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AN ENERGETIC VARIATIONAL APPROACH TO MATHEMATICAL MODELING OF CHARGED FLUIDS: CHARGE PHASES, SIMULATION AND WELL POSEDNESS

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Abstract

In thesis we propose a mathematical model of electrolyte fluid and interface systems. The model is based on a coupling between the Navier-Stokes equations of an incompressible fluid, the Nernst-Plank-Poisson equations of a diffuse, binary electrolyte, and the phase field Allen-Cahn equation. The coupling is derived in the energetic variational framework and guarantees the consistent exchange of the kinetic energy of the fluid, entropic and electric energy of the charge carriers and the surface area of the interface. Using the phase field as a topological labeling of the interface, we introduce a "short range" barrier potential which selectively blocks charge migration across the interface. The model is able to capture the dynamics of both charge induced flow and selection by the interface. This is demonstrated by simulation of the coalesence of two charge selective vesicles by charge induced motion.

We also develope the existence theory for global classical solutions of the NPP equations with smooth data in space dimension $d \leq 3$, global weak solutions to the NPP equations coupled with the NS equations for $d \leq 3$ and global weak solutions for small initial data with the additional phase field Allen Cahn equation in space dimension $d \leq 2$. The NPP equations are a system of second order, divergence form, semilinear, nonlocal parabolic equations. We elucidate many of the special features of the NPP equations which are nonstandard in complex fluid systems.

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Dedication

This thesis is dedicated to my father Rolf, whose reflection I see in myself more and more as I grow older, to my mother Christine, whose constant support, sympathy and compassion are felt even in those around me, to my brother Patrik, whom I dearly miss, to my bff STM, to ACD, who taught me to be brave, and finally, to Aurélie, whose grace and tenderness remind me why life is beautiful.

Chapter 1

Introduction

A well established model for charged fluids is given by the transport and Lorentz force coupling between the Navier-Stokes equations of an incompressible fluid and the transported Poisson-Nernst-Plank (PNP) equations of a binary, diffuse charge system [42, 46, 44, 45]. The equations are

$$\rho(\mathbf{u}_t + \mathbf{u}\cdot\nabla\mathbf{u}) + \nabla\pi = \nu\Delta\mathbf{u} + (n-p)\nabla V, \tag{1.1}$$

$$\nabla\cdot\mathbf{u} = 0, \tag{1.2}$$

$$n_t + \mathbf{u}\cdot\nabla n = \nabla\cdot(D_n\nabla n - \mu_n n\nabla V), \tag{1.3}$$

$$p_t + \mathbf{u}\cdot\nabla p = \nabla\cdot(D_p\nabla p + \mu_p p\nabla V), \tag{1.4}$$

$$\nabla\cdot(\epsilon\nabla V) = n - p. \tag{1.5}$$

$\mathbf{u}$ is the fluid velocity, π is the pressure, ρ is the fluid density and ν the fluid viscocity. n and p are the density of binary diffuse negative and positive charges respectively; D_n, D_p and μ_n, μ_p are their respective diffusivity and mobility tensors. ϵ is the dielectric constant of the fluid. In this work we consider the case $\rho = D_n = D_p = \mu_n = \mu_p = 1$. ϵ is taken to be a constant[1]. In chapter 5, we consider the case stationary solutions of (1.1)-(1.5) when $\epsilon \to 0$.

Several classical and contemporary experimental phenomena can be theoretically and numerically recovered from this system of equations. They include the

[1] $\epsilon^2 = \epsilon_0\epsilon_r kT/(C_\infty L)e^2$, where ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity, kT is thermal energy, C_∞ is the characteristic charge density, e is the elementary charge and L is the characteristic length scale. Typically, ϵ ranges from 10^{-3} to 10^{-6} for realistic systems on the length scale of 10^{-6} to 10^{-3} meters with molarity between 10^{-4} to 1 [47].

motion of charge selective, conducting or polarizable particles and the induced motion of fluids. These phenomena arise as a result of polarized concentration layers at the boundary interface between the charged fluid and inclusions [52, 42, 44]. It is in this charged induced motion that electro kinetics becomes a key tool in micro fluidic devices with applications to fluid pumping and particle selection.

Traditionaly, (1.1)-(1.5) are posed in a fixed domain. In this work we couple equations (1.1)-(1.5) with the Allen-Cahn equation as a diffuse formulation of a moving boundary interface. The boundary interface partitions the domain into a region where the dynamics of the charge system are seperated from the other region. As is the case with many interface boundary systems, the modeling of boundary kinetics becomes difficult due to the mixing of coordinate systems. This problem is especially apparent when the interface is free to move or the functions defined over the regions separated by the interface are coupled through boundary condition. In electrolyte systems especially, many experimental observations have yet to be recovered by correct boundary kinetic formulations. A major focus of studies in electrolyte research attempts to understand the interface boundary condition coupling of the diffuse charged bodies and electrostatic potential. From a theoretical standpoint, the interface also represents a difficulty in the existence and regularity theory. The authors demonstrated in [48] that without the presence of an interface, the system (1.1)-(1.5) is totally dissipative. The presence of a boundary, however, introduces terms which are not amenable to producing apriori estimates. The reader should understand that this irrespective of the zero Debye length limit and is a misfeature of the PDE.

In chapters 4 and 5 we look at the questions of existence of solutions to (1.1)-(1.5), with and without the phase field coupling. In section 4.2, we prove that the PNP equations have classical solutions for smooth data using the usual techniques for second order parabolic equations. We prove the existence of global weak solutions to (1.1) -(1.5) with Dirichelet boundary conditions for bounded domains in space dimension $d \leq 3$. We similarly prove the existence of global weak solutions to the coupling of (1.1)-(1.5) with the Allen-Cahn equation when $d = 2$. When coupled with the Allen-Cahn equation, an aprior estimate for solutions n and p cannot be formulated for $d \geq 4$ due to lack of regularity of solutions to the Allen-Cahn equation. A result for $d = 3$ is attainable if the phase field solves a Cahn-Hilliard

equation. Chapter 5 is devoted to stationary solutions of (1.1)-(1.5) in the limit $\epsilon \to 0$.

The question of existence of classical solutions to the PNP equations (and weak solutions to the PNP and NS coupling) is nontrivial. The PNP equations are a second order, divergence form, semilinear, nonlocal system. The nonlocal convective term in the equations for n and p ∇V is self induced by the Poisson equation (1.5). The potential V is repulsive in the sense that the sign dependence on V in (1.4) and (1.5) is opposite of the sign dependence on n in (1.5) and p in (1.5). Thus the equation dynamic results in a dissipation of the potential energy due to V. If the sign dependence were switched (as is the case for the equations of chemotaxis, see [22]), i.e. the self induced potential is attractive, then such a system is degenerate and exhibits finite-time blow-up solutions. This indicates that the existence of global solutions has a nontrivial dependence on the equation structure.

The PNP system carries two energy laws. The first is the dissipation of internal energy (entropic and electric energy). It is the canonical energy law in the sense that the PNP equations can be formulated as a gradient descent with respect to the the sum of the electric and entropic energy. In many complex fluid systems, useful apriori estimates are a direct consequence of the canonical energy law. This is not the case with the PNP equations because the internal energy density is of the form $f \log(f) + fP$ for a potential P. This energy bound implies that solutions are slightly more than integrable. The only utility of this energy law is in guaranteeing the consistency among the exchange of kinetic energy of the fluid, the phase field energy and the internal energy of the charge system. Remarkably, the PNP equations satisfy a second, stronger energy law that implies the usual apriori estimates of second order parabolic equations. It is an interesting aspect of the system structure that both energy laws hold only for positive solutions. In the Galerkin approximation (and the numerical discretization), positivity is not easily guaranteed by maximum principles since the solution data (e.g. the truncated weak solution of the Navier-Stokes equation) may not be smooth enough. Instead we prove the positivity of weak solutions to the PNP equations for weak data using energy techniques, see lemma 4.

1.1 Permselective Membranes

Equations (1.1)-(1.5) are in the majority studied in the context of permselective membranes[2]. A permselective membrane is the boundary interface between an electrolyte (liquid) solution and a solid or liquid region which is selectively permeable. Selectively permeable means that the junction permits currents of one (or none) of the charge species. Studies of permselective membranes account for the relationship between the current of this particular species and the difference in voltage (potentential) between the boundary interface and the bulk of the electrolyte.

There is a region of concentration polarization near the boundary interface. A concentration polarization refers to the boundary layer at the boundary interface where the charge densities are, in general, different[3]. The structure of the boundary layer has a complicated dependence on the potential difference and the current of the charge species at the junction. The complexity of this boundary layer has historically lead to numerous formulations of boundary conditions and approximations of the governing equations (1.1)-(1.5). It is worth pointing out that no boundary conditions have yet been formulated which satisfactorily account for the experimentally observed relationships between current and voltage. Three interesting, contemporary formulations of the boundary layer structure question the validity of the governing equations in the region of concentration polarization.

One formulation focuses on the ion transport in membranes where the permselective interface is a membrane with open channels. Potassium channels (a typical integral membrane protien) have an overall length of 45 Å and a 10 Å diameter cavity. The differing dielectric properties of the surrounding protien and lipid membrane (solid) and the open channels (aqueous) at a scale comparable to the length scale of the governing equations make it difficult to (formally) calculate the induced surface charge and potential within the channel, [24]. If the radius of hydrogen is 0.5 Å, then such a channel would allow for the presence of atmost $\pi(20)^2 \approx 1200$ particles. Describing this system by a continuum distribution is questionable. Nevertheless such a study is of great importance considering that

[2]Similar equations have been extensively studied in semiconductor device, electrochemical film, and fuel cell models.

[3]In the bulk, electrolyte solutions are charge neutral, i.e. $n = p$.

all extracellular regulatory mechanism occur through a membrane ion transport. A notable study of ion transport in open channels is [51, 40]. Beginning from the equations of motion for individual ions the authors have derived a modified version of the diffuse equations (1.4)-(1.5), to include forces induced by self induced surface charges. They have called this the Coniditional Poisson-Nernst-Plank (CPNP) system. An older study by [18, 19] derives the induced surface charge when an arbitrary charge distribution is given.

Two other areas of study have postulated the existence of additional dynamics at the electrolyte junction. The work by [47] has given convincing numerical evidence that electro-osmotic convection at the electrolyte junction induces a periodic vorticity in the flow along the interface. They claim that the convection due to a fluid instability is the source of overlimiting conductance, rather than the traditional thought that it is simply due to electroconvection. In discussion, though, Rubinstein has conceded that this instability has not been experimentally observed. A more recent attempt by [20] has considered modifying the free energy of the charge system to include steric effects, namely that the charge density at the junction is limited by the finite radius of the individual ions. Following [21], they introduce the additional entropic contribution to account for the order a^3 solvent displacement by ions of radius a. This approach is similar to ours, as we introduce in Chapter 3 a free energy that penalizes for the presence of ions in regions exterior to the electrolyte (see equation (3.14).)

In all the works mentioned above, and other related works known to us, authors formulate fixed boundary conditions and analyze linearly perturbed solutions (with respect to ϵ) of (1.1)-(1.5) either formally or numerically. In view of our theoretic results in Chapter 6, we believe that these models are phenomenologically inconsisent. We begin with the simple assumption that the electrolyte/electrode junction is impermeable to both charge species and that the potential is specified as a Dirichelt boundary condition. (in other formulations, the current of one of the species is specified.) Thus our formulation is infact a simpler, special case of theirs. When the total net charge of the electrolyte is zero, we have proven rigorously that the concentration polarization structure is in total agreement with that predicted by other asymptotic theories as $\epsilon \to 0$. However, when the total net charge is nonzero, we have proven that one of the charge densities necessarily diverge at

the boundary and that the potential ϕ diverges to $\pm\infty$ uniformly away from the interface. The assignment of fixed boundary conditions for either charge species then becomes an unrealistic assumption because the value of either charge species at the interface can be parametrized by ϵ and the total net charge! One might argue, though, that an electrolyte of nonzero net charge does not exist, along with said instability. This is in a sense true, to the degree of what one means by zero net charge. If a current is present at the electrolyte junction, then a change in the net charge, although slight, might be significant with respect to ϵ to induce the above mentioned instability. This being said, we claim that any asymptotic expansion of n, p and ϕ with respect to ϵ is unjustified without first explicitly guaranteeing or specifiying that the total net charge is "small" compared to ϵ. We plan to extend the results of Chapter 6 to more general boundary conditions of the potential ϕ and to include the nonzero current/boundary flux case.

1.2 Energetic Formulation

The charge PNP equations stems from a well defined free energy consisting of the electric and entropic energy. Other energetic contributions, such as those leading to induced surface charges [40], steric effects [20] and other forces can similarly be accounted for by modifications of the free energy. Also, the force induced by the charge system on the fluid, (in our case $(n-p)\nabla V$ in equation (1.1)) is similarly derived from this free energy (see Chapter 2, section 2.2). A major contribution of this work is formulation the hydrodynamic system (1.1)-(1.5) and the PNP equations themselves in terms of energetic principles at the *continuum level*. To clarify, the equations of motion

$$\ddot{\mathbf{x}} - \gamma^{-1}\dot{\mathbf{x}} = \nabla F(\mathbf{x}), \quad \mathbf{x} \in \mathbb{R}^N, \quad N \gg 1$$

with damping used to derive the PNP equations from a particle-particle interaction model are energetic. However, in the derivation of the PNP and similar Fokker-Plank type equations, one assumes that the time scale of the particle acceleration is much smaller than the dynamic in consideration, so that the particles simply satisfy the gradient descent dynamic $\dot{\mathbf{x}} = -\gamma\nabla F(\mathbf{x})$. This velocity field of the

particle positions leads to the the Liouville (conservation of mass) equation. This is our point of departure, namely in correctly formulating the force ∇F in terms of the continuum distribution of $\mathbf{x}$.

There are several consequences of such a formulation. The first and most important consequence is the differential inequality describing the exchange between kinetic and free energy of the charge system (see equation (2.14) with variants (3.30) and (4.31)). We refer to this differential inequality as the canonical energy law. In the mathematical existence theory this DI is the source of apriori bounds which are so critical in the construction of approximate solutions. This object, which is natural to study from the mathematical standpoint, also captures the physical force balance of the system; it states that the exchange of kinetic and free energy is lost to diffusion and viscous damping. In equations (1.4)-(1.5) the fluid imparts a force on the charge system through transport while in equation (1.1) the charge system imparts the Lorentz force on the fluid. From the modeling point of view, any formulation which does not reflect this force balance relationship in an energy law cannot be faithful to the dynamic.

This admonishen holds for numerical approximations as well. In order for the numerical approximation to be faithful to the force balance dynamic it must also satisfy a discrete form of the canonical energy law. For example, in existence proofs found in Sections 4.2 and 4.3, it quickly becomes apparent solutions and solution approximations of the PNP equations must be strictly positive for the canonical energy law to hold. To address this need, we have chosen a numerical discretization[4] of equations (1.4) and(1.5) which preserves the positivity of the diffusion-convection operator under the assumption that the domain triangulation (tetrahedralization in three dimensions) is Delaunay. Furthermore, when the problem being considered has solutions limiting to a simgular problem, e.g. $\epsilon \to 0$ in (1.5), then the only physically relevent approximations captured by the numerical scheme will be those with energies bounded irrespective of ϵ.

[4]Edge Averaged Finite Element scheme [58], see Section 3.6.

Chapter 2

The Energetic Variational Approach

The energetic variational approach to complex fluid problems consists of postulating energies that approximate the energy of internal variables of the complex fluid, and defining energetically consistent evolution equations. By consistent, we mean that the net exchange of the internal variables' energies and kinetic energy, ignoring viscous losses, is zero. A general framework for producing such evolution equations relies on two variation principles; the least action principle and the principle of steepest descent. The least action principles stipulates that the fluid minimizes the loss of kinetic energy to the energy of internal variables. The law of steepest descent stipulates that the internal variable chooses an evolution path which minimizes the internal energy most quickly. The choice of this path is of the gradient descent with respect to the internal energy where the gradient is defined by the admissable perturbations of the internal variable. The consistency of the system is a generic consequence of the coupling through transport and force balance. In some notable cases, the consistency of the complex fluid system is key to developing an existence theory and developing numerical strategies which guarantee stability. This is unfortunately not the case for the system considered in this work.

Two of these notable complex fluid systems are liquid crystals, viscoelastic fluids and fluid structure systems.

In this work, we define an energetic variational framework for the Nernst-Plank-

Poisson (NPP) equations with the presence of an interface for the most simple setting; the evolution of charged fluids where the charge system is simply restricted to the interior of an interace. This system requires us to consider several energetic constructs. The first will be the implicit description of the interface by the phase-field labeling function. We will introduce the necassary variational formalism and derivation of the force balance equations via the least action principle. With these tools we derive the NPP equations and Lorentz force coupling with the fluid. In chapter 3, we introduce an additional interface/phase field dependent potential to charge system.

As elluded to before, the energetic vartional framework guarantees the consistency between the kinetic and internal energy transfer. Additional estimates must be made for the charge densities to gaurantee the existence of solutions with the fluid coupling. The canonical internal energy of diffuse systems implies no additional regularity of solutions other than integrability. Below we give a thorough outline of the implicit description by the phase field internal variable, the derivation of orce balance equations by the least action principle and introduce several notions and aspects of variational derivatives.

2.1 Interfacial Energies

In general, the interface between regions $\Gamma(t)$ evolves according to its interfacial energy dissipation. The interfacial energy, denoted S, is exchanged with the kinetic energy of the surrounding fluid and the energy of other internal variables, e.g. the electric and entropic energy of the charge system. The exchange of energy with the charge system is realized by restriction of the charged bodies to regions specified by the interface. The exchange with kinetic energy is realized through interfacial forces as governed by S. In return, the interface, viewed as a two dimensional region of the fluid, is transported by the fluid flow field.

From the modeling perspective, there are several interface formulations which capture the evolution of $\Gamma(t)$ well. These include the direct, shock wave and level set formulations. However, all but the level set formulations suffer from the inherent mathematical and numerical deficiences due to the fact that the interface is a Lagrangian object while complex fluids, with their flows and internal variables,

are described by Eulerian variables. Traditionaly, there are several well-established methods of analytically and computationally modeling surfaces. Most notably, these include direct methods, the front tracking [1, 2], volume of fluid (VOF) [3], and level set methods [4], [14].

The most straight forward way of handling a moving surface is the direct method. One employs a discretization with grid points on the surface itself, using finite differences, finite-elements, and boundary-integral techniques. Although conceptually convenient, this method inherits the trappings of a moving mesh scheme. Large deformations in the surface may lead to mesh entanglement, and keeping track of the mesh requires a great deal of algorithmic complexity. Most importantly though, it is difficult to couple the surface motion with the field equation of a body force, making interface motion through a fluid difficult to model.

Alternatively, one may fix a discretization of the domain, and represent the surface motion as a vector field distributed along a thin band within which the surface resides. Methods of this type include the level set, VOF, and front tracking methods. The advantage here is that the surface motion, although distributed over a small region, is a bulk quantity and couples easily with other fields. Further, there is no algorithmic overhead in keeping track of the quality of the domain discretization. The above mentioned schemes, however, do not treat the discretization uniformly on the whole domain. Front tracking requires the solution of an auxiliary Riemann problem to extrapolate the difference scheme at the interface. In the other models, the indicator function must be renormalized at each time step, introducing artificial dampening to the surface motion.

Level set methods, on the other hand, describe the interface implicitly by the labeling function ϕ, which is defined as a function in the observer's corrdinate, space, and time. One of these level set functions, the phase field, is particulary useful for energetic variational approaches because its evolution and force balance stem directly from its associated energy and provide a consistent relaxation of the tranpsort equation. Because the relaxation is consistent, the phase field energy remains bounded and thus only those singularities which are meaningful are captured by the dynamic. Further, as is the case with other implicit definitions, the formulation is insensitive to topological changes of the interface, such as coalescence or break up.

The phase field is a topological labeling of the interior and exterior of the interface in the domain $\Omega \subset \mathbb{R}^d$ by the values 1 and -1. The transition region, where ϕ deviates from these two values, is where the associated energy density of S_η and consequently interfacial force are supported. η is the order parameter describing the characteristic thickness of the interfactial region. The interface $\Gamma(t)$ is now loosly associated with this region, motivating another phase field nomenclature, the diffuse interface. In the limit $\eta \to 0$, the phase field approaches the something like the characterstic function of the interior and exterior of $\Gamma(t)$ while the diffuse interface forces heuristically approach those of the the original sharp interface dynamic. The sharp interface limit of phase field dynamics is popular topic of research and the convergence of energy and force terms for all but the most simple energies remain largely unknown. The reader intersted in these results may further investigate the references given herein.

