the flow is more suppressed than when $\zeta = 1$, and the Marangoni stress plays a stronger role in balancing the electric stress than it does when $\zeta = 1$, although the hydrodynamic stress is still the stronger of the two. In this case, the hydrodynamic stress slightly overshoots its steady value as the steady surfactant distribution is established. Consistent with previous studies [Nganguia et al., 2013, Mandal et al., 2016a, Nganguia et al., 2019], the flow is suppressed substantially in the cases $\zeta = 100$ and $\zeta = 1000$, and the Marangoni stress plays a much stronger role in balancing the electric stress than does the hydrodynamic stress. The hydrodynamic stress initially increases quickly in response to the electric stresses, convecting surfactant around the drop. This creates surface tension gradients that lead to a relatively strong Marangoni stress that suppresses the flow and decreases the hydrodynamic stress. Figure 3.2(b) shows the corresponding evolution of the deformation parameter D_Q , and the inset displays an enlarged view of the steady values. As expected, the deformation increases with ζ , and approaches its steady value monotonically as time increases for all of the values of ζ shown.

Next, Figures 3.3(a–c) show the dependence of the steady deformation parameter D_Q of the three drop classes (prolate A, prolate B, and oblate) on ζ for four values of El . Figure 3.3(a) shows results for a prolate A drop with $S = 1/3$, $Q = 1$, Figure 3.3(b) shows results for a prolate B drop with $S = 1/3$, $Q = 7/2$, and Figure 3.3(c) shows results for an oblate drop with $S = 1$, $Q = 2$. In the Taylor regime, the charge distribution q can be written as

$$q = q^* \cos \theta, \quad (3.69)$$

where $q^* = 1 - Q + (2 + Q)P_z$, while the surface tension can be written as

$$\gamma = 1 + \gamma^* P_2(\cos \theta), \quad (3.70)$$

where $\gamma^* = -Ca_E Q_{zz}^\Gamma$ and $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is the second Legendre

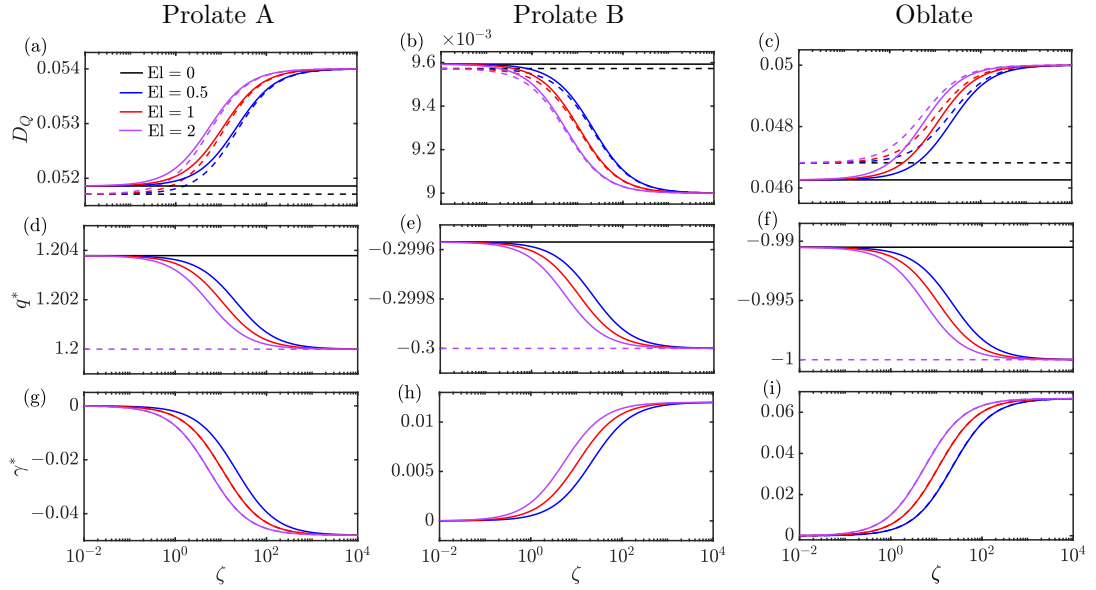


Figure 3.3: Dependence of the steady deformation parameter D_Q of (a) a prolate A drop with $S = 1/3$, $Q = 1$, (b) a prolate B drop with $S = 1/3$, $Q = 7/2$, and (c) an oblate drop with $S = 1$, $Q = 2$ on ζ for $El = 0$ (black lines), 0.5 (blue lines), 1 (red lines) and 2 (purple lines). The solid lines are the results obtained when retaining charge convection, while the dashed lines are the results obtained when neglecting charge convection. (d–f) show the strength of the surface charge distribution, and (g–i) show the strength of the surface tension variations. In all cases, $Ca_E = 0.2$, $Re_E = 1$, and $\lambda = 10$.

polynomial. Figures 3.3(d–f) show q^* , and Figures 3.3(g–i) show γ^* , again as functions of ζ . In all cases in Figure 3.3, $\text{Ca}_E = 0.2$, $\text{Re}_E = 1$, and $\lambda = 10$. The solid lines are the results obtained when retaining charge convection, while the dashed lines are the results obtained when neglecting charge convection. Black lines correspond to a uniform surface tension drop, i.e., $\text{El} = 0$, while the blue, red and purple lines correspond to $\text{El} = 0.5, 1, 2$, respectively. Note that in Figures 3.3(g–i), each dashed line lies almost on top of the solid line of the same colour, indicating that charge convection has a minimal effect. It is helpful to first examine the dashed lines in Figure 3.3, which reveal how the drop dynamics depend on ζ in the absence of charge convection as studied previously [Nganguia et al., 2019]. For all three classes of drops, in the limit of strong surfactant diffusion ($\zeta \rightarrow 0$), Figures 3.3(g–i) show that the surfactant distribution remains uniform regardless of the value of El , and Figures 3.3(a–c) show that all drops of each class thus attain the same deformation as a uniform surface tension drop of the relevant class. As the value of ζ increases, the effect of varying the elasticity number El becomes stronger. In the cases of prolate A and oblate drops, the deformation increases with increasing ζ or El , while both trends are reversed for prolate B drops. However, in the case of prolate B and oblate drops, the surface tension at the poles increases with increasing ζ or El , while the surface tension at the poles of a prolate A drop decreases with increasing ζ or El . As we further increase ζ towards the limit of zero surfactant diffusion ($\zeta \rightarrow \infty$), the flow is completely arrested at steady state. Within each class, all drops converge to the same surface tension profile and deformation. Under these circumstances, the surfactant is redistributed by the initial fluid flow until the Marangoni stresses alone balance the tangential electric stresses, and the degree of deformation depends solely on Ca_E , S , and Q , as can be seen from (3.60). Note that in Figures 3.3(d–f), the dashed lines of all four colours lie exactly on top of each other. This is because in the absence of charge convection, the charge distribution is decoupled from the flow and is found by taking the simplified expression for the dipole

moment (3.57), yielding

$$q = \left(1 - Q + \frac{(2 + Q)(1 - S)}{1 + 2S} \right) \cos \theta \quad (3.71)$$

for the charge. Thus, the surfactant can affect the charge distribution only through modifying the fluid flow appearing in the convective term in the full dipole evolution equation (3.44). Next, we focus on the solid lines in Figure 3.3, which correspond to results obtained when charge convection is retained in the model. Previous studies have found that in the absence of surfactants charge convection increases deformation for prolate drops and decreases deformation for oblate drops [Feng, 1999, Lanauze et al., 2015, Das and Saintillan, 2017b]. We observe the same effects for surfactant covered drops as well for all values of El and ζ . This is clearly shown in Figures 3.3(a,b), in which the solid lines lie above the dashed lines for the prolate drops, and Figure 3.3(c), in which the solid lines lie below the dashed lines for the oblate drops. As noted in previous studies, charge convection has a greater impact on the deformation of oblate drops than prolate ones. The impact on prolate B drops is particularly small; the hydrodynamic stress, which promotes oblate deformation, is slightly weakened compared to the dominant electric stress, which promotes prolate deformation and is strengthened by charge convection. In the limit of strong surfactant diffusion ($\zeta \rightarrow 0$), the surfactant distribution remains uniform regardless of the value of El . The effect of charge convection is strongest in this limit due to the absence of Marangoni stresses. In the limit of zero surfactant diffusion ($\zeta \rightarrow \infty$), the opposite happens and the flow is completely arrested at steady state, hence charge convection has no effect on drop deformation. Within each class, all surfactant-laden drops attain the same degree of deformation, regardless of the value of El , as was shown analytically in §3.3.2.

Figures 3.3(d–f) show that for prolate A drops, small values of ζ lead to a stronger positive charge distribution at the north pole (relative to the direction of the applied field) of the drop, while for oblate and prolate B drops, low values of ζ lead to a weaker negative charge distribution at the north pole of the drop.

In the prolate A class (Figure 3.3(d)), the charge distribution is parallel to the field, and since the interfacial velocity carries charges from the equator to the poles, the charge distribution is strengthened by convection. In the prolate B (Figure 3.3(e)) and oblate classes (Figure 3.3(f)), the charge distribution is antiparallel to the field, and since the interfacial velocity carries charges from the poles to the equator, the charge distribution is weakened by convection. For all three classes, as ζ is increased, the effect of charge convection is diminished because the flow is suppressed, and the value of q^* converges to that in the absence of convection given in (3.71).

Figures 3.3(g–i) show that charge convection has very little impact on the surface tension profile for drops in all three classes for the parameter values used. This is explained by the fact that the flow is suppressed when surfactant diffusion is weak, while the surface tension profile is almost uniform regardless of charge convection when surfactant diffusion is strong.

3.3.4 Quincke regime

In the Quincke regime, the applied electric field exceeds a critical threshold, and the axisymmetric steady state of the drop becomes unstable. When the axisymmetry is broken by a perturbation to the drop shape or dipole moment, the drop tilts relative to the applied field and undergoes steady rotation with a constant angular velocity. In this section, we discuss the effects of surfactant on the drop dynamics in the Quincke regime. As discussed in §2.3, the experiments of Salipante and Vlahovska [2010] demonstrated hysteresis in the angular velocity of drops undergoing Quincke rotation, behaviour which has also been captured theoretically by Peng and Schnitzer [2025]. We first show that the present model captures hysteresis and then explore how it is affected by the presence of a surfactant. The bifurcation diagrams in Figure 3.4 show the angular velocity Ω (Figure 3.4(a)) and the deformation D_Q (Figure 3.4(b)) of the drop as functions of the scaled electric field strength $E_0/E_{c,s}$. In Figure 3.4, solid blue lines denote stable solutions and dashed red lines denote unstable solutions. We show solutions for eleven values of $\zeta = 0.01, 0.1, 0.5, 1, 5, 10, 20, 30, 50, 100, 1000$. Note

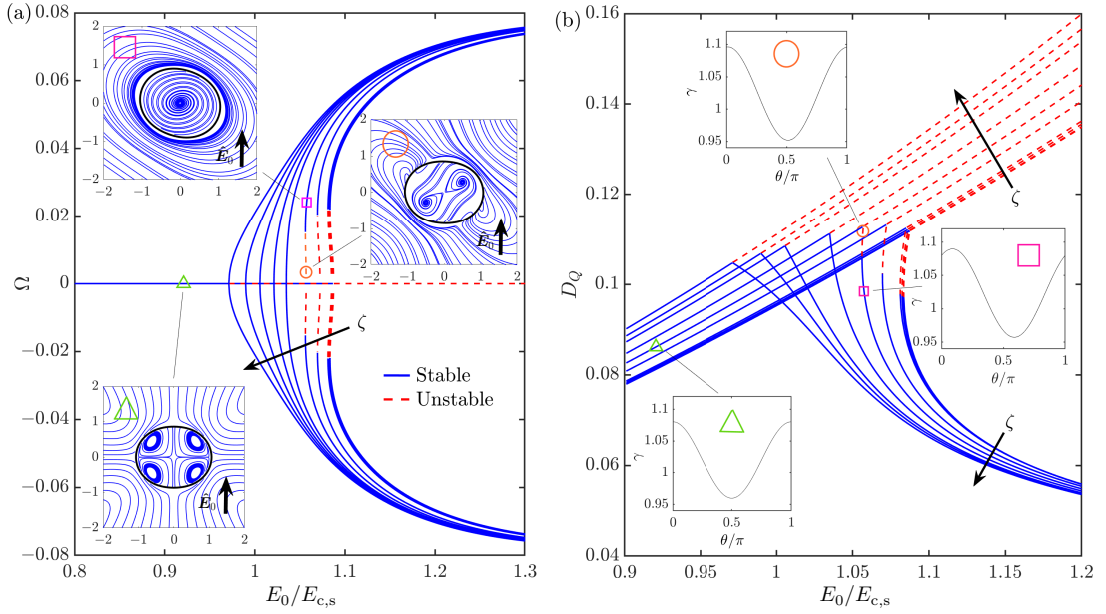


Figure 3.4: Bifurcation diagrams showing (a) the angular velocity Ω and (b) the deformation D_Q of the drop as functions of the scaled electric field strength $E_0/E_{c,s}$ for eleven values of $\zeta = 0.01, 0.1, 0.5, 1, 5, 10, 20, 30, 50, 100, 1000$, where solid blue lines denote stable solutions and dashed red lines denote unstable solutions. The arrows indicate the directions of increasing ζ . The insets in (a) show streamlines around the drop, and the insets in (b) show the corresponding surface tension as a function of θ . In all cases, $El = 0.5$ and the other parameter values are those used by Salipante and Vlahovska [2010], given in Table 2.1.

that in both Figure 3.4(a) and 3.4(b), the curves for $\zeta = 0.01, 0.1, 0.5, 1$ lie almost on top of one another and so appear as a single thick line. The insets in Figure 3.4(a) show streamlines around the drop for three different solutions for the case $\zeta = 10$, and the insets in Figure 3.4(b) show the corresponding surface tension as a function of θ . In all cases, $El = 0.5$ and the other parameter values are those used by Salipante and Vlahovska [2010], given in Table 2.1.

Figure 3.4(a) shows that a stable solution with a straining flow but zero rotational flow (streamlines shown in the inset with the green triangle, with maximum velocity $0.0058a/\tau_{\text{EHD}}$) exists up to a critical electric field strength, at which it becomes unstable and a perturbation to the dipole moment or shape of the drop will lead to steady rotation (streamlines shown in the inset with the pink square, with maximum velocity $0.045a/\tau_{\text{EHD}}$). The present model predicts that hysteresis occurs for the cases in which $\zeta = 10$ or less, and that the critical field strength for rotation decreases substantially as ζ is increased. The suppression of the

straining flow at high values of ζ may contribute to this effect; previous work on drops without surfactant has shown that the critical field strength decreases as the strength of the straining flow decreases [Das and Saintillan, 2021]. Remarkably, for $\zeta = 100$ and $\zeta = 1000$, the model predicts the onset of rotation at a lower critical field strength than that for a solid sphere. In the cases exhibiting hysteresis, the onset of rotation corresponds to a subcritical pitchfork bifurcation, and there is an unstable solution branch on which the drop is tilted and rotates (streamlines shown in the inset with the orange circle, with maximum velocity $0.011a/\tau_{\text{EHD}}$). At higher ζ , the pitchfork bifurcation becomes supercritical, and no unstable rotating solution exists.

Figure 3.4(b) shows the drop deformation corresponding to the angular velocities in Figure 3.4(a). For the given set of parameters, the drop attains an oblate shape in the Taylor regime. Before Quincke rotation begins, the deformation is greater for higher values of ζ than for lower ones, consistent with Figure 3.3(c), and surfactant accumulates at the drop equator and decreases the surface tension there (see the inset marked with the green triangle), as discussed previously. After the onset of rotation, the deformation decreases due to the rotational flow through the term $\mathbf{Q}^{xf}$, as discussed in §3.2.4. The surface tension gradients are largest for solutions on the unstable branch; while increasing the electric field strength increases the surface tension gradients, the rotational component of the flow tends to restore a uniform surfactant distribution through the term $\mathbf{Q}^{x\Gamma}$ in (3.45). This is analogous to the effect of the term $\mathbf{Q}^{xf}$, which acts to restore a spherical drop shape once rotation begins. In the Quincke regime, the inset in Figure 3.4(b) marked with the pink square indicates that there is more surfactant at the equator of the drop than at the poles, just as in the Taylor regime. However, counterintuitively, we find that higher values of ζ lead to less deformation than do lower values of ζ . This is a result of only considering the deformation of the drop in the xz plane; at high ζ , surfactant is transported out of the xz plane and towards the tips of the drops along the axis of rotation. The convection of

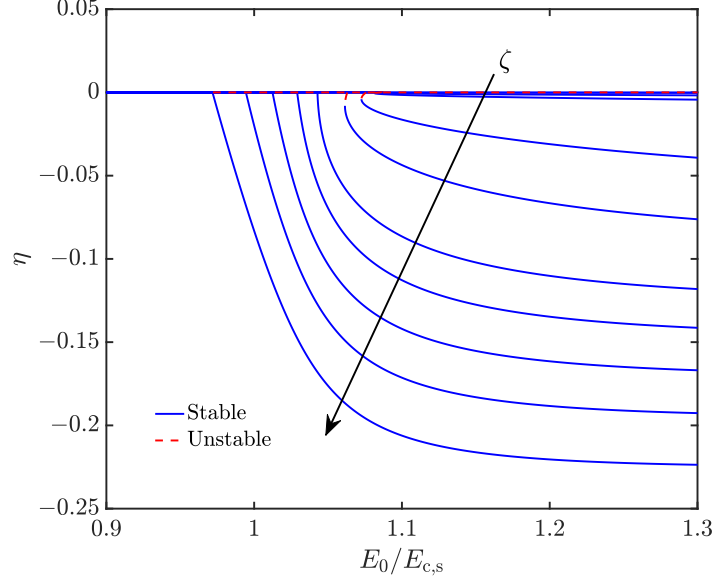


Figure 3.5: Parameter η given by (3.73) as a function of the scaled electric field strength $E_0/E_{c,s}$ for the same parameter values as those used in Figure 3.4. The arrow indicates the direction of increasing ζ .

surfactant out of the xz plane may be quantified by defining the parameter

$$\eta = \frac{1}{2\pi} \int_0^\pi \Gamma(\theta, \phi = 0) + \Gamma(\theta, \phi = \pi) d\theta - \frac{1}{2\pi} \int_0^\pi \Gamma(\theta, \phi = \pi/2) + \Gamma(\theta, \phi = 3\pi/2) d\theta, \quad (3.72)$$

which measures the difference between the average amount of surfactant in the xz plane and that in the yz plane, and takes the simple form

$$\eta = \frac{1}{2}\epsilon (Q_{xx}^\Gamma - Q_{yy}^\Gamma). \quad (3.73)$$

Figure 3.5 shows η as a function of $E_0/E_{c,s}$ for the same parameter values as those used in Figure 3.4. In the Taylor regime, η is zero because the surfactant distribution is axisymmetric. However, once rotation begins, η becomes negative, indicating that surfactant is moving out of the xz plane and accumulating in the yz plane. This effect, which is stronger for higher values of ζ , leads to an increase of the surface tension in the xz plane, which in turn leads to decreased deformation.

As previously discussed, the strength of the straining flow in the Taylor regime depends on the value of ζ . For high values of ζ , the flow is suppressed by the Marangoni stresses. However, in the Quincke regime, the surfactant distribution becomes more uniform, so the Marangoni stresses are diminished and the straining flow may be relatively unsuppressed. The strength of the straining flow is quantified by the trace of $\mathbf{S}^2$, where $\mathbf{S} = (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)/2$ is the rate-of-strain tensor [Das and Saintillan, 2017a]. We evaluate $\text{Tr}(\mathbf{S}^2)$ at the centre of the drop, $\mathbf{r} = \mathbf{0}$, where it is given by

$$\text{Tr}(\mathbf{S}^2)|_{\mathbf{r}=\mathbf{0}} = 8 (q_{xx}^{\phi 2} + q_{zz}^{\phi 2} + q_{xz}^{\phi 2} + q_{xx}^{\phi} q_{zz}^{\phi}) . \quad (3.74)$$

Figure 3.6(a) shows $\text{Tr}(\mathbf{S}^2)|_{\mathbf{r}=\mathbf{0}}$ as a function of $E_0/E_{c,s}$ for the same parameter values as those used in Figures 3.4 and 3.5. As expected, in the Taylor regime, the straining flow becomes weaker for larger values of ζ . In the cases corresponding to $\zeta \leq 30$, the straining flow is weaker in the Quincke regime than it is in the Taylor regime. This is also the case for a clean drop. However, for the cases $\zeta = 50$, $\zeta = 100$, and $\zeta = 1000$, the straining flow is stronger in the Quincke regime than it is in the Taylor regime. This is a direct result of the flow suppression effect in the Taylor regime which becomes less prominent in the Quincke regime. As the electric field strength is increased further, the dependence of strength of the straining flow on ζ decreases because the surfactant distribution becomes more uniform as a result of the strong rotational flow through the term $\mathbf{Q}^{\chi\Gamma}$ in (3.45).

The relative strengths of the straining and rotational components of the flow field can be compared by defining the flow assessment parameter

$$\Xi = \frac{\text{Tr}(\mathbf{S}^2)|_{\mathbf{r}=\mathbf{0}} - \text{Tr}(\mathbf{W}^2)|_{\mathbf{r}=\mathbf{0}}}{\text{Tr}(\mathbf{S}^2)|_{\mathbf{r}=\mathbf{0}} + \text{Tr}(\mathbf{W}^2)|_{\mathbf{r}=\mathbf{0}}} , \quad (3.75)$$

where $\mathbf{W} = (\nabla \mathbf{v} - \nabla \mathbf{v}^T)/2$ is the rate-of-rotation tensor [Das and Saintillan, 2017a]. Thus, $\Xi = 1$ corresponds to purely straining flow and $\Xi = -1$ corresponds to purely rotational flow. Figure 3.6(b) shows Ξ as a function of $E_0/E_{c,s}$ for the same parameter values as in Figures 3.4 and 3.5. In the Taylor regime, $\Xi = 1$ for all values of ζ . Even though the straining flow is strongly suppressed for large

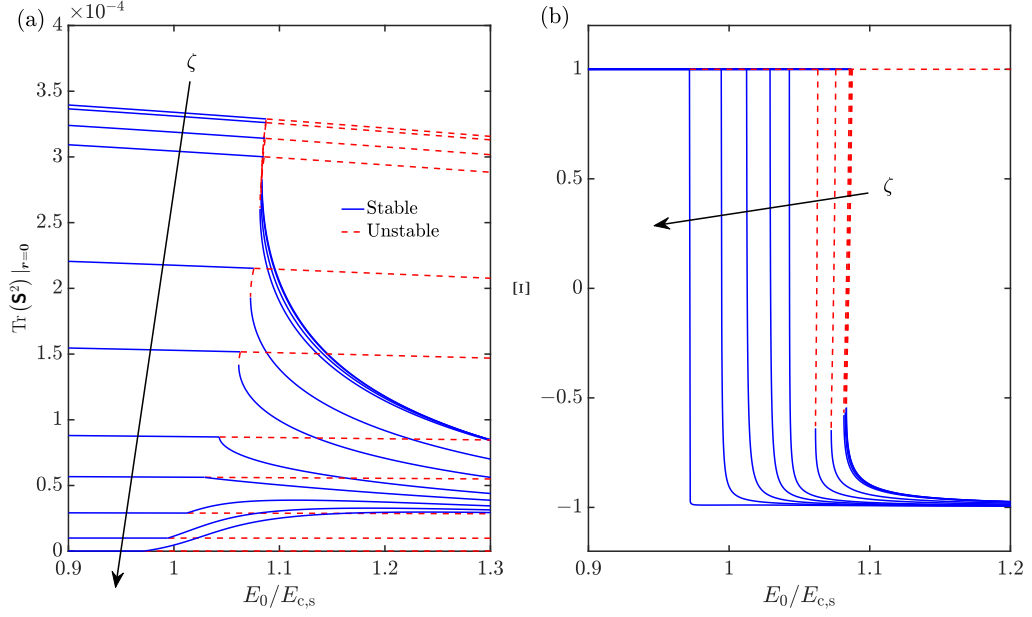


Figure 3.6: (a) Flow field strength $\text{Tr}(\mathbf{S}^2)|_{r=0}$ given by (3.74) and (b) flow assessment parameter Ξ given by (3.75) as functions of the scaled electric field strength $E_0/E_{c,s}$ for the same parameter values as those used in Figures 3.4 and 3.5. The arrows indicate the directions of increasing ζ .

values of ζ , the rotational flow is zero below the critical electric field strength for the bifurcation. Beyond the critical field strength, the value of Ξ drops towards $\Xi = -1$, indicating that the rotational component of the flow is dominant. For large values of ζ , this change is particularly sharp because the straining flow is relatively weak in the Quincke regime compared to that for small values of ζ , consistent with Figure 3.6(a). Conversely, the transition from $\Xi = 1$ towards $\Xi = -1$ is more gradual for smaller values of ζ , for which the straining flow is relatively strong in the Quincke regime. However, as the field strength is increased further, the value of Ξ converges towards -1 for all values of ζ , reflecting the increasing dominance of the rotational flow.

