
THEORY OF CHARGE STORAGE IN NANOSTRUCTURED ELECTRODES

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DECLARATION OF ORIGINALITY

I herewith certify that all material within this document which is not my own has, to the best of my knowledge, been properly declared.

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Abstract

The use of nanostructured electrodes in supercapacitor design have the potential to increase both the specific capacitance, via the superionic effect, and the surface electrode interfacial area optimising the energy stored in such a device. When this increase in specific capacitance was first rationalised the electrodes that formed the supercapacitor were assumed to be ideally metallic. Accordingly, interionic interactions between counterions are exponentially screened by metallic electrons. This allows a denser packing of counter charge than what one would usually assume possible, which in turn leads to an increased specific capacitance. This was named the superionic effect. Modern nanoporous electrodes are predominantly made of carbon materials and are not ideally metallic. To test the applicability of the superionic state to an electrode constructed of non-ideal materials we study Coulomb interaction of charges in cylindrical and slit pores that allow finite electric field penetration into the pore walls. In both geometries the screening is found to be subtly different than in metallic nanopores, but still strong enough to support realization of the superionic state in such pores. Furthermore, the screening is found to be strong enough to neglect long range interactions between ions packed into these pores. Motivated by this we develop several nearest neighbour lattice models of charge storage for electrodes consisting of many similar cylindrical pores wetted with an ionic liquid. Finally, we present a theoretical study of structural deformation that has been seen to occur in carbon electrodes containing pores that are comparable in size to the size of a charging ion. Our model shows qualitative agreement with the features of the experimentally observed expansion caused by variation of electrode potential.

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All of old. Nothing else ever. Ever tried. Ever failed. No matter. Try again. Fail again. Fail better.

— Samuel Beckett

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List of Symbols

This list is not exhaustive but rather includes significant and often used symbols as well as symbols that have several, related meanings, throughout the document. Additionally, symbols referring to common quantities in different models or theories may include a sub/superscript, not listed here, to aid individualization.

Symbol	Description
C	Differential capacitance
e	Elementary charge
E	Energy stored in a pore
f	Free energy per lattice site
F	Total free energy of the system
h	Voltage
h^*	Threshold voltage defined as location of local maximum of χ
H	A canonical Hamiltonian
$\mathcal{H}$	A grand canonical Hamiltonian
J	Interaction energy between charges in the centre of a pore
	Interaction energy between geometrically identical ions in the pore
J_{++}	Interaction energy between cations in the pore
J_{+-}	Interaction energy between cations and anions in the pore
J_{--}	Interaction energy between anions in the pore
ℓ	Axial distance in a cylindrical pore
	The distance between two points located in the centre of a slit pore
	Height coordinate in cylindrical coordinate system
$\ell_{\pm}$	Diameter of a cation or anion
ℓ_0	Diameter of a solvent molecule
L	Length of cylindrical pore
L_{ions}	Length of a chain of N ions in a pore
L_B	Bjerrum length
Continued on next page	

Symbol	Description
L_D	Debye length
$N_{\pm}$	Number of cations, anions or total ions in a pore/sites on a lattice
r	The radius of a cylindrical pore Half the width of a slit pore
s_i	Lattice site spin variable
S	Total spin on a finite lattice
$\underline{T}$	Transfer Matrix
$w_{\pm}$	Energy transfer of a cation and anion from the bulk into the pore
w^*	Threshold energy of transfer between ionophobicities
z	Charge valencies
Z	Canonical partition function
$\mathcal{Z}$	Grand canonical partition function
α	Empirical doping length change constant
δr	Standard deviation of radial distribution
ϵ	Dielectric constant Strain of a pore
κ	Inverse Thomas-Fermi length
$\lambda_+ \lambda_0 \lambda_-$	Eigenvalues of the transfer matrix– $\lambda_+ > \lambda_0 > \lambda_-$ where applicable
$\mu_{\pm}$	Chemical potential of cation and anion
ρ	Radial coordinate in cylindrical coordinate system
$\rho_{\pm} \rho_0$	Density of cations, anion and solvent in pore $\in [0, 1]$
σ	Surface charge density
ϕ	Azimuthal coordinate in cylindrical coordinate system
ψ	Electrostatic potential
χ	Susceptibility
$\langle x \rangle$	The expected quantity x obtained in the mean field The average of quantity x – often averaged between cation and anion
$\tilde{x}$	Difference of a quantity associated with a cation x_+ and the average

Thesis Outline

I have published two first author articles [1, 2] and they form the basis of chapters 2 and 6 respectively. Furthermore, the material presented in chapter 4 is to be published. The thesis was typeset with L^AT_EX using the font Latin Modern. The figures presented were made with Mathematica 10, PowerPoint for Mac 2011 and TikZ.

Outline by Chapter

Chapter 1 - Introduction

We present a brief literature review of electric double layer supercapacitors. Historical models of the double layer in dilute and concentrated electrolytes at a flat electrode are reviewed. Overscreening and lattice saturations effects are discussed, as is Démary's description of overscreening in an ionic liquid [3] which motivated the majority of the work presented in this thesis. Finally, we discuss the use of structured electrodes in supercapacitor design and modern models of the double layer in nanoconfinement.

Chapter 2 - Electrostatic Interactions in Confinement

This chapter is an investigation into the electrostatic interactions of charges inside cylindrical and slit pores that allow electric field penetration into the pore walls. Classical results for the case of an ideal conductor are shown for comparison and completeness while the case of screening in a slit or cylindrical surrounded by a Thomas-Fermi conductor is derived. The results presented in this chapter were published in [1].

Chapter 3 - Charge Storage in Ion Filled Nanotubes

This chapter introduces the concept of mapping ions inside a narrow pore onto a 1D lattice that will be used throughout this thesis, the Ising model of charge storage with ions of the same size and an extension to this Ising model which allows the pore to be charged with ions of different sizes. The material presented in sections 3.1 and 3.2 was first applied to charge storage by Kornyshev [4], the author makes no attempt to claim

the ideas presented here as his own. These sections are included for completeness and pedagogical reasons as Kornyshev's Ising model can be obtained as a particular case of the other lattice models presented in this thesis and it will be illuminating to refer to it when discussing more advanced models. Extending this model to include ions different sizes, section 3.4, is original work of this dissertation.

Chapter 4 - Charge Storage in Solvent Filled Nanotubes

The Ising models of charge storage presented in the previous chapter are both models of a pore fully wetted with ions at all times. In this chapter we present a three species model of charge storage that draws analogies with the Blume-Emery-Griffiths model of magnetism [5]. The trinary nature of this model will allow us to consider a pore that is wetted with ions or a neutral solvent. The state of charging of the pore will be determined by the interplay of the ions interaction with the applied voltage and energetic cost or benefit associated with replacing ions with neutral solvent in the pore. The molecules in the pore are still densely packed and sit in the centre of the pore. To test these assumptions, complimentary Monte Carlo simulations are presented which do not restrict molecules positions within the pore. These simulations agree with the theory. The results presented with ions of the same size was published in [6], the extension to charging the pore with ions of different sized ions is the authors own work and is to be published.

Chapter 5 - Charge Storage in Empty Nanotubes

We introduce a grand canonical model of charge storage in a finite pore. In this model, the spacing between ions will be dependent on the number of ions inside the pore. In many ways, this is a toy model which will allow us to introduce a grand canonical set-up but there is a certain equivalence between this and the BEG model which itself will be interesting to explore.

Chapter 6 - Electroactuation Association with Charge Storage

We present a model of electroactuation of an elastic carbon cylindrical pore. We incorporate changes of the carbon-carbon bond length due to electrochemical doping of the pore walls and steric effects related to counterion insertion into the pore via a modified Ising model of charge storage. When considering the total electrode deformation these effects either compliment or compete with each other depending on the polarisation of the electrode. Our model shows qualitative agreement with the features of the experimentally observed expansion caused by variation of electrode potential. The results presented in this chapter were published in [2].

Chapter 1

Introduction

We present a brief literature review of electric double layer supercapacitors. Historical models of the double layer in dilute and concentrated electrolytes at a flat electrode are reviewed. Overscreening and lattice saturations effects are discussed, as is Démary's description of overscreening in an ionic liquid [3] which motivated the majority of the work presented in this thesis. Finally, we discuss the use of structured electrodes in supercapacitor design and modern models of the double layer in nanoconfinement.

1.1 Electrical Double Layer Capacitors

Electrical double layer capacitors store charge and energy by gathering ions at the surfaces of charged electrodes when polarizing the electrochemical cell to voltages smaller than those required to start electrochemical reactions. The structure of ions that form at the surface of the electrode is called the electrical double layer [7]. The charging and discharging of these devices is relatively fast and can sustain many thousands of cycles without degradation as, ideally, electrochemical reactions at the interface are not involved in capacitive energy storage [8]. This gives double layer capacitors advantages over batteries which have relatively low power density and eventually degrade in time due to electrochemical reactions. The key limitations for such capacitors is that their potential stored energy density is much lower than that usually seen in batteries [9]. As the net electrical capacitance of each electrode is roughly proportional to its accessible surface area electrical double layer capacitors have been made using volume filling porous, nanos-

structured, electrodes. These electrodes, when wetted by electrolyte, can deliver huge interfacial area along which the electrical double layer can form potentially providing a massive increase in energy density [10, 11, 12]. Such devices are called supercapacitors¹ and have found many applications [7, 13, 14].

To understand how supercapacitors store energy we must understand the behaviour of this double layer. In this section we will present an introduction to the theory behind the double layer. We shall start by exploring early attempts to describe the double layer on flat surfaces wetted with dilute electrolyte before moving on to describe the double layer formed on surfaces wetted with ionic liquid. Finally, we will discuss modern models that are required to describe the double layer in the extreme confinement that can arise from using nanostructured electrodes.

1.2 The Double Layer in Dilute Electrolytes

The study of the double layer is not a new field. In 1853 Helmholtz proposed that the application of a voltage to an electrode, wetted with an electrolyte, would cause a single monolayer of counterions in their solvation shells to form adjacent to the electrode and that this layer of ions would screen the electrode linearly across its width [15, 16]. This paper gave the name to the double layer. The Helmholtz double layer is equivalent to a macroscopic parallel plate capacitor with a width comparable to the radius of a solvated ion. As such the capacitance of the Helmholtz layer, C_H , is a constant with regards to the potential applied to the electrode

$$C_H = \frac{\epsilon^*}{4\pi r} \quad (1.1)$$

where ϵ^* is the dielectric constant between the electrode surface and the ions in the double layer, and r is the radius of those solvated ions. Throughout this document we use Gaussian units. Although this model was a large step forward in understanding capacitance it remained unimproved upon for almost 60 years even though this model has several flaws. The most obvious of which is that counterions remain stationary on the surface of the electrode and so there are no thermal variations.

To address this flaw Gouy and Chapman, independently, proposed that the double

¹Devices that store energy via a combination of Faradaic reactions and the electric double layer have also been called supercapacitors but we will not consider that type of device here.

layer could be viewed as a diffusive structure, rather than a rigid one, that would take into account the thermal motion of ions. In this model the electrostatic potential, h , in units of $k_B T/e$, and the concentrations of cations and anions in the electrolyte, $c_{\pm}$, are related via Poisson's equation

$$\frac{d^2 h}{d\ell^2} = -\frac{4\pi e}{\epsilon}(c_+ - c_-) \quad (1.2)$$

where ℓ describes the perpendicular distance away from the electrode surface and $c_{\pm}$ represent the concentration of ions inside the electrolyte². It is assumed that electrolyte is dilute and the concentrations of ions are governed by Boltzmann's equation

$$c_{\pm} = c_0 e^{\mp h} \quad (1.3)$$

where c_0 is the concentration of ions in the bulk. Eqns. (1.2) and (1.3) can be combined to form the Poisson-Boltzmann equation

$$\frac{d^2 h}{d\ell^2} = \frac{8\pi e c_0}{\epsilon} \sinh(h). \quad (1.4)$$

The differential capacitance of the double layer is given by

$$C(h) = \frac{d\sigma}{dh} \quad (1.5)$$

where σ is the surface charge density. Using Gauss' law we can write the surface charge as

$$\sigma = -\frac{\epsilon}{4\pi} \left. \frac{dh}{d\ell} \right|_{\ell=0} \quad (1.6)$$

so that

$$C = -\frac{\epsilon}{4\pi} \frac{d}{dh} \left(\left. \frac{dh}{d\ell} \right|_{\ell=0} \right). \quad (1.7)$$

Eqn. (1.7) and the integral of eqn. (1.4) finally allow us to write down the capacitance in the Gouy-Chapman model

$$C_{GC} = \frac{\epsilon}{4\pi L_D} \cosh(h/2), \quad L_D = \sqrt{\frac{1}{8\pi L_B c_0}}, \quad (1.8)$$

where L_D is called the Debye length and $L_B = e^2/k_B T$ is the Bjerrum length. This Gouy-Chapman model is similar to the Debye-Hückel model³ which describes the ionic atmosphere of an ion in an electrolyte [17, 18]. The differential capacitance, as well

²We consider a 1-1 electrolyte for simplicity.

³The Debye-Hückel model, proposed a decade after the Gouy-Chapman model, is also based on the Poisson-Boltzmann equation.

as the counter charge density and the electrostatic potential in the electrolyte, in this model, are dependent on ion concentration in the solution, temperature and electrostatic potential of the electrode. The counter charge density and the electrostatic potential in the electrolyte both decay with distance away from the electrode while the differential capacitance has a minimum at zero volts and diverges at larger voltages. This divergence arises as ions are considered as point particles. If one increases the electrode potential there is no upper limit on the counter charge density or on the distance that the center of mass of the counter charge distribution can approach the electrode surface. This allows the Gouy-Chapman model to predict an unbounded capacitance as electrode potential increases.

To overcome this problem Stern suggested that it is better to view the double layer as two separate regions, a compact Helmholtz layer, adjacent to the electrode and a diffusive Gouy-Chapman layer extending into the bulk solution [19]. The inclusion of a Helmholtz layer partially addresses the lack of steric interactions near the electrode in the Gouy-Chapman model. The capacitance of this Gouy-Chapman-Stern model is simply the combination of capacitance from the Helmholtz and Gouy-Chapman regimes given by

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{GC}}. \quad (1.9)$$

At small electrode potentials C has a contribution from C_{GC} but as the capacitance of the Gouy-Chapman layer diverges at larger potentials C tends to the constant C_H from below. The compact double layer in this model is dependent only on the radius of the solvated ion and the dielectric constant between the electrode and the ion adjacent to it. It is independent of ionic concentration.

Many more involved models of the double layer on a flat surface with a dilute electrolyte have been developed [20], notably models that incorporate, the specific adsorption of ions [21, 22, 23, 24], the role of polar solvent at the interface [25], electron transfer reactions near at the electrode [26] and models that consider the capacitance of the electrode [27, 28].

Optimising the Energy Stored by the Double Layer

The energy stored per surface area by the double layer, or in fact any capacitor, between zero and h voltages is given by

$$E = \int_0^h \eta C(\eta) d\eta. \quad (1.10)$$

This formula suggests several ways to optimise the total energy stored per volume in a supercapacitor: One can widen the voltage window at which the capacitor can reliably and repeatedly operate, increase the surface area available for the formation of the double layer or increase the capacitance at large voltages. The optimisation of the capacitance can be achieved once we have a suitable model of the double layer, however the optimisation of the voltage window and electrode surface area will dictate the type of model we must use or develop. We shall address these first two points in turn.

1.3 The Double Layer in Ionic Liquids

Increasing the voltage window of the supercapacitor mainly involves an adroit choice of electrolyte. If our electrolyte has an aqueous component then electrolysis will occur at the electrode once a voltage of about 1.25V is applied [29]. This would damage and ultimately destroy the supercapacitor. To move to higher voltages we must use a suitable non-aqueous electrolyte with a wider voltage window. This has driven interest in supercapacitors constructed using ionic liquids, some of which have a stable electrochemical window of 6V [30, 31, 32].

An ionic liquid is a salt in a liquid state. Typically, the ionic liquids that are used for supercapacitor design are liquid at room temperature and atmospheric pressure rather than molten salts which enter a liquid phase at higher temperatures. Naïvely, one would assume that without a neutral solvent to increase the range of interaction between two ionic molecules, a purely ionic material would be solid at room temperature due to the strength of the ionic bond. This is not the case, as size and shape effects between vastly asymmetric ionic molecules can increase the system entropy lowering the melting point to below room temperature [33, 34]. Incorporating this asymmetry between the size of cations and anions will be a priority for any model of the double layer with ionic liquids.

The first room temperature ionic liquids have been known about for more than a century [35] but it was not until the discovery of new moisture stable room temperature ionic liquids [30, 36] less than 20 years ago that ionic liquids found uses in mainstream electrochemistry [37, 38, 39, 40, 41]. Many different ionic liquid forming cations and anions are now known. These ions can be mixed together and, with some trial and error, provide bespoke liquids with a tunable array of properties [33, 34, 42].

Simulations of electrodes wetted with concentrated electrolytes [43, 44], molten salts [45] and early experimental work of flat electrodes wetted with ionic liquids [46, 47, 48] suggested that Gouy-Chapman-Stern theory does not reproduce the behaviour of the double layer. This is to be expected as the Gouy-Chapman component of this theory is derived in the limit of low ion concentration. In higher ionic concentrations steric effects, arising from finite ion size, become important throughout the liquid, not just at the interface, and must be considered.

The Poisson-Boltzmann equation that gave rise to Gouy-Chapman model of the double layer can be modified to include these steric, as well as other, effects between ions and the electrode. For an overview of such models see the reviews [49, 50]. We focus on one such modified Poisson-Boltzmann model that was first proposed as a model of steric effects in concentrated electrolytes by Bikerman in 1942 [51]. This paper was overlooked at the time as it was experimentally difficult to verify but the theory itself has proven resilient being reformulated independently several times [52, 53, 54, 55, 56]. For a full history of this rediscovery see [57]. While Bikerman's approach was to apply volume constraints to the Poisson-Boltzmann theory the same modified Poisson-Boltzmann theory can be derived from a statistical physics viewpoint. We shall discuss this technique here but we shall still call this Bikerman's theory. The method we will discuss was developed and first applied to solvent free ionic liquids in [58].

We consider the electrolyte as a charged 3D lattice gas in contact with the electrode. Cations and anions are physically identical and sit on lattice sites. These sites can either be occupied or empty. The proportion of occupied lattice sites in the bulk is controlled by the parameter γ . This factor can be called the compacity [59] which is the volume fraction filled in a granular medium. A dense system in the bulk is represented by $\gamma = 1$ while a completely dilute and sparse system would have compacity $\gamma = 0$. For $\gamma < 1$ the influences of a local potential can cause a change in local density of the lattice gas. It can be shown in a mean field approximation [58] that excluded volume effects cause the concentration of ions in such a lattice gas to obey Fermi-Dirac like statistics as a function

of potential in the electrolyte

$$c_{\pm} = \frac{c_0 e^{\mp h}}{1 + 2\gamma \sinh^2(h/2)}. \quad (1.11)$$

This is a modification of the Boltzmann equation, eqn. (1.3), that we used when deriving the Gouy-Chapman capacitance. This formula can be adapted to include ion asymmetry [58]. The differential capacitance of an electrode in contact with this lattice gas, C_B , can be obtained by combining equations (1.2), (1.7) and (1.11) giving

$$C_B = \frac{\epsilon}{4\pi L_D} \cosh(h/2) \frac{1}{1 + 2\gamma \sinh^2(h/2)} \sqrt{\frac{2\gamma \sinh^2(h/2)}{\ln(1 + 2\gamma \sinh^2(h/2))}}. \quad (1.12)$$

The behaviour of this capacitance for a variety of compacities is shown in figure 1.1. There are two shapes for capacitance curves, a bell curve for $\gamma \geq 1/3$ and a camel⁴ shaped curved for $\gamma < 1/3$. The Gouy-Chapman capacitance is recovered for a dilute electrolyte, $\gamma \rightarrow 0$. Importantly, for all compacities greater than zero, the capacitance decays at large voltages. This is the lattice saturation effect [58, 60]. It is a steric phenomenon. As lattice sites near the electrode are filled with counterions, additional counterions cannot collect adjacent to the electrode but must instead form a thicker double layer. This causes a decrease in the differential capacitance at large voltages. We shall see similar lattice saturation effects in all the models of capacitance developed in this thesis.

Experimental work carried out after the proposal of eqn. (1.12) have observed bell and camel shaped differential capacitance curves for a flat electrode wetted with various ionic liquids [61, 62, 63]. This mean field theory is not without its limitations. The compacities of an ionic liquid are difficult to estimate ab initio, so that the shape of the differential capacitance curve is not generally known until it is measured. Furthermore, this mean field theory does not tell us anything about the physical structure of the double layer [64]. Importantly, this theory lacks the Coulombic correlations between ionic liquids molecules that one would expect to dominate at low electrode voltages in dense ionic systems. Simulations [65, 66, 67, 68, 69], X-ray relectometry [70] and atomic force microscopy [71] have shown that these short range correlations cause the first layer of counter charge adjacent to the electrode to contain more charge than the electrode at low electrode voltages in dense ionic systems. This effect was called overscreening. In response to this overscreening layer of counterions, a second layer of (co-)ions, with opposite polarity to the first, forms. This process continues as alternating ‘slabs’ of decaying quantities of charge form adjacent to the electrode until the potential is fully

⁴A Bactrian camel.

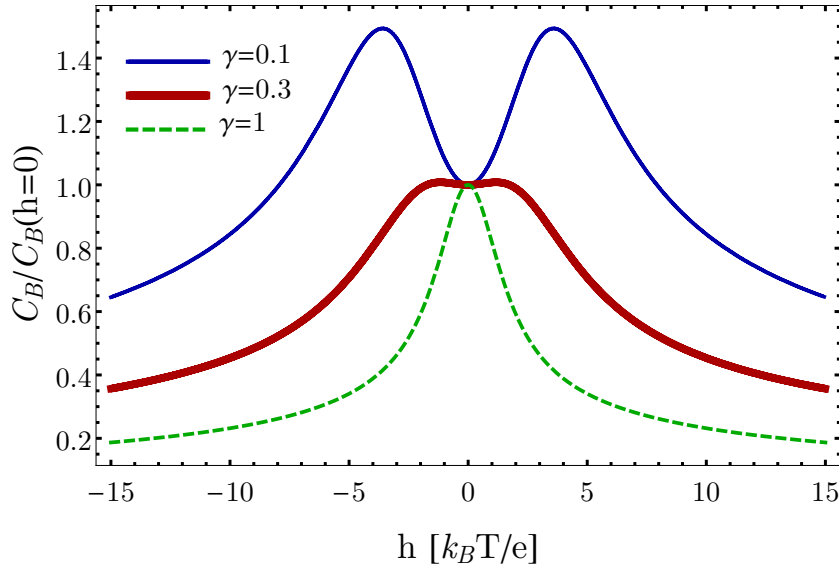


Figure 1.1: Differential capacitance, eqn. (1.12), of a flat electrode wetted by an ionic liquid [58]. The parameter γ is known as the compacity and roughly describes the compressibility of the ionic liquid, an incompressible liquid is described by $\gamma = 1$ and infinitely compressible liquid by $\gamma = 0$.

screened. At larger potentials lattice saturation effects win out and these short ranged correlations become negligible near the electrode, a phenomenological model detailing the transition from overscreening to lattice saturation or crowding, was developed by Bazant et al. [72].

Démery et al. developed a 1D description of the double layer in a dense system using a Coulomb gas model that admits an exact solution [3, 73, 74]. In this model, the 3D electrolyte in contact with the electrode is divided up into 2D slabs of charge. Each layer of charge is then represented by a single site in a 1D lattice running perpendicular to the electrode that could either be filled with a cation, an anion or a void. While this model has its limitations, it did provide a mathematically rigorous basis for the phenomena of overscreening and eqn. (1.12) can be recovered in a mean field approximation. Indeed, this initial work in this area formed the inspiration for the lattice models of charge storage that will be presented in this thesis.

1.4 Confinement – Nanostructured Electrodes

Increasing the surface area of the electrode increases the number of charged ions that can accumulate at the liquid-electrode interface. Accordingly, increasing the surface area of the electrode should increase the total capacitance of the electrode. To achieve this increase without increasing the volume taken up by the electrode we must structure the electrode surface. As one would expect, driven by the potential applications, this field is an active area of research and there have been many recent advances in electrode fabrication techniques. Novel carbon electrode materials such as, activated carbon, templated carbon, carbide derived carbons, carbon fibres, nanotubes, carbon onions and carbon nanohorns are of particular interest and have all been tested for their supercapacitor applications [75, 76, 77, 78, 79, 80, 81]. These carbon materials can be light, good electrical conductors, electrochemically inert at large voltages and importantly are relatively easy to fabricate. The fabrication of carbide derived carbon is especially interesting. It is a porous material and its average pore size can be tuned in the nanometre range by modifying the fabrication technique [82]. The finer the pores, the greater the surface area per unit volume of the electrode and the higher the total capacitance per unit volume, that is as long as the electrolyte can still enter such pores [10, 83, 84].

Experimental investigations of the differential capacitance of electrodes constructed of nanoporous materials have shown an interesting effect [85, 86]. The capacitance per unit surface area, the specific capacitance, initially increases as the average pore size of the electrode becomes smaller than a nanometre and then rapidly decays to zero when the average pore size becomes smaller than the size of the ion. The decay to zero is easy to understand, extremely small pores are inaccessible to ions and there can be no accumulation of charge. However, the increase in capacitance per unit surface area in accessible sub-nanometre pores was a surprise and even earned the title the anomalous increase of the capacitance [85].

Unfortunately, most models of the double layer on flat electrodes can be used only when the size of the double layer is much smaller than the volume adjacent to the electrode in which the double layer forms. These models can be modified to include surface roughness [87, 88] but they are wholly non-applicable to nanostructured electrodes and will not shed any light on this anomalous increase of the capacitance. To rationalise this anomalous capacitance the idea of a superionic state of ions in nanoporous electrodes was introduced via a semi-phenomenological theory [89], statistical mechanical models [90] and computer simulations [90, 91, 92]. It was proposed that electrostatic interaction of

ions inside a conducting nanopore would be exponentially screened by the pore walls [93]. This exponentially strong screening allows the packing of more ions of the same sign into the pore when polarizing it relative to the bulk of electrolyte than it would have been possible if the electrostatic repulsion between them was unscreened. This increases the accumulated surface charge and ultimately the specific capacitance. The decay range of screening grows with pore size. The larger the pore, the stronger the ions will interact with each other, the more difficult it will be to charge the pore, and the smaller the pores specific capacitance. Additionally, the capacitance of a single pore has been seen to oscillate as a function of pore radius in computer simulations [94, 95, 96]. This capacitance oscillation is caused by a layering effect. The capacitance decays as the pore becomes wider, decreasing the screening effect, and then jumps up once the pore is wide enough to admit another row of ions. Such oscillations will be difficult to identify in an electrode with any significant pore width dispersion.

The superionic state and its potential to increase the specific capacitance while increasing the porosity of the electrode and therefore increasing the energy density of a supercapacitor has motivated research in the area of charge storage in nanoconfinement. While computer simulations [92, 97, 98] can cope with a disordered nanoporous electrode a theoretical model usually requires some regularity in the electrode to make it tractable. As such the first theoretical models of these systems focused on charge storage in regular slit or planar pores [89, 90, 91, 99, 100] and cylindrical pores [4, 6, 101]. In these geometries the theory of charge storage can be reduced to a 2 or 1D problem. In chapters 3, 4 and 5 we will introduce several such models of charge storage in cylindrical nanopores. Additionally, early studies of the superionic state considered the electrode, in terms of screening, as an ideal metal [89, 91]. First attempts to move beyond this approximation were reported in [90]. In chapter 2 we will study the effects of non-ideal screening, using the models of field penetration into the electrode for slit and cylindrical pores comparing the results to the respective ideally screening case.

Utilizing nanopores of the order of the size of a few ions can have side effects. It may be impractical for ions to pass each other in such confinement preventing the electrode from fully charging or discharging. Furthermore, molecules moving in narrow channels will incur greater ohmic losses due to Knudsen diffusion [102], slowing the charging dynamics, unless special measures are taken [103]. These side effects are concerned with charging dynamics rather than a supercapacitor's ability to store energy and are not generally destructive to a supercapacitor but they can undermine power delivery. Another, more nefarious, side effect is the potential deformation of the electrode that might result from the charging/discharging process. Nanostructured carbon materials are not absolutely

rigid and electrodes made of such materials have been seen experimentally, via dilatometry studies, to swell upon charging [104, 105, 106], a first model interpretation was given to this effect in [106]. The effect of ‘electrode breathing’ with voltage variation can, after a large number of cycles, wear the system, causing cracks, detachments and even short cuts. This will undermine the longevity of supercapacitors. In chapter 6 we present a statistical-mechanical analysis of this swelling which aims to provide a theoretical understanding of this effect in long narrow pores.

Chapter 2

Electrostatic Interactions in Confinement

This chapter is an investigation into the electrostatic interactions of charges inside cylindrical and slit pores that allow electric field penetration into the pore walls. Classical results for the case of an ideal conductor are shown for comparison and completeness while the case of screening in a slit or cylindrical surrounded by a Thomas-Fermi conductor is derived. The results presented in this chapter were published in [1].

2.1 Cylindrical and Slit Pore Geometries

Interionic interactions in conducting nanopores determine how counterions may be packed in the pores subject to the applied voltage. In ideal metals, interactions are exponentially screened by metallic electrons. However, modern nanoporous electrodes are not necessarily made from ideally screening materials. To what extent is this screening affected by a different mode of dielectric response in such materials? To answer this question we study the Coulomb interaction of charges in cylindrical and slit pores that allow finite electric field penetration into the pore walls and judge if this interaction is screened enough to support realization of the so called superionic state in such pores.

We consider the electrostatic interactions of two point charges in either a cylindrical or a slit geometry. In a cylindrical geometry the two charges, separated by a distance ℓ ,

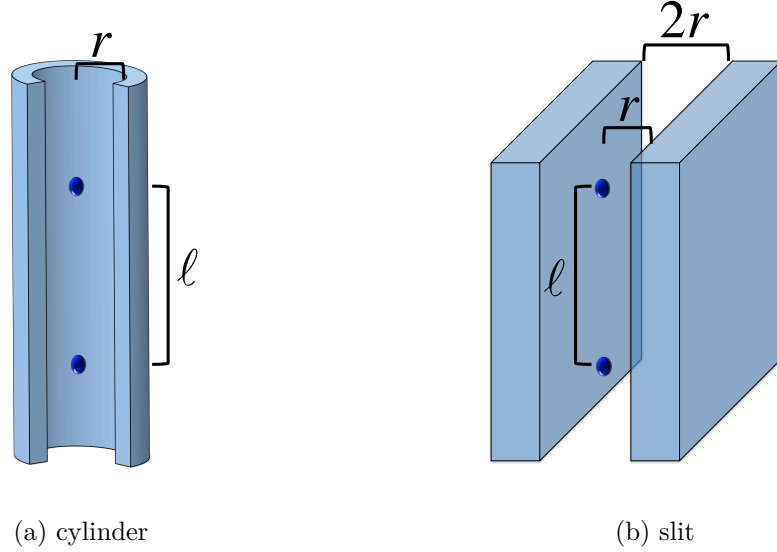


Figure 2.1: Two point charges placed in the center of a cylindrical and slit pore. The interior of the pore is referred to as region 1 in the following section and the screening material, region 2, surrounding the charges is assumed extend to infinity away from the charges.

sit in the centre of an infinitely long cylinder of radius r . This cylinder is surrounded by the material that will screen the interaction between the charges, figure 2.1a. In a slit geometry the two charges, separated by a distance ℓ , sit in between two parallel semi-infinite conducting slabs. The distance to both slabs from both charges is r , the ‘radius’ or rather the half width of the slit, figure 2.1b.

For each geometry we will present expressions for the corresponding Green’s function, $\psi(\ell)$. This is the potential, at a distance ℓ , due to one unit point charge located in the middle of the pore, created on the symmetry axis for a cylindrical pore or the central plane in a slit pore. The interaction energy $J(\ell, r)$ between two charges within the same geometry can be then calculated using

$$J(\ell, r) = z_1 z_2 e^2 \psi(\ell, r) \quad (2.1)$$

where z_1 and z_2 are the respective charge valencies and e elementary charge.

Throughout this document we will use the notion of an effective dielectric constant of the interior of the pore. The nature of the dielectrics contribution to the screening of charge-charge interactions may be different in different contexts. If we intend to describe interionic interactions in a pore fully filled with ionic liquid ions, the dielectric will take

into account the electronic polarizability of the ions. If the ionic liquid is mixed with solvent, the solvent's electronic polarizability as well as vibrational modes may contribute to the value of the dielectric in the interior of the pore. Most importantly, the latter may become dependent on the pore width, which will affect the variation of the interionic pair potential with the width or diameter of the pore. For a discussion of the consequences of such a dependence see [107]. This effect will not be considered in this document.

2.2 Ideal Screening in Cylindrical and Slit Pores

In a slit pore surrounded by ideal metal the potential of a charge is given by

$$\psi = \frac{2}{\epsilon r} \sum_{n=1}^{\infty} K_0 \left((2n-1) \frac{\ell \pi}{2r} \right) \quad (2.2)$$

where $K_0(x)$ is the modified Bessel function of the second kind of zeroth order. Here ϵ is the dielectric constant of the interior of the pore [108]. Using the asymptotic behaviour $K_0(x) \sim e^x \sqrt{\frac{\pi}{2x}}$ for $x \gg 1$ [109], one finds a simple law

$$\psi = \frac{2}{\epsilon \sqrt{r \ell}} \exp \left(-\frac{\ell \pi}{2r} \right), \quad \ell \gg 2r/\pi. \quad (2.3)$$

A similar expression for the potential of a charge in a cylindrical pore, of radius r , surrounded by ideal metal exists [93]

$$\psi = \frac{2}{\epsilon r} \sum_{m=1}^{\infty} \frac{\exp \left(-\frac{k_m \ell}{r} \right)}{k_m [J_1(k_m)]^2} \quad (2.4)$$

here $J_1(k_m)$ is the first order Bessel function and k_m are roots of the Bessel function of zeroth order. For $\ell \gg r$ it is sufficient to keep only the first term of the series, so that

$$\psi \underset{\ell \gg r}{\simeq} \frac{3.08}{\epsilon r} \exp \left(-2.4 \frac{\ell}{r} \right). \quad (2.5)$$

If the radius of a cylindrical pore is the same as the half width of a slit pore then the screening of a charge is stronger in the cylindrical pore as the screening metal surrounds the two charges from all sides in a cylinder. This allows the counter-charge distribution, in the screening metal, to form on all sides around the internal point charge and thus the potential decays more rapidly as you move away from the charge. If we consider

a slit pore of width $2r$ and a cylindrical pore of diameter $2r$, the decay range of the electrostatic interaction is $r/1.67$ in a slit pore, and $r/2.4$ in a cylindrical pore. Although these different geometries provide different screening, there are several common elements to eqns. (2.2) and (2.4). Most importantly, the potential is *exponentially* screened when the separation of two charges is of the order of the pore diameter or larger. If there were a lattice of charges in the centre of the pore with a spacing only slightly smaller than the pore width then only the electrostatic interactions of charges adjacent to each other should be taken into account. The interactions of next nearest neighbour charges and beyond can be neglected.

2.3 Thomas-Fermi Screening in a Cylindrical Pore

We consider a point charge located at the center of a cylinder of radius r surrounded by a Thomas-Fermi metal. We denote the region inside the cylinder as region 1 with dielectric constant ϵ . Region 2, outside the pore, will be characterized by background dielectric constant ϵ_2 and inverse Thomas-Fermi length κ . We use cylindrical polar coordinates: ℓ is the distance along the symmetry axis of the cylinder from the charge, ρ for radial distance and ϕ for the azimuthal angle.

Inside region 1 the potential, ψ , satisfies Laplace's equation, with a delta function source at the origin

$$\nabla^2 \psi = -4\pi \frac{\delta(\rho)}{\epsilon} \frac{\delta(\ell)}{2\pi\ell}. \quad (2.6)$$

Inside region 2 the potential, ψ_2 , satisfies the Thomas-Fermi equation

$$\nabla^2 \psi_2 - \kappa^2 \psi_2 = 0. \quad (2.7)$$

The boundary conditions in this geometry are

$$\psi(\rho = r) = \psi_2(\rho = r), \quad (2.8)$$

$$\epsilon \left[\frac{\partial \psi}{\partial \rho} \right]_{\rho=r} = \epsilon_2 \left[\frac{\partial \psi_2}{\partial \rho} \right]_{\rho=r}. \quad (2.9)$$

We focus on the potential inside region 1. Inside this region the potential, ψ_1 , is given by

$$\psi_1 = \frac{1}{\epsilon_1} \int_0^\infty dk \cos(k\ell) \left[\frac{2}{\pi} K_0(k\rho) + g(k) I_0(k\rho) \right], \quad (2.10)$$

where $g(k)$ is a function to be determined by the boundary conditions.

Inside region 2 the potential, ψ_2 , satisfies the Thomas-Fermi equation, eqn. (2.7). The Thomas-Fermi equation can be solved by separation of variables. Denoting $\psi_2 = P(\rho)\Phi(\phi)\bar{\ell}(\ell)$,

$$\frac{1}{P\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial P}{\partial\rho}\right) + \frac{1}{\Phi\rho^2}\frac{\partial^2\Phi}{\partial\phi^2} - \frac{1}{\bar{\ell}}\frac{\partial^2\bar{\ell}}{\partial\ell^2} - \kappa^2 = 0, \quad (2.11)$$

we let

$$\frac{1}{\bar{\ell}}\frac{\partial^2\bar{\ell}}{\partial\ell^2} = -k^2 \rightarrow \bar{\ell} = A_1 \cos(k\ell) + A_2 \sin(k\ell). \quad (2.12)$$

Substituting this back into eqn. (2.11), we obtain

$$\frac{\rho}{P}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial P}{\partial\rho}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} - (k^2 + \kappa^2)\rho = 0 \quad (2.13)$$

and letting

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2 \rightarrow \Phi = B_1 \sin(m\phi) + B_2 \cos(m\phi)$$

we obtain

$$\frac{\rho}{P}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial P}{\partial\rho}\right) - m^2 - (k^2 + \kappa^2)\rho = 0.$$

The solution of this equation can be expressed using modified Bessel functions

$$P = C_1 I_m\left(\rho\sqrt{k^2 + \kappa^2}\right) + C_2 K_m\left(\rho\sqrt{k^2 + \kappa^2}\right).$$

As $\psi_2 \rightarrow 0$ when $\rho \rightarrow \infty$, we can express ψ_2 in terms of

$$\psi_2 = \int_0^\infty dk \cos(k\ell) f(k) K_0\left(\rho\sqrt{k^2 + \kappa^2}\right). \quad (2.14)$$

where $f(k)$ is a function to be determined by boundary condition matching. Considering the boundary condition in eqn. (2.8) gives

$$K_0(\gamma kr) f(k) = \frac{2}{\pi} K_0(kr) + g(k) I_0(kr), \quad (2.15)$$

where $\gamma = \sqrt{1 + (\kappa/k)^2}$ and the boundary condition in eqn. (2.9) gives

$$-\frac{\epsilon_2}{\epsilon_1} \gamma K_1(\gamma kr) f(k) = g(k) I_1(kr) - \frac{2}{\pi} K_1(kr), \quad (2.16)$$

Substituting eqn. (2.15) in to eqn. (2.16), and after some algebra, we obtain

$$g(k) = \frac{2}{\pi} \frac{K_1(kr) K_0(\gamma kr) - \frac{\epsilon_2}{\epsilon_1} \gamma K_1(\gamma kr) K_0(kr)}{\frac{\epsilon_2}{\epsilon_1} \gamma K_1(\gamma kr) I_0(kr) + I_1(kr) K_0(\gamma kr)}. \quad (2.17)$$

When $\rho = 0$, corresponding to charge on the axis of the cylinder, the potential at a distance ℓ inside the cylinder reads

$$\psi_1 = \frac{1}{\epsilon_1} \int_0^\infty dk \cos(k\ell) \left[\frac{2}{\pi} K_0(k\ell) + g(k) \right]. \quad (2.18)$$

Evaluating the first term in this equations yields the desired result,

$$\psi = \frac{1}{\epsilon\ell} + \frac{2}{\pi\epsilon} \int_0^\infty dk \cos(k\ell) \frac{K_1(kr)K_0(\gamma kr) - \frac{\epsilon_2}{\epsilon}\gamma K_1(\gamma kr)K_0(kr)}{\frac{\epsilon_2}{\epsilon}\gamma K_1(\gamma kr)I_0(kr) + I_1(kr)K_0(\gamma kr)}. \quad (2.19)$$

2.4 Screening in a Slit Pore

Now we consider a slab rather than a cylindrical geometry. We place a point charge in the middle of a slab of width $2r$, this slab we denote as region 1 with dielectric constant ϵ . Either side of region 1 we place semi-infinite slabs. Region 2, outside the middle slab, will be characterized by a background dielectric constant ϵ_2 and inverse Thomas-Fermi length κ . Inside region 1 the potential, ψ , satisfies the Laplace's equation, eqn. (2.6) and inside region 2 the potential, ψ_2 , satisfies the Thomas-Fermi equation, eqn. (2.7). The 4 boundary conditions at the slab interfaces are given by

$$\psi(\rho = \{-r, r\}) = \psi_2(\rho = \{-r, r\}), \quad (2.20)$$

$$\epsilon \left[\frac{\partial \psi}{\partial \rho} \right]_{\rho=\{-r, r\}} = \epsilon_2 \left[\frac{\partial \psi_2}{\partial \rho} \right]_{\rho=\{-r, r\}}. \quad (2.21)$$

To solve these equations we make use of the solution for the electrostatic screening by an ideal metal in the same geometry. To do this we make eqn. (2.6) homogeneous and use the solution to this ideal case as a particular integral for the Thomas-Fermi case.