The interfacial energy $S_\eta(\phi)$ of the phase field ϕ depends on the type of interface being considered. For example, if the interface $\Gamma(t) = \{\phi = 0\}$ models the junction between two immisable fluids, then the energy

$$S_\eta(\phi) = \int_\Omega \frac{1}{2\eta}|\nabla\phi|^2 + \frac{1}{\eta}W(\phi)\,dx, \quad W(\phi) = \frac{1}{4}(\phi^2 - 1)^2 \tag{2.1}$$

approximates the surface area of $\Gamma(t)$ in the limit $\eta \to 0$. Loosly speaking, if S_η is bounded with respect to η, then ϕ is close to ± 1 almost everywhere, while the gradient energy prevents this jump from being sharp. Consequently, both terms approach a δ sequence around the level set $\{\phi = 0\}$ and $S_\eta(\phi) \longrightarrow |\Gamma(t)|$. (2.1) is the simplest phase field energy. In this work, we consider the interfaces of this type, i.e. the associated energy of $\Gamma(t) \approx \{\phi = 0\}$ is (2.1). Two equations derived from the gradient descent of (2.1) are the Allen-Cahn equation, when the addmisable test space is $H^1(\Omega)$, and the Cahn-Hilliard equation, when the admissable test space is $H^2(\Omega)$. Results on the existence of solutions to the Allen-Cahn, Cahn-Hilliard and more general semilinear equations can be found in [34]. For the existence of weak solutions for the coupling of the hydrodynamic coupling of the Allen-Cahn equation and the Navier Stokes (NS) equations, we rely heavily on results by [35]. The asymptotic limit of the Allen-Cahn, Cahn-Hilliard and minimizers of (2.1) as $\eta \to 0$ have also been extensively studied, [5, 6, 7, 8, 9, 10, 12].

Other forms of the functional S_η approximate more general interfacial energies; In the case of membrane vesicles, where $\Gamma(t)$ models a lipid membrane for example

$$\int_\Omega \frac{\eta}{2}\left(\Delta\phi - \frac{1}{\eta^2}W'(\phi)\right)^2 dx \approx \int_{\Gamma(t)} H^2\, dS \tag{2.2}$$

is a good approximation of the mean curvature energy or in the case of the topological index of the vesicle,

$$\int_\Omega \left(\eta\Delta\phi - \frac{1}{\eta}W'(\phi)\right) W'(\phi)\, dx \approx \int_{\Gamma(t)} K\, dS \tag{2.3}$$

approximates the Euler number of $\{\phi = 0\}$. $K = k_1k_2$ and $H = (k_1 + k_2)/2$ are of course the Gaussian and mean curvature of $\Gamma(t)$ respectively. Unlike, (2.1), not a great deal is known about the asymptotic behaviour, existence of minimizers or existence of time dependent solutions given by (2.2) (see [43, 39] for two recent developements). The minimization of (2.2) is related to the Willmore problem from differential geometry, [57]. This author and collaborators have proposed (2.2) and (2.3), and the resulting hydrodynamic equations in the study of vesicle membranes. We have demonstrated the convergence of these functionals to their geometric analogues under the somewhat restrictive ansatz that ϕ satisfy an optimal profile condition [26, 27, 31]. However, our collaborators have simulated the minimization and hydrodynamic coulping of (2.2) and (2.3) which are encouraging results as to the viability of phase field modeling of vesicle membranes, [25, 26, 29, 30].

2.2 Least Action Principle and Variational Derivatives

In the aforementioned energetic coupling of the force balance and steepest descent dynamics, there three important variational derivatives, each depending on the admissable perturbations of internal variables. The duality between these variational derivates is the source of consistency in the energetic variational approach. The three variational derivates are the usual Frechet derivative (variation with respect to the function), the argument derivative (variation of the domain) and the

variation with respect to the predomain.

Assume that $\psi : \Omega \to \mathbb{R}$ is a function, the internal variable, and

$$L(\psi) = \int_\Omega Q(\psi, \nabla\psi)\, dx \tag{2.4}$$

is a functional, the internal energy. A variational derivative of L, if it exists, is defined as the limit

$$\lim_{s\to 0} \frac{1}{s}(L(\psi^s) - L(\psi^0)) \tag{2.5}$$

where ψ^s is a one parameter family of functions chosen with respect to a particular type of test function, or perturbation.

The usual Frechet derivative, denoted simply by L_ψ or L' (in case it is clear that L depends only on one function, the prime $(\cdot)'$ notation is used), is defined by

$$\langle L_\psi, u\rangle = \int_\Omega (Q_\psi - \nabla \cdot Q_{\nabla\psi})u\, dx, \quad \forall u \in C_c^\infty(\Omega).$$

The perturbation in this case is a solution to the equation $\partial_s\psi^s + u = 0,\ \psi^0 = \psi$. The space of test functions for the Frechet derivative are maps from Ω into $\mathbb{R}$ which are added to the functional argument.

In contrast, in the variation of the domain, the variation is chosen from maps from Ω to itself. The test space is the tangent space of diffeomorphisms of Ω The variation of the domain derivative, denoted L_*^ψ, is given by

$$\langle L_*^\psi, \mathbf{u}\rangle = -\int_\Omega (Q_\psi - \nabla \cdot Q_{\nabla\psi})\nabla\psi \cdot \mathbf{u}\, dx, \quad \forall \mathbf{u} \in (C_c^\infty(\Omega))^2. \tag{2.6}$$

In this case, the pertubation occurs within the argument of ψ itself, so that ψ^s solves the transport equation $\partial_s\psi^s + \mathbf{u}\cdot\nabla\psi^s = 0,\ \psi^0 = \psi$. The variation of the domain describes the pertubation of those internal variables which are moving with the fluid, e.g. a material labelings or densities of very small, dilute particles.

If ψ is the density of particles indexed by points in the conitunuum W with positions in Ω, then a third variation is chosen from the tangent space of maps into Ω from the predomain W. The deviation of the the variable ψ is motivated as follows. Suppose that ψ^s is defined as a constant multiple of the Jacobian, J^s of a one-parameter family of maps $x^s : W \to \Omega$; $\psi^s(x^s) = \det(J^s)\psi_0$. Define a vector

field $\mathbf{v} : \Omega \to \mathbb{R}^3$ by $\mathbf{v}(x^s) = \partial_s x^s$. We may compute the deviation of ψ^s as follows; for any $y \in C_0^\infty(\Omega)$,

$$\begin{aligned}
\int_\Omega \partial_s \psi(X) y(X)\, dX &= \frac{d}{ds} \int_\Omega \det(J^s((x^s)^{-1}(X))) \psi_0((x^s)^{-1}(X)) y(X)\, dX \\
&= \frac{d}{ds} \int_W \psi_0(w) y(x^s(w))\, dw \\
&= \int_W \psi_0(w) \nabla y(x^s(w)) \cdot \partial_s x^s(w)\, dw \\
&= \int_\Omega \det(J^s((x^s)^{-1}(X))) \psi_0((x^s)^{-1}(X)) \nabla y(X) \cdot \mathbf{v}(X)\, dX \\
&= -\int_\Omega \nabla \cdot (\psi^s(X)\mathbf{v}(X)) y(X)\, dX.
\end{aligned}$$

As the above identity holds for all y, we have that the class of all admissable perturbations to functions of the form $\psi^s(x^s) = \det(J^s)\psi_0$. is given by solutions to the equation $\partial_s \psi^s + \nabla \cdot (\psi^s \mathbf{v}) = 0$. The derivative with respect to such perturbations, L_ψ^*, is defined where ψ^s is a solution to the convection equation, hence

$$\langle L_\psi^*, \mathbf{u} \rangle = -\int_\Omega \psi \nabla (Q_\psi - \nabla \cdot Q_{\nabla \psi}) \cdot \mathbf{u}\, dx, \quad \forall \mathbf{u} \in (C_c^\infty(\Omega))^2. \tag{2.7}$$

Note that if $\mathbf{u}$ is divergence free, $\langle L_\psi^*, \mathbf{u} \rangle = \langle L_*^\psi, \mathbf{u} \rangle$ as expected. We have chosen the $*$ notation to emphasize the duality between these two forms, $L_\psi^* = \psi \nabla L_\psi$ while $L_*^\psi = L_\psi \nabla \psi$. Furthermore, one immedietly sees that the essential duality between L_ψ, L_*^ψ and L_ψ^* are the identities

$$\langle L_*^\psi, \mathbf{u} \rangle = -\langle L_\psi, \mathbf{u} \cdot \nabla \psi \rangle, \tag{2.8}$$

$$\langle L_\psi^*, \mathbf{u} \rangle = -\langle L_\psi, \nabla \cdot (\psi \mathbf{u}) \rangle, \qquad \forall \mathbf{u} \in (C_c^\infty(\Omega))^2, \tag{2.9}$$

assuming ψ is smooth. The above identities holds for functionals of higher order derivatives of ψ as well.

Let $Q_T = \Omega \times [0, T]$ and assume now that $\psi : Q_T \to \mathbb{R}$ is given. Consider the space of time dependent, volume preserving maps from Ω into Ω,

$$\mathcal{X} = \{\, x(X,t) : \Omega \times [0,T] \to \Omega \,:\, \det \nabla_X x(X,t) = 1, \forall (X,t) \in Q_T \,\}. \tag{2.10}$$

Given $x \in \mathcal{X}$ we may define an action

$$\mathcal{A}(x) = \int_0^T \int_\Omega \frac{1}{2}|x_t(X,t)|^2 \, dX - L(\psi(x)) \, dt. \tag{2.11}$$

If x is a minimizer of $\mathcal{A}$, it will satisfy $\lim_{s\to 0} s^{-1}(\mathcal{A}(x^s) - \mathcal{A}(x^0)) = 0$ for every one paramter family of maps $x^s \in \mathcal{X}$ with $x^0 = x$. Let $y(X,t) = \lim_{s\to 0} s^{-1}(x^s(X,t) - x^0(X,t))$ and $\psi^s(x(X,t)) = \psi(x^s(X,t))$. Further, let $\mathbf{v}(x(X,t)) = y_t(X,t)$ and $\mathbf{u}(x(X,t)) = x_t(X,t)$. By definition, we have then

$$\begin{aligned}
0 = \lim_{s\to 0} s^{-1}(\mathcal{A}(x^s) - \mathcal{A}(x^0)) &= \int_0^T \int_\Omega x_t \cdot y_t \, dX - \lim_{s\to 0} s^{-1}(L(\psi^s) - L(\psi^0)) \, dt \\
&= -\int_0^T \int_\Omega x_{tt} \cdot y \, dX + \lim_{s\to 0} s^{-1}(L(\psi^s) - L(\psi^0)) \, dt \\
&= -\int_0^T \int_\Omega (\mathbf{u}_t + \mathbf{u}\cdot\nabla\mathbf{u}) \cdot \mathbf{v} \, dx + \langle L_*^\psi, \mathbf{v}\rangle \, dt, \\
&\qquad \forall \mathbf{v} \in \{\mathbf{w} \in (C_0^\infty(\Omega))^2 \, : \, \nabla\cdot\mathbf{w} = 0\,\}.
\end{aligned}$$

Writing this last equation in strong form, we recover the force balance equation

$$\mathbf{u}_t + \mathbf{u}\cdot\nabla\mathbf{u} + \nabla p + L_*^\psi = 0, \quad \nabla\cdot\mathbf{u} = 0. \tag{2.12}$$

Suppose that, in addition to (2.12), ψ satisfies a transported gradient descent equation,

$$\psi_t + \mathbf{u}\cdot\nabla\psi = -\gamma K(\psi), \quad \gamma > 0 \tag{2.13}$$

for some operator K. Multiply (2.12) by $\mathbf{u}$ and (2.13) by L_ψ and integrate the two term over Ω. Summing the two equations, we find

$$\frac{d}{dt}\left(\frac{1}{2}\|\mathbf{u}\|^2_{L^2(\Omega)} + L\right) + \langle L_*^\psi, \mathbf{u}\rangle + \langle L_\psi, \mathbf{u}\cdot\nabla\psi\rangle = -\gamma\langle L_\psi, K\rangle.$$

Applying (2.8), we find the conanonical dissipation law

$$\frac{d}{dt}\left(\frac{1}{2}\|\mathbf{u}\|^2_{L^2(\Omega)} + L\right) = -\gamma\langle L_\psi, K\rangle. \tag{2.14}$$

Indeed, it remains only to be shown that $\langle L_\psi, K\rangle \geq 0$. For the case $K = L_\psi$ or $K =$

$-\Delta L_\psi$ this is obvious. If $K = -\nabla\cdot(L_\psi^*)$ we also have, by (2.9), $\langle L_\psi, K\rangle = -\langle L_\psi, \nabla\cdot(L_\psi^*)\rangle = \langle \nabla L_\psi, L_\psi^*\rangle = -\langle \nabla L_\psi^*, \nabla\cdot(\psi\nabla L_\psi)\rangle = (\psi, |\nabla L_\psi|^2)$. This is nonnegative whenever $\psi \geq 0$, i.e. when ψ is a density for example.

2.3 The Nernst-Plank-Poisson Equations

We use this energetic formalism to make a systematic derivation of the NPP equations from the free energy of the binary charge system. Later in chapter 3, we will modify this energy to include the short range repulsion from interfaces. The NPP equations can be rewritten in the form

$$n_t + \nabla\cdot(n(\mathbf{u} + \nabla V + \mathbf{f}) = 0, \tag{2.15}$$

$$p_t + \nabla\cdot(p(\mathbf{u} - \nabla V + \mathbf{g}) = 0, \tag{2.16}$$

$$\epsilon\Delta V = n - p. \tag{2.17}$$

Using the integral representation of solutions to the Poisson equation, we may rewrite

$$V(x) = -\int_\Omega \frac{G(x,y)}{\epsilon}(n(y) - p(y))\,dy \tag{2.18}$$

where $G(x,y)$ is the Green's kernel associated with Ω. We will define a free energy $L_1(n,p)$ so the (2.15)-(2.17) become

$$n_t + \nabla\cdot(n\mathbf{u} + (L_1)_n^* + \mathbf{f}) = 0, \tag{2.19}$$

$$p_t + \nabla\cdot(p\mathbf{u} + (L_1)_p^* + \mathbf{g}) = 0. \tag{2.20}$$

$\mathbf{f}$ and $\mathbf{g}$ are additional data. In this way, we see that the NPP equations are derived from a gradient descent mechanism. The admissable perturbations to the variables n and p are the variations on maps from the particle labeling space to Ω of which n and p are constant multiples (in time) of the determinant. Hence the gradient descent is not with respect to n and p, but to the maps which n and p are determinants of. Define

$$L_1(n,p) = \int_\Omega n\log(n) + p\log(p) + (n-p)\int_\Omega \frac{G(x,y)}{2\epsilon}(n-p)(y)\,dy\,dx. \tag{2.21}$$

Following (2.7), (replace n by $-\nabla\cdot(n\mathbf{y})$ and p by $-\nabla\cdot(p\mathbf{y})$)

$$\begin{aligned}
\langle (L_1)_n^*, \mathbf{y}\rangle &= -\int_\Omega (1+\log(n))\nabla\cdot(n\mathbf{y}) + \nabla\cdot(n\mathbf{y})\int_\Omega \frac{G(x,y)}{2\epsilon}(n-p)(y)\,dy \\
&\quad + (n-p)\int_\Omega \frac{G(x,y)}{2\epsilon}\nabla\cdot(n\mathbf{y})(y)\,dy\,dx \\
&= -\int_\Omega (1+\log(n))\nabla\cdot(n\mathbf{y}) + \nabla\cdot(n\mathbf{y})\int_\Omega \frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\,dx \\
&= \int_\Omega n\nabla(1+\log(n))\cdot\mathbf{y} + n\mathbf{y}\cdot\int_\Omega \nabla\frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\,dx \\
&= \int_\Omega \left(\nabla n + n\int_\Omega \nabla\frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\right)\cdot\mathbf{y}\,dx, \\
&= \int_\Omega (\nabla n - n\nabla V)\cdot\mathbf{y}\,dx,
\end{aligned}$$

$$\begin{aligned}
\langle (L_1)_p^*, \mathbf{y}\rangle &= -\int_\Omega (1+\log(p))\nabla\cdot(p\mathbf{y}) - \nabla\cdot(p\mathbf{y})\int_\Omega \frac{G(x,y)}{2\epsilon}(n-p)(y)\,dy \\
&\quad - (n-p)\int_\Omega \frac{G(x,y)}{2\epsilon}\nabla\cdot(p\mathbf{y})(y)\,dy\,dx \\
&= -\int_\Omega (1+\log(p))\nabla\cdot(p\mathbf{y}) - \nabla\cdot(p\mathbf{y})\int_\Omega \frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\,dx \\
&= \int_\Omega p\nabla(1+\log(p))\cdot\mathbf{y} - p\mathbf{y}\cdot\int_\Omega \nabla\frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\,dx \\
&= \int_\Omega \left(\nabla p - p\int_\Omega \nabla\frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\right)\cdot\mathbf{y}\,dx. \\
&= \int_\Omega (\nabla p + p\nabla V)\cdot\mathbf{y}\,dx.
\end{aligned}$$

The second and seventh equations follow from the symmetry of the Green's function, see [32]. We have shown that $(L_1)_n^* = \nabla n - n\nabla V$ and that $(L_1)_p^* = \nabla p + p\nabla V$, for which (2.19) and (2.20) are consistent with (2.15)-(2.17).

Similarly, we apply a domain variation to L_1, (2.6), to derive the Lorentz force $F = (L_1)_*^n + (L_1)_*^p$. Following (2.6) (replace n by $-\mathbf{v}\cdot\nabla n$ and p by $-\mathbf{v}\cdot\nabla p$) and

again using the symmetry of the Green's function

$$\begin{aligned}\langle F, \mathbf{v}\rangle &= \langle (L_1)^p_*, \mathbf{v}\rangle + \langle (L_1)^n_*, \mathbf{v}\rangle \\ &= -\int_\Omega (1+\log(n))\mathbf{v}\cdot\nabla n + (1+\log(p))\mathbf{v}\cdot\nabla p \\ &\qquad \mathbf{v}\cdot\nabla(n-p)\int_\Omega \frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\,dx \\ &= \int_\Omega (n-p)\nabla\int_\Omega \frac{G(x,y)}{\epsilon}(n-p)(y)\,dy\cdot\mathbf{v}\,dx = -\int_\Omega (n-p)\nabla V\cdot\mathbf{v}\,dx\end{aligned}$$

Note that $\mathbf{v}$ is divergence free, hence the total derivatives $(1+\log(n))\nabla n$ and $(1+\log(p))\nabla p$ vanish.

Assuming that n, p, V and $\mathbf{u}$ are smooth solutions to (2.15)-(2.17), (2.12) and n and p are everywhere positive, then (2.14) immedietly implies that $L_1(t)$ is bounded by $L_1(0)$ for all $t > 0$. Furthermore, (assuming viscocity) the $L^2(\Omega)$ norm and $H^1(\Omega)$ norm of $\mathbf{u}$ are uniformly bounded and square integrable, respectively in time. Unfortunately, L_1 is coercive with respect to n and p only in the uniform, $L^1(\Omega)\log(L^1(\Omega))$ norm and the square $H^1(\Omega)$ of V. This does not give a sufficient apriori bound to construct weak solutions to the NPP and NS coupled equations. Furthermore, positivity of solutions to (2.15) and (2.16) can only be guaranteed when the solutions are smooth. The difficulty in the existence theory, especially for the phasefield coupling in three dimensions, is due to these two deficiences. However, the NPP equations have more structure in the form of stronger apriori bounds and maximum principles. These will be used in constructing solutions to the NPP, NS and Allen Cahn equations later in chapter 4.

Chapter 3

Charge Phases

3.1 Introduction

Electrolytes are an example of a complex fliud which exhibits an interplay between flow fields and electric forces. Within this interplay, the fluids exhibit a variety of electrically induced flow phenomena at the milimeter to nanometer length scale which are not practically achievable by traditional mechanical or pressure driven means and thusly find promising application in microfluidic and material science engineering. The concentration and capture of bioparticles in pathogen detection devices ([59]), micron sized particle coating for drug delivery and mass spectroscopy ([56]) and field induced stiffening of nano particle suspensions ([55]) are three novel examples of electrorheological effects with promising industrial application.

In electrolyte models, charged bodies (ions) are described by a number density. Usually one considers two ion species, one negative, one positive, with number densities n and p respectively. The electrostatic potential, V is defined as the potential due to electric interactions with the ions n and p.

Electrolytes are in part characterized by their dielectric constant[1], ϵ. The flow phenomena observed in electrolytes are strictly due to boundary layer effects where the characteristic thickness of the boundary layer is $\epsilon^{1/2}$. The boundary layer is sometimes called the Debye layer. Consequently, electrolyte models are ubiqui-

[1] $\epsilon^2 = \epsilon_0 \epsilon_r kT/(C_\infty L)e^2$, where ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity, kT is thermal energy, C_∞ is the characteristic charge density, e is the elementary charge and L is the characteristic length scale. Typically, ϵ ranges from 10^{-3} to 10^{-6} for realistic systems on the length scale of 10^{-6} to 10^{-3} meters with molarity between 10^{-4} to 1 [47].