The destabilising effect of a weakly-diffusing surfactant on the Quincke rotation of drops may be useful in practical settings, in which rotation could be induced with a smaller electric field. It is important to bear in mind that this destabilising effect is relative to a uniformly-coated drop with constant surface tension γ_{eq} , rather than to a clean drop with the higher surface tension γ_0 . In other words, it is the spatial variations in the surfactant distribution, rather than

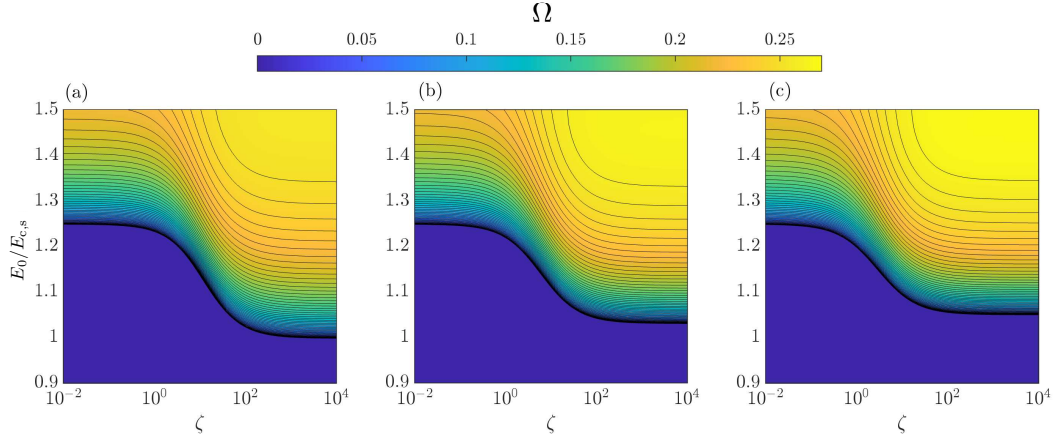


Figure 3.7: Contour plots showing the angular velocity Ω of a drop as a function of the scaled electric field strength $E_0/E_{c,s}$ and ζ for (a) $El = 0.5$, (b) $El = 1$, and (c) $El = 2$. In all cases, $Q = 5$, $S = 30$, $\lambda = 10$, and $0.04 \leq Ca_E \leq 0.1$ and $0.45 \leq Re_E \leq 1.25$ in the range of field strengths shown.

simply its presence, that provide the effect. However, the critical field for a drop with lower constant surface tension is higher than that of one with higher surface tension, so one might expect this effect to be offset by the global reduction of surface tension arising from the addition of surfactant to a clean drop with surface tension γ_0 . However, for the values $\gamma_{eq} = 4.5 \times 10^{-3}$ and $El = 0.5$ used here the corresponding constant surface tension of the same drop without surfactant is $\gamma_0 = 6.75 \times 10^{-3}$. Rescaling the capillary number with this surface tension, the critical field for rotation is around $1.065E_{c,s}$, while the critical field at $\zeta = 0$ and a capillary number based on γ_{eq} is around $1.088E_{c,s}$. The critical field at $\zeta = 1000$ and a capillary number based on γ_{eq} is around $0.97E_{c,s}$. Hence, the increase in the critical field owing to the global reduction in surface tension is much smaller than the decrease in the critical field due to the spatial variations in surface tension at high ζ . Moreover, the present model predicts that this destabilising effect becomes even more significant if El is decreased further, although this prediction should be interpreted with caution since the present asymptotic analysis formally assumes that $El = \mathcal{O}(1)$.

Next, we systematically explore the effects of varying El and ζ on the Quincke rotation of a drop, considering a drop-fluid system for which $Q = 5$, $S = 30$, and $\lambda = 10$. The present model does not predict hysteresis for these parameter values.

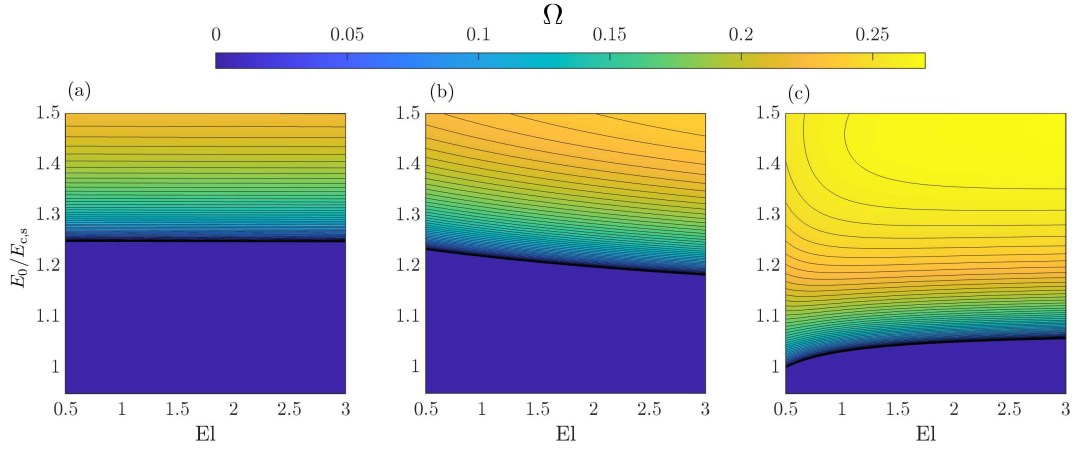


Figure 3.8: Contour plots showing the angular velocity Ω of a drop as a function of the scaled electric field strength $E_0/E_{c,s}$ and the elasticity number El for (a) $\zeta = 0.01$, (b) $\zeta = 1$, and (c) $\zeta = 1000$. All the other dimensionless parameters are the same as those used in Figure 3.7.

These values correspond to an oblate drop, but qualitatively similar results were obtained for a prolate B drop for which $Q = 0.4$, $S = 3$ and $\lambda = 10$. Figure 3.7 shows contour plots of the angular velocity Ω of the drop as a function of the scaled electric field strength $E_0/E_{c,s}$ and ζ at (a) $El = 0.5$, (b) $El = 1$, and (c) $El = 2$. Over the range of field strengths shown, namely $0.9 \leq E_0/E_{c,s} \leq 1.5$, the other dimensionless parameters vary in the ranges $0.04 \leq Ca_E \leq 0.12$ and $0.45 \leq Re_E \leq 1.25$. In the limit of strong diffusion (i.e., $\zeta \rightarrow 0$), the critical field is the same for all three values of El because the surfactant distribution remains uniform. As ζ increases, the critical field decreases and approaches a limiting value as ζ becomes large. This behaviour is qualitatively similar at all three values of El . It is noted that the critical field in the limit of weak diffusion (i.e., $\zeta \rightarrow \infty$) is highest for $El = 2$ and lowest for $El = 0.5$.

Next, we fix ζ and study the effect of changing the scaled electric field strength $E_0/E_{c,s}$ and the elasticity number El on the Quincke rotation of the drop. To this end, Figure 3.8 shows contour plots of the angular velocity Ω of the same drop as in Figure 3.7, but now plotted as a function of $E_0/E_{c,s}$ and El at (a) $\zeta = 0.01$, (b) $\zeta = 1$, and (c) $\zeta = 1000$. In the case of strong diffusion (Figure 3.8(a)), the drop behaves essentially like a uniform surface tension drop, and varying El has little effect on the critical field strength for rotation, which we denote $E_{c,d}$, nor on

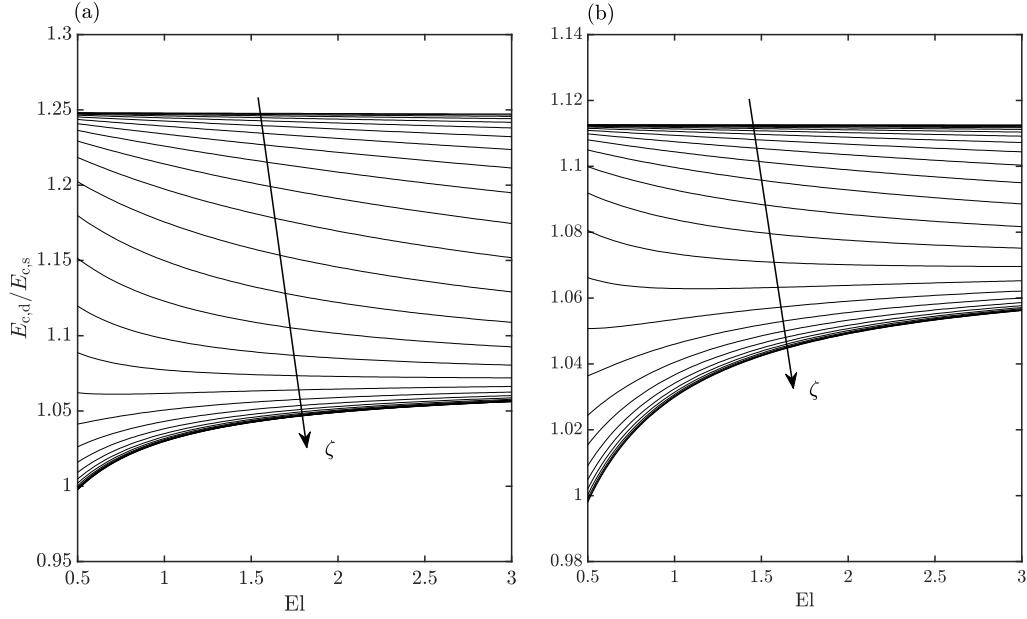


Figure 3.9: Scaled critical electric field strengths for the onset of Quincke rotation $E_{c,d}/E_{c,s}$ as functions of El for thirty logarithmically-spaced values of ζ between 10^{-2} and 10^4 , specifically for $\zeta = 10^{-2+6n/29}$ for $n = 0, 1, 2, \dots, 28, 29$. (a) shows results for $\lambda = 10$, and (b) shows results for $\lambda = 50$. The dimensionless parameters are the same as those used in Figures 3.7 and 3.8.

Ω . When diffusion is moderate (Figure 3.8(b)), increasing El leads to a decrease in $E_{c,d}$ and an increase in Ω . However, when diffusion is weak (Figure 3.8(c)), $E_{c,d}$ instead increases as El increases. In this case, the dependence of Ω on El depends on the field strength. At field strengths only just strong enough to induce rotation (i.e., $E_0/E_{c,s}$ less than approximately 1.1 in Figure 3.8(c)), an increase in El leads to a decrease in Ω . At slightly greater field strengths (i.e., $E_0/E_{c,s}$ around 1.2 in Figure 3.8(c)), an increase in El initially leads to an increase in Ω , before the trend reverses and further increases in El lead to a decrease in Ω . At relatively large field strengths (i.e., $E_0/E_{c,s}$ greater than approximately 1.3 in Figure 3.8(c)), an increase in El initially leads to an increase in Ω , before the effect vanishes and Ω becomes insensitive to further increases in El .

The relationship between the elasticity number El and the critical electric field strength $E_{c,d}$ can be explored further using the linear stability analysis described in §3.3.1. Figure 3.9 shows the critical field strengths for rotation of a drop scaled by that for a solid sphere $E_{c,d}/E_{c,s}$ as functions of El for thirty logarithmically-

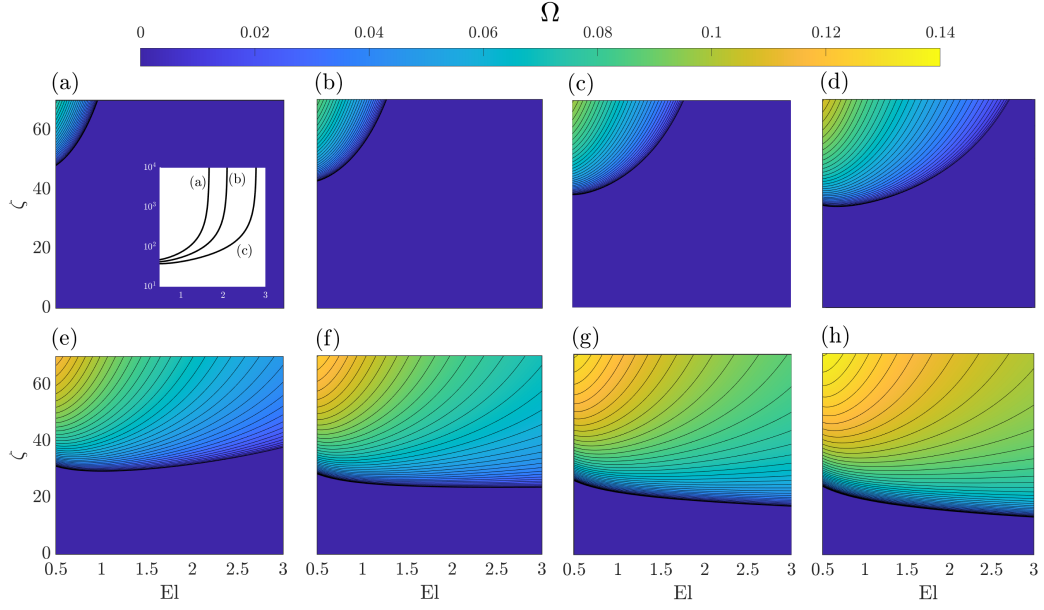


Figure 3.10: Contour plots showing the angular velocity Ω of a drop as a function of ζ and the elasticity number El for eight electric field strengths $E_0/E_{c,s} = 1.045, 1.05, \dots, 1.075, 1.08$. All the other dimensionless parameters are the same as those used in Figures 3.7, 3.8, and 3.9. The inset in (a) displays the marginal curves between the axisymmetric and rotational solution regions as functions of El for (a) $E_0/E_{c,s} = 1.045$, (b) $E_0/E_{c,s} = 1.05$, and (c) $E_0/E_{c,s} = 1.055$ using a logarithmic scale.

spaced values of ζ between 10^{-2} and 10^4 , specifically for $\zeta = 10^{-2+6n/29}$ for $n = 0, 1, 2, \dots, 28, 29$. The curves in Figure 3.9 generated from the linear stability analysis are the same as the marginal curves in Figure 3.8 that separate the Taylor and Quincke regimes. Figure 3.9(a) shows results for $\lambda = 10$, and Figure 3.9(b) shows results for $\lambda = 50$. The other parameters are the same as those used in Figures 3.7 and 3.8. Figure 3.9 indicates that the effect of the surfactant is destabilising over the full range shown of $0.5 \leq El \leq 3$, and that the effect is more pronounced for $\lambda = 10$ than for $\lambda = 50$. It also shows that increasing El leads to a decrease in $E_{c,d}/E_{c,s}$ at lower values of ζ , and that the trend reverses at higher values of ζ , consistent with the results shown in Figure 3.8.

Next, we focus our attention on the effects of varying ζ and the elasticity number El at fixed electric field strengths close to the critical field for Quincke rotation. Firstly, Figure 3.10 shows contour plots of the angular velocity Ω of the drop as a function of ζ and El for eight field strengths increasing in increments of

0.005 from $E_0/E_{c,s} = 1.045$ (Figure 3.10(a)) to $E_0/E_{c,s} = 1.080$ (Figure 3.10(h)). The inset in Figure 3.10(a) displays the marginal curves between the axisymmetric and rotational solution regions as functions of El for (a) $E_0/E_{c,s} = 1.045$, (b) $E_0/E_{c,s} = 1.05$, and (c) $E_0/E_{c,s} = 1.055$ using a logarithmic scale. At each field strength shown, the angular velocity is greatest for the highest values of ζ and the lowest values of El shown. As in Figure 3.7, the critical field strength $E_{c,d}/E_{c,s}$ at which rotation occurs for a given value of El is decreased as ζ is increased. Hence, for a given field strength that is greater than the critical field strength for rotation in the limit $\zeta \rightarrow \infty$ (i.e., the limit of weak surfactant diffusion) but smaller than that in the limit $\zeta \rightarrow 0$ (i.e., the limit of strong surfactant diffusion), there exists a critical value of ζ at which the drop becomes unstable and Quincke rotation occurs. This critical value corresponds to the marginal curves between the axisymmetric and rotational solution regions. At the lowest field strength considered, $E_0/E_{c,s} = 1.045$ (Figure 3.10(a)), the critical value increases sharply as El is increased. As shown in the inset, the critical value diverges as El approaches $El \approx 1.67$. Above $El \approx 1.67$, the field is too weak to induce rotation at any value of ζ . The critical values at the second and third field strengths shown, $E_0/E_{c,s} = 1.05$ and $E_0/E_{c,s} = 1.055$ (Figures 3.10(b) and (c)), diverge as the elasticity number approaches $El \approx 2.1$ and $El \approx 2.78$, respectively. For field strengths at or above that shown in Figure 3.10(d), corresponding to $E_0/E_{c,s} = 1.06$, the critical value of ζ is smaller than $\zeta = 40$ for all values of El in the range shown. Furthermore, when the field strength is at or above $E_0/E_{c,s} = 1.07$, the critical value of ζ decreases with increasing El in the range shown. Hence, the critical value of ζ and the angular velocity of the drop are significantly more sensitive to changes in the field strength for $El = 3$ than they are for $El = 0.5$. On the other hand, the contour lines indicate that for the field strengths shown, Ω is more sensitive to changes in ζ when $El = 0.5$ than when $El = 3$.

Figure 3.11 shows the scaled critical electric field strength for Quincke rotation $E_{c,d}/E_{c,s}$ (Figure 3.11(a)), angular velocity Ω (Figures 3.11(b) and (c)), straining flow strength $\text{Tr}(\mathbf{S}^2)|_{r=0}$ (Figures 3.11(d) and (e)), and deformation parameter

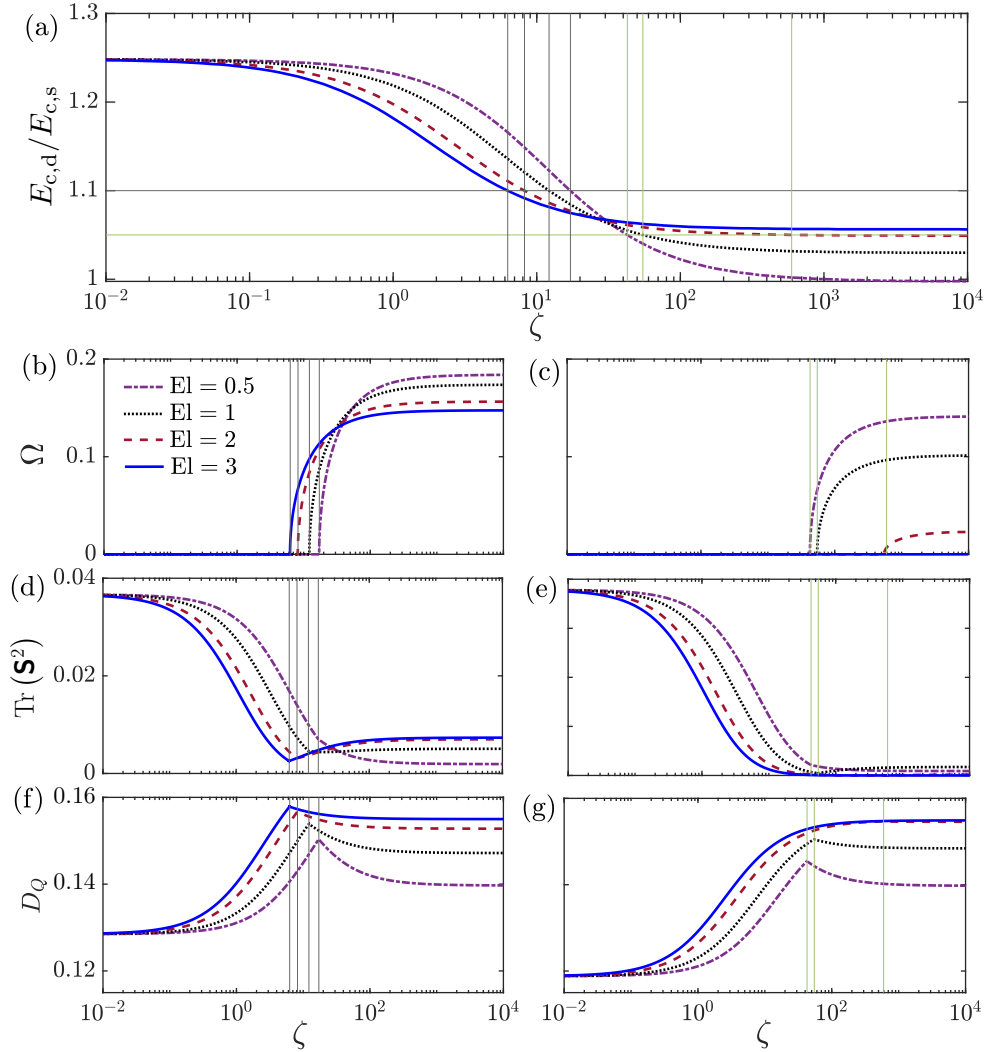


Figure 3.11: (a) Scaled critical electric field strength for Quincke rotation $E_{c,d}/E_{c,s}$, (b,c) angular velocity Ω , (d,e) straining flow strength $\text{Tr}(\mathbf{S}^2)|_{r=0}$, and (f,g) deformation parameter D_Q as functions of ζ for $\text{El} = 0.5$ (purple dash-dotted lines), 1 (black dotted lines), 2 (red dashed lines), and 3 (blue solid lines). (b), (d) and (f) correspond to $E_0/E_{c,s} = 1.1$, while (c), (e) and (g) correspond to $E_0/E_{c,s} = 1.05$. These field strengths are indicated by the thin black and green horizontal lines in (a), respectively, and the predicted critical values of ζ are denoted in the relevant subfigures by the thin vertical green and black lines. We again use $Q = 5$ and $S = 30$, and the other relevant parameters are $\text{Ca}_E = 0.06$ and $\text{Re}_E = 0.6$ at $E_0/E_{c,s} = 1.05$, and $\text{Ca}_E = 0.07$ and $\text{Re}_E = 0.67$ at $E_0/E_{c,s} = 1.1$.