2.4.1 Ideal Screening in a Slit Pore

The potential, ψ , of a charge in the central region (region 1) of a slit pore surrounded by an ideal metal satisfies eqn. (2.6). However, as region 2 consists of ideal metal, the potential is constant in this region and may be taken for zero. Our boundary conditions are enforced by the condition that potential must vanish at the interface between region 1 and 2

$$\psi(\rho = \{-r, r\}) = 0. \quad (2.22)$$

First, we take the Hankel transform of eqn. (2.6)

$$\frac{\partial^2 \hat{\psi}}{\partial \rho^2} - k \hat{\psi} = -2\delta(\rho)/\epsilon \quad (2.23)$$

where

$$\hat{\psi} = \int_0^\infty \psi J_0(k\ell) \ell dk. \quad (2.24)$$

To find the general solution of eqn. (2.23) we divide the ρ axis into two separate domains, $-r < \rho < 0$ and $0 < \rho < r$ such that $\hat{\psi}_- \in -r < \rho < 0$ and $\hat{\psi}_+ \in 0 < \rho < r$. As these domains do not include the δ -function we need to solve the equations

$$\frac{\partial^2 \hat{\psi}_\pm}{\partial \rho^2} - k \hat{\psi}_\pm = 0. \quad (2.25)$$

The solutions of eqn. (2.25) can easily be obtained using the boundary conditions given in eqn. (2.22)

$$\hat{\psi}_+ = A \sinh[k(\rho - r)], \quad (2.26)$$

$$\hat{\psi}_- = B \sinh[k(\rho + r)]. \quad (2.27)$$

We require that $\hat{\psi}$ be continuous over the combined domain $-r < \rho < r$, therefore we require that $\hat{\psi}_+(\rho = 0) = \hat{\psi}_-(\rho = 0)$, implying that $A = -B$. Integrating eqn. (2.23) over the interval $[0^-, 0^+]$ we find that the first derivative of $\hat{\psi}$ is discontinuous,

$$\frac{\partial \hat{\psi}(\rho = 0^+)}{\partial \rho} - \frac{\partial \hat{\psi}(\rho = 0^-)}{\partial \rho} = -2/\epsilon. \quad (2.28)$$

Using the discontinuity of the first derivative one finds

$$A = \frac{1}{\epsilon k \cosh[kr]} \quad (2.29)$$

thus

$$\hat{\psi}_+ = \frac{\sinh[k(\rho - r)]}{\epsilon k \cosh[kr]}, \quad (2.30)$$

$$\hat{\psi}_- = \frac{\sinh[k(\rho + r)]}{\epsilon k \cosh[kr]}. \quad (2.31)$$

Writing this concisely we have

$$\hat{\psi} = \frac{\sinh[k(r - |\rho|)]}{\epsilon k \cosh[kr]}. \quad (2.32)$$

Taking the inverse Hankel transform retrieves the electrostatic potential

$$\psi(\rho, \ell) = \frac{1}{\epsilon} \int_0^\infty J_0(k\ell) \frac{\sinh[k(r - |\rho|)]}{\cosh[kr]} dk. \quad (2.33)$$

In the center of the pore, $\rho = 0$, the potential of a charge screened by two slabs of ideal metal takes a particularly simple form

$$\psi(\rho = 0, \ell) = \frac{1}{\epsilon} \int_0^\infty J_0(k\ell) \tanh(kr) dk. \quad (2.34)$$

Although this equation looks different to the series representation for ψ in a slit pore we gave in eqn. (2.2) all is still well. This integral representation can be converted into eqn. (2.2) by closing a contour around the upper right complex quadrant and then counting the poles generated by the hyperbolic tangent on the positive complex axis in a manner similar to Matsubara Summation.

2.4.2 Thomas-Fermi Screening in a Slit Pore

We begin by taking Hankel transforms of eqn. (2.7) and the homogeneous version of eqn. (2.6), which is now truly Laplace's equation, and look for solutions of the following form:

$$\hat{\psi} = C_1 \exp^{k\rho} + C_2 \exp^{-k\rho} + \frac{\sinh[k(r - |\rho|)]}{\epsilon k \cosh[kr]}, \quad (2.35)$$

$$\hat{\psi}_2 = C_3 \exp^{-\rho\sqrt{k^2 + \kappa^2}} \text{ for } \rho > 0, \quad (2.36)$$

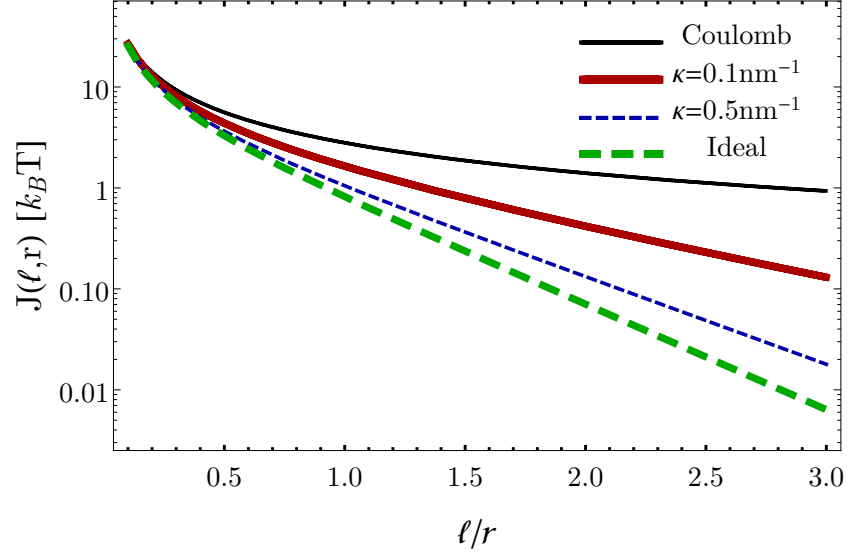
$$\hat{\psi}_2 = C_4 \exp^{\rho\sqrt{k^2 + \kappa^2}} \text{ for } \rho < 0, \quad (2.37)$$

where we have already imposed the trivial boundary conditions that the potential must decay at infinity. The third term on the right of $\hat{\psi}$ is the particular case which will give us our charge and originates from eqn. (2.32). Implementing the other boundary conditions yield

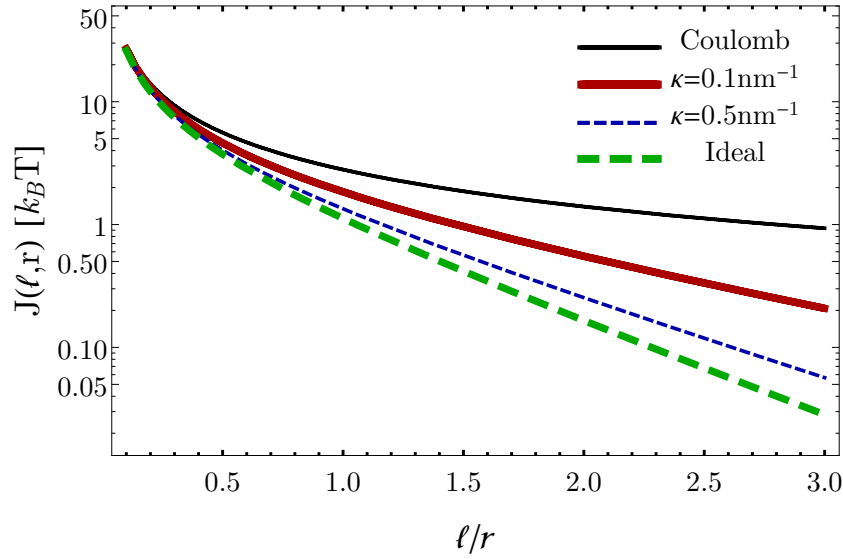
$$\hat{\psi} = \frac{\cosh[k\rho] + \sinh[k(r - |\rho|)](\frac{\epsilon_2}{\epsilon} \frac{\sqrt{k^2 + \kappa^2}}{k} \cosh[kr] + \sinh[kr])}{\epsilon k \cosh[kr](\frac{\epsilon_2}{\epsilon} \frac{\sqrt{k^2 + \kappa^2}}{k} \cosh[kr] + \sinh[kr])} \quad (2.38)$$

and

$$\hat{\psi}_2 = \frac{\exp^{\sqrt{k^2 + \kappa^2}(r - |\rho|)}}{\epsilon k (\frac{\epsilon_2}{\epsilon} \frac{\sqrt{k^2 + \kappa^2}}{k} \cosh[kr] + \sinh[kr])}. \quad (2.39)$$



(a) Cylinder



(b) Slit

Figure 2.2: Comparison of screened electrostatic interaction of two charges in a cylindrical, eqn. (2.19), and slit, eqn. (2.40), pores for various inverse Thomas-Fermi lengths. [Parameters: $r = 1\text{nm}$, $\epsilon = \epsilon_2 = 2$]

Taking the inverse Hankel transform of eqn. (2.38), setting $\rho = 0$ and after some algebra we have the desired result for the potential along the center of the slit pore from a point charge located in the centre of the pore,

$$\psi(\rho = 0) = \frac{1}{\epsilon} \int_0^\infty dk J_0(k\ell) \left(\coth(kr) - \frac{1}{\sinh^2(kr) \left(\coth(kr) + \frac{\epsilon}{\epsilon_2} \frac{k}{\sqrt{k^2 + \kappa^2}} \right)} \right). \quad (2.40)$$

If we allow $\epsilon_2 \rightarrow \infty$ or $\kappa \rightarrow \infty$ in the eqn. (2.40) we recover the screening obtained in ideal case, eqn. (2.34).

2.5 Asymptotic Screening Behaviour in Thomas-Fermi Pores

Although the full formula derived for the electrostatic screening in a cylinder or a slit surrounded by Thomas-Fermi material, eqns. (2.19) and (2.40) respectively, are rather complicated there are some interesting asymptotic limits.

Close to the point charge the effects of the screening material diminish and the short range behaviour of the electrostatic interaction, regardless of the screening material or geometry, resembles the bare Coulomb interaction, viz. $\psi \sim \ell^{-1}$.

In a cylinder surrounded by Thomas-Fermi material, the potential, $\psi(\ell)$, is well reproduced at large ℓ by

$$\psi = \frac{2}{\epsilon r^*} \frac{\exp\left(-\frac{k_1 \ell}{r^*}\right)}{k_1 (J_1(k_1))^2}, \quad \text{for } \ell \gg \frac{\epsilon}{\epsilon_2 \kappa}, \quad (2.41)$$

where

$$r^* = r + \frac{\epsilon}{\epsilon_2 \kappa}. \quad (2.42)$$

r^* can be thought of as the renormalized radius of the cylindrical pore and k_1 is the first root of the Bessel function of zeroth order ($k_1 \approx 2.4$ [110]). In a slit surrounded by Thomas-Fermi material, the potential, $\psi(\ell)$, is well reproduced at large ℓ by

$$\psi(\ell) \simeq \frac{2}{\epsilon} \frac{e^{\frac{-\pi \ell}{2r^*}}}{\sqrt{\ell} r^*}, \quad \text{for } \ell \gg \frac{\epsilon}{\epsilon_2 \kappa}, \quad (2.43)$$

where r^* is now the renormalized half width of the slit pore and is the same form as eqn. (2.42). Comparison and the eventual convergence of the asymptotic approximations

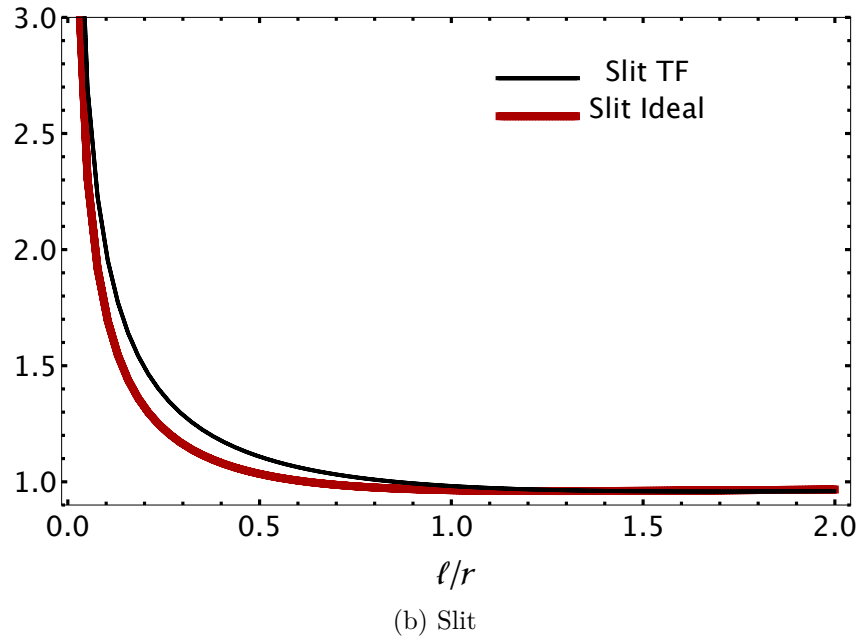
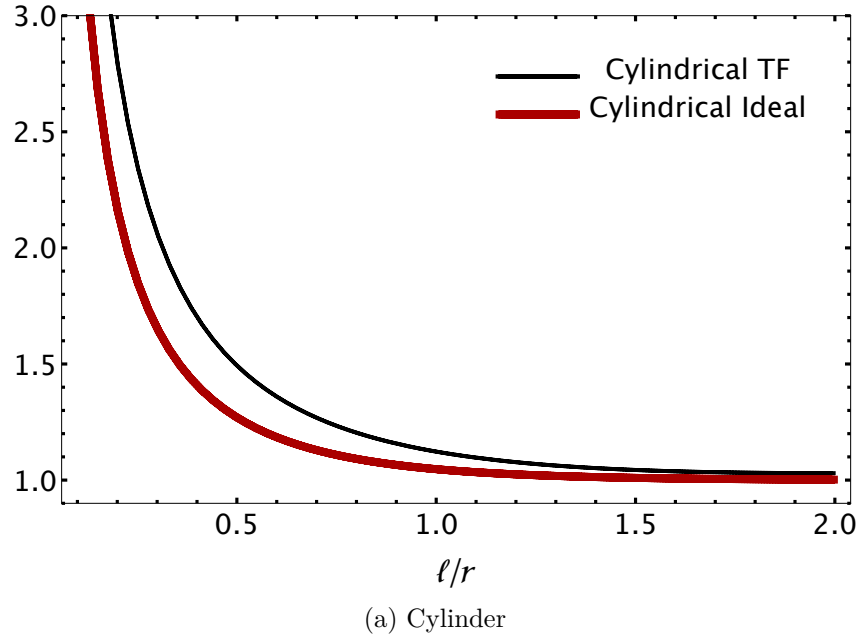


Figure 2.3: Ratio of exact formula for ψ to the corresponding long range asymptotic given in section 2.5. [Parameters: $r = 1\text{nm}$, $\epsilon = \epsilon_2 = 2$, $\kappa = 0.25\text{nm}^{-1}$]

given by Eqns. (2.41) and (2.43) and to the full integrals expression of Eqns. (2.19) and (2.40) is shown in figure 2.3.

2.6 Discussion and Conclusions

The electrostatic potential of a charge screened by a non-ideal, Thomas-Fermi metal, in both a cylinder and a slit is seen to decay exponentially as function of distance away from the charge and so the idea of the superionic state, introduced in [89, 91, 92], can be applied to supercapacitors constructed using non-ideal electrically conducting materials. However, the screening lengths in these systems is slightly larger than in the ideal case. An approximation for this renormalized screening length is given by eqn. (2.42).

Using the distance from the centre of the pore to the ‘physical’ surface of the pore rather than using distance to the centre of mass of the induced screening charge when calculating screened interactions between ions inside the pore, might over or underestimate these interactions. For instance, a charge placed near a plane metal surface induces a screening charge distribution that sits in front of the metals ‘physical’ surface [111], while for a graphite slab the charge distribution resides behind the surface [112]. Calculations carried out by Schmickler et al. [113] suggest that the screening image charge distribution of gold and carbon nanotubes extends into the nanotube interior and therefore an effective screening radius may be used which is smaller than the physical radius of the pore. The position of this effective screening radius is material dependent and also, possibly, dependent on the applied electrode potential. The incorporation of this effect is beyond the scope of the present work.

Figure 2.2 compares Thomas-Fermi screening of a charge placed at the center of a slit and a cylinder as a function of the distance away from the charge along the central axis of the slit or cylinder, ℓ . The diameter of the cylinder corresponds to the width of the slit. Electrostatic screening is stronger in a cylinder than in a slit in the Thomas-Fermi case as it is in the ideal case. The underlying reason is the same even with field penetration into the surrounding material; in a cylinder the charge is surrounded on all sides by electrically responsive material, in the slit the charge is not.

As the inverse Thomas-Fermi length increases the strength of the electrostatic screening increases. This is true for any charge screened by a Thomas-Fermi material. As $\kappa \rightarrow \infty$ or $\epsilon_2 \rightarrow \infty$ then $r^* \rightarrow r$ and the limiting case of ideally metallic screening, Eqns.

$J(\ell, r), k_B T$	Cylinder		Slit	
	Ideal	TF	Ideal	TF
(N. N.)	0.706	6.646	1.654	7.690
(N.N.N.)	0.006	1.371	0.051	1.877

Table 2.1: Charge-charge interaction energy between two hard sphere molecules just smaller than the width of the pore with a single point charge at there centre (Restrictive Primitive Model) at nearest neighbour (N.N.) and next to nearest neighbour (N.N.N.) packing distances. The separation of N.N. ions is approximated as 1 pore width and N.N.N. as 2 pore widths. Cylinder pore radius and slit pore half width width $r = 1\text{nm}$, $\ell = 2r$ or $4r$, $\epsilon = \epsilon_2 = 2$, $\kappa = 0.5\text{nm}^{-1}$.

(2.2) and (2.4), is recovered for both a cylinder and slit pore.

Table (2.1) gives an estimate of the electrostatic interaction energy of two hard spheres with a single charge at their center that are just small enough to fit inside a pore with a constant background dielectric. This is a restrictive primitive model. The nearest neighbour distance between two adjacent tightly packed ions will be approximately the pore width. Electrostatic interactions are heavily screened and an ion will significantly interact only with its nearest neighbours. Thus, when building a model of charge storage in a narrow cylindrical pore we will only consider nearest neighbour electrostatic interactions.

2.6.1 Elliptical Pores

The renormalizing contribution to the width, r^* , of a slit pore is the same as the renormalizing contribution to a cylindrical pore¹. The author firmly believes that this is not a coincidence but rather it is due to the fact that a slit and a cylindrical pore are both special cases of an elliptical pore. A cylindrical pore is an elliptical pore with its foci at the origin and a slit pore is an elliptical pore with an infinitely long semi-major axis. Unfortunately, the author was unable to solve eqns. (2.6) and (2.7) with elliptical boundary conditions and leaves this for further work. The screening formula do suggest that the electrostatic interaction energy of two charges along the central axis of an elliptical pore with semi-minor axis comparable to the radius of of a cylinder or half the slit width would be bounded from below by the electrostatic interaction energy two charges separated by the same distance in a cylindrical pore, eqn. (2.19), and bounded from above by the electrostatic interaction energy two charges separated by the same distance in a slit

¹We note that in [90] Shklovskii et al. suggested a similar renormalization of pore width.

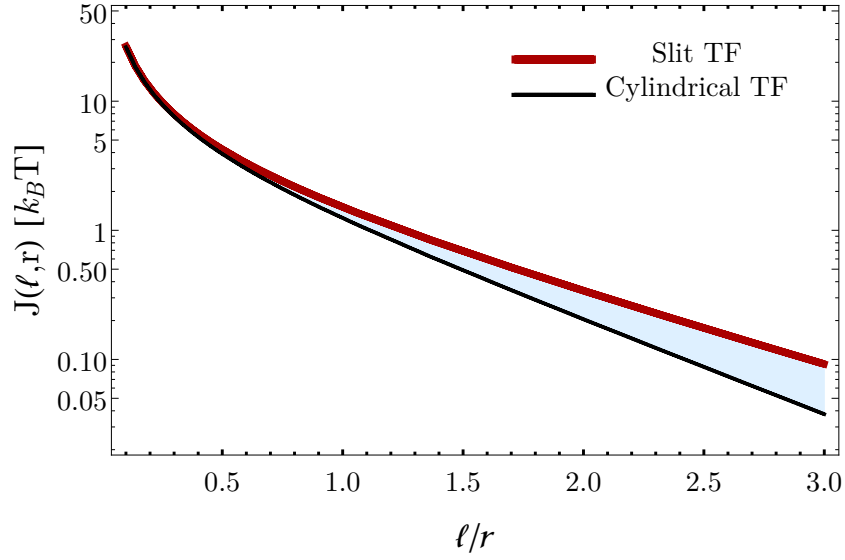


Figure 2.4: Comparison of screened electrostatic interaction energy of two charges in a slit and a cylindrical pore. The shaded area contains the possible values of interaction energy two charges along the central axis of an elliptical pore with semi-minor axis r could possess. [Parameters: $r = 1\text{nm}$, $\epsilon_1 = \epsilon_2 = 2$, $\kappa = 0.25\text{nm}^{-1}$]

pore, eqn. (2.40), shown in figure 2.4. At large ℓ the interaction of two charges decays exponentially in a cylinder and in slit, therefore, we expect potential of a charge to decay exponentially in an elliptical pore also.

Chapter 3

Charge Storage in Ion Filled Nanotubes

This chapter introduces the concept of mapping ions inside a narrow pore onto a 1D lattice that will be used throughout this thesis, the Ising model of charge storage with ions of the same size and an extension to this Ising model which allows the pore to be charged with ions of different sizes. The material presented in sections 3.1 and 3.2 was first applied to charge storage by Kornyshev [4], the author makes no attempt to claim the ideas presented here as his own. These sections are included for completeness and pedagogical reasons as Kornyshev's Ising model can be obtained as a particular case of the other lattice models presented in this thesis and it will be illuminating to refer to it when discussing more advanced models. Extending this model to include ions different sizes, section 3.4, is original work of this dissertation.

3.1 Mapping Ions onto a Lattice

We have seen in chapter 2 that a cylindrical pore screens charge more efficiently than a slit geometry. This should allow a supercapacitor electrode containing cylindrical pores to store more charge per surface area at voltages that are non-destructive to the supercapacitor. This is the superionic effect. Furthermore, an electrode constructed of cylindrical pores, perhaps made of nanotubes, could have a larger porosity, and therefore a higher surface area to volume ratio, than an electrode containing slit pores. This high porosity

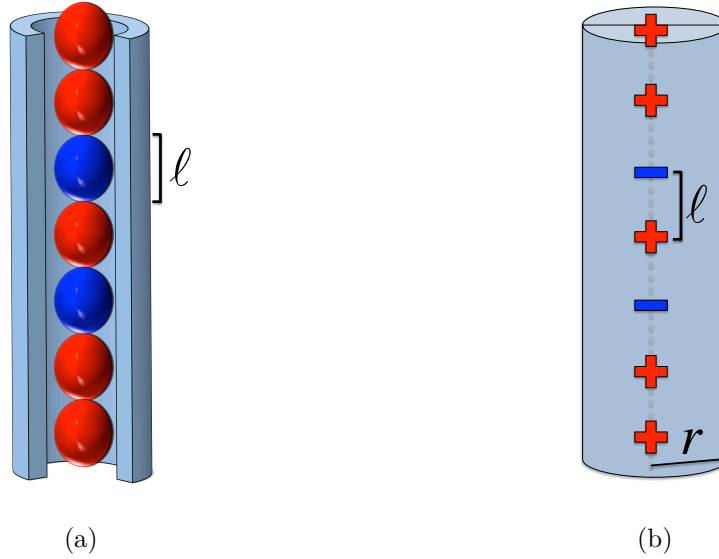


Figure 3.1: a) A schematic representation of ions of diameter ℓ inside a cylindrical pore of radius r . The ions are densely packed and the pore accommodates only one file of ions. The blue ellipsoids represent anions and the red represent cations. b) Ions are mapped to a 1D lattice with uniformly spaced spin s . Cations are mapped to $s = +1$, anions to $s = -1$.

and the efficient superionic effect all should make a supercapcitor built from an electrode containing cylindrical pores a good energy storage device.¹ To investigate how to optimise energy storage and differential capacitance in such a device we will develop a model of charge storage in a single nanotube in this chapter and then apply this theory to an electrode containing a distribution of similar pores. We will charge our pore with neat ionic liquid and we consider our pore to be ionophilic, that is the pore is completely filled with ionic liquid at all voltages. In later chapters we will extend our theory to include solvent and voids.

We examine the charging of a single narrow cylindrical pore with radius, r . The pore radius is large enough for ions to enter the pore and swap positions but still narrow enough to force the ions inside the pore to form a quasi-1D line. The electrostatic interactions between ions in the pore are screened by the electronic polarisation of the pore. For reasonable ion and pore dimensions, which maintain this single file structure of ions, the screening between ions is exponential for both a pore constructed of ideally screening material and a pore that allows Thomas-Fermi field penetration into the pore, section 2.5. For simplicity we assume that screening is ideal. The exponential screening means

¹Compared to other supercapacitors built without nanostructured electrodes and perhaps at the cost of power delivery.

that only significant electrostatic interactions between a row of ions within the pore will be between adjacent ions. In other words, the electrostatic interactions of all ions other than those between nearest neighbour ions are negligible. The ionic liquid is assumed to fully wet the pore, i.e. the pore is ionophilic and the ions inside of it are densely packed even when the electrode is not polarised.

The ionic liquid itself consists of identical spherical anions and cations of diameter ℓ . The requirement to maintain a quasi-1D structure of ions places bounds on the radius of the cylindrical pore. Strictly, the ion must be small enough to fit inside the pore and the pore radius must not be large enough to admit two ions parallel to the radial plane of the pore. To maintain the structure of a file of spherical ions within the pore r must obey the sterical constraint $\ell/2 < r < \ell$.

The charge of a spherical ion is assumed to sit at its centre which itself is located at the centre on the central axis of the pore. This is a primitive restrictive model, a hard sphere with its charge located at its centre and a background dielectric. The charge of an ion is mapped onto a lattice with spacing ℓ between sites. Each site is characterised by a spin, s , that, in this chapter, can take one of two values. If a site is occupied by a cation s will take the value of $+1$ and $s = -1$ for an anion. A schematic of a pore and this mapping is shown in figure 3.1. To charge our pore we will apply a potential to the pore. It is assumed that this potential acts uniformly throughout the pore so that it will affect each charge in an identical way.

Now that we have introduced the notion of mapping ions in a pore onto a lattice we will introduce the Ising model and demonstrate how it can be used to describe charge storage in a pore.

3.2 Ising Model of Charge Storage

The 1D Ising model, with an external field, is exactly solvable. This has made it a common pedagogical tool and a staple of undergraduate statistical physics courses. Although the Ising model started as a simple description of magnetism [114] it has been used to describe physical systems such as lattice gases [115] and spin glasses [116], the activity of neurons [117], finance [118], and it has even found applications describing social interactions [119]. Here we introduce the Ising model and demonstrate how it can be applied to the problem of charge storage in a narrow pore.

We consider a set of N sites arranged onto a 1D lattice chain. Each site, s_i , $i \in \{1, 2, \dots, N\}$, only interacts with its two nearest neighbours, through the coupling constant J , and an external field, h' . The Hamiltonian for such a system is

$$H_I = J \sum_{\langle i, j \rangle} s_i s_j + h' \sum_i s_i \quad (3.1)$$

where $\langle i, j \rangle$ represents combinations of nearest neighbours sites. If the Ising model were to be used as a description of magnetism in 1D we would associate $J > 0$ with an antiferromagnetic interaction between nearest neighbour sites and h' with a magnetic field [120]. To apply the Ising model to our charge storage problem we map the ions in the pore onto a lattice as described in section 3.1. We associate J with the electrostatic interaction energy between point charges representing two densely packed ions in a conducting cylindrical pore and h' is the total non-interacting energy of a single charge in the pore² so that

$$h' = eh - \tilde{w} \quad (3.2)$$

where h is the applied voltage and $\tilde{w}$ is the ‘energy benefit’ to move a cation from the pore into the bulk and replace it with an anion. The electrostatic interaction energy between two point charges in an ideally screening cylindrical pore is well described by a combination of eqns. (2.1) and (2.5). Accordingly the coupling constant between two monovalent adjacent ions of the same diameter, ℓ , in units of $k_B T$, is defined as

$$J \equiv J(\ell, r) = \frac{3.08 L_B}{r} \exp\left(-2.4 \frac{\ell}{r}\right) \quad (3.3)$$

where $L_B = e^2 / \epsilon k_B T$ is the Bjerrum length and ϵ is the dielectric constant in the interior of the pore. We will assume, throughout the rest of this document, that $\epsilon = 2$.

We wish to calculate the canonical partition function, Z_I , for this system,

$$Z_I = \sum_{\{s\}} e^{-H_I} \quad (3.4)$$

where summation is over all configurations of $\{s\}$. To evaluate this summation we use the transfer matrix method to rewrite the partition function as a matrix multiplication rather than a summation and implement periodic boundary conditions on the lattice chain to form a ring, viz. site s_N is now adjacent to site s_1 . Periodic boundary conditions are not required to solve this problem however they simplify the analysis. Furthermore, we expect the contribution to the partition function from the boundary conditions to decrease as

²Specifically, here non-interacting means not interacting with other molecules in the pore.

the size of the system increases.

$$Z_I = \sum_{\{s\}} e^{-h's_1} e^{-Js_1s_2} e^{-h's_2} e^{-Js_2s_3} \dots e^{-h's_N} e^{-Js_Ns_1} = \sum_{\{s\}} T_{s_1,s_2} T_{s_2,s_3} \dots T_{s_N,s_1} \quad (3.5)$$

where

$$T_{s_i,s_j} = e^{\frac{-h'}{2}s_i} e^{-Js_is_j} e^{\frac{-h'}{2}s_j} = \underline{T} = \begin{pmatrix} e^{-(J+h')} & e^J \\ e^J & e^{-(J-h')} \end{pmatrix}. \quad (3.6)$$

For finite coupling constants T_{ij} is not defective and therefore diagonalisable. If the two eigenvalues of $\underline{T}$ are $\lambda_{\pm}$, where $\lambda_+ > \lambda_-$, we can rewrite the partition function as

$$Z_I = \text{tr}(\underline{T}^N) = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}^N \quad (3.7)$$

where

$$\lambda_{\pm} = e^{-J} \cosh h' \pm \sqrt{e^{-2J}(\sinh h')^2 + e^{2J}}. \quad (3.8)$$

Finally, after carrying out the matrix multiplication the canonical partition function is found in a compact form

$$Z_I = \lambda_+^N + \lambda_-^N. \quad (3.9)$$

The free energy per lattice site of the system is related to the partition function via

$$f = -\frac{1}{N} \ln(Z_I). \quad (3.10)$$

In the thermodynamic limit when $N \rightarrow \infty$ the partition function is dominated by its leading term and the free energy per lattice site takes a particularly simple form,

$$\begin{aligned} f &= -\ln(\lambda_+) \\ &= -\ln\left(e^{-J} \cosh h' + \sqrt{e^{-2J}(\sinh h')^2 + e^{2J}}\right). \end{aligned} \quad (3.11)$$

From the free energy per site we can obtain the mean spin per site (magnetisation), $\langle s \rangle$, and the susceptibility, χ , of the lattice spin with regards to the applied voltage

$$\langle s \rangle = -\frac{\partial f}{\partial h'}, \quad \chi = \frac{\partial^2 f}{\partial h'^2}. \quad (3.12)$$

The surface area of the interior of a cylindrical pore with length, L , and radius, r , is $2\pi rL$. The surface charge density of the pore, σ , is therefore

$$\sigma = \frac{eN\langle s \rangle}{2\pi rL}. \quad (3.13)$$

As the sites are separated by a lattice constant, ℓ , the length of the pore that surrounds N ions is $L = N\ell$ and

$$\begin{aligned}\sigma &= -\frac{e}{2\pi r\ell} \langle s \rangle \\ &= \frac{e}{2\pi r\ell} \frac{\sinh(h')}{\sqrt{\sinh^2(h') + e^{4J}}}.\end{aligned}\tag{3.14}$$

The differential capacitance per unit surface area of the pore, C , is then the susceptibility rescaled by the dimensions of the ion and the pore

$$\begin{aligned}C &= \frac{\partial \sigma}{\partial h} = \frac{e^2}{2\pi r\ell} \chi \\ &= \frac{e^2}{2\pi r\ell} \frac{e^{-2J} \cosh(h')}{\sqrt{1 + e^{-4J} \sinh^2(h')}}.\end{aligned}\tag{3.15}$$

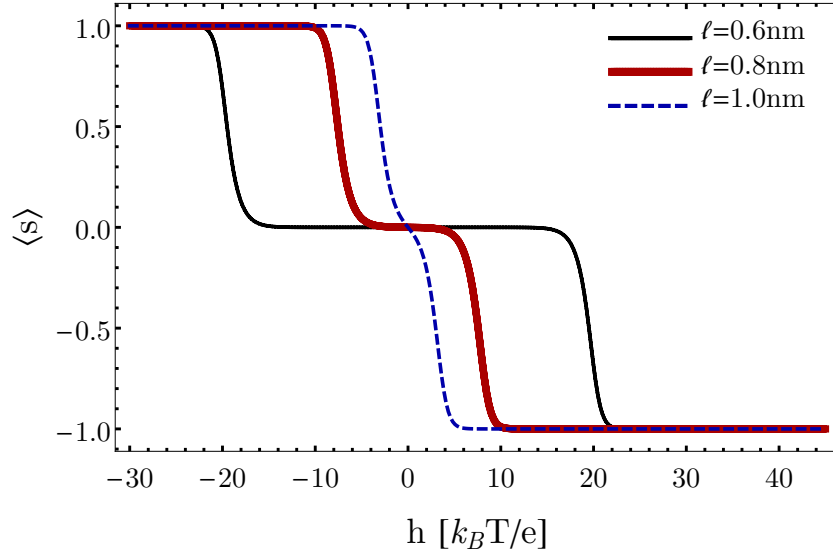
The total energy stored in the pore between zero and h voltages is given by

$$E = \int_0^h \eta C(\eta) d\eta.\tag{3.16}$$

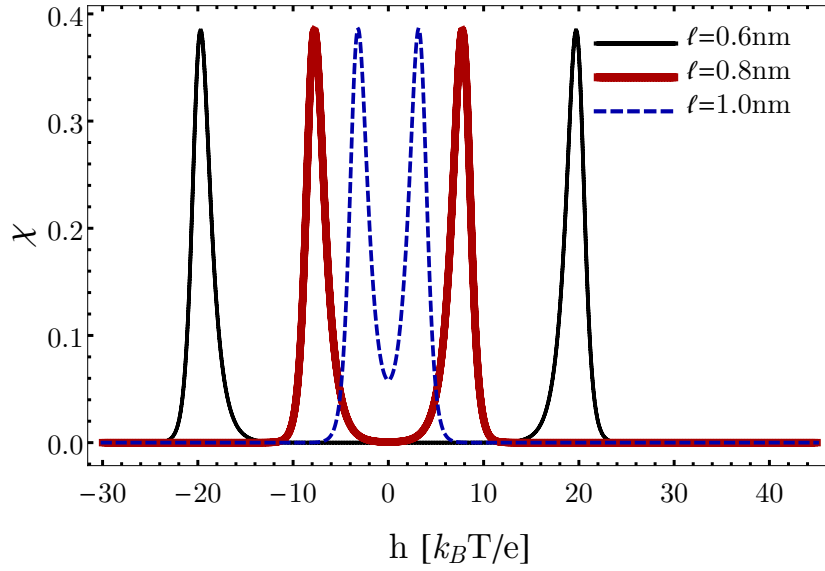
3.2.1 Differential Capacitance for a Single Ising Pore

Figure 3.2 shows the mean charge and susceptibility of a narrow cylindrical pore as a function of voltage. At low voltages relative to the magnitude of $\tilde{w}/e$, specifically when $(\tilde{w} - 2J) < eh < (\tilde{w} + 2J)$, the pore is neutral and $\langle s \rangle = 0$. Each ion inside the pore is surrounded by two ions of opposite charge so that a chain of alternating charges exist in the pore. At large voltages relative to the magnitude of $\tilde{w}/e$, $eh < (\tilde{w} - 2J)$ and $(\tilde{w} + 2J) < eh$, the pore is fully charged and each ion sits next to another one with the same charge. The susceptibility peaks around the threshold voltages $h^* \approx (\tilde{w} \pm 2J)/e$. We can understand the location of the susceptibility peaks intuitively and mathematically.

To begin mathematically we define the charging threshold voltage, h^* , to be a local maximum in the susceptibility. To find these maxima we consider the derivative of the susceptibility with respect to the applied voltage look to see where this derivative equals



(a) Average charge per site



(b) Susceptibility

Figure 3.2: Effect of ion size on the properties of a Ising model applied to the problem of charge storage in nanopores. [Parameters: $r = 0.5\text{nm}$, $\tilde{w} = 0k_B T$.]

zero.