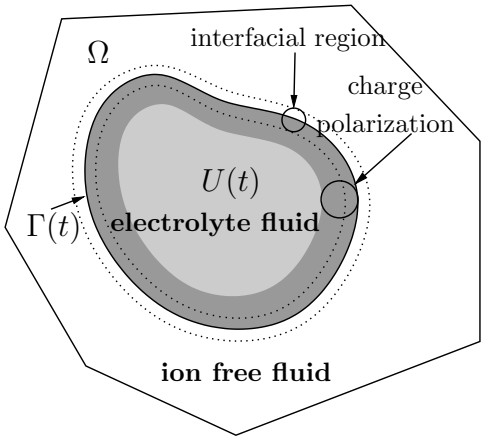

Figure 3.1. Two phase fluid model of electrolyte droplet.

tously formulated in the context of an interface and electrolyte system. In traditional approaches, the interface is stationary and is considered part of the domain boundary, $\partial\Omega$. The electric properties of the material opposite the electrolyte with respect to the interface boundary are described by boundary conditions of the variables n, p and V. From a physical standpoint, one must take care in summarizing the electric properties of the interface and region exterior to the electrolyte by boundary conditions (see [48].) Further, in many cases it is desirable that the interface be mobile. Freely floating inclusions such as large colloids ([16]) or vesicle membranes ([38]) are two important examples where a moving interface is present in an electrolyte.

The approach we take to an electrolyte interface formulation is similar in spirit the study of steric effects in the electrolyte double layer taken in [20] and [21]. In these works, the authors reevaluated the ion free energy by introducing an energetic term to account for the finite exclusion of solvent by ions of fixed radius. [40] and [51] similarly considered additional energetic terms stemming from induced surface charges in ion channels. We reevaluate the electrolyte free energy in terms of a domain dependent barrier functional (3.2) which restricts the motion of ions to mobile subregions of the domain.

3.2 Phase field barrier functional

In this chapter we propose a strategy to model the electrolyte and inclusions as a mixture of two incompressible fluids. We view the region occupied by the electrolyte as a time dependent subregion $U(t)$ of the domain Ω. The interface is the boundary of this subregion, $\Gamma(t) := \partial U(t)$. To achieve this end, we employ a phase field representation of the subregion $U(t)$ by assigning

$$U(t) := \{\phi < 0\}, \quad \Gamma(t) := \{\phi = 0\} \tag{3.1}$$

where $\phi : \Omega \times [0, T] \to \mathbb{R}$ is the phase field indicator function. The phase field has an associated length scale η which is the characteristic thickness of the interfacial region. The interfacial region is, roughly speaking, the region where ϕ is close to 0.

The intial data n_0 and p_0 of the variables n and p respectively are chosen so that the support of n_0 and p_0 are contained in $U(0) = \{\phi(t = 0) < 0\}$. The ions are, however, diffuse, and will tend to migrate to the exterior of $U(t)$ as the system evolves. To ensure that this is not the case, we employ the following penalty formulation. We introduce the phase field barrier functional

$$B_M(\phi, n, p) := \int_\Omega M(\phi + 1)(n + p)\, dx. \tag{3.2}$$

Owing to the special feature of the phase field function, ϕ is close to -1 in $U(t)$ and 1 in the exterior of $U(t)$,

$$\lim_{\eta \to 0} B_M(\phi, n, p) = M \int_{\Omega \setminus U(t)} n + p\, dx. \tag{3.3}$$

Ideally, if $B_M(\phi, n, p)$ remains bounded independently of t and M, then $n = p = 0$ in $\Omega \setminus U(t)$ as $M \to \infty$.

There are three length scales associated with this model. They are the characteritic flow length scale Re, the thickness of the interfacial region η and the thickness of the charge boundary layer $\epsilon^{1/2}$. In order to ensure that the charge boundary layer is resolved, η is chosen smaller than $\epsilon^{1/2}$ and $\epsilon^{1/2}$ smaller than Re.

There are also three energy scales. That of the interfacial energy, the electric

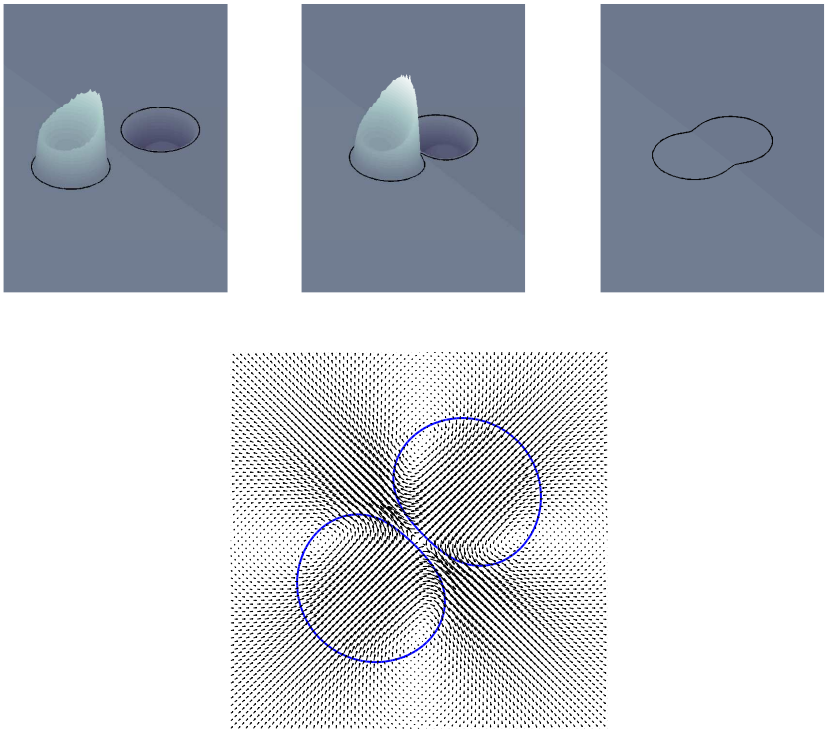

Figure 3.2. Finite element simulation of droplet coalescence

energy and the mixing energy of the barrier potential. The mixing energy is of order M while the electric energy is of order $\epsilon^{-1/2}$. To ensure that the barrier potential energy is stronger than the electric energy, M is chosen larger than the electric energy scale. In simulation we consider the regime

$$\eta \ll \epsilon^{1/2} \ll Re, \quad M^{-1} \ll \epsilon^{1/2}. \tag{3.4}$$

The choice of the barrier functional (3.2) was motivated by the following

Proposition 1. *Suppose that* $\mathbf{v}$ *is divergence free and* c *and* b *satisfies*

$$\begin{cases} c_t + \mathbf{v} \cdot \nabla c = \Delta c + M \nabla \cdot (c \nabla b) \\ b_t + \mathbf{v} \cdot \nabla b = 0 \end{cases}$$

where initially $\int_\Omega c_0 b_0 \, dx = 0$, $c_0 > 0$ *and* $c|_{\partial\Omega} = \exp(-M)$ *and* $b|_{\partial\Omega} = 1$. *Then*

$$\int_\Omega cb \, dx \leq M^{-1} \left(\int_\Omega c_o \log(c_0) \, dx + e^{-1} |\Omega| \right).$$

Proof. Consider the energy density $A(c) = c\log(c) + Mcb$. By maximum principles, $c(x,t) \geq 0$ for all $x \in \Omega$ and all $t \in [0,T]$. Hence, $A(c)$ is always defined. Note that $A_c = 1 + \log(c) + Mb$ and $\nabla A_c = c^{-1}\nabla c + M\nabla b$. A brief calculation then shows that

$$\frac{d}{dt}\int_\Omega A(c)\,dx = -\int_\Omega c|\nabla A_c|^2\,dx. \tag{3.5}$$

(3.5) simply says that $\int_\Omega A(c)\,dx$ is decreasing in time. Consequently

$$\int_\Omega A(c)\,dx \leq \int_\Omega A(c_0)\,dx = \int_\Omega c_0\log(c_0)\,dx.$$

For $c > 0$, we have that $c\log(c) > -\exp(-1)$. Bounding the leftmost term in the above inequality from below, we find

$$-e^{-1}|\Omega| + M\int_\Omega cb\,dx \leq \int_\Omega c_0\log(c_0)\,dx.$$

□

The above proposition states that in the ideal case when the indicator function b is transported, the integral (mass) of the density function c over the preimage of the value of b greater than any number is bounded uniformly in time. This integral can be made arbitrarily small for all time by chosing M large.

The barrier functional can further be motivated by considering the potential energy as due to shorter range interactions than the usual inverse distance electrostatic interaction. Assuming x is sufficiently far from the boundary of Ω, we formaly write

$$\phi(x) = \int_\Omega \frac{1}{|x-y|}\Delta\phi(y)\,dy \approx \int_{\Omega\setminus U(t)} \frac{2d-2}{|x-y|^3}\,dy$$

The last equation is meaningless since $|x-y|^{-3}$ is not integrable for dimension less than 3. However, the the integrand $(n+p)M(\phi+1)$ in $L(n,p)$ indicates that the particles are repelled from the interface $\Gamma(t) = \{\phi = 0\}$ by a "shorter range" third order potential $|x-y|^{-3}$, in comparison to the first order potential $G(x,y)$. In this way, it is energetically favourable that n and p should remain supported in the interior of $U(t)$.

3.3 A model of electrolyte droplets

We consider the following system of the hydrodynamic flow of two incompressible fluids; the first fluid is an electrolyte, while the second fluid ion free; it has no or very little ions.

$$\rho(\mathbf{u}_t + \mathbf{u}\cdot\nabla\mathbf{u}) + \nabla\pi = \nu\Delta\mathbf{u} + (n-p)\nabla V - \nabla\cdot(\nabla\phi\otimes\nabla\phi), \tag{3.6}$$

$$\nabla\cdot\mathbf{u} = 0, \tag{3.7}$$

$$n_t + \mathbf{u}\cdot\nabla n = \nabla\cdot(D_n\nabla n - \mu_n n\nabla V + Mn\nabla\phi), \tag{3.8}$$

$$p_t + \mathbf{u}\cdot\nabla p = \nabla\cdot(D_p\nabla p + \mu_p p\nabla V + Mp\nabla\phi), \tag{3.9}$$

$$\nabla\cdot(\epsilon\nabla V) = n - p, \tag{3.10}$$

$$\phi_t + \mathbf{u}\cdot\nabla\phi = \gamma(\Delta\phi - \eta^{-2}W'(\phi)) \tag{3.11}$$

Equations (3.6) and (3.7) are the Navier-Stokes (NS) equations where $\mathbf{u}$ is the fluid velocity of the electrolyte fluid, π is the pressure, ρ is the fluid density and ν the fluid viscocity. In equation (3.6), $(n-p)\nabla V$ is the macroscopic Lorentz (or Coulomb) force. Similarly, $\nabla\cdot(\nabla\phi\otimes\nabla\phi)$ approximates the surface tension of the interface, see [37].

Equations (3.8) and (3.9) are the Nernst-Plank equations of a binary charge system, n and p are the densities of diffuse, negative and positive charges respectively. D_n, D_p are the respective diffusivity constants and μ_n, μ_p are the respective mobility constants. μ_n, μ_p and D_n and D_p are related by Einstein's relation and the valence of the charged bodies. For example, in a solution of potassium chloride (KCl), the negative and positive valences are 1, $(\mathrm{Cl}^-, \mathrm{K}^+)$. In equations (3.8) and (3.9) the convection involving ∇V is the migration of charge bodies due to the microscopic Coulomb's force experienced by the charged bodies in the direction of the electric field $(-\nabla V)$. The convective term $M\nabla\phi$ in (3.8) and (3.9), as we will see later, is derived from the mixing energy (3.2).

Equation (3.10) is the Poisson equation for the electrostatic potential V. ϵ is the dielectric constant of the fluid. Collectivelly, (3.8)-(3.10) are called the Poisson-Nernst-Plank (PNP) equations. In this chapter, ϵ is taken to be a small constant.

Equation (3.11) is the Allen-Cahn equation. As $\gamma \to 0$, ϕ is a viscocity solution

of the transport equation

$$\phi_t + \mathbf{u} \cdot \nabla \phi = 0.$$

In this chapter we simply let $\rho = D_n = D_p = \mu_n = \mu_p = 1$. We consider the case when

$$\mathbf{u}\big|_{\partial\Omega} = 0, \quad n|_{\partial\Omega} = f > 0, \quad p|_{\partial\Omega} = g > 0, \tag{3.12}$$

$$V\big|_{\partial\Omega} = V_0, \quad \phi\big|_{\partial\Omega} = 1. \tag{3.13}$$

3.4 Free energy variation

In this section we derive equations (3.6)-(3.11) from a free energy using variational principles. We define the internal energy of the electrolyte-interface system

$$\begin{aligned} L(n,p) = \int_\Omega n\log(n) + p\log(p) + V(p-n)\,dx \\ + B_M(\phi,n,p) + S_\eta(\phi). \end{aligned} \tag{3.14}$$

Here V is a solution of the Poisson equation (3.10) and thus may written explicitly in terms of convolution with the Green's kernel $G(x,y)$.

$$V(x) = \int_\Omega \frac{G(x,y)}{2\epsilon}(n(y) - p(y))\,dy.$$

We may rewrite (3.14)

$$\begin{aligned} L(n,p) = \int_\Omega n\log(n) + p\log(p)\,dx \\ + \iint_{\Omega^2} \frac{G(x,y)}{2\epsilon}(n-p)(y)(n-p)(x)\,dy\,dx \\ + B_M(\phi,n,p) + S_\eta(\phi). \end{aligned} \tag{3.15}$$

$B_M(\phi,n,p)$ was defined in (3.2) and

$$S_\eta(\phi) = \int_\Omega \frac{\eta}{2}|\nabla\phi|^2 + \frac{1}{4\eta}(\phi^2-1)^2\,dx. \tag{3.16}$$

In this form, we see that the free energy (3.15) is composed of entropic contributions (the logarithmic terms), electrostatic interaction (Green's kernel), the barrier functional and the interface surface area.

We define the chemical potential $\beta(n)$ and $\beta(p)$ as the usual Frechet derivatives of L with respect to n and p respectively;

$$\begin{aligned} \beta(n) &= 1 + \log(n) - V + M(\phi + 1), \\ \beta(p) &= 1 + \log(p) + V + M(\phi + 1). \end{aligned} \tag{3.17}$$

The fluxes $J(n)$ and $J(p)$ are defined as the gradient of $\beta(n)$ and $\beta(p)$, scaled by n and p respectively (Fick's Law);

$$J(n) = n\nabla\beta(n), \quad J(p) = p\nabla\beta(p). \tag{3.18}$$

If, in addition, n and p are macroscopically transported by the fluid velocity $\mathbf{u}$ and $J(n)$ and $J(p)$ are the fluxes of n and p, then the conservation of mass implies that

$$n_t + \mathbf{u} \cdot \nabla n = \nabla J(n), \quad p_t + \mathbf{u} \cdot \nabla p = \nabla J(p). \tag{3.19}$$

In contrast, we will now show that (3.18) and (3.19) are also variational in structure. We elaborate briefly. n and p are both a number density corresponding to the position of the negative and positive ions (particles) respectively. In particular, n and p can be written in terms of the inverse Jacobian of the map which specifies the position of these particles. The only variation which can occur in the physical system is with respect to the particle positions. This variation corresponds to the usual variation of the function, where the function is the particle position map. Suppose that the particle positions are perturbed by the field $\mathbf{v}$. It is not hard to check that the deviation n^s and p^s of n and p respectively then satisfy

$$\begin{gathered} \delta n^s + \nabla \cdot (n^s \mathbf{v}) = 0, \quad \delta p^s + \nabla \cdot (p^s \mathbf{v}) = 0, \\ n^0 = n, \quad p^0 = p. \end{gathered}$$

Consider now the variation of L with respect to the above deviation in the variable

n;

$$\begin{aligned}\frac{d}{ds}\Big|_{s=0} L(n^s, p) &= -\int_\Omega \beta(n)\nabla\cdot(n\mathbf{v})\,dx \\ &= \int_\Omega n\mathbf{v}\cdot\nabla\beta(n)\,dx = \int_\Omega n\mathbf{v}\cdot\left(\frac{\nabla n}{n} - \nabla V\right)\,dx \\ &= \int_\Omega \mathbf{v}\cdot J(n)\,dx\end{aligned}$$

We see that the flux $J(n)$ is the microscopic force experienced by the particle system. Because the motion of the particles is damped by fluid, the sum of microscopic forces $J(n)$ translates into convection (net particle velocity.) Furthermore, if we define a variational derivative $\delta L/\delta n$ of L by

$$\int_\Omega \frac{\delta L}{\delta n} w\,dx = -\frac{d}{ds}\Big|_{s=0} L(n^s, p), = \int_\Omega J(n)\cdot\nabla w\,dx \qquad \forall w \in C_0^\infty(\Omega) \tag{3.20}$$

where ∇w replaces $\mathbf{v}$ in (3.20), we see that (3.8) is a transported, gradient descenct equation $n_t + \mathbf{u}\cdot\nabla n = -\delta L/\delta n$ where the gradient direction is defined directly above. Analogous considerations hold for equation (3.9) and the variable p.

3.5 Verification for transport case

We will now study smooth solutions of (3.6-3.11) in the case when the phase field is purely transported, i.e. $\gamma = 0$. We will reproduce a similar result to Proposition 1. The difference here is that in addition to transport limited diffusion found in Proposition 1, the system (3.6-3.11) has the additional internal electrostatic coupling.

Suppose that $\mathbf{u}$, n, p, and ϕ are C^1 in time and C^2 in space and solve (3.6-3.11) with initial data satisfying

$$n_0 > 0, \quad p_0 > 0, \quad \int_\Omega (\phi_0 + 1)(n_0 + p_0)\,dx = 0.$$

We discuss the following Dirichlet data of n, p and V. These data must be chosen so that energy is not begin added to the system as time progresses. In

particular, no far electric fields may be present, i.e. $V_0 =$ constant. (3.6-3.11) are invariant under translations of the Dirichlet data for V. We thus choose

$$V_0 = 0. \tag{3.21}$$

Furthermore, we require that the chemical potential $\beta(n)$ and $\beta(p)$ vanish at the boundary;

$$n\big|_{\partial\Omega} = \exp(1-2M), \quad p\big|_{\partial\Omega} = \exp(1-2M). \tag{3.22}$$

This implies that $n, p > 0$ on the boundary of $\Omega \times [0,T]$. A simple maximum principle then shows that n and p are strictly positive in the interior as well.

