

Mathematical modelling of electronic contact mechanisms in silicon photovoltaic cells



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Abstract

In screen-printed silicon-crystalline solar cells, the contact resistance of a thin interfacial glass layer between the silicon and the silver electrode plays a limiting role for electron transport. The motivation of this project is to gain increased understanding of the transport mechanisms of the electrons across this layer, which can be exploited to provide higher performance crystalline silicon solar cells. Our methodology throughout is to formulate and analyse mathematical models for the electron transport, based on the drift diffusion equations.

In the first chapter we outline the problem and provide a summary of relevant theory. In Chapter 2 we formulate a one-dimensional model for electron transport across the glass layer, that we solve both numerically and by employing asymptotic techniques. Chapter 3 extends the model presented in Chapter 2 to two dimensions. To solve the two-dimensional model numerically we devise and validate a new spectral method. The short circuiting of current through thinner regions of the glass layer enables us to find limiting asymptotic expressions for the average current density for two different canonical glass layer profiles. In Chapter 4 we include quantum mechanical effects into the one-dimensional model outlined in Chapter 2 and find that they have a negligible effect on the contact resistance of the glass layer. We model the boundary effects present at the silicon emitter-glass interface in Chapter 5. Finally, in Chapter 6 we summarise our key results, suggest possible future work, and outline the implications of our work to crystalline silicon solar cell manufacturers.

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Chapter 1

Introduction

The photovoltaic solar cell industry grew by 34% over the two year period from 2012–2013 with an expected 100 GW annual deployment in 2018. This means that solar is expected to compete directly with more traditional forms of energy generation and increase to 3% of the total global power supply [94]. In the period up to 2018, it is predicted that 91% of the solar cells installed will be crystalline silicon (c-Si) [94]. In the production of c-Si solar cells a silicon wafer is doped to form the p-n junction, essential for charge separation. The typically n-type emitter is then covered in a silicon nitride passivation layer that also provides an antireflection coating. To form the front contact, silver paste is patterned by screen printing onto the emitter before being fired in a furnace. This thesis aims to use mathematical modelling to increase the understanding of the transport mechanisms of electrons from the silicon emitter into the silver electrode. In this chapter we provide a summary of the theory required to model current flow in semiconductors and outline what is known about the formation and conduction mechanisms present at the front contact of a silicon solar cell.

1.1 Contact formation

The silver paste used to form the front contact of a silicon solar cell must etch through the antireflection layer and make a contact with low electrical resistance and good mechanical adhesion. The main constituents of commercial silver pastes tend to be silver powders, lead borosilicate glass and an organic vehicle system [52]. During the firing process, the organics are combusted off and sintering of the silver particles occurs to form a connected interface layer. The lead borosilicate glass wets the silver particles and the silicon nitride. The lead borosilicate glass then etches through the silicon nitride and reacts with the silicon to form SiO_2 and lead.

The removal of the silicon nitride allows the following reaction to take place



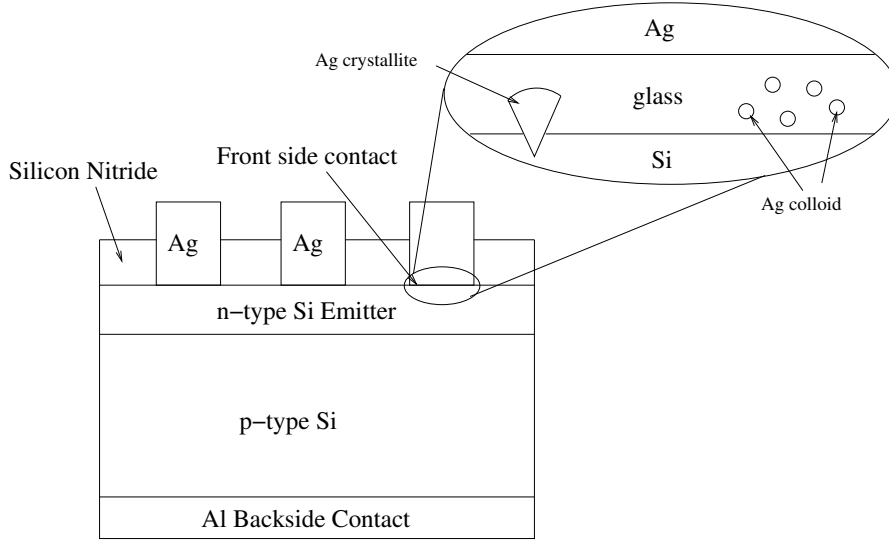


Figure 1.1: Schematic diagram of a solar cell after firing. The detail shows the different possible geometries of silver inclusions: “crystallite” and “colloid”.

that leads to the formation of silver crystallites embedded in the silicon and/or silver precipitates (nano-Ag colloids) [39, 86]. The general structure of the front contact is therefore a layer of silver, a glass layer (SiO_2 and transition metals [50]) containing nano-Ag colloids, and a silicon emitter with silver crystallites embedded. The glass layer is not uniform and can vary from $\sim 10\text{nm} - 1000\text{nm}$ [64, 65, 103]. The exact structure of the front contact depends on a number of factors including: the emitter doping [29], the size of the silver particles in the paste [49], the surface structure of the silicon emitter [58] and the firing temperature [44, 53, 64, 65, 81, 86]. A schematic of the geometry is illustrated in figure 1.1.

1.2 Band theory

When considering the electronic properties of different materials it is common to use band theory. Here, we give a brief summary of the key concepts, for a more complete description see [74, 95].

In band theory the available energies for an electron in a solid are divided into different energy levels (bands). An electron that is involved in bonding between atoms is thought to be in the valence band E_v . An electron that is free to move within the solid and therefore able to transport charge and energy is in the conduction band E_c . The region between these two bands is known as the band gap E_g . Electrons are forbidden from existing within the band gap.

Metals are thought to have zero band gap allowing easy conduction of charge. In semiconductors an electron must be excited from the valence band into the conduction band to contribute to current flow. When an electron is excited from the valence band into the conduction band it leaves behind a positively charged vacancy ('hole'). The movement of electrons in the conduction band and holes in the valence band are the cause of current flow in semiconductors.

Two additional energy levels to consider are the Fermi level E_F and the vacuum level E_{vac} . The Fermi level is the energy level corresponding to the chemical potential of an electron in the solid. The vacuum level is the energy level an electron must reach to be free of all forces from the solid. The different energy levels in a semiconductor are related by the following¹ (see figure 1.2(a))

$$E_c = E_{\text{vac}} + \chi_n, \quad (1.2.1)$$

$$E_v = E_{\text{vac}} + \chi_n - E_g = E_{\text{vac}} + \chi_p, \quad (1.2.2)$$

$$E_F = E_c - k_B T \log\left(\frac{g_c}{n}\right) = E_v + k_B T \log\left(\frac{g_v}{p}\right), \quad (1.2.3)$$

where χ_n is the electron affinity, χ_p is the ionisation potential, k_B is Boltzmann's constant, T is absolute temperature, g_c is the conduction band effective density of states, g_v is the valence band effective density of states, n is the density of electrons (in the conduction band) and p is the density of holes (in the valence band).

The product of the electron and hole densities in a semiconductor is constant when the semiconductor is in equilibrium and is therefore used to define the intrinsic carrier density of the semiconductor n_i . Using (1.2.3) we find n_i is given by

$$n_i^2 = pn = g_c g_v \exp\left(-\frac{E_g}{k_B T}\right). \quad (1.2.4)$$

It is usual to think of a metal having only the E_{vac} and E_F energy levels, with

$$E_F = E_{\text{vac}} - W_{\text{metal}}, \quad (1.2.5)$$

where W_{metal} is the workfunction of the metal. A schematic of the band diagram for a metal is given in figure 1.2(b).

¹Equation 1.2.3 only holds for nondegenerate semiconductors. A nondegenerate semiconductor is where n (p) is always less than g_c (g_v) [95].

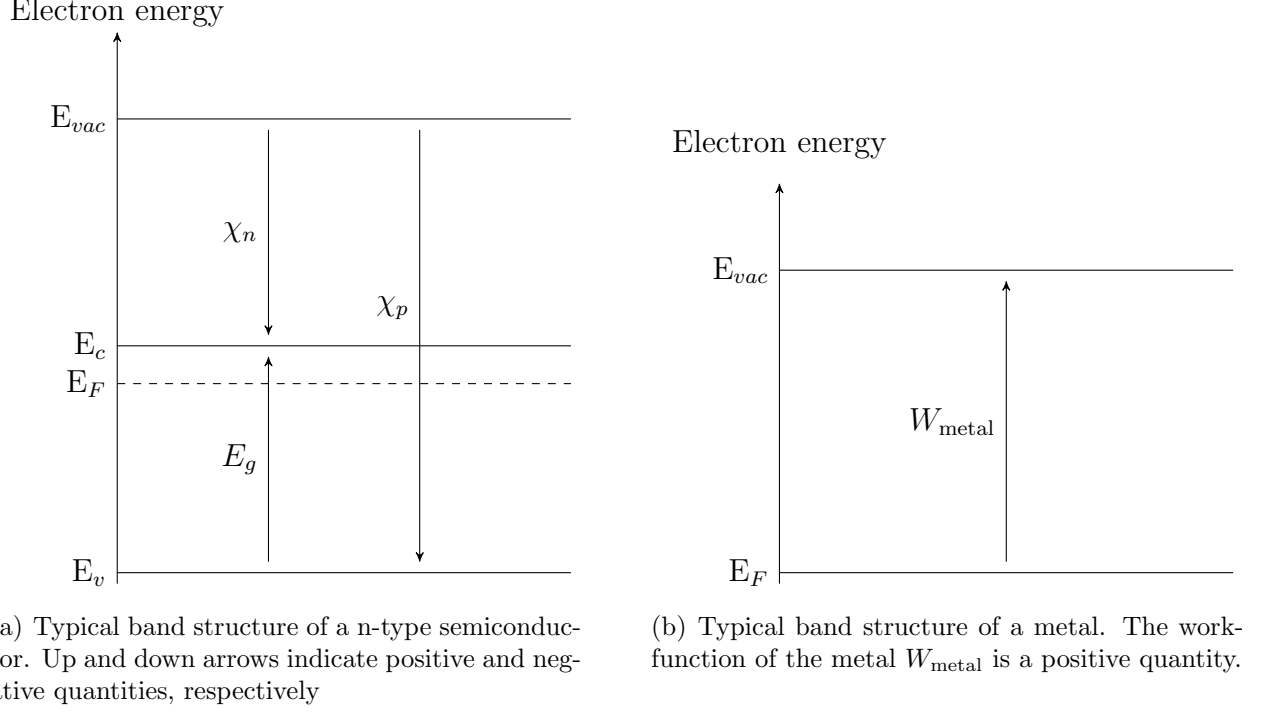


Figure 1.2: Schematics of the band structure of a semiconductor (a) and a metal (b).

1.3 Semiconductor-metal contact

1.3.1 Schottky contact

For illustrative purposes we consider the case of a semiconductor doped with donor impurities (n-type) contacting a metal. Away from the contact the semiconductor is electrically neutral, and the electron and hole densities take their equilibrium values. The electron density must then be approximately equal to the concentration of donor impurities N_D ($n \approx N_D$), whilst the hole density is found using (1.2.4) ($p \approx n_i^2/N_D$).

When the materials are brought into electronic contact, to reach equilibrium, the Fermi levels of the semiconductor and metal must align [95]. Typically, the electron affinity of a semiconductor (χ_n) is smaller in magnitude than the workfunction of a metal (W_{metal}) and therefore near to the metal, in order for the Fermi levels to align, the valence, conduction, and vacuum band bend ‘upwards’. We assume that there is no band bending in the metal because the Debye length in a metal is extremely short. A typical band diagram for a n-type semiconductor-metal contact is shown in figure 1.3. The difference between the workfunction of the metal and the electron affinity of the semiconductor is often known as the ‘Schottky barrier height’ θ_{MB} . The band bending occurs through the transfer of electrons from the semiconductor into the metal [74]. Using (1.2.3) we realise that the upwards bending of the valence band leads to an increase in the number

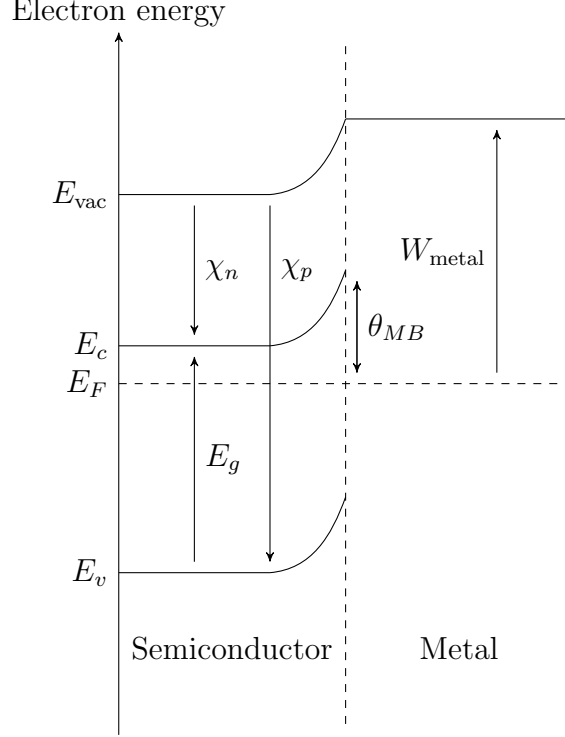


Figure 1.3: Band diagram for n-type semiconductor-metal contact.

of holes present at the contact. However, the concentration of holes is still very small and it is well known that the current transport at a semiconductor-metal contact is mainly due to the majority carrier (electrons in a n-type semiconductor and holes in a p-type semiconductor) [95].

The transfer of electrons from the semiconductor into the metal leads to an area near the contact with relatively few charge carriers. This region is often called the ‘depletion region’ [74] and leads to the formation of a ‘potential barrier’ that electrons must surmount for current to flow between the semiconductor and metal [95]. A schematic of the variation of electron density at the semiconductor-metal contact is given in figure 1.4. If an electric potential is applied so that the semiconductor has a negative polarity and the metal has a positive polarity the system is in forward bias. In forward bias, the depletion region decreases in size and therefore the current density increases rapidly. At high forward biases the current density will be limited by the series resistance of the semiconductor. If an electric potential is applied so that the semiconductor has positive polarity and the metal a negative polarity the system is in reverse bias and the depletion region increases in size. The large depletion region means that only a small current flows (that is approximately constant) as the reverse bias is increased [95]. This means that the contact will pass current preferentially in one direction and have ‘rectifying’ characteristics [74].