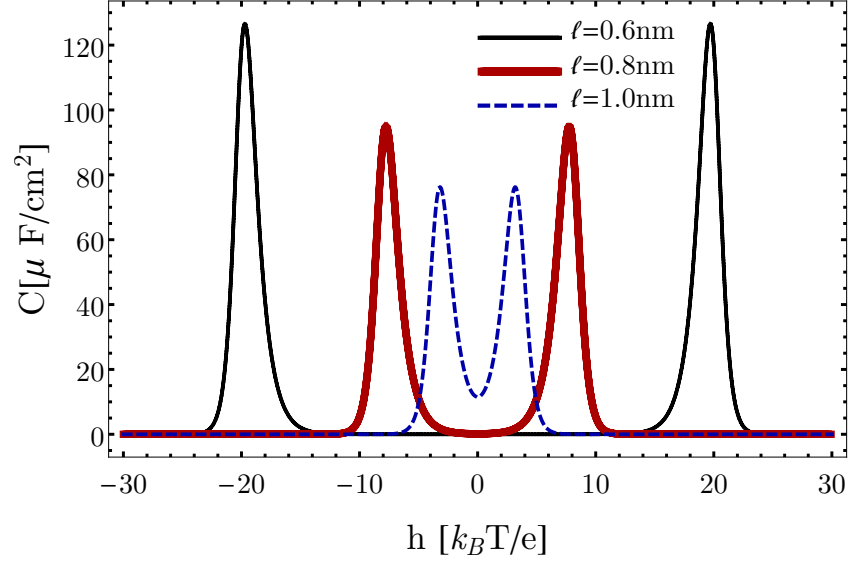
$$\begin{aligned} \frac{\partial \chi}{\partial h'} &= 0 \\ \frac{e^{2J} \sinh(h') \left(-\cosh(2h') + e^{4J} - 2 \right)}{\left(\sinh^2(h') + e^{4J} \right)^2 \sqrt{e^{-4J} \sinh^2(h') + 1}} &= 0 \end{aligned} \quad (3.17)$$

we can see that there is a turning point at $h' = 0$ from the hyperbolic sine. This corresponds to the local minimum in susceptibility at the centre of the two peaks, figure 3.2b. To find the locations of the two local maxima we consider the parentheses in the numerator of eqn. (3.17)

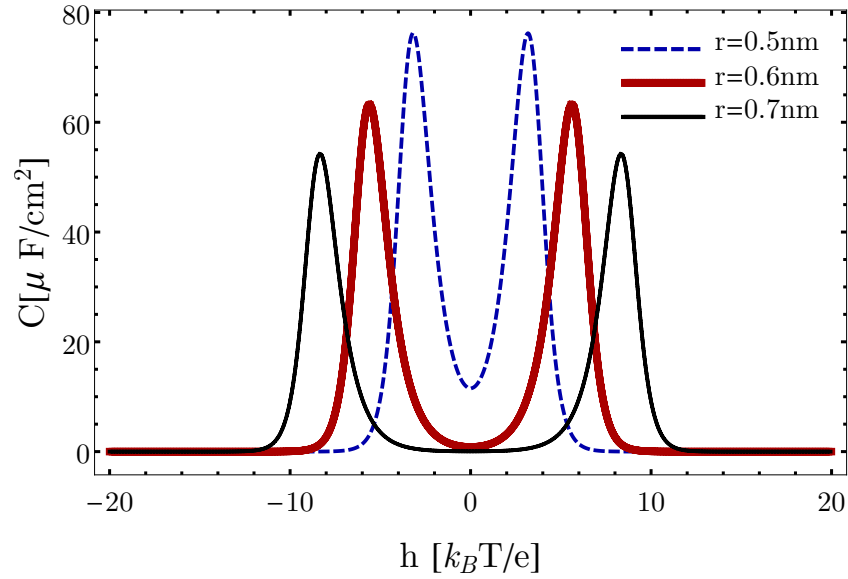
$$\begin{aligned} e^{4J} - 2 &= \cosh(2h') \\ e^{4J} &\approx \cosh(2h') \quad \text{for } J \gg 1 \\ h' &\approx \pm 2J \\ h^* &\approx \frac{1}{e}(\tilde{w} \pm 2J). \end{aligned} \quad (3.18)$$

To understand this result intuitively we consider the energy, at $h' = 0$, of an ion in an alternating series of charges and the energy of an ion in a fully charged configuration. The energetic contribution to the Hamiltonian, eqn. (3.1), of the central ion in the configuration $+-+$ is from electrostatic interactions $-J$, while in configuration $+++$ it is J . The difference between these energies is what the non-interacting energy of the ion, h' , needs to compensate for when charging the pore and, once $\tilde{w}$ is considered, it is this difference that defines the magnitude of the threshold voltage. As the ions decrease in size or as the pore widens, J increases and it becomes increasingly difficult to cause any change in the state of charge held within the pore.

The differential capacitance of the pore is shown in figure 3.3. The differential capacitance is the susceptibility rescaled. Therefore, the maxima of the susceptibility, at the threshold voltages $h^* \approx (\tilde{w} \pm 2J)/e$, will also be the maxima of the differential capacitance. Increasing the pore radius or decreasing the ion size increases the voltage required to start the charging process. Unlike the susceptibility the height of the peaks in the differential capacitance is not constant but rather proportional to $1/(r\ell)$. The energy stored in a pore is given by eqn. (3.16). Large values for total energy storage effectively correspond to large values of differential capacitance at high voltages. Decreasing the size of ions that charge the pore both increases the height of the corresponding differential capacitance peak and increases J so that higher voltages are needed to reach this peak thus optimising energy storage, figure 3.3a. Changing the pore radius produces less of



(a) Changing ion size



(b) Changing pore radii

Figure 3.3: Differential capacitance of an ionophilic cylindrical nanopore as a function of ion and pore sizes. [Parameters: $\tilde{w} = 0k_B T$, a) $r = 0.5\text{nm}$ b) $\ell = 1\text{nm}$.]

an effect on energy storage. Increasing the pore radius does increase the voltage required to charge the pore however this effect is offset by decreasing the height of the differential capacitance peak as you have also increased the surface area of the pore, figure 3.3b.

3.3 The Electrode - Averaging Over Many Pores

The differential capacitance shown in figure 3.3 applies only to a single pore and not an electrode. We would wish to extend our model of a pore to that of an electrode but there are obvious limitations. Our model describes single file charge storage and we cannot use it to analyse charge storage in any larger, higher dimensional, pores. We could use our model to describe charge storage in approximately monodisperse and monomorphic nanostructured electrodes that consist of many cylindrical pores. We admit that a real porous electrode is a much more disordered structure than what we will describe [121], even if it is possible to constrain the size of very narrow pores in certain electrodes to nanometre accuracy [82], but by studying this idealised case, we hope to obtain valuable qualitative information on the nature and main features of the differential capacitance of real ultra-nanoporous electrodes. With this in mind we average our results for a single pore over a normal pore size distribution. We will refer to this collection of pores of different radii as the electrode.

We define the probability density function of the normal distribution with mean $\langle r \rangle$ and standard deviation δr as

$$\mathcal{N}(r|\langle r \rangle, \delta r) \equiv \frac{1}{\delta r \sqrt{2\pi}} \exp \left\{ \frac{-(r - \langle r \rangle)^2}{2 \delta r^2} \right\}. \quad (3.19)$$

As the normal distribution has an infinite domain we apply upper and lower bounds, r_{max} and r_{min} , ensuring that the dimensions of any pore in the electrode is such that the ions can fit inside the pore while maintaining their 1D file like structure. The lower bound of this distribution will be a weak inequality while the upper bound is a strict inequality, $r \in [r_{min}, r_{max})$. To truncate the normal distribution in this manner we define the error function as

$$\text{erf}(x) \equiv 2 \int_0^x \mathcal{N}(r|0, 1/\sqrt{2}) \, dr \quad (3.20)$$

and a normalised weight function as

$$w(r|\langle r \rangle, \delta r, r_{min}, r_{max}) = \frac{2\mathcal{N}(r|\langle r \rangle, \delta r)}{\text{erf}\left(\frac{\langle r \rangle - r_{min}}{\sqrt{2} \delta r}\right) - \text{erf}\left(\frac{\langle r \rangle - r_{max}}{\sqrt{2} \delta r}\right)}. \quad (3.21)$$

Now to average our capacitance, $C(r)$, or indeed any function, over a set of normally distributed pore radii centred on $\langle r \rangle$, with standard deviation δr we compute the weighted average numerically using

$$\langle C \rangle \equiv \sum_{m=0}^{M-1} C \left(r_{\min} + \frac{m(r_{\max} - r_{\min})}{M} \right) \times w \left(r_{\min} + \frac{m(r_{\max} - r_{\min})}{M} \mid \langle r \rangle, \delta r, r_{\min}, r_{\max} \right) \frac{(r_{\max} - r_{\min})}{M} \quad (3.22)$$

where M is an integer large enough accurately sample all facets of the possibly sharp peaked weight function.

3.3.1 Differential Capacitance of Many Ising Pores

Figure 3.4 demonstrates the effects of the averaging process, defined by eqns. (3.21) and (3.22), has on the differential capacitance of the Ising model of charge, eqn. (3.15), with maximum and minimum pore radii given by³

$$r_{\max} = \ell, \quad r_{\min} = \ell/2. \quad (3.23)$$

We see that the differential capacitance peaks are extremely sensitive to any dispersion in pore radii. Increasing the standard deviation associated with the pore radii distribution both widens the voltage window where you find significant values of capacitance and also decreases the relative values of capacitance. Both effects can be explained by thinking of capacitance as a resonance phenomenon centred at h^* . Capacitance is very sharply peaked around h^* and the value of h^* is exponentially sensitive to changes in r via the electrostatic interactions between ions in the pore, eqn. (3.3). There is limited overlap for capacitance curves for individual pores with different radii and, as such, any averaging process will reduce and fatten the peaks seen in the capacitance.

3.4 Charge Storage with Ions of Different Sizes

In sections 3.1 and 3.2 we made the assumption that the anions and cations that charge the pore are the same size, however, if a room temperature ionic liquid were made up of ions of the same size it would most likely freeze. It is the asymmetry in the shape and size

³See section 3.1 for a discussion on the motivation of these bounds.

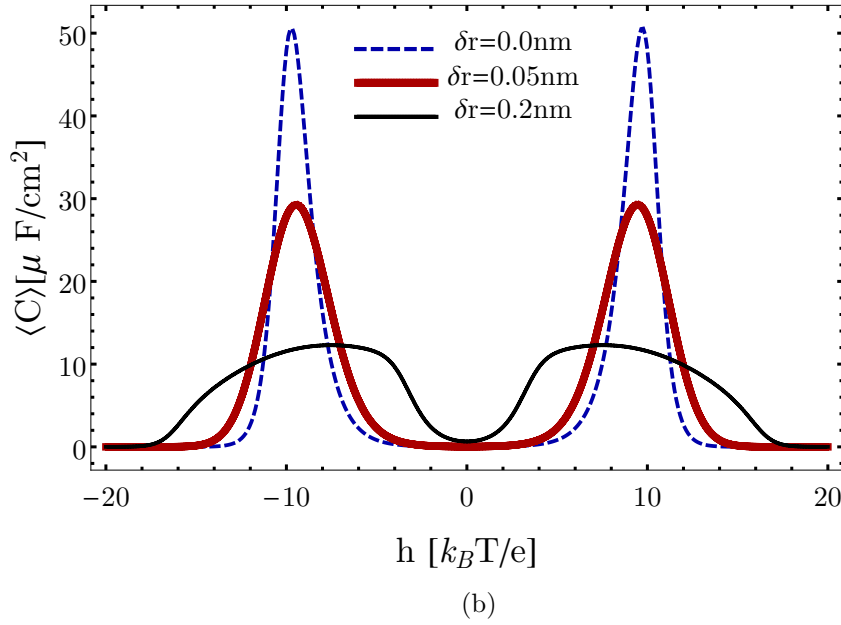
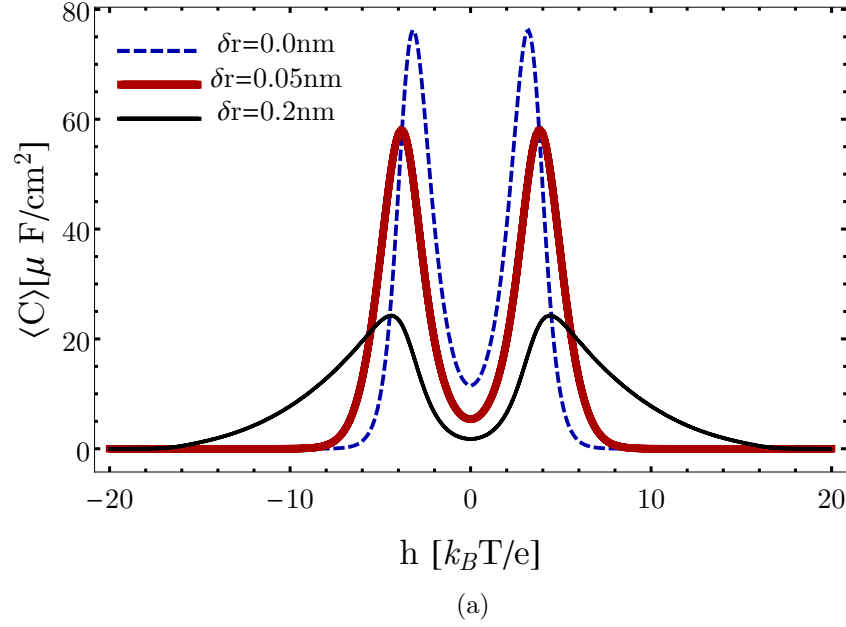


Figure 3.4: Average capacitance of many Ising pores with truncated normally distributed pore radii. a) The blue curve ($\delta r = 0\text{nm}$) is identical to both blue curves in figure 3.3 that were generated using the same parameters. [Parameters: $\ell = 1\text{nm}$, $\tilde{w} = 0k_B T$ a) $\langle r \rangle = 0.5\text{nm}$. b) $\langle r \rangle = 0.75\text{nm}$.]

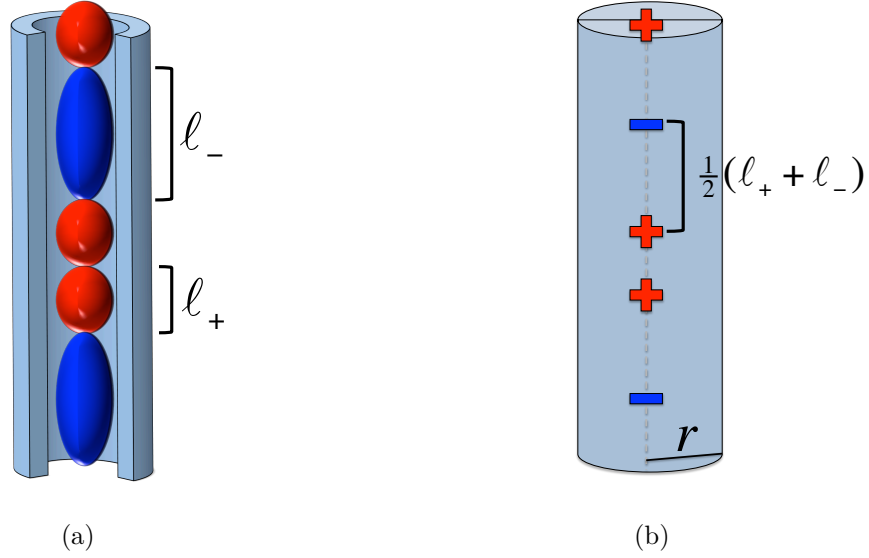


Figure 3.5: a) A schematic representation of ions of different sizes inside a cylindrical pore. The blue ellipsoids represent anions and the red represent cations. b) A visualisation of the mapping of the ions shown in the pore to a variable lattice.

of the ions that form an ionic liquid that keep the ionic liquid a liquid at low temperatures [33, 34]. To produce a more robust theory of pore charging we must try to include an element of this ion asymmetry. To do this we allow the distance between adjacent ions to depend on the charge of the respective ions. Thus, the strength of nearest neighbour electrostatic interactions will now become a function of s_i and s_j . We define J_{s_i, s_j} via

- Cation-cation interactions $\equiv J_{+1, +1} = J\left(\frac{\ell_+ + \ell_+}{2}, r\right)$,
- Cation-anion interactions $\equiv J_{+1, -1} = J_{-1, +1} = J\left(\frac{\ell_+ + \ell_-}{2}, r\right)$,
- Anion-anion interactions $\equiv J_{-1, -1} = J\left(\frac{\ell_- + \ell_-}{2}, r\right)$.

where ℓ_+ is diameter of a cation and ℓ_- is the diameter of an anion, shown in figure 3.5. To maintain dimensionality in our pore we limit the radius of the pore such that $\max(\ell_+/2, \ell_-/2) \leq r < \min(\ell_+, \ell_-)$. This ensures that the largest ion can fit into the pore while two of the smallest ions are prevented from packing parallel to the radial plane of the pore. After incorporating this species dependent coupling into our, now modified, Ising Hamiltonian is given by

$$H_A = \sum_{\langle i j \rangle}^N J_{s_i, s_j} s_i s_j + h' \sum_i^N s_i \quad (3.24)$$

where we notice that the coupling constant has moved inside the summation over nearest neighbours. The partition function for this Hamiltonian is given by

$$Z_A = \sum_{\{s\}} e^{-H_A}. \quad (3.25)$$

Kornyshev's original Ising model of charge storage [4], presented in section 3.2, can be obtained from this one when $\ell_+ = \ell_- = \ell$. This partition function can be calculated using an analogous transfer matrix method as described in section 3.2. The transfer matrix we will use to calculate the summation in this partition function is

$$\underline{T}_A = \begin{pmatrix} e^{-(J_{++}+h')} & e^{J_{+-}} \\ e^{J_{+-}} & e^{-(J_{--}-h')} \end{pmatrix} \quad (3.26)$$

where we have used the short hand

$$J_{s_i, s_j} = \begin{cases} J_{++} & \text{if } s_i = +1, \ s_j = +1. \\ J_{+-} & \text{if } s_i = \pm 1, \ s_j = \mp 1. \\ J_{--} & \text{if } s_i = -1, \ s_j = -1. \end{cases} \quad (3.27)$$

The eigenvalues, $\lambda_{\pm}$, of this transfer matrix $\underline{T}_A$ are

$$\lambda_{\pm} = \frac{1}{2} \left(e^{-(J_{++}+h')} + e^{-(J_{--}-h')} \right. \\ \left. \pm \sqrt{(e^{-(J_{++}+h')} + e^{-(J_{--}-h')})^2 - 4(e^{-(J_{--}+J_{++})} - e^{2J_{+-}})} \right). \quad (3.28)$$

In the thermodynamic limit the partition function is again determined by the largest of these eigenvalues. Once the partition function is computed then the free energy, charge density and susceptibility of the pore can be obtained from λ_+ following the prescription detailed at the end of section 3.2,

$$f = -\ln(\lambda_+), \quad \langle s \rangle = -\frac{\partial f}{\partial h'}, \quad \chi = \frac{\partial^2 f}{\partial h'^2}. \quad (3.29)$$

Unfortunately, the surface charge, differential capacitance and stored energy are not obtained so easily. By allowing the nearest neighbour coupling constant to be dependent on the species of adjacent ions and therefore on the length of these ions, we have created a model in which the separation of lattice sites is not constant. Each pair of adjacent lattice sites can be separated by three different distances. Should we apply an external field that

favours larger ions, then our lattice will expand. Conversely, applying a field favouring smaller ions will cause a contraction. Unfortunately, this means that the surface charge density and the differential capacitance of the pore per surface area do not follow from eqn. (3.14) and (3.15) where we assumed that the length of the pore that included N ions was a constant. Now that cations and anions are different sizes we define the length of the pore that surrounds a chain of N ions as

$$\begin{aligned}
 L &= N_+ \ell_+ + N_- \ell_- \\
 &= \left(N + \sum_i^N s_i \right) \ell_+ + \left(N - \sum_i^N s_i \right) \ell_- \\
 &= \left(\frac{\ell_+ + \ell_-}{2} \right) N + \left(\frac{\ell_+ - \ell_-}{2} \right) \sum_i^N s_i \\
 &= \langle \ell \rangle N + \tilde{\ell} \sum_i^N s_i \\
 &\approx N(\langle \ell \rangle + \tilde{\ell} \langle s \rangle)
 \end{aligned} \tag{3.30}$$

where $N_{\pm}$ is the number of cations/anions in the pore and rather than consider individual cation and anion length, the average length of cations and anions, $\langle \ell \rangle$, and the difference in length of a cation from the average length, $\tilde{\ell}$, have been introduced via

$$\langle \ell \rangle = \frac{\ell_+ + \ell_-}{2}, \quad \tilde{\ell} = \frac{\ell_+ - \ell_-}{2}. \tag{3.31}$$

Finally, we have also made the mean field approximation

$$\sum_i^N s_i \approx N \langle s \rangle \tag{3.32}$$

in the final line of eqn. (3.30). The average lattice spacing as a function of voltage is shown in figure 3.7a. If the ions are the same size then there is no change in the average separation between lattice sites but if the ions are different sizes then the application of a voltage that favours the smaller ions does shrink the lattice and vice versa for larger ions.

We now have everything to calculate the differential capacitance of the system

$$\begin{aligned}
 C &= \frac{\partial \sigma}{\partial h} = \frac{\partial}{\partial h} \left(\frac{Ne\langle s \rangle}{2\pi r L} \right) \\
 &= \frac{e^2}{2\pi r} \frac{\partial}{\partial h} \left(\frac{\langle s \rangle}{(\langle \ell \rangle + \tilde{\ell}\langle s \rangle)} \right) \\
 &= \frac{e^2}{2\pi r} \frac{\langle \ell \rangle \chi}{(\langle \ell \rangle + \tilde{\ell}\langle s \rangle)^2}.
 \end{aligned} \tag{3.33}$$

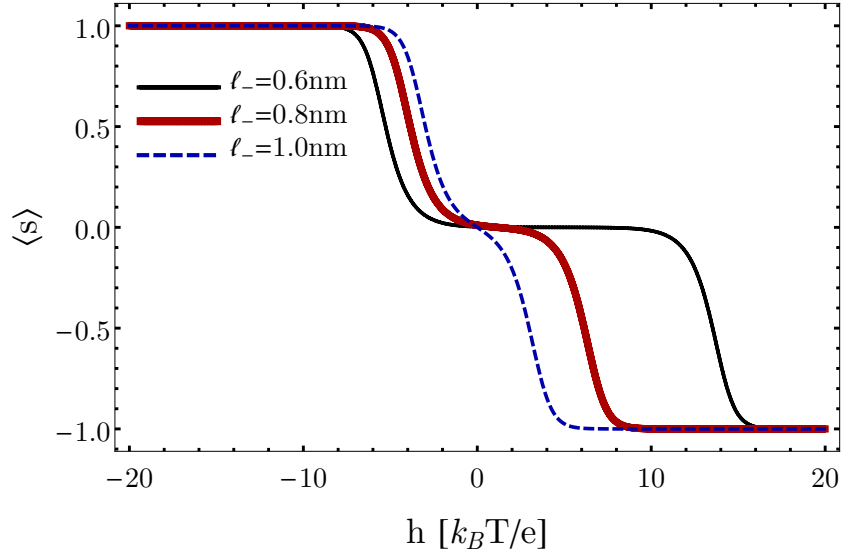
Once an expression for the differential capacitance of the pore is known the energy stored in the pore follows from combining this expression with eqn. (3.16).

3.4.1 A Single Pore Charged with Ions of Different Sizes

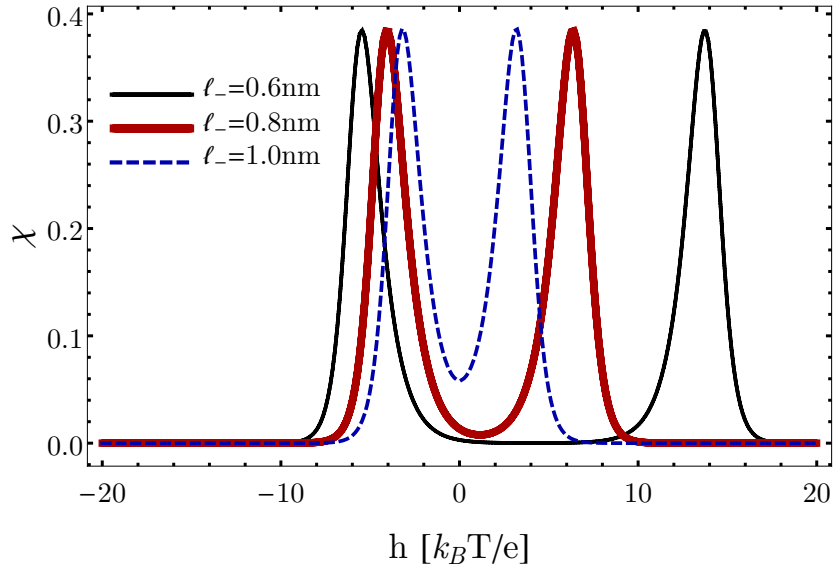
Figure 3.6 shows the charge density and susceptibility of a pore with filled with ions of different sizes. As in section 3.2 the electrostatic interactions between two smaller neighbouring ions are stronger than the interaction of larger ions, thus, a larger voltage is required to change the charge density within the pore. The voltage thresholds required to change the charge density in the pore are now $eh^* \approx \{-(J_{++} + J_{+-} - \tilde{w}), J_{--} + J_{+-} + \tilde{w}\}$ rather than $eh^* \approx \{\tilde{w} + 2J, \tilde{w} - 2J\}$ in the case of ions of the same size. Intuitively, we require an energy of J_{+-} to unbind two oppositely charged nearest neighbours and then an energy of J_{++} or J_{--} to force counterions into the pore. To derive this mathematically we need to find the turning points of the susceptibility. The susceptibility has three turning points, two of which will be the local maxima we are looking for while one will be the local minima that split the maxima. We define h^* to be the value of the voltage at the local maxima. To find these turning points we look to see where the third derivative of the free energy⁴ equals zero. This is particularly messy but we will attempt to tidy things up by only keeping the terms that can equal zero and bundling the rest up in the strictly negative ζ which is a function of all three electrostatic coupling constants and the potential.

$$\begin{aligned}
 \frac{\partial^3 f}{\partial h^3} &= 0 \\
 &= \left(e^{2h' + J_{++}} - e^{J_{--}} \right) \left(2e^{2(h' + J_{--} + J_{+-} + J_{++})} - 4e^{2h' + J_{--} + J_{++}} - e^{4h' + 2J_{++}} - e^{2J_{--}} \right) \zeta.
 \end{aligned} \tag{3.34}$$

⁴This is the first derivative of the susceptibility.



(a) Average charge per site



(b) Susceptibility

Figure 3.6: Properties an ionophilic nanopore filled with ions of different sizes. [Parameters: $\ell_+ = 1\text{nm}$, $r = 0.5\text{nm}$, $\tilde{w} = 0k_B T$]

As ζ is strictly negative the turning points of the susceptibility will be found by setting the arguments of the two parenthesis equal in eqn. (3.34) to zero. We consider the simplest looking bracket first and look for turning points such that

$$\begin{aligned} \left(e^{2h'+J_{++}} - e^{J_{--}} \right) &= 0 \\ \Rightarrow h' &= \frac{J_{--} - J_{++}}{2}. \end{aligned} \quad (3.35)$$

Unfortunately, this is not the location of one of the two local maxima but rather the location of the local minima in between the two peaks. I do not attempt to show this directly but rather I will use the location of this minima to simplify the task of finding the two maxima. The other two turning points must be found by setting the argument of the second parenthesis in eqn. (3.34) equal to zero. On first inspection of this parenthesis solving for h' does not look very hospitable. To simplify the problem we make the transformation

$$h' = \hat{h} + \frac{J_{--} - J_{++}}{2} \quad (3.36)$$

in eqn. (3.34). We are motivated to do this as we suspect the local minima will be in the centre between the two local maxima. If this is the case then such a transformation will shift the two roots to a position where they are both equidistant from $\hat{h} = 0$. Following this transformation the second parenthesis becomes

$$\begin{aligned} \left(2e^{2(h'+J_{--}+J_{+-}+J_{++})} - 4e^{2h'+J_{--}+J_{++}} - e^{4h'+2J_{++}} - e^{2J_{--}} \right) &= 0 \\ e^{2J_{--}} \left(1 + e^{2\hat{h}} \left(4 + e^{2\hat{h}} - 2e^{J_{--}+2J_{+-}+J_{++}} \right) \right) &= 0 \end{aligned} \quad (3.37)$$

after some rearrangement we find that the turning points are located at

$$\begin{aligned} \cosh \hat{h} &= e^{J_{--}+2J_{+-}+J_{++}} - 2 \\ \hat{h} &\approx \{ \pm(J_{--} + 2J_{+-} + J_{++}) \} \\ h' &\approx \{ -(J_{++} + J_{+-}), (J_{--} + J_{+-}) \} \quad \text{for } J \gg 1 \\ eh^* &\approx \{ -(J_{++} + J_{+-} - \tilde{w}), (J_{--} + J_{+-} + \tilde{w}) \}. \end{aligned} \quad (3.38)$$

These are the exact threshold voltages that we expected to find.

Several differential capacitance curves for pores charged with anions of various sizes are shown in figure 3.7b. We can see that the threshold to start charging and, thus, the differential capacitance peaks occur at larger voltages when charging with smaller ions. This follows from eqn. (3.38) once we note that the susceptibility and the differential capacitance are proportional to one another.

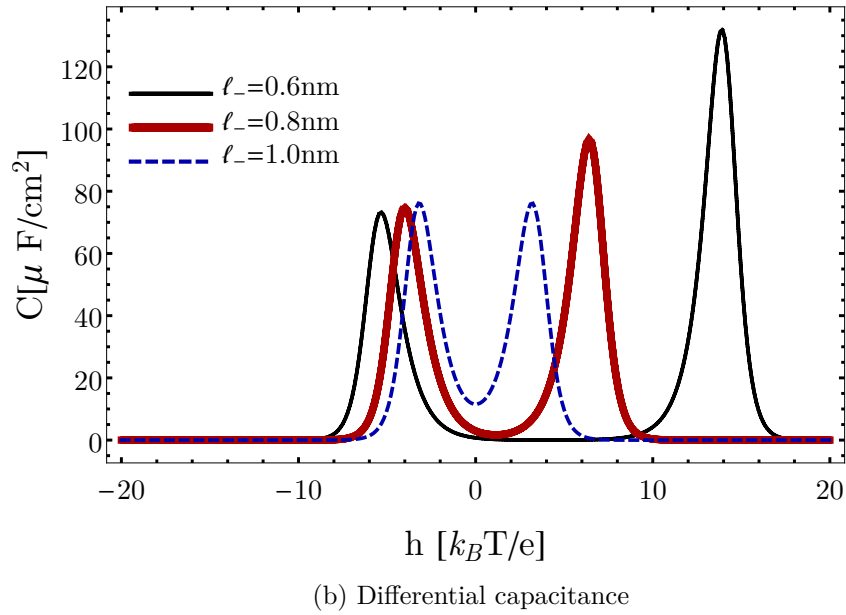
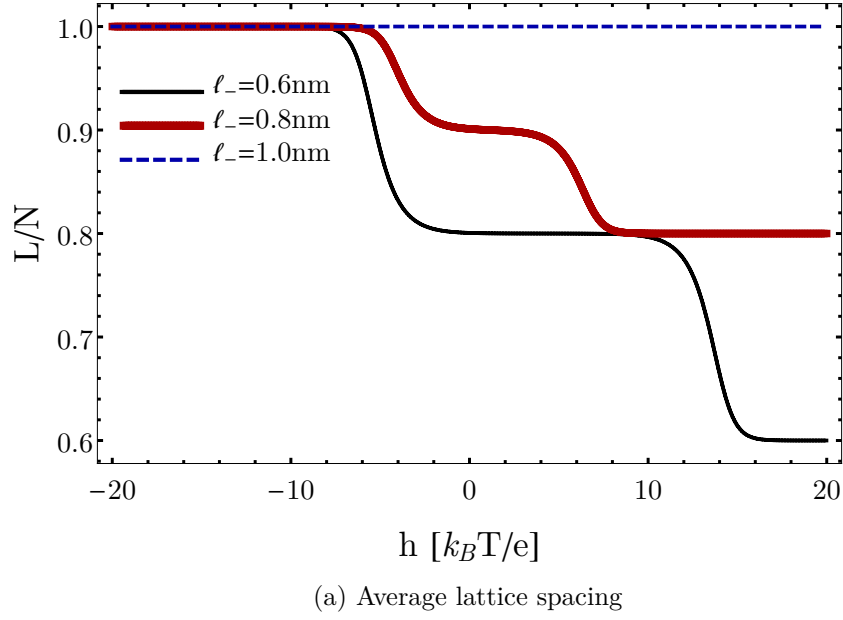


Figure 3.7: Properties an ionophilic nanopore filled with ions of different sizes. [Parameters: $\ell_+ = 1\text{nm}$, $r = 0.5\text{nm}$, $\tilde{w} = 0k_B T$]

The height of the capacitance peaks corresponding to charging with smaller ions is also higher. This can be understood by considering that when charging the pore with smaller ions the surface area taken up by an ion decreases, the total charge that can be packed into a pore of finite length increases and the differential capacitance per unit area of the pore correspondingly increases.

3.4.2 Many Pores Charged with Ions of Different Sizes

The average capacitance of many pores of differing radii charged with ions of different sizes can be seen in figure 3.8. To achieve this the averaging prescription, described in section 3.3, was combined with eqn. (3.33) with the maximum and minimum pore radii in the electrode

$$r_{min} = \max(\ell_+/2, \ell_-/2), \quad r_{max} = \min(\ell_+, \ell_-). \quad (3.39)$$

As in the case of charging with ions of the same size, figure 3.4, averaging over a pore size distribution reduces the height of the capacitance peaks. As dispersion increases these peaks fall further still. This reduces the overall asymmetry in the height of the two capacitance peaks however the asymmetry in the threshold voltage is still apparent. As such, the differential capacitance of a collection of pores decays to negligible levels at higher voltages when the pores are filled with smaller ions no matter what size the pore. Smaller ions still require larger voltages to be coaxied into the pore than larger ones.

3.5 Energy Storage

The energy stored by a pore is given by combining eqn. (3.16) and the differential capacitance defined by eqn. (3.33), when considering ions of different sizes, or by eqn. (3.15), in the special case of identically sized ions. Whatever the form of the capacitance, to maximise the energy stored in the pore upon charging we need a large value of differential capacitance at a large voltage. Should we be in a situation where the optimisation of the differential capacitance and the voltage is not possible simultaneously it is clear from eqn. (3.16) that, as a rule of thumb, the optimisation of the voltage window should take priority. One would expect a pore with a small capacitance at a large voltage is likely to store more energy than a large capacitance at a small voltage. We note that if the differential capacitance is symmetric about zero volts then the same amount of energy

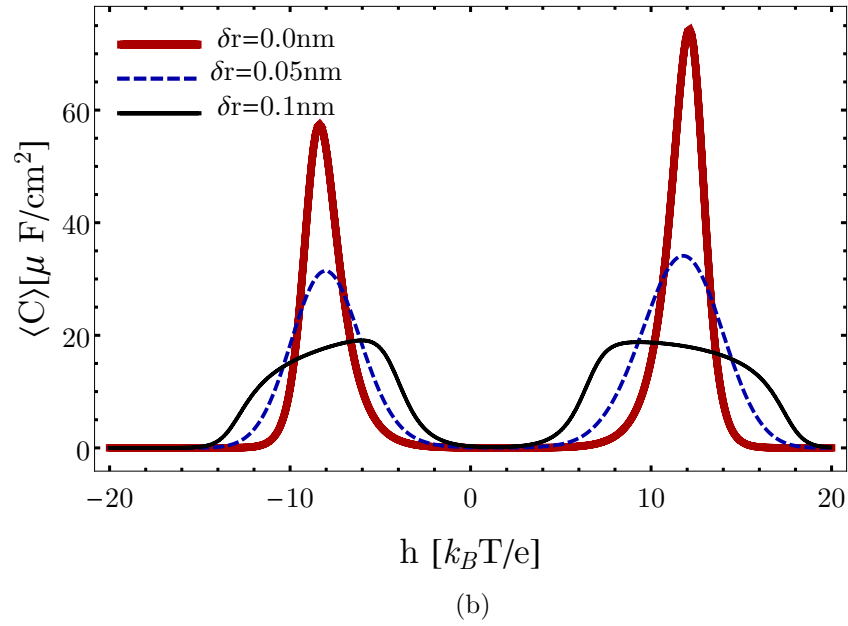
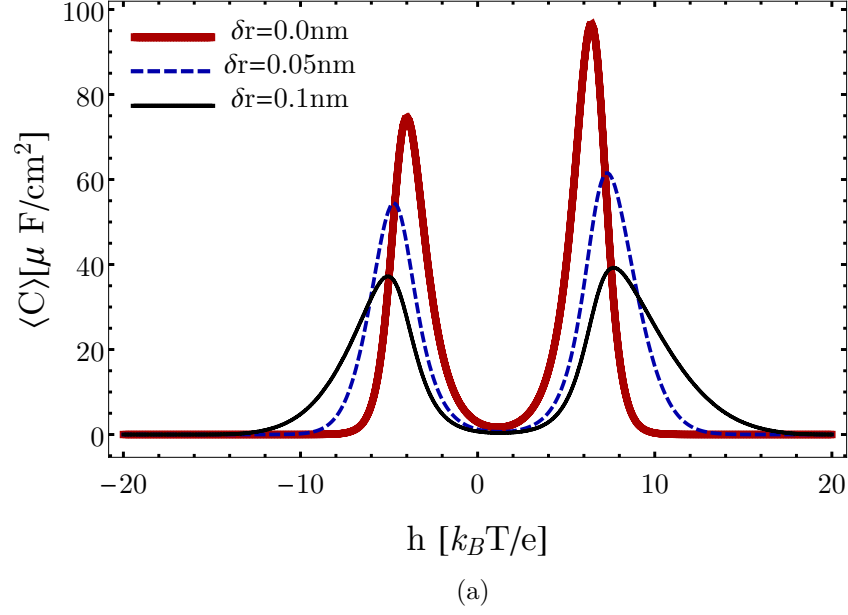


Figure 3.8: Average capacitance of many pores with truncated normally distributed pore radii filled with cations and anions of different sizes. [Parameters: $\ell_+ = 1\text{nm}$, $\ell_- = 0.8\text{nm}$, $\tilde{w} = 0k_B T$. a) $\langle r \rangle = 0.5\text{nm}$. b) $\langle r \rangle = 0.65\text{nm}$.]

will be stored when the pore is charged to the same positive or negative voltage.

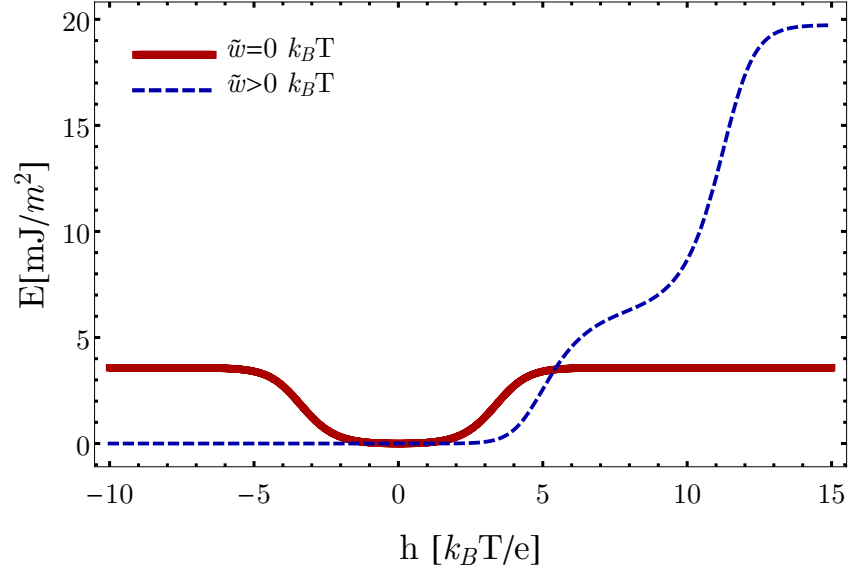
If we consider the differential capacitance of a pore filled with ions of the same size, as shown in figure 3.3, it is clear that decreasing the ion size will optimise energy storage as it increases the capacitance threshold voltage and maximises the height of the differential capacitance peak. Increasing the pore radius also increases energy storage as it increases the threshold voltage for charging however this effect is offset by the increase in surface area of the pore.