Multiply equation (3.6) by the solution $\mathbf{u}$ and integrate by parts. One finds

$$\frac{1}{2}\frac{d}{dt}\|\mathbf{u}\|^2_{L^2(\Omega)} + \nu\|\nabla\mathbf{u}\|^2_{L^2(\Omega)} = \int_\Omega (n-p)\nabla V\cdot\mathbf{u} + \Delta\phi\nabla\phi\cdot\mathbf{u}\,dx. \tag{3.23}$$

Next, multiply (3.11) by $\Delta\phi - W'(\phi)/\eta^2 + M(n+p)$. Note that $W'(\phi)\nabla\phi$ is a total derivative;

$$\frac{d}{dt}S_\eta(\phi) + \int_\Omega M\phi_t(n+p) + \Delta\phi\nabla\phi\cdot\mathbf{u} + M(n+p)\nabla\phi\cdot\mathbf{u}\,dx = 0 \tag{3.24}$$

Finaly mutliply (3.8) by $\beta(n)$ and (3.9) by $\beta(p)$. Recall that $\beta(n) = \beta(p) = 0$ on $\partial\Omega$ and $(1+\log(c))\nabla c$ is a total derivative for $c = n, p$.

$$\begin{aligned}&\int_\Omega (n_t + \mathbf{u}\cdot\nabla n)\beta(n)\,dx = \\ &\qquad \int_\Omega (n\log(n))_t + (M(\phi+1)-V)(n_t+\mathbf{u}\cdot\nabla n) = -\int_\Omega n|\nabla\beta(n)|^2\end{aligned} \tag{3.25}$$

$$\begin{aligned}&\int_\Omega (p_t + \mathbf{u}\cdot\nabla p)\beta(p)\,dx = \\ &\qquad \int_\Omega (p\log(p))_t + (M(\phi+1)+V)(p_t+\mathbf{u}\cdot\nabla p) = -\int_\Omega p|\nabla\beta(p)|^2\end{aligned} \tag{3.26}$$

where the right hand sides above come from integration by parts. Also, $(n-p)V_t = \Delta V V_t$ and $(V_0)_t = 0$ so that

$$\int_\Omega (p-n)V_t\,dx = -\int_\Omega \Delta V V_t = \frac{d}{dt}\int_\Omega \frac{1}{2}|\nabla V|^2\,dx \tag{3.27}$$

Summing (3.24)-(3.27), taking care account for the total derivatives

$$\int_\Omega M(\phi_t + \mathbf{u}\cdot\nabla\phi)(n+p) + M(\phi+1)(n_t + p_t + \mathbf{u}\cdot\nabla(n+p))\,dx = \int_\Omega M[(\phi+1)(n+p)]_t + \mathbf{u}\cdot\nabla[(\phi+1)(n+p)]\,dx$$

one finds

$$\begin{aligned}\frac{d}{dt}L(\phi,n,p) - \frac{1}{2}\frac{d}{dt}\|\nabla V\|^2_{L^2(\Omega)} \\ = -\int_\Omega (n-p)\nabla V\cdot\mathbf{u} + \Delta\phi\nabla\phi\cdot\mathbf{u}\,dx \\ -\int_\Omega n|\nabla\beta(n)|^2 + p|\nabla\beta(p)|^2\,dx\end{aligned} \tag{3.28}$$

Note that

$$\|\nabla V\|^2_{L^2(\Omega)} = \int_{\partial\Omega} V_0\nabla V\cdot\mathbf{n}\,dS - \int_\Omega (n-p)V\,dx$$

so that we may rewrite (3.28)

$$\begin{aligned}\frac{d}{dt}\tilde{L}(\phi,n,p) = -\int_\Omega (n-p)\nabla V\cdot\mathbf{u} + \Delta\phi\nabla\phi\cdot\mathbf{u}\,dx \\ -\int_\Omega n|\nabla\beta(n)|^2 + p|\nabla\beta(p)|^2\,dx\end{aligned} \tag{3.29}$$

where

$$\begin{aligned}\tilde{L} &:= \int_\Omega n\log(n) + p\log(p) + \frac{1}{2}V(p-n)\,dx + B_M(\phi,n,p) + S_\eta(\phi) \\ &= L - \frac{1}{2}\|\nabla V\|^2_{L^2(\Omega)}.\end{aligned}$$

Summing (3.29) with (3.23), we finally have

$$\frac{d}{dt}(\|\mathbf{u}\|^2_{L^2(\Omega)} + \tilde{L}) + \nu\|\nabla\mathbf{u}\|^2_{L^2(\Omega)} \le 0. \tag{3.30}$$

(3.30) is the canonical energy inequality associated with (3.6-3.11) and captures the dissipation of kinetic and internal energy. It implies that $\|\mathbf{u}(t)\|^2_{L^2(\Omega)} + \tilde{L}(t) < \|\mathbf{u}(0)\|^2_{L^2(\Omega)} + \tilde{L}(0)$ for any $t \in [0,T]$. If c_0 is a constant which bounds $\|\mathbf{u}(0)\|^2_{L^2(\Omega)} +$

$\tilde{L}(0)$ from above, then this inequaltiy implies

$$\int_\Omega (\phi + 1)(n + p)\, dx \leq M^{-1}(2e^{-1}|\Omega| + c_0), \quad \forall t \in [0, T].$$

This inequality is the same as found in Proposition 1. It is remarkable that it still holds despite the presence of a possible competing internal dynamic.

On solution existence

We will briefly discuss the existence of weak solutions to (3.6-3.11). Due to regularity considerations, it is necassary to assume that $\gamma > 0$. In this case, the procedure in the above section fails to produce an energy inequality of the form (3.30). This in part due to the fact that the variational structures which determine ϕ differs from that of n and p.

Note that intrinsicly (3.30) is not a sufficient apriori estimate to produce a weak solutions to (3.8) and (3.9), as it implies that n and p are only slightly more than integrable in space. Instead, depending on the regularity of ϕ, solutions of (3.8) and (3.9) satisfy a stronger energy inequality of the type usually derived for parabolic PDE. When ϕ solves (3.11), this stronger inequality holds for space dimension 2 and implies the existence of weak solutions for sufficiently small initial data. In summary, one may prove the following small data, global in time, existence theorem:

Theorem 1. *Let $\Omega \subset \mathbb{R}^2$ be bounded with smooth boundary. For $\|n_0\|_{L^2(\Omega)}$, $\|p_0\|_{L^2(\Omega)}$ and $\|\nabla\phi_0\|_{L^2(\Omega)}$ sufficiently small, there exist a Leray solution of (3.6-3.11) satifying boundary conditions* (3.22) *and* (3.21).

The ability to construct a Galerkin approximate solution to (3.6-3.11) is highly dependent on the sign relationship between n, p and V and also the positivity of n and p. In general, positivity is difficult to ascertain for a Galerkin (or numerical) approximation, due to a lack of smoothness. However, one may prove the maximum principle, Lemma 4 found in the next chapter.

The proof of Theorem 1 and Proposition 4 will involve a modified Galerkin's scheme together with all the energy estimates [49]. These results are the subject of Chapter 4.

3.6 Simulation

We present several numerical simulations of equations (3.6-3.11). These simulations serve three purposes. The first is to demonstrate concretely the dynamic interaction between electrostatic, interfacial and fluid forces. The second is to verify the potency of the phase field barrier functional, (3.2), in restricting densities to subregions of the domain. Finally, researchers traditionally avoid solving (3.6-3.11) numerically due to the boundary layer structure. Our algorthim, however, clearly preserves the boundary layer structure and resolves the Reynolds, Debye, and interfacial length scale without difficulty. Below we describe some of the features of this algorithm, in particular we elaborate on the finite elements used to discretize (3.6-3.11).

The following simulations were performed for a 1 by 1 unit square. The grid points were chosen uniformly with a mesh size of $h = .01$ We use Delaunay triangulations (generated by [53]) and a fully implicit forward Euler time stepping scheme with time step $\tau = 4 \times 10^{-2}$.

The viscocity ν and Reynolds number Re was 1. η was chosen as 10^{-2}. Although η is comparable to the mesh length h the interfacial region was clearly resolved, as is seen from the numerical experiments. The dielectric ϵ was chosen to be 10^{-2}. Thus $\eta \ll \epsilon^{1/2} \ll Re$, as is desired by (3.4). A penalty coefficient of $M = 5$ was sufficient to almost entirely restrict the discrete densities to the droplet interior. This was suprising because the electric potential characteristically was only of one magnitude less. We chose $\gamma = 10^{-3}$ so that the change in volume of the droplet did not signficanlty affect the dynamic of the simulation.

A simple iteration between equations (3.6)-(3.11) leads to a fixed point solution of the nonlinear couplings. We used Newton's method to solve (3.11) for each time step.

In our numerical simulations, the intertial term $\mathbf{u} \cdot \nabla \mathbf{u}$ is set to zero in the Navier-Stokes equation. This is by no means is a restriction for the model as we are considering a flow with a relatively small Reynolds number 1. We discretized this linearized Navier-Stokes equations with the MINI element [15], that is, the velocity $\mathbf{u}$ was discretized by piecewise linear elements enriched with bubble functions (one per triangle of the triangulation). For every triangle T the bubble functions are

defined by $B^3_{T,h} = \lambda_{1,T}\lambda_{2,T}\lambda_{3,T}$, where $\{\lambda_i\}_{i=1}^3$ are the barycentric coordinates associated with T. The pressure π was discretized by piecewise linear continuous elements. As it is well known, that the continuous, piecwise linear plus bubble velocity and continuous piecewise linear pressure is a stable finite element pair for the Stokes equation, namely, it satisfies the inf-sup condition [15], [17].

In our calculations, we have used a direct method to solve the Stokes equation since our problem was relatively small, of size $O(10^4)$. However, for smaller values of the characteristic mesh size h, it will be necassary to use iterative methods. such as the Uzawa method [17], [54] and augmented Lagrangian algorithm [17].

At each time step, we discretize the operators in (3.8),(3.9) and (3.11) by the EAFE scheme proposed in [58]. The EAFE scheme is type of upwinding scheme for finite elements with automatic choice of the upwind direction. Such a discretization is monotone for Delaunay triangulations, that is, the resulting stiffness matrix corresponding to the bilinear form of the convection diffusion equation, (with continuous convection and diffusion coefficients) is an M matrix if and only if the usual stiffness matrix corresponding to the Poisson equation is also an M matrix. In the time stepping procedure, in the the fixed point iteration of the charge densities and during the Netwon iteration for the phase field, we must solve convection diffusion equations of the form

$$\nabla \cdot (\nabla u + u\beta) = f. \tag{3.31}$$

Note that the analysis presented in section 3.5 hints that the stability of the numerical scheme is related to maintaining the monotonicity of the operators found in (3.8), (3.9) and (3.11). By monotonicity, we mean that charge density and phase field equations have an associated maximum principle which guarantee that the smooth charge solutions by positive and smooth phase field solutions be bounded by 1 and -1. Hence, it is important both mathematically and in order that solutions be physical that the discretization of (3.31) maintain this property, namely the discrete solutions densities be positive and discrete phase field be bounded by 1 and -1 as well.

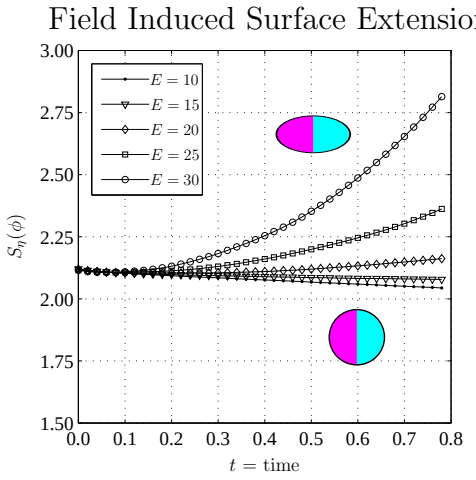

Figure 3.3. Evolution of phase field energy $S_\eta(\phi)$ for a variety of applied fields E.

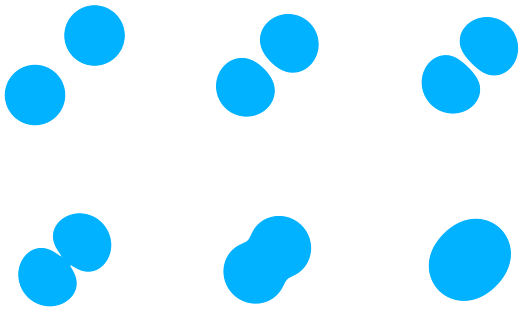

Figure 3.4. Evolution of phase field for two oppositely charged droplets.

Field induced extension

The first class of simulations we present demonstrates the competition between electostatic forces and interfacial forces. We demonstrate this by applying an electric field across an initially neutral electrolyte droplet by specifying the boundary conditions

$$V(x, y) = Ex, \quad (x, y) \in \partial([0, 1] \times [0, 1]). \tag{3.32}$$

ϕ was initially chosen so that $U(0)$ was a ball centered at $(1/2, 1/2)$ and n and p where chosen to be identically 0.5 in this ball and 0 outside this ball.

The field induces a polarization of the droplet, namely n becomes large in the left of the ball and p becomes large in the right. The polarization induces the Lorentz force which causes the fluid to move horizontally in opposite directions

w.r.t. the $x = 1/2$ axis and consequently stretch the droplet interface. For small fields the surface tension of the interface is sufficient to withstand the force induced by this polarization, and the droplet surface area decreases[2]. For large electric fields, the polarization induced force overcomes the surface tension and the surface area increases. Figure 3.3 compares this growth in surface area with respect to time for several different applied field strengths E. We point out that from the energetic point of view, the system is converting electric energy from E into surface energy $S_\eta(\phi)$.

Charge induced coalescence

Next we consider two electrolyte droplets with opposite charge seperated over some distance.

ϕ is initially chosen so that $U(0)$ is the union of two balls a distance apart. n is initally chosen to be a constant 0.5 in the first ball, zero elsewhere and p is chosen to be 0.5 in the second ball and zero elsewhere. V satisfies zero boundary conditions.

The charge seperation produces a gradient in electric potential which in turn causes fluid motion through the Lorentz force. This causes the two seperated phases to move toward each other until they merge. The two phases coalesce at a close enough distance, widening the support of the negative charge density to that of the positive charge density and vic versa. The densities migrate into the other phase until a single, charge neutral phase is reached. At this point, interfacial forces dominate the motion of the phase and the droplet evolves under surface tension.

The dynamics of these two droplets are such that the electric energy is dissipated into kinetic energy in order to resolve the topological seperation. As the droplets are close enough, the energy of the topological seperation is lost. This can be seen in figure 3.6 as the sharp drop in surface energy $S_\eta(\phi)$.

Figures 3.5 and 3.6 clearly demonstrate the utility of our phase field barrier

[2]The phase field equation is *not* volume preserving in our simulation. Such a modification is possible by considering the Cahn-Hilliard equation instead of the Allen-Cahn equation for instance. For γ very small, the volume of the droplet changes little with respect to the experiment time scale.

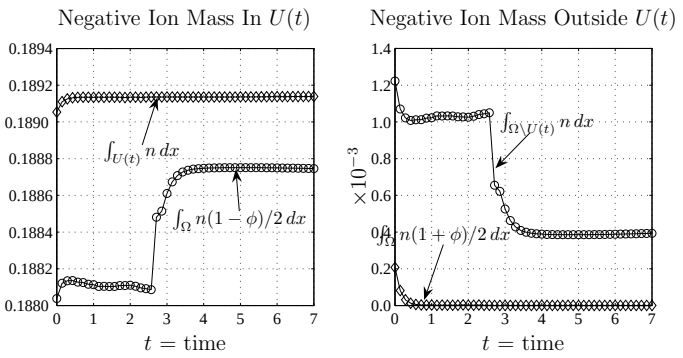

Figure 3.5. Mass conservation with respect to $U(t)$

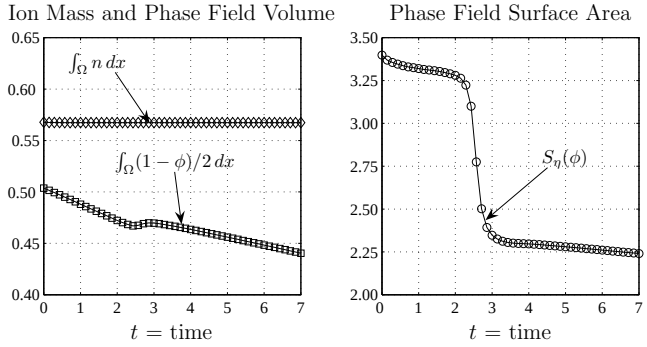

Figure 3.6. Mass conservation in domain and change in surface energy

formulation. In figures 3.5 we see that the total density (mass) n interior to $U(t)$ changes less than one hundreth of the total mass. Similarly, the mass exterior to droplet, despite diffusion and electric convection, is less than one hundreth of the total mass. Moreover, in figure 3.6, the total mass of n is almost constant in time while the phase field surface area $S_\eta(\phi)$ drops by 10% in the simulation time.

3.7 Conclusion

In this chapter, we have used the phase field method to capture the hydrodynamic system of an electrolyte which involves free interface motions. The key advantage of the formulation allowed us to employ different variational procedures to derived all the coupled subsystems from one single energy law. The approach guarantees that the resulting systems be consistent with the second law of thermodynamics (the energy dissipation laws). As a simple example, we have introduced a penalty

formulation based on a barrier functional for restricting the support of solutions of the hydrodynamic Poisson-Nernst-Plank equations to the evolving subregions of the domain. We validated the model by energetic arguments and several dynamic, finite element simulations.

Future work will include modeling cell membranes by interfaces with elastic bending energy and spontaneous curvature [25], [26], as well as variable permeabilities of the interface to ions [24], [40]. With an elastic interface, a particulary interesting application of our formulations would be to electric cell lysis, [38].

The free energy variation partially extends to the case when the charged bodies are polarized colloids as well, i.e. when the electric potential is a dipole interaction, [41], [55].

Chapter 4

Classical and Weak Solutions

4.1 Preliminaries

We introduce the usual notation and spaces associated with the Navier-Stokes and other second order, time dependent equations. The inner product of two functions u and v in $L^2(\Omega)$ and two functions $\mathbf{u}$ and $\mathbf{v}$ in $(L^2(\Omega))^2$ is denoted by (u, v) and $(\mathbf{u}, \mathbf{v})$ respectively. $\mathcal{V}$ is the space $\{\mathbf{v} \in (C_0^\infty(\Omega))^3 \,:\, \nabla \cdot \mathbf{v} = 0\}$ and H and V are the closure of $\mathcal{V}$ in $L^2(\Omega)$ and $H_0^1(\Omega)$ respectively. We choose a basis $\{\mathbf{v}_i\}_{i=1}^\infty$ for H which satisfies $(\mathbf{v}_i, \mathbf{v}_j) = \delta_i^j$ and $(\nabla \mathbf{v}_i, \nabla \mathbf{v}_j) = 0$ if $i \neq j$ (see [54].) we define the forms

$$b(\mathbf{u}, v, w) = \int_\Omega \mathbf{u} \cdot \nabla v w \, dx, \quad \mathbf{b}(\mathbf{u}, \mathbf{v}, \mathbf{w}) = \sum_{i=1}^{3} b(\mathbf{u}, \mathbf{v}^i, \mathbf{w}^i)$$

for all $v, w \in H^1(\Omega)$ and $\mathbf{u}, \mathbf{v}, \mathbf{w} \in (H^1(\Omega))^2$. In three space dimensions, b and $\mathbf{b}$ are continuous and trilinear with respect to the $H_0^1(\Omega)$ norm. Using the same notation, we will consider maps from $[0, T] \subset \mathbb{R}$ into the spaces X, whose norms are bounded in L^p for $1 \leq p \leq \infty$. For example, $L^p([0, T]; X)$ (also written $L^p(X)$ when the interval of dependence is clear) is defined as

$$u : [0, T] \to X \,:\, \int_0^T \|u\|_X \, dt < \infty.$$

The space $Y(\alpha_1, \alpha_2; X_1, X_2)$ is space of maps $u \in L^{\alpha_1}(X_1)$ with $u' \in L^{\alpha_2}(X_2)$. Q_T is the cylinder $\Omega \times [0, T]$. We will frequently use

Lemma 1. *For $u \in H_0^1$ and $\Omega \in \mathbb{R}^3$ bounded with smooth boundary*

$$\|u\|_{L^4(\Omega)} \leq \|u\|_{L^2(\Omega)}^{1/4} \|u\|_{H_0^1(\Omega)}^{3/4}. \tag{4.1}$$

We define a second trilinear form, $\theta(u, f, v)$ for $u, f \in H^1(\Omega)$, $v \in H_0^1(\Omega)$ as follows,

$$\theta(u, f, v) = \int_\Omega \nabla \cdot (u \nabla W) v \, dx = -\int_\Omega u \nabla W \cdot \nabla v \, dx,$$

whenever $\Delta W = f$ with $W|_{\partial\Omega} = 0$. With $f \in H^1(\Omega)$, W is differentiable so that the above integrals make sense. Furthermore, one has

Lemma 2. *If $u, f \in H^1(\Omega)$ and $v \in H_0^1(\Omega)$, then*

$$\begin{aligned} |\theta(u, f, v)| &\leq c_0 \|u\|_{H^1(\Omega)} \|f\|_{H^1(\Omega)} \|v\|_{L^2(\Omega)}, & (4.2) \\ |\theta(u, f, v)| &\leq c_2 \|u\|_{L^2(\Omega)} \|f\|_{H^1(\Omega)} \|v\|_{H_0^1(\Omega)}. & (4.3) \end{aligned}$$

for some constants c_0 and c_2 depending only on Ω. Furthermore, if $u \in H_0^1(\Omega)$ then

$$\theta(u, f, u) = \int_\Omega \frac{1}{2} u^2 f \, dx. \tag{4.4}$$

Proof. By elliptic regularity, $W \in C^1(\Omega)$ with $\|\nabla W\|_{C^0(\Omega)} \leq c_0 \|f\|_{H^1(\Omega)}$ for some $c_0 = c_0(\Omega)$ when $d \leq 3$. Then

$$|\theta(u, f, v)| = \left| \int_\Omega u \nabla W \cdot \nabla v \, dx \right| \leq c_0 \|u\|_{L^2(\Omega)} \|\nabla v\|_{L^2(\Omega)} \|f\|_{H^1(\Omega)}$$

This implies (4.3). Also

$$\begin{aligned} |\theta(u, f, v)| &= \left| \int_\Omega (\nabla u \nabla W + u \Delta W) v \, dx \right| = \left| \int_\Omega (\nabla u \nabla W + u f) v \, dx \right| \\ &\leq c_0 \|\nabla u\|_{L^2(\Omega)} \|v\|_{L^2(\Omega)} \|f\|_{H^1(\Omega)} + \|u\|_{L^4(\Omega)} \|f\|_{L^4(\Omega)} \|v\|_{L^2(\Omega)} \\ &\leq c_1 \|u\|_{H^1(\Omega)} \|f\|_{H^1(\Omega)} \|v\|_{L^2(\Omega)} \end{aligned} \tag{4.5}$$

where c_1 is c_0 plus the norm of the embedding $L^4(\Omega) \subset H^1(\Omega)$. This implies (4.2).