D_Q (Figures 3.11(f) and (g)) as functions of ζ for $El = 0.5$ (purple dash-dotted lines), 1 (black dotted lines), 2 (red dashed lines), and 3 (blue solid lines). Figures 3.11(b), (d) and (f) correspond to $E_0/E_{c,s} = 1.1$, while Figures 3.11(c), (e) and (g) correspond to $E_0/E_{c,s} = 1.05$. We again use $Q = 5$ and $S = 30$, and the other relevant parameters are $Ca_E = 0.06$ and $Re_E = 0.6$ at $E_0/E_{c,s} = 1.05$, and $Ca_E = 0.07$ and $Re_E = 0.67$ at $E_0/E_{c,s} = 1.1$. These field strengths are marked by the thin horizontal lines in Figure 3.11(a), in which the green line marks $E_0/E_{c,s} = 1.05$ and the black line marks $E_0/E_{c,s} = 1.1$. The predicted critical values of ζ at the given field strengths are given by the ζ coordinates of the intersections of these horizontal lines and the solution curves in Figure 3.11(a), and are denoted in the relevant subfigures by the thin vertical green and black lines. The critical field strengths $E_{c,d}/E_{c,s}$ shown in Figure 3.11(a) are obtained from the linear stability analysis described in §3.3.1, and are the same as the marginal curves separating the Taylor and Quincke regimes in Figure 3.7. Similarly, Figures 3.11(b) and (c) correspond to horizontal slices of Figure 3.7. At $E_0/E_{c,s} = 1.05$, the critical value of ζ is lower for lower values of El than for higher ones, and indeed no bifurcation occurs at all for the case $El = 3$. However, the trend reverses at $E_0/E_{c,s} = 1.1$, and the critical value of ζ decreases as El is increased. Figures 3.11(b) and (c) show that at both of these field strengths, the angular velocity is larger for lower values of El than for higher ones as ζ grows large, even though drops with higher El destabilise at lower values of ζ at $E_0/E_{c,s} = 1.1$. Figures 3.11(d) and (e) show that as ζ is increased, the straining flow is weakened due to the increasing Marangoni stresses. However, beyond the critical value of ζ , the straining flow is strengthened with further increases in ζ for the cases $El = 1, 2$, and 3 at $E_0/E_{c,s} = 1.1$ (Figure 3.11(d)) and for the cases $El = 1$ and 2 at $E_0/E_{c,s} = 1.05$ (Figure 3.11(e)). On the other hand, for $El = 0.5$, the straining flow continues decreasing in strength as ζ is increased beyond its critical value at both field strengths considered. Figures 3.11(f) and (g) show that in the limit of strong diffusion (i.e., in the limit $\zeta \rightarrow 0$), in which all of the drops are in the Taylor regime, all of the drops have the same deformation at a given field strength because the surfactant distribution remains uniform in all

cases, as is the case for the results shown in Figure 3.3. As ζ is increased, the deformation increases due to the accumulation of surfactant around the equator, with the deformation becoming greater for greater values of El . However, above the critical value of ζ , the deformation begins to decrease as ζ increases. The reduction of the deformation in the Quincke regime becomes more pronounced as El is decreased. Thus, in the limit of zero diffusion (i.e., in the limit $\zeta \rightarrow \infty$) the deformation of surfactant-laden oblate drops increases as El is increased in the Quincke regime, unlike in the Taylor regime, in which the deformation is the same for all values of El .

3.4 Conclusions

In this chapter, we have described a three-dimensional phenomenological model for an almost spherical, leaky dielectric drop coated with a dilute monolayer of insoluble apolar surfactant and subjected to a uniform DC electric field. The novelty of our work lies in the retention of charge convection in the transport equation for the surface charge, which allows the model to capture Quincke rotation. We have examined the combined effects of surfactant and charge convection on drop deformation in the Taylor regime, and found that the two effects work cooperatively to promote increased deformation of prolate A drops, but that they work antagonistically in the cases of prolate B and oblate drops. Our model predicts that the presence of a weakly-diffusing surfactant can eliminate the hysteresis that occurs in the angular velocity of drops undergoing Quincke rotation and can significantly decrease the critical electric field strength for the onset of rotation from that for a drop of constant surface tension. We find that for an oblate drop in the Quincke regime, the surfactant is transported out of the rotational plane and accumulates at the tips of the drop along the axis of rotation.

A linear stability analysis of the system reveals that for strongly-diffusing surfactants (i.e., for low values of ζ), an increase in El leads to a decrease in the critical electric field strength for the onset of rotation $E_{c,d}$, while the opposite is true for weakly-diffusing surfactants (i.e., for high values of ζ). We have explored

the effects of varying ζ and the elasticity number El on the deformation and angular velocity of an oblate drop at fixed electric field strengths. We find that larger values of El lead to larger deformation than do smaller ones across the whole range of ζ studied, and smaller values of El lead to larger angular velocity than do larger ones in the limit of large ζ . At intermediate values of ζ , the relationship between the angular velocity and El depends on the field strengths: at larger field strengths, drops with larger values of El begin rotating at a smaller critical value of ζ than do drops with smaller values of El . At smaller field strengths, the opposite is true, and drops with smaller values of El begin rotating at smaller critical values of ζ , while drops with larger values of El may not rotate at all, even in the limit of large ζ .

Chapter 4

An Interacting Pair of Clean Drops

As discussed in §1.4, several authors have studied the electrohydrodynamic interactions between a pair of drops theoretically [Sozou, 1975, Mhatre et al., 2015, Zabaranin, 2020, Sorgentone et al., 2021, Kach et al., 2022], computationally [Baygents et al., 1998, Lin et al., 2012, Mhatre et al., 2015, Dong and Sau, 2018, Sorgentone and Vlahovska, 2022, Dong et al., 2024], and experimentally [Mhatre et al., 2015, Kach et al., 2022]. However, with the exception of the work of Dong et al. [2024] on a pair of two-dimensional counterrotating drops, none of these theoretical or computational studies have considered the effect of charge convection, and have thus been unable to capture Quincke rotation. Hence, in this chapter, we present a three-dimensional phenomenological model that captures the interactions between a pair of drops, retaining charge convection so as to allow for Quincke rotation. This chapter is organized as follows. In §4.1, we outline the problem under consideration, recapitulating the governing equations and boundary conditions. In §4.2, we present our approach to solving the problem, focusing in particular on the necessary additions to the equations for an isolated drop presented in Chapter 2. In §4.3, we present the results of our model, first for freely suspended drops and then for drops fixed in space. Finally, in §4.4, we summarize the key findings of the present model.

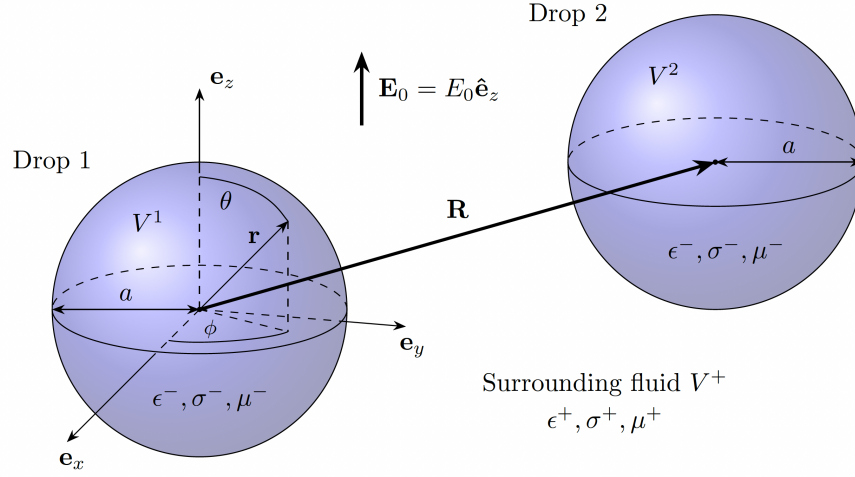


Figure 4.1: Two identical drops of a leaky dielectric fluid suspended in another fluid and exposed to a uniform electric field $\mathbf{E}_0 = E_0 \hat{\mathbf{e}}_z$.

4.1 Problem formulation

Consider two initially spherical leaky dielectric drops with initial radius a and identical material properties suspended in another leaky dielectric fluid and exposed to a uniform DC electric field $\mathbf{E}_0$ as shown in Figure 4.1. We use the same spherical coordinate system (radial distance r , polar angle θ , azimuthal angle φ) as in Chapters 2 and 3, now defined such that the origin is at the centre of one of the drops, which we call drop 1. The position of the centre of the second drop, which we call drop 2, is given by the separation vector $\mathbf{R} = (r = R, \theta = \theta_R, \phi = \phi_R)$. Electrical permittivity (dielectric constant), electrical conductivity and viscosity are again denoted ϵ, σ and μ , respectively, and $+$ and $-$ superscripts denote the values of these parameters in the surrounding fluid and the drops, respectively. We denote the unbounded domain of the surrounding fluid by V^+ , the domains of the two drops by V_1 and V_2 , and the drop interfaces by ∂V_1 and ∂V_2 , respectively. We will also define V^- to denote the domain of either drop 1 or 2, since the same governing equations apply in each drop domain. With the assumption of charge-free bulk fluids, the electric potential $\varphi^\pm(\mathbf{r}, t)$ satisfies Laplace's equation in all three domains,

$$\nabla^2 \varphi^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm. \quad (4.1)$$

The electric field is denoted by $\mathbf{E}^\pm(\mathbf{r}, t) = -\nabla\varphi^\pm$, and the charge distribution $q_i(\mathbf{r}, t)$ on the interface of drop i is given by Gauss's Law:

$$q_i = \llbracket \epsilon \mathbf{E} \cdot \mathbf{n}(\mathbf{r}, t) \rrbracket_i \quad \text{for } \mathbf{r} \in \partial V_i, \quad i = 1, 2. \quad (4.2)$$

Here, the notation $\llbracket f(\mathbf{r}) \rrbracket_i = f^+(\mathbf{r}) - f^-(\mathbf{r})$, $\mathbf{r} \in \partial V_i$ is used to denote the discontinuity of a field variable f over the interface of drop i and $\mathbf{n}_i$ is the outward-pointing unit vector normal to the interface of drop i . The electric potential and the tangential electric field are both continuous across both drop interfaces:

$$\llbracket \varphi \rrbracket_i = 0, \quad \llbracket \mathbf{E} \cdot (\mathbf{l} - \mathbf{n}\mathbf{n}) \rrbracket_i = \mathbf{0} \quad \text{for } \mathbf{r} \in \partial V_i, \quad i = 1, 2. \quad (4.3)$$

The transport equation for the surface charge (2.4) applies to the charge distribution of each drop, that is,

$$\frac{\partial q_i}{\partial t} + \llbracket \sigma \mathbf{E} \cdot \mathbf{n} \rrbracket_i + \nabla_{s,i} \cdot (q_i \mathbf{v}_i^\pm) = 0 \quad \text{for } \mathbf{r} \in \partial V_i, \quad i = 1, 2. \quad (4.4)$$

Here, $\mathbf{v}_i^\pm(\mathbf{r}, t)$ is the fluid velocity and $\nabla_{s,i} = (\mathbf{l} - \mathbf{n}_i \mathbf{n}_i) \cdot \nabla$ is the surface gradient operator for the i th drop interface. The fluid flow is governed by the Stokes equations in all three domains:

$$\mu^\pm \nabla^2 \mathbf{v}^\pm = \nabla p^\pm, \quad \nabla \cdot \mathbf{v}^\pm = 0 \quad \text{for } \mathbf{r} \in V^\pm, \quad (4.5)$$

where $p^\pm(\mathbf{r}, t)$ is the pressure. The fluid velocity is continuous across the interface of each drop:

$$\llbracket \mathbf{v} \rrbracket_i = \mathbf{0} \quad \text{for } \mathbf{r} \in \partial V_i, \quad i = 1, 2. \quad (4.6)$$

The interfaces are defined implicitly as

$$\xi_i(\mathbf{r}, t) = 0 \quad \text{for } \mathbf{r} \in V^\pm, \quad (4.7)$$

and are advected with the flow, so the kinematic boundary condition is written

$$\frac{\partial \xi_i}{\partial t} + \mathbf{v}_i \cdot \nabla \xi_i = 0 \quad \text{for } \mathbf{r} \in \partial V_i, \quad i = 1, 2. \quad (4.8)$$

Finally, the electrohydrodynamic stress balance (1.54) applies at the interface of each drop, i.e.,

$$[\![\mathbf{f}^E]\!]_i + [\![\mathbf{f}^H]\!]_i = 2\gamma\kappa_i \mathbf{n}_i \quad \text{for } \mathbf{r} \in S_i, \quad i = 1, 2, \quad (4.9)$$

where $[\![\mathbf{f}^E]\!]_i(\mathbf{r}, t)$ and $[\![\mathbf{f}^H]\!]_i(\mathbf{r}, t)$ are the electric and hydrodynamic traction jumps across the interface of drop i , respectively, γ is the constant surface tension coefficient, and $\kappa_i(\mathbf{x}, t) = (\nabla_{\mathbf{s}} \cdot \mathbf{n})_i/2$ is the mean surface curvature of drop i .

4.1.1 Nondimensionalisation and scaling assumptions

The length and time scales for the problem are again taken to be the initial drop radius a and the electrohydrodynamic flow time τ_{EHD} , respectively. Then, the nondimensional stress balance (2.13) applies at the interface of each drop,

$$[\![\mathbf{f}^E]\!]_i + [\![\mathbf{f}^H]\!]_i = \frac{2}{\text{Ca}_E} \kappa_i \mathbf{n}_i, \quad (4.10)$$

as does the dimensionless charge transport equation (2.15),

$$\frac{\partial q_i}{\partial t} + \frac{1}{\text{Re}_E} [\![\mathbf{j} \cdot \mathbf{n}]\!]_i + \nabla_{\mathbf{s},i} \cdot (q_i \mathbf{v}_i^\pm) = 0, \quad (4.11)$$

where

$$[\![\mathbf{j} \cdot \mathbf{n}]\!]_i = \mathbf{E}_i^+ \cdot \mathbf{n}_i - \frac{1}{S} \mathbf{E}_i^- \cdot \mathbf{n}_i \quad (4.12)$$

is the discontinuity in the current across the interface of drop i in the normal direction. As in Chapters 2 and 3, we assume that small deviations of both drop shapes from sphericity are proportional to $\delta \ll 1$. In addition, we assume $\text{Re}_E = \mathcal{O}(1)$, and $\lambda \gg 1$. Interactions between the drops are handled using the method of reflections [Happel and Brenner, 1965, Hetsroni and Haber, 1978, Das and Saintillan, 2013], which is valid for widely-separated drops. The leading-

order interactions between the drops are the translational velocities of each drop induced by Quincke rotation of the other, appearing at $\mathcal{O}(R^{-2})$, as will be shown in §4.2.3. However, these interactions only affect the drop shapes, flow fields and charge distributions through modifying $\mathbf{R}$, and terms of $\mathcal{O}(R^{-2})$ do not appear in any of the equations other than those governing the translation of the drops. The disturbance to the electric field experienced by drop 1 due to the polarisation of drop 2, as well as gradients in the ambient velocity field experienced by drop 1 due to the presence of drop 2, appear at $\mathcal{O}(R^{-3})$. Hence, we take $R^{-3} \ll 1$ as the third small parameter in our analysis. Finally, it will be shown in §4.2.6 that $\delta \sim \text{Ca}_E$. Thus, in summary, we assume that R^{-3} , λ^{-1} , Ca_E and δ are small and of the same order; that is,

$$\delta \sim \text{Ca}_E \sim \lambda^{-1} \sim R^{-3} \ll 1, \quad (4.13)$$

and retain all terms to leading order in any of these three parameters. In some cases, to capture additional physical effects such as DEP, we retain higher order terms, but the model is asymptotically correct to $\mathcal{O}(\delta + \lambda^{-1} + R^{-3})$.

4.2 Problem solution

In this section, we outline the solution to the problem formulated in section 4.1. We focus on solving the governing equations for the flow fields and shape of drop 1. The corresponding analysis for drop 2 is conducted similarly, with appropriate adjustments to the subscripts. In §4.2.1, we describe the parameterisation of the shape of drop 1 and the calculation of the corresponding curvature and unit normal vector. In §4.2.2, we solve Laplace's equation (4.1) for the electric potential. §4.2.3 addresses the solution of the Stokes equations (4.5) for the fluid velocity and pressure. In §4.2.4, we obtain the translational velocities of the drops induced by electrohydrodynamic and dielectrophoretic interactions. §4.2.5 applies the kinematic boundary condition to establish relationships between the flow fields and the drop shape. §4.2.6 focuses on balancing electric and hydrody-

dynamic stresses at the drop interface. Finally, in §4.2.7, we derive the evolution equations for the surface charge, which are then solved numerically.

4.2.1 Drop shapes

We parameterise the interface of drop 1 as

$$\xi_1 = r - [1 + \delta f_1(\theta, \phi, t)] = 0, \quad (4.14)$$

where $\delta \ll 1$ (to be defined in §4.2.6). Deviations of the interface from a spherical shape are captured by $f_1 = f_1(\theta, \phi, t)$ which is expanded as a series of spherical harmonics. Here, we only retain the second order harmonics, in anticipation of the form of the electric stress [Das and Saintillan, 2021],

$$f_1 = \mathbf{Q}_1^f : \hat{\mathbf{r}}\hat{\mathbf{r}}. \quad (4.15)$$

Using the definition in (4.14), the surface normal $\mathbf{n}_1$ and the curvature κ_1 of the interface of drop 1 are given by

$$\mathbf{n}_1 = \frac{\nabla \xi_1}{|\nabla \xi_1|} = \hat{\mathbf{r}} - 2\delta(\mathbf{Q}_1^f \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}), \quad \kappa_1 = \frac{1}{2} \nabla_{s,1} \cdot \mathbf{n}_1 = 1 + 2\delta \mathbf{Q}_1^f : \hat{\mathbf{r}}\hat{\mathbf{r}}. \quad (4.16)$$

4.2.2 Electrostatics

To satisfy Laplace's equation (4.1), we use a similar multipole expansion to that employed in Chapters 2 and 3. However, in contrast to the case of an isolated drop, the electric potential and the corresponding electric field in the vicinity of drop 1 are modified by the polarisation of drop 2. This interaction means that the electric field experienced by drop 1 is generally nonuniform, and so gives rise to higher-order multipoles beyond the dipole moment in the surface charge of drop 1. Specifically, the effective external electric potential experienced by drop 1 is

$$\varphi_1^\infty = -\hat{\mathbf{E}}_0 \cdot \mathbf{r} + \frac{\mathbf{P}_2 \cdot (\mathbf{r} - \mathbf{R})}{|\mathbf{r} - \mathbf{R}|^3}, \quad (4.17)$$

where $\mathbf{P}_2(t)$ is the induced dipole moment of drop 2. However, expanding the associated electric field for large R/r shows that the leading-order (i.e., the $\mathcal{O}(R^{-3})$) effect of drop 2 is a uniform correction to the applied field, while spatial variations appear only at $\mathcal{O}(R^{-4})$. Specifically, the electric field experienced by drop 1 can be written

$$\mathbf{E}_1^\infty = \hat{\mathbf{E}}_0 - R^{-3} \mathbf{P}_2 \cdot (\mathbf{I} - 3\hat{\mathbf{R}}\hat{\mathbf{R}}) + \mathcal{O}(R^{-4}), \quad (4.18)$$

where $\hat{\mathbf{R}} = \mathbf{R}/R$ is the unit vector in the direction of $\mathbf{R}$. Hence, by retaining only the leading order effect of drop 2 on the electric field near drop 1, $\mathbf{E}_1^\infty$ remains uniform and so does not induce any higher order charge multipoles. The charge distribution on drop 1 may then still be described solely by the dipole moment, as for the case of an isolated drop. With this approximation, the electric potentials inside and outside drop 1 can be written as

$$\varphi_1^- = \varphi_1^\infty + \mathbf{P}_1 \cdot \mathbf{r}, \quad \varphi_1^+ = \varphi_1^\infty + r^{-3} \mathbf{P}_1 \cdot \mathbf{r}, \quad (4.19)$$

respectively. Here, $\mathbf{P}_1(t)$ denotes the induced dipole moment of drop 1. The potentials resulting from the drop's own dipole $\mathbf{P}_1$ inside and outside the drop are given by growing and decaying harmonics, respectively. As will be seen in §4.2.7, hydrodynamic interactions between the drops can also give rise to higher-order multipoles scaling as R^{-3} . However, the effect of these multipoles on the flow fields and shape of drop 1 appear at $\mathcal{O}(\lambda R^{-3})$, so they are not retained in (4.19) at this order of approximation. The associated electric fields, $\mathbf{E}_1^\pm = -\nabla \varphi_1^\pm$, inside and outside drop 1 are given by

$$\mathbf{E}_1^- = \mathbf{E}_1^\infty - \mathbf{P}_1, \quad \mathbf{E}_1^+ = \mathbf{E}_1^\infty - r^{-3} \mathbf{P}_1 \cdot (\mathbf{I} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}). \quad (4.20)$$

After calculating the electric stress tensors inside and outside drop 1, the traction jump across the interface is given by

$$\llbracket \mathbf{f}^E \rrbracket_1 = \llbracket \boldsymbol{\tau}^E \rrbracket_1 \cdot \hat{\mathbf{r}} = p_1^E \hat{\mathbf{r}} + \mathbf{Q}_{1,\hat{\mathbf{r}}}^E : \hat{\mathbf{r}}\hat{\mathbf{r}}\hat{\mathbf{r}} + \left(\mathbf{Q}_{1,\hat{\mathbf{t}}}^E \cdot \hat{\mathbf{r}} \right) \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}) + \mathbf{T}_1^E \times \hat{\mathbf{r}}, \quad (4.21)$$

where

$$p_1^E = -\frac{1-Q}{6}(E_1^\infty)^2 + \frac{4-Q}{3}(\mathbf{E}_1^\infty \cdot \mathbf{P}_1) + \frac{Q+2}{6}P_1^2, \quad (4.22a)$$

$$\begin{aligned} \mathbf{Q}_{1,\hat{\mathbf{r}}}^E &= (1-Q)\mathbf{E}_1^\infty \mathbf{E}_1^\infty + \frac{1+2Q}{2}(\mathbf{E}_1^\infty \mathbf{P}_1 + \mathbf{P}_1 \mathbf{E}_1^\infty) + \frac{5-2Q}{2}\mathbf{P}_1 \mathbf{P}_1 \\ &+ \left[-\frac{1-Q}{3}(E_1^\infty)^2 - \frac{1+2Q}{3}(\mathbf{E}_1^\infty \cdot \mathbf{P}_1) - \frac{5-2Q}{6}P_1^2 \right] \mathbf{I}, \end{aligned} \quad (4.22b)$$

$$\begin{aligned} \mathbf{Q}_{1,\hat{\mathbf{t}}}^E &= (1-Q)\mathbf{E}_1^\infty \mathbf{E}_1^\infty + \frac{1+2Q}{2}(\mathbf{E}_1^\infty \mathbf{P}_1 + \mathbf{P}_1 \mathbf{E}_1^\infty) - (2+Q)\mathbf{P}_1 \mathbf{P}_1 \\ &+ \left[-\frac{1-Q}{3}(E_1^\infty)^2 - \frac{1+2Q}{3}(\mathbf{E}_1^\infty \cdot \mathbf{P}_1) + \frac{2+Q}{3}P_1^2 \right] \mathbf{I}, \end{aligned} \quad (4.22c)$$

$$\mathbf{T}_1^E = \frac{3}{2}\mathbf{P}_1 \times \mathbf{E}_1^\infty. \quad (4.22d)$$

As before, p_1^E is the isotropic electric pressure on the surface of drop 1, $\mathbf{Q}_{1,\hat{\mathbf{r}}}^E$ and $\mathbf{Q}_{1,\hat{\mathbf{t}}}^E$ are the quadrupolar stresses, and $\mathbf{T}_1^E$ is the torque.