In all of the figures we have previously discussed the energy benefit to move a cation into the bulk and replace it with an anion has been zero. In other words, the pores we have not ‘preferred’ to be filled with either cations or anions at low voltages. We have neglected this when considering the surface charge or differential capacitance as the effects of this bias are trivial. $\tilde{w} \neq 0$ simply produces a translation in the voltage axis according to eqn. (3.2). However, when considering energy storage the effects can be highly non-trivial. The energy stored when $\tilde{w} \neq 0$, figure 3.9a, is no longer symmetric around zero volts as the differential capacitance itself is no longer symmetric around zero volts. Specifically, the application of a voltage to the pore with opposite polarity to this preferred ion will cause the pore to store less energy compared to the case of a pore with no ion bias. In the extreme case when the pore is completely filled with one ion at zero volts the application of a voltage favouring this ion will cause no change in the pore and no energy will be stored. Such a case, labelled $\tilde{w} > 0$, is shown in figure 3.9a. The application of a voltage with the same polarity as the preferred ions has the opposite effect increasing energy storage, figure 3.9a. This applied voltage first needs to overcome the bias favouring coions and then overcome the usual electrostatic barriers to form a file of counterions, eqn. (3.38). As these electrostatic barriers are broken at higher voltages than in the case of no bias the energy stored is increased. Furthermore, due to the nature of eqn. (3.16) this increase in energy stored is not linear but rather roughly quadratic.

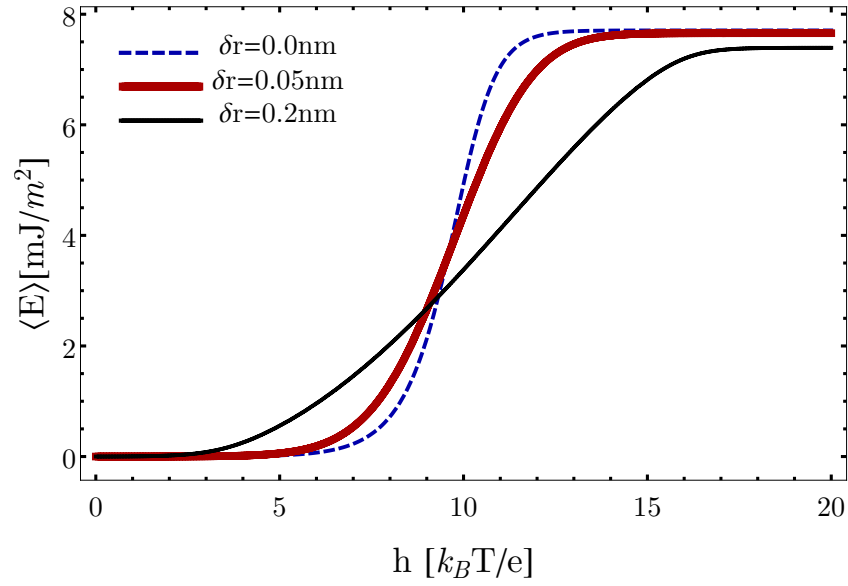
The energy stored in an array of pores with normally distributed pore radii can be obtained by replacing the differential capacitance of one pore with the differential capacitance of many $\langle C \rangle$, in eqn. (3.16) so that

$$\langle E \rangle = \int_0^h \eta \langle C(\eta) \rangle d\eta. \quad (3.40)$$

We will refer to this as the energy stored in the electrode. Figure 3.9b shows how increasing the standard deviation of the pore radii in the electrode affects the energy stored within it. We can see that as the pore radii dispersion increases energy storage becomes



(a) Single Pore



(b) Electrode

Figure 3.9: Effects of $\tilde{w} \neq 0$ and electrode radial dispersion on energy storage. b) The differential capacitance of identical electrodes is shown in figure 3.4b. [Parameters: $\ell = 1 \text{ nm}$, a) $r = 0.5 \text{ nm}$, $\tilde{w} = 8k_B T$. b) $\tilde{w} = 0k_B T$, $\langle r \rangle = 0.75 \text{ nm}$.]

more gradual and less step-like as a function of voltage. This is a result of the ‘smearing’ out of the differential capacitance upon averaging. The high resonance peaks, which cause the step-like energy storage are reduced and broadened causing a more gradual change. The amount of energy stored in the electrode depends on how the averaging process affects the differential capacitance of the electrode. If increasing the dispersion creates significant values of differential capacitance at larger voltages, as in the cases of figures 3.4a and 3.8a, then increasing the dispersion will also increase the energy storage. However, if increasing the dispersion creates significant differential capacitance at lower voltages then increasing the dispersion may not increase energy storage, as in the cases of figures 3.4b, 3.8b and 3.9b.

3.6 Discussion and Conclusions

Electrodes composed of cylindrical and other extremely narrow pores have obvious drawbacks in terms of power storage but they are a natural apex when one attempts to optimise the porosity of an electrode. Encouragingly, the Ising models of charge storage presented in this chapter lead to analytical expressions for accumulated surface charge and differential capacitance that demonstrate the interplay between voltage, transfer energy and the interionic electrostatic interactions within the pore.

We have found that for an ionophilic pore that, unless there is a transfer energy preferencing one ion species over another, a file of ions of alternating species are present in the pore at low voltages. This alternating change is reasonably stable until a threshold voltage is reached at which point the pore is charged by expelling coions and filling with counterions. Once the pore is filled with counterions a lattice saturation effect prevents the accumulation of any more charge at any larger voltage. This threshold voltage is larger when the counterions are smaller and the corresponding differential capacitance peak is large due to the increased charge density associated with a smaller ion. Averaging over a pore radius distribution to make our results applicable to a approximately monodisperse and monomorphic nanostructured electrode causing a smearing of the capacitance peak as a function of voltage, however, this smearing may have little affect on the energy stored per unit surface area of the electrode if significant values of differential capacitance are accessed at higher voltages. The optimisation of energy storage for a single pore is achieved when the pore is filled with smaller counterions or when the transfer energy favours coions.

The assumption of the electrode behaving as an ideal metal is a good one for many

metallic electrodes. If our electrode was not constructed of an ideal metal then, as we have seen in chapter 2, field penetration into the pore walls would increase the screening length, which would itself increase the electrostatic interactions between ions causing the threshold voltages to increase. Should these voltages be accessible to the supercapacitor this would increase the total energy that would be possible to store in the electrode.

The requirement for the ionic liquid to be composed of spherical ions, a restrictive primitive model, is a strong assumption which we do not necessarily need to take. We could have charged our pore with ellipsoidal anions and cations, as shown in figure 3.5, with a semi-major axis of length, ℓ . Where the largest dimension of the ion would be assumed to sit parallel to the cylinder so that these ellipsoidal ions are specifically prolate spheroids or spheres in the degenerate case of the semi-major axis have the same magnitude as the semi-minor axis. To maintain dimensionality of a pore charged with ellipsoids one dimension of both ions must be small enough to allow the ion to fit inside the pore and the pore radius must not be large enough to admit two ions parallel to the radial plane of the pore. This would require the specification of the size of the semi-minor axis of the ellipsoidal ions, however, the author is pained to define another parameter of this model and so our ions remain spherical.

Chapter 4

Charge Storage in Solvent Filled Nanotubes

The Ising models of charge storage presented in the previous chapter are both models of a pore fully wetted with ions at all times. In this chapter we present a three species model of charge storage that draws analogies with the Blume-Emery-Griffiths model of magnetism [5]. The trinary nature of this model will allow us to consider a pore that is wetted with ions or a neutral solvent. The state of charging of the pore will be determined by the interplay of the ions interaction with the applied voltage and energetic cost or benefit associated with replacing ions with neutral solvent in the pore. The molecules in the pore are still densely packed and sit in the centre of the pore. To test these assumptions, complimentary Monte Carlo simulations are presented which do not restrict molecules positions within the pore. These simulations agree with the theory. The results presented with ions of the same size was published in [6], the extension to charging the pore with ions of different sized ions is the authors own work and is to be published.

4.1 A Blume-Emery-Griffiths Model

We wish to build a model of charge storage similar to the one discussed in section 3.4 but now we want to include the possibility that solvent can enter the pore. To do this we must move beyond the two species Ising model of charge storage and use a three species model where the additional species will represent the solvent. As this three species

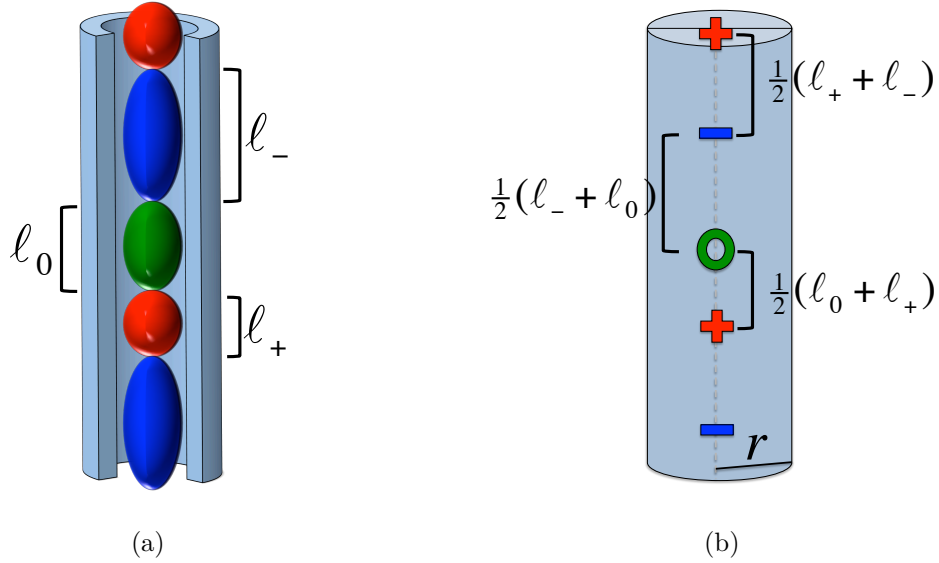


Figure 4.1: A schematic representation of ions and solvent of different sizes inside a cylindrical pore and the mapping of these molecules to a variable lattice. The blue ellipsoids represent anions, red ellipsoids cations and green ellipsoids solvent.

model of charge storage will be analogous to the Blume-Emery-Griffiths (BEG) model of magnetism we will refer to it as the BEG model of charge storage. Much of the following set up is similar to that detailed in chapter 3.

Molecules inside the pore will again be represented by spheres. A cation will have a diameter of ℓ_+ , an anion a diameter of ℓ_- and a solvent molecule a diameter of ℓ_0 . The charge of an ion will again reside at its centre and we will map the centre of each molecule in the pore onto a site on a lattice that runs through the cylindrical pore. A solvent molecule will have no charge. As the molecules in the pore can all be different sizes the distance between adjacent lattice sites is dependent on the nature of the molecule sitting on that site, figure 4.1. The charge of a molecule is represented on the lattice at each site by a spin, s_i , which can take the values $s_i \in \{+1, 0, -1\}$ corresponding to the polarity of the molecule.

Electrostatic interactions between ions inside the pore are screened by the metallic cylindrical pore in a similar manner to section 3.4. The interactions between ions will be represented in the Hamiltonian via J_{s_i, s_j} , defined in section 3.4, with the extension that there is no electrostatic interaction between any molecule and a neutral solvent, $J_{+0} = J_{-0} = J_{00} = 0$ and so forth. In other words, the solvent is not polarizable. The strength of the screening inside the pore allows us to neglect long range interactions and

only consider nearest neighbour electrostatic interactions; two ions separated by a solvent molecule do not interact.

The electrode itself is polarised by a potential, h , relative to the bulk of the solvent. The energy of a single charge in this potential is eh . Cations and anions have an associated transfer energy from the bulk into the pore, w_+ and w_- respectively. These parameters characterise the propensity for cations and anions to occupy the pore, at $h = 0$, relative to the neutral solvent and include the self interaction of the ion with its own induced charge distribution in the pore walls. We refrain from calling w_+ and w_- the chemical potential of cations or anions as the change in free energy of the system that occurs when one ion is added to the pore cannot be defined with respect to that species alone but must also include a reference to the solvent species.

The Hamiltonian, H_{BEG} , and partition function, Z_{BEG} , relevant to the system described above is

$$H_{BEG} = \sum_{\langle i,j \rangle} J_{s_i,s_j} s_i s_j + \sum_i h_{s_i} s_i, \quad Z_{BEG} = \sum_{\{s\}} \exp(-H_{BEG}) \quad (4.1)$$

where $\langle i,j \rangle$ represents the sum over nearest neighbours, the sum in the partition function runs over all ion configurations of $\{s\}$ and h_{s_i} is net transfer energy required to swap an ion from the bulk with a solvent in the pore at a certain voltage defined via

$$h_{s_{\pm 1}} = eh \mp w_{\pm}, \quad h_{s_0} = 0. \quad (4.2)$$

This Hamiltonian is similar to a modified BEG model in the theory of magnetism where J_{s_i,s_j} would play the role of the spin-spin coupling and h_{s_i} a spin dependent magnetic field coupling.

To obtain an analytic expression for the partition function, eqn. (4.1), we consider the transfer matrix

$$\underline{T}_{BEG} = \begin{pmatrix} e^{-J_{++}-h_+} & e^{-h_+/2} & e^{J_{+-}-(h_+-h_-)/2} \\ e^{-h_+/2} & 1 & e^{h_-/2} \\ e^{J_{+-}-(h_+-h_-)/2} & e^{h_-/2} & e^{-J_{--}+h_-} \end{pmatrix} \quad (4.3)$$

where for brevity, we will use the shorthand

$$h_{\pm} \equiv h_{s_{\pm 1}}. \quad (4.4)$$

This is a 3×3 rather than a 2×2 matrix as we now have three species inside our pore and each one is represented by a column and a row. As in section 3, for finite coupling constants this transfer matrix is not defective and therefore diagonalisable. The three eigenvalues of $\underline{T}_{BEG}$ are λ_+ , λ_0 and λ_- where $\lambda_+ > \lambda_0 > \lambda_-$, we can rewrite the partition function as

$$Z_{BEG} = \text{tr} \left(\underline{T}_{BEG}^N \right) = \begin{pmatrix} \lambda_+ & 0 & 0 \\ 0 & \lambda_0 & 0 \\ 0 & 0 & \lambda_- \end{pmatrix}^N \quad (4.5)$$

$$= \lambda_+^N + \lambda_0^N + \lambda_-^N. \quad (4.6)$$

In the thermodynamic limit the partition function and the Helmholtz free energy per site of the system, f , can be defined by the largest eigenvalue of the transfer matrix, eqn. (4.3),

$$f = -\frac{1}{N} \ln(Z_{BEG}) \quad (4.7)$$

$$f \approx -\ln(\lambda_+). \quad (4.8)$$

As $\underline{T}_{BEG}$ is Hermitian this eigenvalue is real. The closed form of this eigenvalue is un-gainly, a property that holds true for many eigenvalues of larger matrices and so it is not reproduced in the text but it can be found via methods detailed in [122, 123].

To obtain observables we differentiate this free energy with regards to the relevant conjugate variable. The mean field density of cations, $\langle \rho_+ \rangle$, anions, $\langle \rho_- \rangle$, and solvent, $\langle \rho_0 \rangle$, in the pore, can be obtained from the free energy

$$\langle \rho_+ \rangle = \frac{\partial f}{\partial w_+}, \quad \langle \rho_- \rangle = \frac{\partial f}{\partial w_-}, \quad \langle \rho_0 \rangle = 1 - \langle \rho_+ \rangle - \langle \rho_- \rangle. \quad (4.9)$$

and the mean spin and the susceptibility of the pore via

$$\langle s \rangle = -\frac{\partial f}{\partial h_{s_i}} = \langle \rho_+ \rangle + \langle \rho_- \rangle, \quad \chi = -\frac{\partial \langle s \rangle}{\partial h_{s_i}}. \quad (4.10)$$

The surface charge accumulated per unit area of the pore is

$$\sigma = \frac{e}{(2\pi r) \langle \ell \rangle} \langle s \rangle \quad (4.11)$$

where

$$\langle \ell \rangle = \ell_+ \langle \rho_+ \rangle + \ell_- \langle \rho_- \rangle + \ell_0 \langle \rho_0 \rangle \quad (4.12)$$

is the average (mean field) lattice spacing. To calculate the differential capacitance of

the pore we need to take the derivative of the surface charge with respect to the applied voltage

$$C = \frac{\partial \sigma}{\partial h}. \quad (4.13)$$

The total energy stored in a BEG pore follows from combining eqns. (3.16) and (4.13), and can be calculated numerically once the differential capacitance is known.

4.2 Results for a Single Pore

The BEG model of charge storage has a large number of parameters, w_+ , w_- , ℓ_+ , ℓ_- , ℓ_0 , r and h . Exploring this large parameter space will require a thorough investigation. We begin by discussing the effects of asymmetric transfer energy and how they can be related to a pore with a single transfer energy for both ions, reducing our parameter space by one dimension. Following that we will introduce the terms ionophobicity and ionophilicity to characterise a pore charged with ions of the same size according to the charging mechanisms and threshold voltages present when both ions have the same transfer energy. This classification system will eventually be expanded to include ions of different sizes and will ultimately allow us to understand the behaviour of a pore at any position in the parameter space.

4.2.1 Asymmetric transfer energy

Our model allows the energetic cost, or benefit, for ions to enter the pore to be species dependent. We do not force $w_+ = w_-$ but these two parameters are not so unrelated as we might first think. The system studied when $w_+ \neq w_-$ is analogous to a system where both ions have a single average transfer energy given by

$$\langle w \rangle = w_+ = w_- = \frac{1}{2}(w_+ + w_-) \quad (4.14)$$

and the curves produced by this single transfer energy system are translated on the voltage axis by a shift of

$$\begin{aligned} \hat{h} &\longrightarrow h - \frac{1}{2e}(w_+ - w_-) \\ \hat{h} &\longrightarrow h - \tilde{w}/e \end{aligned} \quad (4.15)$$

where we have defined $\tilde{w}$ the difference between w_+ and $\langle w \rangle$. To see this consider the effects this transformation has on eqn. (4.2),

$$\begin{aligned} eh \mp w_{\pm} &= e\hat{h} + \tilde{w} \mp w_{\pm} \\ &= e\hat{h} \mp \frac{1}{2}(w_+ + w_-) \\ &= e\hat{h} \mp \langle w \rangle. \end{aligned} \tag{4.16}$$

In effect, by altering the individual transfer energies of cations and anions we have rebased the point of zero charge of the system and the system now prefers one ion species over another.

In what follows we will directly consider pores with only one average transfer energy $w_+ = w_- \equiv \langle w \rangle$. Should one wish to consider a pore that prefers one ion over the other we will be able to transform the relevant results produced with one average transfer energy into the asymmetric case via eqns. (4.14) and (4.15).

4.2.2 Ionophobicity and Ionophilicity

We wish to introduce some new terminology to describe the regime where the pore is devoid of solvent and when it is not. Our first attempt is to say that a BEG pore is ionophilic/solvent-phobic (ion-loving/solvent-hating) when solvent does not enter the pore and ionophobic/solvent-philic (ion-hating/solvent-loving) when solvent plays a role in the charging process. This is all well and good but to what parameter regime does our new nomenclature belong? The average transfer energy plays a role in determining if the pore prefers to be filled with solvent or ions and it is the obvious candidate to provide a threshold between these two regimes but it is not the only factor that affects the composition of the pore before a voltage is applied. The electrostatic interactions of nearest neighbours ions inside the pore also play an important role. For example, a chain of ions of alternating polarity is energetically stable. Naïvely, one might think that any negative transfer energy would expel all ions from the pore at low voltages but if this transfer energy is not large enough to overcome the electrostatic bonding between alternating ions it will not. A threshold must be crossed to break this stable chain. With this in mind rather than classifying a pore as ionophilic or -phobic we define a BEG pore to be

- *Strongly ionophilic* if there is no significant amount of solvent in the pore for any

voltage and the pore has the same charging mechanisms and thresholds as an equivalent Ising pore, section 3.2.

- *Weakly Ionophilic* if the pore has the same charging thresholds as an Ising pore but some solvent can enter the pore near these thresholds.
- *Weakly Ionophobic* if the solvent in the pore affects the charging mechanisms and thresholds but the pore does not prefer solvent enough to break the chain of alternating ions that exist in the pore at low voltages.
- *Strongly Ionophobic* if the pore is filled with solvent at zero volts.

To elucidate these classifications we will consider a BEG pore charged with ions of the same size before moving onto the more complicated case of ions of different sizes.

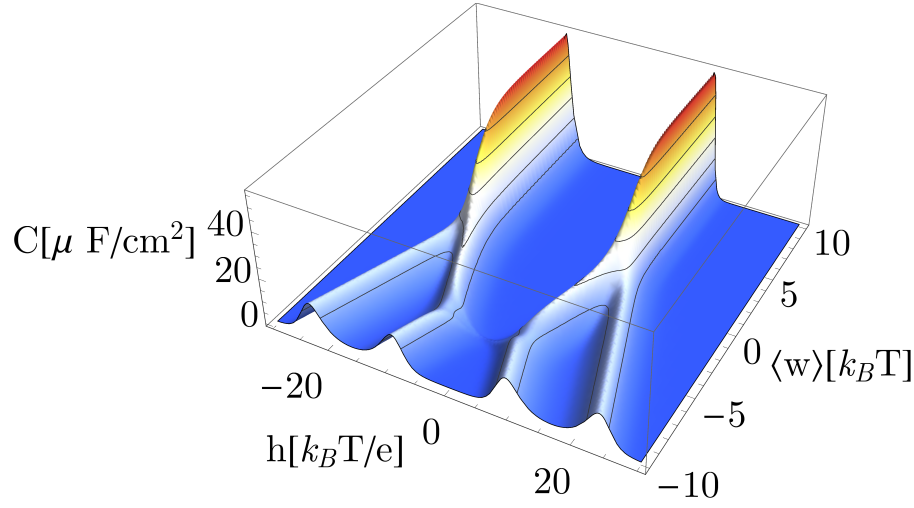
4.2.3 Charging with Ions and Solvent of the Same Size

Figure 4.2 shows the differential capacitance of a BEG pore as a function of voltage and average transfer energy. At this point, we will confine ourselves to examining the case of charging with identically sized molecules $\ell_+ = \ell_- = \ell_0$ thus $J_{++} = J_{+-} = J_{--} \equiv J$. The accompanying figure 4.3 shows several cross sections of this differential capacitance surface at a progression of average transfer energies and the corresponding molecule densities in the pore. The values of the transfer energy used to create these cross sections are indicated via gray broken lines on the contour plot, figure 4.2b. We will discuss the results at each transfer energy in turn, starting with the largest positive transfer energy which should create the most ionophilic pore and proceed to look at smaller and eventually negative transfer energies that should create ionophobic pores. We will focus on understanding the composition of the interior of the pore, the charging mechanisms and the locations of the charging thresholds¹ at various voltages and transfer energies.

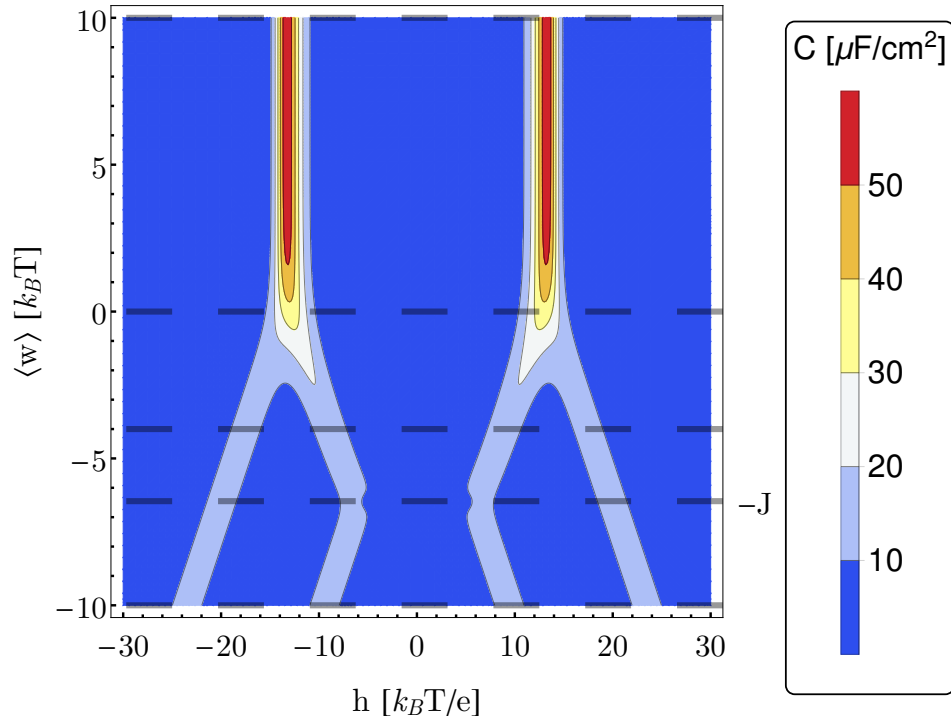
When $\langle w \rangle \gg 1$ all is familiar. There is no solvent in the pore at any voltage² and we recover the two species Ising model of pore charging with ions of the same size detailed in section 3.2. The pore is strongly ionophilic. At low voltages cations and anions form an alternating chain in the pore, we represent such configurations graphically as $+ - +$ or $- + -$. As cations are not preferred relative to anions the pore begins to charge when

¹Recall from section 3 that the threshold voltages correspond to the local maxima of the susceptibility.

²Strictly speaking, for finite parameters, there is always solvent in a BEG pore, $\langle \rho_0 \rangle \in (0, 1)$, but in very small amounts it can be neglected.



(a) 3D Surface.



(b) Contour Plot

Figure 4.2: 3D Differential capacitance surface of a pore as a function of voltage h and average transfer energy $\langle w \rangle$, and the corresponding contour plot of this surface. Cross sections of this surface, at constant $\langle w \rangle$ are shown in figure 4.3 and are indicated on this contour plot as horizontal gray broken lines. The value for the coupling constant $-J$ is shown on the contour plot. [Parameters: $\ell_+ = \ell_- = \ell_0 = 0.9\text{nm}$, $r = 0.75\text{nm}$.]

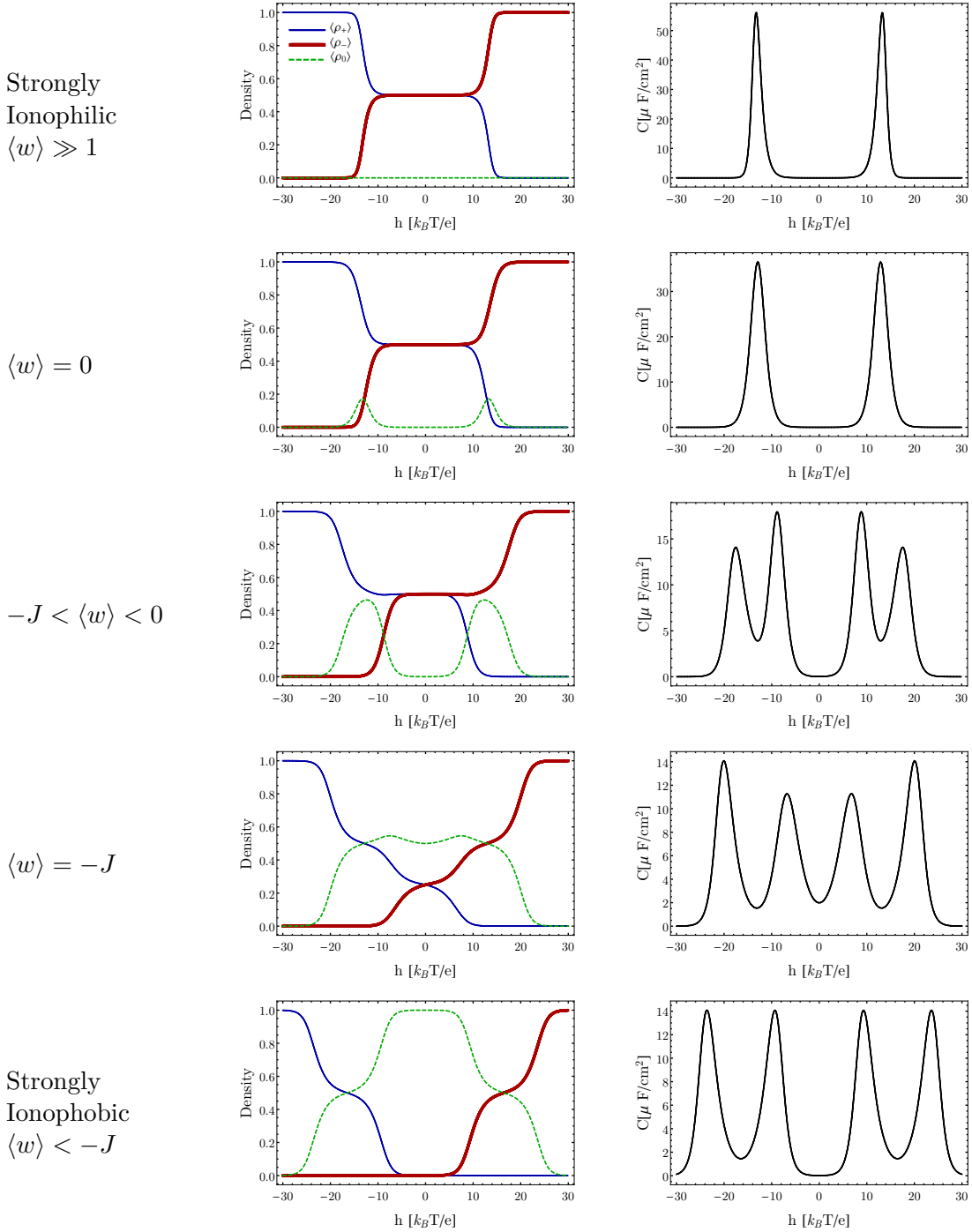


Figure 4.3: An array of graphs detailing the change in the differential capacitance surface, shown in figure 4.2, as the ionophilicity/phobicity of the pore changes. All pores are geometrically identical. Each row corresponds to a specific transfer energy, $w_- = w_+ \equiv \langle w \rangle$, shown in the left column. Ion and solvent densities are shown in the centre column and differential capacitance is shown in right column. [Parameters: $\ell_+ = \ell_- = \ell_0 = 0.9\text{nm}$, $r = 0.75\text{nm}$.]

the magnitude of the applied voltage reaches the threshold $|h^*| \approx 2J/e$, eqn. (3.18). The pore is fully charged once $|h| \gg 2J/e$. The only charging mechanisms in this case are $+ - + \rightarrow + + +$ or $- + - \rightarrow - - -$ depending on the polarity of the applied voltage. The difference in transfer energies of the BEG model, $\tilde{w}$, is the energy benefit to move a cation from the pore into the bulk and replace it with an anion. We recall that $\tilde{w}$ is also a parameter in the Ising model. We will need to decrease the average transfer energy to see the aspects of our three species model.

When the transfer energy gives no preference to whether an ion or solvent is in the pore, $\langle w \rangle = 0$, the density and corresponding differential capacitance graphs look similar to the strongly ionophilic case but there is an important difference. At low voltages cations and anions still form an alternating chain in the pore but now as the pore charges, near the threshold voltage, $|h^*| \approx 2J/e$, solvent molecules start to enter the pore. These solvent molecules are soon forced out of the pore but they do play an important role in the charging of the pore. We consider a cation or anion in an alternating chain of ions that would exist in a pore at low voltages. In the strongly ionophilic (solvent-phobic) case there is a large energetic cost for solvent molecules to enter the pore compared to ions, accordingly, this central anion is simply replaced by a cation once the relevant threshold voltage is reached. When there is little or no transfer energy discouraging solvent from entering the pore, $\langle w \rangle \gtrsim 0$, solvent molecules can enter the pore but only near the threshold voltage. The pore is weakly ionophilic. The solvent molecules allow an alternate charging mechanism.

Let us consider, for a moment, the charging of a pore, with $\langle w \rangle = 0$, via the application of a negative voltage. At low voltages an alternating chain of ions is still energetically favourable and charging can proceed directly as in the ionophilic case $+ - + \rightarrow + + +$ or it can proceed via an intermediate state. Near the threshold voltage the bonding between alternating charges is lessened and solvent molecules can play the role of a buffer separating two counterions. At higher voltages this neutral buffer molecule is itself forced out of the pore to make way for a counterion, $+ - + \rightarrow + \circ + \rightarrow + + +$ ³. The inclusion this intermediate state serves to reduce the height and increase the width of the peaks of the associated differential capacitance curve.

The first time we notice a striking change in the shape of the differential capacitance curve is when the average transfer energy of the pore is in the range $-J < \langle w \rangle < 0$. Where once we had one peak either side of $h = 0$, we now have two, four in total. The differential

³Charging follows the same mechanisms after the application of a positive voltage but the polarity of the molecules that leave and enter the pore is swapped.

capacitance has two local minima at $|h| \approx 2J/e$ in the centre of two sets local maxima at $|h^*| \approx (2J \pm w)/e$. The locations of the minima correspond to the locations of the maxima of the differential capacitance curve for an ionophilic pore. As the parameter $\langle w \rangle$ becomes negative each single peak splits in a manner resembling a pitchfork bifurcation into two new peaks and a minima, see figure 4.2. The inner peaks in each polarisation, relative to $h = 0$, corresponds to the formation the $+\circ+$ and $-\circ-$ intermediate states which have now become distinct from the fully charged $---$ or $+++$ states. We can see this clearly from the ion density curves in figure 4.3. At low voltages a chain of alternating ions exist but at a threshold of $|h^*| \approx (2J + \langle w \rangle)/e$ this chain is deconstructed and replaced with a chain of alternating counterions and solvent molecules. The pore is weakly ionophobic and $\langle w \rangle^* = 0$ is the threshold for the transition from the ionophilic regimes into this weakly ionophobic case. At $|h^*| \approx (2J - \langle w \rangle)/e$ the voltage is large enough to expel solvent ions from the pore and force counterions into a densely packed configuration beginning the second phase of charging.

Deriving the threshold voltages in this weakly ionophobic regime mathematically is impractical, the eigenvalues of $\underline{T}_{BEG}$ and the resulting closed form expressions for the free energy, spin and susceptibility of the system are too ungainly. However, the threshold voltages can be understood intuitively. To charge the pore we need to break the chain of alternating ions with an energetic cost of $2J$ but we also need to overcome the preference the pore now has for solvent molecules rather than ions requiring an energetic cost of $\langle w \rangle$. This gives a total energy cost of $2J - \langle w \rangle$ to fully charge the pore from neutral. The argument for the value of the threshold voltage of the intermediate state is the same as above but now the solvent molecule provides an energetic benefit reducing the energy required to reach this state. The inner differential capacitance peaks label by $-J < \langle w \rangle < 0$ in figure 4.3 are taller than the outer two showing that there is still some overlap in the voltage regimes where each charging mechanism operates. Finally, as the solvent density never reaches $\langle \rho_0 \rangle = 0.5$ we never have a pore completely filled with alternating counterions and solvent.

When the average transfer energy is the same magnitude as the nearest neighbour electrostatic coupling constant, $\langle w \rangle = -J$, we see that half of the pore is filled with solvent while the other half shared by an equal amount of cations and anions. All of the ions inside the pore are separated by a single solvent molecule, for example $\circ - \circ - \circ +$. The charging mechanisms and threshold voltages are the same as in the weakly ionophobic case but decomposition of the ion chain at low voltages signals that $\langle w \rangle^* = -J$ is the threshold that separates the weakly and strongly ionophobic regimes.

Once $\langle w \rangle < -J$ we no longer see any ions in the pore at low voltages, the alternating chain of ions has been totally replaced by the more energetically favourable row of solvent molecules. All four peaks in the differential capacitance are the same height and the two charging mechanism operate distinctly. The pore is strongly ionophobic. Intuitively⁴, we would assume, correctly, that the inner peaks are located at $|h^*| \approx -\langle w \rangle / e$ as this is the voltage required to replace a solvent with an ion in the pore and, as such, the inner peaks are associated with the charging processes $\circ \circ \circ \longrightarrow \circ + \circ$ and $\circ \circ \circ \longrightarrow \circ - \circ$. The outer peaks should be associated with the charging processes $\circ + \circ \longrightarrow + + +$ and $\circ - \circ \longrightarrow - - -$ and are located at $|h^*| = (2J - \langle w \rangle) / e$ as this is the voltage required to swap solvent with ions *and* overcome the electrostatic repulsion needed to form a chain of counterions. Increasing the ionophobicity past this point simply increases the separation of the two sets of peaks around $h = 0$.

To summarise, ions form an alternating chain in the pore at low voltages unless the pore is ionophobic enough to break up this chain and replace it with solvent. We say the pore is

- *Strongly Ionophilic* when $\langle w \rangle \gg 1$. The pore is filled with an equal amount of anions and cations at $h = 0$. There are only two differential capacitance maxima for $J > 1k_B T$. No solvent enters the pore in any significant quantities and we reproduce the Ising model of charge storage, section 3.2.
- *Weakly Ionophilic* when $\langle w \rangle \gtrsim 0$. The pore is filled with an equal amount of anions and cations at $h = 0$. There are only two differential capacitance maxima for $J > 1k_B T$. Some solvent can enter the pore near the charging thresholds $|h^*| \approx 2J/e$
- *Weakly Ionophobic* when $-J < \langle w \rangle < 0$. The pore is filled with an equal amount of anions and cations at $h = 0$ but no solvent. There are four differential capacitance maxima but the distance between two peaks in one polarity is sensitive to changes in $\langle w \rangle$.
- *Strongly Ionophobic* when $\langle w \rangle < -J$. The pore is filled with solvent at $h = 0$. There are four differential capacitance maxima and the distance between two peaks in one polarity is fixed.

The charging mechanisms and threshold voltages for each type of pore are summed up in Table 4.1 and depicted graphically in a flowchart in Figure 4.4. It is important to

⁴We will derive the location of the charging thresholds for a strongly ionophobic pore mathematically in section 4.2.4.

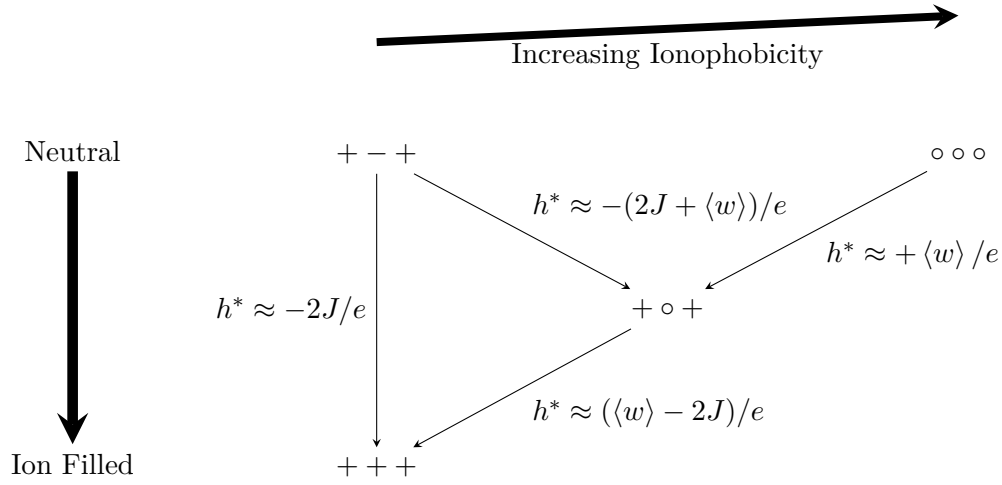


Figure 4.4: Flowchart summarising the typical configurations of ions inside a pore and the charging mechanisms present in the BEG model of charge storage with $\ell_+ = \ell_- = \ell_0$ upon the application of a negative voltage. Charging mechanisms are shown as arrows and the corresponding threshold voltage labels each arrow. A mixture of charging mechanisms can be present for certain ionophobicities.