So far we have considered an ‘ideal’ contact between the semiconductor and metal

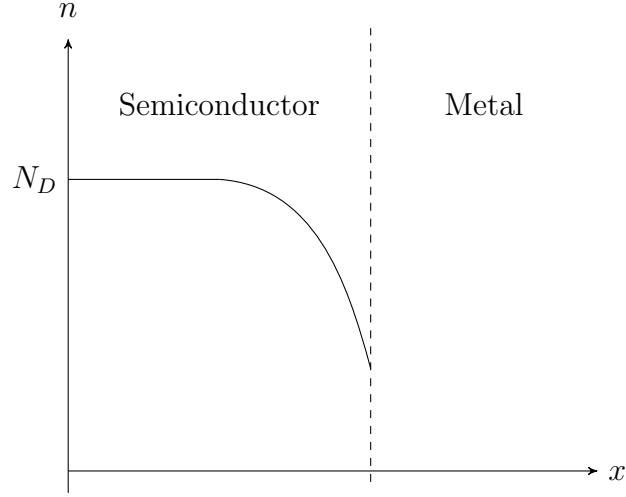


Figure 1.4: Schematic of electron density variation at n-type semiconductor-metal contact.

by neglecting (i) the Schottky effect and (ii) interface states that in practice can have a profound effect on the current-voltage characteristics:

1. The Schottky effect (also known as image-force lowering) occurs when an electron in the semiconductor approaches the metal and generates a positive image charge. The attractive force between the electron and positive image charge favours electron transport from the semiconductor into the metal and therefore further contributes to the rectifying nature of the semiconductor-metal contact [95].
2. The surface of a semiconductor is likely to contain interface states (defects and impurities) that introduce electrons or trap electrons (introduce holes). This change in charge carrier density will affect the ‘potential barrier’ at the contact and therefore the current-voltage characteristics of the contact [74].

1.3.2 Ohmic contact

An Ohmic contact is a low resistance contact where current flows easily in both directions. For a n-type semiconductor-metal junction an Ohmic contact exists if $(-\chi_n) \gtrsim W_{\text{metal}}$ ($(-\chi_p) \lesssim W_{\text{metal}}$ for a p-type semiconductor-metal junction) [74]. In this case, the electronic contact leads to electrons moving from the metal to the semiconductor. There then exists an accumulation of charge carriers at the contact allowing current to pass easily in each direction. Ohmic contacts also arise when a degenerate semiconductor is contacted to a metal ($N_D > g_c$) [95]. For degenerate semiconductors the relation (1.2.3) does not hold and the drift diffusion equations are not valid [68].

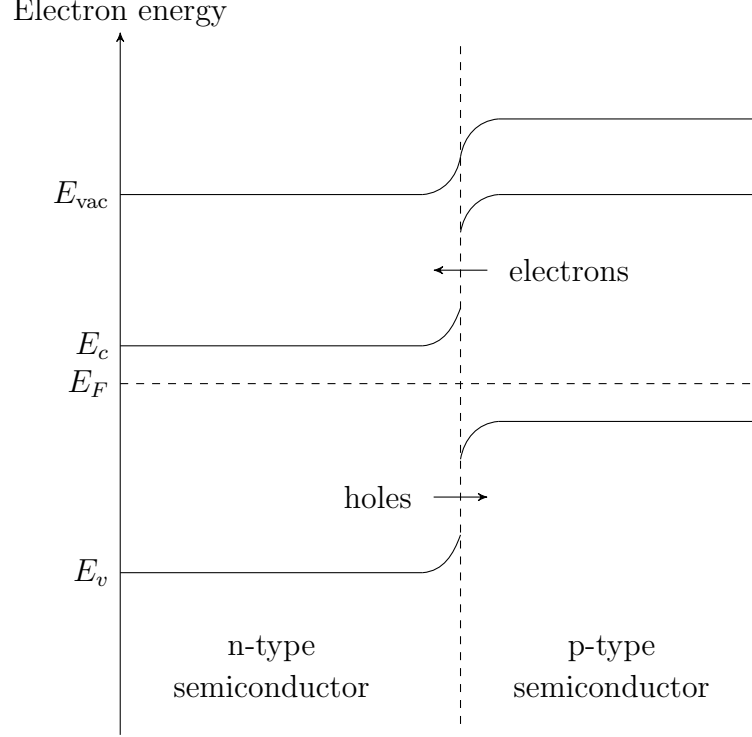


Figure 1.5: Band diagram for n-type semiconductor-p-type semiconductor contact. The arrows indicate the effective field on the electrons and holes.

1.4 Semiconductor-semiconductor contact

When two semiconductors are brought together with differing electron affinity and ionisation potential, there are discontinuities in the conduction and valence band edges. The potential step leads to effective fields on electrons and holes, with electrons preferring to move ‘down’ a potential gradient and holes ‘up’ a potential gradient [74]. A band diagram of the contact between an n-type and p-type semiconductor with differing electron affinity and ionisation potential is shown in figure 1.5.

1.5 Conduction mechanisms

Meier & Schroder [71] give the following definition of contact resistance

Contact resistance refers to the resistance associated with the metal/semiconductor barrier at the interface between the semiconductor and metal contact.

An increased understanding of the local electron transport mechanisms present at the front contact of a screen-printed crystalline silicon solar cell will aid in the development of silver pastes that achieve low contact resistance ($\leq 5\text{m}\Omega\text{cm}^2$ [63]) and, consequently, enable the production of higher efficiency solar cells. In addition, the contacting of lower

doped emitters to the silver electrode is of interest because it leads to a reduction in recombination losses [41, 63, 87].

It is clear that the glass layer between the silver electrode and the silicon emitter plays a limiting role for electron flow across the interface [14]. However, there are at least two different hypotheses about the dominant conduction mechanism of electrons. The first is that the electrons flow through the silver crystallites embedded in the silicon that are either separated from the silver electrode by an ultrathin glass layer or in direct contact with it [14, 26–28, 33, 41, 48, 51, 60–62, 86, 88, 89]. There are opposing views as to whether direct contact between the silicon and silver crystallites is actually present at the interface. Jeong et al. [56], Li et al. [65] and Lin et al. [66] find no evidence of direct contact during their experiments, whilst Cabrera et al. [27] and Cooper et al. [33] believe their experiments show the presence of direct contacts and that it is through these contacts that the majority of current flows. Despite the fact it has been found that these crystallites do not cause junction shunting² [57, 89], they do cause junction degradation [57] and lead to recombination losses [29, 75]. The second hypotheses is that nano-Ag colloids in the interfacial glass layer aid the electron transport across the interface [31, 53, 64–66].

Evidently there is wide disagreement over the dominant conduction mechanism with Cabrera et al. [28] stating

The growth of Ag crystallites into Si is essential for the current conduction from the Si emitter to the silver finger.

and Li et al. [64] stating

Ag crystallites are not needed for efficient current collection.

However, it is generally accepted in the literature that these two conduction mechanisms could be operating at the same time [44, 64, 65, 80, 88]. A further factor that needs to be taken into account is that different pastes and firing conditions will be used in different experiments and this could affect which conduction mechanism is dominant [63].

Attempts to model the electronic properties of the front contact have been made by Kim et al. [59] who reduce the whole glass layer to a Schottky barrier and assume that an increase in thickness of the glass layer causes the Schottky barrier height to increase. Similarly, Cooper et al. [33] use the Schottky barrier model by fitting an effective barrier height to experimental data. It is common to assume that the conduction process is either direct quantum mechanical tunnelling or multi-step tunnelling via the nano-Ag colloids [14, 31, 44, 48, 53, 56, 63–66, 80, 86, 88, 89, 103]. An investigation into the viability of

²Junction shunting is the penetration of the Ag crystallites into the p - n junction [48].

this hypothesis was carried out by Hoenig et al. [50] who found that the electrons always have to overcome glass layer distances $\geq 10\text{nm}$ and therefore the electrical current can not be explained by tunnelling theories alone.

We focus our attention on the resistance of the glass layer itself by analysing a mathematical model of electron transport based on the drift diffusion equations, commonly used to model current flow in semiconductors [68]. A modified drift diffusion theory (outlined in §1.8) is investigated in Chapter 4 to consider the impact of quantum mechanical effects. This novel approach to modelling contact resistance enables us to determine systematically how the resistance changes as various physical properties are varied.

1.6 Drift-diffusion equations

The drift diffusion equations identify the two main sources of current flow as:

1. Diffusion of electrons and holes due to the gradient in carrier concentration $\mathbf{J}_n^{\text{diff}}$, $\mathbf{J}_p^{\text{diff}}$.
2. Drift of electrons and holes, where the electric field is the driving force $\mathbf{J}_n^{\text{drift}}$, $\mathbf{J}_p^{\text{drift}}$.

Here we have used the subscript n to denote electrons and subscript p to denote holes. The total current density is then found by linearly superimposing these two processes [68]

$$\mathbf{J}_n = \mathbf{J}_n^{\text{diff}} + \mathbf{J}_n^{\text{drift}}, \quad (1.6.1)$$

$$\mathbf{J}_p = \mathbf{J}_p^{\text{diff}} + \mathbf{J}_p^{\text{drift}}. \quad (1.6.2)$$

The current density due to diffusion is given by Fick's law [95]

$$\frac{\mathbf{J}_n^{\text{diff}}}{q} = D_n \nabla n, \quad (1.6.3)$$

$$\frac{\mathbf{J}_p^{\text{diff}}}{q} = -D_p \nabla p, \quad (1.6.4)$$

where D_n and D_p are the diffusion coefficients for electrons and holes and q is the magnitude of charge on an electron. The diffusion coefficients D_n , D_p are given by the following Einstein relation, which holds if the semiconductor is non-degenerate [68]

$$D_n = \frac{k_B T \mu_n}{q}, \quad (1.6.5)$$

$$D_p = \frac{k_B T \mu_p}{q}, \quad (1.6.6)$$

where k_B is Boltzmann's constant, T is temperature and μ_n and μ_p are the electron and hole mobilities.

The current densities due to the electric field are given by [68]

$$\mathbf{J}_n^{\text{drift}} = -qn\mathbf{v}_n^{\text{drift}} = qn\mu_n\mathbf{E}, \quad (1.6.7)$$

$$\mathbf{J}_p^{\text{drift}} = qp\mathbf{v}_p^{\text{drift}} = qp\mu_p\mathbf{E}, \quad (1.6.8)$$

where $\mathbf{v}_n^{\text{drift}}$ and $\mathbf{v}_p^{\text{drift}}$ are the drift velocities and $\mathbf{E}$ is the electric field. The assumption that the drift velocity is proportional to the electric field strength is valid for moderate fields, but at sufficiently high electric field levels there can be nonlinearity in the mobilities and saturation of the drift velocity [95]. In the high field limit it is possible instead to use Monte Carlo methods to simulate charge transport; see [54].

To relate the charge and the electric field we use Gauss' law

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\hat{\epsilon}}, \quad (1.6.9)$$

where $\hat{\epsilon}$ is the absolute permittivity and ρ is the total charge density. We can use the relation $\mathbf{E} = -\nabla\phi$, where ϕ is the electric potential to write (1.6.9) as

$$\nabla^2\phi = \frac{q(n - p + N_A - N_D)}{\hat{\epsilon}}. \quad (1.6.10)$$

The terms N_A and N_D are present since semiconductors are often doped, and they represent the concentration of acceptor impurities and donor impurities respectively; N_A and N_D can be taken to be constant or dependent on position. In contrast with electrons and holes, these are fixed charges and do not contribute to the current densities [79].

Conservation of electrons and holes leads to the equations

$$\frac{\partial n}{\partial t} - \frac{1}{q}\nabla \cdot \mathbf{J}_n = G_n - U_n, \quad (1.6.11)$$

$$\frac{\partial p}{\partial t} + \frac{1}{q}\nabla \cdot \mathbf{J}_p = G_p - U_p, \quad (1.6.12)$$

where G_n and G_p are the generation rates of electrons and holes respectively and U_n and U_p are the recombination rates [95]. In summary, the basic drift diffusion model consists of (1.6.10)–(1.6.12), with the total current densities given by

$$\mathbf{J}_n = \mu_n k_B T \nabla n - q\mu_n n \nabla \phi, \quad (1.6.13)$$

$$\mathbf{J}_p = -\mu_p k_B T \nabla p - q\mu_p p \nabla \phi. \quad (1.6.14)$$

1.7 Applications of drift diffusion equations

The drift diffusion equations are often used to model current flow in various devices. These can be electrochemical, such as microbatteries or water desalination apparatus, or they

can be semiconductor devices, for example, a p - n junction, metal-oxide semiconductor (MOS) diodes, transistors, and organic semiconductors; see [16, 17, 19, 24, 32, 42, 43, 67, 69, 70, 73, 79, 82, 85, 100, 101, 105] .

Please [79] noted that in one dimension (1.6.13) can be written as

$$J_n = nq\mu_n \frac{d}{dx} \left(\frac{k_B T}{q} \log(n) - \phi \right). \quad (1.7.1)$$

Hence the gradient of the electrochemical potential, $\left(\frac{k_B T}{q} \log(n) - \phi \right)$; sometimes known as the quasi-fermi potential), moves the electrons. A corresponding electrochemical potential for holes can be found. This also leads to the common assumption that ϕ scales with $k_B T/q$ (known as the thermal voltage) to ensure that the drift and diffusion terms are in balance [30].

The boundary conditions that are applied to the drift diffusion equations will depend on the device under consideration. For example, in electrochemical thin films Butler-Volmer boundary conditions are needed to describe the reaction kinetics for electron transfer [16, 24, 32]. For this thesis, important boundary conditions to consider are those specified at semiconductor-metal contacts present in semiconductor devices. An electric potential difference is always specified over a semiconductor device [42, 43, 67, 69, 70, 79, 82, 85, 105]. When specifying the electric potential difference it is important to take into account that the total electric potential difference of the device will also contain the built-in electric potential V_{bi} . The built-in electric potential is determined by the electric potential difference between the anode and cathode of the device at equilibrium [43]. We note that if the anode and cathode are made of the same material $V_{bi} = 0$.

We now discuss a number of different formulations for the boundary conditions on the electron density n and hole density p at a metal-semiconductor contact. ‘Perfect Ohmic boundary conditions’ make the assumption of no space charge and thermal equilibrium, and therefore

$$n - p + N_A - N_D = 0, \quad np = n_i^2, \quad (1.7.2)$$

at the contact. The boundary conditions used by [42, 43, 82] assume that the Fermi level of the semiconductor and metal align, and therefore by making use of (1.2.1)–(1.2.3) and (1.2.5) we find

$$n = g_c \exp \left(-\frac{\chi_n + W_{\text{metal}}}{k_B T} \right), \quad p = g_v \exp \left(\frac{\chi_p + W_{\text{metal}}}{k_B T} \right), \quad (1.7.3)$$

at the contact. The boundary conditions (1.7.3) do not depend on the applied potential and have therefore been previously described as ‘Ohmic boundary conditions’ [42, 43, 82].