4.2.3 Hydrodynamics

As in Chapters 2 and 3, we use the general solution of Lamb [1932] to the Stokes equations (4.5). However, in contrast to the case of an isolated drop, hydrodynamic interactions between a pair of drops must be accounted for. The pressures inside and outside drop 1 are

$$p_1^- = \sum_{n=0}^{\infty} p_{1,n} \quad (4.23)$$

and

$$p_1^+ = p_1^\infty + \sum_{n=0}^{\infty} p_{1,-(n+1)}, \quad (4.24)$$

and the velocities are

$$\begin{aligned} \mathbf{v}_1^- &= \sum_{n=1}^{\infty} \nabla \times (\mathbf{r} \chi_{1,n}) \\ &+ \nabla \phi_{1,n} + \frac{n+3}{2(n+1)(2n+3)\lambda} r^2 \nabla p_{1,n} - \frac{n}{\lambda(n+1)(2n+3)} \mathbf{r} p_{1,n} \end{aligned} \quad (4.25)$$

and

$$\begin{aligned} \mathbf{v}_1^+ &= \mathbf{v}_1^\infty + \sum_{n=1}^{\infty} \nabla \times (\mathbf{r} \chi_{1,-(n+1)}) \\ &\quad + \nabla \phi_{1,-(n+1)} + \frac{2-n}{2n(2n-1)} r^2 \nabla p_{1,-(n+1)} + \frac{n+1}{n(2n-1)} \mathbf{r} p_{1,-(n+1)}. \end{aligned} \quad (4.26)$$

In (4.24) and (4.26), we have included an external pressure $p_1^\infty(\mathbf{r}, t)$ and velocity $\mathbf{v}_1^\infty(\mathbf{r}, t)$, which represent the hydrodynamic effect of drop 2 on drop 1. To calculate these, we note that at leading order (i.e., in the absence of hydrodynamic interactions), the pressure and velocity fields outside drop 2 are those given for an isolated drop in (2.55) and (2.57). These are denoted $p_{2,0}^+$ and $\mathbf{v}_{2,0}^+$ and are expanded for small r/R to approximate their values near drop 1. Keeping terms up to $\mathcal{O}(R^{-3})$, the pressure and velocity fields around drop 1 arising from hydrodynamic interactions with drop 2 are

$$p_1^\infty = p_{2,0}^+|_{\mathbf{r}=\mathbf{R}} = R^{-1} M_{2,0}^p + R^{-3} \mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}} + \mathcal{O}(R^{-4}) \quad (4.27)$$

and

$$\mathbf{v}_1^\infty = \mathbf{v}_{2,0}^+|_{\mathbf{r}=\mathbf{R}} = R^{-2} \mathbf{N}_1^\infty + R^{-3} \mathbf{S}_1^\infty \cdot \mathbf{r} + R^{-3} \boldsymbol{\omega}_1^\infty \times \mathbf{r} + \mathcal{O}(R^{-4}), \quad (4.28)$$

where

$$\mathbf{N}_1^\infty = -\mathbf{D}_{2,0}^\chi \times \hat{\mathbf{R}} - \frac{1}{2} \mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}} \hat{\mathbf{R}}, \quad (4.29a)$$

$$\begin{aligned} \mathbf{S}_1^\infty &= -\frac{3}{2} ((\mathbf{D}_{2,0}^\chi \times \hat{\mathbf{R}}) \hat{\mathbf{R}} + \hat{\mathbf{R}} (\mathbf{D}_{2,0}^\chi \times \hat{\mathbf{R}})) - \frac{5}{2} \mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}} \hat{\mathbf{R}} \hat{\mathbf{R}} \\ &\quad + \frac{1}{2} \left(\hat{\mathbf{R}} (\mathbf{Q}_{2,0}^p \cdot \hat{\mathbf{R}}) + (\mathbf{Q}_{2,0}^p \cdot \hat{\mathbf{R}}) \hat{\mathbf{R}} \right) + \frac{1}{2} \left(\mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}} \right) \mathbf{I}, \end{aligned} \quad (4.29b)$$

$$\boldsymbol{\omega}_1^\infty = -\frac{1}{2} \mathbf{D}_{2,0}^\chi \cdot (\mathbf{I} - 3\hat{\mathbf{R}} \hat{\mathbf{R}}) + \frac{1}{2} (\mathbf{Q}_{2,0}^p \cdot \hat{\mathbf{R}}) \times \hat{\mathbf{R}}. \quad (4.29c)$$

Here, $M_{2,0}^p$, $\mathbf{D}_{2,0}^\chi$, and $\mathbf{Q}_{2,0}^p$ represent the exterior isotropic pressure of drop 2, the angular velocity, and the exterior pressure distribution ($n = 2$ mode), respectively, when computed without hydrodynamic interactions. These quantities will be defined precisely in §4.2.7. $\mathbf{N}_1^\infty$ is a uniform flow field containing contributions

from the rotational and straining flows produced by drop 2, and is the leading-order translational velocity of drop 1 in the large R limit. $\mathbf{S}_1^\infty$ is a second-order tensor containing the straining component of the ambient flow field. $\boldsymbol{\omega}_1^\infty$ is the angular velocity of drop 1 resulting from the ambient flow field $\mathbf{v}_1^\infty$, and equals half the vorticity of $\mathbf{v}_1^\infty$. The hydrodynamic traction associated with the ambient flow is

$$\begin{aligned} \llbracket \boldsymbol{\tau}^\infty \rrbracket_1 \cdot \hat{\mathbf{r}} &= (-p_1^\infty \mathbf{I} + \nabla \mathbf{v}_1^\infty + \nabla \mathbf{v}_1^{\infty T}) \cdot \hat{\mathbf{r}} \\ &= -\left(R^{-1} M_{2,0}^p + R^{-3} \mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}}\right) \hat{\mathbf{r}} + 2R^{-3} \mathbf{S}_1^\infty \cdot \hat{\mathbf{r}}, \end{aligned} \quad (4.30)$$

which reveals that no new flow modes are excited by the ambient flow at this order of approximation beyond those already excited by the electric stress on an isolated drop. Accordingly, the velocities take the same form as those in (2.56) and (2.57), with the addition of $\mathbf{v}_1^\infty$ to the exterior flow field:

$$\mathbf{v}_1^- = \mathbf{d}_1^\chi \times \mathbf{r} + \mathbf{d}_1^\phi + 2\mathbf{q}_1^\phi \cdot \mathbf{r} + \frac{r^2 \mathbf{q}_1^p \cdot \mathbf{r}}{21\lambda} \cdot (5\mathbf{I} - 2\hat{\mathbf{r}}\hat{\mathbf{r}}), \quad (4.31)$$

$$\mathbf{v}_1^+ = r^{-3} \mathbf{D}_1^\chi \times \mathbf{r} + r^{-5} \frac{\mathbf{Q}_1^p : \mathbf{r} \mathbf{r} \mathbf{r}}{2} + r^{-5} \left(\mathbf{Q}_1^\phi \cdot \mathbf{r} \right) \cdot (2\mathbf{I} - 5\hat{\mathbf{r}}\hat{\mathbf{r}}) + \mathbf{v}_1^\infty. \quad (4.32)$$

Similarly, the hydrodynamic stress takes the same form as that in (2.53) but with the addition of (4.30),

$$\begin{aligned} \llbracket \mathbf{f}^H \rrbracket_1 &= (m_1^p - M_1^p - p_1^\infty) \hat{\mathbf{r}} + \left(24\mathbf{Q}_1^\phi - 3\mathbf{Q}_1^p - 4\lambda \mathbf{q}_1^\phi + \frac{\mathbf{q}_1^p}{7} + 2R^{-3} \mathbf{S}_1^\infty \right) : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}} \\ &+ \left[\left(-16\mathbf{Q}_1^\phi + \mathbf{Q}_1^p - \frac{16\mathbf{q}_1^p}{21} - 4\lambda \mathbf{q}_1^\phi + 2R^{-3} \mathbf{S}_1^\infty \right) \cdot \hat{\mathbf{r}} \right] \cdot (\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}) - 3\mathbf{D}_1^\chi \times \hat{\mathbf{r}}. \end{aligned} \quad (4.33)$$

While the hydrodynamic interactions do not generate a hydrodynamic torque on drop 1 [Hetsroni and Haber, 1970], they will still alter the angular velocity of drop 1 through charge convection and flow vorticity.

4.2.4 Drop translation

Unlike an isolated drop, a pair of interacting drops generally undergo translational motion. As discussed in §1.4, the translational velocity of drop 1, denoted by $\mathbf{U}_1(t)$ consists of two parts: one originating from hydrodynamics, found using Faxén's law for drops [Hetsroni and Haber, 1978], and another originating from electrostatics via the DEP force $\mathbf{f}_1^{\text{DEP}}$:

$$\mathbf{U}_1 = \left(1 + \frac{\lambda}{2(2+3\lambda)} \nabla^2\right) \mathbf{v}_1^\infty|_{r=0} - \frac{1}{2\pi} \frac{1+\lambda}{2+3\lambda} \mathbf{f}_1^{\text{DEP}}. \quad (4.34)$$

The DEP force exerted on the dipole of drop 1 is $\mathbf{f}_1^{\text{DEP}} = 4\pi \mathbf{P}_1 \cdot \nabla \mathbf{E}_1^\infty|_{r=0}$ [Jones, 1979], which can be expanded using (4.18) as

$$\mathbf{f}_1^{\text{DEP}} = -12\pi R^{-4} \left[(\mathbf{P}_1 \cdot \hat{\mathbf{R}}) \mathbf{P}_2 + (\mathbf{P}_2 \cdot \hat{\mathbf{R}}) \mathbf{P}_1 \right. \quad (4.35)$$

$$\left. + (\mathbf{P}_1 \cdot \mathbf{P}_2) \hat{\mathbf{R}} - 5(\mathbf{P}_1 \cdot \hat{\mathbf{R}})(\mathbf{P}_2 \cdot \hat{\mathbf{R}}) \hat{\mathbf{R}} \right]. \quad (4.36)$$

We retain the DEP force in the problem even though it is $\mathcal{O}(R^{-4})$ since it causes the important effect of chaining in real systems, whereby attractive interactions between polarised particles in a suspension lead to the formation of chains of particles along the field direction, which can increase the viscosity of the suspension and introduce non-Newtonian features such as yield stresses [Halsey, 1992]. The translational velocity of drop 2, denoted by $\mathbf{U}_2(t)$, can be found by applying the same procedure as outlined here to drop 2. The relative velocity of the pair of drops $\mathbf{U}_{21} = \mathbf{U}_2 - \mathbf{U}_1$ and hence the evolution of the separation vector $\mathbf{R}$ can be easily found,

$$\mathbf{U}_{21} = \frac{d\mathbf{R}}{dt} = \mathbf{U}_2 - \mathbf{U}_1. \quad (4.37)$$

Note that in previous models of interacting drops in the Taylor regime [Sorgentone et al., 2021, Kach et al., 2022], the interactions between identical drops are reciprocal, i.e., $\mathbf{U}_{21} = 2\mathbf{U}_2$. However, it will be seen in §4.3 that the same is not true for drops undergoing Quincke rotation.

4.2.5 Kinematic boundary condition

The kinematic boundary condition (4.8) for interacting drops is the same as that used for an isolated drop in Chapters 2 and 3, but the velocities appearing must also include the ambient flow $\mathbf{v}_1^\infty$. First, the no-slip condition gives the relations

$$R^{-3}\boldsymbol{\omega}_1^\infty + \mathbf{D}_1^\chi = \mathbf{d}_1^\chi, \quad R^{-2}\mathbf{N}_1^\infty = \mathbf{d}_1^\phi, \quad R^{-3}\mathbf{S}_1^\infty + 2\mathbf{Q}_1^\phi = 2\mathbf{q}_1^\phi + \frac{5\mathbf{q}_1^p}{21\lambda}. \quad (4.38)$$

Substituting the expression for ξ_1 given in (4.14) into (4.8) yields:

$$\mathbf{v}_1^- \cdot \hat{\mathbf{r}} - \delta \mathbf{v}_1^- \cdot \nabla f_1 = \mathbf{v}_1^+ \cdot \hat{\mathbf{r}} - \delta \mathbf{v}_1^+ \cdot \nabla f_1 = \delta \frac{\partial f_1}{\partial t}. \quad (4.39)$$

As before, the velocities $\mathbf{v}_1^\pm$ appearing in the nonlinear convective products $\mathbf{v}_1^\pm \cdot \nabla f_1$ include only the leading order flow components, i.e., $\mathbf{D}_1^\chi$ and $\mathbf{d}_1^\chi$, which are independent of λ . At leading order, $\mathbf{d}_1^\chi = \mathbf{D}_1^\chi$ from (4.38), and hence $\delta \mathbf{v}_1^+ \cdot \nabla f = \delta \mathbf{v}_1^- \cdot \nabla f$. The kinematic condition (4.39) at leading order reads

$$\mathbf{v}_1^- \cdot \hat{\mathbf{r}} = \mathbf{v}_1^+ \cdot \hat{\mathbf{r}} = \delta \left(\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \nabla f_1 \right), \quad (4.40)$$

where

$$\mathbf{v}_1 \cdot \nabla f_1 = \left(\varepsilon_{lkj} Q_{1,li}^f D_{1,k}^\chi + \varepsilon_{lki} Q_{1,lj}^f D_{1,k}^\chi \right) \hat{r}_i \hat{r}_j = \mathbf{Q}_1^{\chi f} : \hat{\mathbf{r}} \hat{\mathbf{r}} \quad (4.41)$$

and

$$Q_{1,ij}^{\chi f} = \varepsilon_{lkj} Q_{1,li}^f D_{1,k}^\chi + \varepsilon_{lki} Q_{1,lj}^f D_{1,k}^\chi. \quad (4.42)$$

Using (4.40) in tandem with the relations given in (4.38) yields similar relations to those in (2.64) and (3.31), but now also involving $\mathbf{S}_1^\infty$:

$$\mathbf{Q}_1^\phi = \frac{1}{6} \mathbf{Q}_1^p - \frac{\delta}{3} \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) + \frac{1}{3} R^{-3} \mathbf{S}_1^\infty, \quad (4.43a)$$

$$\mathbf{q}_1^p = \frac{7\lambda}{2} \mathbf{Q}_1^p - \frac{35\lambda\delta}{2} \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) + \frac{35\lambda}{2} R^{-3} \mathbf{S}_1^\infty, \quad (4.43b)$$

$$\mathbf{q}_1^\phi = -\frac{1}{4} \mathbf{Q}_1^p + \frac{7\delta}{4} \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) - \frac{5}{4} R^{-3} \mathbf{S}_1^\infty. \quad (4.43c)$$

The hydrodynamic traction jump (4.33) is then written as

$$\llbracket \mathbf{f}^H \rrbracket_1 = \llbracket \boldsymbol{\tau}_1^H \rrbracket \cdot \hat{\mathbf{r}} = p_1^H \hat{\mathbf{r}} + \mathbf{Q}_{1,\hat{\mathbf{r}}}^H : \hat{\mathbf{r}} \hat{\mathbf{r}} \hat{\mathbf{r}} + \left(\mathbf{Q}_{1,\hat{\mathbf{t}}}^H \cdot \hat{\mathbf{r}} \right) \cdot (\mathbf{I} - \hat{\mathbf{r}} \hat{\mathbf{r}}) + \mathbf{T}_1^H \times \hat{\mathbf{r}}, \quad (4.44)$$

where

$$p_1^H = m_1^p - M_1^p - R^{-1} M_{2,0}^p - R^{-3} \mathbf{Q}_{2,0}^p : \hat{\mathbf{R}} \hat{\mathbf{R}}, \quad (4.45a)$$

$$\mathbf{Q}_{1,\hat{\mathbf{r}}}^H = \frac{2+3\lambda}{2} \mathbf{Q}_1^p - \frac{16+19\lambda}{2} \delta \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) + \frac{20+15\lambda}{2} R^{-3} \mathbf{S}_1^\infty, \quad (4.45b)$$

$$\mathbf{Q}_{1,\hat{\mathbf{t}}}^H = -\frac{5(1+\lambda)}{3} \mathbf{Q}_1^p + \frac{16+19\lambda}{3} \delta \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) - \frac{10+25\lambda}{3} R^{-3} \mathbf{S}_1^\infty, \quad (4.45c)$$

$$\mathbf{T}_1^H = -3\mathbf{D}_1^\chi. \quad (4.45d)$$

4.2.6 Stress balance

Given that the drops are clean, the nondimensional stress balance (4.10) to be satisfied at the interface of each drop is the same as that used for an isolated drop in Chapter 2, which reads

$$\llbracket \mathbf{f}^E \rrbracket_1 + \llbracket \mathbf{f}^H \rrbracket_1 = \frac{2}{\text{Ca}_E} \left[\hat{\mathbf{r}} - 2\delta (\mathbf{Q}_1^f \cdot \hat{\mathbf{r}}) \cdot (\mathbf{I} - 2\hat{\mathbf{r}} \hat{\mathbf{r}}) \right]. \quad (4.46)$$

As before, the radial component of (4.46) yields a scalar equation for the pressures and a tensor equation for the radial quadrupolar stresses,

$$p_1^E + p_1^H = \frac{2}{\text{Ca}_E}, \quad (4.47)$$

$$\mathbf{Q}_{1,\hat{\mathbf{r}}}^E + \mathbf{Q}_{1,\hat{\mathbf{r}}}^H = \frac{4\delta}{\text{Ca}_E} \mathbf{Q}_1^f, \quad (4.48)$$

and we again take

$$\delta = \frac{3\text{Ca}_E}{4(1+2S)^2}. \quad (4.49)$$

The tangential component of (4.46) yields a vector equation for the torques and a tensor equation for the tangential quadrupolar stresses,

$$\mathbf{T}_1^E + \mathbf{T}_1^H = \mathbf{0}, \quad (4.50)$$

$$\mathbf{Q}_{1,\hat{\mathbf{t}}}^E + \mathbf{Q}_{1,\hat{\mathbf{t}}}^H = \mathbf{0}. \quad (4.51)$$

The torque balance (4.50) yields

$$\mathbf{D}_1^\chi = \frac{1}{2} \mathbf{P}_1 \times \mathbf{E}_1^\infty, \quad (4.52)$$

while combining (4.48) and (4.51) gives an expression for the flow coefficients $\mathbf{Q}_1^p$ as well as a system of ODEs for the shape coefficients $\mathbf{Q}_1^f$, which are similar to (2.73) and (2.74) but also involve $\mathbf{S}_1^\infty$ in the case of interacting drops:

$$\mathbf{Q}_1^p = \frac{2}{3+2\lambda} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}_1^f + \mathbf{Q}_{1,\hat{\mathbf{r}}}^E + \frac{3}{2} \mathbf{Q}_{1,\hat{\mathbf{t}}}^E \right] + \frac{10(1-\lambda)}{3+2\lambda} R^{-3} \mathbf{S}_1^\infty, \quad (4.53)$$

$$\begin{aligned} \frac{\partial \mathbf{Q}_1^f}{\partial t} &= \frac{10(1+\lambda)}{\delta(16+19\lambda)(3+2\lambda)} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}_1^f + \mathbf{Q}_{1,\hat{\mathbf{r}}}^E + \frac{6+9\lambda}{10(1+\lambda)} \mathbf{Q}_{1,\hat{\mathbf{t}}}^E \right] \\ &\quad + \frac{5}{\delta(3+2\lambda)} R^{-3} \mathbf{S}_1^\infty - \mathbf{Q}_1^{\chi f}. \end{aligned} \quad (4.54)$$

The flow and shape coefficients defining $\mathbf{v}_1^\infty$ and p_1^∞ are given by the corresponding equations for drop 2 without any hydrodynamic interactions, which take the same form as (2.73) and (2.74):

$$\mathbf{D}_{2,0}^\chi = \frac{1}{2} \mathbf{P}_2 \times \mathbf{E}_2^\infty, \quad (4.55)$$

$$\mathbf{Q}_{2,0}^p = \frac{2}{3+2\lambda} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}_2^f + \mathbf{Q}_{2,\hat{\mathbf{r}}}^E + \frac{3}{2} \mathbf{Q}_{2,\hat{\mathbf{t}}}^E \right], \quad (4.56)$$

$$\begin{aligned} \frac{\partial \mathbf{Q}_{2,0}^f}{\partial t} &= \frac{10(1+\lambda)}{\delta(16+19\lambda)(3+2\lambda)} \left[-\frac{3}{(1+2S)^2} \mathbf{Q}_2^f + \mathbf{Q}_{2,\hat{\mathbf{r}}}^E + \frac{6+9\lambda}{10(1+\lambda)} \mathbf{Q}_{2,\hat{\mathbf{t}}}^E \right] - \mathbf{Q}_2^{\chi f}. \end{aligned} \quad (4.57)$$

4.2.7 Charge conservation

We now apply the dimensionless charge conservation equation (4.4) at the interface of drop 1,

$$\frac{\partial q_1}{\partial t} + \frac{1}{\text{Re}_E} [\mathbf{j} \cdot \mathbf{n}]_1 + \nabla_{s,1} \cdot (q_1 \mathbf{v}_1) = 0. \quad (4.58)$$

The dimensionless charge distribution q_1 introduced in (4.2) is

$$q_1 = (1 - Q) \mathbf{E}_\infty \cdot \hat{\mathbf{r}} + (2 + Q) \mathbf{P}_1 \cdot \hat{\mathbf{r}}. \quad (4.59)$$

From (4.58), we obtain a system of ODEs for the dipole moment of drop 1,

$$\begin{aligned} \frac{d\mathbf{P}_1}{dt} = & -\frac{1 + 2S}{S(2 + Q)\text{Re}_E} \mathbf{P}_1 - \frac{S - 1}{S(2 + Q)\text{Re}_E} \mathbf{E}_1^\infty + \boldsymbol{\Omega}_1 \times \left(\frac{1 - Q}{2 + Q} \mathbf{E}_1^\infty + \mathbf{P}_1 \right) \\ & + \left(\frac{1 - Q}{2 + Q} \mathbf{E}_1^\infty + \mathbf{P}_1 \right) \cdot \left[\frac{1}{5} \mathbf{Q}_1^p - \frac{6}{5} \delta \left(\frac{\partial \mathbf{Q}_1^f}{\partial t} + \mathbf{Q}_1^{\chi f} \right) + R^{-3} \mathbf{S}_1^\infty \right] \\ & + R^{-3} \frac{1 - Q}{2 + Q} \frac{d\mathbf{P}_2}{dt} \cdot (\mathbf{I} - 3\hat{\mathbf{R}}\hat{\mathbf{R}}), \end{aligned} \quad (4.60)$$

where $\boldsymbol{\Omega}_1 = \mathbf{D}_1^\chi + R^{-3} \boldsymbol{\omega}_1^\infty$ is the total angular velocity of drop 1, containing both a self-induced contribution due to Quincke rotation and a contribution arising from hydrodynamic interactions with drop 2, with the latter scaling as $\mathcal{O}(R^{-3})$. The final term in (4.60) appears because the ambient electric field $\mathbf{E}_\infty$ appearing in the definition of the charge distribution (4.59) involves a contribution from $\mathbf{P}_2$. In the case of interacting drops, the angular velocity of drop 1 is generally nonzero even when the field strength is too weak to induce Quincke rotation, because the contribution from drop 2, $\boldsymbol{\omega}_1^\infty$, involves the straining flow $\mathbf{Q}_{2,0}^p$, as can be seen from (4.29c). Hence, if the electric field is sufficiently weak, drop 1 rotates only as a result of electrohydrodynamic interactions with drop 2. We refer to this type of behaviour as the Taylor regime, in which the impact of charge convection scales like the straining flow as $\mathcal{O}(\lambda^{-1})$, as seen in (4.53). In sufficiently strong fields, self-induced rotation is possible in both drops. We refer to this type of behaviour as the Quincke regime, in which drop rotation is the dominant contribution to the fluid velocity, and convection, like the solid-body rotation, is $\mathcal{O}(1)$. An equation similar to (4.60) can be obtained for the dipole moment of drop 2.