Ionophobicity	Transfer Energy	Thresholds (eh^*)	Charging Mechanisms
Strongly ionophilic	$\langle w \rangle \gg 0$	$2J$ $-2J$	$- + - \rightarrow - - -$ $+ - + \rightarrow + + +$
Weakly ionophilic	$\langle w \rangle \gtrsim 0$	$2J$	$- + - \rightarrow - o -$ $- o - \rightarrow - - -$ $- + - \rightarrow - - -$
		$-2J$	$+ - + \rightarrow + o +$ $+ o + \rightarrow + + +$ $+ - + \rightarrow + + +$
Weakly ionophobic	$-J \leq \langle w \rangle \leq 0$	$(2J + w)$ $2J - \langle w \rangle$ $-(2J + \langle w \rangle)$ $\langle w \rangle - 2J$	$- + - \rightarrow - o -$ $- o - \rightarrow - - -$ $+ - + \rightarrow + o +$ $+ o + \rightarrow + + +$
Strongly ionophobic	$\langle w \rangle < -J$	$-\langle w \rangle$ $2J - \langle w \rangle$ $\langle w \rangle$ $\langle w \rangle - 2J$	$o o o \rightarrow o - o$ $o - o \rightarrow - - -$ $o o o \rightarrow o + o$ $o + o \rightarrow + + +$

Table 4.1: Summary of the charging mechanisms and voltage thresholds in BEG pores of various ionophobicities charged with ions and solvent of the same size. The strongly ionophilic case is comparable to the Ising model, section 3.2. The strongly ionophobic pore can be described by a two state model consisting of solvent and ions which is discussed in section 4.2.4.

note that the differential capacitance of ionophilic pores have a single peak per polarity while the ionophobic pores have two peaks per polarity. The number of peaks present in the differential capacitance will be the tell-tale sign indicating if a BEG pore is behaving ionophobically or -philically. It is clear from figure 4.2 that the location of the maxima and thus the charging thresholds undergo a smooth transition between the ionophilic, weakly ionophobic and strongly ionophobic regimes.

4.2.4 Threshold Voltages of Strongly Ionophobic Pores

We notice the similarity that each pair of peaks, at positive or negative polarity, in a strongly ionophobic pore, labelled $\langle w \rangle < -J$ in figure 4.3, has with the simple two state Ising model of charge storage described in section 3.2. The two peaks in the same polarity are separated by the same voltage, $h \approx 2J/e$ but these peaks are smaller than the peaks in Ising model. This is to be expected, as we have increased the ionophobicity of our pore we have removed any voltage regime where all three molecules can enter the pore at the same time in any significant quantities. Positive voltages regimes are occupied by anions and solvent while negative voltages by cations and solvent alone. In each of these regimes we have a two species system, similar to what we considered with the Ising model, however, the charging mechanisms are now very different. The charging mechanism in the Ising model of charge storage were $- + - \rightarrow - - -$ and $+ - + \rightarrow + + +$. Now, in the BEG model we have $- \circ - \rightarrow - - -$ in the region of positive voltage and $+ \circ + \rightarrow + + +$ in the region of negative voltage. The total charge accumulated in one voltage regime is halved compared to the Ising model which considers charge accumulated in both voltage regimes. This accounts for the lower height of the differential capacitance peaks. Recall that the surface charge accumulated between two voltages h_1 and h_2 is the integral of the differential capacitance with regards to voltage

$$\sigma(h_2) - \sigma(h_1) = \frac{1}{e} \int_{h_1}^{h_2} C(\eta) d\eta. \quad (4.17)$$

The reduction of the system into isolated two state subsystems in each polarity allows us to mathematically, rather than just intuitively, explain the location of the differential capacitance threshold voltages. We consider the two state system consisting of anions and solvent ($2S^-$) to find the charging thresholds at positive voltages described

by the partition function⁵

$$H_{2S-} = \sum_{\langle i,j \rangle} J_{s_i, s_j} s_i s_j + \sum_i h_{s_i} s_i, \quad Z_{2S-} = \sum_{\{s\}} \exp(-H_{2S-}) \quad (4.18)$$

where $s \in \{0, -1\}$ and

$$h_{s_{-1}} \equiv h_- = eh + w_-, \quad h_{s_0} = 0. \quad (4.19)$$

To evaluate this partition function we consider the transfer matrix

$$\underline{T}_{2S-} = \begin{pmatrix} 1 & e^{h_-/2} \\ e^{h_-/2} & e^{-J_{--}+h_-} \end{pmatrix}. \quad (4.20)$$

We note that this transfer matrix is the lower right 2×2 sub-matrix of the BEG transfer matrix, eqn. (4.3). Following the transfer matrix methods that we have employed in sections 3.2, 3.4 and 4.1 we proceed by finding the largest eigenvalue of $\underline{T}_{2S-}$

$$\lambda_+ = \frac{1}{2} \left(1 + e^{h_- - J_{--}} + \sqrt{(1 + e^{h_- - J_{--}})^2 - 4(e^{h_- - J_{--}} - e^{h_-})} \right). \quad (4.21)$$

In the thermodynamic limit we can use this eigenvalue to obtain the free energy per site of the system and from this the susceptibility

$$\chi = \frac{2e^{J_{--}} \cosh\left(\frac{1}{2}(J_{--} - h_-)\right)}{(2 \cosh(J_{--} - h_-) + 4e^{J_{--}} - 2)^{3/2}}. \quad (4.22)$$

To obtain the location of the threshold voltages we look for the maxima of this susceptibility

$$\begin{aligned} \frac{\partial \chi}{\partial h_-} &= 0 \\ &= (e^{h_-} - e^{J_{--}}) (e^{2h_-} + e^{2J_{--}} + 4e^{h_-+J_{--}} - 2e^{h_-+2J_{--}}) \zeta \end{aligned} \quad (4.23)$$

where we have introduced the strictly positive function ζ to encapsulate the sections of eqn. (4.23) that are unimportant when looking for the threshold voltages. The location of one turning point, $h_- = J$, comes from setting the argument of the first parenthesis equal to zero. Unfortunately, this is not one of the maxima we are looking for but rather the minima that separate them. The two maxima must be found by setting the argument of the second parenthesis equal to zero. To simplify the problem we make the transformation

⁵We do not make the simplification that $\ell_+ = \ell_- = \ell_0$ but consider the general case.

in the second parenthesis

$$h_- = \hat{h} - J_{--} \quad (4.24)$$

so that

$$\begin{aligned} (e^{2h_-} + e^{2J_{--}} + 4e^{h_-+J_{--}} - 2e^{h_-+2J_{--}}) &= 0 \\ 2e^{\hat{h}} (2 - e^{J_{--}} + \cosh(\hat{h} - 2J_{--})) &= 0 \\ \implies \hat{h} &= \{J_{--}, 3J_{--}\} \quad \text{for } J_{--} \gg 1 \\ h_- &= \{0, 2J_{--}\} \\ h^* &= \frac{1}{e} \{-w_-, (2J_{--} - w_-)\} \end{aligned} \quad (4.25)$$

In the special case of ions of the same size ($J_{++} = J_{+-} = J_{--} = J$) and symmetric transfer energy ($w_+ = w_- = \langle w \rangle$) eqn. (4.25) gives us the exact threshold voltages we expected to find at positive voltages for a strongly ionophobic pore, table 4.1. To find the negative threshold voltages we need to consider the two state system consisting of cations and solvent only ($2S+$). The relevant transfer matrix for such a system is the upper left 2×2 sub-matrix of $\underline{T}_{BEG}$

$$\underline{T}_{2S+} = \begin{pmatrix} e^{-J_{++}-h_+} & e^{-h_+/2} \\ e^{-h_+/2} & 1 \end{pmatrix}. \quad (4.26)$$

This system can be analysed in exactly the same way as the ($2S-$) system revealing the negative threshold voltages to be

$$h^* = \frac{1}{e} \{(w_+ - 2J_{++}), w_+\}. \quad (4.27)$$

The full set of threshold voltages (locations of the peaks of differential capacitance) for a strongly ionophobic BEG pore with symmetric transfer energy ($w_+ = w_- = \langle w \rangle$) are given by

$$h^* = \frac{1}{e} \{\langle w \rangle - 2J_{++}, \pm \langle w \rangle, 2J_{--} - \langle w \rangle\}. \quad (4.28)$$

4.2.5 Changing Ion Size

We wish to understand how the differential capacitance surface of a BEG pore changes as we include ion asymmetry, $\ell_- \neq \ell_+$. The major difference between charging with molecules of different sizes and charging with identically sized molecules is that there is no longer a single electrostatic coupling constant, J . The different sizes of the ions imply

that there are three electrostatic couplings J_{++} , J_{+-} and J_{--} but given our experience examining the charging a BEG pore wetted with identically sized molecules, section 4.2.3, we do have some idea of what to expect. We start by discussing the limits of ionophobicity where we already understand what is happening in the pore and then we will consider what will happen in the regions of ionophobicity which we are unable to analyse mathematically. Once we have our predictions we will apply this knowledge to explain the results shown in figures 4.6 and 4.7.

Predictions

We expect we will be able to classify our pores as strongly ionophilic, weakly ionophilic, weakly ionophobic and strongly ionophobic. A strongly ionophilic pore will not admit solvent and we will reproduce the Ising model of charge storage wetted with ions of different sizes, section 3.4. The charging thresholds for a pore in this regime will be $h^* = \{J_{--} + J_{+-}, -(J_{++} + J_{+-})\}/e$. A strongly ionophobic pore will be filled with solvent at low voltages and the BEG model will reduce to the two species models detailed in section 4.2.4. The charging thresholds for such a pore will be $h^* = \{\langle w \rangle - 2J_{++}, \pm \langle w \rangle, 2J_{--} - \langle w \rangle\}/e$, eqn. (4.28). Between these two extremes we expect to find the weakly ionophilic and weakly ionophobic regimes. The charging thresholds in a weakly ionophilic pore will, by definition, be identical to the charging thresholds of a strongly ionophilic pore but the charging thresholds for a weakly ionophobic pore will not come so easily and will need consideration.

A pore in a weakly ionophobic regime is filled with ions of alternating charges at low voltages. There are two charging mechanisms, the swapping of coions for solvent ($- + - \rightarrow - \circ -$ or $- + - \rightarrow + \circ +$) and the eventual swapping of these solvent molecules for counterions at larger voltages ($- \circ - \rightarrow - - -$ or $+ \circ + \rightarrow + + +$). We consider, at first, the swapping of positive coions with solvent on the application of a positive voltage. To remove a cation from the alternating ion chain we need to break the electrostatic bonds between two neighbouring anions, this has an energetic cost of $2J_{+-}$. The insertion of a solvent molecule has the energetic cost/benefit of $\langle w \rangle$. In total the energetic cost associated with the charging mechanism $- + - \rightarrow + \circ +$ is $2J_{+-} + \langle w \rangle$ and its threshold voltage will be $h^* = (2J_{+-} + \langle w \rangle)/e$. The argument for the threshold voltage associated with the charging mechanism $- + - \rightarrow - \circ -$ in the opposite polarity is the same, resulting in $h^* = -(2J_{+-} + \langle w \rangle)/e$. At larger voltages this solvent molecule will be replaced by a counterion in the pore. The energetic cost/benefit of excluding a solvent

from the pore is $-\langle w \rangle$. The insertion of a counterion between two other ions with the same charge will come with an energetic cost of $2J_{++}$ or $2J_{--}$ depending on the polarity of the voltage applied. Thus, the total energetic cost of the second charging processes will be $2J_{--} - \langle w \rangle$ or $2J_{++} - \langle w \rangle$. Therefore, the charging process $-\circ- \rightarrow - - -$ will occur at a threshold voltage $h^* = (2J_{--} - \langle w \rangle)/e$ and the process $+\circ+ \rightarrow + + +$ at $h^* = -(2J_{++} - \langle w \rangle)/e$.

The mathematical analysis of the charging thresholds of the ionophilic and strongly ionophobic regimes combined with the intuitive analysis of the charging thresholds of the weakly ionophobic regimes have given us insight into what will happen in a pore once we have classified its ionophobicity. Unfortunately, we cannot use this analysis at the moment as we do not know to what values of average transfer energy the terms strongly ionophilic, weakly ionophilic, weakly ionophobic and strongly ionophobic apply to a BEG pore charged with ions of different sizes. We do know that in the special case of identically sized ions each ionophilic charging threshold splits into two weakly ionophobic thresholds and these thresholds themselves smoothly transitioned into the strongly ionophobic thresholds, figure 4.2b. We expect that the charging thresholds of BEG pore filled with ions of different sizes to do the same. Therefore, to find the value of the transfer energy that separates the ionophilic and ionophobic regimes we look for the value of $\langle w \rangle$ at which the two weakly ionophobic thresholds split from the single ionophilic threshold. At positive voltages we have

$$\begin{aligned} eh^* &= J_{--} + J_{+-} = 2J_{+-} + \langle w \rangle = 2J_{--} - \langle w \rangle \\ \implies \langle w \rangle^* &= J_{--} - J_{+-} \end{aligned} \quad (4.29)$$

and at negative voltages we have

$$\begin{aligned} eh^* &= J_{++} + J_{+-} = 2J_{+-} + \langle w \rangle = 2J_{++} - \langle w \rangle \\ \implies \langle w \rangle^* &= J_{++} - J_{+-}. \end{aligned} \quad (4.30)$$

The two different thresholds between ionophobic and ionophilic behaviour imply that the effective ionophobicity of the pore is polarity dependent. In other words, it will be possible for the differential capacitance of a BEG pore to have a single maximum in one voltage polarity (ionophilic behaviour) and a double peak (ionophobic behaviour) in the other. The threshold energies $J_{--} - J_{+-}$ and $J_{++} - J_{+-}$ are the difference in magnitude of an interaction between adjacent like and unlike ions in a pore.

The equations for the outer threshold voltages, relative to $h = 0$, are the same for

both weakly ionophobic behaviour and strongly ionophobic behaviour but we can match the inner thresholds to find the crossover between the two ionophobic regimes. At positive voltages we have

$$\begin{aligned} eh^* &= 2J_{+-} + \langle w \rangle = -\langle w \rangle \\ \implies \langle w \rangle^* &= -J_{+-} \end{aligned} \quad (4.31)$$

and at negative voltages

$$\begin{aligned} eh^* &= -(2J_{+-} + \langle w \rangle) = \langle w \rangle \\ \implies \langle w \rangle^* &= -J_{+-}. \end{aligned} \quad (4.32)$$

The crossover between weakly and strongly ionophobic regimes is the same for both polarities and, somewhat expectantly, it is the transfer energy required to deconstruct a chain of alternating ions and fill the pore with solvent at low voltages. All of the charging mechanisms and thresholds predicted for a BEG pore filled with ions of different sizes are summarised in table 4.2 and depicted graphically in the flowchart shown in figure 4.5.

Results

We present the differential capacitance surface of BEG pore charged with ions of different sizes in similar manner to section 4.2.3 as function of voltage and average transfer energy in figure 4.6. The accompanying figure 4.7 shows several cross sections of this differential capacitance surface, again the values of the transfer energy used to create these cross sections are shown on the contour plot, figure 4.6b. We will examine each of these cross sections of the differential capacitance surface in turn.

The differential capacitance and molecule density curves with a transfer energy of $\langle w \rangle \gg J_{++} - J_{+-}$ correspond to the most ionophilic pore shown in figure 4.7. Indeed, at this transfer energy the pore is strongly ionophobic for both voltage polarities and the Ising model of charge storage with different sized ions is recovered.

The second set of graphs, labelled $\langle w \rangle = J_{++} - J_{+-}$ in figure 4.7, are the first we have seen that show polarity dependent ionophobicity. The differential capacitance in negative voltages is weakly ionophilic, while at positive voltages it is strongly ionophilic. $\langle w \rangle = J_{++} - J_{+-}$ corresponds to a transfer energy at the ionophilic/ionophobic boundary for negative voltages. The negative peak of the differential capacitance has decreased in

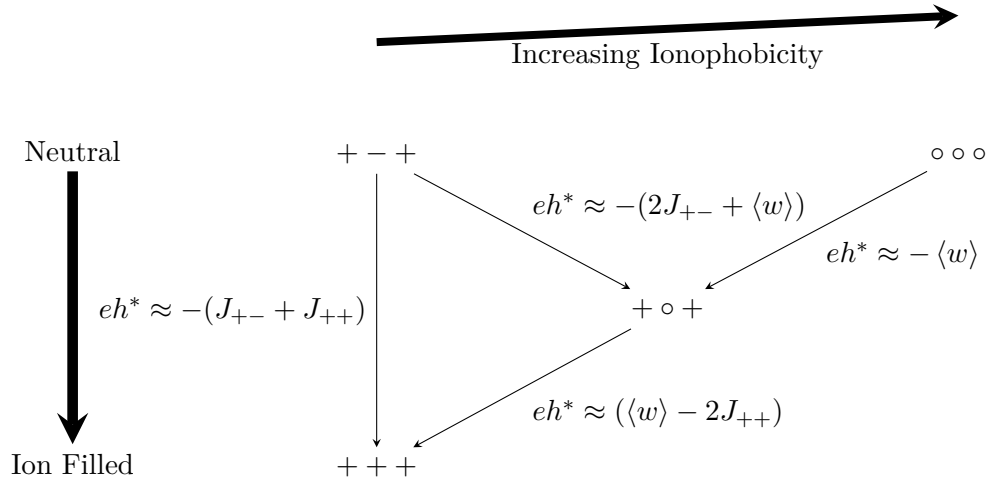
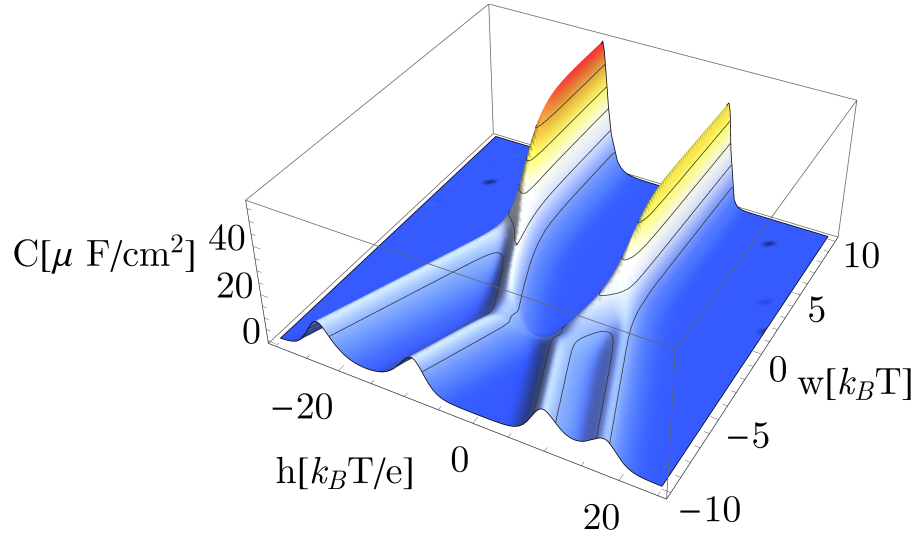


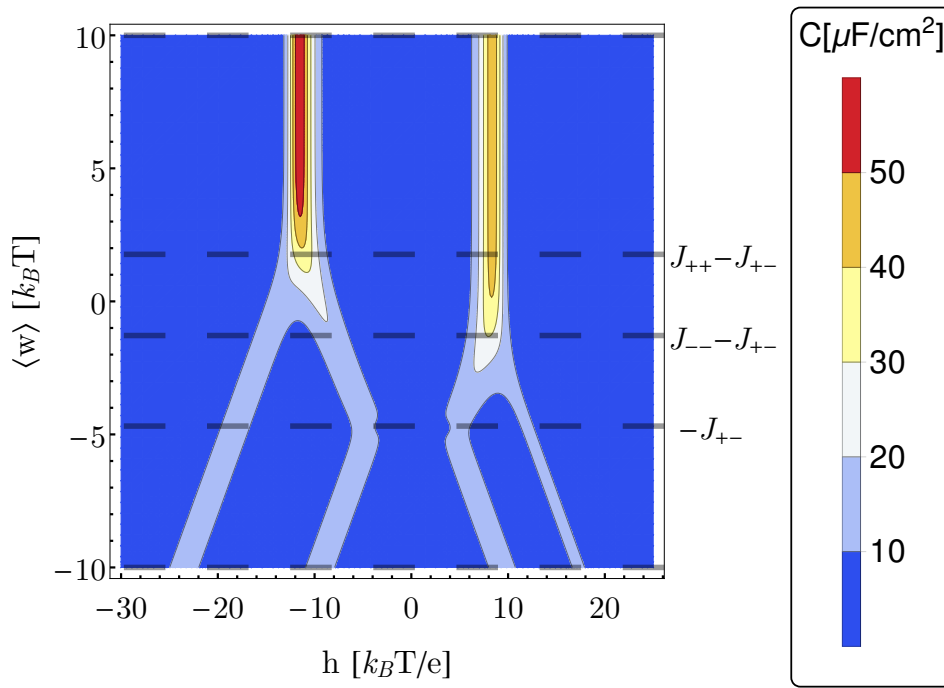
Figure 4.5: Flowchart summarising the typical configurations of ions inside a pore and the charging mechanisms present in the BEG model of charge storage with $\ell_+ \neq \ell_- = \ell_0$ upon the application of a negative voltage. Charging mechanisms are shown as arrows and the corresponding threshold voltage labels each arrow. A mixture of charging mechanisms can be present for certain ionophobicities.

Ionophobicity	Transfer Energy	Thresholds (eh^*)	Mechanisms
Strongly ionophilic	$\langle w \rangle \gg J_{--} - J_{+-}$	$(J_{+-} + J_{--})$	$-+- \rightarrow ---$
	$\langle w \rangle \gg J_{++} - J_{+-}$	$-(J_{+-} + J_{++})$	$+-+ \rightarrow +++$
Weakly ionophilic	$\langle w \rangle \gtrsim J_{--} - J_{+-}$	$(J_{+-} + J_{--})$	$-+- \rightarrow -o-$
			$-o- \rightarrow ---$
			$-+- \rightarrow ---$
	$\langle w \rangle \gtrsim J_{++} - J_{+-}$	$-(J_{+-} + J_{++})$	$+-+ \rightarrow +o+$
Weakly ionophobic	$-J_{+-} \leq \langle w \rangle < J_{--} - J_{+-}$	$(2J_{+-} + \langle w \rangle)$	$-+- \rightarrow -o-$
		$(2J_{--} - \langle w \rangle)$	$-o- \rightarrow ---$
	$-J_{+-} \leq \langle w \rangle < J_{++} - J_{+-}$	$-(2J_{+-} + \langle w \rangle)$	$+-+ \rightarrow +o+$
		$-(2J_{++} - \langle w \rangle)$	$+o+ \rightarrow +++$
Strongly ionophobic	$\langle w \rangle < -J_{+-}$	$-\langle w \rangle$	$ooo \rightarrow o-o$
		$(2J_{--} - \langle w \rangle)$	$o-o \rightarrow ---$
		$\langle w \rangle$	$ooo \rightarrow o+o$
		$-(2J_{++} - \langle w \rangle)$	$o+o \rightarrow +++$

Table 4.2: Summary of the charging mechanisms and voltage thresholds in BEG pores of various ionophobicities charged with ions and solvent of different sizes. The strongly ionophilic case is comparable to the Ising pore wetted with ions of different sizes, section 3.4. The strongly ionophobic pore can be described by a two state model consisting of solvent and ions, section 4.2.4.



(a) 3D Surface.



(b) Contour Plot

Figure 4.6: 3D Differential capacitance surface of a pore as a function of voltage h and average transfer energy $\langle w \rangle$ charged with ions of different sizes $\ell_+ \neq \ell_-$ and the corresponding contour plot of this surface. Cross sections of this surface, at constant $\langle w \rangle$ are shown in figure 4.7 and are indicated on this contour plot as horizontal gray broken lines. The coupling constants combinations relevant to the ionophobicity/ionophilicity thresholds are shown on the contour plot. [Parameters: $\ell_- = 1.1\text{nm}$, $\ell_+ = \ell_0 = 0.9\text{nm}$, $r = 0.75\text{nm}$.]

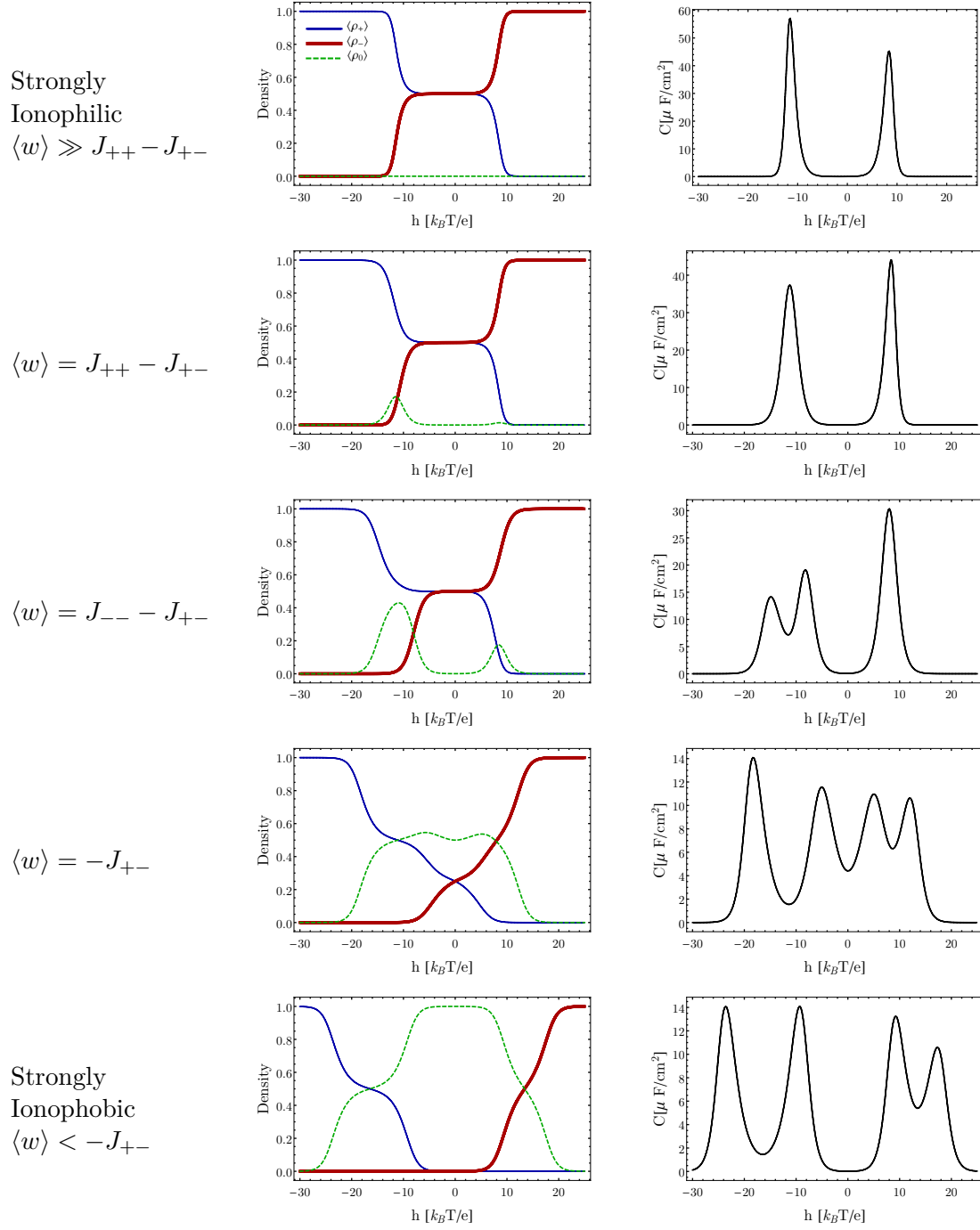


Figure 4.7: An array of graphs detailing the change in the differential capacitance surface, shown in figure 4.6b, as the ionophilicity/phobicity of the pore changes. All pores are geometrically identical. Each row corresponds to a specific transfer energy, $w_- = w_+ \equiv \langle w \rangle$, shown in the left column. Ion and solvent densities are shown in the centre column and differential capacitance is shown in right column. [Parameters: $\ell_- = 1.1\text{nm}$, $\ell_+ = 0.9\text{nm}$, $r = 0.75\text{nm}$.]

height and widened, when compared to the strongly ionophilic peak, as a result of the significant amount of solvent that enters pore near the charging threshold. The positive peak is still relatively untouched as the current transfer energy is still larger than the ionophilic/ionophobic boundary at positive voltages, $J_{++} - J_{+-} > J_{--} - J_{+-}$. Physically, solvent aids charging by acting as a buffer between the counterions. The asymmetry in solvent density ultimately stems from the fact that this solvent buffer is in greater demand when the pore is charged with smaller ions with larger the electrostatic interactions.

The graphs labelled $\langle w \rangle = J_{--} - J_{+-}$ in figure 4.7 correspond to a transfer energy at the ionophilic/ionophobic boundary for positive voltages. In negative voltages the pore behaves weakly ionophobically as $J_{++} - J_{+-} > J_{--} - J_{+-} > J_{+-}$. We also notice the solvent density near the positive threshold voltage at this transfer energy is comparable to the solvent density near the negative threshold voltage $\langle w \rangle = J_{++} - J_{+-}$. This is understandable as both solvent densities are at the same effective ionophobicity.

From the graphs labelled $\langle w \rangle = -J_{+-}$ in figure 4.7 we can see that anions and cations occupy half of the sites in the pore at zero voltage, the other half is occupied by solvent and the differential capacitance has two peaks in both polarities signifying ionophobic behaviour. This is the boundary between weak and strong ionophobicity. The differential capacitance peaks at this ionophobicity decrease in height from right to left as larger more positive voltages favour larger counterions ($\ell_- > \ell_+$) that have a lower charge density and thus accumulate a lower surface charge per unit area.

The final set of graphs, labelled $\langle w \rangle < -J_{+-}$ in figure 4.7, depict a pore that favours solvent enough to be occupied by it at low voltages. This pore is strongly ionophobic. The differential capacitance peaks at negative polarity are the same height as the solvent molecules and anions are the same size. However, the inner differential capacitance peak at positive polarity is higher than the outer one as the solvent is smaller than an anion in this figure the charging mechanism $\circ \circ \circ \longrightarrow \circ - \circ$ accumulates more charge per unit length than the mechanism $\circ - \circ \longrightarrow - - -$. This means that the change in surface charge per unit length of the pore is greater in the initial phase of charging than in the second in this polarity accounting for the higher peak.

The results seen in figures 4.6 and 4.7 have confirmed the predictions made earlier in this section. All that is needed to predict the location and number of the maxima in the differential capacitance of a BEG pore filled an interacting chain of ions is table 4.2. For example, figure 4.8a shows the effects of changing the size of the cation charging a strongly ionophobic pore. Cations do not enter the pore at positive voltages resulting

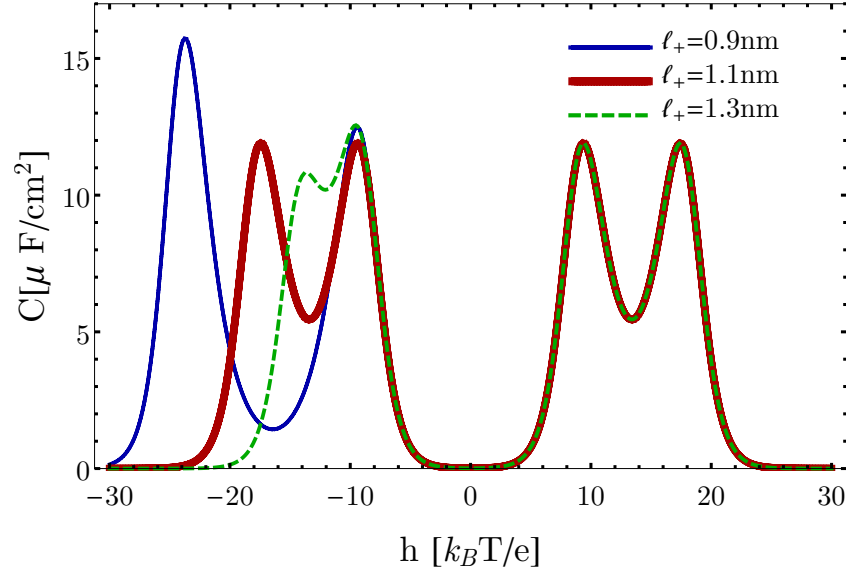
in the unchanged differential capacitance curves. The inner negative peak is located at $h^* = \langle w \rangle / e$ while the outer is located at $h^* = -(2J_{++} - \langle w \rangle) / e$. The inner negative peak is resilient to change in the cation size as its threshold is not a function of cation size. The outer negative peak is found at lower voltages when the ion is smaller as J_{++} increases as the cation shrinks, eqn. (3.3). Again, the outer peak is higher as smaller ions have a larger charge density.

4.2.6 Changing Solvent Size

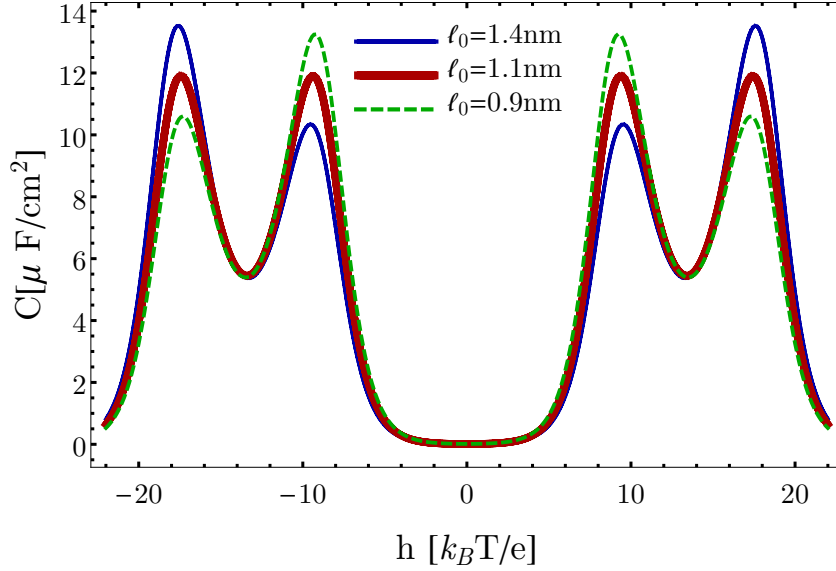
Solvent size does not affect the charging thresholds or mechanisms in our model. This parameter only enters via the average lattice spacing, $\langle \ell \rangle$, which acts to normalise the differential capacitance, eqn. (4.12). We have seen some effects from unequal sized ions and solvent in section 4.2.5 but it will be worthwhile to specifically look at how changing solvent size affects the differential capacitance. Figure 4.8b shows the effects of varying solvent size has on differential capacitance of a pore charged with ions of the same size ($\ell_+ = \ell_-$). Decreasing the size of the solvent molecule increases the height of the inner peaks in the differential capacitance. These inner peaks correspond to the charging mechanisms $+ - + \rightarrow + \circ +$ and $- + - \rightarrow - \circ -$. Replacing a larger ion with a smaller solvent molecule in your pore allows more molecules into a pore of finite length. The charge accumulated in these processes is larger accounting for the higher peaks. The outer peaks are reduced as you are now forcing out a smaller solvent molecule to make way for a larger ion in the charging mechanisms $+ \circ + \rightarrow + + +$ and $- \circ - \rightarrow - - -$. If the solvent molecule is larger than the ions this trend is reversed. The inner peaks become smaller and the outer peaks are taller.

4.3 Monte Carlo Simulations of a Single Pore

Complementary Monte Carlo simulations were preformed in collaboration with the author's colleague Dr. Svyatoslav Kondrat, at the time of writing, of Forschungszentrum Jülich GmbH previously of Prof. Kornyshev's Group at Imperial College London. Importantly, in these simulations the molecules within the pore are not constrained to sit in the centre of the pore. These simulations are similar to those performed by Dr. Kondrat in [91] regarding the charging of slit pores and [6] which considered the charging of cylindrical pores. We will only summarise the simulation method here and refer the reader to the aforementioned publications for full details.



(a) Changing cation size



(b) Changing solvent size

Figure 4.8: Differential capacitance a BEG pore with ions and solvent of different sizes. The differential capacitance curves produced from changing anion size are equivalent to the curves produced after changing cation size and making a reflection in the line $h = 0$. [Parameters: $r = 0.75\text{nm}$, $\ell_- = 1.1\text{nm}$. a) $\ell_0 = 1.1\text{nm}$. b) $\ell_+ = 1.1\text{nm}$.]

Hard sphere ions of different sizes with a point charge at their centre are placed inside an ideally screening cylindrical pore. These ions interact with each other, their own image charge and are influenced by a chemical potential. These ions cannot overlap and two monovalent ions centred at $(0, \bar{\rho}, 0)$ and (ℓ, ρ, ϕ) have an interaction energy of

$$J(\ell, \rho, \bar{\rho}, \phi) = \frac{e^2}{\epsilon} \frac{2}{r} \sum_{m=0}^{\infty} a_m \cos m\phi \sum_{n=1}^{\infty} \frac{J_m(k_{nm}\bar{\rho}/r) J_m(k_{nm}\rho/r)}{k_{nm} Y_{m+1}(k_{nm})^2} e^{-k_{nm}|\ell/r|} \quad (4.33)$$

where $a_m = 1$ if $m = 0$ and $a_m = 2$ otherwise, $J_m(x)$ and $Y_m(x)$ are the Bessel functions of the first and second kind and k_{nm} is the n^{th} positive root of $J_m(x)$. In the special case of $\bar{\rho} = \rho = 0$ this formula reduces to eqn. (3.3), see [124] for a full derivation. The energy of interaction between a charge located at $(0, \bar{\rho}, 0)$ and own induced image charge is given by

$$U(\bar{\rho}, r) = -\frac{e^2}{\epsilon} \frac{1}{2\pi^2 r} \sum_{m=0}^{\infty} a_m \int_0^{2\pi} d\phi \cos m\phi \int_0^{\infty} d\xi \frac{I_m(\xi\bar{\rho}/r)}{I_m(\xi)} K_0\left(\frac{\xi}{r} \sqrt{\bar{\rho}^2 + r^2 - 2r\bar{\rho} \cos \phi}\right) \quad (4.34)$$

where $I_m(x)$ and $K_m(x)$ are the modified (or hyperbolic) Bessel functions of the first and second kind respectively. Molecules are forced into the pore by a chemical potential, $\mu_{\pm}$ for cations and anions and μ_0 for a solvent. The transfer energy described in the theory is related to this chemical potential via

$$-w_{\pm} = U(\bar{\rho}, r) + \mu_{\pm}^{(sim)} - \mu_0^{(sim)}. \quad (4.35)$$

Note that in simulations we distinguish between a solvent and voids and therefore we have additionally chemical potential of a solvent, $\mu_0^{(sim)}$, which had to be fitted to compare with the theory. We choose $\mu_0^{(sim)}$ such that a pore is nearly fully occupied at any voltage either by ions or by solvent to more closely correspond to the theoretical model. It must be noted however that eqn. (4.35) does not give a satisfactory quantitative agreement between the theory and simulations, most likely due to the lateral entropy and the shift in the interaction potentials (ions in simulations are free to locate at the pore wall and are not restricted to the middle axis as in the theory), both ignored in the theory but which would modify eqn. (4.35). Nevertheless the qualitative agreement between the theory and simulations is excellent, figure 4.9.