The Schottky effect has been incorporated through ‘Schottky boundary conditions’ where n and p at the contact are given by [68, 95]

$$\mathbf{J}_n \cdot \mathbf{n} = -qv_n(n - n_{eq}), \quad \mathbf{J}_p \cdot \mathbf{n} = qv_p(p - p_{eq}), \quad (1.7.4)$$

where $\mathbf{n}$ is the unit normal to the contact, v_n, v_p are thermionic recombination velocities and n_{eq}, p_{eq} are the ‘equilibrium values’ of the electron density and hole density. Markowich et al. [70] determine n_{eq} and p_{eq} by solving

$$n_{eq} \exp\left(\frac{\chi_n + W_{\text{metal}}}{k_B T}\right) - p_{eq} \exp\left(-\frac{\chi_p + W_{\text{metal}}}{k_B T}\right) + N_A - N_D = 0, \quad n_{eq} p_{eq} = 1. \quad (1.7.5)$$

However, Crowell & Begulwala [34] use the relation (1.7.3) to determine n_{eq} and p_{eq} . We see that using (1.7.3) to determine n_{eq} and p_{eq} means that (1.7.4) reduces to (1.7.3) for infinite thermionic recombination velocities and using (1.7.5) to determine n_{eq} and p_{eq} means that (1.7.4) reduces to (1.7.2) for $(-\chi_n) = (-\chi_p) = W_{\text{metal}}$ and infinite thermionic recombination velocities.

It is important to differentiate between a Schottky contact, an Ohmic contact, Schottky boundary conditions and Ohmic boundary conditions. A Schottky contact is one showing the qualitative behaviour described in §1.3.1 whereas Schottky boundary conditions are those incorporating the Schottky effect. Similarly, an Ohmic contact is one showing the qualitative behaviour described in §1.3.2 whereas Ohmic boundary conditions are those that do not depend on the applied electric potential. This is highlighted through the work in Appendix C where we demonstrate that by applying the Ohmic boundary conditions (1.7.3) to a n-type semiconductor-metal contact one can reproduce the qualitative behaviour of an ideal Schottky contact and an Ohmic contact. To avoid confusion we thus refer to the Ohmic boundary conditions (1.7.3) as ‘Ideal boundary conditions’ henceforth.

It is common for asymptotic methods to be used to obtain solutions to the drift diffusion equations [16, 17, 19, 24, 32, 42, 43, 67, 69, 70, 79, 82]. The studies [16, 17, 19, 24, 32, 43, 67, 69, 70] employ asymptotic methods by exploiting the smallness of the following dimensionless parameter, that is the ratio of the Debye length³ to device length:

$$\nu = \sqrt{\frac{\epsilon k_B T}{q^2 l^2 C_c}}. \quad (1.7.6)$$

Here l is the device length and C_c is the scaling for the charge carrier density in (1.6.10)–(1.6.14). The semiconductor papers [67, 69, 70] take C_c to be the maximal magnitude of

³Debye length is the characteristic length for semiconductors over which charge varies.

the doping concentration in the semiconductor, Foster et al. [43] take C_c to be the typical charge density in the organic solar cell, and the electrochemical studies [16, 17, 19, 24, 32] take C_c to be the average ion concentration. Richardson et al. [82] and Foster, Kirkpatrick, & Richardson [42] apply asymptotic methods to the drift diffusion equations by considering different limits of current size. Finally, Please [79] applied asymptotic methods in the highly doped limit, meaning N_A and N_D in (1.6.10) will be much larger than n and p . In such asymptotic calculations the authors are often considering an interface, for example Please [79] considers a $p - n$ junction, Markowich [67] considers a semiconductor-oxide interface, Richardson, Please & Kirkpatrick [82] consider the interface between two different organic materials, and Bonnefont, Argoul & Bazant [24] consider an aqueous solution bounded by electrodes. In the asymptotic limits examined it is consistently found that boundary layers in the charge carriers and ϕ exist at these interfaces [16, 17, 19, 24, 32, 42, 43, 67, 69, 70, 79, 82]. However, if Perfect Ohmic boundary conditions (1.7.2) are specified these boundary layers are not present [70]. Rather than calculate the potential in the boundary layer present at a $p - n$ junction, as Please [79] did, Schmeiser & Steinrück [85], and Ward, Reyna & Odeh [105] take there to be a jump in the potential at the junction and then obtain this jump by assuming continuity of quasi-fermi potentials.

The drift diffusion equations have also been solved using numerical methods with the most common techniques being the finite-difference and finite-element methods [93]. A popular finite difference method is to use the Scharfetter-Gummel scheme [84], where (1.6.13) and (1.6.14) are treated as differential equations in n and p with $\mathbf{J}_n$, $\mathbf{J}_p$, μ_n , μ_p and $\mathbf{E}$ assumed to be constant between nodes. This substitution is often used when simulating semiconductor devices where both types of carrier are accounted for [93]. When using Chebyshev polynomials as basis functions spectral methods are known to be good at resolving boundary layers and have been successfully employed in one dimension by Chu and Bazant [32] and through Chebfun [97, 98] by [42, 43]. Two-dimensional numerical methods are discussed in Chapter 3 where we formulate a novel 2D spectral method.

1.8 Density gradient theory

Quantum mechanical effects may be modelled using a modified drift diffusion theory with an additional longer-range interaction term [9], making (1.6.13)–(1.6.14) become

$$\mathbf{J}_n = \mu_n k_B T \nabla n - q \mu_n n \nabla \phi - \frac{\mu_n \hbar^2}{2m_n^* r_n} n \nabla \left(\frac{\nabla^2 \sqrt{n}}{\sqrt{n}} \right), \quad (1.8.1a)$$

$$\mathbf{J}_p = -\mu_p k_B T \nabla p - q \mu_p p \nabla \phi + \frac{\mu_p \hbar^2}{2m_p^* r_p} p \nabla \left(\frac{\nabla^2 \sqrt{p}}{\sqrt{p}} \right), \quad (1.8.1b)$$

where $\hbar$ is Planck's constant, m_n^* is the electron effective mass, m_p^* is the hole effective mass and r_p , r_n are statistical factors⁴. The values of the effective masses and the statistical factors are not well known and therefore they are often used as fitting parameters when matching with experiments or alternative quantum mechanical simulations [6]. The addition of a higher order term to the drift diffusion equations means that more boundary conditions are required. Quantum mechanical effects are assumed not to be present in the electrodes of the semiconducting material of interest and therefore an appropriate boundary condition is to let the the final term in (1.8.1a) and (1.8.1b) be zero at the boundaries [76]. The quantum behaviour manifested by the additional term becomes most evident when there are steep gradients in the charge densities [12].

The modified drift diffusion theory (often known as density gradient confinement theory or quantum drift diffusion theory) was first formulated by Ancona & Tiersten [9] by assuming that the non-locality of quantum mechanics could be approximated by letting the energy densities of the electron and hole gases depend on the spatial gradient of the charged particles densities. The modification means that the electrochemical potential for electrons in density gradient confinement theory is given by

$$\frac{k_B T}{q} \log n - \phi - \frac{\hbar^2}{2q m_n^* r_n} \frac{\nabla^2 \sqrt{n}}{\sqrt{n}}; \quad (1.8.2)$$

see (1.7.1) for comparison with the classical electrochemical potential. The density gradient confinement equations have since been derived in various ways; for example Cumberbatch, Uno & Abebe [35] demonstrated that they can be obtained directly from quantum mechanics by expressing the Schrödinger wave function for electrons in amplitude/phase form. The final term in (1.8.2) is known as the quantum or Bohm potential and it provides an additional non-local driving force for the electrons [10, 83, 106]. The coefficient of the final term in (1.8.2) is a measure of the strength of the gradient dependence of the electrons [4, 11], its smallness means that there is often a small parameter multiplying the highest derivative making the equations suitable for singular perturbation analysis. However, singular perturbation analysis of the density gradient confinement equations has only been carried out in a select few studies [35, 99].

The density gradient confinement equations are the lowest-order quantum correction and therefore are only strictly applicable when quantum effects can be considered as a small perturbation to a classical system [7]. However, they give good qualitative agreement with tunnelling experiments [6, 12, 106] and therefore have been used in number of studies to model metal-oxide-semiconductor (MOS) devices where quantum mechanical effects are significant [1, 6, 10, 12, 13, 35, 99].

⁴The factors r_n , r_p are set to unity if the Pauli exclusion principle is ignored [6].

On the $O(1)$ nm length scale the mean free path of an electron is typically greater than the length of the device under consideration and therefore scattering of charged particles is negligible and the conduction of electrons is ballistic dominated [6]. In the ballistic dominated regime quantum tunnelling effects have been modelled by making further modifications to the drift diffusion equations [4,8,11]. The modifications that are made to (1.6.10)–(1.6.14) are:

- Recombination and generation is neglected.
- The longer-range interaction term in (1.8.1) is included.
- As the scattering of charged particles off the semiconductor lattice is assumed to be negligible the limit of $\mu_n \rightarrow \infty$ and $\mu_p \rightarrow \infty$ is considered. The electron and hole density therefore becomes the tunnelling electron density n_t and tunnelling hole density p_t . In this limit the quasi-fermi level is constant and therefore the system is in quasi-thermal equilibrium.
- An additional term to include inertial effects is added to (1.6.13)–(1.6.14).

The resulting equations (known as density gradient tunnelling theory) are therefore

$$\nabla^2 \phi = \frac{q(n_t - p_t + N_A - N_D)}{\hat{\epsilon}}, \quad (1.8.3a)$$

$$\frac{1}{q} \nabla \cdot \mathbf{J}_n = \frac{\partial n_t}{\partial t}, \quad (1.8.3b)$$

$$\frac{1}{q} \nabla \cdot \mathbf{J}_p = -\frac{\partial p_t}{\partial t}, \quad (1.8.3c)$$

$$m_n^* \frac{D^n \mathbf{v}_n}{Dt} = \nabla \left(-k_B T \log n_t + q\phi + \frac{\hbar^2}{2m_n^* r_n} \frac{\nabla^2 \sqrt{n_t}}{\sqrt{n_t}} \right), \quad (1.8.3d)$$

$$m_p^* \frac{D^p \mathbf{v}_p}{Dt} = \nabla \left(-k_B T \log p_t - q\phi + \frac{\hbar^2}{2m_p^* r_p} \frac{\nabla^2 \sqrt{p_t}}{\sqrt{p_t}} \right), \quad (1.8.3e)$$

where

$$\frac{D^n}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}_n \cdot \nabla, \quad \frac{D^p}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}_p \cdot \nabla \quad (1.8.4)$$

and $\mathbf{v}_n$, $\mathbf{v}_p$ are the electron and hole gas velocities respectively. Furthermore, since there is negligible interaction between the charge carriers, the electron/hole populations that are injected from different electrodes must have their own transport equations [4,8,11]. Making use of fitting parameters, good agreement with experiment has been found when using (1.8.3) to model tunnelling in ultrathin MOS capacitors [11].

The density gradient confinement theory outlined in (1.8.1) is employed by engineers to simulate quantum semiconductor devices as it has the advantage of being easy to

couple to existing drift diffusion codes and is numerically efficient when compared with alternative quantum mechanical simulation frameworks [6, 77]. On the other hand, the density gradient tunnelling theory is sparingly used by the device research community [6] where nonequilibrium Green's function methods are preferred [36, 37]. A possible reason is that the use of a continuum approach to model a discrete quantum effect seems counterintuitive.

1.9 Thesis outline

The aim of this thesis is to formulate and analyse models for electron transport across the front contact of a silicon solar cell to better understand the important conduction mechanisms.

In Chapter 2 we analyse a simple one-dimensional model for electron transport across the glass layer, based on the drift diffusion equations. In practice there are large variations in the glass layer thickness, and the resulting two dimensional effects on electron flow are investigated in Chapter 3. In Chapter 4 we introduce quantum effects into our one-dimensional model, since quantum mechanical tunnelling is often cited as a conduction mechanism. The role that the boundary effects present at the silicon emitter-glass interface play in determining the resistance of the glass layer is explored in Chapter 5. Finally, in Chapter 6 we summarise the main results of our work, discuss possible areas for future research and lay out our key findings of interest to manufacturers of crystalline silicon solar cells.

1.10 Statement of originality

The models presented in Chapters 2 and 3 are new and the original results are presented in [23] and [22], respectively.

The model analysis carried out in §4.2 of Chapter 4 is new. The model presented in §4.3 is taken from [4] and the asymptotic outer solutions (4.3.36) and (4.3.42) have previously been derived in [4]. On the other hand, all other asymptotic analysis and the numerical method presented in Chapter 4 are new.

The entirety of Chapter 5 is new.

The semiconductor-metal contact problem presented in Appendix C is well studied in the literature; however, the model and numerical solutions are novel.

Chapter 2

One-dimensional modelling

2.1 Introduction

Current flow through the glass layer plays an important role in the contact resistance present at the front side of a screen printed silicon solar cell [50]. In this chapter we investigate the resistive properties of the glass layer by analysing a simple model for electron transport across the layer. In §2.2.1–2.2.3 we formulate the governing equations and boundary conditions of our mathematical model. In §2.2.4 we solve the resulting equations analytically and numerically. Approximate expressions for the resistance of the glass layer are obtained in §2.3 by using asymptotic techniques. We show that, depending on the values of the physical parameters, the resistance of the glass layer may be a monotonic increasing, monotonic decreasing, or non-monotonic function of the electron flux in §2.4.

2.2 Mathematical model

2.2.1 Formulation of the problem

We assume that the width of the glass layer is much bigger than its thickness and hence reduce the problem to one-dimensional conduction through a layer of thickness H driven by an imposed electric potential difference $(-\Phi)$. We consider two different possible systems, namely a glass layer separating either (i) the silicon emitter from the silver electrode (Si-glass-Ag system); (ii) a silver crystallite from the silver electrode (Ag-glass-Ag system). A schematic of the two systems is given in figure 2.1.