4.2.8 Model summary

The system of ODEs describing the evolution of the dipole moments and shape coefficients of drops 1 and 2 and the separation vector $\mathbf{R}$ can be written succinctly as

$$\frac{d}{dt} \begin{bmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \\ \mathbf{Q}_1^f \\ \mathbf{Q}_2^f \\ \mathbf{R} \end{bmatrix} = \mathcal{F} \left(\mathbf{P}_1, \mathbf{P}_2, \mathbf{Q}_1^f, \mathbf{Q}_2^f, \mathbf{R}; \text{Ca}_E, \text{Re}_E, Q, S, \lambda \right). \quad (4.61)$$

This system of ODEs is integrated numerically with initial conditions corresponding to initially spherical drops, $\mathbf{Q}_1^f(0) = \mathbf{Q}_2^f(0) = \mathbf{0}$, and zero surface charge density $q_1(\mathbf{r}, 0) = q_2(\mathbf{r}, 0) = 0$. The charge density conditions when substituted into (4.59) gives us initial conditions for both dipole moments,

$$\mathbf{P}_1(0) = \mathbf{P}_2(0) = \frac{R^3}{\frac{Q+2}{Q-1}R^3 + 1} \hat{\mathbf{E}}_0 \cdot \left(\mathbf{I} + \frac{3}{\frac{Q+2}{Q-1}R^3 - 2} \hat{\mathbf{R}}\hat{\mathbf{R}} \right). \quad (4.62)$$

When simulating the trajectories of freely suspended drops, we apply small perturbations to $\mathbf{P}_1(0)$ and $\mathbf{P}_2(0)$ in order to induce Quincke rotation in different directions, leading to a range of different behaviours.

4.3 Results and discussion

In this section, we present results obtained from the model described in §4.2. We consider the effect of EHD interactions between the pair of drops in two scenarios. First, in §4.3.1, we consider drops which are free to translate. Next, in §4.3.2, we consider drops which are fixed in space. Unless otherwise stated, we use the parameter values from the experiments of Salipante and Vlahovska [2010] as given in Table 2.1.

4.3.1 Freely suspended pairs of drops

First, we examine the behaviour of pairs of drops that are free to translate as a result of hydrodynamic and DEP interactions. Specifically, the rotational flow of one drop provides the dominant contribution to the translational velocity of the other, while straining flow and DEP forces provide higher-order corrections. In practical settings, the drops may come into contact and coalesce, but the present model does not account for coalescence and will predict unphysical behaviour when the separation distance between the drops is smaller than two drop radii, i.e., when the drops overlap. Hence, to prevent the drops from coming into contact or overlapping, we impose a short-range repulsive force [Bossis and Brady, 1984, Takamura et al., 1981] along the line joining the centres of the two drops, denoted by $\mathbf{F}_R$ and given by

$$\mathbf{F}_R = -A \frac{e^{-B(R-2.01)}}{1 - e^{-B(R-2.01)}} \hat{\mathbf{R}}, \quad (4.63)$$

where A and B are adjustable nondimensional parameters. In our simulations, we found the values $A = B = 200$ to be sufficient to avoid overlaps. In most cases when a pair of drops attract one another, this repulsive force will balance the attractive electrohydrodynamic or DEP interactions and the separation distance R will settle to a value slightly above 2. It is important to remember that the present model is formally only valid for widely separated drops, which is clearly violated when the repulsive force (4.63) is active. Nevertheless, including it allows the model to capture the sustained translation of counter-rotating pairs of drops, which has recently been studied numerically [Dong et al., 2024] and has been captured by a theoretical model for solid spheres [Das and Saintillan, 2013]. We separate our results into two categories based on the electric field strength: weak fields (i.e., the Taylor regime), wherein the drop trajectories are driven solely by induced straining flows and DEP forces, and strong fields (i.e., the Quincke regime), wherein drop rotation is also present and the drop trajectories are characterised by complex spiraling motions due to the rotational flows. First, we validate the present model against the results reported in previous publications concerning drop trajectories in the Taylor regime. Next, we report new results for

drop trajectories in the Quincke regime. In simulating the trajectories of freely suspended drops in the Quincke regime, we apply small perturbations to $\mathbf{P}_1(0)$ and $\mathbf{P}_2(0)$ in order to induce Quincke rotation in different directions, leading to a range of different behaviours. In practical settings, specific perturbations may be deliberately applied via an imposed fluid flow, electric field asymmetry or mechanical disturbance, or random perturbations may be introduced by weak residual flows or electrostatic disturbances.

4.3.1.1 Taylor regime

We first compare our results with previous work concerning drop trajectories in the Taylor regime, in which Quincke rotation is absent, and drop translation is driven by induced straining flows and DEP. As a result of the axisymmetry of the flow fields and shapes of the drops, the trajectories of pairs of drops in the Taylor regime are two dimensional, remaining in the plane containing the initial drop separation vector and the applied field. An initial perturbation to the dipole moments in a direction out of that plane may have a short transient impact but will decay. Figure 4.2 compares the drop trajectories predicted by the present model with those predicted by the boundary element simulations of Sargentone et al. [2021] (taken from their Figure 9). In the present simulations, we forgo the parameter values of Table 2.1 and instead directly prescribe values of the nondimensional parameters Q , S , λ and Ca_E in order to match the values used by Sargentone et al. [2021]. The permittivity and conductivity ratios Q and S change between the four different cases shown in Figure 4.2, while $\lambda = 1$ and $\text{Ca}_E = 0.1$ in all cases. Furthermore, since the simulations of Sargentone et al. [2021] neglect charge relaxation and convection, we initially remove these effects from the present model for the purposes of the comparison. Instead, we impose the simpler condition $[\mathbf{j} \cdot \hat{\mathbf{r}}] = 0$, in which case the dipoles of the two drops are identical and are given by

$$\mathbf{P}_1 = \mathbf{P}_2 = \frac{1}{\frac{1+2S}{1-S} + R^{-3}} \hat{\mathbf{E}}_0 \cdot \left(\mathbf{I} + \frac{3R^{-3}}{\frac{1+2S}{1-S} - 2R^{-3}} \hat{\mathbf{R}} \hat{\mathbf{R}} \right). \quad (4.64)$$

As Figure 4.2 shows, there is good agreement between the two-dimensional trajectories predicted by the simulations of Sorgentone et al. [2021], shown in black dotted lines, and those predicted by the present model, shown in blue solid lines, when charge convection and relaxation are neglected. This is perhaps surprising given the small initial separation distances ($R = 4$) and drop viscosities ($\lambda = 1$) involved, since our model is valid for widely separated and highly viscous drops. In the cases shown in Figures 4.2(a) and (d), for which (a) $S = 10$, $Q = 1$, $\theta_R(t = 0) = 60^\circ$ and (d) $S = 0.01$, $Q = 1$, $\theta_R(t = 0) = 80^\circ$, the drops initially repel one another and the line joining their centres rotates towards the direction of the applied field (i.e., the z direction), before the drops change direction and attract one another. Ultimately, the drops reach a steady state in which they are aligned parallel to the applied field (i.e., $\hat{\mathbf{R}} \parallel \hat{\mathbf{E}}_0$). Conversely, in the cases shown in Figures 4.2(b) and (c), for which (b) $S = 1$, $Q = 10$, $\theta_R(t = 0) = 45^\circ$ and (c) $S = 1$, $Q = 0.1$, $\theta_R(t = 0) = 65^\circ$, the drops exhibit so-called ‘kiss and run’ dynamics, initially drifting towards and then away from each other.

To investigate the role of charge convection on the drop trajectories, we numerically integrate the complete system of ODEs (4.61) for both $\text{Re}_E = 0.5$ and $\text{Re}_E = 1$. The resulting drop trajectories are denoted with orange ($\text{Re}_E = 0.5$) and green ($\text{Re}_E = 1$) dashed lines in Figure 4.2. The effect of convection is small in all of the cases shown, but is most noticeable in Figure 4.2(b). In this case, when $\text{Re}_E = 0.5$ the drops come slightly closer together before repelling than they do when convection is neglected, and when $\text{Re}_E = 1$ the drops do not repel one another at all. Instead, as shown in the inset, the drops attract one another until they reach the steady separation $R \approx 2$, after which the line joining their centres rotates towards the direction of the applied field. The strength of convection can be increased by increasing Re_E further, and when Re_E is sufficiently large, the present model predicts that the “kiss and run” behaviour no longer occurs in cases (b) and (c). Instead, the lines joining the centres of the drops rotate counterclockwise and the drops initially repel before attracting one another (not shown in plots), in a manner similar to cases (a) and (d). We note that when Re_E is very large, charge convection is very strong, giving rise to additional charge

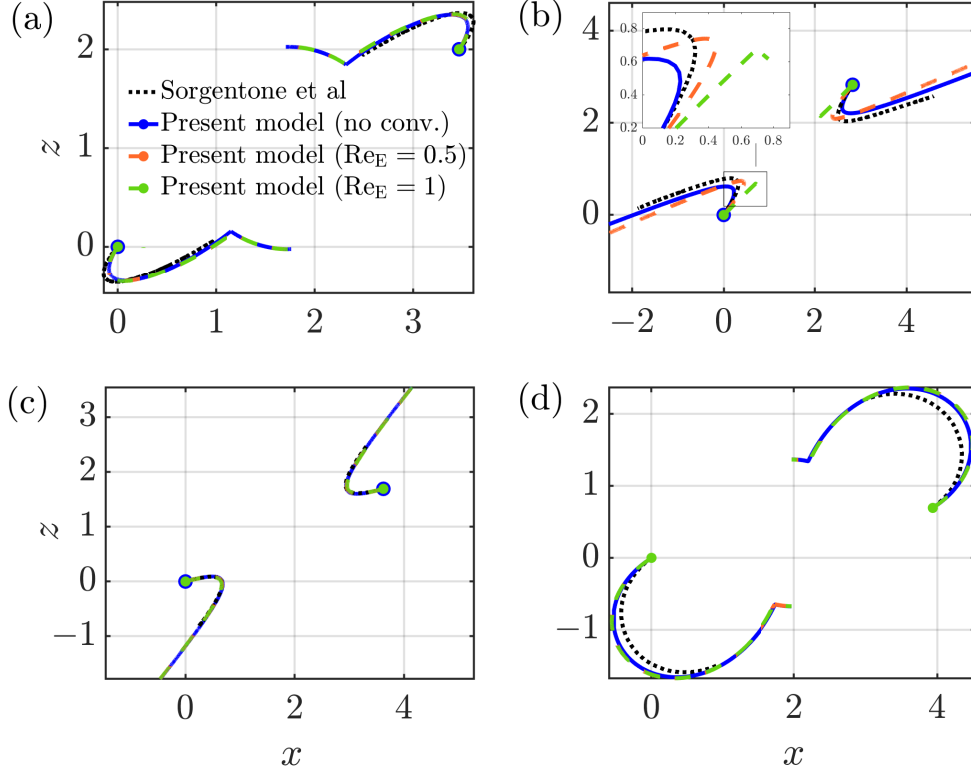


Figure 4.2: Four examples of two-dimensional drop trajectories when the electric field is applied in the z direction. In each case, $R(t=0) = 4$, $\lambda = 1$ and $\text{Ca}_E = 0.1$. Other parameter values are as follows: (a) $S = 10$, $Q = 1$, $\theta_R(t=0) = 60^\circ$; (b) $S = 1$, $Q = 10$, $\theta_R(t=0) = 45^\circ$; (c) $S = 1$, $Q = 0.1$, $\theta_R(t=0) = 65^\circ$; (d) $S = 0.01$, $Q = 1$, $\theta_R(t=0) = 80^\circ$. Solid blue lines denote the trajectories predicted by the present model, with the dots marking the initial positions of the drops. Black dotted lines denote the corresponding trajectories predicted by the boundary element simulations of Sargentone et al. [2021] (reproduced from their Figure 9). Orange and green dashed lines denote the corresponding trajectories when charge convection is retained, with $\text{Re}_E = 0.5$ and $\text{Re}_E = 1$, respectively.

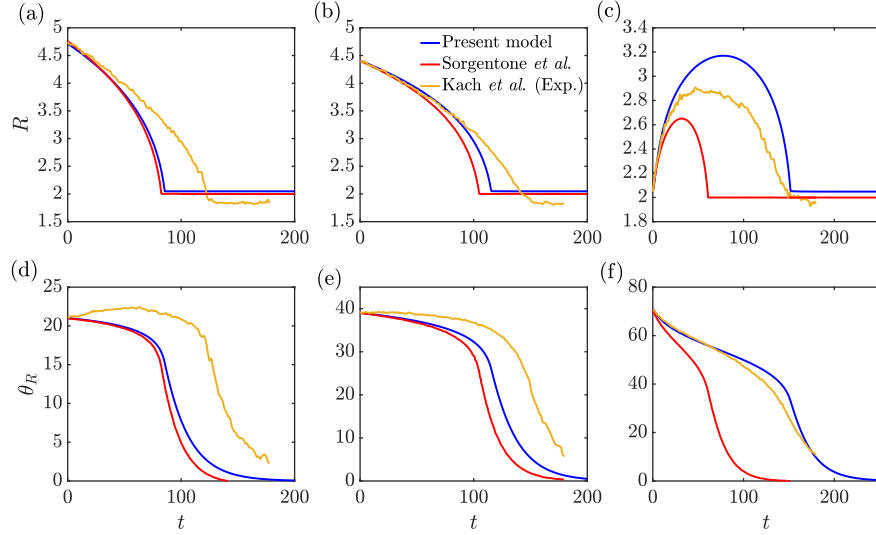


Figure 4.3: Evolution of the separation distance R and angle θ_R of the separation vector for a pair of drops in the Taylor regime. In each case, $\lambda = 0.39$, $Q = 0.57$, $S = 29$, $\text{Re}_E = 1.05$ and $\text{Ca}_E = 0.19$. The initial spatial configurations of the drops are as follows: (a) $\theta_R(t=0) = 21^\circ$, $R(t=0) = 4.7$; (b) $\theta_R(t=0) = 39^\circ$, $R(t=0) = 4.4$; (c) $\theta_R(t=0) = 71^\circ$, $R(t=0) = 2.04$. Blue lines denote the predictions of the present small deformation model, red lines denote the predictions of the small deformation model of Sorgentone et al. [2021], and yellow lines denote the experimental findings of Kach et al. [2022].

multipoles which have been neglected in the present model. Hence, full simulations are better suited for predicting drop dynamics in such systems with strong charge convection. In cases (a) and (b), if the electric field is sufficiently strong and charge convection is present, Quincke rotation may occur, as we discuss in the next section. In addition to their boundary element simulations, Sorgentone et al. [2021] developed an asymptotic theory neglecting some physical effects to allow for closed-form solutions for the fluid velocities and DEP forces. In particular, the only electrostatic interactions present in their theory are the DEP forces on the drops, and the only hydrodynamic interactions are those driving drop translation through the Faxén’s law. Charge convection and relaxation are absent, as is drop deformation, although the authors extended their theory to account for transient deformations, as described in their appendix. The theory of Sorgentone et al. [2021] neglecting drop deformation was subsequently compared with experiments by Kach et al. [2022]. Here, we include additional physical effects (namely, charge convection, relaxation, transient deformation and higher-order electrostatic and

hydrodynamic interactions), and demonstrate that doing so improves the agreement with the experimental drop trajectories. Figure 4.3 shows the predictions of the present model (blue lines) with experimental results of Kach et al. [2022] (yellow lines) and the theory of Sargentone et al. [2021] (red lines). Three cases with different initial spatial configurations of the drops are shown. Figures 4.3(a), (b) and (c) display the evolution of the separation distance R in each case, while Figures 4.3(d), (e) and (f) display the corresponding evolutions of the angle between the applied field direction and the line of centres of the drops in each case. In these simulations, we use the same parameter values as those used by Kach et al. [2022], namely, $\lambda = 0.39$, $Q = 0.57$, $S = 29$, $\text{Re}_E = 1.05$ and $\text{Ca}_E = 0.19$. In the first two cases (Figures 4.3(a) and (d), and Figures 4.3(b) and (e)), the initial separation angle $\theta_R(t = 0)$ is sufficiently small such that the drops monotonically attract while rotating around one another so that the separation angle approaches zero. In these cases, the inclusion of the additional physical effects mentioned above provides a modest improvement over the theory of Sargentone et al. [2021] when compared to the experimental results, but underpredicts the time it takes for the separation distance to reach the steady value $R \approx 2$. In the third case (Figures 4.3(c) and (f)), the initial separation angle is larger than in the first two cases, and the drops initially repel one another while the separation angle again decreases, but eventually, the drops change direction and begin to attract. Compared to the experimental results [Kach et al., 2022], the present model slightly overpredicts the time it takes for the separation distance to reach the steady value $R \approx 2$; however, the agreement between theory and experiment is substantially improved by retaining the additional physical effects.

4.3.1.2 Quincke regime

In the Quincke regime, the drop trajectories are primarily influenced by the rotational flows, almost always leading to complex spiraling motions. A variety of qualitatively different trajectories are obtained for a pair of drops of given material properties depending on the initial positions of the drops and the perturbations to their initial surface charge densities. Figures 4.4(a–c) show three representative

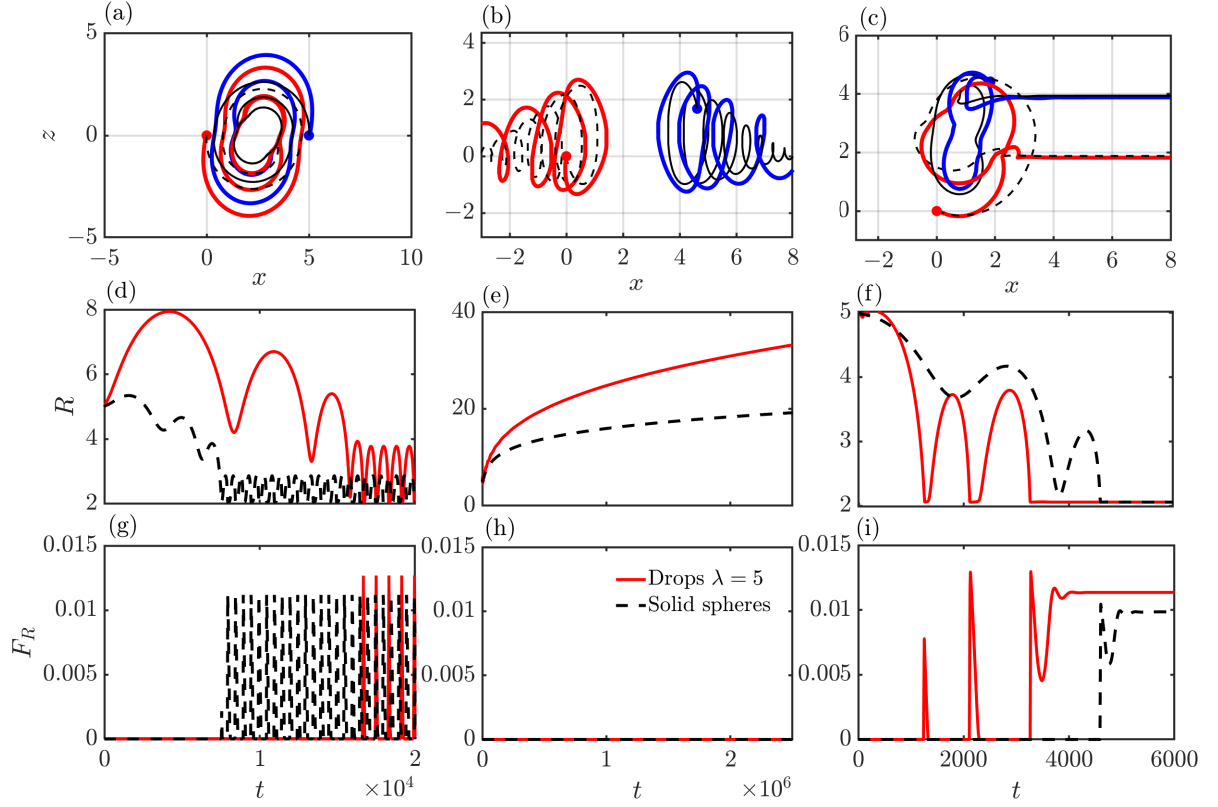


Figure 4.4: Trajectories of freely suspended drops and spheres (a–c), the corresponding evolutions of the separation distance R (d–f), and the corresponding evolutions of the magnitude F_R of the repulsive force $\mathbf{F}_R$ defined in (4.63) (g–i), plotted as functions of time t . The electric field is applied in the z direction. The thick blue and red lines denote the trajectories of drops with $\lambda = 5$, and the thin black lines denote the trajectories of solid spheres with the same initial conditions. Dots denote the initial positions of the drops. In all cases, $E_0/E_{c,s} = 3$.

examples of different types of behaviour, with the trajectories of the drops shown with thick blue and red lines, and those of solid spheres with identical initial conditions shown with thin black lines. Figures 4.4(d–f) show the corresponding plots of the separation distance R as functions of time t . Figures 4.4(g–i) show the corresponding plots of the magnitudes F_R of the repulsive force $\mathbf{F}_R$ defined in (4.63) as functions of time t . In the case shown in Figure 4.4(a), the drops and spheres spiral around and attract one another while remaining confined to the x - z plane. The solid spheres, which attract one another more quickly than the drops, follow spiraling trajectories around one another. In contrast, the drops exhibit peanut-shaped trajectories due to the straining flows either pushing the drops further apart or pulling them closer together as they spiral around one another. Figure 4.4(d) illustrates the corresponding oscillations in the separation distance R , as a function of time and clearly shows larger oscillations for the drops than for the spheres. This type of behaviour can occur when identical perturbations are applied to both drops, leading to corotation, or when no perturbation is applied, in which case hydrodynamic interactions lead to rotation, with the spirals confined to the plane defined by the applied field vector $\hat{\mathbf{E}}_0$ and the separation vector $\hat{\mathbf{R}}$. The special planar case shown in Figure 4.4(a) will occur less frequently in practical settings than the other two cases shown in Figure 4.4, as any perturbation in the third dimension will cause the drops and spheres to move out of the plane, leading to one of the other two cases discussed subsequently. In the case shown in Figure 4.4(b), the drops and spheres undergo a spiraling motion while moving apart. Figure 4.4(e) shows the separation distance increasing with time. The drops separate more quickly than the spheres, as the additional influence of the straining flow is repulsive when the angle between the separation vector and the applied field is greater than approximately $\arccos(1/3) \approx 54.7^\circ$, as discussed later in §4.3.2.3. In the case shown in Figure 4.4(c), the drops and spheres attract one another again but follow complex trajectories around one another before settling into a steady configuration in which they counter-rotate while translating as a pair in a direction perpendicular to the applied field. This behaviour is closely related to the self-propulsion of solid spheres under Quincke rotation on surfaces

(Quincke rollers), which has garnered significant interest in the active matter community [Bricard et al., 2013, 2015]. The counter-rotating self-propelling case has been explored for two-dimensional drops recently in the simulations of Dong et al. [2024]. As shown in Figure 4.4(f), the separation distance between the drops or spheres eventually settles at $R \approx 2$ due to the repulsive force given in (4.63).