For (4.4),

$$\theta(u, f, u) = -\int_\Omega u\nabla W\nabla u\, dx = -\int_\Omega \frac{1}{2}\nabla u^2\nabla W\, dx = \int_\Omega \frac{1}{2}u^2 f\, dx.$$

□

4.2 Classical Solutions to PNP Equations

Setting $\epsilon = M = 1$, we rewrite (3.8)-(3.10) in the following form

$$\begin{aligned} n_t &= \nabla\cdot(\nabla n + n(\nabla\phi - \nabla V - \mathbf{u})),\\ p_t &= \nabla\cdot(\nabla p + p(\nabla\phi + \nabla V - \mathbf{u})),\\ \Delta V &= n - p. \end{aligned}$$

This motivates the following

Theorem 2. *Let $n_0, p_0 \in C^\infty(\Omega)$ and $\beta_1, \beta_2 \in C^\infty(\overline{Q}_T)$ and $k > 0$ a constant. Then there exists unique, positive $n, p \in C^\infty(\overline{Q}_T)$ satisfying $n, p|_{\partial\Omega} = k$ for all $t \in [0, T]$, $n, p|_{t=0} = n_0, p_0$ and*

$$n_t = \nabla\cdot(\nabla n + n(\beta_1 - \nabla V)), \tag{4.6}$$

$$p_t = \nabla\cdot(\nabla p + p(\beta_2 + \nabla V)), \tag{4.7}$$

$$\Delta V = n - p. \tag{4.8}$$

Theorem 2 is nontrivial in the sense that if one were to switch the sign of V, i.e. V solves $\Delta V = p - n$, then [22] have shown that finite time blow-up solutions exist for sufficiently large initial data. We show in lemma 3 that (4.6)-(4.8) has a small time weak solution, in lemma 4 that this solution is positive and then extend the solution globally.

Lemma 3. *Assume the hypothesis of theorem 2. Then there exist*

$$\tilde{n}, \tilde{p} \in Y([0, \delta); 2, 1; H_0^1(\Omega), H^{-1}(\Omega))$$

with $\tilde{n} + k$ and $\tilde{p} + k$ satisfying (4.6)-(4.8) weakly for some sufficiently small $\delta > 0$.

Proof. We construct a weak solution to (4.6)-(4.8) as the limit of a Galerkin approximation. Let $\{v_i\}_{i=1}^{\infty}$ be an L^2 orthonormal and H^1 orthogonal basis of $H_0^1(\Omega)$. Consider solutions a_i and e_i for $i = 1, \ldots, \mu$ of the following system

$$a_i'(t) + \lambda_i a_i(t) = (B_1)_{ij}(t)a_j(t) - D_{ij}^k a_j(t)(a_k(t) - e_k(t)) \tag{4.9}$$

$$e_i'(t) + \lambda_i e_i(t) = (B_2)_{ij}(t)e_j(t) + D_{ij}^k e_j(t)(a_k(t) - e_k(t)) \tag{4.10}$$

where $\lambda_i = (\nabla v_i, \nabla v_i)$, and

$$(B_w)_{ij} := b(\beta_w, v_j, v_i) - k((-1)^w \lambda_k^{-1}(v_k, v_j) + (\beta_w, \nabla v_j)), \quad w = 1, 2.$$
$$D_{ij}^k := \lambda_k^{-1}\theta(v_j, v_k, v_i).$$

The intial conditions are $a_i = (n_0, v_i)$ and $e_i = (p_0, v_i)$. Note that we are using the repeated index summation. a_i and e_i depend on μ. (We have subtracted k from n and p in (4.7),(4.8).) Define

$$n_\mu = a_i v_i, \quad p_\mu = e_i v_i.$$

(4.9) and (4.10) have a continuous dependence on $a_i(t)$ and $e_i(t)$ so that a continuous solution exists for some finite interval dependent on μ.

Multiply (4.9) and (4.10) by $a_i(t)$ and $e_i(t)$ and sum from $i = 1$ to μ. Define $\rho(t) = \|n_\mu\|_{L^2(\Omega)}^2 + \|p_\mu\|_{L^2(\Omega)}^2$ and $\sigma(t) = \|\nabla n_\mu\|_{L^2(\Omega)}^2 + \|\nabla p_\mu\|_{L^2(\Omega)}^2$. Note that $\rho(0) \le \|n_0\|_{L^2(\Omega)}^2 + \|p_0\|_{L^2(\Omega)}^2$ for all μ. ρ and σ satisfy

$$\begin{aligned}\frac{1}{2}\rho'(t) + \sigma(t) &= -\theta(n_\mu, n_\mu - p_\mu, n_\mu) + \theta(p_\mu, n_\mu - p_\mu, p_\mu) \\ &\quad + b(\beta_1, n_\mu, n_\mu) + b(\beta_2, p_\mu, p_\mu) \\ &\quad + k\|n_\mu - p_\mu\|_{L^2(\Omega)}^2 + k(\beta_1, \nabla n_\mu) + k(\beta_2, \nabla p_\mu) \\ &= I + II + III\end{aligned}$$

As n_μ and p_μ may not be strictly positive, the sign of the I is indeterminant. If n_μ and p_μ are positive, then $I \le 0$. This is infact the case, as we will see later in

theorem 4. We have

$$|II| \leq \sup_{t\in[0,T]} \max_{w=1,2} \|\nabla \cdot \beta_w\|_{C^0(\Omega)}(\|n_\mu|^2_{L^2(\Omega)} + \|p_\mu\|^2_{L^2(\Omega)}) \leq c_1\rho(t)$$

for some constant c_1. Further

$$|III| \leq k(1 + \sup_{t\in[0,T]} \max_{w=1,2} \|\nabla \cdot \beta_w\|_{C^0(\Omega)})(\|n_\mu|^2_{L^2(\Omega)} + \|p_\mu\|^2_{L^2(\Omega)}) \leq c_2\rho(t)$$

for some other constant c_2. Lastly, by (4.4),

$$\begin{aligned}
|I| &= \left|\int_\Omega (n_\mu + p_\mu)(n_\mu - p_\mu)^2\, dx\right| \\
&\leq \|n_\mu + p_\mu\|_{L^2(\Omega)}\|(n_\mu - p_\mu)^2\|_{L^2(\Omega)} \\
&\leq \|n_\mu + p_\mu\|_{L^2(\Omega)}\|(n_\mu - p_\mu)\|^{1/2}_{L^2(\Omega)}\|\nabla(n_\mu - p_\mu)\|^{3/2}_{L^2(\Omega)} \\
&\leq \frac{1}{4\eta}\|n_\mu + p_\mu\|^4_{L^2(\Omega)}\|n_\mu - p_\mu\|^2_{L^2(\Omega)} + \frac{3\eta}{4}\|\nabla(n_\mu - p_\mu)\|^2_{L^4(\Omega)} \\
&\leq \frac{1}{2\eta}\rho^3(t) + \frac{3\eta}{2}\sigma(t).
\end{aligned}$$

Choosing $\eta < 1/3$ we find

$$\frac{1}{2}\rho'(t) + \frac{1}{4}\sigma(t) \leq \rho^3(t) + c_3\rho(t) \tag{4.11}$$

for some constant c_3. This inequality implies that $\rho(t)$ is bounded and continuous on some interval $[0, \delta)$ where δ depends only on $\rho(0)$ independently of μ. Furthermore, n_μ and p_μ are bounded in $L^2([0,\delta); H^1_0(\Omega))$ independently of μ.

Letting $\mu \to \infty$, we find $n_\mu, p_\mu \to \tilde{n}, \tilde{p} \in L^2([0,\delta); H^1)$ strongly in $L^2([0,\delta); L^2)$, weakly in $L^2([0,\delta); H^1_0(\Omega))$ and weak star in $L^\infty([0,\delta); L^2(\Omega))$ for some subsequence also indexed by μ. If we define $\Delta V_\mu = n_\mu - p_\mu$, then we additionaly see that $V_\mu \to \tilde{V}$ strongly in $L^2([0,\delta), H^2(\Omega))$ where $\Delta\tilde{V} = \tilde{n} - \tilde{p}$. □

Using the structure of (4.17) and (4.18), we show that the solutions guaranteed by lemma 3 must be positive on the interval where they are defined.

The following lemma is a weaker version of the usual positivity maximum principle, and only requires that solutions lie in $L^2([a,b]; H^1_0(\Omega))$ on some interval and

a compatability in the sign of the nonlinear convective terms. In particular, the data need only lie $L^\infty([a,b];L^\infty(\Omega))$.

Lemma 4 (Positivity for Weak Solutions)**.** *For $\delta > 0$, let*

$$f \in Y([0,\delta);2,1;H^1(\Omega),H^{-1})$$

be a solution of the following equation

$$\langle f', v\rangle + b(\mathbf{u}, f, v) = -\int_\Omega (\nabla f + f\beta)\cdot\nabla v\, dx, \quad \forall v \in H_0^1(\Omega) \tag{4.12}$$

where $f|_{t=0} = f_0 \in L^2(\Omega)$ is strictly positive, $f-k \in H_0^1(\Omega)$ for some $k>0$, $\nabla\cdot\mathbf{u} = 0$ and $\beta \in L^\infty\left(\overline{\Omega}\times[0,\delta)\right)$ is a vector field satisfying the following compatibility condition;

$$\nabla\cdot\beta = g - f + \nabla\cdot\beta_2, \quad g \geq 0, \quad \nabla\cdot\beta_2 \in L^\infty(\overline{\Omega}\times[0,\delta)).$$

Then, f is strictly positive for all $t \in [0,\delta)$.

Proof. The proof is based on energy techniques. We construct an energy which necessarily diverges if f takes negative values. Consider the cut-off function

$$l(t) = \begin{cases} t & t \geq \zeta, \\ \zeta\exp((t-\zeta)/\zeta) & t < \zeta, \end{cases}$$

for ζ sufficiently small. l is continuous, positive and has two well defined derivatives over the reals. Further, $ll'' - (l')^2$ is identically 0 for $t < \zeta$ and is identically -1 for $t \geq \zeta$. Consider the test function $v = l'(f)/l^2(f) - l'(k)/l^2(k)$. Since l is bound away from zero, v and its gradient are continuous functions of $f \in H^1(\Omega)$ which are bounded independently of f and so $v \in H_0^1(\Omega)$. Consider (4.12) for this choice of test function v; $v\nabla f$ is the total gradient $-\nabla(1/l(f))$ and so $b(\mathbf{u},f,v) = 0$.

$$\frac{d}{dt}\left(\int_\Omega \frac{1}{l(f)}\,dx - c_1\int_\Omega f\,dx\right) = \int_\Omega (\nabla f + f\beta)\cdot\nabla\left(\frac{l'(f)}{l^2(f)}\right)dx$$

where $c_1 = l'(k)/l^2(k) = 1/k$ is a constant for sufficiently small ζ. Let $\rho(t) = \int_\Omega l^{-1}(f)\,dx$ and $r(t) = \int_\Omega f\,dx$. Note also that $f\nabla(l'(f)/l^2(f)) = \nabla(fl'(f)/l^2(f) +$

$1/l(f)$). We compute

$$\begin{aligned}
&\rho'(t) - c_1 r'(t) \\
&\quad = \int_\Omega \frac{l(f)l''(f) - (l'(f))^2}{l^3(f)} |\nabla f|^2 + \beta \cdot \nabla \left(\frac{f l'(f)}{l^2(f)} + \frac{1}{l(f)} \right) dx \\
&\quad = -\int_{\{f>\zeta\}} \frac{1}{f^3} |\nabla f|^2 + \beta \cdot \nabla \left(\frac{f l'(f)}{l^2(f)} + \frac{1}{l(f)} \right) dx \\
&\quad \le c_2 \|\beta\|_{L^\infty(\overline{\Omega}\times[0,\delta))} |\partial\Omega| + \int_\Omega \nabla \cdot \beta \left(\frac{f l'(f)}{l^2(f)} + \frac{1}{l(f)} \right) dx \\
&\quad \le C_1 + \int_\Omega (g - f + \nabla \cdot \beta_2) \left(\frac{f l'(f)}{l^2(f)} + \frac{1}{l(f)} \right) dx \\
&\quad \le C_1 + 2|\Omega| + 2\|\nabla \cdot \beta_2\|_{L^\infty(\Omega\times[0,\delta))} \int_\Omega \frac{1}{l(f)} \, dx
\end{aligned}$$

where $c_2 = (kl'(k)/l^2(k) + 1/l(k)) = 2/k$ is a constant for sufficiently small ζ and $C_1 = c_2\|\beta\|_{L^\infty(\Omega\times[0,\delta))}|\partial\Omega|$. The last inequality follows for $g \ge 0$ and because $0 < l'(t) < 1$ and $t < l(t)$ for all t. Let $c_3 = 2\|\nabla \cdot \beta_2\|_{L^\infty(\Omega\times[0,\delta))}$. $\rho(t)$ and $r(t)$ satisfy the following differential inequality

$$\rho'(t) - r'(t) \le C_1 + 2|\Omega| + c_3\rho(t).$$

Applying the Gronwall's inequality,

$$\rho(r) \le \rho(0) + e^{c_3 a} \int_0^r (C_1 + 2|\Omega| + c_3 r(s)) e^{-c_3 s} \, ds, \quad \forall \zeta > 0, r < \delta.$$

Since $f \in L^1([0,\delta); L^1(\Omega))$, the right hand side is bounded.

Suppose now $f \le 0$ for some $t^* \in (0,\delta)$. Then $\int_U f \, dx|_{t=t^*} \le 0$ and

$$\lim_{\zeta\to 0} \int_U l(f) \, dx|_{t=t^*} = 0$$

for some measurable set U. Applying Jensen's inequality for convex functions, e.g. $1/l(t)$, we find

$$\infty = \lim_{\zeta\to 0} \left(\int_U l(f) \, dx \right)^{-1} \le \lim_{\zeta\to 0} \int_U \frac{1}{l(f)} \, dx \le \lim_{\zeta\to 0} \rho(t^*).$$

Since the latter quantity is uniformly bounded in $[0, \delta)$, we arrive at a contradiction. $\square$

The obvious objection to this lemma is that we are trying to prove that both n and p are positive. If we take $f = n$ and $g = p$ in the above theorem, then g is not necassarily positive. We overcome this problem with a slight modification to the proof. Consider the above argument for the energy $\rho(t) = \int_\Omega l^{-1}(n) + l^{-1}(p)\, dx$. Following the same calculation, we find

$$\rho'(t) - r'(t) \leq C_1 \int_\Omega \frac{l(p)}{l(n)} + \frac{l(n)}{l(p)}\, dx + C_2\rho(t) + C_3$$

for some constants C_1, C_2 and C_3. Replacing the integrand by the quotient of $l^2(n) + l^2(p)$ with $l(n)l(p)$, and using the inequality

$$\begin{aligned}
&\int_\Omega \frac{l^2(n) + l^2(p)}{l(n)l(p)}\, dx \\
&\qquad \leq \int_{\{n,p\geq 1\}} l^2(n) + l^2(p)\, dx + \int_{\{n,p<1\}} \frac{l(n) + l(p)}{l(n)l(p)}\, dx \\
&\qquad \leq \|n\|^2_{L^2(\Omega)} + \|p\|^2_{L^2(\Omega)} + \rho(t),
\end{aligned}$$

we arrive at exactly the same conclusion. We will apply this reasoning into the following existence result on all of $[0, T]$.

We are now in a position to prove theorem 2.

Proof of theorem 2. Let $t^* \in (0, T]$ be least upper bound of the set of t for which $n = \tilde{n} + k$ and $p = \tilde{p} + k$ given by lemma 3 are positive on $[0, t]$. If $t^* = T$ then we are done. Otherwise, assume $t^* < T$. Let $\rho(t) = \|n\|^2_{L^2(\Omega)} + \|p\|^2_{L^2(\Omega)}$ and $\sigma(t) = \|\nabla n\|^2_{L^2(\Omega)} + \|\nabla p\|^2_{L^2(\Omega)}$. Note that $C(n, p) := -\int_\Omega (n + p)(n - p)^2\, dx \leq 0$ for $t \in [0, t^*]$. Then, the following energy estimate also holds for n and p;

$$\begin{aligned}
\frac{1}{2}\rho'(t) + \sigma(t) &\leq C(n, p) + (1 + k) \max_{w=1,2} \|\nabla \cdot \beta_w\|_{C^0(\overline{Q}_T)}(\|n\|_{L^2(\Omega)} + \|p\|_{L^2(\Omega)}) \\
&\leq c_0\rho(t)
\end{aligned}$$

for some constant c_0. We infer that

$$\rho(t^*) + e^{c_0 t} \int_0^{t^*} e^{c_0 t} \sigma(s)\, ds \leq \rho(0), \tag{4.13}$$

or, $\rho(t^*) \leq \rho(0)$. By lemma 3, n and p may be extended to $[0, t^* + \delta_1)$ for $\delta_1 = \delta(\|n\|_{L^2(\Omega)}(t), \|p\|_{L^2(\Omega)}(t), \phi)$, since $\|n\|_{L^2(\Omega)}, \|p\|_{L^2(\Omega)}|_{t=t^*} \leq \|n_0\|_{L^2(\Omega)}, \|p_0\|_{L^2(\Omega)}$. By lemma 4, n and p are strictly positive on $[0, t^* + \delta)$. Thus, $t^* = t^* + \delta$, a contradiction when $\delta > 0$. We infer that $t^* = T$ and n and p are strictly positive in Ω a.e.

If there are two such solutions, n_1, p_1 and n_2, p_2, consider $\bar{n} = n_1 - n_2$ and $\bar{p} = p_1 - p_2$. Denote by $\bar{V} = V_1 - V_2$ as well, where V_1 and V_2 correspond to n_1, p_1 and n_2, p_2 respectively. Repeating the energy estimate for $\bar{n}$, we find

$$\begin{aligned}
&\frac{d}{dt}\frac{1}{2}\|\bar{n}\|^2_{L^2(\Omega)} + \|\nabla \bar{n}\|^2_{L^2(\Omega)} \\
&\quad = \theta(\bar{n}, n_1 - p_1, \bar{n}) + \theta(n_2, \bar{n} - \bar{p}, \bar{n}) + b(\beta_1, \bar{n}, \bar{n}) \\
&\quad \leq \alpha(t)\|\bar{n}\|_{L^2(\Omega)}(\|\bar{n}\|_{H^1_0(\Omega)} + \|\bar{p}\|_{H^1_0(\Omega)}) + C_1\|\bar{n}\|^2_{L^2(\Omega)}
\end{aligned}$$

for some constant C_1 and $\alpha(t) \leq \|n_1\|_{H^1_0(\Omega)} + \|p_1\|_{H^1_0(\Omega)} + \|n_2\|_{H^1_0(\Omega)} + \|p_1\|_{H^1_0(\Omega)} \in L^2([0,T])$. A similar estimate holds for $\bar{p}$, so that in total we find

$$\|\bar{n}\|^2_{L^2(\Omega)} + \|\bar{p}\|^2_{L^2(\Omega)} + e^{k(t)} \int_0^t e^{-k(s)} \left(\|\bar{n}\|^2_{L^2(\Omega)}(s) + \|\bar{p}\|^2_{L^2(\Omega)}(s) \right) ds \leq 0$$

where $k(s) = \int_0^t \alpha^2(s) - 2C_1\, ds$. Hence $n_1 = n_2$ and $p_1 = p_2$ for a.e. $t \in [0,T]$. The usual bootstrap arguments show that n and p are infact smooth solutions (4.6)-(4.8). □

Following the same line of reasoning as in the proof of theorem 2 we have

Corollary 1. *Let $n_0, p_0 \in L^2(\Omega)$, $\mathbf{v} \in L^2([a,b]; V)$ and $k > 0$ be a constant. Then there exists unique, positive*

$$n, p \in Y([a,b]; 2, 4/3; H^1_0(\Omega), H^{-1}(\Omega))$$

with $n(a), p(a) = n_0, p_0$ *in* $L^2(\Omega)$, $n-k, p-k \in H_0^1$ *and*

$$\langle n', v\rangle + b(\mathbf{v}, n, v) = -(\nabla n, \nabla v) - \theta(n, n-p, v), \tag{4.14}$$

$$\langle p', v\rangle + b(\mathbf{v}, n, v) = -(\nabla p, \nabla v) + \theta(p, n-p, v), \quad \forall v \in H_0^1(\Omega). \tag{4.15}$$

Moreover n *and* p *satisfy*

$$\|n\|_{L^2(\Omega)}(t) + \|p\|_{L^2(\Omega)}(t) \leq \|n_0\|_{L^2(\Omega)} + \|p_0\|_{L^2(\Omega)}, \ \forall t \in [a, b],$$

$$\int_a^b \|\nabla n\|^2_{L^2(\Omega)} + \|\nabla p\|^2_{L^2(\Omega)}\, dt \leq \|n_0\|^2_{L^2(\Omega)} + \|p_0\|^2_{L^2(\Omega)}.$$

Proof. Following the proof of lemma 3, there exist n and p satisfying the claim of this corollary for $[a, a+\delta)$ for some sufficiently small $\delta = \delta(\|n_0\|_{L^2(\Omega)}, \|p_0\|_{L^2(\Omega)})$. By lemma 4 with $\mathbf{v} = \mathbf{u}$ and $\beta = \nabla V$, n and p are positive. Shift equations (4.14) and (4.15) by k and write n in place of $n-k$ and p in place of $p-k$. Multiply these equations by n and p respectively, sum the two and integrate over Ω. Integrating by parts one finds

$$\begin{aligned}\frac{1}{2}\frac{d}{dt}(\|n\|^2_{L^2(\Omega)} + \|p\|^2_{L^2(\Omega)}) + \|\nabla n\|^2_{L^2(\Omega)} + \|\nabla p\|^2_{L^2(\Omega)} \\ = -\int_\Omega \frac{1}{2}(n^2 - p^2)(n-p) + k(n-p)^2\, dx \leq 0.\end{aligned}$$

Thus $\|n\|_{L^2(\Omega)}(t), \|p\|_{L^2(\Omega)}(t) \leq \|n_0\|_{L^2(\Omega)}, \|p_0\|_{L^2(\Omega)}$ for $t \in [a, a+\delta)$. Applying this result recursively the claim is proved. □

4.3 PNP and NS Coupling

Weak Formulation

We choose the following weak formulation of equations (3.6)-(3.11) when $\phi \equiv 0$.