Considering the Ag-glass-Ag system, neglecting the Schottky effect and applying the Ideal boundary conditions at the glass-silver interfaces we find that the electron and hole densities at the silver crystallite-glass interface (n_0, p_0) are equal to the electron and hole

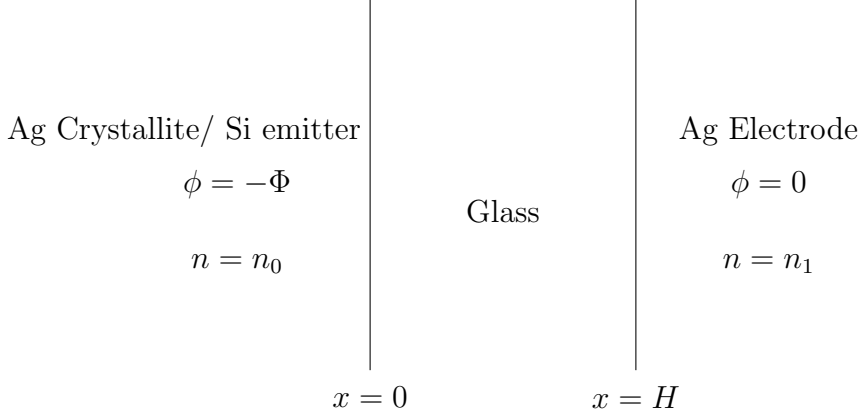


Figure 2.1: Schematic of the two systems considered.

densities at the glass-silver electrode interface (n_1, p_1) and given by

$$n_0 = n_1 = \bar{g}_c \exp\left(-\frac{\bar{\chi}_n + W_{\text{Ag}}}{k_B T}\right), \quad p_0 = p_1 = \bar{g}_v \exp\left(\frac{\bar{\chi}_p + W_{\text{Ag}}}{k_B T}\right), \quad (2.2.1)$$

where $\bar{g}_c$ is the conduction band effective density of states in the glass, $\bar{g}_v$ is the valence band effective density of states in the glass, $\bar{\chi}_n$ is the electron affinity of the glass, $\bar{\chi}_p$ is the ionisation potential of the glass, and W_{Ag} is the workfunction of the silver. In principle, it is now possible to determine the values of n_0 , n_1 , p_0 , and p_1 , but, unfortunately the electronic properties of the glass are not well known.

It is known that the glass layer consists of SiO_2 and transition metals [50] and if we take the electron affinity and ionisation potential of SiO_2 that are -0.9eV and -9.9eV , respectively, as well as the workfunction of silver 4.3eV [95], Boltzmann's constant, k_B $1.38 \times 10^{-23} \text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$, and let absolute temperature T be 300K we find (irrespective of the values of $\bar{g}_c$ and $\bar{g}_v$) that there are no electrons or holes in the glass layer and therefore no conduction takes place. This is obviously not the case, and since the glass layer thickness is too large for conduction to be explained by tunnelling theories alone [50] we make the assumption that the glass layer has been formulated by the industrialists so that $|\bar{\chi}_n| \gtrsim W_{\text{Ag}}$ making $n_0, n_1 \gg 0$ whilst $p_0, p_1 \approx 0$ and therefore the glass layer can be modelled as an n-type semiconductor where the charge is predominantly carried by electrons.

In the Si-glass-Ag system the value of n_1 is given by (2.2.1), on the other hand, n_0 will be dependent on the electron density profile in the silicon emitter. For simplicity in this chapter we take n_0 in the Si-glass-Ag system to be a known constant where it seems reasonable to expect $n_0 < n_1$, however, in Chapter 5 we see that counterintuitively it is possible for $n_0 > n_1$.

We model charge transport through the glass layer with the drift diffusion equations and therefore take the model presented in (1.6.10)–(1.6.14), reduce it to one dimension,

and make the following assumptions.

- The charge is predominantly carried by electrons rather than by holes. We therefore neglect the motion of holes henceforth.
- There is no generation or recombination of electrons in the glass.
- The system operates in a quasi-steady state.
- There is no doping present in the glass layer.
- An electric potential difference ($-\Phi$) is applied across the glass layer.

We therefore arrive at the following system of equations:

$$\frac{dj_n}{dx} = 0, \quad (2.2.2)$$

$$\frac{d^2\phi}{dx^2} = -\frac{qn}{\epsilon}, \quad (2.2.3)$$

$$j_n = \mu \left(-n \frac{d\phi}{dx} + \frac{k_B T}{q} \frac{dn}{dx} \right), \quad (2.2.4)$$

where j_n is the electron flux, n is the density of free electrons, ϕ is the electric potential, μ is the electron mobility in the glass, k_B is Boltzmann's constant, T is the absolute temperature, ϵ is the absolute permittivity of the glass and q is the charge on an electron. The boundary conditions are

$$n(0) = n_0, \quad \phi(0) = -\Phi, \quad n(H) = n_1, \quad \phi(H) = 0. \quad (2.2.5)$$

Equations (2.2.2)–(2.2.4) comprise a third-order system with four boundary conditions (2.2.5), making the problem overdetermined. In a given situation we can therefore either specify the potential difference ($-\Phi$) and try to determine the corresponding electron flux j_n or *vice versa*.

2.2.2 Nondimensionalisation

For the nondimensionalisation we scale the electron density with the electron density at the silver-glass layer interface (n_1), we take the length scale to be the thickness of the glass layer (H) and scale the potential with $-k_B T/q$. We choose the scaling for reasons outlined in §1.7 and introduce the minus sign so that we have a nondimensionalisation that is convenient for dealing with electron transport. We scale the electron flux with $\mu k_B T n_1 / (qH)$ to ensure all terms in (2.2.4) are balanced and drop the standard subscript

n as we are solely dealing with electron flux. The nondimensionalisation then proceeds as follows:

$$x = Hx^*, \quad n = n_1 n^*, \quad \phi = -\frac{k_B T}{q} \phi^*, \quad \Phi = -\frac{k_B T}{q} \Phi^*, \quad j_n = \frac{\mu k_B T n_1}{q H} j^*. \quad (2.2.6)$$

Substituting (2.2.6) into (2.2.3) and (2.2.4) and dropping the starred notation we obtain

$$j = -n \frac{d\phi}{dx} - \frac{dn}{dx}, \quad (2.2.7)$$

$$\nu^2 \frac{d^2 \phi}{dx^2} = -n, \quad (2.2.8)$$

where the electron flux j is constant. The boundary conditions (2.2.5) become

$$n(0) = \alpha, \quad \phi(0) = \Phi, \quad n(1) = 1, \quad \phi(1) = 0. \quad (2.2.9)$$

The dimensionless parameters are

$$\alpha = \frac{n_0}{n_1} \quad \text{and} \quad \nu = \frac{H_D}{H} = \sqrt{\frac{\epsilon k_B T}{q^2 H^2 n_1}}, \quad (2.2.10)$$

where H_D is the Debye length. Applying Ideal boundary conditions $\alpha = 1$ in the Ag-glass-Ag system and in the Si-glass-Ag system we focus on examples where $\alpha < 1$, however, in Chapter 5 we demonstrate it is possible for $\alpha > 1$. We expect the parameter ν to be small since it is well known the glass layer plays a limiting role for electron flow across the interface [14] and that the thickness of the glass layer does not allow the electrical current to be explained by quantum tunnelling alone [50]. To estimate a value of ν we assume the absolute permittivity ϵ is that of silicon dioxide $3.45 \times 10^{-11} \text{ Fm}^{-1}$; Boltzmann's constant, k_B , is $1.38 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$ and the charge on an electron, q , is $1.6 \times 10^{-19} \text{ C}$; the absolute temperature T is 300K and the estimated average thickness of the glass layer H is $5 \times 10^{-7} \text{ m}$. We presume that electron density at the glass silver interface is bounded from above by the electron density in the silver, 10^{28} m^{-3} , and by making the small ν assumption we presume that $n_1 \gtrsim 10^{20} \text{ m}^{-3}$, since, we find with $n_1 = 10^{28} \text{ m}^{-3}$, $\nu = 8.2 \times 10^{-5}$ and with $n_1 = 6.7 \times 10^{19} \text{ m}^{-3}$, $\nu = 1$. We note that ν in (2.2.10) is equivalent to ν in (1.7.6).

2.2.3 Resistance

Rewriting (2.2.7) as¹

$$j = -n(\phi + \log n)', \quad (2.2.11)$$

¹Here and henceforth using ' as shorthand for d/dx .

where $\phi + \log n$ is the electrochemical potential, we see that when there is no electron flow, we can use (2.2.9) to determine that the built in potential $\Phi_{bi} = -\log \alpha$. We therefore define the effective resistance of the layer as

$$R = \frac{\Phi + \log \alpha}{j}, \quad (2.2.12)$$

where we have subtracted the built in potential $(-\log \alpha)$ from Φ before dividing by the electron flux. The quantity $\Phi + \log \alpha$ is the total potential difference V_{tot} . In this chapter, motivated by the problem of contact resistance in solar cells, we will only consider cases where $V_{\text{tot}} > 0$ ($j > 0$). Physically this means that the electrons are always flowing into the silver electrode.

2.2.4 Analytical and numerical solution

Eliminating n between (2.2.7) and (2.2.8), we find

$$\frac{j}{\nu^2} = \phi''\phi' + \phi'''. \quad (2.2.13)$$

Now integrating (2.2.13) and using the Riccati substitution (see for example [18]) $u = e^{\phi/2}$ we find that u satisfies

$$u''(x) = \left(\frac{jx}{2\nu^2} - C \right) u(x), \quad (2.2.14)$$

and the boundary conditions

$$u(0) = e^{\Phi/2}, \quad \alpha = 2\nu^2 (u'(0)^2 e^{-\Phi} + C), \quad (2.2.15a)$$

$$u(1) = 1, \quad 1 = 2\nu^2 \left(u'(1)^2 - \frac{j}{2\nu^2} + C \right), \quad (2.2.15b)$$

where C is an unknown constant of integration. To derive (2.2.15) we make use of the relation

$$n = 2\nu^2 \left[\left(\frac{u'}{u} \right)^2 - \left(\frac{jx}{2\nu^2} - C \right) \right]. \quad (2.2.16)$$

A similar system is solved in [42] and [82].

The general solution to (2.2.14) is

$$u = \hat{a} \text{Ai}(\chi x - \hat{C}) + \hat{b} \text{Bi}(\chi x - \hat{C}), \quad (2.2.17)$$

where Ai and Bi are Airy functions,

$$\hat{C} = C \left(\frac{2\nu^2}{j} \right)^{2/3}, \quad \chi = \left(\frac{j}{2\nu^2} \right)^{1/3}, \quad (2.2.18)$$

and $\hat{a}$, $\hat{b}$ are constants of integration. We will discover shortly that j/ν^2 is a key parameter of the problem. By substituting (2.2.17) into (2.2.15), we obtain

$$\hat{a} \text{Ai}(\chi - \hat{C}) + \hat{b} \text{Bi}(\chi - \hat{C}) = 1, \quad (2.2.19a)$$

$$\hat{a} \text{Ai}(-\hat{C}) + \hat{b} \text{Bi}(-\hat{C}) = e^{\Phi/2}, \quad (2.2.19b)$$

$$2\chi^2 \left\{ (\hat{a} \text{Ai}'(-\hat{C}) + \hat{b} \text{Bi}'(-\hat{C}))^2 e^{-\Phi} + \hat{C} \right\} = \frac{\alpha}{\nu^2}, \quad (2.2.19c)$$

$$2\chi^2 \left\{ (\hat{a} \text{Ai}'(\chi - \hat{C}) + \hat{b} \text{Bi}'(\chi - \hat{C}))^2 + \hat{C} - \chi \right\} = \frac{1}{\nu^2}. \quad (2.2.19d)$$

In principle, elimination of $\hat{a}$, $\hat{b}$ and $\hat{C}$ between the four transcendental equations (2.2.19) leads to a functional relation between j and Φ . For example, numerical solution of (2.2.19) with $\alpha = 1$, $\nu = 1$ and $j = 1$ gives $\Phi = 1.078$ to three decimal places, and we plot the resulting solutions $\phi(x)$ and $n(x)$ in figure 2.2. However, this approach is unwieldy in practice: the oscillatory nature of the Airy functions gives rise to multiple solution branches of (2.2.19), and one must pick the first root to ensure that the solution is physical. Unphysical solutions contain non-physical negative values of the electron density n . Foster, Kirkpatrick & Richardson [42] demonstrated the presence of these unphysical solutions by carrying out phase plane analysis on (2.2.13).

In contrast, it is straightforward to solve the boundary-value problem (2.2.7)–(2.2.9) numerically. We rewrite the governing equations (2.2.7) and (2.2.8) in the form

$$\nu^2 \phi'' = -n, \quad n'' = -n' \phi' + \frac{n^2}{\nu^2}, \quad (2.2.20)$$

and use the boundary conditions (2.2.9), therefore specifying the value of Φ . We then calculate j by first taking (2.2.11) and rearranging to find

$$\frac{j}{n} = -\frac{d}{dx}(\phi + \log n), \quad (2.2.21)$$

and second integrating over the domain and applying the boundary conditions (2.2.9) to give

$$j = \frac{\Phi + \log \alpha}{\int_0^1 \frac{dx}{n(x)}}. \quad (2.2.22)$$

The numerical solution of (2.2.20) and the evaluation of the integral in (2.2.22) are both implemented using the spectral software package **Chebfun** [97,98]. Figure 2.2 demonstrates the excellent agreement between the analytical and numerical solutions when $\nu = 1$, $\alpha = 1$, $j = 1$ and $\Phi = 1.078$.

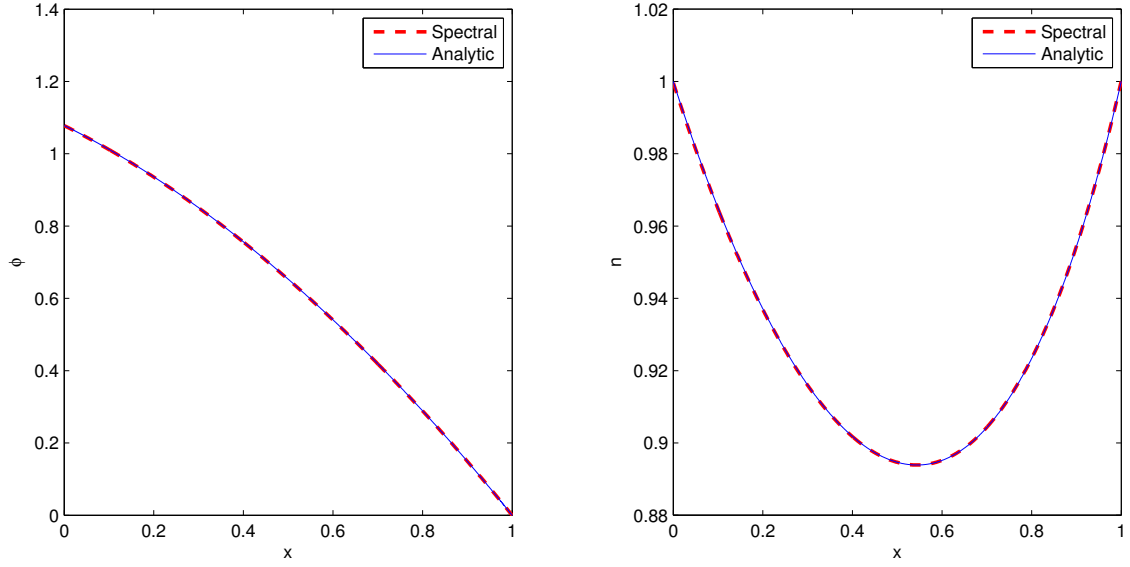


Figure 2.2: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 1$ and $\alpha = 1$. The spectral solution is found by specifying $\Phi = 1.078$ to determine $j \approx 1$. The analytic solution is found by specifying $j = 1$ to determine $\Phi \approx 1.078$.