4.3.2 Fixed pairs of drops

Although the case of moving drops is the most general and relevant to experiments and other practical settings, steady solutions to the system of equations (4.61) do not exist in most cases because the separation vector $\mathbf{R}$ between the drops changes continuously. To gain a better understanding of the electrohydrodynamic interactions in a simplified setting, the relative positions of the two drops can be fixed, so that the separation vector $\mathbf{R}$ is constant. Doing so allows steady solutions of the resulting simplified system of equations to be obtained.

In the Taylor regime, the flow fields and shape of an isolated drop are axisymmetric, so the problem of a pair of drops can be formulated in two dimensions without any loss of generality. The spatial configuration can be fully described using only the separation distance R and the angle θ_R between the applied field and the line connecting the centres of the two drops. In the Quincke regime, however, the situation is more complex because the flow fields and shape of an isolated drop are not axisymmetric after the onset of rotation. If random initial perturbations are applied to the drops, such that their rotational axes are generally misaligned, the ensuing transient dynamics are fully three dimensional. However, the effect of the perturbations decays in time and at steady state, the spatial configuration determines the rotational axes, and the drops either corotate (i.e., $\mathbf{\Omega}_1 = \mathbf{\Omega}_2$) or counter-rotate (i.e., $\mathbf{\Omega}_1 = -\mathbf{\Omega}_2$) in the plane containing the separation vector $\mathbf{R}$. In this section we present steady state results, and hence we will consider the behaviour of pairs of unperturbed drops, except in the symmetric configurations of $\theta_R = 0$ and $\theta_R = \pi/2$. In these symmetric configurations, unperturbed drops do not rotate, so we introduce perturbations leading to corotation of the drops. In any other configuration, unperturbed drops will naturally tend to corotate in

the plane containing the separation vector $\mathbf{R}$ due to the straining flows. Since the drops are identical and all interactions, except for the translational velocities of the drops, are quadratic in $\hat{\mathbf{R}}$, the dipole moments, shapes, and flow fields of both drops are identical. Thus, we write $\mathbf{P} = \mathbf{P}_1 = \mathbf{P}_2$, $\mathbf{Q}^f = \mathbf{Q}_1^f = \mathbf{Q}_2^f$, $\mathbf{Q}^p = \mathbf{Q}_1^p = \mathbf{Q}_2^p$, $\mathbf{\Omega} = \mathbf{\Omega}_1 = \mathbf{\Omega}_2$, and so on for the remaining variables to simplify the following presentation. We can simplify the analysis of the unperturbed system by invoking symmetry arguments. Firstly, there is periodicity in π ; by setting $\theta_R = \pi + \theta'_R$, we have $\hat{\mathbf{R}} = -\hat{\mathbf{R}}'$, and we need only interchange the names of the drops to recover the original problem. Secondly, moving drop 2 from $\theta_R = \theta'_R$ to $\theta_R = \pi - \theta'_R$, i.e., switching the sign of $\hat{R}_z$, results in a change of sign in the initial condition of P_x , as seen from (4.62). However, P_z remains unchanged. As a result, the shape of both drops as well as their dipole moments tilt in the opposite direction, and the sign of the rotation of the drops is reversed. Due to these symmetries, it is sufficient to restrict our analysis to spatial configurations corresponding to $0 \leq \theta_R \leq \pi/2$. In the following subsections, we report results pertaining to the onset of rotation of interacting pairs of drops, as well as the shapes of the drops and the attractive or repulsive nature of the drop interactions.

4.3.2.1 Angular velocity

The onset of Quincke rotation in interacting pairs of solid spheres is largely similar to that of an isolated sphere; the instability corresponds to a supercritical pitchfork bifurcation, but the critical field at which bifurcation occurs is offset from that for an isolated sphere depending on the spatial configuration of the pair of spheres [Das and Saintillan, 2013]. However, the onset of rotation of interacting pairs of drops is rather different to that of an isolated drop. When two identical drops interact, the angular velocity of each drop undergoes a pitchfork bifurcation only in certain symmetric configurations, specifically when the separation vector $\mathbf{R}$ between the drops is either perfectly parallel ($\theta_R = 0$) or perpendicular ($\theta_R = \pi/2$) to the applied field. In more general configurations, the symmetry around drop 1 is broken by the straining flow produced by drop 2, and vice versa, leading to an imperfect bifurcation.

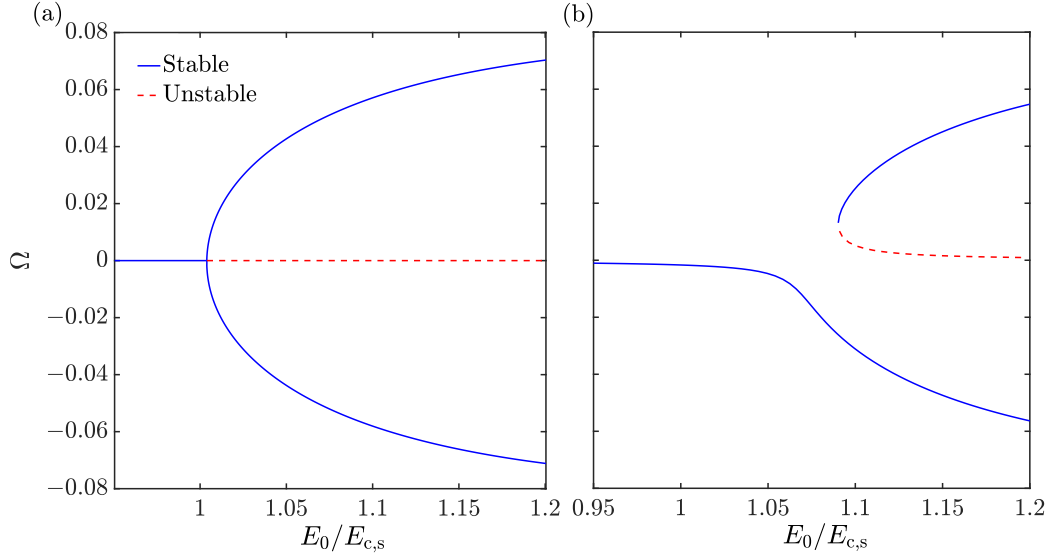


Figure 4.5: Bifurcation diagrams for pairs of (a) solid spheres and (b) spherical drops with $\lambda = 5$, both with $\theta_R = \pi/4$ and $R = 5$.

As discussed in §4.2.7, the straining flow, which is present even in subcritical fields, produces weak rotation in drop 1 through $\boldsymbol{\omega}^\infty$ and $\mathbf{S}^\infty$, which both scale as $\mathcal{O}(\lambda^{-1}R^{-3})$. This straining flow convects charge around the surface of drop 1 and misaligns its dipole with the local electric field. Figure 4.5 displays bifurcation diagrams for pairs of (a) solid spheres and (b) spherical drops, with $\theta_R = \pi/4$ in both cases. In the former case, a supercritical pitchfork bifurcation occurs at some critical field which is offset slightly from $E_{c,s}$ because of electrostatic interactions, scaling as $\mathcal{O}(R^{-3})$. In the latter case, no critical field exists and instead the angular velocities of the drops increase steadily as $E_0/E_{c,s}$ is increased. At a certain electric field, a saddle node bifurcation occurs, giving rise to new unstable and stable branches. To capture the unsteady solution branches, Figure 4.5 is obtained via arclength continuation.

Figure 4.6 displays the magnitude of the steady state angular velocity attained by deforming drops for three values of θ_R as well as for an isolated drop and sphere as functions of the electric field strength. Black lines, corresponding to solid spheres, clearly exhibit a pitchfork bifurcation for each value of $\theta_R = 0$ (solid lines), $\theta_R = \pi/4$ (dashed lines), and $\theta_R = \pi/2$ (dotted lines), as well as for the isolated case. On the other hand, pitchfork bifurcations occur only for the drops in the isolated case and for $\theta_R = 0$ and $\theta_R = \pi/2$. However, when $\theta_R = \pi/4$, the

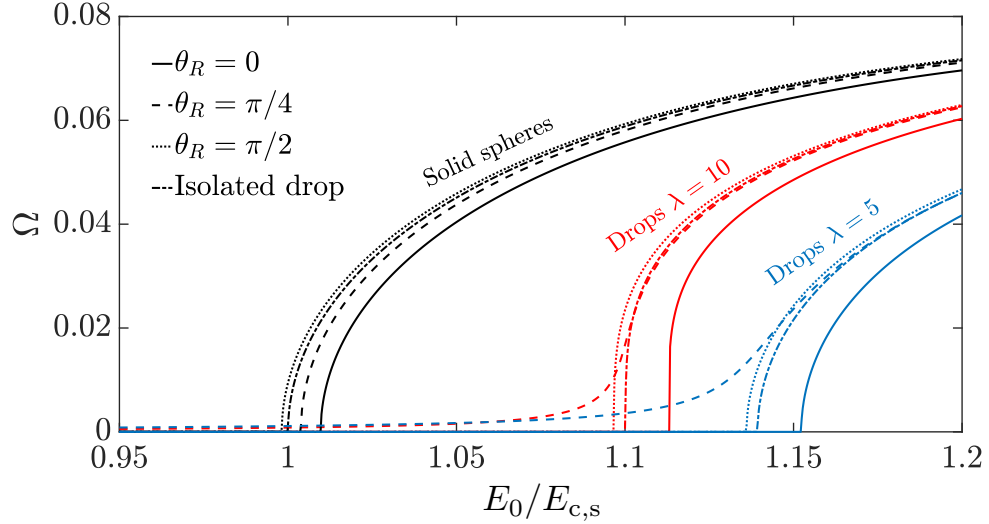


Figure 4.6: Steady angular velocity magnitudes for corotating solid spheres (black lines) and drops with $\lambda = 10$ (red lines) and $\lambda = 5$ (blue lines) as functions of $E_0/E_{c,s}$ at different values of θ_R , as well as the values for an isolated sphere and drop. In all cases involving interactions, $R = 5$.

angular velocity of the drops is nonzero for all electric field strengths regardless of the value of λ , corresponding to an imperfect bifurcation. For $\theta_R = 0$ and $\theta_R = \pi/2$, the critical field for rotation of drops (shown with blue and red lines) is greater than that for solid spheres (shown with black lines). The critical field is greater for the less viscous drop (shown with the blue line) when compared to the more viscous one (shown with the red line). The magnitude of the angular velocity at a given electric field strength is always smaller for drops than for solid spheres in all spatial configurations. This is primarily because the straining flows produced by drops convect charge from the poles to the equator of the drop and hence weaken the dipole moment. We note also that the angular velocity of solid spheres or drops is higher for $\theta_R = \pi/2$, and lower for $\theta_R = 0$, and the critical field for rotation is higher for $\theta_R = 0$, and lower for $\theta_R = \pi/2$, than for an isolated sphere or drop. Hence, the interactions between drops in the parallel configuration ($\theta_R = 0$) have a stabilising effect while interactions between drops in the perpendicular configuration ($\theta_R = \pi/2$) have a destabilising effect on the pair of drops, when compared to an isolated drop.

Figure 4.7 displays the magnitude of the angular velocity of each drop as a

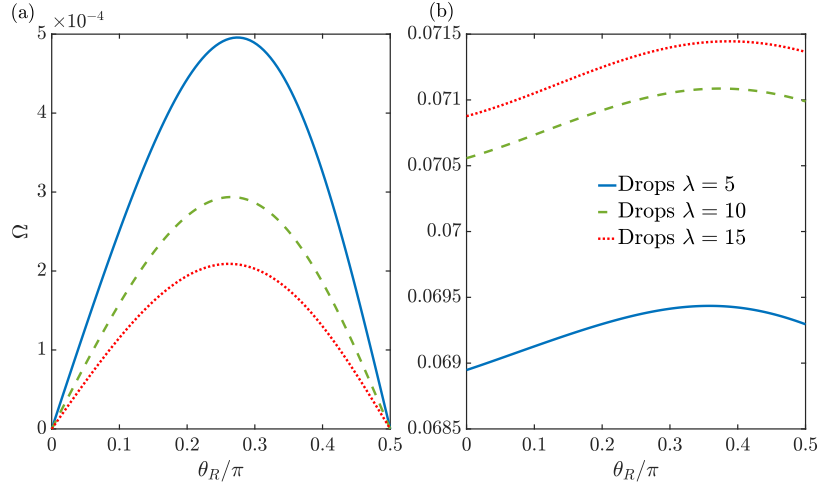


Figure 4.7: Steady angular velocity as functions of θ_R with $R = 5$ at (a) $E_0/E_{c,s} = 0.8$ and (b) $E_0/E_{c,s} = 1.8$ for three values of λ .

function of θ_R for two electric field strengths, namely $E_0/E_{c,s} = 0.8$ and $E_0/E_{c,s} = 1.8$. As shown in Figure 4.6, the angular velocity of the drop in the weaker field vanishes at $\theta_R = 0$ and $\theta_R = \pi/2$, and peaks shortly after θ_R exceeds $\pi/4$. Since rotation of one drop is driven by the straining flow produced by the other drop in this regime, decreasing the viscosity ratio increases the magnitude of the angular velocity. Conversely, in the stronger field, the trend with respect to λ is reversed, and drops with greater viscosity attain a greater angular velocity. This is because the dominant contribution to the angular velocity in this case is Quincke rotation, which is stronger for high viscosity drops than low viscosity ones.

As the drop viscosity becomes large, we expect to recover the supercritical pitchfork bifurcation that occurs for solid spheres. Figure 4.8 displays the magnitude of the angular velocity Ω as functions of $E_0/E_{c,s}$ for logarithmically-spaced values of λ between 10^0 and 10^3 , specifically $\lambda = 10^{3n/14}$ for $n = 0, 1, 2, \dots, 13, 14$. At low values of the viscosity ratio, the angular velocity increases smoothly and continuously as the electric field strength is increased. As the viscosity ratio is increased, discontinuous jumps in the angular velocity characteristic of the hysteresis discussed in §2.3.2 occur. Finally, as the viscosity ratio becomes large, the jumps become progressively smaller until the supercritical bifurcation is eventually recovered.

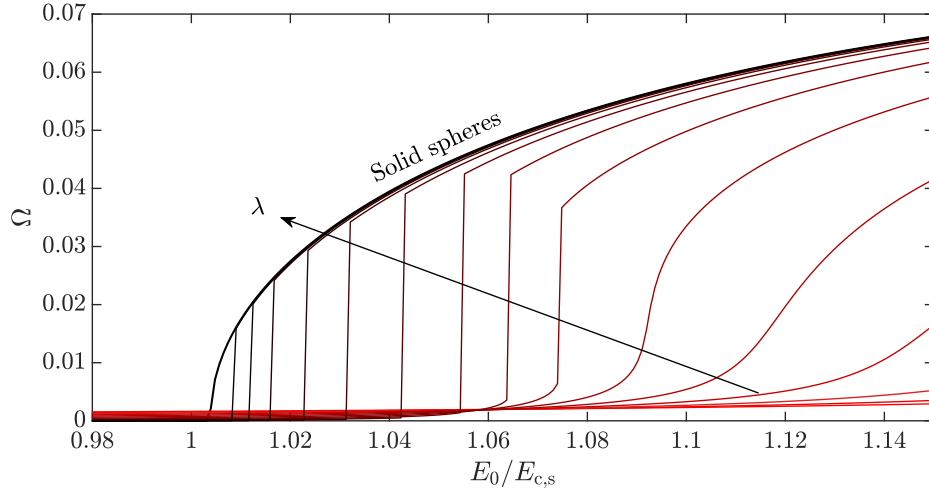


Figure 4.8: Steady angular velocity of corotating drops as functions of $E_0/E_{c,s}$ at different values of λ , corresponding to $\lambda = 10^{3n/14}$ for $n = 0, 1, 2, \dots, 13, 14$. In all cases $R = 5$, $\theta_R = \pi/4$.

4.3.2.2 Drop shape

We now turn our attention to the shapes of the drops, focusing on the effects of the interactions between the drops. First, we validate the results of the present model against those of Zabaranin [2020]. In that work, the separation vector between the drops is perfectly parallel to the applied field (i.e., $\theta_R = 0$) and charge convection is absent, so the system is axisymmetric. Since the work of Zabaranin [2020] is valid for dissimilar drops, it also applies to the identical drops considered here. In the axisymmetric configuration, $\mathbf{Q}^f$ is a diagonal traceless tensor, and the shapes of the drops are characterized by a single shape coefficient, Q_{zz}^f . Thus, (4.14) reduces to

$$\xi_1 = r - [1 + \delta Q_{zz}^f P_2(\cos \theta)] = 0. \quad (4.65)$$

In the absence of charge convection, the dipole moments (given by (4.64)) can be approximated by the asymptotic expansion

$$\mathbf{P}_1 = \mathbf{P}_2 = \frac{1-S}{1+2S} \left(1 + 2R^{-3} \frac{1-S}{1+2S} \right) \hat{\mathbf{E}}_0 + \mathcal{O}(R^{-6}). \quad (4.66)$$

The electric stresses in (4.22) can then be calculated using these expressions. Solving for $\mathbf{S}_1^\infty$, $\mathbf{Q}_1^p$, and $\mathbf{Q}_1^f$ via (4.29b), (4.53), and (4.54) gives the required shape coefficient as

$$Q_{1,zz}^f = \mathcal{F}_d \left(1 + 4R^{-3} \frac{1-S}{1+2S} \right) + R^{-3} \frac{3S(QS-1)(16+19\lambda)}{5(1+\lambda)^2} + \mathcal{O}(R^{-6}), \quad (4.67)$$

precisely as found by Zabaranin [2020], where $\mathcal{F}_d$ is as defined in (1.36). Since the present model can handle arbitrary drop configurations, we explore the effects of varying θ_R on the drop shape. For arbitrarily positioned pairs of drops, electrostatic and hydrodynamic interactions give rise to non-axisymmetric drop shapes even in the Taylor regime. We measure the degree of deformation and the tilt angle, defined as the angle between the major axes of the drops and the x -axis. Using the shape coefficients in $\mathbf{Q}^f$, the tilt angle θ_T is given by

$$\theta_T = \frac{1}{2} \arctan \left(\frac{2Q_{xz}^f}{Q_{xx}^f - Q_{zz}^f} \right). \quad (4.68)$$

It is important to emphasise that θ_T is not measured in the same way as other occurrences of θ in the present work. Measuring θ_T from the positive x -axis ensures consistency with previous works on isolated drops [Salipante and Vlahovska, 2010, Das and Saintillan, 2021], but it must be borne in mind that the angle denoted by θ_T is given by $\pi/2 - \theta$ in our spherical coordinate system, in which θ is measured from the positive z direction. We calculate the semi-major and semi-minor axes of the drop as $l = 1 + \delta f(\theta = \pi/2 - \theta_T, \phi = 0)$ and $b = 1 + \delta f(\theta = -\theta_T, \phi = 0)$, and hence determine the deformation parameter D_Q to be

$$D_Q = \frac{1}{2} \delta |Q_{1,xx}^f - Q_{1,zz}^f| \sqrt{1 + \left(\frac{2Q_{1,xz}^f}{Q_{1,xx}^f - Q_{1,zz}^f} \right)^2} + \mathcal{O}(\delta^2). \quad (4.69)$$

The tilt angle is zero for an isolated drop in the Taylor regime and for axisymmetric pairs of drops. However, it is nonzero for a rotating isolated drop [Das and Saintillan, 2021] or for non-axisymmetric pairs of drops.

Figure 4.9(a) shows the difference between the deformation parameter for in-

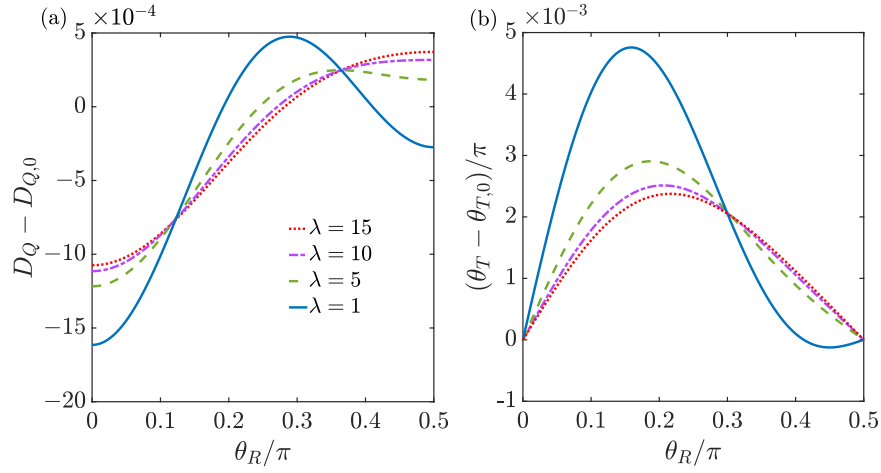


Figure 4.9: Deviation of (a) deformation parameter D_Q and (b) scaled tilt angle θ_T/π for interacting drops in the Taylor regime from the corresponding values for an isolated drop, $D_{Q,0}$ and $\theta_{T,0}/\pi$, as functions of θ_R for $E_0/E_{c,s} = 0.8$ for various viscosity ratios. See Table 4.1 for the values of $D_{Q,0}$ and $\theta_{T,0}$ for each λ . In all cases, $R = 5$.

interacting drops, D_Q , and that of an isolated drop in the Taylor regime ($E_0/E_{c,s} = 0.8$), denoted $D_{Q,0}$, as functions of θ_R for a range of viscosity ratios. Values of $D_{Q,0}$ are listed in Table 4.1. For all viscosity ratios studied, the deformation is smallest when the drops are aligned perfectly with the field. However, the separation angle θ_R corresponding to the maximum deformation depends on the viscosity ratio. More viscous drops (e.g., $\lambda = 10, 15$) deform most when perpendicular to the field, while less viscous drops (e.g., $\lambda = 1, 5$) experience maximum deformation at intermediate angles, which decrease with the viscosity ratio. Note that as a consequence of the symmetries discussed at the beginning of §4.3.2, Q_{xx}^f and Q_{zz}^f are symmetric and Q_{xz}^f is antisymmetric around $\theta_R = \pi/2$, so from (2.83) we see that D_Q is also symmetric around $\theta_R = \pi/2$.