Problem A. *Let* $n_0, p_0 \in C^\infty(\Omega)$ *and* $\mathbf{u}_0 \in H$ *and* $k > 0$ *be a constant. Find* $n-k, p-k \in L^2(H_0^1(\Omega))$ *with* $n', p' \in L^1(H^{-1}(\Omega))$ *and* $\mathbf{u} \in L^2(V)$ *with* $\mathbf{u}' \in L^1(V^{-1})$ *satifying*

$$\langle \mathbf{u}', \mathbf{v}\rangle + \mathbf{b}(\mathbf{u}, \mathbf{u}, \mathbf{v}) = -\nu(\nabla \mathbf{u}, \nabla \mathbf{v}) + \langle \mathbf{f}, \mathbf{v}\rangle, \quad \forall \mathbf{v} \in V \tag{4.16}$$

$$\langle n', u\rangle + b(\mathbf{u}, n, u) = \langle L_n^*, v\rangle, \tag{4.17}$$

$$\langle p', u\rangle + b(\mathbf{u}, p, u) = \langle L_p^*, v\rangle, \qquad \forall u \in H_0^1(\Omega), \tag{4.18}$$

$$n(0), p(0), \mathbf{u}(0) = n_0, p_0, \mathbf{u}_0, \quad \textit{in } L^2(\Omega). \tag{4.19}$$

where $\mathbf{f}$*,* L_n^* *and* L_p^* *are defined as*

$$\langle \mathbf{f}, \mathbf{v}\rangle := \int_\Omega (n-p)\nabla V \cdot \mathbf{v}\, dx, \qquad \forall \mathbf{v} \in V,$$

$$\langle L_p^*, u\rangle := \int_\Omega (\nabla n - n\nabla V)\nabla u\, dx,$$

$$\langle L_n^*, u\rangle := \int_\Omega (\nabla p + p\nabla V)\nabla u\, dx, \quad \forall u \in H_0^1(\Omega).$$

The function V *is defined;*

$$\Delta V(x) = n - p, \quad V\big|_{\partial\Omega} = 0. \tag{4.20}$$

We will produce a solution to (4.16)-(4.18) as the limit of a so called modified Galerkin sequence. The strategy is as follows; first we construct unique, weak solutions to (4.17) and (4.18) when $\mathbf{u}$ is a given velocity field in the space $\mathcal{W}_\mu = \{\mathbf{u} = \sum_{i=1}^{\mu} g_i(t)\mathbf{v}_i(x)\}$ This constructs a map from $\mathcal{W}_\mu$ to itself by entering these weak solutions into a truncated form of (4.16). The fixed point of this map, $\mathbf{u}_\mu$ defines the modified Galerkin approximation $\mathbf{u}_\mu$, $n_\mu = n(\mathbf{u}_\mu)$ and $p_\mu = p(\mathbf{u}_\mu)$. Roughly speaking, n_μ and p_μ solve (4.17)-(4.18) exactly while $\mathbf{u}_\mu$ solves the projection of (4.16) onto $\text{span}(\mathbf{v}_1, \ldots, \mathbf{v}_\mu)$. Passing to the limit, $\mu \to \infty$, the approximation converges to a solution $\mathbf{u}, n$ and p in the requisite spaces.

We have demonstrated that (4.17) and (4.18) are uniquely and strongly solvable when $\mathbf{u}$ is smooth on Q_T, see theorem 2. We reiterate that despite the parabolic structure of (4.17), (4.18), the existence of solutions is nontrivial and highly reliant on the sign of the convective term ∇V. Furthermore, this sign dependence follows only if n and p are positive. In the weak and Galerkin formulations, the positivity of n and p cannot be guaranteed by maximum principles. Either the Galerkin approximation takes negative values or the smoothness of the weak solution required for the maximum principle is exactly that which is being ascerted. However, since $\mathbf{u}_\mu$ is divergence free, we may aply (4) to find $n_\mu, p_\mu > 0$ for a.e. t in the solution

domain. Later, in section 4.4, where the additional convective term $\nabla\phi$ is smooth, but because $\mathbf{u}_\mu$ does not necassarily have arbitrarily many time derivatives, this lemma becomes especially important.

An interesting aspect of this system is that the canonical, force balance energy esitmate (2.14) and (4.31) associated with (4.16)-(4.18) implies the usual $L^\infty(H)$ and $L^2(V)$ apriori estimates of the velocity Galerkin solution $\mathbf{u}_\mu$, but only uniform integrability in time for n_μ and p_μ. This is a ubiquitous feature of Fokker-Plank type equations. Fortunately, the potential V of n and p is self induced, so that additional apriori estimates (4.26),(4.27) which are independent of the force balance can be derived. When (4.16)-(4.18) is further coupled with the Allen-Cahn equations, and the potential of n and p is dependent on ϕ, these additional esitmates are lost.

Following [35], we assert the existence of $\mathbf{u}_\mu = \sum_{i=1}^{\mu} g_i(t)v_i \in W_\mu$, n_μ, p_μ satifying a truncated form of (4.16)-(4.18);

$$g_i'(t) + g_j(t)g_k(t)b(\mathbf{v}_j, \mathbf{v}_k, \mathbf{v}_i) + \lambda_i g_i(t) = \langle \mathbf{f}, v_i\rangle, \quad \text{for } i = 1, \dots, \mu, \tag{4.21}$$

$$(n_\mu)_t + \mathbf{u}_\mu \cdot \nabla n_\mu = \Delta n_\mu - \nabla \cdot (\nabla n_\mu \nabla V_\mu), \tag{4.22}$$

$$(p_\mu)_t + \mathbf{u}_\mu \cdot \nabla p_\mu = \Delta p_\mu + \nabla \cdot (\nabla p_\mu \nabla V_\mu), \tag{4.23}$$

$$\Delta V_\mu = n_\mu - p_\mu, \quad V_\mu|_{\partial\Omega} = 0, \tag{4.24}$$

$$n_\mu(0), p_\mu(0) = n_0, p_0 > 0, \text{ in } L^2(\Omega), \quad g_i(0) = (\mathbf{u}_0, \mathbf{v}_i). \tag{4.25}$$

Following a general fixed point procedure, [35], we have

Theorem 3. *For $k > 0$, there exists $\mathbf{u}_\mu \in W_\mu$, positive*

$$n_\mu, p_\mu \in Y([0, T_0]; 2, 1; H^1(\Omega), H^{-1}(\Omega))$$

with $n_\mu - k, p_\mu - k \in L^2(H_0^1(\Omega))$ satisfying (4.21)-(4.25) for $T_0 > 0$ sufficiently small.

Lemma 5. *Let $\mathbf{u}_\mu$,n_μ and p_μ be any solution of (4.21)-(4.25) on the interval $[0, T_1]$. Then*

$$\|V_\mu\|_{H_0^1(\Omega)}(t), \|n_\mu\|_{L^2(\Omega)}(t), \|p_\mu\|_{L^2(\Omega)}(t) \le c_0, \quad \forall t \in [0, T_1] \tag{4.26}$$

$$\int_0^{T_1} \|\nabla n_\mu\|_{L^2(\Omega)}^2 + \|\nabla p_\mu\|_{L^2(\Omega)}^2 \, dt \le c_1, \tag{4.27}$$

for some constants c_0 and c_1 independent of μ and T_1.

Proof. This is corollary 1 with $a = 0, b = T_1$ and $\mathbf{v} = \mathbf{u}_\mu$. □

Lemma 6. *Let $\mathbf{u}_\mu$, n_μ and p_μ be any solution of (4.21)-(4.25) on the interval $[0, T_1]$. Then*

$$\|\mathbf{u}_\mu\|_{L^2(\Omega)}(t) \leq c_2, \ \forall t \in [0, T_1], \quad \int_0^{T_1} \|\nabla \mathbf{u}_\mu\|^2_{L^2(\Omega)} \, dt \leq c_3, \tag{4.28}$$

for some constants c_2 and c_3 independent of μ and T_1.

Proof. We will duplicate (2.14) for the weak formulation. Although n_μ and p_μ are positive, their logarithms may not be bounded. Similarly to lemma 4, we construct an appropriate cutoff function, evaluate the logarithm with this cutoff function, and take the limit $\zeta \to 0$. Consider $\log(l(u))$ for $l(t)$ bounded away from zero. Consider for example,

$$l(t) = \begin{cases} t & t \geq \zeta, \\ \zeta t^2 + (1 - 2\zeta^2)t + \zeta^3 & 0 \leq t < \zeta. \end{cases}$$

Let $Q(t) = l(t)\log(l(t))$, and $q(t) = Q'(t)$. For this particular choice of l we will later need the bounds

$$0 \leq q'(t), \quad |q'(t)t + 1| \leq C_0, \quad \forall t \in [0, \zeta]$$

for some C_0 independent of ζ. Note that $q'(n_N) = n_\mu^{-1}$ on the $\{x \in \Omega \, : \, n_\mu(x) \geq \zeta\}$. Consider the energy

$$\tilde{L}(n_\mu, p_\mu) := \int_\Omega Q(n_\mu) + Q(p_\mu) + (p_\mu - n_\mu)V_\mu \, dx.$$

By lemma 4, n_μ and p_μ are positive so that $\tilde{L}$ is well defined. We compute

$$\begin{aligned} \frac{d}{dt}\tilde{L}(n_\mu, p_\mu) = &\int_\Omega (q(n_\mu) - q(k) - V_\mu)(n_\mu)_t + (q(p_\mu) - q(k) + V_\mu)(p_\mu)_t \, dx \\ &+ q(k)\frac{d}{dt}\left(\int_\Omega n_\mu + p_\mu \, dx\right) + \int_\Omega ((p_\mu) - (n_\mu))(V_\mu)_t \, dx. \end{aligned}$$

Note that

$$\int_\Omega (p_\mu - n_\mu)V_\mu \, dx = \int_\Omega \Delta V_\mu V_\mu \, dx = \frac{1}{2}\int_\Omega |\nabla V_\mu|^2 \, dx$$

and

$$\int_\Omega (p_\mu - n_\mu)(V_\mu)_t \, dx = \int_\Omega \Delta V_\mu (V_\mu)_t \, dx = \frac{1}{2}\frac{d}{dt}\int_\Omega |\nabla V_\mu|^2 \, dx$$

and define the test functions $w_1 = q(n_\mu) - q(k) - V_\mu$ and $w_2 = q(p_\mu) - q(k) + V_\mu$. Then

$$\frac{d}{dt}\tilde{L}(n_\mu, p_\mu) = \frac{d}{dt}\left(q(k)\int_\Omega n_\mu + p_\mu \, dx + \frac{1}{2}\|\nabla V_\mu\|^2_{L^2(\Omega)}\right) + ((n_\mu)_t, w_1) + ((p_\mu)_t, w_2).$$

Note that $w_1, w_2 \in H^1_0(\Omega)$ and $q(k) = k$ for $\zeta \le k$. Multiply (4.22) and (4.23) by w_1 and w_2 respectively. Note that $(q(n_\mu) - q(k))\nabla n_\mu$ and $(q(p_\mu) - q(k))\nabla p_\mu$ are total gradients. One has

$$((n_\mu)_t, w_1) + ((p_\mu)_t, w_2) = b(\mathbf{u}_\mu, p_\mu - n_\mu, V_\mu) + \langle L^*_n, w_1\rangle + \langle L^*_p, w_2\rangle.$$

This and the previous identity imply

$$\begin{aligned}\frac{d}{dt}\int_\Omega Q(n_\mu) + Q(p_\mu) + \frac{1}{2}|\nabla V_\mu|^2 - k(n_\mu + p_\mu) \, dx \\ = b(\mathbf{u}_\mu, n_\mu - p_\mu, V_\mu) + \langle L^*_n, w_1\rangle + \langle L^*_p, w_2\rangle.\end{aligned} \tag{4.29}$$

Multiply (4.21) by g_i. The sum of these expresssions for $i = 1, \dots, \mu$ is

$$\frac{d}{dt}\frac{1}{2}\|\mathbf{u}_\mu\|^2_{L^2(\Omega)} + \|\nabla \mathbf{u}_\mu\|^2_{L^2(\Omega)} = b(\mathbf{u}_\mu, V_\mu, n_\mu - p_\mu). \tag{4.30}$$

Adding (4.29) and (4.30);

$$\begin{aligned}&\frac{d}{dt}\left(\int_\Omega Q(n_\mu) + Q(p_\mu) + \frac{1}{2}|\nabla V_\mu|^2 - k(n_\mu + p_\mu) \, dx + \|\mathbf{u}_\mu\|^2_{L^2(\Omega)}\right) + \|\nabla \mathbf{u}\|^2_{L^2(\Omega)} \\ &\quad = b(\mathbf{u}_\mu, n_\mu - p_\mu, V_\mu) + b(\mathbf{u}_\mu, V_\mu, n_\mu - p_\mu) + \langle L^*_n, w_1\rangle + \langle L^*_p, w_2\rangle \\ &\quad = \langle L^*_n, w_1\rangle + \langle L^*_p, w_2\rangle.\end{aligned} \tag{4.31}$$

The proof is complete once we have shown that $\langle L_n^*, w_1\rangle + \langle L_p^*, w_2\rangle$ is bounded in the limit $\zeta \to 0$.

$$\begin{aligned}\langle L_n^*, w_1\rangle &= -\int_\Omega (q'(n_\mu)\nabla n_\mu + \nabla V_\mu)\cdot(\nabla n_\mu + n_\mu \nabla V_\mu)\, dx \\ &= -\int_{\{n_\mu \geq \zeta\}} \frac{1}{n_\mu}|\nabla n_\mu + n_\mu \nabla V_\mu|^2\, dx \\ &\quad -\int_{\{n_\mu<\zeta\}} q'(n_\mu)|\nabla n_\mu|^2 + (q'(n_\mu)n_\mu + 1)\nabla n_\mu \cdot \nabla V_\mu + n_\mu|\nabla V_\mu|^2\, dx \\ &\leq \int_{\{n_\mu<\zeta\}} (q'(n_\mu)n_\mu + 1)\nabla n_\mu \cdot \nabla V_\mu\, dx,\end{aligned}$$

the last inequality following from the positivity of $q'(t)$ and n_μ. Continuing,

$$\langle L_n^*, \partial_n \tilde{L}\rangle \leq \int_{\{n_\mu \leq \zeta\}} (q'(n_\mu)n_\mu + 1)\nabla n_\mu \cdot \nabla V_\mu\, dx \leq C_0 \|\nabla n_\mu\|_{L^2(\Omega)} \|\nabla V_\mu\|_{L^2(\Omega)}.$$

A similar estimate holds for $\langle L_p^*, \partial_p \tilde{L}\rangle$. By (4.26) and (4.27)

$$|\langle L_n^*, \partial_n \tilde{L}\rangle + \langle L_p^*, \partial_p \tilde{L}\rangle| \leq C_0 c_0 (\|\nabla n_\mu\|_{L^2(\Omega)} + \|\nabla p_\mu\|_{L^2(\Omega)}) := \alpha(t)$$

where $\|\alpha(t)\|_{L^2([0,T_1])} \leq C_0 c_0 c_1$ independently of μ and T_1. Note that

$$Q(n_\mu), Q(p_\mu) \geq -e^{-1}, \quad \forall \zeta > 0, x \in \Omega.$$

This, along with (4.31), then implies (4.28). □

Remark 1. There is actually a much faster way to prove (4.28), namely by multiplying the difference of (4.22) and (4.23) by V_μ and integrating by parts. It happens by coincidence that $(\Delta(n_\mu - p_\mu), V) = \|n_\mu - p_\mu\|^2_{L^2(\Omega)} \geq 0$. This is due to the fact that $\epsilon = 1$ is a constant. Indeed, it is sometimes desirable that V satisfy the Poisson equation with a variable coefficient $\epsilon = \epsilon(x,t)$, in which case this "trick" no longer works. The inequality (4.31) would still hold though, along with more general potentials than V.

Theorem 4. *Given $T > 0$, there exists $n, p \in Y([0,T]; 2, 4/3; H^1, H^{-1})$ and $\mathbf{u} \in$*

$Y([0,T];2,4/3;H^1,H^{-1})$ *satisfying* (4.16)-(4.19). *Moreover,* n, p *and* $\mathbf{u}$ *satisfy*

$$\mathbf{u} \in L^\infty([0,T];H) \cap L^2([0,T];V),$$
$$n,p \in L^\infty([0,T];L^2(\Omega)) \cap L^2([0,T];H^1(\Omega)).$$

Proof. By lemma 5 and lemma 6, the solution of (4.16)-(4.19) guaranteed by theorem 3 for the interval $[0,T_0]$ also satisfies

$$\|n_\mu\|_{L^2(\Omega)}(T_0), \|p_\mu\|_{L^2(\Omega)}(T_0), \|\mathbf{u}_\mu\|_H(T_0) \leq C$$

for some constant C independenlty of μ and T_0. Hence the solution $n_\mu, p_\mu, \mathbf{u}_\mu$ extends to $[0, T_0+\delta]$ for some $\delta = \delta(C)$. Since C and $\delta(C)$ are independent of μ and t, the solution extends to all of $[0,T]$.

Again, by lemma 5, n_μ and p_μ stay bounded in a subset of $L^2([0,T];H^1) \cap L^\infty([0,T];L^2)$ as $\mu \to \infty$. By lemma 6, $\mathbf{u}_\mu$ also stays in a bounded subset of $L^2([0,T];V) \cap L^\infty([0,T];H)$ as $\mu \to \infty$. We may thus extract a subsequence, also indexed by μ satisfying

$$n_\mu, p_\mu \rightharpoonup n, p \in L^2(H^1) \cap (L^\infty(L^2))^*,$$
$$\mathbf{u}_\mu \rightharpoonup \mathbf{u} \in L^2(V) \cap (L^\infty(H))^*,$$

Following [35], we have $\|\mathbf{u}'_\mu\|_{H^{-1}} \in L^{4/3}([0,T])$, if we can demonstrate that $\mathbf{f} \in L^{4/3}([0,T];H^{-1})$. Recall that $\langle \mathbf{f}, \mathbf{v}\rangle = \int_\Omega (n_\mu - p_\mu)\nabla V_\mu \cdot \mathbf{v}\, dx$. By elliptic regularity,

$$|\langle \mathbf{f}, \mathbf{v}\rangle| \leq \|n_\mu - p_\mu\|_{L^2(\Omega)} \|\nabla V_\mu\|_{L^\infty(\Omega)} \|\mathbf{v}\|_H \leq C\|n_\mu - p_\mu\|_{H^1_0(\Omega)} \|\mathbf{v}\|_V$$

so that $\|\mathbf{f}\|_{H^{-1}} \leq C\|n_\mu - p_\mu\|_{H^1_0(\Omega)} \in L^2([0,T])$. In addition, $\mathbf{u}_\mu, \mathbf{u}$ are bounded in $Y(2,4/3;V,H^{-1}(\Omega))$ and n_μ, p_μ, n, p are bounded in $Y(2,4/3;H^1(\Omega),H^{-1}(\Omega))$. If X_0 is compactly embedded in X, and X is continuously embedded in X_1, then $Y(\alpha_0,\alpha_1;X_0,X_1) \subset L^2(X)$ compactly whenever $\alpha_0, \alpha_1 > 1$ (see [54].) Thus, we have additionally, $\mathbf{u}_\mu \to \mathbf{u}$ strongly in $L^2(H)$. As $n_\mu, p_\mu \to n, p \in L^2(L^2(\Omega))$, $V_\mu \to V$ strongly in $L^2(H^1)$ also. By the usual arguments, $\mathbf{u}, n$ and p satisfy (4.16)-(4.19). ∎

4.4 PNP, NS, Allen-Cahn Coupling

The following existence result is for small data in space dimension $d \leq 2$. When the PNP equations are coupled by the additional convective term $\nabla\phi$, the completely dissipative energy law, corollary 1, is lost. This is a technical difficulty by the following reasoning. For $d \leq 3$, if the weak formulation requires ϕ to solve a higher order equation, such as the transported Cahn-Hilliard, then one has an apriori bound of the Galerkin solution, $\|\Delta\phi_\mu\|_{L^2(\Omega)} \leq C$ for some constant C independent of μ and n_μ and p_μ by the canonical energy law. One then recovers the apriori estimates found in corollary 1. From the modeling standpoint this is natural since the equation satisfied by ϕ is to be viewed as a viscocity (relaxed) solution of the transport equation. For the sake of completeness we neverless expose the small data, global existence of weak solutions to (3.6)-(3.11).