Interaction potentials eqns. (4.33) and (4.34) have been implemented in MCCCSTowhee simulation package [125, 126]. Our system constitutes a single cylindrical pore which was 25nm long and periodic boundary conditions were applied along the pore. The grand-canonical Monte Carlo simulations consisted of the standard Widom insertion/deletion [127] and translational moves, but additionally we used a molecular type

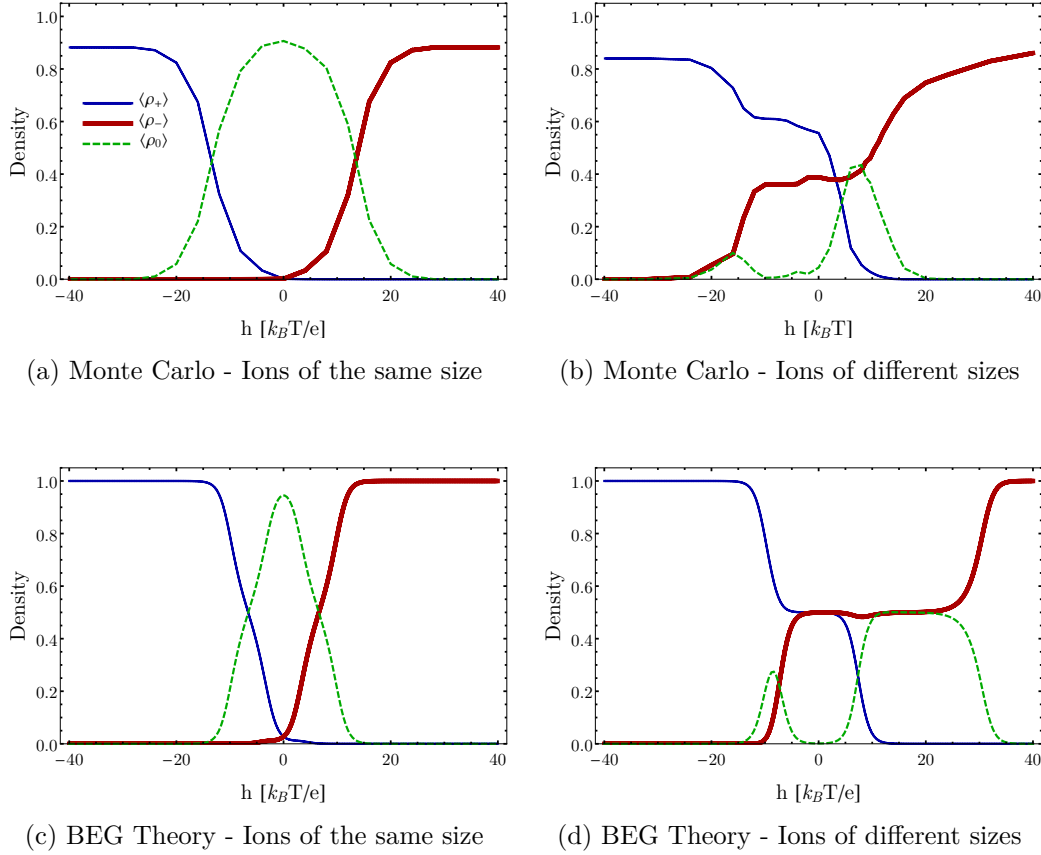


Figure 4.9: Comparison of observed Monte Carlo molecule densities and those predicted by the BEG theory. The first row shows simulation data and the second theory. Both columns have the same parameters. The first column shows charging with $\ell_+ = \ell_-$ and the second compared charging with $\ell_+ > \ell_-$. Both simulation and theory are in good agreement. [Parameters: $\ell_+ = \ell_0 = 0.7\text{nm}$, $r = 0.75\text{nm}$, $\langle w \rangle = -4k_B T$, a) & c) $\ell_- = 0.7\text{nm}$, b) & d) $\ell_- = 0.45\text{nm}$.]

swap move in which a randomly picked molecule is replaced by a molecule of a different type provided it fits into the emptied space. [91] The total number of simulation steps was $5 \times 10^6 - 10^7$ in the equilibration runs and 2×10^7 in the production runs. To obtain better results in some cases we performed a second round of simulations starting from the saved molecular configurations from the previous runs.

4.4 Results for Many Pores

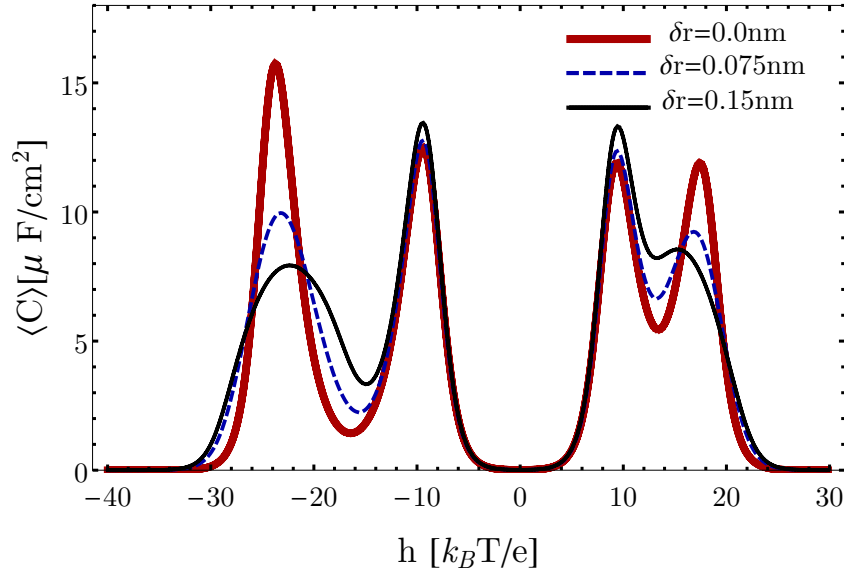
We wish to extend our BEG model of charge storage in a single pore to a model of charge storage in a electrode in a similar way to that discussed in section 3.3. We can use eqns. (3.21) and (3.22) to obtain the average differential capacitance of many BEG pores almost without modification. However, now that we have a three rather than a two species model we will have to ensure that both the ions and solvent can enter the pore while still maintaining the single file structure of the molecules in the pore. To do this we set the minimum and maximum radii used to the truncated normal pore size distribution, eqn. (3.22), such that

$$r_{max} = \min(\ell_+, \ell_-, \ell_0), \quad r_{min} = \max(\ell_+/2, \ell_-/2, \ell_0/2). \quad (4.36)$$

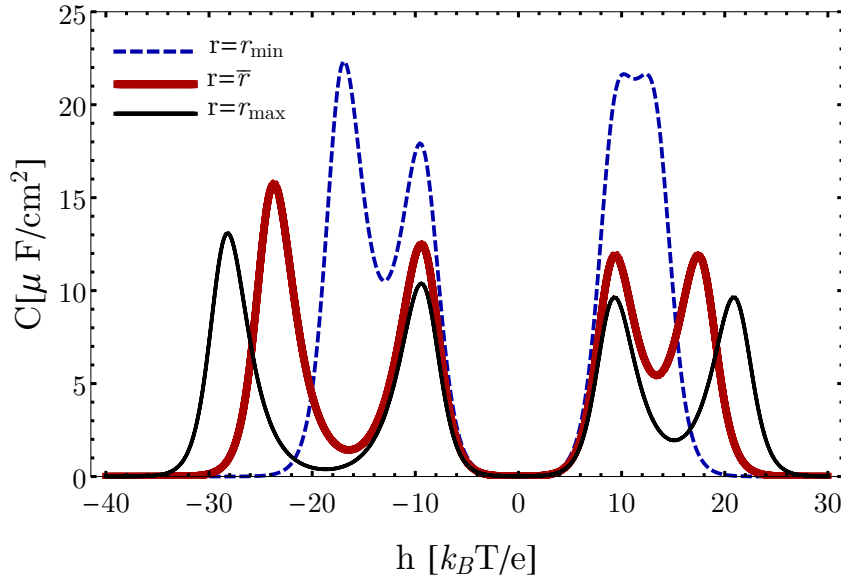
4.4.1 Many Strongly Ionophobic Pores

Figure 4.10 shows the effects of applying the pore size distribution defined by eqns. (3.21), (3.22) and (4.36) to the differential capacitance of many strongly ionophobic, $\langle w \rangle < -J_{+-}(r_{max})$ BEG pores charged with ions of different sizes. The differential capacitance of the largest, smallest and average BEG pores corresponding to the truncated normal pore distribution using in figure 4.10a are shown in figure 4.10b.

We can see from figure 4.10a that increasing the standard deviation of the pore size distribution has little effect on the inner peaks. To understand this we have to recall that for a strongly ionophobic pore there are no ions in the pore at low voltages and the pore is filled with solvent only. Half of the solvent in such a pore will swap for counterions at the threshold voltage $|h^*| \approx -\langle w \rangle / e$. This is not dependent on pore radius so long as the radius does not increase to a point where it is energetically favourable to form a chain of alternating ions at low voltages. As we have defined that ionophobicity of our electrode is such that $\langle w \rangle < -J_{+-}(r_{max})$ this will not happen in any pore. As each pore



(a) Capacitance of many BEG pores



(b) Capacitance of a single pore

Figure 4.10: Average capacitance of many BEG pores over a truncated normal pore radii distribution and the differential capacitance curves of the max, min and average radii pores associated with that truncated distribution, defined in section 4.4. All pores have symmetric transfer energy and are charged with ions of different sizes, $\ell_- \neq \ell_+$. The red curves are identical on both figures. [Parameters: $\ell_+ = 0.9\text{nm}$, $\ell_- = \ell_0 = 1.1\text{nm}$, $\bar{r} = 0.75\text{nm}$, $w_+ = w_- = \langle w \rangle = -10k_B T$.]

we average over half fills with counterions at this threshold voltage the height and shape of the inner average differential capacitance peaks remain unchanged as we increase the standard deviation of the pore radius distribution of the electrode.

Increasing the standard deviation of the pore size distribution does have a large effect on the outer peaks, decreasing their size. These outer peaks correspond to the second phase of charging, $+ \circ + \rightarrow + + +$ and $- \circ - \rightarrow - - -$. Here counterions need to enter the pore and overcome the electrostatic interaction with their two new neighbours in the pore. These outer peaks are located at $h^* = \{2J_{--}(r) - \langle w \rangle, -(2J_{++}(r) - \langle w \rangle)\}/e$. The electrostatic part of this threshold voltage is exponentially sensitive to changes in the radius of the pore that the counterions are entering. This second phase of charging starts at lower voltages for smaller pores, where the screening between nearest neighbour ions is the strongest and at higher voltages in larger pores, where screening is the smallest. This can be seen in figure 4.10b. The dependence that the outer peaks location has on pore radius causes the outer peaks to be smeared out as we increase the standard deviation of the electrode pore radius distribution. This also decreases their height and slightly fills in the trough between the inner and outer peaks.

4.4.2 Many Weakly Ionophobic or Ionophilic Pores

Should we consider a weakly ionophobic electrode, that is one in which all pores are weakly ionophobic, $-J_{+-} \leq \langle w \rangle < J_{--} - J_{+-}$ or $-J_{+-} \leq \langle w \rangle < J_{++} - J_{+-}$ depending on polarity. Then every pore in the electrode will be at least partially filled with ions at low voltages. The first charging process in any pore in this electrode would be the removal of coions and their replacement with solvent molecules, $+ - + \rightarrow + \circ +$ or $- + - \rightarrow - \circ -$. The inner peaks of our differential capacitance are associated with this charging process and are located at $|h^*| \approx (2J_{+-}(r) + w)/e$. The location of these inner peaks is now sensitive to pore radii and so we expect any averaging to smear the inner peaks as well as the outer peaks. Indeed, one would expect the inner peaks to be smeared out by exactly the same amount as the outer peaks as both the inner and outer peaks, in each polarisation, are symmetric around the minima located at $h \approx (J_{+-} + J_{--})/e$ and $h \approx -(J_{+-} + J_{++})/e$. However, averaging over a collection of only slightly ionophobic pores places could place stricter constraints on the allowed pore radius than our dimensionality arguments presented in section 4.4 which allowed us to arrive at eqn. (4.36). To ensure that all pores are only slightly ionophobic we would need to add the criterion that no

radius $r \in [r_{min}, r_{max}]$ could violate the inequalities

$$J_{+-}(r) \leq \langle w \rangle < J_{--}(r) - J_{+-}(r) \quad \wedge \quad -J_{+-}(r) \leq \langle w \rangle < J_{++}(r) - J_{+-}(r). \quad (4.37)$$

As this would place further limits on the system this is not a constraint that we are willing to implement. If we carry out a weighted average over a collection of pores, then all the pores with a radius such that $-\langle w \rangle > J(r_{min} < r < r_{max})$ will be at least partially filled with ions at low voltages while the pores with $-\langle w \rangle \leq J(r_{min} < r < r_{max})$ will be filled with solvent. Averaging the differential capacitance over this distribution would not symmetrically smear out both the inner and outer peaks. The averaged inner peaks will still have a bias towards $|h| \approx -\langle w \rangle$ from the contribution from the solvent filled pores while the outer peaks receive no such reinforcement at a single value of potential.

The effects of averaging in strongly ionophilic pores has been discussed in sections 3.3 and 3.4.2. Both charging thresholds in a strongly ionophilic pore are dependent on the electrostatic interaction between ions in the pore and therefore the pore radius. Any averaging process smears out the features present in the differential capacitance curve and reduces the height of the peaks present. The charging thresholds for a weakly ionophilic pore are the same as for a strongly ionophilic pore and any averaging process causes similar smearing of this resonance peak.

4.5 Energy Storage

The total energy stored in a BEG pore can be obtained from combining eqns.(3.16) and (4.13). The key to optimising total energy storage capacity of a pore is to optimise the differential capacitance at large voltages. We saw in section 3.5 that this can be achieved in two ways, by charging the pore with smaller ions or by changing the transfer energy of the pore, $\tilde{w}$, and then charging the pore with the unfavoured ion. In the BEG model both of these changes still optimise the maximum energy that can be stored in a pore or an electrode for that matter. Additionally, in the BEG model we can also vary the size of the solvent molecule and the ionophobicity of the pore on the whole, $\langle w \rangle$.

Figure 4.11a shows a contour plot of the total energy stored in a pore charged with identically sized ions and solvent between a voltage of 0 and $h k_B T/e$ as a function of average ionophobicity. Figures 4.11b and 4.11c show cross sections of this contour plot at constant ionophobicity and voltage respectively, the location of these cross sections

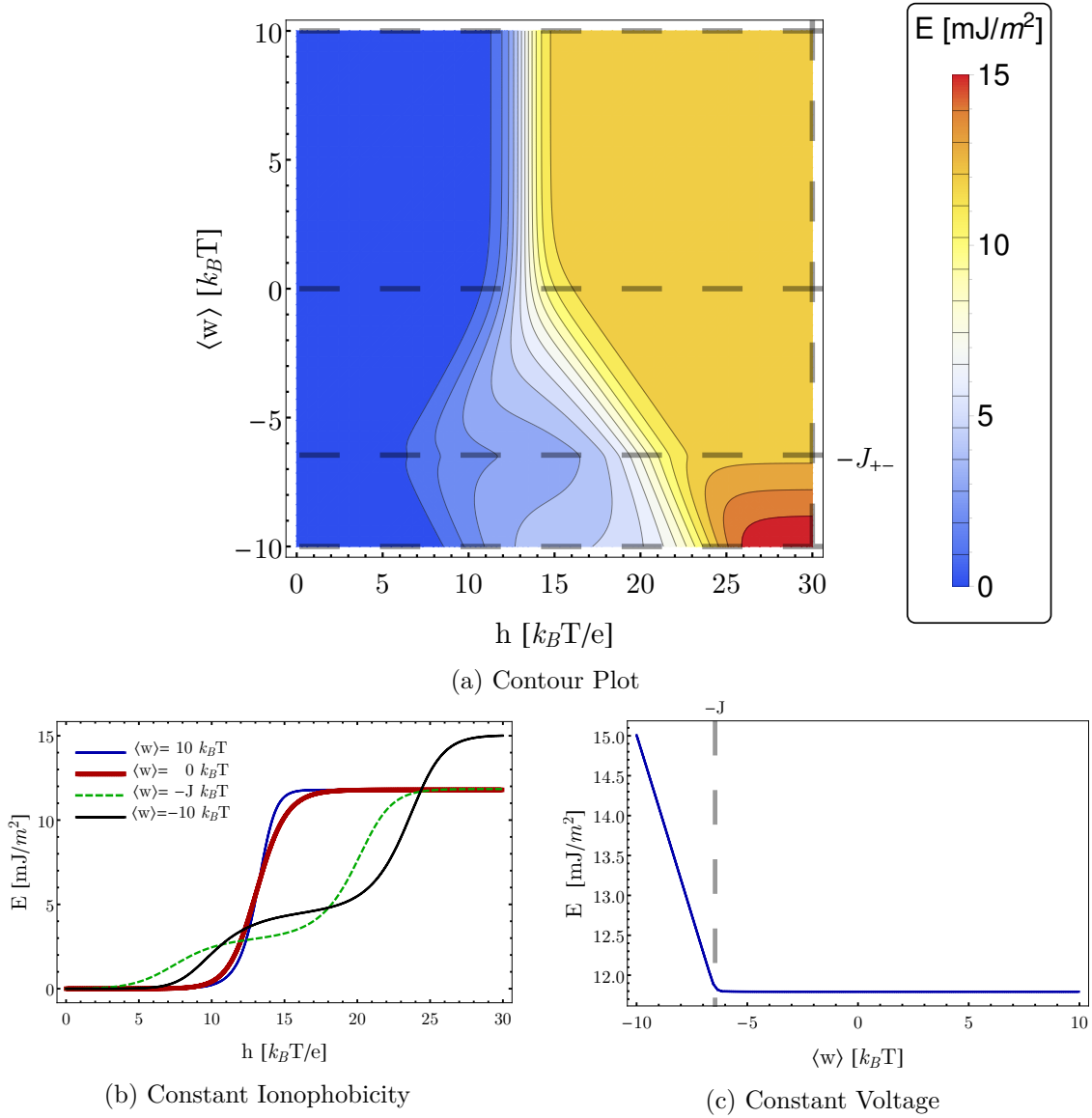


Figure 4.11: (a) A contour plot of the total energy stored in a pore charged with identically sized ions and solvent between a voltage of 0 and $h k_B T$ as a function of average ionophobicity. The differential capacitance corresponding to this energy surface is shown in figures 4.2 and 4.3. Cross sections of this energy surface at constant Ionophobicity are shown in (b) and at constant voltage in (c). These cross sections are indicated on the contour plot via broken gray lines. The value for the coupling constant $-J_{+-}$ is on (a) and (c). [Parameters: $\ell_+ = \ell_- = \ell_0 = 0.9\text{nm}$, $r = 0.75\text{nm}$.]

are indicated on the contour plot via broken gray lines. The differential capacitance corresponding to this energy surface is shown in figures 4.2 and 4.3. We can see that for ionophilic pore, $\langle w \rangle > 0$, the ionophobicity does not affect the total energy stored in the pore. For a weakly ionophobic pore, $-J_{+-} < \langle w \rangle < 0$, the total energy that can be stored in the pore is the same as in the ionophilic case but larger voltages are required to fully charge the pore. In this regime increasing the ionophobicity causes the separation of the differential capacitance to increase; the inner differential capacitance peak stores less energy as it is found at a lower voltage while the outer one stores more at a higher voltage but both of these changes are balanced. In a strongly ionophilic pore, $\langle w \rangle < -J_{+-}$, increasing the ionophobicity moves both differential capacitance peaks to larger voltages, this greatly increases the energy storage. While we have only considered the case of identically sized ions directly identical trends are observed for when $\ell_+ \neq \ell_-$, average ionophobicity only affects the maximum energy can be stored significantly when the pore is strongly ionophobic in the charging polarity.

In a strongly or weakly ionophobic pore using a larger solvent increases height of the outer differential capacitance peaks and reduces the inner peaks, figure 4.8b. This increases the total energy that could be stored in a pore or an electrode as the differential capacitance has been optimised at larger voltages at a cost of the lower voltages which are less important for energy storage.

We have not directly considered the energy stored in an electrode but this is not necessary. What optimises the differential capacitance at large voltages in a pore also optimises the differential capacitance in an electrode. To optimise energy stored in a pore you must

- Decrease the size of the counterion.
- Make the pore favour coions over counterions.
- Increase the total ionophobicity so that the pore is filled with solvent at low voltages, this can be achieved by varying the transfer energy or the radius of the pore.
- Use a larger solvent molecule.

Additionally, the averaging process will decrease the height of any peak in the differential capacitance whose location is dependent on pore radius but much depends on how the averaging process smears the differential capacitance maxima. If significant values of differential capacitance are created at higher voltages as well as at lower there may be

little difference between the energy stored in an electrode and the energy stored in a pore with the mean radius of this electrode per surface area, figure 3.9b. However, if the differential capacitance is smeared to lower voltages then the energy stored per surface area in an electrode may be significantly less than in a pore with the mean radius of the pores in the electrode.

4.6 Discussion and Conclusions

We have successfully extended our Ising model of charge storage, section 3.4, to include third neutral species. Complimentary Monte Carlo simulations were preformed in collaboration with Dr. Kondrat that did not require the ions to reside in the middle of the pore or be densely packed. Molecule densities observed in simulations agreed with those predicted by theory.

Three different charging mechanisms were identified in the BEG theory, coion swapping for counterion, coion swapping for solvent which itself is replaced by counterions and finally, solvent for counterions. The ionophobicity of a pore decided which charging mechanism was used, see table 4.2 for a summary. Increasing ionophobicity only increased the total energy storage once the pore was filled with solvent at low voltages. Interestingly, less ionophobic pores did stored more energy at lower voltages, figure 4.11b. To optimise the total energy stored in the pore one needed to use a smaller counterion, make the pore favour coions, increases the ionophobicity so that ions must be forced into the pore and use a larger solvent. The effect of averaging over an array of similar pores decreased the height of the differential capacitance peaks if they were a function of pore radius, there may be some resonance about $h = \pm \langle w \rangle$ which could be an interesting test for ionophobicity. The energy stored in a electrode is very much dependent on the averaging scheme used.

The Ising model of charge storage is recovered from the BEG model in the limiting case of an ionophilic pore. The parameters $\tilde{w}$ in this limit are identical in both models. We defined the threshold between strong and weakly ionophilic regimes to be when the solvent content in the pore became negligible, this somewhat arbitrary. The solvent content of a BEG pore, for finite parameters, is always greater than zero. While this could easily be defined the author was pained to introduce another model parameter.

We have assumed that the solvent is simply a hard-sphere buffer in a pore with

an average background dielectric. This is a 3-component model and a simplification. As mentioned earlier, when an ionic liquid is mixed with solvent, the solvent's electronic polarizability as well as vibrational modes, which may be pore width dependent [107], will contribute to the value of the dielectric in the interior of the pore. As ionic liquids are often diluted with acetonitrile which has a dielectric constant of 37 and they sorb water from atmosphere which has a dielectric of 80⁶ the inclusion of the polarizability of solvent could be an important effect to consider. Although we will argue in chapter 5 the solvent in this model could be also be viewed as a discrete sized void, instead of a solvent molecule we do not wish to abandon the possibility of solvent entering the pore. The author firmly believes that inclusion of polarizability effects or dipolar solvent would form the most interesting avenue of further work.

⁶We note that the dielectric constants listed here are obtained in the bulk and confinement might reduce a polar molecules ability to respond which will lower the associated dielectric.

Chapter 5

Charge Storage in Empty Nanotubes

We introduce a grand canonical model of charge storage in a finite pore. In this model, the spacing between ions will be dependent on the number of ions inside the pore. In many ways, this is a toy model which will allow us to introduce a grand canonical set-up but there is a certain equivalence between this and the BEG model which itself will be interesting to explore.

5.1 A Grand Canonical Ising model?

We wish to build a model of charge storage in a cylindrical pore that removes the constraint of densely packed molecules inside the pore by allowing voids between ions. To do this we will move out of the thermodynamic limit and consider a finite sized pore with a variable number of ions inside of it. We do not allow solvent to enter the pore. One would think that we could do this by simply adding a chemical potential, μ , coupled to the total particle number, N . Extending our current Ising Hamiltonian describing charging of a pore with different sized ions, equation (3.24), to a grand canonical ensemble after summing over all possible values for N .

$$\mathcal{H} = \sum_{\langle i j \rangle}^N J_{s_i, s_j} s_i s_j + h' \sum_i^N s_i - \mu N, \quad (5.1)$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{s\}} e^{-\mathcal{H}}. \quad (5.2)$$

This naïve approach is unfortunately flawed. There is no constraint on the number of lattice sites inherent in this Hamiltonian. If it is energetically favourable to increase the number of lattice sites for a certain value of applied potential then the number of lattice sites will diverge. This is not physical. We must include some sort of a constraint on the energy required to create a lattice site. In this section we will impose this constraint by imposing a distance of closest approach between ions in a finite and rigid pore while in chapter 6 we impose this constraint via a tight packing condition in an elastic pore.

5.2 A Grand Canonical Ising Model for an Empty Pore

We consider the Hamiltonian

$$\mathcal{H}_{I\delta}(\lambda) = J(\lambda, r) \sum_{\langle i j \rangle}^N s_i s_j + \sum_i^N h' s_i - \langle \mu \rangle N \quad (5.3)$$

and the grand canonical partition function

$$\mathcal{Z}_{I\delta} = \int_{\ell}^{\infty} \sum_{N=0}^{\infty} \sum_{\{s\}} e^{-\mathcal{H}_{I\delta}(\lambda)} \delta\left(\lambda - \frac{L}{N}\right) d\lambda \quad (5.4)$$

where $J(\lambda, r)$ is defined via eqn. (3.3) and $s \in \{-1, +1\}$. Our Hamiltonian is similar to that of equation (5.1) but we have dropped the electrostatic interactions dependence on s_i and s_j . Instead all ions in the pore will have the same spacing λ . We have also introduced an average chemical potential for both ions to enter to enter the pore from the bulk

$$\langle \mu \rangle = \frac{(\mu_+ + \mu_-)}{2} \quad (5.5)$$

where μ_+ and μ_- are the individual chemical potential of cations and anions. This allows us to define a shifted ‘voltage’

$$\begin{aligned} h' &= eh - \frac{(\mu_+ - \mu_-)}{2} \\ h' &= eh - \tilde{\mu}. \end{aligned} \quad (5.6)$$

where again we use tilde to define the difference of a quantity associated with cations, in this case the positive chemical potential, from the average. The grand canonical partition

function has several new features. While the sum over all configurations of $\{s\}$ remains, we have also included a discrete Gibbs summation ranging over all possible numbers of ions, an integral over the continuous degree of freedom in ion spacing and a δ -function to provide a constraint to this lattice spacing degree of freedom. We will refer to this model as the Ising-Delta model ($I\delta$) model of charge storage reminding us of the use of the δ -function to enforce lattice/ion spacing.

The Gibbs summation is the easiest to understand, we wish to include contributions to the partition function from states that include a different number of lattice sites. For each possible number of ions in the pore will compute the summation over all configurations in $\{s\}$. The integral and the δ -function, as usual, act together and together they will remove any divergences from the infinite Gibbs summation. This forces all ions inside the finite pore to be equally spaced. The limits of this integral set the domain of the allowed ion spacing. Importantly, the lower bound of the integral passes information to the partition function about the size of ions in the pore and imposes a distance of closest approach between ions in the pore. The spacing between the centre of two ions is not allowed to be less than ℓ , thus overlapping of ions is prohibited. The δ -function passes information about the length of the pore to the partition function. This removes any divergences associated with an infinity long chain of ions.

The integral in our partition function can be quickly calculated so that

$$\mathcal{Z}_{I\delta} = \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} \sum_{\{s\}} e^{-\mathcal{H}_{I\delta}(L/N)}. \quad (5.7)$$

The summation over all configurations of $\{s\}$ can now be treated using the transfer matrix method developed in section 3.2. The transfer matrix associated with $\mathcal{Z}_{I\delta}$ is

$$\underline{\mathbf{T}}_{I\delta} = e^{-\mu} \begin{pmatrix} e^{-J(L/N,r)+h'} & e^{J(L/N,r)} \\ e^{J(L/N,r)} & e^{-J(L/N,r)-h'} \end{pmatrix}. \quad (5.8)$$

$\underline{\mathbf{T}}_{I\delta}^N$ can be rewrote in terms of its two eigenvalues λ_+ and λ_- where $\lambda_+ > \lambda_-$

$$\mathcal{Z}_{I\delta} = \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} \sum_{\{s\}} e^{-\mathcal{H}_{I\delta}(L/N)} = \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} \underline{\mathbf{T}}_{I\delta}^N = \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} \lambda_+^N + \lambda_-^N. \quad (5.9)$$

Initially, we are cautious about dropping the smaller eigenvalue as our Gibbs summation does consider small values of N . These terms invalidate the large N argument. Instead, we make the assumption that we will always consider large pores, with a large surface area,

then any contributions to the surface charge, capacitance or energy stored per surface area from small N will be negligible. For our purposes we can drop the smaller eigenvalue from the partition function

$$\begin{aligned} \mathcal{Z}_{I\delta} &\approx \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} \lambda_+^N \\ &\approx \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} e^{\mu N} \left(e^{-J(L/N,r)} \cosh h' + \sqrt{e^{-2J(L/N,r)} (\sinh h')^2 + e^{2J(L/N,r)}} \right)^N. \end{aligned} \quad (5.10)$$

It no longer makes sense to consider the free energy per site of our system as we have a variable number of lattice sites within the pore. Instead we will consider the total free energy of the system, F , normalised to the pore length, L ,

$$F/L = -\frac{1}{L} \ln(\mathcal{Z}_\delta) \quad (5.11)$$

$$F/L \approx -\frac{1}{L} \ln \sum_{N=0}^{\lfloor \frac{L}{\ell} \rfloor} e^{\mu N} \left(e^{-J(L/N,r)} \cosh h' + \sqrt{e^{-2J(L/N,r)} (\sinh h')^2 + e^{2J(L/N,r)}} \right)^N. \quad (5.12)$$

For $L \gg \ell$ this normalised quantity and all that are derived from it are independent of the pore length. The density of cations, $\langle \rho_+ \rangle$, and anions, $\langle \rho_- \rangle$, in the pore can be obtained from

$$\langle \rho_+ \rangle = \frac{\ell}{L} \frac{\partial F}{\partial w_+}, \quad \langle \rho_- \rangle = \frac{\ell}{L} \frac{\partial F}{\partial w_-}. \quad (5.13)$$

The density of ions in the pore, the quantity we use in this section, and the density per site of ions in the pore, discussed in section 4, are derived from subtly different points, to all intensive purposes both sets of quantities describe the same characteristics of a pore and are comparable. As in section 4, $\langle \rho_+ \rangle$ and $\langle \rho_- \rangle$ are restricted to the unit range $(0, 1)$. $\langle \rho_\pm \rangle = 0$ signifies a pore clear of cations or anions, while $\langle \rho_\pm \rangle = 1$ signifies a pore fully filled with one species of ion. Importantly, the sum of cation and anion densities in the pore need not equal one. We define the density of voids in the pore, $\langle \rho_0 \rangle$, via

$$\langle \rho_0 \rangle = 1 - \langle \rho_+ \rangle - \langle \rho_- \rangle. \quad (5.14)$$

In this chapter $\langle \rho_0 \rangle$ is a measure of the free space within the pore between ions and not the solvent density we encountered in section 4. However, we use the same notation as we will see parallels between the space between ions filled with continuous voids and discrete solvent molecules. Once the ion density of the pore is known the surface charge per unit

surface area of the pore can be calculated

$$\sigma = -\frac{e}{2\pi r}(\langle\rho_+\rangle - \langle\rho_-\rangle), \quad (5.15)$$

equivalently this can be derived by differentiating the free energy per unit length by h

$$\sigma = -\frac{\ell}{2\pi r L} \frac{\partial F}{\partial h}. \quad (5.16)$$

The differential capacitance, C , per unit surface area of the pore follows via

$$C = \frac{\partial \sigma}{\partial h} = -\frac{\ell}{2\pi r L} \frac{\partial^2 F}{\partial h^2} \quad (5.17)$$

and the energy stored in the pore between zero and h voltages, E , follows the usual formula, first described in eqn. (3.16), reproduced here for convenience

$$E = \int_0^h \eta C(\eta) d\eta. \quad (5.18)$$

5.3 Results for a Single Pore

Interplay between the individual ion chemical potentials, electrostatic interactions between nearest neighbour ions and the applied voltage will decide the density and configuration of ions inside the pore. Higher densities of ions inside the pore will increase the electrostatic interactions between ions inside the pore that might help or hinder the charging of the pore but this cost could be offset by the contributions to the Hamiltonian from the chemical potential and the charge of an ion in the applied voltage. We will explore the behaviour of an I δ pore starting off with a quick discussion of asymmetric chemical potentials and then move on to consider the interplay of an average chemical potential with electrostatic interaction between ions in the pore and the voltage.

5.3.1 Asymmetric Ion Chemical Potentials

The effects of changing the individual ion chemical potentials on ion density and differential capacitance are easy to understand. Any results produced with asymmetric individual chemical potentials are identical to results produced with an average chemical potential translated on the voltage axis, eqn. (5.6). Once this is understood all that is required is

a thorough understanding of pores with $\mu_+ = \mu_- \equiv \langle \mu \rangle$. This is similar to the discussion of asymmetric transfer energies in the BEG model, section 4.2.1.

5.3.2 Changing the Average Chemical Potential

Figure 5.1 shows the ion and void densities, and the differential capacitance for an $I\delta$ pore described in section 5.2 for a variety of average chemical potentials. The parameters and graphs shown in figure 5.1 are comparable to those shown in figure 4.3 where the Blume-Emery-Griffiths model was used to describe a pore densely packed with ions and solvent molecules in a thermodynamic limit. Both models show similar characteristics but there are several important differences notably stemming from the now continuous spacing between ions in the pore, the lack of solvent and the finiteness of the system.

The ion density and differential capacitance plots labelled $\langle \mu \rangle \gg 0$ in figure 5.1 correspond to $I\delta$ pores with a large energetic bias to be filled with ions. In this limit, we again recover the Ising model of charge storage described in section 3.2. The large chemical potential forces ions to enter the pore from the bulk, these ions form a densely packed alternating row of cations and anions in the pore for $|h| < 2J(\ell, r)$ which smoothly transitions into a fully packed, fully charged configuration containing only one species of ion when $|h| > 2J(\ell, r)$. We will call $I\delta$ pores with an average chemical potential $\langle \mu \rangle \gg 0$ strongly ionophilic due to their similarity with the strongly ionophilic pores in the BEG model charged with ions of the same size.

In pores with little or no chemical potential discouraging ions from entering the pore, the graphs labelled $\langle \mu \rangle = 0$ and $-J(\ell, r) < \langle \mu \rangle < 0$ in figure 5.1, we still see an alternating configuration of densely packed anions and cations for small voltages $|h| < (2J(\ell, r) + \langle \mu \rangle)/e$ but the change away from this state is now abrupt rather than smooth and resembles a phase transition. Once the voltage is increased to the point where it and the chemical potential can overcome the nearest neighbour attraction between oppositely charged ions *all* of the coions in the alternating chain are forced out of the pore and some counterions enter the pore. This rapid change of charge inside the pore causes the divergent looking peaks in the corresponding differential capacitance graphs. Closer inspection of these peaks show that they are not truly divergent but merely extremely pronounced facets. Increasing the magnitude beyond the threshold voltage of $|h^*| = (2J(\ell, r) + \langle \mu \rangle)/e$ compresses the chain of equally spaced counterions in the pore decreasing the empty space in between the ions until the ions approach a tightly

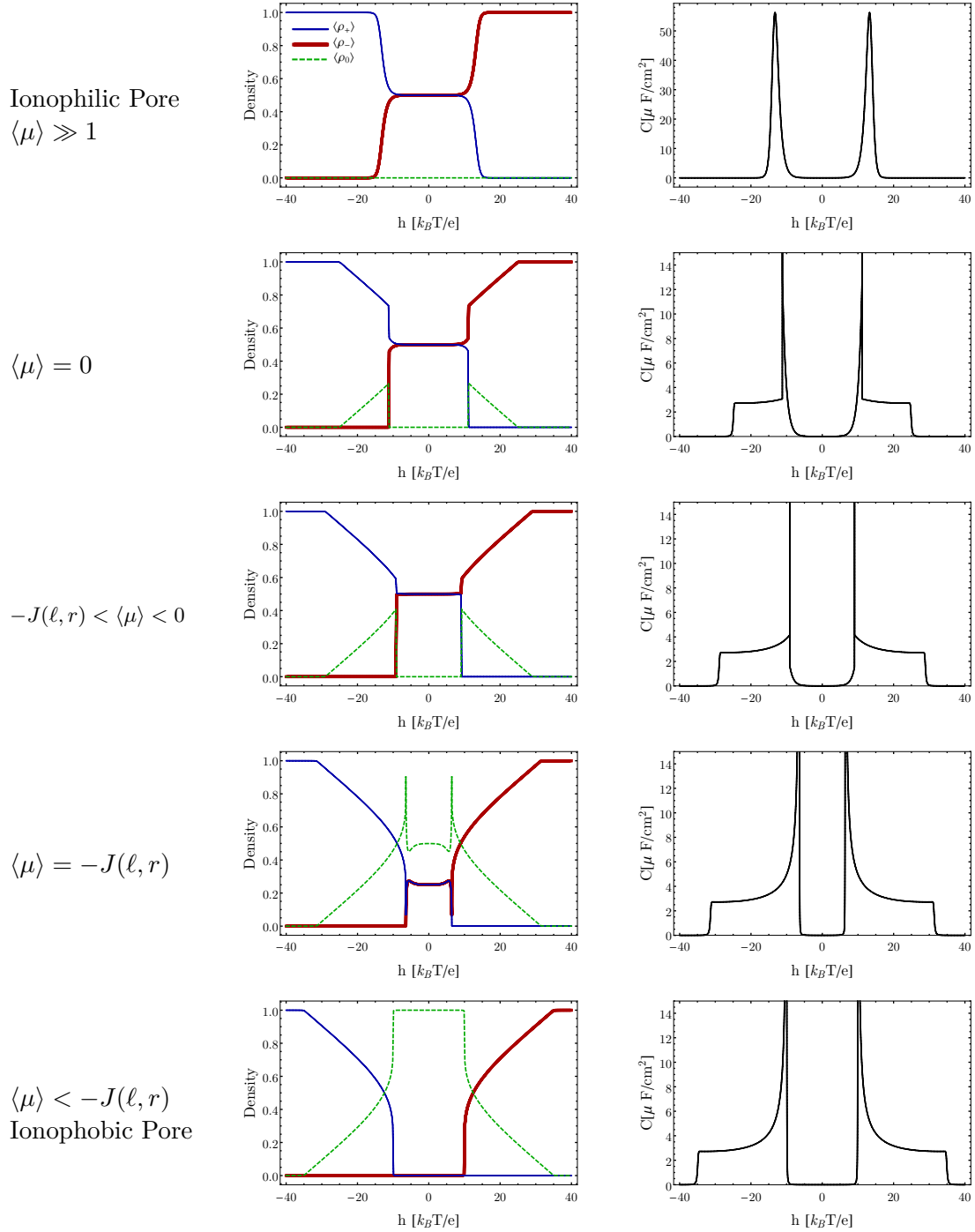


Figure 5.1: An array of graphs detailing the change in differential capacitance and molecule densities inside similar $I\delta$ pores all charged with identical ions at various average chemical potentials. Each row corresponds to a specific chemical potential shown in the left column. Ion and void densities are shown in the centre column and differential capacitance is shown in right column. [Parameters: $\ell = 0.9\text{nm}$, $r = 0.75\text{nm}$, $\mu_+ = \mu_- = \langle \mu \rangle$, $L = 2000\text{nm}$.]

packed configuration. Initially, the compression of this chain of counterions is relatively easy. The exponential screening between ions in a cylindrical pore, section 2, means that there is little energetic cost associated with moving two well separated ions slightly closer to one another. The majority of the energy gained from another counterion entering the pore and being subjected to the applied voltage is used to overcome the ionophobic chemical potential. As the ions are squeezed into a densely packed configuration the repulsive electrostatic interaction between counterions grows exponentially and the magnitude of the differential capacitance curve decays finally reaching zero when the counterions are densely packed. We will call I δ pores with an average chemical potential $-J(\ell, r) < \langle \mu \rangle < 0$ weakly ionophobic due to their similarity with the weakly ionophobic pores in the BEG model charged with identically sized ions.