Figure 4.9(b) shows the scaled tilt angle in a subcritical electric field. Note that the tilt angle of an isolated drop, denoted by $\theta_{T,0}$ in the Taylor regime is zero. The value of θ_R that maximizes the tilt angle also depends on the viscosity ratio. High-viscosity ratio drops tilt most around $\theta_R = \pi/4$, while for lower viscosity ratios, this angle decreases towards alignment with the field (i.e., towards $\theta_R = 0$). For all cases except $\lambda = 1$, the tilt angle is greater than that for the isolated drop across the full range of θ_R ; for $\lambda = 1$, there is a short range of θ_R near

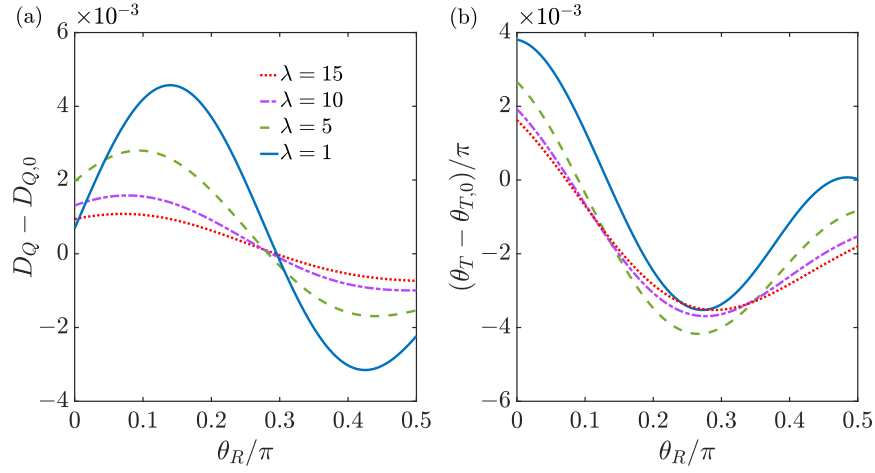


Figure 4.10: Deviation of (a) deformation parameter D_Q and (b) scaled tilt angle θ_T/π of corotating drops in Quincke rotation from the corresponding values for an isolated drop, $D_{Q,0}$ and $\theta_{T,0}$, as functions of θ_R for $E_0/E_{c,s} = 1.8$ for various viscosity ratios. See Table 4.1 for the values of $D_{Q,0}$ and $\theta_{T,0}/\pi$ for each λ . In all cases, $R = 5$.

perpendicular alignment within which the tilt angle is smaller than that of an isolated drop.

Figure 4.10(a) displays the difference in the deformation parameter for corotating drops and for an isolated drop in the Quincke regime ($E_0/E_{c,s} = 1.8$). In general, interactions between the drops increase their deformation compared to that of an isolated drop when the pair of drops is aligned nearly parallel to the applied field (i.e., near $\theta_R = 0$) and decrease it when the alignment is close to perpendicular (i.e., near $\theta_R = \pi/2$). The precise value of θ_R at which this behaviour changes is close to $\pi/4$ and depends on the viscosity ratio. The values of θ_R corresponding to the maximum and minimum deformation also depend on the viscosity ratio.

The effect of interactions on the tilt angle of corotating drops is shown in Figure 4.10(b). For all viscosity ratios studied, the largest tilt angle occurs when $\theta_R = 0$. The alignment corresponding to the smallest tilt is near to $\theta_R = \pi/4$, although this depends nonlinearly on the viscosity ratio. Drops with $\lambda = 5$ reach their minimum tilt angle at a smaller value of θ_R than either lower viscosity drops ($\lambda = 1$) or higher viscosity drops ($\lambda = 10, 15$). While Figures 4.9 and 4.10(a) show the largest impact of interactions on deformation and tilt angle for drops with

λ	$E_0/E_{c,s} = 0.8$		$E_0/E_{c,s} = 1.8$	
	$D_{Q,0}$	$\theta_{T,0}/\pi$	$D_{Q,0}$	$\theta_{T,0}/\pi$
1	0.047	0	0.129	0.217
5	0.058	0	0.083	0.345
10	0.061	0	0.051	0.385
15	0.062	0	0.036	0.4

Table 4.1: Isolated drop deformation $D_{Q,0}$ and scaled tilt angle $\theta_{T,0}/\pi$ in the Taylor regime ($E_0/E_{c,s} = 0.8$) and corotating in a stronger field ($E_0/E_{c,s} = 1.8$).

$\lambda = 1$, Figure 4.10(b) shows that the tilt angle for drops with $\lambda = 5$ deviates more from the value for an isolated drop than it does for drops with $\lambda = 1$.

4.3.2.3 Attraction and repulsion between pairs of drops

We now explore the effect of the separation angle θ_R on the attractive or repulsive nature of the interactions between drops, as quantified by the component of the relative velocity of the pair of drops in the $\hat{\mathbf{R}}$ direction, $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$. For identical, unperturbed drops, $\mathbf{U}_{21} = 2\mathbf{U}_2 = -2\mathbf{U}_1$. By definition, a positive value of $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$ indicates repulsion, while a negative value indicates attraction. We also determine the contributions to drop attraction or repulsion from straining flows and DEP. It is important to bear in mind that $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$ is evaluated with the drops fixed in space, and hence these results show the nature of the interactions that would result if the drops were suddenly allowed to move freely after the drop shapes and dipole moments had reached their steady values [Saintillan, 2008]. Previous work by Sargentone et al. [2021] on drops in the Taylor regime (in which charge relaxation and convection are neglected and constant dipole moments $\mathbf{P} = (1 - S)/(1 + 2S)\hat{\mathbf{E}}_0$ are assumed) has shown that the radial components of both the induced straining flow and the DEP force vary as $P_2(\cos \theta)$ around each drop. From this, it follows that drops with $SQ > 1$ will attract for $\theta_R < \arccos(1/3) \approx 54.7^\circ$ and will repel otherwise. Although the rotational flows dominate the fluid velocities in strong fields, they do not directly appear in the radial component of the relative velocity of the pair of drops, as is evident from the definition of $\mathbf{N}^\infty$ in (4.29a).

Figure 4.11 shows the radial component of the relative velocity of a pair of

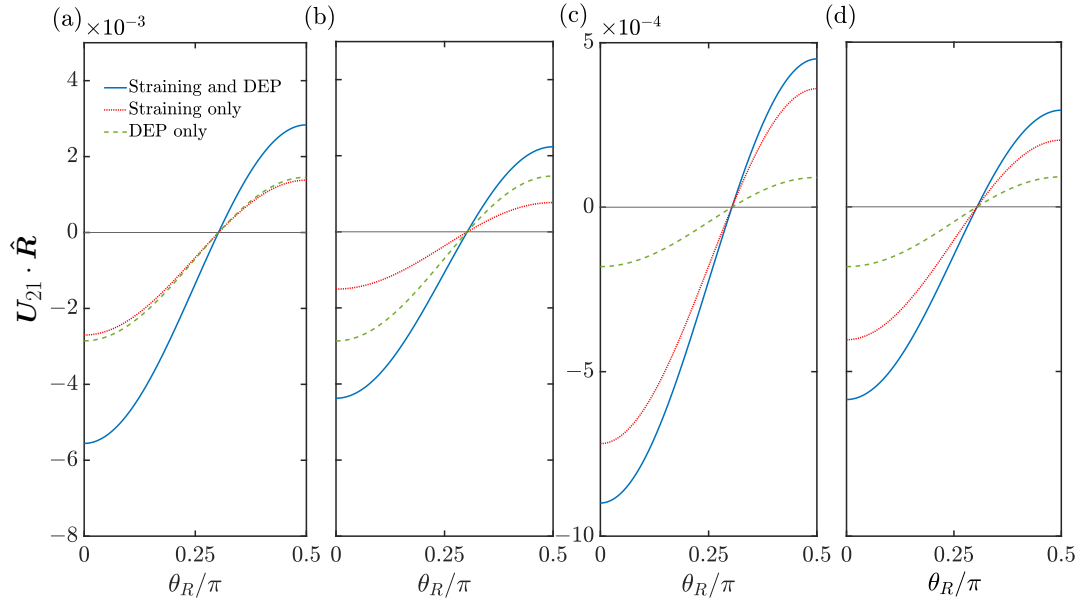


Figure 4.11: The radial component of the relative velocity of a pair of drops in the Taylor regime ($E_0/E_{c,s} = 0.8$), plotted as functions of θ_R in four cases: (a) $R = 5$, $\lambda = 5$, (b) $R = 5$, $\lambda = 10$, (c) $R = 10$, $\lambda = 5$, and (d) $R = 10$, $\lambda = 10$. Note that the y axis values in (a) apply to (a) and (b), and the y axis values in (c) apply to (c) and (d). The blue solid line represents the radial component of the total pair velocity $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$, while the red dotted line and green dashed line represent the contributions from straining flow and DEP, respectively.

drops in the Taylor regime ($E_0/E_{c,s} = 0.8$) plotted as functions of θ_R . Figure 4.11 includes results for four cases: (a) $R = 5$, $\lambda = 5$, (b) $R = 5$, $\lambda = 10$, (c) $R = 10$, $\lambda = 5$, and (d) $R = 10$, $\lambda = 10$. The separation angles θ_R corresponding to attraction and repulsion are consistent with the results of earlier work in which charge convection and relaxation were neglected [Sorgentone et al., 2021]. In all cases, the interactions are attractive when the drops are nearly parallel to the field and repulsive when they are nearly perpendicular, with maximum attraction and repulsion occurring at exactly parallel and perpendicular configurations, respectively. More precisely, the interactions switch from attraction to repulsion at approximately $\theta_R = 54.4^\circ$ when $R = 5$, and $\theta_R = 54.7^\circ$ when $R = 10$, suggesting that charge relaxation and convection have little impact on the attractive or repulsive nature of drop interactions in the Taylor regime. DEP and straining flows act cooperatively for all angles θ_R , but their relative strengths depend on R and λ . Since straining scales as $\mathcal{O}(R^{-2}\lambda^{-1})$ and DEP as $\mathcal{O}(R^{-4})$, DEP is the stronger effect at the smaller separation distance considered (namely, $R = 5$, as shown in (a) and (b)), while straining dominates at the larger separation distance (namely, $R = 10$, shown in (c) and (d)). For both separation distances, increasing the viscosity ratio reduces the straining flow, weakening the overall attraction or repulsion.

Figure 4.12 shows $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$ for corotating drops in the Quincke regime, for the same values of R and λ as used in Figure 4.11. As in the Taylor regime, the strongest attraction occurs when the drops are exactly parallel to the field (i.e., when $\theta_R = 0$), and increasing θ_R reduces the attraction, which eventually switches from attraction to repulsion. However, unlike in the weaker field, the strongest repulsion does not occur when the drops are precisely perpendicular to the field due to the tilted dipole moments. Further increases to the electric field strength enhance the transverse dipole component, shifting the separation angle corresponding to the maximum repulsion away from $\theta_R = \pi/2$. Additionally, the separation angle at which interactions switch between attractive and repulsive depends on both λ and R , but in all cases, the range of separation angles corresponding to repulsion is larger than that corresponding to attraction. For

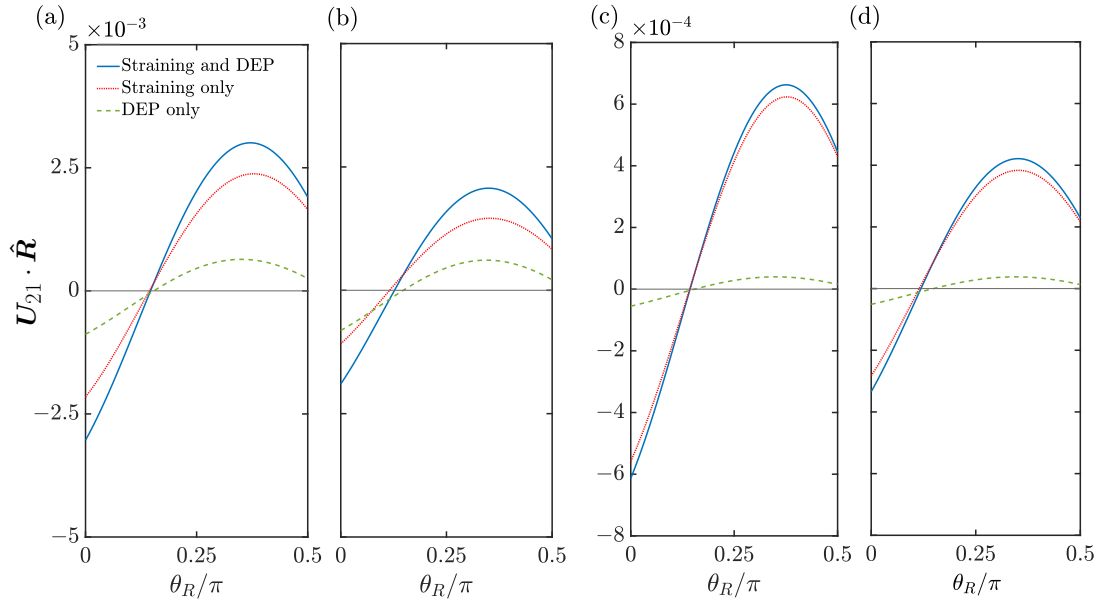


Figure 4.12: The radial component of the relative velocity of a pair of drops corotating in the Quincke regime ($E_0/E_{c,s} = 1.8$) plotted as functions of θ_R in four cases: (a) $R = 5$, $\lambda = 5$, (b) $R = 5$, $\lambda = 10$, (c) $R = 10$, $\lambda = 5$, and (d) $R = 10$, $\lambda = 10$. Note that the y -axis values in (a) apply to (a) and (b), and the y -axis values in (c) apply to (c) and (d). The blue solid line represents the radial component of the total pair velocity $\mathbf{U}_{21} \cdot \hat{\mathbf{R}}$, while the red dotted line and green dashed line represent the contributions from straining flow and DEP, respectively.

the four cases examined, the switch occurs approximately at (a) $\theta_R = 26.3^\circ$, (b) $\theta_R = 22.9^\circ$, (c) $\theta_R = 27.3^\circ$, and (d) $\theta_R = 21.3^\circ$. Since DEP and straining contributions do not change sign at the same value of θ_R , there are configurations where they oppose each other. This is most apparent in Figure 4.12(b), where there is a small range of angles (around 6°) within which straining is repulsive and DEP is attractive. Straining is the stronger of the two effects at most separation angles, except near the points where it changes sign.

4.4 Conclusions

In this chapter, we have presented a three-dimensional phenomenological model to capture electrohydrodynamic interactions between a pair of identical leaky dielectric drops exposed to a spatially uniform DC electric field. Our model demonstrates good agreement with previous theoretical [Zabarankin, 2020, Sargentone et al., 2021], numerical [Sargentone et al., 2021], and experimental [Kach et al., 2022] studies on drop dynamics in the weak-field Taylor regime.

In the Quincke regime, freely suspended drops exhibit a range of distinct trajectories based on their initial positions and perturbations to their dipole moments. Drop trajectories are primarily influenced by rotational flows, leading to behaviours such as attraction, repulsion, and sustained pair translation. To gain deeper insights into EHD interactions, we analyse drops fixed in a plane but free to rotate and deform. By varying the viscosity ratio and spatial configurations of the drops, we investigate the effects of interactions on the angular velocity, deformation, and tilt angle of the drops. We observe that the onset of Quincke rotation, which corresponds to a pitchfork bifurcation in isolated drops or pairs of fixed solid spheres, is instead associated with an imperfect bifurcation in pairs of fixed drops due to symmetry-breaking hydrodynamic interactions arising from the straining flows. These interactions cause unperturbed drops to corotate in the plane defined by the applied field and the line joining the drop centres, with the rotation direction determined by the angle between the line of centres and the applied field. Electrohydrodynamic interactions can either inhibit or promote

drop rotation, depending on the relative drop positions. We also find that drop deformation and tilt angle vary non-monotonically with the angle between the applied field and the line connecting the drop centres, as well as with the viscosity ratio. Finally, we examine the effects of DEP forces and straining flows on drop attraction and repulsion across different spatial configurations for two viscosity ratios.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

In this thesis, the effects of surfactants and pair interactions on the electrohydrodynamics of leaky dielectric drops have been explored. In particular, we have derived semi-analytical theories including these effects in addition to charge convection, which allows us to obtain novel results concerning drops undergoing Quincke rotation. In this chapter, we briefly recapitulate the main findings of the previous three chapters, highlight the limitations of our theories and suggest some directions for future work to further build on the physical completeness and accuracy of our theories.

In Chapter 2, we introduced the small deformation theory of a clean isolated drop of Das and Saintillan [2021] using the notation and scaling used in the rest of the thesis. We presented novel results on the effects of charge convection in both the Taylor and Quincke regimes. We demonstrated that the theory captures the experimentally observed hysteresis associated with the onset of Quincke rotation of a drop, and attributed this behaviour to the ability of the drop to deform. Furthermore, we derived a novel expression for the critical field strength for Quincke rotation of a spherical drop, which reduces to the well-known result of Jones [1984] for a solid sphere in the limit $\lambda \rightarrow \infty$.

In Chapter 3, we developed a small deformation theory for a surfactant-laden drop and explored the effects of spatially varying surface tension on the dynamics

of a drop in both the Taylor and Quincke regimes. In particular, the presence of weakly-diffusing surfactant can significantly lower the critical field strength for Quincke rotation of a drop, and can eliminate the hysteresis occurring at onset of rotation. The electrohydrodynamic straining flow, which is suppressed by Marangoni stresses in the Taylor regime (and entirely arrested in the limit of zero surfactant diffusion, i.e., $\zeta \rightarrow \infty$), may be relatively unsuppressed in the Quincke regime due to the reduction of surface tension gradients by the rotational flow. We systematically studied the effects of varying El and ζ on the onset of Quincke rotation using both pseudo-arclength continuation and a linear stability analysis and found that larger values of El lead to a lower critical field for rotation when diffusion is strong (low ζ), while the opposite is true for high values of ζ . This chapter represents the first study on the effects of surfactant on the Quincke rotation of drops.

In Chapter 4, we developed a small deformation theory for a pair of clean drops and explored the effects of electrohydrodynamic and dielectrophoretic interactions on the dynamics of both freely suspended drops and drops which are fixed in space. We found a range of qualitatively different types of behaviour of freely suspended drops. In a somewhat artificial case in which both drops are perturbed in the plane containing the vector separating their centres, the drops spiral around one another in two dimensions while attracting one another. In more general settings, the drops may either repel one another or form a counterrotating pair which exhibit indefinite self-propelled translation motion. In the case of fixed pairs of drops, we find that the critical field strength for Quincke rotation is increased from that of an isolated drop if the drops are aligned parallel to the electric field, while the critical field strength is decreased if the drops are aligned perpendicular to the field. However, if, more realistically, the drops are not in one of these symmetric configurations, symmetry breaking hydrodynamic interactions lead to an imperfect bifurcation at the onset of rotation and no critical field can be established. We also found that the deformation and tilt angle of the drops can be either increased or decreased from those of an isolated drop depending on the alignment of the drops relative to the field. The material presented in this

chapter advances the understanding of electrohydrodynamic drop interactions, particularly in the context of Quincke rotation.

5.2 Limitations of the present work and suggested future work

Several potentially fruitful avenues exist to build upon the work presented in this thesis. Most importantly, full numerical simulations of a surfactant-laden drop or a pair of interacting drops under Quincke rotation would be highly desirable in order to validate the novel results presented in this thesis. The model of Das and Saintillan [2021] described in Chapter 2 is one of several theoretical models of drops undergoing Quincke rotation which have been contributed to the literature, and which explore various physical effects including deformation [He et al., 2013, Das and Saintillan, 2021], surface conduction [Tyatyushkin, 2017] and charge shocks [Peng and Schnitzer, 2025]. A physically comprehensive model retaining all of these effects would be likely to provide the most accurate prediction of the behaviour observed in experiments and would constitute a valuable advancement to the existing body of knowledge.

In the model for a surfactant-laden drop presented in Chapter 3, the linearisation of the Langmuir equation (3.9) is convenient for the spherical harmonic representation used in our theory, but restricts the theory to dilute concentrations of surfactant, and the theory thus fails to capture some of the qualitative features of surfactant effects at higher concentrations as found by Nganguia et al. [2019]. For example, their spheroidal theory predicts that the deformation of prolate A drops decreases and that of prolate B drops increases with increasing surfactant coverage for strongly diffusing surfactants, while the opposite is true for weakly-diffusing surfactants. However, the coverage is assumed to be small in the theory, so this complexity is lost. Full simulations using a finite or boundary element method may be used to explore nondilute coverages [Eggleton et al., 1999]. Moreover, it is important to note that the theory is restricted to apolar and insoluble surfactant molecules. The transport of polar surfactant molecules may be

strongly affected by the applied electric field and complex nonlinear interactions may exist between polar molecules, the surface charge and the induced electrohydrodynamic flow. By limiting the surfactant gradients, surfactant solubility may have a similar effect to diffusion, leading to a reduction in the destabilising effect of non-diffusing surfactant and reducing the flow suppression effect in the Taylor regime, thus allowing charge convection to play a stronger role in the drop dynamics. The inclusion of any of these physical effects is likely to lead to a more complete picture of the impact of surfactant on drop deformation, and would constitute a valuable advancement to the framework presented in this thesis. Our model also represents a first step towards understanding the electrorheology of emulsions of drops covered with surfactants, which could be achieved either using particle-based simulations [Das and Saintillan, 2023] or by coarse-graining the governing equations [Vlahovska, 2011]. Additionally, our model can be extended to incorporate interfacial rheological effects, such as surface viscosities [Scriven, 1960, Mandal and Chakraborty, 2017b, Nganguia et al., 2023], while retaining charge convection in three dimensions, to study their influence on Quincke rotation.