Weak Formulation

We choose the following weak formulation of equations (3.6)-(3.11) for $\phi \neq 0$.

Problem B. *Let $\Omega \subset \mathbb{R}^2$ be bounded with smooth boundary. Let $-1 \leq \phi_0 \leq 1 \in H^1(\Omega)$, $n_0, p_0 \in C^\infty(\Omega)$ and $\mathbf{u}_0 \in H$ and $k > 0$ be a constant. Find $\phi - 1 \in L^\infty(H_0^1(\Omega))$ with $\phi' \in L^1(H^{-2}(\Omega))$, $n - k, p - k \in L^2(H_0^1(\Omega))$ with $n', p' \in L^1(H^{-1}(\Omega))$ and $\mathbf{u} \in L^2(V)$ with $\mathbf{u}' \in L^1(V^{-1})$ satifying*

$$\langle \mathbf{u}', \mathbf{v}\rangle + \mathbf{b}(\mathbf{u}, \mathbf{u}, \mathbf{v}) = -\nu(\nabla\mathbf{u}, \nabla\mathbf{v}) + \langle \mathbf{f}, \mathbf{v}\rangle, \quad \forall \mathbf{v} \in V \tag{4.32}$$

$$\langle n', u\rangle + b(\mathbf{u}, n, u) = -(\nabla n + n\nabla(\phi - V), \nabla u) \tag{4.33}$$

$$\langle p', u\rangle + b(\mathbf{u}, p, u) = -(\nabla p + p\nabla(\phi + V), \nabla u), \tag{4.34}$$

$$\langle \phi', u\rangle + b(\mathbf{u}, \phi, u) = -\gamma[(\nabla\phi, \nabla u) + (W'(\phi), u)], \quad \forall u \in H_0^1(\Omega), \tag{4.35}$$

$$n(0), p(0), \mathbf{u}(0), \phi(0) = n_0, p_0, \mathbf{u}_0, \phi_0 \quad \textit{in } L^2(\Omega), \tag{4.36}$$

where

$$\langle \mathbf{f}, \mathbf{v}\rangle := \int_\Omega -(\nabla\phi \otimes \nabla\phi) \cdot \nabla v(n - p)\nabla V \cdot \mathbf{v}\, dx, \qquad \forall \mathbf{v} \in V.$$

The existence of a modified Galerkin sequence ϕ_μ, n_μ, p_μ and $\mathbf{u}_\mu$ defined on

the interval $[0, T_0]$ for some sufficiently small $T_0 > 0$ with n_μ and p_μ positive follows identically from the results in section 4.3. We will refer to (4.32)-(4.36) and the Galerkin formulation interchangebly. Following lemma 6, in (4.36) let $u = \Delta\phi_\mu + W'(\phi_\mu) + (n_\mu + p_\mu)$, in (4.34) and (4.35) let $u = q(n_\mu) - q(k) - V_\mu + \phi_\mu$ and $u = q(p_\mu) - q(k) + V_\mu + \phi_\mu$ respectively and let $\mathbf{v} = \mathbf{u}_\mu$ in the truncated form of (4.32). Recall that q and Q are defined in terms of the truncation function l. One finds the canonical energy law

$$\begin{aligned} \frac{d}{dt}\left(\frac{1}{2}\|\mathbf{u}_\mu\|^2_{L^2(\Omega)} + \|\nabla\phi_\mu\|^2_{L^2(\Omega)} + \int_\Omega Q(n_\mu) + Q(p_\mu) - k(n_\mu + p_\mu)\,dx\right) \\ + \|\nabla\mathbf{u}\|^2_{L^2(\Omega)} + \gamma\|S'_\eta(\phi_\mu)\|_{L^2(\Omega)}(1 - \|n_\mu\|^2_{L^2(\Omega)} - \|p_\mu\|^2_{L^2(\Omega)}) \\ \leq c_0(\|\nabla n_\mu\|_{L^2(\Omega)} + \|\nabla p_\mu\|_{L^2(\Omega)})\|\nabla\phi\|_{L^2(\Omega)} \end{aligned} \tag{4.37}$$

for some constant c_0 independent of δ and μ. Similarly, letting $u = n_\mu$ in $u = p_\mu$ in (4.33) and (4.34) respectively, one finds

$$\begin{aligned} \frac{1}{2}\frac{d}{dt}\left(\|n_\mu\|^2_{L^2(\Omega)} + \|p_\mu\|^2_{L^2(\Omega)}\right) + \|\nabla n_\mu\|^2_{L^2(\Omega)} + \|\nabla p_\mu\|^2_{L^2(\Omega)} \\ \leq \int_\Omega (n_\mu\nabla n_\mu + p_\mu\nabla p_\mu)\nabla\phi_\mu\,dx. \end{aligned} \tag{4.38}$$

For $d \leq 2$, we may bound the righthand side of (4.38) by

$$\frac{1}{2}\left(\|\nabla n_\mu\|^2_{L^2(\Omega)} + \|\nabla p_\mu\|^2_{L^2(\Omega)}\right) + \frac{1}{2}(\|n\|^2_{L^2(\Omega)} + \|p\|^2_{L^2(\Omega)})\|\phi\|^2_{H^2(\Omega)}.$$

We have used the inequality (4.1) and the interpolation inequality

$$\|\nabla\phi\|_{L^4(\Omega)} \leq \|\phi\|^{1/2}_{L^\infty(\Omega)}\|\phi\|^{1/2}_{H^2(\Omega)}, \quad \forall\phi \in H^2(\Omega)$$

with $-1 \leq \phi_\mu \leq 1$ a.e. Furthermore,

$$\|\phi_\mu\|_{H^2(\Omega)} \leq c_1(\|\Delta\phi_\mu\|_{L^2(\Omega)} + 1) \leq c_2(\|S'_\eta(\phi_\mu)\|_{L^2(\Omega)} + 1)$$

for some constants c_1, c_2 dependening only on Ω. Combining these estimates with

(4.37), for some constant c_3 independent of μ,

$$\begin{aligned}\frac{d}{dt}\Bigg(\frac{1}{2}\|\mathbf{u}_\mu\|^2_{L^2(\Omega)} + \|\nabla\phi_\mu\|^2_{L^2(\Omega)} + \int_\Omega Q(n_\mu) + Q(p_\mu) - k(n_\mu + p_\mu)\,dx \\ + \frac{1}{2}\|n_\mu\|^2_{L^2(\Omega)} + \frac{1}{2}\|p_\mu\|^2_{L^2(\Omega)}\Bigg) + \|\nabla\mathbf{u}\|^2_{L^2(\Omega)} \\ + \gamma\|S'_\eta(\phi_\mu)\|^2_{L^2(\Omega)}\Big(1 - c_3\big(\|n_\mu\|^2_{L^2(\Omega)} + \|p_\mu\|^2_{L^2(\Omega)}\big)\Big) \\ + \Big(\|\nabla n_\mu\|_{L^2(\Omega)} + \|\nabla p_\mu\|_{L^2(\Omega)}\Big)\Big(1/2 - c_0\|\nabla\phi\|_{L^2(\Omega)}\Big) \le 0\end{aligned}$$

For $\|\nabla\phi_0\|_{L^2(\Omega)}, \|n_0\|_{L^2(\Omega)}$ and $\|p_0\|_{L^2(\Omega)}$ sufficiently small, this inequality implies that ϕ_μ stays bounded in $L^\infty(H^1(\Omega)) \cap L^2(H^2(\Omega))$, n_μ and p_μ stay bounded in $L^\infty(L^2(\Omega)) \cap L^2(H^1(\Omega))$ and $\mathbf{u}_\mu$ stays bounded in $L^\infty(H) \cap L^2(V)$ where the time interval is $[0, T_0]$. This implies that the solution and the above inequality extend to $[0, T]$. Similarly, following [35], we have $\phi'_\mu, n'_\mu, p'_\mu$ and $\mathbf{u}'_\mu$ in $L^{4/3}([0,T]; H^{-1})$. Hence ϕ_μ, n_μ, p_μ and $\mathbf{u}_\mu$ converge (in the approriate sense) to a solution ϕ, n, p and $\mathbf{u}$ of (4.32)-(4.36). This proves

Theorem 5. *For $\|\nabla\phi_0\|_{L^2(\Omega)}, \|n_0\|_{L^2(\Omega)}$ and $\|p_0\|_{L^2(\Omega)}$ sufficiently small, there exist a solution to Problem B.*

Chapter 5

Special Solutions

5.1 Introduction

In this chapter we define the equations of stationary electrokinetics, demonstrate the existence of solutions to these equations and discuss the qualitative properties of limiting stationary solutions as $\epsilon \to 0$. The electric potential of the stationary solution solves a Poisson-Boltzmann type equation. We derive explicit bounds as the dielectric constant ϵ approaches zero for solution extrema and boundary gradients in one space dimension. A major feature of the system is a nonlocal integral term in the nonlinearity on the righthand side of the Poisson equation which arises from the charge density conservation. In contrast to other Poisson-Boltzmann equations, this nonlocal dependence is responsible for the fact that solutions blow up like $\log(\epsilon)$ in certain cases. We present some numerical results to exemplify the three important cases and provide evidence for an upper growth bound.

The stationary equations presented below are not new and in fact are a simplified version of the those equations widely studied in the literature. No-flux boundary conditions are chosen to allow for a decoupling of the Nernst-Plank equations from the Poisson equation through the Boltzmann distribution. In other works though, the flux at the boundary of the domain is representative of the current/voltage relationship. The majority of the research in electrokinetics attempts to recover the experimentally observed current/voltage relationship by carefully postulating potential and charge dynamics at the interface of electrolyte and elec-

trode. Due to nonlinearity, verifying these theoretical hypotheses can only be achieved by numerical solution of the equations themselves or low order expansions of these equations. The stability of numerical schemes with respect to these equations or even of the asymptotic expansions is virtualy nonexistent. Motivated by these problems, we have chosen to study these equations from a variational PDE point of view to determine to what extent these claims are true. Concretely, we demonstrate that in some sense, the no-flux equations lack a limiting asymptotic solution. The no-flux boundary conditions imply mass conservation of charge species; in a binary electrolyte these masses are identical. However, the limiting solution is necassarily asymptotically unstable with respect to these masses. In the case of nonzero flux, where the charge masses fluctuate, it is not clear then that an expanded limiting solution represents anything other than one of many particular solutions in the zero Debye length limit.

5.2 Stationary Solutions

Recall equations (1.1)-(1.5) and suppose that n and p satisfy the natural boundary conditions

$$(\nabla n - n\nabla V) \cdot \mathbf{n}\big|_{\partial\Omega} = 0, \tag{5.1}$$

$$(\nabla p + p\nabla V) \cdot \mathbf{n}\big|_{\partial\Omega} = 0. \tag{5.2}$$

If $\mathbf{u}$ satisfies the no slip boundary condition $\mathbf{u}\big|_{\partial\Omega} = 0$, then

$$\frac{d}{dt}\int_\Omega n\,dx = \int_\Omega n_t\,dx = -\int_{\partial\Omega} (\nabla n - n\nabla V)\cdot\mathbf{n} + n\mathbf{u}\cdot\mathbf{n}\,dS - \int_\Omega n\nabla\cdot\mathbf{u}\,dx = 0,$$
$$\frac{d}{dt}\int_\Omega p\,dx = \int_\Omega p_t\,dx = -\int_{\partial\Omega} (\nabla p + p\nabla V)\cdot\mathbf{n} + n\mathbf{u}\cdot\mathbf{p}\,dS - \int_\Omega p\nabla\cdot\mathbf{u}\,dx = 0.$$

Thus the integrals of n and p are conserved. This motivates defining the stationary problem ($\mathbf{u} = 0$ and $n_t = p_t = 0$)

$$\nabla\cdot(\nabla n - n\nabla V) = 0, \tag{5.3}$$

$$\nabla\cdot(\nabla p + p\nabla V) = 0, \tag{5.4}$$

$$\epsilon \Delta V = n - p, \tag{5.5}$$

with boundary conditions/constraints (5.1), (5.2) and

$$\int_\Omega n\,dx = \alpha > 0, \quad \int_\Omega p\,dx = \beta > 0, \quad V\big|_{\partial\Omega} = V_0 \in C^0(\partial\Omega). \tag{5.6}$$

We study qualitative properties of solutions to (5.3)-(5.5) with (5.1), (5.2) and (5.6) as $\epsilon \to 0$. Note that

$$n = \alpha \frac{e^V}{\int_\Omega e^V\,dx}, \quad p = \beta \frac{e^{-V}}{\int_\Omega e^{-V}\,dx}. \tag{5.7}$$

are solutions to (5.3),(5.4). Combining (5.7) with (5.5), one finds

$$\epsilon \Delta V = \alpha \frac{e^V}{\int_\Omega e^V\,dx} - \beta \frac{e^{-V}}{\int_\Omega e^{-V}\,dx}, \quad V\big|_{\partial\Omega} = V_0. \tag{5.8}$$

We point out that (5.10) is the Euler-Lagrange equation of the energy

$$E[u] = \frac{\epsilon}{2}\|\nabla u\|^2_{L^2(\Omega)} + \alpha \log\left(\int_\Omega e^u\,dx\right) + \beta \log\left(\int_\Omega e^{-u}\,dx\right).$$

The existence of a unique solution to (5.10) and consequently the existence of a unique stationary solution of (5.3)-(5.5) is guaranteed by the direct method of the calculus of variations;

Theorem 6. *Let Ω be a bounded, open subset of $\mathbb{R}^n$ with smooth boundary and $V_0 \in C^0(\bar{\Omega})$. Then there exists at most one $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ satisfying* (5.8).

Proof. We begin by demonstrating that E is a convex functional bounded from below. By the convexity of the exponential, and the Poincire inequality,

$$\begin{aligned}
E(u) &\geq \frac{\epsilon}{2}\|\nabla u\|^2_{L^2(\Omega)} + \alpha \int_\Omega u\,dx - \beta \int_\Omega u\,dx \\
&\geq \frac{\epsilon}{2}\|\nabla u\|^2_{L^2(\Omega)} - c_0\|u\|_{L^1(\Omega)} \\
&\geq \frac{\epsilon}{2}\|\nabla u\|^2_{L^2(\Omega)} - c_0|\Omega|^{1/2}(\|V_0\|_{L^2(\Omega)} + C\|\nabla V_0\|_{L^2(\Omega)} + C\|\nabla u\|_{L^2(\Omega)}) \\
&\geq -c_0|\Omega|^{1/2}(\|V_0\|_{L^2(\Omega)} + C\|\nabla V_0\|_{L^2(\Omega)}) - \frac{C^2|\Omega|c_0^2}{2\epsilon}
\end{aligned}$$

where $c_0 = |\alpha - \beta|$ and C is the Poincire constant. The convexity of E follows from a straightforward application of Hölder's inequality

$$\log\left(\int_\Omega e^{\lambda_1 u_1 + \lambda_2 u_2}\,dx\right) \le \log\left(\left(\int_\Omega e^{u_1}\,dx\right)^{\lambda_1}\left(\int_\Omega e^{u_2}\,dx\right)^{\lambda_2}\right)$$
$$= \lambda_1 \log\left(\int_\Omega e^{u_1}\,dx\right) + \lambda_2 \log\left(\int_\Omega e^{u_2}\,dx\right)$$

The convexity of the Dirichelet energy is a standard result. □

Properties of Equation (5.8).

Let V be a solution of (5.8). Note that solutions commute with translation of V_0, i.e. $V + c$ is a solution to (5.10), if V_0 is replaced by $V_0 + c$ for $c \in \mathbb{R}$. Consequently, in the lemma and theorem statements below, we may without loss of generality shift the boundary data.

The major difficulty in the analysis of V is the nonlocal terms in (5.8). The righthand side of (5.8) does, however, have several properties that can be taken advantage of. We introduce the following notation related to the right hand side of (5.8); given a continuous function W, define $b(W) : \mathbb{R} \to \mathbb{R}$ by

$$b(W)(t) = \alpha \frac{e^t}{\int_\Omega e^{W(y)}\,dy} - \beta \frac{e^{-t}}{\int_\Omega e^{-W(y)}\,dy}. \tag{5.9}$$

Further, define $a(W) : \mathbb{R} \to \mathbb{R}$ by $a(W)(t) = b(W)'(t)$. Note that $a(W)(t) > 0$ for all t and $b(W)(t)$ is strictly increasing in t. Also, define $B(W), A(W) : \Omega \to \mathbb{R}$ by $B(W)(x) = b(W)(W(x))$ and $A(W)(x) = a(W)(W(x))$. Equation (5.8) is then equivalent to

$$\epsilon \Delta V(x) = B(V)(x), \quad \forall x \in \Omega. \tag{5.10}$$

Lemma 7. *Let $V \in C^0(\bar{\Omega})$. Then*

1. $\int_\Omega B(V)\,dx = \alpha - \beta$ and $\int_\Omega A(V)\,dx = \alpha + \beta$.

2. $\nabla B(V) = A(V)\nabla V$ and $\nabla A(V) = B(V)\nabla V$.

3. $B(V)$ is monotone with respect to V in the sense that if $V(x) < V(y)$, then $B(V)(x) < B(V)(y)$.

4. There exists a unique $V_* \in \mathbb{R}$ *such that* $B(V)(x) = a(V)(V_*)\sinh(V(x) - V_*)/2$ *and* $a(V)(V_*) \leq \min_{x\in\Omega} A(V)(x)$.

Proof. (1) and (2) follow immedietly from the definition of $B(V)$ and $A(V)$. (3) follows from the fact $b(V)$ is strictly increasing so that $B(V)(x) = b(V)(V(x)) < b(V)(V(y)) = B(V)(y)$. V_*, the unique zero of $b(V)$ and consequently unique critical point of $a(V)$ can be calculated as:

$$e^{2V_*} = \frac{\beta \int_\Omega e^V \, dy}{\alpha \int_\Omega e^{-V} \, dy}.$$

It is clear that $a(V)(V_*)$ minimizes $a(V)$ and consequently $A(V)$. We check the identity in (4) directly;

$$a(V)(V_*)\sinh(V - V_*) = \alpha\frac{e^V - e^{-V}e^{2V_*}}{\int_\Omega e^V \, dy} - \beta\frac{e^{-V} - e^V e^{-2V_*}}{\int_\Omega e^{-V} \, dy} = 2B(V).$$

□

The above properties hold for all continuous functions V. If, however, V solves (5.10) and $V|_{\partial\Omega} = V_0 \in C^0(\partial\Omega)$ then $B(V)$ and $A(V)$ have additional structures. Lemma 2 shows that $B(V)$ solves a second order equation with a negative zeroth order coefficient bound away from zero. Although the boundary values of $B(V)$ are not known, the equation it solves, in contrast to (5.10), is local and linear. Below we develope positivity criterion for extremal values and comparison functions for $B(V)$. These become important in proving that all non-electroneutral ($\alpha \neq \beta$) solutions diverge as $\epsilon \to 0$ (see Lemma 9, theorem 9.)

Lemma 8. *If* $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ *satisfies* (5.10)*, then* $B(V)$ *has no positive internal local maxima and no negative internal local minima. Further, there exist* $\mu, \theta > 0$ *independent of* ϵ *such that* $\theta \leq a(V)(V_*) \leq \mu$ *for all* $\epsilon \neq 0$ *where* V_* *is given in Lemma 7.*

Proof. Consider the following; $\Delta B(V) = \nabla \cdot (A(V)\nabla V) = B(V)|\nabla V|^2 + A(V)\Delta V$. Note that $\epsilon\Delta V = B(V)$, so that $B(V)$ satisfies

$$\epsilon\Delta B(V) = B(V)(\epsilon|\nabla V|^2 + A(V)). \tag{5.11}$$

Since $A(V) > 0$, it follows that if $B(V)(x_*) > 0$ for some $x_* \in \Omega$, then

$$\Delta B(V)(x_*) > 0$$

so that $B(V)(x_*)$ cannot be a local maximum. Similarly, a negative value cannot be a local mimimum.