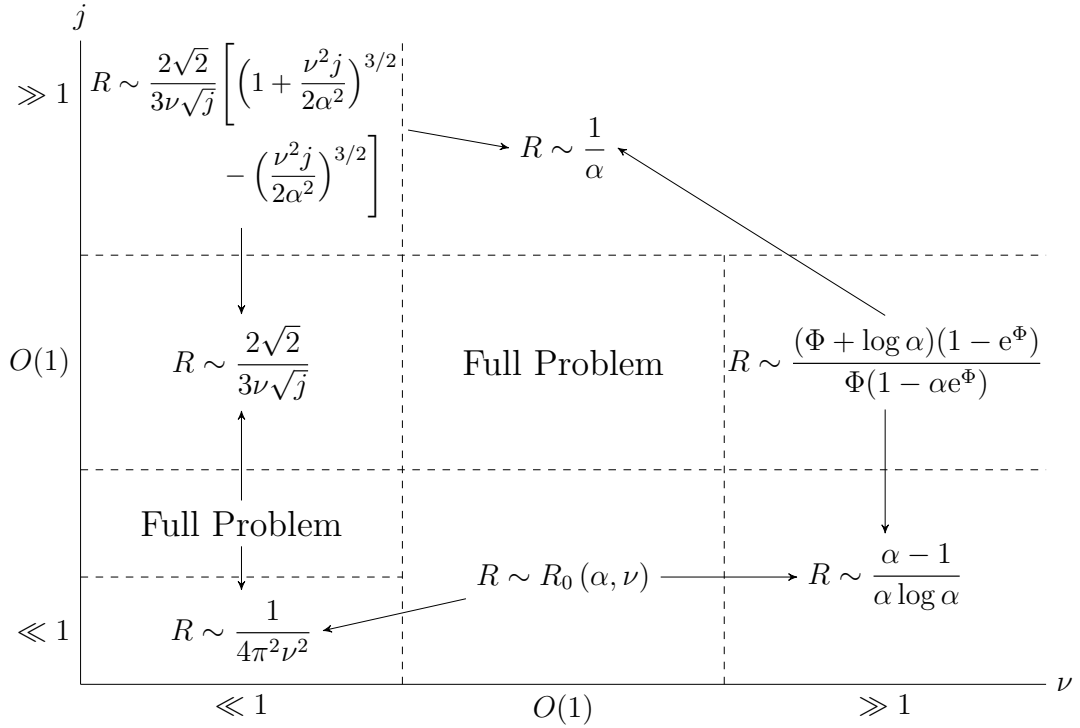


Figure 2.3: Diagram showing different asymptotic analytic expressions for resistance in different asymptotic regions.

2.3 Asymptotic analysis

2.3.1 Overview

In this section, we use asymptotic techniques to find approximate expressions for the resistance of the glass layer as j and ν vary. Our aim is to determine how the resistance R is affected by the values of the various parameters, where ν is a material parameter of the system and j will vary as the electric potential changes. Figure 2.3 depicts the different asymptotic expressions for R that we will derive, where the arrows linking different regions show how the regions may be matched by taking appropriate intermediate limits. The presence of ‘Full Problem’ in figure 2.3 indicates regions where it is not possible to obtain a significantly simplified analytic expression for R .

2.3.2 Small electron flux: $j \ll 1$

Here it is helpful to start from the Airy equation (2.2.14) and boundary conditions (2.2.15), rewritten in the form

$$u''(x) + Cu(x) = \chi^3 x u(x), \quad (2.3.1)$$

$$u(0) = e^{\Phi/2}, \quad u'(0)^2 = \left(\frac{\alpha}{2\nu^2} - C\right) e^{\Phi}, \quad u(1) = 1, \quad u'(1)^2 = \frac{1}{2\nu^2} - C + \chi^3, \quad (2.3.2)$$

where $j/2\nu^2 = \chi^3 \ll 1$.

Now we seek the solution $u(x)$ and the constants Φ and C as asymptotic expansions in powers of χ^3 , that is,

$$u(x) \sim u_0(x) + \chi^3 u_1(x) + \chi^6 u_2(x) + \dots, \quad (2.3.3a)$$

$$\Phi \sim \Phi_0 + \chi^3 \Phi_1 + \chi^6 \Phi_2 + \dots, \quad (2.3.3b)$$

$$C \sim C_0 + \chi^3 C_1 + \chi^6 C_2 + \dots, \quad (2.3.3c)$$

and therefore

$$R \sim R_0 + \chi^3 R_1 + \dots. \quad (2.3.4)$$

We recall from Section 2.2.3 that

$$\Phi_0 = -\log \alpha \quad (2.3.5)$$

is the electric potential difference at zero electron flux.

To leading order we find

$$u_0 = \operatorname{cosec} \left(\sqrt{C_0} \right) \sin \left(\sqrt{C_0} x \right) + e^{\Phi_0/2} \operatorname{cosec} \left(\sqrt{C_0} \right) \sin \left(\sqrt{C_0} (1 - x) \right), \quad (2.3.6)$$

and by substituting (2.3.6) into (2.3.2) we obtain the relation

$$\nu^2 = \frac{e^{-\Phi_0/2} \sin^2(\sqrt{C_0})}{4C_0 [\cosh(\Phi_0/2) - \cos(\sqrt{C_0})]}. \quad (2.3.7)$$

The integration constant C_0 is in principle determined as a function of α and ν by (2.3.5) and the implicit equation (2.3.7). By requiring ν to be real and positive, we find that C_0 lies in the range $(-\Phi_0^2/4, \pi^2)$, with $C_0 \rightarrow -\Phi_0^2/4 = -(\log \alpha)^2/4$ as $\nu \rightarrow \infty$, and $C_0 \rightarrow \pi^2$ as $\nu \rightarrow 0$. Figure 2.4 shows a plot of ν vs C_0 and the leading-order solutions for ϕ and n are plotted in figure 2.5.

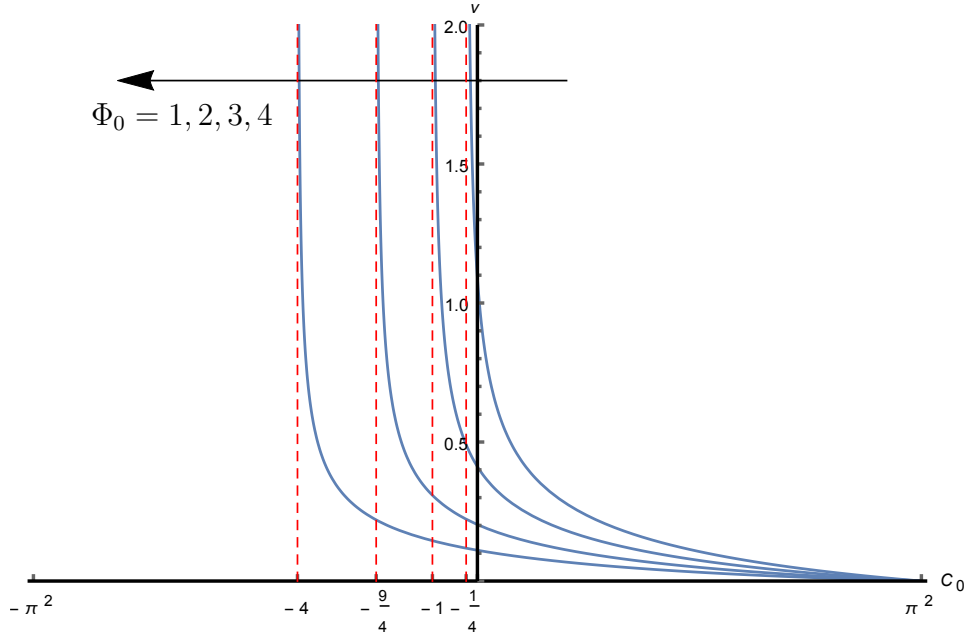


Figure 2.4: Dimensionless Debye length ν plotted against the integration constant C_0 for various values of the potential difference Φ . The blue curves are ν as a function of C_0 , (2.3.7), and the red dashed lines are the appropriate values of $-\Phi_0^2/4$.

The limiting resistance (2.2.12) at zero electron flux is given by

$$R_0 = \frac{\Phi_1}{2\nu^2}. \quad (2.3.8)$$

Fortunately we can avoid the need to calculate the first correction $u_1(x)$ by rewriting (2.3.1) as

$$\frac{d}{dx}(u'^2 + (C - \chi^3 x)u^2) = -\chi^3 u^2 \quad (2.3.9)$$

and integrating across the domain to obtain the identity

$$e^\Phi \alpha - 1 = 2\chi^3 \nu^2 \int_0^1 u^2 dx. \quad (2.3.10)$$

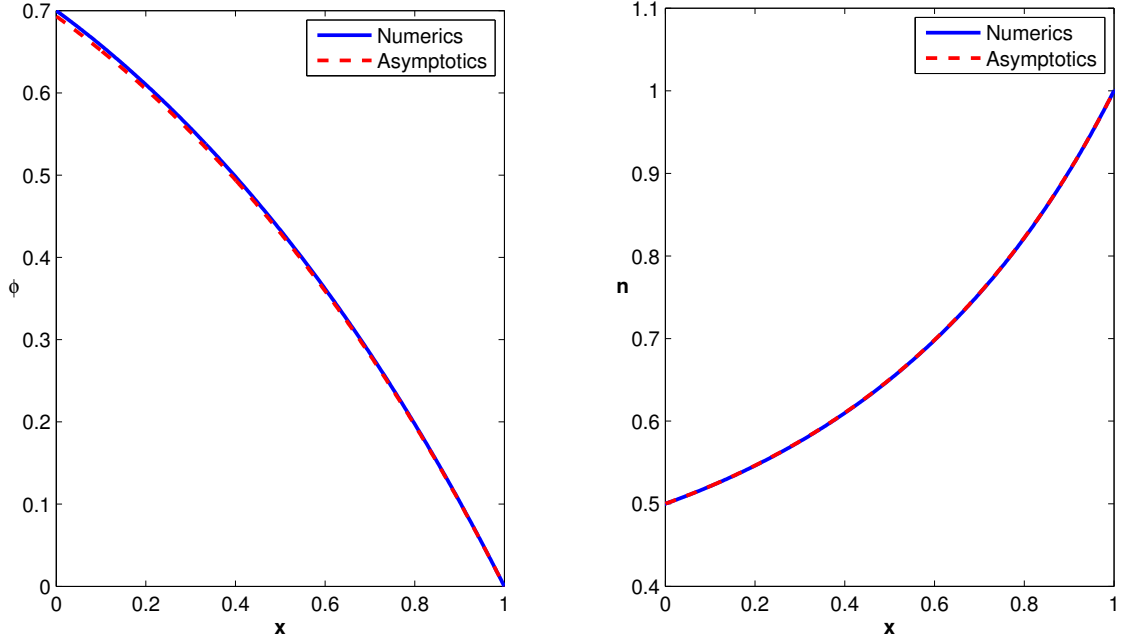


Figure 2.5: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 1$, $\alpha = 0.5$ and $C_0 \approx 0.22$. The numerical solution is found by specifying $\Phi = 0.7$ to determine $j \approx 0.0045$. The asymptotic solution is found by specifying $j = 0.0045$ to determine $\Phi \approx 0.7$.

Hence the resistance is given by the exact formula

$$R = \frac{1}{2\chi^3\nu^2} \log \left(1 + 2\chi^3\nu^2 \int_0^1 u(x)^2 dx \right). \quad (2.3.11)$$

In particular, the limiting resistance as $\chi^3 \rightarrow 0$ may be obtained using only the leading-order solution:

$$\begin{aligned} R_0 &= \int_0^1 u_0(x)^2 dx \\ &= \frac{e^{\Phi_0/2} [\cosh(\Phi_0/2) - \cos(\sqrt{C_0})]}{\sin^2(\sqrt{C_0})} - \frac{e^{\Phi_0/2} [\cosh(\Phi_0/2) \cos(\sqrt{C_0}) - 1]}{\sqrt{C_0} \sin(\sqrt{C_0})}. \end{aligned} \quad (2.3.12)$$

For a given value of α (and therefore of Φ_0), equations (2.3.7) and (2.3.12) determine R_0 parametrically as a function of ν , with the parameter C_0 varying in the range $(-\Phi_0^2/4, \pi^2)$. This functional relation is plotted in figure 2.6 for various values of α . By analysing the behaviour as $C_0 \rightarrow \pi^2$ and as $C_0 \rightarrow -\Phi_0^2/4$, we obtain the limiting forms

$$R_0 \sim \frac{1}{4\pi^2\nu^2} \quad \text{as } \nu \rightarrow 0, \quad R_0 \sim \begin{cases} \frac{\alpha - 1}{\alpha \log \alpha} & \text{if } \alpha \neq 1, \\ 1 & \text{if } \alpha = 1, \end{cases} \quad \text{as } \nu \rightarrow \infty, \quad (2.3.13)$$

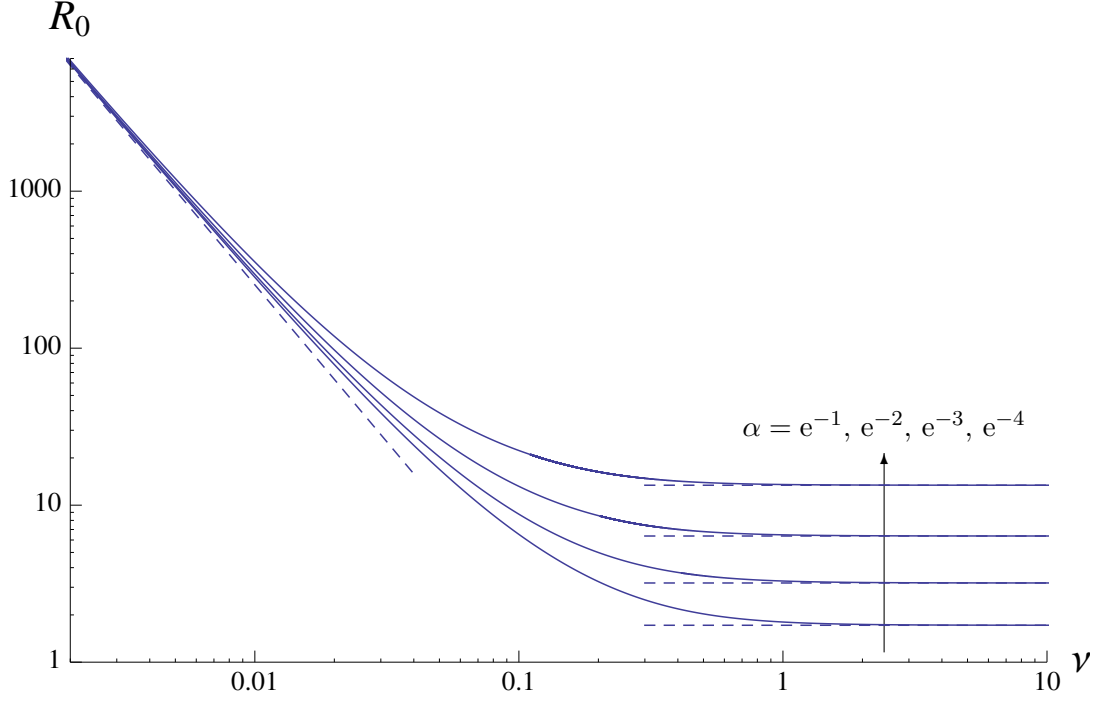


Figure 2.6: The resistance R_0 at zero electron flux plotted versus the dimensionless Debye length ν for different values of the density ratio $\alpha = e^{-1}, e^{-2}, e^{-3}, e^{-4}$. The dashed curves show the asymptotic limits (2.3.13) as $\nu \rightarrow 0$ and as $\nu \rightarrow \infty$.

which are plotted as dashed curves in figure 2.6. The expressions in (2.3.13) show that, when $\nu \gg 1$, the value of α plays the dominant role in determining the value of R_0 but, if ν is decreased sufficiently, the resistance becomes independent of α .