While the model of interacting drops presented in Chapter 4 demonstrates excellent agreement with weak-field trajectories computed numerically, it is not expected to yield accurate results for drops in close contact, which may experience lubrication effects or coalescence. Modelling interactions at close contact could be achieved using numerical techniques including boundary element [Das and Saintillan, 2017c, Firouznia et al., 2023], finite element [Wagoner et al., 2021], immersed interface [Hu et al., 2015] or volume-of-fluid [López-Herrera et al., 2011] methods. Furthermore, since experimental or industrial drop systems are rarely truly clean, considering the added influence of surfactant would likely lead to a more complete picture of drop interactions and may further improve the agreement between the theory and experimental data. In particular, a weakly-diffusing apolar surfactant may strongly impede the induced straining flow while leaving the surface charge relatively unchanged (except for weakening the effect of charge convection), thus allowing for control of the relative strengths of electrohydrodynamic

and DEP interactions. Another valuable extension to the material in Chapter 4 would be to consider the interactions between a pair of dissimilar drops, following the works of Kach et al. [2022] and Sorgentone and Vlahovska [2022], who highlighted the intriguing possibility of sustained pair translation of dissimilar drops in the Taylor regime. An analogous study of dissimilar drops in the Quincke regime is likely to reveal a rich range of intriguing behaviours. Furthermore, with straightforward extensions, the framework can be adapted to systems of three or more drops, which would be a valuable next step for studying emulsions in strong electric fields undergoing Quincke rotation, where drop rotation significantly influences bulk rheology. Experiments by Lobry and Lemaire [1999] on suspensions of solid particles undergoing Quincke rotation showed significant reductions in the apparent viscosity of the suspension, but a similar study for drops has not been conducted, either experimentally or theoretically. While Quincke rotation of solid particles has been exploited to create self-propelled rollers and helices relevant for active matter studies [Bricard et al., 2013, 2015, Das and Lauga, 2019], analogous systems for deformable drops under Quincke rotation remain unexplored. Furthermore, Das and Saintillan [2023] observed chaining in a suspension of solid particles, but straining flows may have a destabilising effect on these chains and the resulting dynamics may be richer. As mentioned in §1.4, interactions between three or more identical drops have been studied experimentally and theoretically by Kach et al. [2022]. However, charge convection was neglected in these works, so no results for drops undergoing Quincke rotation have been reported. A system of three drops can be analysed by assuming each drop undergoes pairwise interactions with every other drop, which can simply be summed to determine the ultimate effect of the interactions on each drop [Klingenberg et al., 1989, Park and Saintillan, 2010, Kach et al., 2022]. Figure 5.1 presents a range of trajectories of a three drop system calculated using this approach for the parameter values of Salipante and Vlahovska [2010] given in Table 2.1. The other relevant parameter values are $\lambda = 14.1$ and $E_0/E_{c,s} = 3$. For initial conditions exhibiting various symmetries, the trajectories observed for three drops can be closely related to the trajectories of two drops shown in Figure 4.4. In particular, Figure 5.1(a)

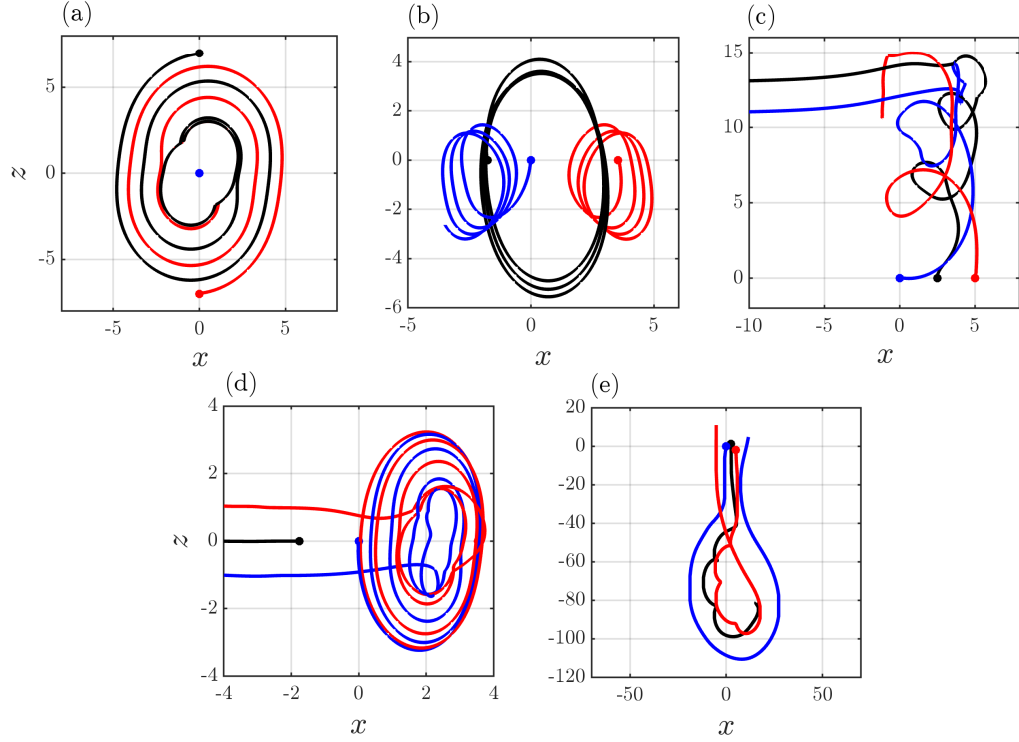


Figure 5.1: Examples of trajectories of a three drop system for the parameter values of Salipante and Vlahovska [2010] given in Table 2.1. In addition, $\lambda = 14.1$ and $E_0/E_{c,s} = 3$.

shows three drops initially aligned with the electric field with one drop exactly halfway between the other two, and all three drops are perturbed in the same direction. In this case, two drops spiral around one another in two dimensions while attracting one another, while the third remains stationary due to the symmetric interactions with the other two drops. This behaviour is similar to that of a drop pair shown in Figure 4.4(a). In the case shown in Figure 5.1(b), the three drops are initially located at the vertices of an equilateral triangle in the plane normal to the applied field, and all three drops are perturbed in a direction perpendicular to one of the sides of the triangle. In this case, two drops repel one another, much like in Figure 4.4(b), while the third drop follows a spiralling trajectory in the plane exactly halfway between the other two. In the case shown in Figure 5.1(c), which occurs most frequently for random initial drop positions and perturbations, the drops initially undergo complex three body interactions before two drops form a counterrotating pair like in Figure 4.4(c), while the third drop is left alone. In the case shown in Figure 5.1(d), the drops are again initially

located at the vertices of an equilateral triangle in the plane normal to the applied field, and all three drops are perturbed in a direction parallel to one of the sides of the triangle. Two of the drops (red and blue lines) follow a spiralling motion reminiscent of that of Figure 4.4(a), but the trajectories are not two dimensional due to the repulsion of both drops from the third drop. The spiralling drops form a corotating pair which moves towards the third drop and collects it before the three translate as a triplet. The axis of rotation of the third drop is parallel to the direction of translation, which may ultimately cause an abrupt change in the direction of translation, at which point one drop may be left behind while the other two continue as a counterrotating pair. In the case shown in Figure 5.1(e), which is not closely related to any behaviour observed for two drops and does not require any particular symmetric initial conditions, all three drops initially translate a large distance in the opposite direction to the applied field. All three drops then loop around and begin translating back in the direction of the applied field, but one stops moving while the other two trace out a large teardrop-shaped trajectory before slowly repelling one another. A thorough investigation into these behaviours and their implications for the bulk rheology of electrohydrodynamic emulsions of rotating drops would be highly desirable, and the material presented in this thesis presents a valuable first step towards studying such systems.

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Appendix A

Nomenclature

The following defines the frequently-used symbols used in this thesis.

Chapter 2

Symbol	Quantity	Definition
$\epsilon^\pm$	Absolute electric permittivity of drop or surrounding fluid	-
$\sigma^\pm$	Electric conductivity of drop or surrounding fluid	-
$\mu^\pm$	Dynamic viscosity of drop or surrounding fluid	-
$V^\pm$	Domain of drop or surrounding fluid	-
∂V	Interface between drop and surrounding fluid	-
a	Initial drop radius	-
$\mathbf{E}_0$	Applied electric field	-
E_0	Magnitude of applied electric field	$E_0 = \mathbf{E}_0 $
$\hat{\mathbf{E}}_0$	Unit vector in direction of applied electric field	$\hat{\mathbf{E}}_0 = \mathbf{E}_0/E_0$
$\mathbf{r}$	Position vector	-
r	Magnitude of position vector	$r = \mathbf{r} $
$\hat{\mathbf{r}}$	Unit vector in direction of position vector	$\hat{\mathbf{r}} = \mathbf{r}/r$
$\mathbf{E}^\pm$	Electric field in drop or surrounding fluid	(2.30)

Chapter 2 cont.

Symbol	Quantity	Definition
$\varphi^\pm$	Electric potential in drop or surrounding fluid	(2.28), (2.29)
$\mathbf{n}$	Unit vector normal to drop interface	(2.22)
q	Interfacial charge density	(2.3)
∇_s	Surface gradient operator	$\nabla_s = (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \nabla$
$\mathbf{v}^\pm$	Fluid velocity in drop or surrounding fluid	(2.56) (2.57)
$p^\pm$	Pressure in drop or surrounding fluid	(2.54) (2.55)
ξ	Interface level set function	(2.17)
$[\![\mathbf{f}^E]\!]$	Electric traction jump	(2.32)
$[\![\mathbf{f}^H]\!]$	Hydrodynamic traction jump	(2.65)
γ	Surface tension	-
κ	Mean surface curvature	(2.22)
$[\![\boldsymbol{\tau}^E]\!]$	Electric stress tensor	(2.10)
$[\![\boldsymbol{\tau}^H]\!]$	Hydrodynamic stress tensor	(2.11)
τ_{EHD}	Electrohydrodynamic flow time	(2.12)
Ca_E	Electric capillary number	(2.14)
δ	Small parameter characterising drop deformation	(2.70)
$\mathbf{j}$	Ohmic current	$\mathbf{j} = \sigma \mathbf{E}$
Re_E	Electric Reynolds number	(2.16)
λ	Viscosity ratio	$\lambda = \mu^- / \mu^+$
f	Shape function	(2.20)
$\mathbf{Q}^f$	Shape coefficients	-
$\mathbf{P}$	Induced dipole moment	-
p^E	Isotropic electric pressure	(2.33a)
$\mathbf{Q}_{\hat{\mathbf{r}}}^E$	Radial quadrupolar electric stresses	(2.33b)
$\mathbf{Q}_{\hat{\mathbf{t}}}^E$	Tangential quadrupolar electric stresses	(2.33c)
$\mathbf{T}^E$	Electric torque	(2.33d)
Q	Permittivity ratio	$Q = \epsilon^- / \epsilon^+$
S	Conductivity ratio	$S = \sigma^+ / \sigma^-$
m^p	Interior isotropic hydrodynamic pressure	-
M^p	Exterior isotropic hydrodynamic pressure	-
$\mathbf{q}^p$	Interior quadrupolar pressure distribution coefficients	(2.64b)

Chapter 2 cont.

Symbol	Quantity	Definition
$\mathbf{Q}^p$	Exterior quadrupolar pressure distribution coefficients	(2.73)
$\mathbf{q}^\phi$	Interior potential driven straining flow coefficients	(2.64c)
$\mathbf{Q}^\phi$	Exterior potential driven straining flow coefficients	(2.64a)
$\mathbf{d}^\chi$	Interior rotational flow coefficients	(2.58)
$\mathbf{D}^\chi$	Exterior rotational flow coefficients	(2.75)
$\mathbf{Q}^{\chi f}$	Convective shape derivative	(2.62)
p^H	Isotropic hydrodynamic pressure	(2.66a)
$\mathbf{Q}_{\hat{\mathbf{r}}}^H$	Radial quadrupolar hydrodynamic stresses	(2.66b)
$\mathbf{Q}_{\hat{\mathbf{t}}}^H$	Tangential quadrupolar hydrodynamic stresses	(2.66c)
$\mathbf{T}^H$	Hydrodynamic torque	(2.66d)
D_Q	Deformation parameter	(2.83)
Ω	Drop angular velocity	$\Omega = \mathbf{D}^\chi $
$E_{c,s}$	Critical field strength for rotation of sphere	(1.60)
E_c^{SN}	Critical field strength for saddle node bifurcation in drops	-
E_c^{P}	Critical field strength for pitchfork bifurcation in drops	-
E_{c,d^*}	Critical field strength for rotation of spherical drop	(2.91)

Chapter 3

Many of the symbols in Chapter 3 are identical to those in Chapter 2.

These symbols are not listed here unless the definition has changed as a result of the presence of surfactant.

Symbol	Quantity	Definition
γ	Surface tension	(3.18)
Γ	Surfactant concentration	(3.20b)
Γ_∞	Maximum surfactant concentration	-
γ_0	Surface tension with no surfactant	-
$\mathbf{v}_s$	Tangential surface velocity	$\mathbf{v}_s = (\mathbf{I} - \mathbf{n}\mathbf{n}) \cdot \mathbf{v}$
Γ_{eq}	Equilibrium surfactant concentration	-
γ_{eq}	Equilibrium surface tension	-
D_s	Surfactant surface diffusivity	-
Ca_E	Electric capillary number	(3.13)
Pe_s	Surface Péclet number	(3.16)
ζ	Inverse diffusivity parameter	(3.17)
El	Elasticity number	(3.19)
$\mathbf{Q}^\Gamma$	Surfactant concentration coefficients	-
ϵ	Small parameter quantifying surfactant gradients	(3.38)
$\mathbf{Q}^p$	Exterior quadrupolar pressure distribution coefficients	(2.73)
$\mathbf{Q}^{\chi\Gamma}$	Convective surfactant derivative	(3.46)
$\mathbf{S}$	Rate-of-strain tensor	$\mathbf{S} = (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) / 2$
$E_{c,d}$	Critical field strength for rotation of drop (in cases with no hysteresis)	-

Chapter 4

Many of the symbols in Chapter 4 are identical to those in Chapter 2, but with the addition of a 1 or 2 subscript to denote the association of the quantity with drop 1 or drop 2. These are not listed unless the definition differs from the corresponding definition in Chapter 2.

Symbol	Quantity	Definition
$\mathbf{R}$	Separation vector between drop centres	-
R	Distance between drop centres	$R = \mathbf{R} $
$\hat{\mathbf{R}}$	Unit vector in direction of $\mathbf{R}$	$\hat{\mathbf{R}} = \mathbf{R}/R$
θ_R	Angle between applied field direction and separation vector	$\theta_R = \arccos(\hat{\mathbf{R}} \cdot \hat{\mathbf{E}}_0)$
q_1	Charge distribution on interface of drop 1	(4.2)
$\mathbf{Q}_1^f$	Shape coefficients of drop 1	-
φ_1^∞	Effective external potential experienced by drop 1	(4.17)
$\mathbf{P}_1$	Induced dipole moment of drop 1	-
$\mathbf{E}_1^\infty$	Effective external electric field experienced by drop 1	(4.18)
$\varphi_1^\pm$	Electric potential inside or outside drop 1	(4.19)
$\mathbf{E}_1^\pm$	Electric field inside or outside drop 1	(4.20)
p_1^E	Isotropic electric pressure on drop 1	(4.22a)
$\mathbf{Q}_{1,\hat{\mathbf{r}}}^E$	Radial quadrupolar electric stresses on drop 1	(4.22b)
$\mathbf{Q}_{1,\hat{\mathbf{t}}}^E$	Tangential quadrupolar electric stresses on drop 1	(4.22c)
$\mathbf{T}_1^E$	Electric torque on drop 1	(4.22d)
p_1^∞	Ambient pressure experienced by drop 1	(4.27)
$p_{2,0}^+$	Hydrodynamic pressure outside drop 2 without hydrodynamic interactions	-
$M_{2,0}^p$	Isotropic contribution to hydrodynamic pressure outside drop 2 without hydrodynamic interactions	-
$\mathbf{Q}_{2,0}^p$	Exterior quadrupolar pressure distribution coefficients of drop 2 without hydrodynamic interactions	(4.56)
$\mathbf{v}_1^\infty$	Ambient velocity experienced by drop 1	(4.28)

Chapter 4 cont.

Symbol	Quantity	Definition
$\mathbf{v}_{2,0}^+$	Velocity outside drop 2 without hydrodynamic interactions	-
$\mathbf{N}_1^\infty$	Ambient uniform flow field experienced by drop 1	(4.29a)
$\mathbf{S}_1^\infty$	Ambient straining flow experienced by drop 1	(4.29b)
$\boldsymbol{\omega}_1^\infty$	Ambient rotational flow experienced by drop 1	(4.29c)
$\mathbf{D}_{2,0}^\chi$	Rotational flow outside drop 2 without hydrodynamic interactions	(4.55)
$\mathbf{v}_1^+$	Fluid velocity outside drop 1	(4.32)
$[\![\mathbf{f}^H]\!]_1$	Hydrodynamic traction jump over interface of drop 1	(4.44)
$\mathbf{U}_1$	Translational velocity of drop 1	(4.34)
$\mathbf{f}_1^{\text{DEP}}$	Hydrodynamic force on drop 1	(4.35)
$\mathbf{U}_{21}$	Relative velocity of pair of drops	(4.37)
$\mathbf{q}_1^p$	Interior quadrupolar pressure distribution coefficients of drop 1	(4.43b)
$\mathbf{q}_1^\phi$	Interior potential driven straining flow coefficients of drop 1	(4.43c)
$\mathbf{Q}_1^\phi$	Exterior potential driven straining flow coefficients of drop 1	(4.43a)
p_1^H	Isotropic hydrodynamic pressure on drop 1	(4.45a)
$\mathbf{Q}_{1,\mathbf{f}}^H$	Radial quadrupolar hydrodynamic stresses on drop 1	(4.45b)
$\mathbf{Q}_{1,\mathbf{\hat{t}}}^H$	Tangential quadrupolar hydrodynamic stresses on drop 1	(4.45c)
$\mathbf{T}_1^H$	Hydrodynamic torque on drop 1	(4.45d)
$\boldsymbol{\Omega}_1$	Rotational velocity of drop 1	$\boldsymbol{\Omega}_1 = \mathbf{D}_1^\chi + R^{-3}\boldsymbol{\omega}_1^\infty$
$\mathbf{F}_R$	Artificial short-range repulsive force	(4.63)
F_R	Magnitude of artificial short-range repulsive force	$F_R = \mathbf{F}_R $
$\boldsymbol{\Omega}$	Rotational velocity of corotating drops	$\boldsymbol{\Omega} = \boldsymbol{\Omega}_1 = \boldsymbol{\Omega}_2$
θ_T	Tilt angle of corotating drops	(4.68)

Appendix B

Jacobian Matrix Elements

In this appendix, for completeness, we give the elements of the Jacobian matrix in the linear system of equations (3.55).

$$\begin{aligned}
 J_{11} = & -\frac{1+2S}{S(2+Q)\text{Re}_E} - \frac{1-Q}{2(2+Q)} + \frac{(1-Q)(1-4Q)}{30(3+2\lambda)(2+Q)} \\
 & + P_{0,z} \left(-\frac{1}{2} + \frac{1}{5(3+2\lambda)} \left[\frac{5-8Q}{6} - \frac{9(14+11\lambda)(1-Q)}{(16+19\lambda)(2+Q)} \right] \right) \\
 & + P_{0,z}^2 \frac{2}{15(3+2\lambda)} \left(2+Q - \frac{9(14+11\lambda)}{16+19\lambda} \right) \\
 & + Q_{0,xx}^f \frac{6(14+11\lambda)}{5(16+19\lambda)(3+2\lambda)(1+2S)^2} - Q_{0,xx}^\Gamma \frac{2(8+5\lambda)}{(16+19\lambda)(3+2\lambda)},
 \end{aligned} \tag{B.1}$$

$$J_{15} = \left(P_{0,z} + \frac{1-Q}{2+Q} \right) \frac{6(14+11\lambda)}{5(16+19\lambda)(3+2\lambda)(1+2S)^2}, \tag{B.2}$$

$$J_{18} = - \left(P_{0,z} + \frac{1-Q}{2+Q} \right) \frac{2(8+5\lambda)}{(16+19\lambda)(3+2\lambda)}, \tag{B.3}$$

$$\begin{aligned}
 J_{22} = & -\frac{1+2S}{S(2+Q)\text{Re}_E} - \frac{6(1-Q^2)}{15(3+2\lambda)(2+Q)} \\
 & + P_{0,z} \frac{4}{15(3+2\lambda)} \left(-3Q - \frac{9(14+11\lambda)(1-Q)}{(16+19\lambda)(2+Q)} \right) \\
 & + P_{0,z}^2 \frac{2}{5(3+2\lambda)} \left[2+Q - \frac{9(14+11\lambda)}{16+19\lambda} \right] \\
 & + Q_{0,zz}^f \frac{6(14+11\lambda)}{5(16+19\lambda)(3+2\lambda)(1+2S)^2} - Q_{0,zz}^\Gamma \frac{2(8+5\lambda)}{(16+19\lambda)(3+2\lambda)},
 \end{aligned} \tag{B.4}$$

$$J_{24} = J_{15}, \quad J_{27} = J_{18}, \tag{B.5}$$

$$J_{32} = -\frac{1+2Q}{3\delta(3+2\lambda)} - \frac{2}{3\delta(3+2\lambda)} \left(\frac{45(1+\lambda)}{16+19\lambda} - (2+Q) \right) P_{0,z}, \tag{B.6}$$

$$J_{33} = -\frac{30(1+\lambda)}{\delta(16+19\lambda)(3+2\lambda)(1+2S)^2}, \tag{B.7}$$

$$J_{36} = \frac{2(4+\lambda)\epsilon\text{El}}{\text{Ca}_E\delta(16+19\lambda)(3+2\lambda)}, \tag{B.8}$$

$$J_{42} = -2J_{32}, \quad J_{44} = J_{33}, \quad J_{47} = J_{36}, \quad (\text{B.9})$$

$$J_{51} = -\frac{3}{2}J_{32} + \frac{1}{2}\left(Q_{0,xx}^f - Q_{0,zz}^f\right), \quad (\text{B.10})$$

$$J_{55} = J_{44} = J_{33}, \quad J_{58} = J_{47} = J_{36}, \quad (\text{B.11})$$

$$J_{62} = -\frac{(1+2Q)}{3\epsilon(3+2\lambda)} + \frac{2(68+47\lambda+Q(16+19\lambda))}{3\epsilon(16+19\lambda)(3+2\lambda)}P_{0,z}, \quad (\text{B.12})$$

$$J_{63} = \frac{6(4+\lambda)}{\epsilon(16+19\lambda)(3+2\lambda)(1+2S)^2}, \quad (\text{B.13})$$

$$J_{66} = -\left(\frac{6}{\zeta\text{Re}_E} + \frac{2(32+23\lambda)\text{El}}{\text{Ca}_E(16+19\lambda)(3+2\lambda)}\right), \quad (\text{B.14})$$

$$J_{72} = -2J_{62}, \quad J_{74} = J_{63}, \quad J_{77} = J_{66}, \quad (\text{B.15})$$

$$J_{81} = -\frac{3}{2}J_{62} + \frac{1}{2}\left(Q_{0,xx}^\Gamma - Q_{0,zz}^\Gamma\right), \quad (\text{B.16})$$

$$J_{85} = J_{74} = J_{63}, \quad J_{88} = J_{77} = J_{66}. \quad (\text{B.17})$$