By Lemma 7 (4),

$$2\sqrt{\alpha\beta}\left(\int_\Omega e^V\,dx\int_\Omega e^{-V}\,dx\right)^{-\frac{1}{2}} = a(V)(V_*) \le \min_{x\in\Omega} A(V)(x).$$

The lemma is proved if we can show that $\int_\Omega e^V\,dx\int_\Omega e^{-V}\,dx$ is bounded above and below independently of $\epsilon \neq 0$. We have shown that $B(V)$ has no negative internal local minima. Without loss of generality, assume that $\underline{V_0} := \min_{\partial\Omega} V_0 \le 0$. Then $\min\{0, \min B(V)(\underline{V_0})\} \le B(V)(x)$ for all $x \in \Omega$. In particular,

$$-\beta\frac{e^{-V_0(-1)}}{\int_\Omega e^{-V}\,dy} \le \min\{0, B(V)(\underline{V_0})\}$$

which, after some arithmetic, implies that

$$e^{-2V(x)} \le \frac{\alpha\int_\Omega e^{-V}\,dy}{\beta\int_\Omega e^V\,dy} + e^{-V_0(-1)}e^{-V(x)} \quad \forall x \in \Omega.$$

Integrating this inequality over Ω, by Hölder's inequality, we find

$$\frac{1}{2}\left(\int_\Omega e^{-V}\,dx\right)^2 \le \int_\Omega e^{-2V}\,dx \le 2\frac{\alpha\int_\Omega e^{-V}\,dx}{\beta\int_\Omega e^V\,dx} + e^{-\underline{V_0}}\int_\Omega e^{-V}\,dx.$$

Multiplying by $2\int_{-1}^1 e^V\,dx/\int_{-1}^1 e^{-V}\,dx$, we find the inequality below;

$$\int_{-1}^1 e^{-V}\,dx\int_{-1}^1 e^V\,dx \le 4\frac{\alpha}{\beta} + 2e^{-\underline{V_0}}\int_{-1}^1 e^V\,dx. \tag{5.12}$$

Similarly, $B(V)$ has no positive internal maxima so that $B(V)(x) \le \max\{0, B(\overline{V_0})\}$ for all $x \in \Omega$, where $\overline{V_0} = \max_{\partial\Omega} V_0$. An analogous argument to the one above will

give the inequality

$$\int_\Omega e^{-V}\,dx \int_\Omega e^{V}\,dx \le 4\frac{\beta}{\alpha} + 2e^{V_0(1)} \int_\Omega e^{-V}\,dx. \tag{5.13}$$

Finally, we claim that (5.12) and (5.13) imply the result

$$\int_\Omega e^{-V}\,dx \int_\Omega e^{V}\,dx \le C$$

for some $C = C(\alpha, \beta, V_0)$. To see this, let $x = \int_\Omega e^V\,dx$, $y = \int_\Omega e^{-V}\,dx$, $c_1 = 4\alpha/\beta$, $c_2 = 2e^{-\underline{V_0}}$, $c_3 = 4\beta/\alpha$, and $c_4 = 2e^{V_0(1)}$. Then x and y satisfy $xy \le c_1 + c_2 x$ and $xy \le c_3 + c_4 y$. If $x \le y$, then $x^2 \le xy \le c_1 + c_2 x \le c_1 + c_2^2/\eta + \eta x^2$ so that $x \le C(c_1, c_2)$ after choosing η sufficiently less than 1. But then $xy \le c_1 + c_2 x \le c_1 + c_2 C(c_1, c_2)$. If $x \ge y$, the same holds true for $C = C(c_3, c_4)$.

To produce a lower bound, Hölder's inequality shows that

$$4 = \left(\int_\Omega e^{V/2} e^{-V/2}\,dx\right)^2 \le \int_\Omega e^{-V}\,dx \int_\Omega e^{V}\,dx.$$

□

Summary of One Dimensional Results

An interpretation of the one dimensional problem is that of a stationary diffuse charge system, enclosed by two infinite, nonreactive plates with fixed voltage. In the remainder of this section we restrict ourselves to the one dimensional problem, $\Omega = (-1, 1)$, although many othe results extend readily to radially symmetric domains in arbitrary dimensions. The three limiting properties for $\epsilon \to 0$ are

1. If $\alpha = \beta$, then V stays bounded and converge uniformly in the interior to the average of the boundary values. The boundary layer has an ϵ thickness and the limiting profile is exponential.

2. If $\alpha < \beta$, then for sufficiently small ϵ, solutions are convex and converge uniformly to a constant (w.r.t. x) in the interior. This constant is asymptotic to $\log(\epsilon^{-1})$; the lower bound is rigorous, while the upper bound can be demonstrated numericaly.

3. Analogous results hold for $\alpha > \beta$.

Limiting Behaviour in Several Classes

Here we consider solutions of (5.10) for $\Omega = (-1, 1)$ as $\epsilon \to 0$. Two distinct limiting behaviours emerge depending solely on the ratio of α to β. In the case when $\alpha = \beta$ (called electroneutral), theorem 7 demonstrates that solutions stay bounded. For $\alpha \neq \beta$ (non-electroneutral case), Lemma 9 demonstrates that solutions diverge with the order $\log(\epsilon^{-1/2})$. By a bootstrap argument, theorem 9 increases the growth order to $\log(\epsilon^{-1})$. Numerical solutions suggest that this is infact an upper bound on growth as well. All results for $\alpha < \beta$ below have an analogous result for $\alpha > \beta$, where convexity is replaced by concavity, etc.

Theorem 7 demonstrates that electroneutral solutions converge exponentially to the average value of the boundary data, $(V_0(-1)+V_0(1))/2$. These solutions have a boundary layer of thickness ϵ, and exponential boundary layer profile. In particular, the boundary gradients are of order $\epsilon^{-1/2}$. In constrast, non-electroneutral solutions have boundary gradients of order ϵ^{-1}. See theorem 8.

Theorem 7. *Let $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ satisfy (5.10) for $\alpha = \beta$ and $-V(-1) = -V_0(-1) = V(1) = V_0(1) \geq 0$. Then V is odd, monotone, convex for $x \in (0, 1)$ and concave for $x \in (-1, 0)$, and there exist $\eta_{1,2}$ and $g \in C_c^\infty([0, 1))$ independent of ϵ such that*

$$V_0(1)[e^{\eta_1(x-1)/\sqrt{\epsilon}} - e^{-\eta_1/\sqrt{\epsilon}} g] \leq V(x) \leq V_0(1) e^{\eta_2(x-1)/\sqrt{\epsilon}}, \quad x \in (0, 1). \tag{5.14}$$

where $g(0) = 1$ and $g'(0) = 0$.

Remark 2. Commutativity of solutions with the boundary data with respect to addition of a constant implies that we may without loss of generality shift the boundary data so that it is odd.

With g compactly supported in $[0, 1)$, (5.14) implies that $V'(1) = V'(-1)$ is bounded above and below by constant multiples of ϵ^{-1}.

Proof. It is immediate to check that if V satisfies (5.10), then ψ defined by $\psi(x) = -V(-x)$ does as well. By the uniqueness of solutions to (5.10) with given boundary data, $\psi = V$ and consequently V is odd.

Using the oddness of V, one may check that $\int_{-1}^{1} e^V dx = \int_{-1}^{1} e^{-V} dx$. Along with $\alpha = \beta$, this implies that $b(V)(0) = 0$ so that in lemma 7 (4), $V_* = 0$. By lemma 7 (4), we may rewrite (5.10) as

$$\epsilon^2 V'' = \rho \sinh(V)$$

where $\rho = a(V)(V_*)/2 > 0$. Note that $V(-1) \leq 0$ and $V(0) = 0$. Suppose that V is positive somewhere in $(-1, 0)$. Then V has a positive maximum at $x_0 \in (-1, 0)$ such that $0 \leq \epsilon^2 V''(x_0) = \rho \sinh(V(x_0)) > 0$, a contradiction. Thus $V(x) \leq 0$, is convex, and consequently monotone for $x \in (-1, 0)$. By oddness, V is concave and monotone on $(0, 1)$ as well. In particular, $V_0(-1) \leq V(x) \leq V_0(1)$ for all $x \in (-1, 1)$.

By lemma 8 and the above remark, ρ and V are bounded above and below independently of ϵ. Thus there exist $C_{1,2} > 0$ independent of ϵ such that $C_2 V \leq \rho \sinh(V) \leq C_1 V$ for $x \in (0, 1)$. Certainly there exists a g satisfying the hypothesis. (5.14) is then obtained by ODE comparison from above and below with the right and left hand sides of (5.14) respectively, with $\eta_2^2 \leq C_2$ and $\eta_1^2 \geq C_1(1 + \max_{x\in[0,1]} |g(x)|) + \epsilon \max_{x\in[0,1]} |g''(x)|$. □

Lemma 9. *If $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ satisfies (5.10) for $\alpha < \beta$, and $V(-1) = V_0(-1)$, $V(1) = V_0(1)$, then*

$$\max_{x\in(-1,1)} V(x) \geq \log(\epsilon^{-1/2}) + C$$

for some $C = C(\alpha, \beta, V_0)$ independent of ϵ.

Proof. Without loss of generality, assume that $V_0(-1) \leq V_0(1)$. Then, by lemma 7 (1) and lemma 8, $B(V)$ takes a negative value and thus $B(V)(-1) < 0$. Consider the auxiliary function $v(x) = B(V)(-1)[\exp(-\eta(x + 1)/\sqrt{\epsilon}) + \exp(\eta(x - 1)/\sqrt{\epsilon})]$ for $\theta > \eta > 0$ independent of ϵ where θ is the constant given in lemma 8. Note that $v < 0$, $v(\pm 1) \leq B(V)(\pm 1)$ and

$$\epsilon v'' - (\epsilon(V')^2 + A(V))v = v[\eta^2 - \epsilon(V')^2 - A(V)] > 0.$$

By ODE comparison, $v(x) \leq B(V)(x)$ for all $x \in (-1,1)$. Also,

$$\frac{2\sqrt{\epsilon}}{\eta} B(V)(-1)(1 - e^{-2\eta/\sqrt{\epsilon}}) = \int_{-1}^{1} v \, dx \leq \int_{-1}^{1} B(V) \, dx = \alpha - \beta.$$

It follows that $\int_{-1}^{1} e^{-V} \, dx \leq C\sqrt{\epsilon}$ for some $C = C(\alpha, \beta, \eta)$ and thus $V(x_0) \geq \log(\epsilon^{-1/2}) + \log(C)$ for some $x_0 \in (-1,1)$. □

Theorems 8 and 9 both characterize the case $\alpha \neq \beta$. Theorem 9 deals with general boundary values while theorem 8 deals with the specific zero voltage case, $V_0(-1) = V_0(1)$.

Theorem 8. *Let $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ satisfy (5.10) and $V(-1) = V_0(-1)$, $V(1) = V_0(1)$ for $\alpha < \beta$ and $V_0(-1) = V_0(1) = 0$. Then V is even, concave,*

$$V'(-1) = -V'(1) = \frac{(\beta - \alpha)}{2\epsilon} \tag{5.15}$$

and

$$V(0) \geq \log(\epsilon^{-1}) + C \tag{5.16}$$

for some C independent of ϵ.

Proof. Again, one may check that $\psi(x) = V(-x)$ also satisfies (5.10) and $V(-1) = V_0(-1)$, $V(1) = V_0(1)$ and thus $\psi = V$ is an even function.

Differentiating $\epsilon V'' = B(V)$ with respect to x and multiplying by V' we find

$$\epsilon V''' V' = B'(V)(V')^2 = A(V)(V')^2.$$

Due to evenness, $V'(-x) = -V'(x)$ and $V''(x) = V''(-x)$ for all $x \in (-1,1)$. Integrating the above expression over $(-a, a)$ for $0 < a < 1$ gives

$$2\epsilon V''(a)V'(a) = \epsilon V'' V' \Big|_{-a}^{a} = \int_{-a}^{a} (V')^2 + A(V)(V')^2 \, dx.$$

The right hand side is nonnegative so that $V''(a)V'(a) \geq 0$ for all $0 < a < 1$. In particular, this implies that V'' does not change sign on $(0,1)$. Since

$$\alpha - \beta = \epsilon \int_{-1}^{1} V'' \, dx = 2\epsilon \int_{-1}^{0} V'' \, dx,$$

$V'' < 0$ if $\alpha < \beta$. Thus V is convex and positive with maximum $V(0)$.

Integrating $\epsilon V'' = B(V)$ over $(-1, 1)$ with $V'(-1) = -V(1)$ will give (5.15). Mutliplying $\epsilon V'' = B(V)$ by V' we find

$$\frac{\epsilon}{2}((V')^2)' = (A(V))'.$$

Integrating this expression over $(-1, 0)$, $V'(0) = 0$ and (5.15) imply that

$$\frac{(\alpha - \beta)^2}{8\epsilon} = \alpha \frac{1 - e^{V(0)}}{\int_{-1}^{1} e^V \, dx} + \beta \frac{1 - e^{-V(0)}}{\int_{-1}^{1} e^{-V} \, dx}.$$

Certainly, $\int_{-1}^{1} e^V \, dx \leq 2e^{V(0)}$ and $\int_{-1}^{1} e^{-V} \, dx \geq 2e^{-V(0)}$, giving the upper bound

$$\frac{(\alpha - \beta)^2}{4\epsilon} \leq \alpha e^{-V(0)} + \beta e^{V(0)} - (\alpha + \beta).$$

Taking $e^{-V(0)} < 1$,

$$V(0) \geq \ln\left(\frac{(\alpha - \beta)^2}{4\beta\epsilon} + 1\right).$$

□

Theorem 9. *Let $V \in C^\infty(\Omega) \cap C^0(\bar{\Omega})$ satisfy (5.10) and $V(-1) = V_0(-1)$, $V(1) = V_0(1)$ for $\alpha < \beta$ and $V_0(-1) < V_0(1)$. Then there exist $\epsilon_* > 0$ such that for $\epsilon < \epsilon_*$, V is convex and*

$$\max_{x \in (-1,1)} V(x) \geq \log(\epsilon^{-1}) + C_1 \tag{5.17}$$

for some C_1 independent of ϵ. Further,

$$|V(y) - V(x)| \leq \frac{C_2}{\epsilon} e^{-\eta/\sqrt{\epsilon}} (\sinh(\eta y/\sqrt{\epsilon}) - \sinh(\eta x/\sqrt{\epsilon})), \quad 0 < x, y < 1 \tag{5.18}$$

for some $C_2, \eta > 0$ independent of ϵ.

Remark 3. The estimate (5.18) shows that for any compact subset K of $(-1, 1)$, the difference between any two values in this set converges exponentialy to zero, since $-1 + \delta < x$ and $y \leq 1 - \delta$ for some δ depending only on K. Consequently, V converges uniformly to a constant value, e.g. $V(0)$, on K.

Remark 4. Compare the lower bound (5.17) with the numerical upper bound in

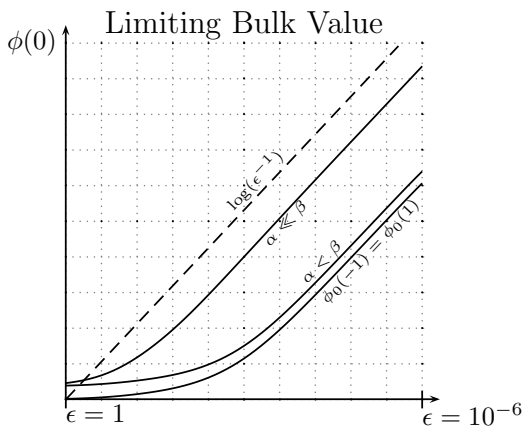

Figure 5.1. Numerical demonstration of upper bound of solution maximum.

figure 5.1.

Proof. By lemma 9, there exists C independent of ϵ and $\epsilon_* > 0$, such that for all $\epsilon < \epsilon_*$, there exists a $y_0 \in (-1, 1)$ for which $V(y_0) > V_0(1)$. In particular, V has an interior maximum for some $x_0 \in (-1, 1)$. Then

$$0 \geq \epsilon V''(x_0) = B(V)(x_0).$$

However, by lemma 7 (3), $B(V)$ is monotone with respect to V, so that $B(V)(y) \leq B(V)(x_0) \leq 0$ for all $y \in (-1, 1)$. Consequently, V is convex and $-V'(-1)$ and $V'(1)$ share the same sign. Thus $\max\{V'(-1), -V'(1)\} \geq \epsilon^{-1}(\beta - \alpha)/2$. Without loss of generality, assume that $V'(-1) = \max\{V'(-1), -V'(1)\}$ and $V_0(-1) = 0$. Following theorem 8, multiplying $\epsilon V'' = B(V)$ by V' and integrating over $(-1, x_0)$, gives

$$\frac{(\alpha - \beta)^2}{8\epsilon} \leq \frac{\epsilon}{2}(V'(-1))^2 = \alpha \frac{1 - e^{V(x_0)}}{\int_\Omega e^V \, dx} + \beta \frac{1 - e^{-V(x_0)}}{\int_\Omega e^{-V} \, dx}.$$

Then the bound $V(x_0) \geq \log(\epsilon^{-1}) + C$ follows exactly as in theorem 8.

Consider, $\epsilon((V')^2)''/2 = \epsilon(V'')^2 + A(V)(V')^2$. By ODE comparison, $(V')^2/2 \leq v$ where $v = (V'(-1))^2/2[\exp(-\eta(x+1)/\sqrt{\epsilon}) + \exp(\eta(x-1)/\sqrt{\epsilon})]$ for $\theta \geq \eta > 0$.

Then

$$\begin{aligned}|V(y)-V(x)| &= \left|\int_x^y V'(s)\,ds\right| \le \left(\int_x^y (V'(s))^2\,ds\right)^{\frac{1}{2}} \\ &\le |V'(-1)|\int_x^y \exp(-\eta(s+1)/\sqrt{\epsilon}) + \exp(\eta(s-1)/\sqrt{\epsilon})\,ds \\ &= |V'(-1)|\frac{2\sqrt{\epsilon}}{\eta}e^{-\eta/\sqrt{\epsilon}}(\sinh(\eta y/\sqrt{\epsilon}) - \sinh(\eta x/\sqrt{\epsilon})).\end{aligned}$$

The theorem follows by noting that $|V'(-1)| \le (\beta-\alpha)/\epsilon$ for $\epsilon \le \epsilon_*$. □

Many of the results in this paper may be generalized to higher dimensions. In particular, lemma 9 holds for all dimensions and domains. If Ω is star shaped, a result similar to theorem 9 follows for the case when V_0 is a constant. In the cases when Ω and V_0 are radially symmetric, most of the above arguments follow with slight modifications. Nevertheless, to be coherent, we have illustrated the properties for solutions of the one dimensional problem only.

5.3 Plug Flow

One of the applications of the theoretical bounds on the structure of solutions to the stationary nonlocal Poisson-Boltzmann equation is in demonstrating the slip velocity induced plug flow phenomena which is not based on asymptotic formalism. In fact, if V can formally be written as a solution to $\epsilon\Delta V = B(V)$ for some function B, then seperation of variables gives the treatment of Poiseuille flow with a Lorentz force.

Consider the infinite channel $U = \Omega\times[-\infty,\infty]$ which is coordinatized by (x,z). We seek solutions to (1.1)-(1.5) of the form $\mathbf{u} = (0,u(x))$, $n = n(x)$, $p = p(x)$ and $V_0 = Ez$ for some constant E. Note that $\mathbf{u}\cdot\nabla n = (0,u(x))\cdot(\nabla_x n, 0) = 0$. Similarly $\mathbf{u}\cdot\nabla\mathbf{u}$ and $\mathbf{u}\cdot\nabla p$ are zero. Applying the previous discussion, we find that for fixed z, $V(x,z)$ is a solution to $\epsilon\Delta V = \epsilon\Delta_x V(x,z) = B(V(x,z))$ and so $\partial_z V = E$. Applying this reasoning, the system (1.1)-(1.5) reduces to the following two equations;

$$\begin{aligned}\nabla_x\pi &= B(V)\nabla_x V \\ \partial_z\pi &= \nu\Delta_x u + B(V)E\end{aligned}$$

The first equation resolves easily since $B(V) = A'(V)$, i.e $\pi = A(V) + f(z)$ for some function f. Differentiating π twice with respect to z and noting that π_z is infact only dependent on x, gives that $f(z)$ is a linear funtion in z. It follows that π_z is a constant, P_0, the pressure drop along the length of the channel. The velocity field is then given by solving the Poisson equation;

$$\Delta_x u = \frac{1}{\nu}(B(V)E + P_0) = \frac{1}{\nu}\Delta(E\epsilon V + Q_0)$$

where Q_0 is the solution of $\Delta P_0 = Q_0$ with $Q_0|_{\partial\Omega} = 0$. Without loss of generality, we assume that $z = 0$ so that, by uniqueness of solutions to the Poisson equation, u may explicetly be expressed

$$u = \frac{E\epsilon}{\nu}V + Q_0.$$

By theorem 8, V exponentially takes atleast the value $\log(\epsilon) + C$ for some $C = C(\alpha - \beta)$ independent of ϵ, in the interior, so that asymoptotically, $u \sim E\epsilon \log(\epsilon)/\nu$ exponentialy into the interior and $u = 0$ at the boundary.

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Vita

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