Figure 2.6 demonstrates that the resistance can vary by orders of magnitude depending on the value of ν . In particular, the fact that $R_0 \rightarrow \infty$ as $\nu \rightarrow 0$ suggests that there may be a new distinguished limit where j and ν are both small. We will return to this possibility below in Section 2.3.5.

2.3.3 Large electron flux: $j \gg 1$

In the limit of large electron flux we let $j = \hat{j}/\delta_1$, where $\delta_1 \ll 1$. In this limit we expect $\Phi = O(j)$ and therefore make the scalings $\Phi = \hat{\Phi}/\delta_1$ and $\phi = \hat{\phi}/\delta_1$. We then expand $\hat{\phi}$, n and $\hat{\Phi}$ in terms of δ_1

$$\hat{\phi} = \hat{\phi}_0 + \delta_1 \hat{\phi}_1 + \dots, \quad (2.3.14a)$$

$$n = \hat{n}_0 + \delta_1 \hat{n}_1 + \dots, \quad (2.3.14b)$$

$$\hat{\Phi} = \hat{\Phi}_0 + \delta_1 \hat{\Phi}_1 + \dots \quad (2.3.14c)$$

Applying the rescaling to j , substituting (2.3.14) into (2.2.7)–(2.2.9) and solving to leading order we obtain the solutions

$$\hat{\phi}_0 = \frac{\hat{j}}{\alpha}(1-x), \quad (2.3.15a)$$

$$\hat{n}_0 = \alpha. \quad (2.3.15b)$$

Unless $\alpha = 1$ the boundary condition $\hat{n}_0(1) = 1$ is not satisfied by (2.3.15b) and so we solve for a boundary layer by applying the rescaling $x = 1 - \delta_1 X_L$ and return to the variable ϕ to find

$$\hat{n}_0 = \alpha + (1 - \alpha)e^{-\hat{j}X_L/\alpha}. \quad (2.3.16)$$

Representing n as the composite of the solution found in the boundary layer and the constant solution found elsewhere in the domain, we find the leading-order approximations are

$$\phi \sim \frac{j(1-x)}{\alpha}, \quad (2.3.17a)$$

$$n \sim \alpha + (1 - \alpha)e^{-j(1-x)/\alpha}. \quad (2.3.17b)$$

Figure 2.7 plots the expressions given in (2.3.17) and demonstrates their good agreement with the numerical solution.

Making use of (2.2.12), we therefore find that at large j the resistance of the glass layer tends to the constant value

$$R_\infty = \frac{1}{\alpha}. \quad (2.3.18)$$

We conclude that in the situation where the applied potential difference is much greater than the thermal voltage, we will always be in the $j \gg 1$ regime and here the glass behaves like a ‘normal’ Ohmic resistor with contact resistance independent of the electron flux. We note that neither the leading-order solution (2.3.17) nor the limiting resistance R_∞ depends on ν . This is due to the high electric potential difference flooding the glass layer with charge carriers so the Debye length is no longer an important factor. Indeed, (2.3.17) shows that the electron density n is approximately constant outside a boundary layer at $x = 1$ whose thickness scales with one over the electric field.

2.3.4 Large Debye length: $\nu \gg 1$

In this section we examine the limit where $\nu \rightarrow \infty$. Unlike the other sections of this chapter it is more convenient here to suppose that Φ is known and determine how j varies.

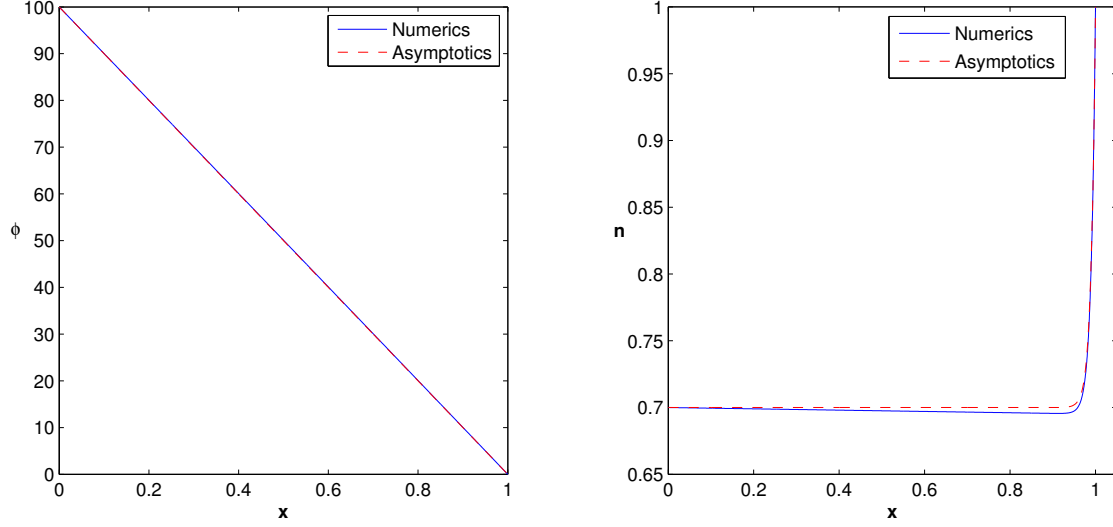


Figure 2.7: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 1$ and $\alpha = 0.7$. The numerical solution is found by specifying $\Phi = 100$ to determine $j \approx 70$. The asymptotic solution is found by specifying $j = 70$ to determine $\Phi \approx 100$.

Equations (2.2.7)–(2.2.8) to leading order in the limit $\nu \rightarrow \infty$ are

$$j = -n\phi' - n', \quad (2.3.19a)$$

$$\phi'' = 0. \quad (2.3.19b)$$

Solving (2.3.19) by making use of boundary conditions (2.2.9) we find the approximate relations

$$\phi \sim \Phi(1 - x), \quad (2.3.20a)$$

$$n \sim \left(\alpha - \frac{1 - \alpha e^\Phi}{1 - e^\Phi} \right) e^{\Phi x} + \frac{1 - \alpha e^\Phi}{1 - e^\Phi}, \quad (2.3.20b)$$

$$j \sim \Phi \frac{1 - \alpha e^\Phi}{1 - e^\Phi}. \quad (2.3.20c)$$

Figure (2.8) plots the expressions given in (2.3.20) and demonstrates their excellent agreement with the numerical solution.

The relation (2.2.12) is used to find that in the large Debye length limit

$$R \sim \frac{(\Phi + \log \alpha)(1 - e^\Phi)}{\Phi(1 - \alpha e^\Phi)}. \quad (2.3.21)$$

We note that when $\alpha = 1$; $n \sim 1$, $j \sim \Phi$ and $R \sim 1$. Taking the limit $\Phi + \log \alpha \rightarrow \infty$ we regain the relation (2.3.18) and in the limit $\Phi + \log \alpha \rightarrow 0$ we find

$$R \sim \frac{\alpha - 1}{\alpha \log \alpha}. \quad (2.3.22)$$

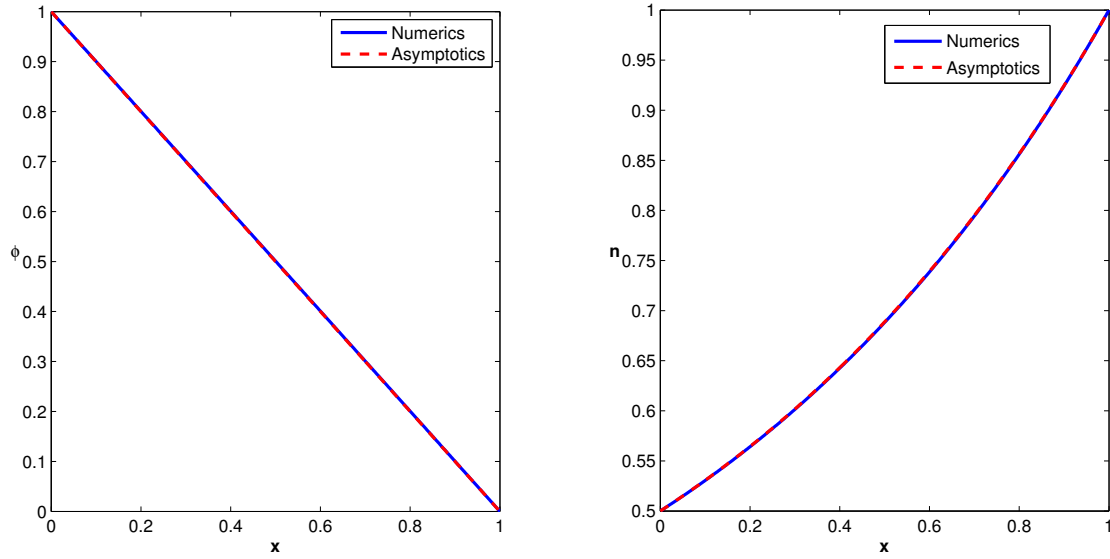


Figure 2.8: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 10$, $\alpha = 0.5$, $\Phi = 1$ and $j \approx 0.21$.

We conclude that in the limit of large Debye length the resistance of the glass layer is dominated by the ratio α between the electron densities at the two electrodes. In the Ag-glass-Ag system ($\alpha \approx 1$) the glass layer behaves like a ‘normal’ resistor with a linear electric potential and a constant electron density and resistance.

2.3.5 Small Debye length: $\nu \ll 1$

2.3.5.1 Introduction

In this section we consider the limit where $\nu \rightarrow 0$, in a similar manner to [16, 17, 19, 24, 32, 67, 69, 70, 100]. This corresponds to the situation where the glass layer is much thicker than the Debye length, as is expected to be the case in practice. Examining the governing equations and boundary conditions (2.2.7)–(2.2.9) we hypothesise that if $\Phi = O(1)$, in the limit $\nu \rightarrow 0$, then the corresponding electron flux $j = O(\nu^2)$. Also we expect to find that $n = O(\nu^2)$ away from the boundaries and there are boundary layers to satisfy the $O(1)$ boundary conditions for n at $x = 0$ and $x = 1$. In the following sections we will derive and asymptotically match leading-order solutions in the outer region and in each boundary layer.

2.3.5.2 Boundary layers

First considering the boundary layer at $x = 0$, we make the rescaling $x = \nu X_0$ before letting $\nu \rightarrow 0$ so that (2.2.7) and (2.2.8) become

$$n \frac{d\phi}{dX_0} + \frac{dn}{dX_0} = 0, \quad (2.3.23)$$

$$\frac{d^2\phi}{dX_0^2} = -n. \quad (2.3.24)$$

Substituting (2.3.24) into (2.3.23), integrating, and using the substitution $\phi = 2 \log \psi$ gives

$$\frac{d^2\psi}{dX_0^2} - \frac{K_1}{2} \frac{d\psi}{dX_0} = 0, \quad (2.3.25)$$

where K_1 is a constant of integration. We find $K_1 = 0$ to match with the outer solution, to be discussed later in §2.3.5.3, and therefore using the boundary conditions (2.2.9) we obtain the leading-order solutions

$$\phi \sim \Phi + 2 \log \left(1 + X_0 \sqrt{\frac{\alpha}{2}} \right), \quad n \sim \alpha \left(1 + X_0 \sqrt{\frac{\alpha}{2}} \right)^{-2}. \quad (2.3.26)$$

Considering the boundary layer at $x = 1$ we make the substitution $x = 1 - \nu X_1$, and following a similar method obtain the leading-order solution

$$\phi \sim 2 \log \left(1 + \frac{X_1}{\sqrt{2}} \right), \quad n \sim \left(1 + \frac{X_1}{\sqrt{2}} \right)^{-2}. \quad (2.3.27)$$

Since the width of these boundary layers scales with the Debye length ν , they are Debye layers and will be used to provide matching conditions for the outer region analysed in the following section. The boundary layer solutions given in (2.3.26) and (2.3.27) along with the outer solution found in §2.3.5.3 are plotted in figure 2.9.