The graphs labelled $\langle \mu \rangle = -J(\ell, r)$ in figure 5.1 show the lowest chemical potential where ions still inhabit the pore at low voltages. These ions are no longer densely packed in the pore. Crossing the threshold voltages $|h^*| = (2J(\ell, r) + \langle \mu \rangle) = J(\ell, r)$ causes coions and some counterions to leave the pore. This exodus causes the spikes in the differential capacitance and increases the average spacing between the counterions that remain in the pore. I δ pores with chemical potentials $-J(\ell, r) = \langle \mu \rangle$ are similar to BEG pores that are on the boundary between weakly ionophobic and strongly ionophobic regions.

The alternating chain of ions is no longer present in the pores labelled $\langle \mu \rangle < -J(\ell, r)$ in figure 5.1. In these pores this configuration is no longer energetically favourable, at low voltages, and so the pore is empty. Once the voltage applied to the pore overcomes the chemical potential keeping the pore empty ions rush in to fill the void. This, again, causes spikes in the differential capacitance at a threshold of $|h^*| = -\langle \mu \rangle / e$. As in the case of pores with a higher chemical potential, counterions in the pore are compressed by larger voltages eventually forming a densely packed chain. We will call I δ pores with an average chemical potential $\langle \mu \rangle < -J(\ell, r)$ strongly ionophobic due to their similarity with the strongly ionophobic pores in the BEG model charged with ions of the same size.

5.4 Results For Many Pores

We can find the average differential capacitance of the I δ model for many pores of by combining eqn. (5.17) with the averaging prescription put forward in section 3.3. This averaging procedure requires the pore radius distribution to be bounded so that we will maintain the file like structure of the ions inside the pore. The minimum radius is the

smallest radius that allows ions to enter the pore and the maximum radius is the the width of the pore when it is large enough to admit two ions side by side. As, in this chapter, all of the ions are of the same size ℓ these bounds are given by

$$r_{min} = \ell/2, \quad r_{max} = \ell. \quad (5.19)$$

For pores with a selection of pores with large positive chemical potential the $I\delta$ model reproduces the Ising model. The process of averaging such pores is equivalent to averaging a group of Ising pores. The reader is referred to section 3.3.1 for a full discussion.

Figure 5.2a shows the effects of applying this averaging procedure to a group of weakly and strongly ionophobic $I\delta$ pores. In the larger pores in the electrode the electrostatic bonding between anions and cations is strong enough to fill the pore with a file of ions of alternating polarity. The stronger screening in the smaller pores decreases this bonding allowing the chemical potential, which favours an empty pore, to expel the ions. In the individual $I\delta$ pores that make up this electrode, figure 5.2b, the first influx of ions into strongly ionophobic pores and the dismantling of the alternating chain of ions in weakly ionophobic pores produced divergent spikes in the differential capacitance at the thresholds $|h^*| = -\langle\mu\rangle/e$ and $|h^*| = (2J(\ell, r) + \langle\mu\rangle)/e$ respectively. Once we apply the averaging procedure, even over a distribution with a very small standard deviation, these resonance spikes are removed, figure 5.2a. The differential capacitance curves of an $I\delta$ electrode have one peak centred on $|h^*| = (2J(\ell, \bar{r}) + \langle\mu\rangle)/e$, this is the location of the charging threshold of the central pore, with radius $\bar{r}$, in the electrode pore radius distribution.

The smearing of the differential capacitance when we average over an electrode containing weakly ionophobic pores occurs because the weakly ionophobic charging threshold is indirectly a function of pore radius through the electrostatic coupling $J(\lambda, r)$, figure 5.2b. However, if all pores were strongly ionophobic then the location of the sharp peak at the charging threshold would depend only of the the average chemical potential and not be a function of radius in our model. In this case, the the averaging procedure would not smooth out this peak.

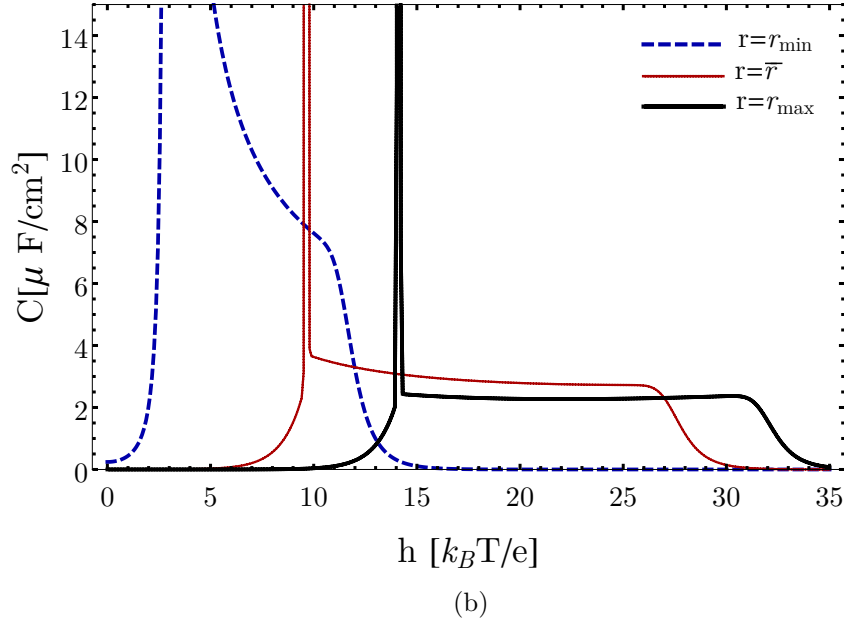
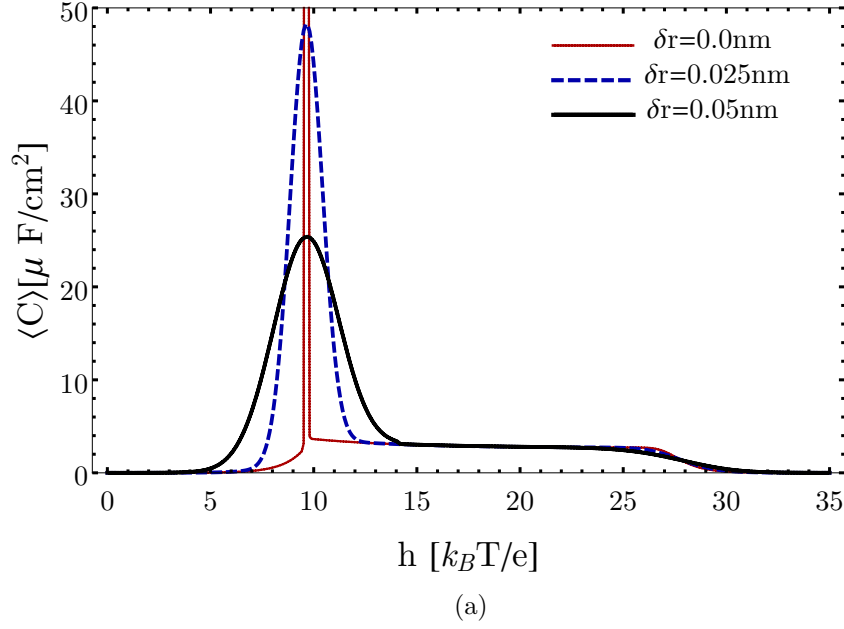


Figure 5.2: a) Average capacitance of many $\text{I}\delta$ pores, eqn. (5.17), over a truncated normal pore radii distribution, section 3.3. b) the differential capacitance curves of the max, min and average radii pores, eqn. (5.19), associated with that truncated distribution, defined in section 5.4. The pore at the centre of the distribution is equivalent to the pore labelled $-J(\ell, r) < \langle \mu \rangle < 0$ in figure 5.1. All ions have the same chemical potential. The capacitance is symmetric about zero volts. [Parameters: $\ell = 0.9\text{nm}$, $\bar{r} = 0.75\text{nm}$, $\langle \mu \rangle = -3k_B T$, $L = 2000\text{nm}$.

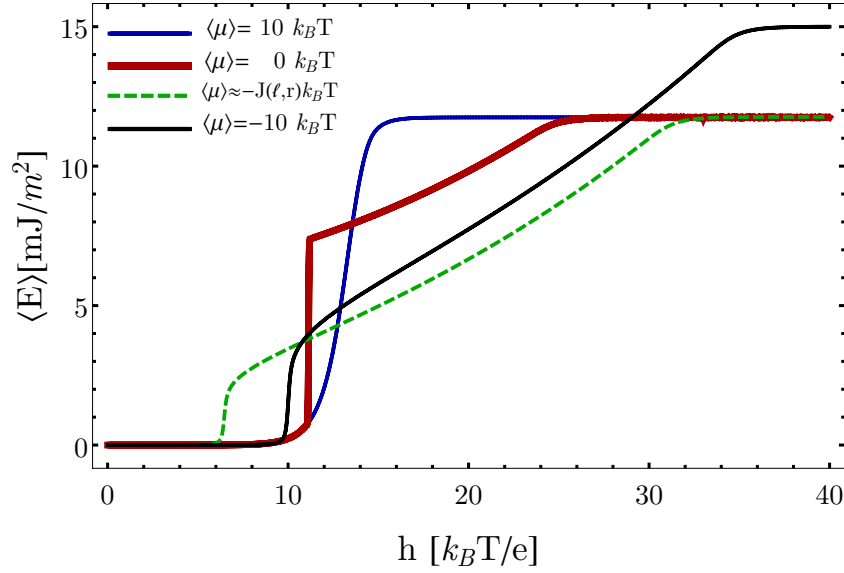


Figure 5.3: Energy stored in I δ pores at various chemical potentials. The differential capacitances and ion densities of the I δ pores at each chemical potential are shown in figure 5.1. [Parameters: $\ell = 0.9\text{nm}$, $r = 0.75\text{nm}$, $\mu_+ = \mu_- = \langle \mu \rangle$, $L = 2000\text{nm}$.]

5.5 Energy Storage

The energy stored in I δ pores can be obtained by combining Eqns. (5.17) and (5.18). This is shown for identical I δ pores at various chemical potential in figure 5.3. The corresponding differential capacitances and ion densities for I δ pores at the same chemical potentials are shown in figure 5.1. The jumps in the stored energy correspond to the spikes in the differential capacitance curves in figure 5.1 which themselves correspond to the charging thresholds of the individual pores. Like BEG pores, figure 4.11, the maximum energy stored does not increase until the pore is strongly ionophobic although different ionophobicities might be more effective at storing energy if the voltage window is limited.

The methods required to increase the total energy stored for an I δ pore are similar to the methods required to increase the energy storage in a BEG pore:

- Decrease the size of the counterion, this increases the initial charging threshold for ionophilic and weakly ionophobic pores and increases the surface charge that can be accommodated per unit length of the pore.
- Make the pore favour coions over counterions, this increases the voltages at which counterions enter the pore optimising eqn. (5.18).

- Increase the total ionophobicity so that the pore is filled with voids at low voltages, we have seen from figure 5.3 that increasing the ionophobicity in a strongly ionophobic pore increases the total energy density. This can be achieved by varying the chemical potential or the radius of the pore.

These three methods are direct analogies to what is required to optimise a BEG pore, only the use of a larger solvent molecule is missing from this list.

The effects of applying the pore radius averaging procedure, section 3.3.1, to the energy stored in I δ pores is very much dependent on the limits of the averaging process and the location of the average pore radius of the electrode within these limits. What is assured is that for electrodes that contain ionophilic or weakly ionophobic pores the sharp spike in capacitance is removed, figure 5.2a, and energy stored in the electrode will be a smoother process than energy stored in a pore, figure 5.3. In general, what improves energy storage in the average pore in an electrode will improve average energy storage in the electrode.

5.6 Comparison of BEG and I δ Models

Figures 5.4 and 5.5 show several comparisons between the BEG and I δ pores. All show remarkable agreement. Figure 5.4 compares the ion density in similar BEG and I δ pores. Although, the ion densities inside I δ pores are much more sharp edged than similar curves produced using the BEG model the density of ions in the pore at all voltages is comparable in both models. Figure 5.5a compares the ion density in similar BEG and I δ pores at zero applied voltage as a function of chemical potential or transfer energy. Pores of both models become strongly ionophobic at corresponding values of chemical potential and transfer energy. Again, the transition in I δ pores is much more abrupt than in BEG pores. Finally, figures 5.5b and 5.5c compare the energy stored in I δ pores and BEG pores respectively. The total energy stored in both models at each value of chemical potential or transfer energy is identical.

While the BEG and I δ models look very similar, importantly the BEG model incorporates a transfer energy between ions and solvent to control ionophobicity while in the I δ model ionophobicity is controlled by a chemical potential. The equivalence shown in figures 5.4 and 5.5 suggest a link between chemical potential and transfer energy. This link exists because of the simplified solvent that we incorporated in the BEG model.

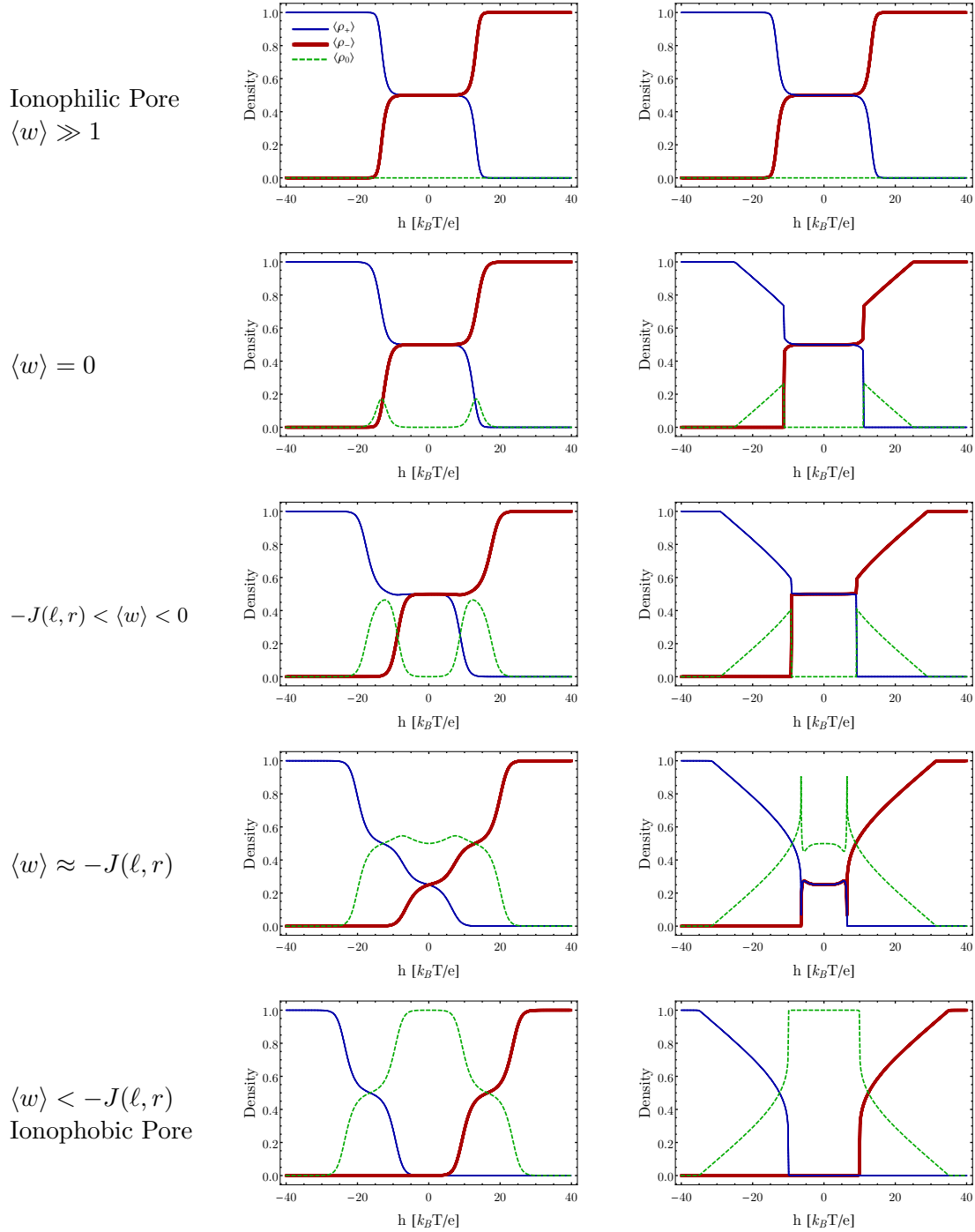


Figure 5.4: Comparison of the ion densities inside identical BEG, centre column, and I δ pores, right column, charged with identical ions. The average transfer energy used to plot the BEG curves is the same as the average chemical potential used in plotting the I δ curves. Identical BEG ion densities are shown in figure 4.3, while identical I δ ion densities are shown in figure 5.1. [Parameters: $\ell_+ = \ell_- = \ell_0 = \ell = 0.9\text{nm}$, $r = 0.75\text{nm}$, $w_+ = w_- = \langle w \rangle = \mu_+ = \mu_- = \langle \mu \rangle$, $L = 2000\text{nm}$.]

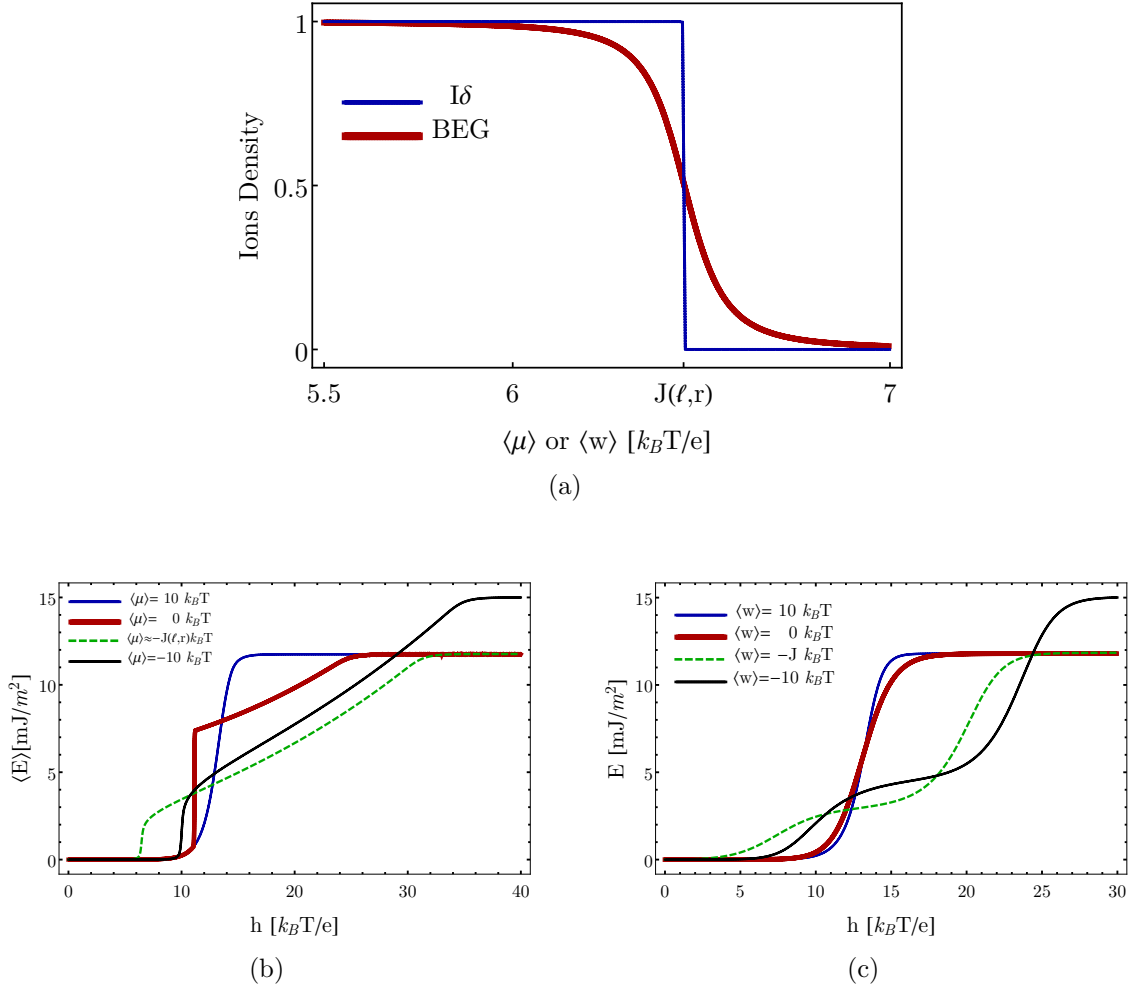


Figure 5.5: a) Comparison of the total ion density of a BEG and I δ pore as a function of average transfer energy and chemical potential respectively at zero applied voltage. The magnitude of the electrostatic coupling constant between two adjacent ions inside the pore is shown on the x-axis. b) Energy stored in I δ pores at various average chemical potentials c) Energy Stored in BEG pores at various average transfer energies. The chemical potentials and the transfer energies shown in b) and c) take the same values and the corresponding curves on both graphs are labelled identically. [Parameters: $\ell_+ = \ell_- = \ell_0 = \ell = 0.9\text{nm}$, $r = 0.75\text{nm}$, $w_+ = w_- = \langle w \rangle = \mu_+ = \mu_- = \langle \mu \rangle$, $L = 2000\text{nm}$. a) $h = 0 k_B T$.]

The solvent is considered only as a non-polarizable buffer. The space that this buffer takes up in the pore could also be thought of as a discrete void. If we think of the solvent in the BEG pore as a discrete void then the ions in this model no longer have a transfer energy into the pore relative to solvent but rather a chemical potential. This explains the correspondence between the BEG and $I\delta$ models. The smooth transitions seen in the BEG corresponding to the abrupt transitions in the $I\delta$ model stem from the fact that the BEG model is in the thermodynamic limit while the $I\delta$ model has a finite lattice.

5.7 Discussion and Conclusions

The differential capacitance of an $I\delta$ pore can be roughly categorised depending on whether the pore is strongly ionophilic in nature or (weakly or strongly) ionophobic. The strongly ionophilic pores exactly reproduce the Ising model of charge storage presented in section 3.2. In an ionophobic pore the capacitance is zero until a threshold is reached and then there is a sharp peak. The charging mechanisms are coion exclusion with counterion inclusion into the pore or simply counterion inclusion depending on the ionophobicity. The pore accumulates a large amount of surface charge at this threshold accounting for the notably lower values of differential capacitance at higher voltages in these ionophobic pores compared to the scale of the ionophilic pores. The total amount of charge and energy stored in similar $I\delta$ and BEG pores is the same.

Averaging over a pore size distribution that contains weakly ionophobic pores creates a similar rounded maximum in the differential capacitance as that seen in the ionophilic pores and the Ising model of charge storage, section 3.2. The averaging process has little effect on the differential capacitance of strongly ionophilic pores as the charging threshold at this ionophobicity is not a function of pore radius. We note that equivalent charging process in strongly ionophobic BEG pores has this same independence of pore radius. If this model were to hold true then looking for this spike could form an interesting test to see if a electrode is empty at low voltages. However, the author believes that the chemical potential will be dependent on the radius of the pore in a non-trivial manner and so averaging over a pore size distribution will smear this peak once this dependence is taken into account. Unfortunately, the study of the chemical potential dependence on radius is far beyond the scope of this work.

To calculate the electrostatic interaction between ions inside the pore we used a background dielectric of the interior of the pore and set its value to 2. This value can

only be justified when the ions are touching. However, when there is a large spacing between the ions we expect the exponential screening of the pore walls to isolate the ions electrostatically and so any contribution from the $1/\epsilon$ factor in eqn. (3.3) will be unimportant. There will also be a crossover regime when the ions in the pore are near enough to each other to feel some electrostatic interaction but not yet in contact with each other but this will only produce effects in a small voltage range.

The discontinuities in the ion densities and the corresponding spike in the differential capacitance look like artefacts of our model but we must proceed with caution as similar discontinuities of the ion densities inside slit pores have been seen in grand canonical simulations of narrow planar pores [89, 128, 129]. The simulations of Kiyhara et al. in particular also show ion densities¹ qualitatively similar to those shown by the strongly ionophobic pore (labelled $\langle\mu\rangle < J(\ell, r)$) in figure 5.1 although they do not show saturation of the pore with counter charge at large voltages. If these discontinuities are artefacts of our model then they could, in the authors opinion, come from two sources, the finiteness of the $I\delta$ lattice or the lack of clustering of ions inside the pore. More research is needed to track down this seemingly artificial behaviour. Thankfully, the BEG model does not have either of these flaws, it is in the thermodynamic limit and it does include clustering but it forces us to make the assumption that voids in the pore have a discrete size. The agreement of both of these models with differing strengths and weaknesses lends credibility to the results that both models agree on, particularly, the total energy stored in a pore and how to optimise this quantity.

¹Kiyhara actually shows the accumulated surface charge but this is proportional the ion density in this case.

Chapter 6

Electroactuation Associated with Charge Storage

We present a model of electroactuation of an elastic carbon cylindrical pore. We incorporate changes of the carbon-carbon bond length due to electrochemical doping of the pore walls and steric effects related to counterion insertion into the pore via a modified Ising model of charge storage. When considering the total electrode deformation these effects either compliment or compete with each other depending on the polarisation of the electrode. Our model shows qualitative agreement with the features of the experimentally observed expansion caused by variation of electrode potential. The results presented in this chapter were published in [2].

6.1 Breathing Electrodes

Using nanopores of dimensions of the order of the size of a few ions has side effects. First the charging dynamics may be slowed. Secondly, electrodes made of nanostructured, usually carbon materials are not absolutely rigid, and may experience elastic deformation in the result of the charging/discharging process. This was experimentally demonstrated recently by dilatometry studies [104, 105, 106], and a first model interpretation was given to this effect in [106]. The effect of ‘electrode breathing’ with voltage variation can, after a large number of cycles, wear the system, causing cracks, detachments and even short cuts. This will undermine the longevity of supercapacitors.

The observed breathing of the carbon electrodes was found to be asymmetric to the sign of the applied potential, specifically, when the electrode was polarised with a positive potential its observed expansion was greater than when it was polarised with a negative potential. The swelling of the electrodes is related to the accommodation of an increasing number of counterions. However, this effect by itself does not explain the asymmetry of the swelling, which requires a competing effect. Density functional theory calculations have shown that electrochemical doping of graphite and single wall carbon nanotubes can cause asymmetrical in-plane structural changes. Negative charge injection results in an expansion of the carbon-carbon bond length while positive charge injection causes contraction [130]. Such effects have been harnessed in carbon nanotube based electroactuators [131, 132].

We will focus on a model of a pore charged with neat ionic liquids as electrolytes because these are expected to deliver the largest voltage window within which the electrolyte does not participate in electrochemical reactions. We will assume, as we did in chapter 3, that the ionic liquid fully wets the interior of the pores, i.e. they are filled with cations and anions, even when the electrode is not polarized. We have seen in chapters 4 and 5 that the ionophilicity-ionophobicity of the pore plays an important role in the energy storage capacity. However, unless special measures are taken, typical pores in carbon materials were found to be ionophilic [133, 134]. Thus, as a starting point we will study a model in which the pores are filled with ions, even when non-polarized, the electrode polarization only serves to rearrange the relative weight of counterions and coions in the pore.

We will allow the cylindrical pores to swell or contract longitudinally and for simplicity neglect any radial changes as it is most likely that longitudinal changes to the pore length, rather than small radial changes, will affect the number of ions that can be absorbed into the pore. The set-up will be similar to chapters 3, 4 and 5. Ions inside the pore will be screened electrostatically by the pore, chapter 2, and we will map the ions onto a grand canonical lattice that will allow us to include steric effects from the electrosorption of ions into the tubular pores as well as effects due to the excess or depletion of electrons in the electrode. These competing effects will determine the overall longitudinal swelling and shrinking of the pore. Once we understand swelling in a single pore we will apply the averaging procedure depicted in section 3.3 to make these results applicable to a nanostructured electrode.

6.2 An Elastic Pore

We focus on describing the longitudinal dimensional change, caused by charging, of a single narrow cylindrical pore of constant radius, r , and relaxed length, L . The pore radius is large enough for ions to enter the pore, and swap positions, but still narrow enough to force the ions inside to form a quasi-1D line. The electrostatic interactions between ions inside the pore are ideally screened by the electronic polarisation of the pore. This screening allows us to neglect all electrostatic interactions other than those between nearest neighbours, section 2.6. As the dimensional change of the pore is caused by charging we do not examine the case of an ionophobic pore but instead we assume that the ionic liquid fully wets the pore, i.e. the pore is strongly ionophilic and is densely packed even when not polarised. The ionic liquid itself consists of spherical anions and cations of diameter, ℓ_- and ℓ_+ respectively. The pore is connected to an ion reservoir allowing the total number of ions in the pore to change if the length of the pore changes. Finally, we consider only long pores that can hold a large number of ions.

We allow deformation of the pore simultaneously via two mechanisms, elastically to accommodate more ions and in response to the electrochemical doping of the pore walls that occurs as the pore is charged. The charge of an ion is assumed to sit on the central axis of the pore and is mapped onto a lattice with N sites. Each site in the lattice is assumed to be occupied by an ion. If it is a cation we assign a positive spin, $s = 1$ to this site and, a negative one, $s = -1$ if it is an anion. There is no solvent in our system. As the ions are different sizes the spacing between adjacent sites is dependent on the nature of the ions present on these sites. Two adjacent sites occupied by cations are separated by ℓ_+ , anions by ℓ_- and the sites represented an adjacent cation and anion are separated by $(\ell_+ + \ell_-)/2$. This mapping of ions onto a lattice is the same as described in section 3.4 and shown in figure 3.5.

Our grand canonical Hamiltonian for actuation H_{act} is composed of three parts. The first will be the canonical Hamiltonian for charge storage with ions of different sizes H_A described in section 3.4, the second controls the energetic benefit of ions entering the pore and the third the energetic cost of actuation, E_{act} ,

$$H_{\text{act}} = H_A - \langle \mu \rangle N + E_{\text{act}}. \quad (6.1)$$

The canonical Hamiltonian for charge storage with ions of different sizes itself contains

the terms

$$H_A = \sum_{\langle i,j \rangle}^N J_{s_i s_j} s_i s_j + (eh - \tilde{\mu}) \sum_i^N s_i. \quad (6.2)$$

The first term in H_A describes the ideally screened electrostatic interactions between nearest neighbours ions in a pore. As such, $J_{s_i s_j}$ is the electrostatic interaction energy of two adjacent charges on the lattice defined via eqns. (3.3) and (3.27). The second term of H_A describes the interaction of the ions inside the pore with the applied electrode potential so that eh is the energy of a cation in the electrostatic potential inside the pore relative to the bulk electrolyte. We have replaced the transfer energy that is found in the Hamiltonian described in section 3.4 with $\tilde{\mu}$, this is the difference between the chemical potential of a cation and an anion

$$\tilde{\mu} = \frac{\mu_+ - \mu_-}{2} \quad (6.3)$$

where μ_+ and μ_- are the individual chemical potential of cations and anions respectively. We have made this semantic change as it is now possible to remove a cation from the pore and *not* replace it with anion.

The third term in eqn. (6.1) describes average energetic benefit of cations and anions entering the pore

$$\langle \mu \rangle = \frac{\mu_+ + \mu_-}{2}. \quad (6.4)$$

As our pore is ionophilic we assume that the average chemical potential is positive, $\langle \mu \rangle > 0$. This is supported by recent calculations that have suggested that the inclusion of an ion inside a carbon nanotube is an exothermic process [113].

The final term on the right of eqn. (6.1) describes the energy cost associated with actuation of the pore. There are two ways that the length of the pore can change: The pore can stretch or contract in response to the charged electrochemical doping of the pore walls as the pore is charged. This doping produces a change in the carbon-carbon bond length. We make the first approximation that the relaxed length of the pore, L , itself expands and contracts linearly as the charge density inside the pore, $\sum s_i/N$, varies so that the length of the doped pore is

$$L_{\text{dope}} = L \left(1 - \alpha \sum_i^N s_i/N \right). \quad (6.5)$$

The magnitude of this doping effect is controlled by the empirical coupling constant α . The pore can also expand or contract elastically to accommodate more ions. This steric

effect of packing the pore competes with the effect of electrochemical doping, resulting in an overall dimensional change of the pore. If the total length of ions in the pore is L_{ions} and the pore must stretch from its doped length to accommodate the ions inside of it then the total elastic energy of the pore is

$$E_{\text{act}} = \frac{1}{2}k(L_{\text{dope}} - L_{\text{ions}})^2 \quad (6.6)$$

where k is the stiffness of the pore. L_{ions} can be rewritten in a manner similar to eqn. (3.30) and after introducing the average ion length, the deviation from the average ion length both defined in eqn. (3.31) and a shorthand for the net number of charges inside the pore $S = \sum_i^N s_i$ we have

$$\begin{aligned} L_{\text{ions}} &= N_+ \ell_+ + N_- \ell_- \\ &= \left(N + \sum_i^N s_i \right) \ell_+ + \left(N - \sum_i^N s_i \right) \ell_- \\ &= \left(\frac{\ell_+ + \ell_-}{2} \right) N + \left(\frac{\ell_+ - \ell_-}{2} \right) \sum_i^N s_i \\ &= \langle \ell \rangle N + \tilde{\ell} S \end{aligned} \quad (6.7)$$

and

$$E_{\text{act}} = \frac{1}{2}k \left(L \left(1 - \alpha \sum_i^N s_i / N \right) - (\langle \ell \rangle N + \tilde{\ell} S) \right)^2. \quad (6.8)$$

Our actuation Hamiltonian has now become

$$\mathcal{H}_{\text{act}} = \sum_{\langle i,j \rangle}^N J_{s_i s_j} s_i s_j + (eh - \tilde{\mu})S - \langle \mu \rangle N + \frac{1}{2}k \left(L(1 - \alpha S/N) - \langle \ell \rangle N - \tilde{\ell} S \right)^2. \quad (6.9)$$

6.3 Calculating the Partition Function

To calculate any observable from the Hamiltonian, eqn. (6.9), we must find a practical expression for the grand canonical partition function

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{s\}} \frac{1}{N_+! N_-!} e^{-\mathcal{H}_{\text{act}}} \quad (6.10)$$

where N_+ is the number of cations in the pore, N_- the number of anions and the sum runs over all possible charge configurations of $\{s\}$. The pre-factor, $(N_+! N_-!)^{-1}$, in

the partition function of eqn. (6.10) creates a difficulty as N_+ and N_- are functions of N and the net number of charges inside the pore

$$\frac{1}{N_+!N_-!} = \frac{1}{\left(\frac{N+S}{2}\right)!\left(\frac{N-S}{2}\right)!}. \quad (6.11)$$

To compute $\mathcal{Z}$ we will need to make approximations.