2.3.5.3 Outer solution

Away from the boundary layers we introduce the variables $N_\nu = n/\nu^2$ and $J_\nu = j/\nu^2$ so that (2.2.7) and (2.2.8) take the form

$$J_\nu = -N_\nu \phi' - N'_\nu, \quad \phi'' = -N_\nu. \quad (2.3.28)$$

We follow a similar method to that outlined in Section 2.2.4 by eliminating N_ν from (2.3.28) and making the substitution $\phi = 2 \log(U/\nu)$. The parameter ν is included for matching purposes. We then obtain the general solution

$$U(x) = a_0 \text{Ai}(\chi x - w) + b_0 \text{Bi}(\chi x - w), \quad (2.3.29)$$

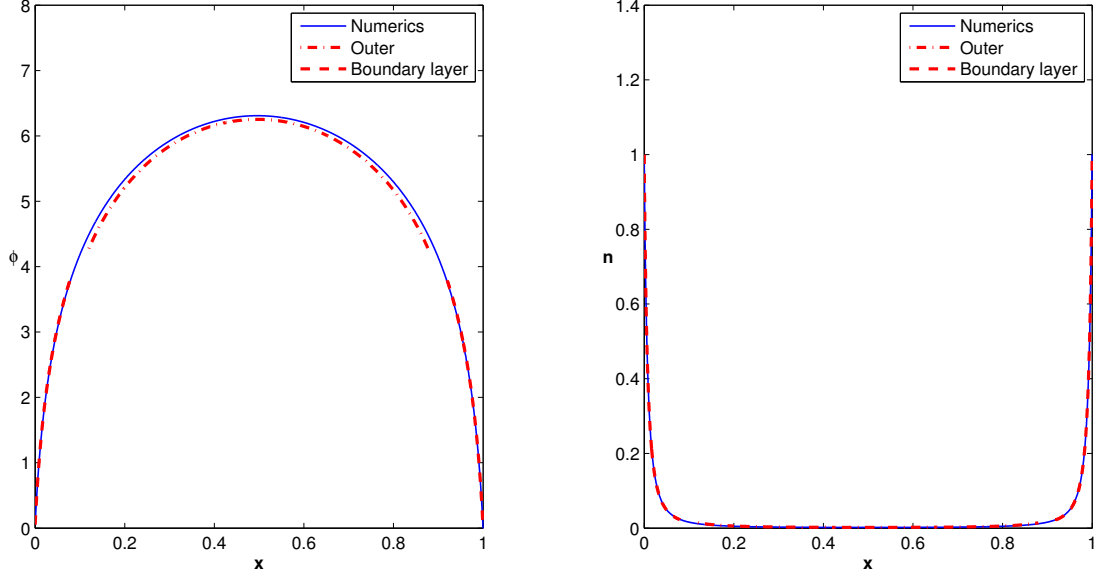


Figure 2.9: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 0.01$ and $\alpha = 1$. The numerical solution is found by specifying $\Phi = 0.0507$ to determine $j \approx 0.0002$. The asymptotic solution is found by specifying $j = 0.0002$ to determine $\Phi \approx 0.0507$.

where a_0 , b_0 and w are integration constants and $\chi = (J_\nu/2)^{1/3} = (j/2\nu^2)^{1/3}$ as in (2.2.18). This agrees with equation (51) of [32] for example. By matching (2.3.29) with (2.3.26) and (2.3.27) as $x \rightarrow 0$ and $x \rightarrow 1$ respectively, we obtain the following system of four equations:

$$a_0 \text{Ai}(-w) + b_0 \text{Bi}(-w) = 0, \quad (2.3.30a)$$

$$a_0 \text{Ai}(\chi - w) + b_0 \text{Bi}(\chi - w) = 0, \quad (2.3.30b)$$

$$\chi \{a_0 \text{Ai}'(-w) + b_0 \text{Bi}'(-w)\} = e^{\Phi/2} \sqrt{\frac{\alpha}{2}}, \quad (2.3.30c)$$

$$\chi \{a_0 \text{Ai}'(\chi - w) + b_0 \text{Bi}'(\chi - w)\} = -\frac{1}{\sqrt{2}}, \quad (2.3.30d)$$

which are evidently a simplified limit of the full transcendental system (2.2.19).

2.3.5.4 Resistance

A starting point for analysis of (2.3.30) is noticing that (2.3.30a) and (2.3.30b) admit nontrivial solutions for a_0 and b_0 if and only if the relation

$$\frac{\text{Ai}(-w)}{\text{Ai}(\chi - w)} = \frac{\text{Bi}(-w)}{\text{Bi}(\chi - w)} \quad (2.3.31)$$

is satisfied. By writing (2.3.30a) and (2.3.30c) as a matrix equation and then taking advantage of Airy's equation being of Sturm-Liouville form, with Wronskian equal to $1/\pi$, we find

$$\begin{pmatrix} a_0 \\ b_0 \end{pmatrix} = \pi \begin{pmatrix} \text{Bi}'(-w) & -\text{Bi}(-w) \\ -\text{Ai}'(-w) & \text{Ai}(-w) \end{pmatrix} \begin{pmatrix} 0 \\ \frac{e^{\frac{\Phi}{2}}}{\chi} \sqrt{\frac{\alpha}{2}} \end{pmatrix}, \quad (2.3.32)$$

while applying a similar method to (2.3.30b) and (2.3.30d) gives

$$\begin{pmatrix} a_0 \\ b_0 \end{pmatrix} = \pi \begin{pmatrix} \text{Bi}'(\chi - w) & -\text{Bi}(\chi - w) \\ -\text{Ai}'(\chi - w) & \text{Ai}(\chi - w) \end{pmatrix} \begin{pmatrix} 0 \\ -\frac{1}{\chi\sqrt{2}} \end{pmatrix}. \quad (2.3.33)$$

Hence we can simply equate (2.3.32) and (2.3.33) to eliminate a_0 and b_0 , making the four equations (2.3.30a)–(2.3.30d) reduce to:

$$-\sqrt{\alpha}e^{\Phi/2} = \frac{\text{Bi}(\chi - w)}{\text{Bi}(-w)} = \frac{\text{Ai}(\chi - w)}{\text{Ai}(-w)}. \quad (2.3.34)$$

It is helpful to combine the two equations in (2.3.34) into a single complex relation, namely

$$-\sqrt{\alpha}e^{\Phi/2} \equiv -e^{jR/2} = \frac{\text{Ai}(\chi - w) + i\text{Bi}(\chi - w)}{\text{Ai}(-w) + i\text{Bi}(-w)}. \quad (2.3.35)$$

The imaginary part of (2.3.35) in principle determines w as a function of χ ; one must be careful always to choose the smallest (in magnitude) root for w to prevent zeros of $U(x)$ occurring in the interval $[0, 1]$ since these would correspond to unphysical singularities in $\phi(x)$. The functional relation $w = f(\chi)$ is shown in figure 2.10. The real part of (2.3.35) then gives a leading-order approximation for the resistance R in terms of j and χ , that is valid when $j = O(\nu^2)$ and $\nu \ll 1$. In general, therefore, it is still necessary to solve a transcendental equation in this asymptotic regime and there is not a significantly simplified analytic expression for the resistance. However, we can find the small- and large-electron flux limits by analysing the relation (2.3.35) as $\chi \rightarrow 0$ and as $\chi \rightarrow \infty$ respectively.

First taking $\chi \rightarrow 0$, we find that a balance in (2.3.35) requires w to tend to infinity, specifically $w = O(\chi^{-2})$. By expanding (2.3.35) in powers of χ and equating the imaginary part to zero, we find that

$$w \sim \frac{1}{\chi^2} \left(\pi^2 + \frac{\chi^3}{2} - \frac{(15 - \pi^2)\chi^6}{48\pi^4} + \frac{(1980 - 210\pi^2 + \pi^4)\chi^{12}}{2304\pi^{10}} + O(\chi^{15}) \right) \quad (2.3.36)$$

and

$$jR \sim \frac{\chi^3}{2\pi^2} - \frac{(10 - \pi^2)\chi^9}{32\pi^8} + O(\chi^{15}) \quad (2.3.37)$$

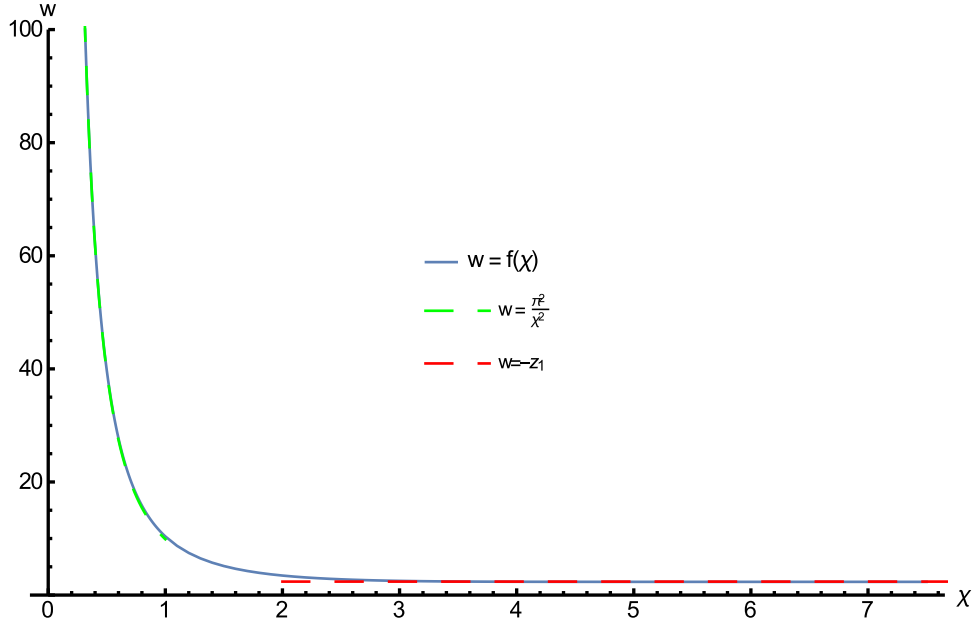


Figure 2.10: Plot of w versus χ . The blue curve is the numerical solution of the imaginary part of (2.3.35). The green dashed line and the red dashed line show the asymptotic behaviour of w as $\chi \rightarrow 0$ namely (2.3.36) and $w \rightarrow -z_1$ (the first zero of the Airy function Ai) as $\chi \rightarrow \infty$ respectively.

as $\chi \rightarrow 0$. A more detailed description of how these relations were obtained is given in Appendix A.2. Substituting for χ from (2.2.18), we thus obtain the approximate resistance in the form

$$R \sim \frac{1}{4\pi^2\nu^2} - \frac{(10 - \pi^2)j^2}{256\pi^8\nu^6} + \dots, \quad (2.3.38)$$

which is valid when $j \ll \nu^2 \ll 1$. Hence the resistance again approaches a constant positive value as the electron flux tends to zero, and this reproduces the small- ν limit of R_0 found previously in (2.3.13).

On the other hand, by taking the limit $\chi \rightarrow \infty$ in (2.3.35), we find that $w \rightarrow -z_1$, where z_1 is the first zero of Ai , and then, making use of the expansions in Appendix A.3,

$$e^{jR/2} \sim \frac{\text{Bi}(\chi + z_1)}{-\text{Bi}(z_1)} + \text{exponentially small terms}. \quad (2.3.39)$$

Hence we obtain the following approximation for the resistance

$$R \sim \frac{2\sqrt{2}}{3\nu\sqrt{j}} + O(\nu^{-1/3}j^{-5/6}), \quad (2.3.40)$$

which is valid when $\nu \ll 1$ and $j = O(1)$.

The approximation (2.3.40) suggests that the resistance of the layer falls to zero as the electron flux increases, which is physically unreasonable and contradicts the large-electron flux limit (2.3.18) obtained previously. This implies the existence of a new distinguished limit when j is large and ν is small, which we examine below.

2.3.5.5 Distinguished limit: $\nu \ll 1$, $\nu\sqrt{j} = O(1)$

We recall that the approximation (2.3.18) was obtained by letting $j \rightarrow \infty$ and then $\nu \rightarrow 0$, while (2.3.40) was obtained by taking the limits in the reverse order. By comparing the two expressions, we deduce that an intermediate regime will occur when $\nu \rightarrow 0$ with $\nu^2 j = O(1)$. To analyse this regime, we perform the rescalings

$$\phi = \nu^{-2}\hat{\psi}, \quad \Phi = \nu^{-2}\hat{\Psi}, \quad j = \nu^{-2}\hat{J}, \quad (2.3.41)$$

so that the problem (2.2.7)–(2.2.9) becomes

$$\hat{J} = -n \frac{d\hat{\psi}}{dx} - \nu^2 \frac{dn}{dx}, \quad \frac{d^2\hat{\psi}}{dx^2} = -n, \quad (2.3.42)$$

subject to

$$n(0) = \alpha, \quad \hat{\psi}(0) = \hat{\Psi}, \quad n(1) = 1, \quad \hat{\psi}(1) = 0. \quad (2.3.43)$$

The leading-order solutions as $\nu \rightarrow 0$ are

$$\hat{\psi} = \frac{2\sqrt{2\hat{J}}}{3} \left[\left(1 + \frac{\hat{J}}{2\alpha^2}\right)^{3/2} - \left(x + \frac{\hat{J}}{2\alpha^2}\right)^{3/2} \right], \quad n = \sqrt{\frac{\hat{J}}{2}} \left(x + \frac{\hat{J}}{2\alpha^2}\right)^{-1/2}. \quad (2.3.44)$$

The boundary condition $n(1) = 1$ is not satisfied by (2.3.44). Thus there is a boundary layer near $x = 1$ and following similar boundary layer analysis to §2.3.3 we obtain the composite approximate expressions

$$\phi \sim \frac{2\sqrt{2j}}{3\nu} \left[\left(1 + \frac{\nu^2 j}{2\alpha^2}\right)^{3/2} - \left(x + \frac{\nu^2 j}{2\alpha^2}\right)^{3/2} \right], \quad (2.3.45a)$$

$$n \sim \nu \sqrt{\frac{j}{2}} \left(x + \frac{\nu^2 j}{2\alpha^2}\right)^{-1/2} + \left(1 - \nu \sqrt{\frac{j}{2}} \left(1 + \frac{\nu^2 j}{2\alpha^2}\right)^{-1/2}\right) \exp \left\{ - \left[\frac{\sqrt{2j}}{\nu} \left(1 + \frac{\nu^2 j}{2\alpha^2}\right)^{1/2} (1-x) \right] \right\}, \quad (2.3.45b)$$

valid where $\nu\sqrt{j} = O(1)$. Thus, in contrast with the analysis where $j = O(\nu^2)$ carried out above, there is now just one boundary layer at, $x = 1$. Moreover, as in Section 2.3.3, the boundary layer thickness scales not with the Debye length (i.e. with ν) but the reciprocal of the electric field. In figure (2.11), we plot the expressions given in (2.3.45), where we see excellent agreement between the numerical solution and the full problem.

By evaluating (2.3.45a) at $x = 0$ we obtain a leading-order approximation for Φ in this regime, and hence for the resistance, namely

$$R = \frac{2\sqrt{2}}{3\nu\sqrt{j}} \left[\left(1 + \frac{\nu^2 j}{2\alpha^2}\right)^{3/2} - \left(\frac{\nu^2 j}{2\alpha^2}\right)^{3/2} \right], \quad (2.3.46)$$

valid when $j = O(\nu^{-2}) \gg 1$. The intermediate approximation (2.3.46) reduces to (2.3.40) when $j = O(1)$ and also agrees with (2.3.18) when $j\nu^2 \gg 1$.