6.3.1 A Mean Field Approximation

One way to make eqn. (6.10) tractable is to make the mean field approximation $S = \langle s \rangle N$ in pre-factor shown in equation eqn. (6.11) where $\langle s \rangle$ is the average charge per site of the canonical partition function, Z_A , defined as

$$Z_A = \sum_{\{s\}} e^{-H_A} \quad (6.12)$$

and described in detail in section 3.4. When we make this approximation we are neglecting any contribution that effects the average charge inside the pore from the chemical potential or the energetic cost of actuation. With this approximation we can define the mean field grand canonical partition function

$$\mathcal{Z}_{\text{MF}} = \sum_{N=0}^{\infty} \frac{1}{(N(1 + \langle s \rangle)/2)!} \frac{1}{(N(1 - \langle s \rangle)/2)!} \sum_{\{s\}} \exp \{-\mathcal{H}_{\text{act}}\}. \quad (6.13)$$

where we have extend the domain of the factorial beyond integers using the gamma function, $n! = \Gamma(n+1)$. To find the more practical expression for the mean field partition function we consider the sum over all configurations of $\{s\}$ at fixed N ,

$$\zeta_N \equiv \sum_{\{s\}} \exp \{-H_{\text{act}}\}. \quad (6.14)$$

Expanding out the actuation term in eqn. (6.9) and collecting terms in powers of S we have

$$\mathcal{H}_{\text{act}} = a' + \sum_{\langle i,j \rangle}^N J_{s_i s_j} s_i s_j + h' S + \frac{1}{2} c' S^2 \quad (6.15)$$

where we have introduced the rescaled coefficients

$$a' = \frac{1}{2}k(L - \langle \ell \rangle N)^2 - \langle \mu \rangle N, \quad (6.16)$$

$$h' = (eh - \tilde{\mu}) - k(L - \langle \ell \rangle N) \left(\frac{\alpha L + N\tilde{\ell}}{N} \right), \quad (6.17)$$

$$c' = k \left(\frac{\alpha L + N\tilde{\ell}}{N} \right)^2. \quad (6.18)$$

As S^2 term couples each lattice site with all other lattice sites it prohibits direct calculation of the sum over all configurations of $\{s\}$ using the transfer matrix methods that were employed in the previous sections. However, the S^2 term can be addressed using the Hubbard-Stratonovich transformation [135, 136]. In this transform one uses the Gaussian integral identity

$$\exp \left\{ -\frac{c'}{2} S^2 \right\} = \sqrt{\frac{1}{2\pi c'}} \int_{-\infty}^{\infty} \exp \left\{ -\frac{y^2}{2c'} - iSy \right\} dy \quad (6.19)$$

to remove the S^2 term at the cost of introducing a new scalar auxiliary field, y , coupled to S , which is to be integrated over, so that

$$\zeta_N = \sum_{\{s\}} \sqrt{\frac{1}{2\pi c'}} \int_{-\infty}^{\infty} \exp \left\{ - \left(a' + \sum_{\langle i,j \rangle}^N J_{s_i s_j} s_i s_j + (h' + iy)S + \frac{y^2}{2c'} \right) \right\} dy. \quad (6.20)$$

Now, the sum over all configurations of $\{s\}$ can be computed using a similar transfer matrix method to that detailed in section 3.4

$$\zeta_N = \sqrt{\frac{1}{2\pi c'}} \int_{-\infty}^{\infty} \exp \left\{ - \left(a' + \frac{y^2}{2c'} \right) \right\} (\lambda_+^N + \lambda_-^N) dy \quad (6.21)$$

where λ_+ and λ_- are the two eigenvalues of the transfer matrix, $\underline{\mathbb{T}}$, given by

$$\underline{\mathbb{T}} = \begin{pmatrix} e^{-(J_{++}+h'-iy)} & e^{J_{+-}} \\ e^{J_{+-}} & e^{-(J_{--}-h'+iy)} \end{pmatrix}. \quad (6.22)$$

In closed form these eigenvalues are

$$\begin{aligned} \lambda_{\pm} = & \frac{1}{2} \left(e^{(J_{++}+h'+iy)} + e^{(J_{--}-h'-iy)} \right. \\ & \left. \pm \sqrt{e^{(J_{++}+h'+iy)} + e^{(J_{--}-h'-iy)} - 4(e^{-(J_{++}+J_{--})} - e^{2J_{+-}})} \right). \end{aligned} \quad (6.23)$$

The first inspection of the integrand of eqn. (6.21) does not fill us with hope. The square root present in the eigenvalues of $\underline{\mathbf{T}}$ is the cause of most of our problems. Indeed if we make the usual approximation that $(\lambda_+^N + \lambda_-^N) \approx \lambda_+^N$ for large N the author believes that the integral of eqn. (6.21) diverges. However, if we keep both eigenvalues the problems caused by the square root in one eigenvalue are cancelled out by the identical square root with opposite sign in the other, smaller, eigenvalue. To see this consider that the eigenvalues of a 2×2 matrix have the form

$$\lambda_{\pm} = \frac{1}{2} \left(\text{tr} \underline{\mathbf{T}} \pm \sqrt{(\text{tr} \underline{\mathbf{T}})^2 - 4 \det \underline{\mathbf{T}}} \right). \quad (6.24)$$

If we consider the sum of these eigenvalues, each raised to the power of N we have

$$\lambda_+^N + \lambda_-^N = \frac{1}{2^N} \left[\left(\text{tr} \underline{\mathbf{T}} + \sqrt{(\text{tr} \underline{\mathbf{T}})^2 - 4 \det \underline{\mathbf{T}}} \right)^N + \left(\text{tr} \underline{\mathbf{T}} - \sqrt{(\text{tr} \underline{\mathbf{T}})^2 - 4 \det \underline{\mathbf{T}}} \right)^N \right] \quad (6.25)$$

and thus

$$2^N (\lambda_+^N + \lambda_-^N) = 2 \sum_{k=0}^{\lfloor N/2 \rfloor} \binom{N}{2k} (\text{tr} \underline{\mathbf{T}})^{N-2k} \left(\sqrt{(\text{tr} \underline{\mathbf{T}})^2 - 4 \det \underline{\mathbf{T}}} \right)^{2k}. \quad (6.26)$$

Simplifying and expanding further, we obtain

$$\lambda_+^N + \lambda_-^N = \frac{1}{2^{N-1}} \sum_{k=0}^{\lfloor N/2 \rfloor} \sum_{m=0}^k \binom{N}{2k} \binom{k}{m} (\text{tr} \underline{\mathbf{T}})^{N-2m} (-4 \det \underline{\mathbf{T}})^m. \quad (6.27)$$

We can now rewrite and then evaluate the summation over k ,

$$\begin{aligned} \lambda_+^N + \lambda_-^N &= \frac{1}{2^{N-1}} \sum_{m=0}^{\lfloor N/2 \rfloor} \sum_{k=m}^{\lfloor N/2 \rfloor} \binom{N}{2k} \binom{k}{m} (\text{tr} \underline{\mathbf{T}})^{N-2m} (-4 \det \underline{\mathbf{T}})^m \\ &= \sum_{m=0}^{\lfloor N/2 \rfloor} \binom{N-m}{m} \frac{N}{N-m} (\text{tr} \underline{\mathbf{T}})^{N-2m} (-\det \underline{\mathbf{T}})^m \end{aligned} \quad (6.28)$$

where we have used the identity

$$\frac{1}{2^{N-1}} \sum_{k=m}^{\lfloor N/2 \rfloor} \binom{N}{2k} \binom{k}{m} = \frac{1}{2^{2m}} \binom{N-m}{m} \frac{N}{N-m} \quad (6.29)$$

which can be found in [137] to get to the last line. Putting all this together we have

$$\begin{aligned} \zeta_N &= \sqrt{\frac{1}{2\pi c'}} \sum_{m=0}^{\lfloor N/2 \rfloor} \frac{1}{2^{2m}} \binom{N-m}{m} \frac{N}{N-m} (-\det \underline{\mathbb{T}})^m \exp \{-a'\} \\ &\quad \times \int_{-\infty}^{\infty} \exp \left\{ -\frac{y^2}{2c'} \right\} (\text{tr} \underline{\mathbb{T}})^{N-2m} dy \end{aligned} \quad (6.30)$$

where we have taken $(-\det \underline{\mathbb{T}})^m$ and a' out of the integral as they are not functions of y , however the trace of $\underline{\mathbb{T}}$ is a function of y ,

$$\text{tr} \underline{\mathbb{T}} = \exp \{-J_{++} - h' - iy\} + \exp \{-J_{--} + h' + iy\}. \quad (6.31)$$

The integral in eqn. (6.30) can now be computed

$$\mathbb{I} = \int_{-\infty}^{\infty} \exp \left\{ -\frac{y^2}{2c'} \right\} (\text{tr} \underline{\mathbb{T}})^{N-2m} dy \quad (6.32)$$

$$\begin{aligned} &= \int_{-\infty}^{\infty} \exp \left\{ -\frac{y^2}{2c'} \right\} \sum_{t'=0}^{N-2m} \binom{N-2m}{t'} \\ &\quad \times \exp \left\{ -[(N-2m-t')(J_{++} + h' + iy) + t'(J_{--} - h' - iy)] \right\} dy \end{aligned} \quad (6.33)$$

$$\begin{aligned} &= \sum_{t'=0}^{N-2m} \binom{N-2m}{t'} \exp \left\{ -[(N-2m-2t')(J_{++} + h) + t'(J_{++} + J_{--})] \right\} \\ &\quad \times \int_{-\infty}^{\infty} \exp \left\{ -\frac{y^2}{2c'} - iy(N-2m-2t') \right\} dy \end{aligned} \quad (6.34)$$

$$\begin{aligned} &= \sqrt{2\pi c'} \sum_{t'=0}^{N-2m} \binom{N-2m}{t'} \\ &\quad \times \exp \left\{ - \left[(N-2m-2t')(J_{++} + h') + t'(J_{++} + J_{--}) + \frac{c'}{2}(N-2m-2t')^2 \right] \right\} \end{aligned} \quad (6.35)$$

where we first expanded out the trace of $\underline{\mathbb{T}}$ binomially and then used the Hubbard-Stratonovich identity, eqn. (6.19), to evaluate this now Gaussian integral. Putting all of this together we have

$$\begin{aligned} \zeta_N &= \sum_{m=0}^{\lfloor N/2 \rfloor} \sum_{t'=0}^{N-2m} \binom{N-m}{m} \binom{N-2m}{t'} \frac{N}{N-m} (-\det \underline{\mathbb{T}})^m \\ &\quad \times \exp \left\{ - \left[a' + (N-2m-2t')(J_{++} + h') + t'(J_{++} + J_{--}) + \frac{c'}{2}(N-2m-2t')^2 \right] \right\} \end{aligned} \quad (6.36)$$

after making the change of variables $t = t' + m$, noticing that for $N - m \geq t \geq m$ the equality

$$\binom{N-m}{m} \binom{N-2m}{t-m} = \binom{N-m}{t} \binom{t}{m} \quad (6.37)$$

holds and as $\det \underline{A} = \exp\{-J_{++} - J_{--}\} - \exp\{-2J_{+-}\}$ we have

$$\begin{aligned} \mathcal{Z}_{\text{MF}} = & \sum_{N=0}^{\infty} \sum_{m=0}^{\lfloor \frac{N}{2} \rfloor} \sum_{t=m}^{N-m} \frac{1}{(N(1 + \langle s \rangle)/2)!} \frac{1}{(N(1 - \langle s \rangle)/2)!} \\ & \times \binom{N-m}{t} \binom{t}{m} \frac{N}{N-m} (\exp\{-2J_{+-}\} - \exp\{-J_{++} - J_{--}\})^m \\ & \times \exp \left\{ - \left[a' + (N-2m)J + (N-2t)h' + \frac{1}{2}c'(N-2t)^2 \right] \right\}. \end{aligned} \quad (6.38)$$

The expected number of ions in the pore, $\langle N \rangle$ can be obtained from the partition function via

$$\langle N \rangle = \frac{1}{\mathcal{Z}_{\text{MF}}} \frac{\partial \mathcal{Z}_{\text{MF}}}{\partial \langle \mu \rangle} \quad (6.39)$$

and expected *total* charge in the pore, $\langle S \rangle$ can be obtained from the partition function via

$$\langle S \rangle = - \frac{1}{\mathcal{Z}_{\text{MF}}} \frac{\partial \mathcal{Z}_{\text{MF}}}{\partial h}. \quad (6.40)$$

Once $\langle N \rangle$ and $\langle S \rangle$ are known, the expected number of cations and anions in the pore can be found

$$\langle N_+ \rangle = \frac{\langle N \rangle + \langle S \rangle}{2} \quad \langle N_- \rangle = \frac{\langle N \rangle - \langle S \rangle}{2} \quad (6.41)$$

and the expected total length of ions in the pore $\langle \ell \rangle \langle N \rangle + \tilde{\ell} \langle S \rangle$ is trivially found, but very cumbersome. We reiterate that since the ions form a densely packed column inside the pore this is approximately the expected length of the pore, $\langle L \rangle$,

$$\langle L \rangle \approx \langle \ell \rangle \langle N \rangle + \tilde{\ell} \langle S \rangle. \quad (6.42)$$

6.3.2 A Steepest Decent Approximation

Equations (6.38)–(6.42) provide the algorithm for the calculation of $\langle L \rangle$. However, this prescription is rather cumbersome and does not allow an easy grasp of $\langle L \rangle$ in parameter space. To gain insight into the behaviour of $\langle L \rangle$ we look at the special case of identically sized ions so that

$$\ell_+ = \ell_- = \langle \ell \rangle \implies \tilde{\ell} = 0 \quad \& \quad J_{++} = J_{+-} = J_{--} \equiv J \quad (6.43)$$

and carry out a further mean field approximation. We define H_{SD} and $\mathcal{Z}_{\text{SD}}$ as the result of making the following replacements

$$\sum_{\langle i,j \rangle}^N s_i s_j \rightarrow N \langle s \rangle^2, \quad \sum_i^N s_i \rightarrow N \langle s \rangle, \quad (6.44)$$

in the partition function given in eqn. (6.9) so that

$$\mathcal{Z}_{\text{SD}} = \sum_{N=0}^{\infty} \frac{1}{(N/2(1 + \langle s \rangle))!} \frac{1}{(N/2(1 - \langle s \rangle))!} \exp \{-\mathcal{H}_{\text{SD}}\} \quad (6.45)$$

$$\mathcal{H}_{\text{SD}} = J \langle s \rangle^2 N + (eh - \tilde{\mu}) \langle s \rangle N - \langle \mu \rangle N + \frac{1}{2} k (L(1 - \alpha \langle s \rangle) - \langle \ell \rangle N)^2 \quad (6.46)$$

For large $k \langle \ell \rangle$ we can now make a steepest decent (SD) approximation to identify which term from the Hamiltonian $\mathcal{H}_{\text{SD}}$ gives the largest contribution to $\mathcal{Z}_{\text{SD}}$ from the Gibbs sum over N . We define the most significant term in the Hamiltonian, $\mathcal{H}_{\text{SD}}$, as N_{SD} such that

$$\left. \frac{\partial \mathcal{H}_{\text{SD}}}{\partial N} \right|_{N=N_{\text{SD}}} = 0 \quad (6.47)$$

N_{SD} is thus the number of ions inside the pore in this steepest decent approximation. We use the same trick as before assuming the length of the pore in this approximation, L_{SD} , is the cumulative length of the densely packed ions inside of it

$$L_{\text{SD}} \approx \langle \ell \rangle N_{\text{SD}} = \frac{\langle \mu \rangle - (eh - \tilde{\mu}) \langle s \rangle - J \langle s \rangle^2}{k \langle \ell \rangle} + L(1 + \alpha \langle s \rangle), \quad (6.48)$$

where the right hand side is based on the solution N_{SD} of (6.47). The two terms on the right hand side of eqn. (6.48) explicitly demonstrate how the overall length change of the pore emerges a competition between steric packing effects, the first term, and electrochemical doping effects, the second. To obtain such a compact expression in this approximation we have considered only the largest term in the in the grand-canonical partition sum eqn. (6.45) and neglected the effects from the normalising pre-factor $(N_+!N_-!)^{-1}$ in the partition function, eqn. (6.10). This factor can of course be included in the Hamiltonian via a Stirling's formula but doing so removes the possibility of solving eqn. (6.47) algebraically for N_{SD} . The inclusion of the normalising pre-factor was found to make a small correction to eqn. (6.48) damping contributions from larger N to the partition function, therefore, N_{SD} and L_{SD} are slight be overestimates of $\langle N \rangle$ and $\langle L \rangle$ respectively. We will compare formula with and without this normalising factor analytically in Section 6.4.2.

6.4 Results for a Single Pore

6.4.1 Composition of the Pore Interior

Before we look at how the length of the pore could change we need to understand the composition of the chain of ions inside the pore. Figure 6.1a shows the total number of cations and anions, eqn. (6.41), and the total number of ions, eqn. (6.39), in a pore as a function of applied voltage.

The first point to note is that at small voltages the pore contains the same amount of anions as it does cations. Thus, an alternating chain of ions is present in the pore at low voltages. The thresholds to deconstruct this chain are the same as the thresholds in the Ising model of charge storage with ions of different sizes, section 3.4. These threshold voltages are $|h^*| = \{-(J_{++} + J_{+-}), (J_{--} + J_{+-})\}/e$. This is to be expected as H_A is a only part of the actuation Hamiltonian, eqn. (6.1) that contains terms pertaining to the spin of lattice site. Physically, the same amount of energy is required in both models to unbind a chain of alternating ions (J_{+-}) and then force counterions into a chain within the pore (J_{++} or J_{--}).

At voltages with a larger magnitude than these thresholds the pore rapidly charges and becomes fully filled with one type of ion. If these ions are smaller than the ions they are replacing then the number of ions in the pore increases on charging and conversely if the ions are larger then the number of ions in the pore decreases on charging. Once the pore is fully charged with counterions the number of counterions in the pore can still increase albeit slowly, this increase is associated with the steric length change of the pore. The pore expands to include additional ions that are favoured by the applied voltage.

6.4.2 The Strain of a Pore

To examine how the pore expands (or contracts) upon charging we define the strain of a pore to be the relative length change of the pore normalised to its relaxed length at zero potential so that

$$\langle \epsilon \rangle = \frac{\langle L(h) \rangle}{\langle L(h=0) \rangle} - 1, \quad \epsilon_{SD} = \frac{L_{SD}(h)}{L_{SD}(h=0)} - 1. \quad (6.49)$$

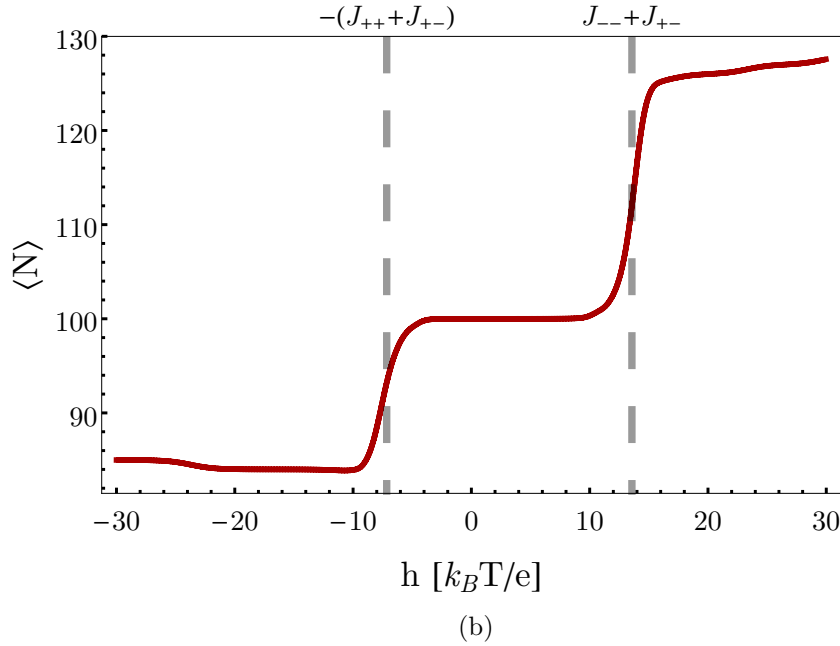
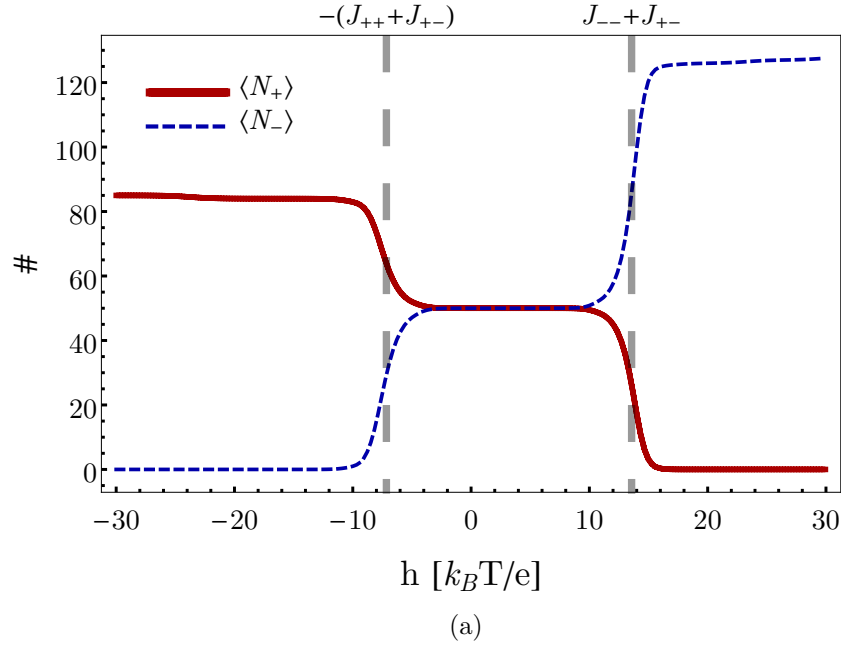


Figure 6.1: a) Expected number of cations, $\langle N_+ \rangle$, and anions, $\langle N_- \rangle$, inside a pore. b) Total number of ions inside a the same pore, $\langle N \rangle = \langle N_+ \rangle + \langle N_- \rangle$, The asymmetry arises as anions are smaller than cations. [Parameters: $\ell_+ = 1.2\text{nm}$, $\ell_- = 0.8\text{nm}$, $L = 100\text{nm}$, $k = 10k_B T/\text{nm}^2$, $\mu = 0k_B T$, $\alpha = 0$]

In figure 6.2a, we compare the strain of the pore, obtained in the steepest decent approximation, ϵ_{SD} , and the more general result $\langle\epsilon\rangle$. We can see that while ϵ_{SD} slightly overestimates $\langle\epsilon\rangle$ it has the same qualitative behaviour as a function of h . The strain obtained via the steepest decent method is only valid to describe a pore with identically sized ions $\ell_+ = \ell_- \equiv \langle l \rangle$ and so cannot be used to grasp the full behaviour of $\langle\epsilon\rangle$ but this specific case will give us a handle on the more general.

To understand how ϵ_{SD} , eqn. (6.48), behaves we recall that $\langle s \rangle$, eqn. (3.29), is a function of electrode potential, h . This dependence is shown in the inset in figure 6.2b. There is little change in $\langle s \rangle$ for small voltages as the potential cannot overcome the electrostatic nearest neighbour attraction between opposite charges. So for small potentials there is no change in $\langle\epsilon\rangle$ or ϵ_{SD} . This agrees with what is seen in figure 6.1. As the potential reaches a threshold, $|h^*| \approx 2J/e$, it overcomes the nearest neighbour affinity between opposite charges and unbinds the ion pairs, $\langle s \rangle$ changes sharply and electrochemical doping occurs in the pore walls in response to the change in ion charge inside the pore¹. This doping causes positive strain for a negative applied potential and negative strain for a positive applied potential. The larger the nearest neighbour interaction the greater the required electrode potential to start the charging process. Once the pore is fully charged strain increases in an approximately linear elastic manner driven by the inclusion of new ions in the pore. There is a small staircase effect seen in the wings of the curves in figures 6.1 and 6.2a. This is a finite size effect corresponding to the inclusion of individual ions into the pore. This is an artefact of the idealised nature of our model and is not present in ϵ_{SD} where a stronger approximation is used.

The parameter α controls the asymmetry in ϵ_{SD} with respect to the sign of the electrode potential, as shown in figure 6.2b. For positive electrode polarisation the electrochemical doping of the pore walls causes contraction which competes with the steric effect of ion insertion. For negative potentials both swelling mechanisms complement each other and the swelling is greater.

The strain, ϵ_{SD} , of pores with various radii can be seen in figure 6.3a. In larger pores the screening is weaker, J is larger, the magnitude of the threshold, h^* , is greater and therefore a larger potential is required to start the charging process and thus the swelling.

¹We note that the charging threshold is now $|h^*| \approx 2J/e$ rather than $|h^*| = \{-(J_{++} + J_{+-}), (J_{--} + J_{+-})\}/e$ as we are in the special case where we charge the pore with identically sized ions so that $J_{++} = J_{+-} = J_{--} = J$.

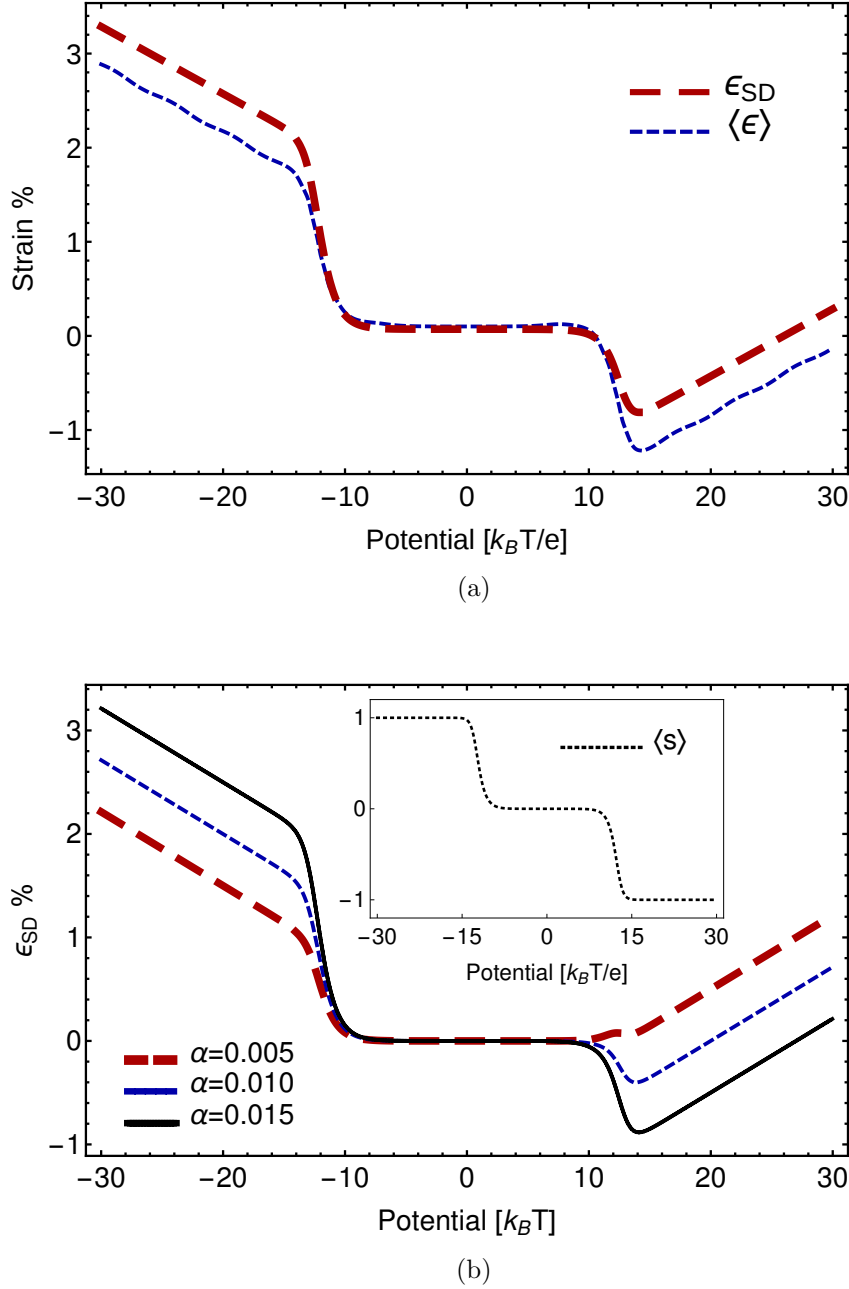


Figure 6.2: a) Comparison of the strain of a single pore vs. potential obtained without a steepest decent approximation, $\langle \epsilon \rangle$, and with a steepest decent approximation, ϵ_{SD} , eqn. (6.49). The staircase effect seen in the wings of $\langle \epsilon \rangle$ corresponds to the inclusion of ions into the pore from the bulk. This is an artefact of the idealised nature of our model. The stronger approximation used to obtain ϵ_{SD} neglects this effect. b) Strain, ϵ_{SD} , for different values of the parameter α , which accounts for electrochemical doping of the nanotube. The corresponding mean field order parameter $\langle s \rangle$, eqn. (3.12), is shown in the inset. [Parameters: $\ell_+ = \ell_- = 0.7\text{nm}$, $L = 200\text{nm}$, $\langle \mu \rangle = 1k_B T$, $r = 0.5\text{nm}$, $k = 10k_B T/\text{nm}^2$. a) $\alpha = 0.015$.]

Once the pore is fully charged with ions, $\langle s \rangle = \pm 1$, there is no change in the electrochemical doping of the pore walls and the only length change is from the steric ion insertion term in eqn. (6.48). In the limit of large electrode polarisation, positive or negative, both $\langle \epsilon \rangle$ and ϵ_{SD} increase at the same rate with respect to potential; we can see from eqn. (6.48) that this gradient is $\pm 1/(k\ell)$. As only one species of ion is present in the pore at these large voltages. The strain a pore in this regime charged with ions of different sizes will have the gradient $1/(k\ell_-)$ for a positive polarisation and the gradient $-1/(k\ell_+)$ for a negative polarisation.

6.4.3 Result for Many Pores

An electrode contains many pores of differing radii. With this in mind we average our results for the strain for a single pore over a normal pore size distribution, with mean, $\langle r \rangle$, and variance $(\delta r)^2$. We do this using the prescription described in section 3.3 but we replace the capacitance in eqn. (3.22) with a strain², ϵ_{SD} , to obtain the average strain $\langle \epsilon_{SD} \rangle$. We again apply the upper and lower bounds $r_{max} = \ell$ and $r_{min} = \ell/2$ to the radial distribution ensuring that the chain of ions in the pore maintains its 1D nature. As usual, we will refer to this collection of pores of different radii as the electrode.

As a potential is applied to the electrode the pores with the smaller radii, and therefore stronger screening, start to swell first, figure 6.3a. Recall, the potential required to start charging a single pore wetted with ions of the same size is $|h^*| \approx 2J/e$. As the potential is increased, larger pores are activated and they then contribute to the total swelling of the electrode. The near linear Hookean expansion of a single fully charged pore is now replaced by an asymmetric parabola formed from the linear contributions of individual pores in various states of charge. Once we reach a large potential all of the pores are fully filled with ions of one species and swelling will again be linear. This is an artefact of our model, specifically due to the upper cut-off we put in place to maintain the single file structure of ions inside the pore. In reality, once all of the smaller quasi-1D pores in an electrode are filled by the charging process, ions will be forced to pack in larger pores. In these larger spaces conventional double layers will be able to form and electrode expansion can be driven by the interaction of overlapping double layers. This will be energetically more costly than filling smaller pores due to reduced electronic screening in the less confined geometry and so swelling in these larger pores will occur at larger potentials.

²We choose to average ϵ_{SD} rather than $\langle \epsilon \rangle$ for computational reasons.

The expansion of several carbon electrodes characterised by various pore size distributions, wetted with several ionic liquids is described in [104, 105, 106]. The swelling of all of these electrodes follow a similar qualitative trend - the electrode swells parabolically as a function of applied potential with larger swelling observed at negative potentials regardless of the nature of the carbon electrode or the ionic liquid that wets it.

Figure 6.3b shows the experimental observations of the swelling of a porous carbon electrode (YP17) when it is charged with an ionic liquid ([EMIM][BF₄]) [104]. To obtain this data an electrode is confined on all but one side and the electrode potential is repeatedly increased and decreased at a slow scan rate causing charging and discharging. The relative height change of the free side is measured as the voltage is cycled. This finite time charging and discharging cycle causes hysteresis in the experimental results, present in the paper by Hantel et al. but for clarity we have averaged out this hysteresis in figure 6.3b.

We relate the experimentally measured relative height change of the electrode to the strain of many pores predicted with the model detailed in this article in figure 6.3b. While the macroscopically measured relative electrode height is not the same as the strain of many aligned nanopores, that we describe with our model, the expansion of many individual nanopores will cause an expansion of the electrode. Indeed, the results from our model, averaged over many pores can be quantitatively fit to the experimentally measured effect.

6.5 Discussion and Conclusions

Decreasing the size of the nanoscale pores in a carbon electrode causes greater swelling as the supercapacitor is charged [104]. The features of the expansion of such electrodes can be explained by two effects occurring simultaneously. Calculations of carbon structures show expansion, when charge is added to the electrode, and contraction, when charge is removed [130]. Experimental studies into the swelling of a carbon electrode wetted with an ionic liquid show asymmetric expansion depending on electrode polarisation [131, 132]. Kaasik et al. noted that in Debye-Hückel theory the proportionality between repulsive pressure of two overlapping double layers and square of the accumulated charge could be used to explain electrode swelling [106]. While this model predicts expansion in both polarisations and can be fitted to experimental data we expect models originating from conventional double layer theory to be applicable to larger pores, for ultra-narrow pores a different approach

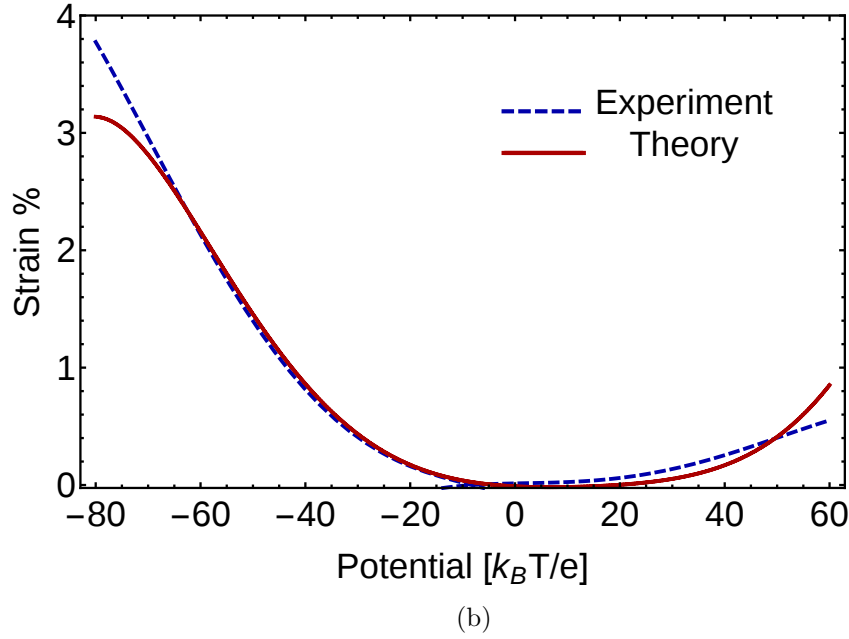
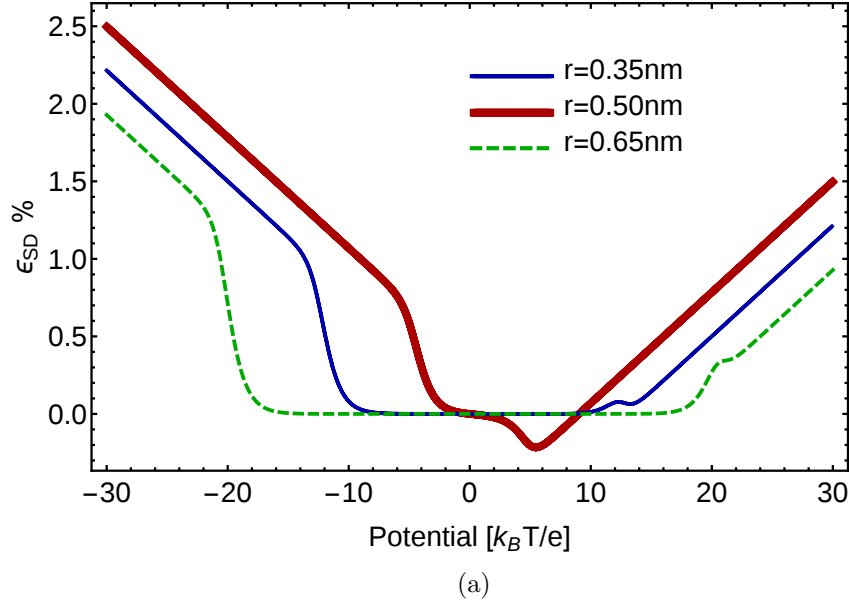


Figure 6.3: a) Strain, ϵ_{SD} , of 3 pores with a range of radii, r . Larger pores, that screen charge less, require larger applied potential to start the swelling process. b) Experimental observations of macroscopic carbon electrode strain compared to the theoretical average strain of many pores with normally distributed radii. Experimental data obtained from M.M. Hantel et al. [104]. The empirical parameter α has been fitted to the experimental data. [Parameters: $\langle\mu\rangle = 1k_B T$, $k = 10k_B T/\text{nm}^2$, $\alpha = 0.005$ a) $\ell_+ = \ell_- = 0.7\text{nm}$, $L = 200\text{nm}$ b) $\ell_+ = \ell_- = 0.35\text{nm}$, $r_0 = 0.4\text{nm}$, $\delta r_0 = 0.1\text{nm}$, $L = 500\text{nm}$.]

is needed. Our model considers discreteness of charge in a quasi-1D arrangement of ions in a pore, screening of electrostatic interactions between the ions by the free electrons of the electrode, and the electron doping effect on the density of carbon. Steric ion insertion which always promotes expansion competes with electrochemical doping effects when the electrode is polarised anodically (positively) and complement each other for cathodic (negative) polarisations.

We weigh the results obtained for one pore radius with a Gaussian pore size distribution making our results applicable to approximately monodisperse and monomorphic nanostructured electrodes. Our electrode swells in both polarisations and this swelling is greater when it is charged with cations than anions. This is in qualitative agreement with experimental results.

In reality, a porous electrode consists of pores of all sizes, many of which are not quasi-1D and not orientated parallel to each other. Our theory predicts that the smallest pores swell the most at low voltages because electrostatic screening is strongest in small pores allowing them to be charged first and swell first. At larger voltages the swelling of wider pores is activated. At very large voltages double layer forces from large 3D pores will contribute to the overall swelling of the electrode as considered in earlier work [106]; as yet, we do not have a unified theory which will could include that limit.

Chapter 7

Conclusions and Outlook

7.1 Summary

We have shown in Chapter 2 that narrow cylindrical and slit pores that do not screen charge ideally but do allow some field penetration into the electrode walls still screen charge-charge interactions within the pore exponentially as a function of charge separation. This supports the applicability of the superionic state in such non-ideal pores. Furthermore, we have argued upper and lower bounds to the screening of a charge in an elliptical pore.

Motivated by the exponential screening that is present even in non-ideal electrodes we have introduced and developed several nearest neighbour lattice models of charge storage in a quasi-1D cylindrical pore, Chapters 3, 4 and 5. These models agreed, where applicable, on the measures required to optimise energy storage. One must decrease the size of the counterion, engineer the pore to favour coions over counterions, increase the ionophobicity of the pore so that it is devoid of ions at low voltages or use a larger solvent molecule to dilute the ionic liquid. Additionally, increasing the radius of the pore can increase the differential capacitance at high voltages but this is offset by increases to the surface area of the electrode, furthermore, such increases in differential capacitance may be outside the voltage window of the electrolyte and inaccessible. We did not consider the capacitance of the electrode itself which, will be material specific and, will be important if it is small. We note that energy storage may be improved if the two electrodes in the electrochemical cell are engineered separately and are individually

optimised with regards to each electrodes charging counterion. Our theories of charge storage are thermodynamic in nature and as such we do not address the dynamics of the charging process but we do note that empty ionophobic pores, which would be optimum for charge and energy storage, should charge faster than filled pores [138].

Finally, in Chapter 6 we developed a model of potentially unwanted electroactuation that is associated with the charging process in electrodes containing cylindrical pores. This model incorporated steric packing and electrochemical doping effects that contributed to the swelling of a pore. We demonstrated that individually linearly swelling pores that are activated at different voltages could produce the parabolic electrode swelling seen experimentally [104, 105, 106] and that charging with smaller ions will cause more swelling of the electrode.

7.2 Further Work

There are many possible avenues of further work that would be interesting to study:

- The author would like to solve the system given by eqns. (2.6) and (2.7) in an elliptical coordinate system as discussed in section 2.6.1.
- The incorporation of effective screening radius and a physical radius. This would be easy to do within our theory but this would require research into electrode material specific properties.
- The effects of thin pore walls, both on screening and on charge storage in adjacent pores.
- Chemical potential or transfer energy should be dependent on the pore radius, through image forces, the study of such an effect would be interesting and perhaps remove the polarity dependence of ionophobicity seen in the BEG model in figure 4.6.
- The dielectric of the interior of the pore might also be dependent on the pore radius in a non-trivial way. Some work on this has already been performed [107] but further investigation would be interesting.
- The inclusion of an electrode capacitance. Again, this is very easy to include in our model, the electrode capacitance and the pore capacitance would simply add in series but it would require research into electrode material specific properties.

- The optimisation of energy storage often involved increasing the capacitance at larger voltages but if these voltages were out of the electrolytes voltage window then achieving this increase in capacitance would be inaccessible. The author would like to investigate how molecule size, optimum pore radius and ionophobicity can be optimised within an electrolyte specific voltage window.
- As discussed in section 4.6 the author would like to develop a lattice model that includes electrostatic interaction of ions with dipolar solvent molecules. This could be done by considering a 4 by 4 transfer matrix with an extra row and column that would depict interactions ion-solvent, solvent-solvent and void-solvent interactions. Research would be required to ascertain the form of these interactions within a confined geometry.
- The $I\delta$ model was originally intended to include ion clustering within the pore rather than the equal spacing approximation that we presented but this line of research was abandoned due to time constraints. The author would like to look at this problem again.

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Postface

Oh. And how is ‘education’ supposed to make me feel smarter? Besides, every time I learn something new, it pushes some old stuff out of my brain. Remember when I took that home wine-making course and I forgot how to drive?

— H.J. Simpson