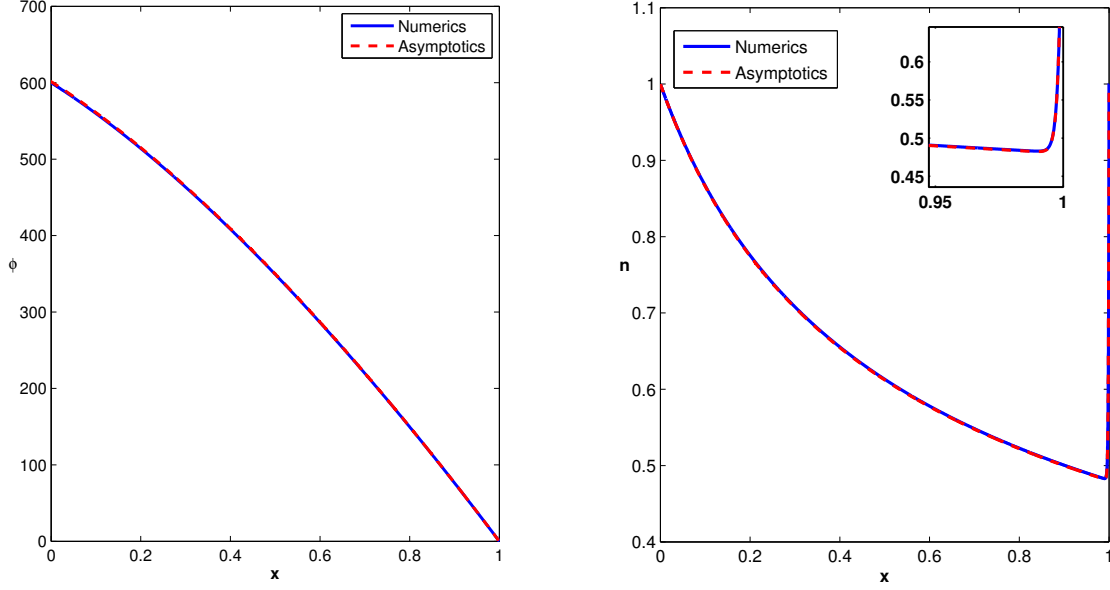


Figure 2.11: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 0.04$ and $\alpha = 1$. The numerical solution is found by specifying $\Phi = 600$ to determine $j \approx 375$ and hence $\nu\sqrt{j} \approx 0.77$. The asymptotic solution is found by specifying $j = 375$ to determine $\Phi \approx 600$.

2.3.6 Comparison between asymptotics and numerics

In figure 2.12 we plot the resistance R versus the electron flux j with parameters values $\alpha = 1$ and $\nu = 0.01$. The solid curve shows the results of numerical solutions obtained using **Chebfun**. As $j \rightarrow 0$, we see that R approaches a constant value that is well predicted by (2.3.13), shown as a dotted line. When $1 \ll j \ll \nu^{-2}$, the resistance decreases, approximately obeying the inverse square root law (2.3.40), plotted using triangles. The transition between these two regimes is governed by the solution of the transcendental equations outlined in Section 2.3.5.4. As $j \rightarrow \infty$, the resistance again approaches a constant value, in agreement with the prediction (2.3.18), plotted using circles. The transition to this constant value from the power-law behaviour is governed by the intermediate asymptotic expression (2.3.46), plotted using squares.

2.3.7 Current-voltage relationship

In this thesis we are investigating the contact resistance present at the front side of a screen printed silicon solar cell and we therefore focus on determining how the resistance of the glass layer depends on various parameters. However, when using the drift diffusion equations to investigate the properties of a semiconducting material it is common to consider the current-voltage relationship [42, 43, 79, 82]. In this section we therefore

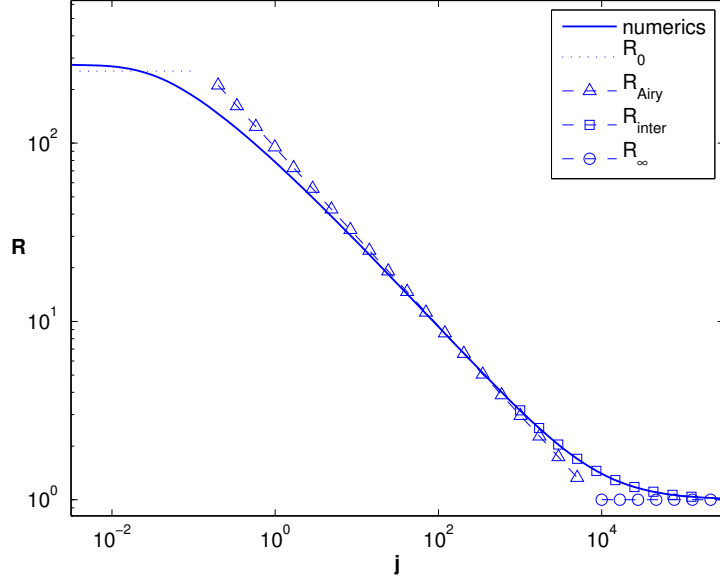


Figure 2.12: Resistance R plotted against electron flux j with $\alpha = 1$ and $\nu = 0.01$: numerical solution (solid); small- j estimate (2.3.13) (dotted); $j \gtrsim 1$ approximation (2.3.40) (triangles); intermediate approximation (2.3.46) (squares); large- j limit (2.3.18) (circles).

consider the relationship between the electron flux j and the total potential difference V_{tot} ($\Phi + \log \alpha$) in the physically relevant small ν limit.

The asymptotic expressions (2.3.13), (2.3.40), (2.3.46), and (2.3.18) can be rearranged to determine

$$j \sim 4\pi^2 \nu^2 V_{\text{tot}}, \quad \text{where } \nu \ll 1, V_{\text{tot}} \ll 1, \quad (2.3.47)$$

$$j \sim \frac{9}{8} \nu^2 V_{\text{tot}}^2, \quad \text{where } \nu \ll 1, V_{\text{tot}} = O(1), \quad (2.3.48)$$

$$V_{\text{tot}} \sim \frac{2\sqrt{2j}}{3\nu} \left[\left(1 + \frac{\nu^2 j}{2\alpha^2} \right)^{3/2} - \left(\frac{\nu^2 j}{2\alpha^2} \right)^{3/2} \right], \quad \text{where } \nu \ll 1, \nu^2 V_{\text{tot}} = O(1) \quad (2.3.49)$$

$$j \sim \alpha V_{\text{tot}}, \quad \text{where } V_{\text{tot}} \gg 1. \quad (2.3.50)$$

We note that (2.3.49) is an implicit relation between the electron flux j and the total potential difference V_{tot} .

In figure 2.13 we plot the electron flux j against the total potential difference V_{tot} where good agreement between the numerical solution obtained using **Chebfun** and the asymptotic relations (2.3.47)–(2.3.50) is evident.

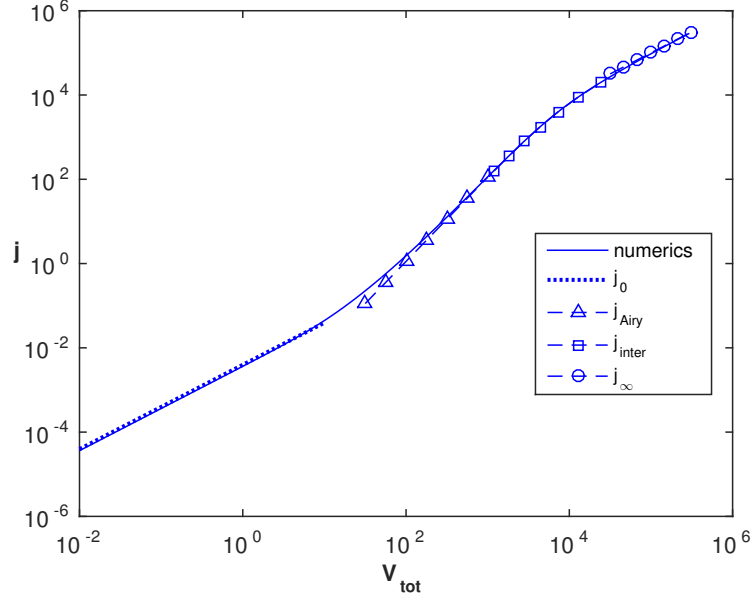


Figure 2.13: Electron flux j plotted against total potential difference V_{tot} with $\alpha = 1$ and $\nu = 0.01$: numerical solution (solid); small- V_{tot} estimate (2.3.47) (dotted); $V_{\text{tot}} \gtrsim 1$ approximation (2.3.48) (triangles); intermediate approximation (2.3.49) (squares); large- V_{tot} limit (2.3.50) (circles).

2.4 Variation of resistance with electron flux

2.4.1 Small- and large-flux limits

In Sections 2.3.2 and 2.3.3, we showed that the resistance R tends to constant values R_0 as $j \rightarrow 0$ and R_∞ as $j \rightarrow \infty$. In figure 2.12 it is evident that $R_0 > R_\infty$ and indeed that R is a monotonic decreasing function of j . However, one can easily find values of ν and α for which the situation is reversed, that is, for which R is an increasing function of j and hence $R_0 < R_\infty$. The curve delineating the regions of (α, ν) parameter space in which R_0 exceeds R_∞ and *vice versa* may be found by setting $R_0 = R_\infty$. By combining equations (2.3.5), (2.3.12) and (2.3.18), we find that the values of α and C_0 for which $R_0 = R_\infty$ satisfy the equation

$$\alpha - 4\sqrt{\alpha} \left(\frac{\sqrt{C_0} \cos(\sqrt{C_0}) - \sin(\sqrt{C_0})}{2\sqrt{C_0} - \sin(2\sqrt{C_0})} \right) + 1 - \frac{4\sqrt{C_0} \sin^2(\sqrt{C_0})}{2\sqrt{C_0} - \sin(2\sqrt{C_0})} = 0. \quad (2.4.1)$$

The physical (real positive) root of (2.4.1) is given by

$$\alpha = \left(\frac{\sin(2\sqrt{C_0}) - 2\sqrt{C_0} \cos(2\sqrt{C_0})}{(2 + \sqrt{\Delta}) \sin(\sqrt{C_0}) - 2\sqrt{C_0} \cos(\sqrt{C_0})} \right)^2, \quad (2.4.2)$$

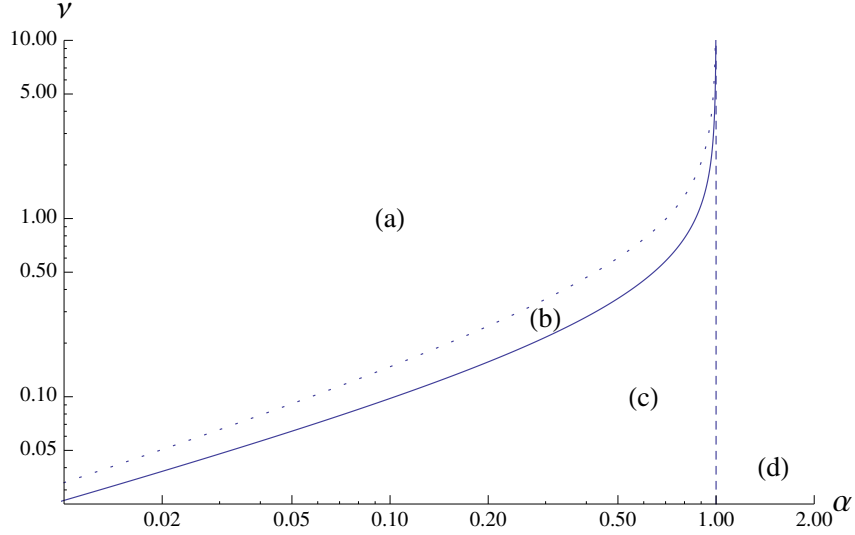


Figure 2.14: Parameter space of dimensionless Debye length ν versus electron density ratio α . The solid curve, given parametrically by (2.4.2) and (2.4.4) shows the parameter values for which $R_0 = R_\infty$. The dashed line indicates $\alpha = 1$, for which the first-order correction R_1 to the resistance as $j \rightarrow 0$ is zero. The dotted curve plots the values satisfying $\nu = (-\alpha/2 \log \alpha)^{1/2}$, for which the first-order correction to the large- j expansion (2.4.22) is zero. The labels (a)–(d) indicate the regions of parameter space in which the qualitative behaviour of the resistance versus electron flux resembles the corresponding plots in figure 2.17.

where Δ is used as shorthand for the discriminant

$$\Delta = \left[2\sqrt{C_0} - \sin(2\sqrt{C_0}) \right]^2 + 4\sin^4(\sqrt{C_0}). \quad (2.4.3)$$

Substitution into (2.3.7) then gives an expression for ν^2 when $R_0 = R_\infty$, namely

$$\nu^2 = \frac{\left(\sin(2\sqrt{C_0}) - 2\sqrt{C_0} \cos(2\sqrt{C_0}) \right)^2}{4C_0 \left[4C_0 + \left(1 - \cos(2\sqrt{C_0}) - 2\sqrt{C_0} \sin(2\sqrt{C_0}) \right) (2 + \sqrt{\Delta}) \right]}. \quad (2.4.4)$$

Equations (2.4.2) and (2.4.4) parameterise the required curve in the (α, ν) -plane; the parameter C_0 takes values in the range $(0, C_*)$, where $C_* \approx 5.048$ is the root of the equation $\tan(2\sqrt{C_*}) = 2\sqrt{C_*}$ in the range $C_* \in (0, \pi^2)$. As $C_0 \rightarrow C_*$, both α and ν tend to zero, with

$$\frac{\nu^2}{\alpha} \rightarrow \frac{1}{4C_*} \left(1 + \frac{1}{\sqrt{1 + 4C_*}} \right) \approx 0.06029 \quad \text{as } \alpha \rightarrow 0. \quad (2.4.5)$$

On the other hand, as $C_0 \rightarrow 0$, we find that $\alpha \rightarrow 1$ and $\nu \rightarrow \infty$, with

$$\nu \sim \frac{1}{\sqrt{6(1 - \alpha)}} \quad \text{as } \alpha \rightarrow 1. \quad (2.4.6)$$

The curve in the (α, ν) -plane parameterised by equations (2.4.2) and (2.4.4) is shown as a solid curve in figure 2.14. For parameter values lying above this curve, $R_0 < R_\infty$ so

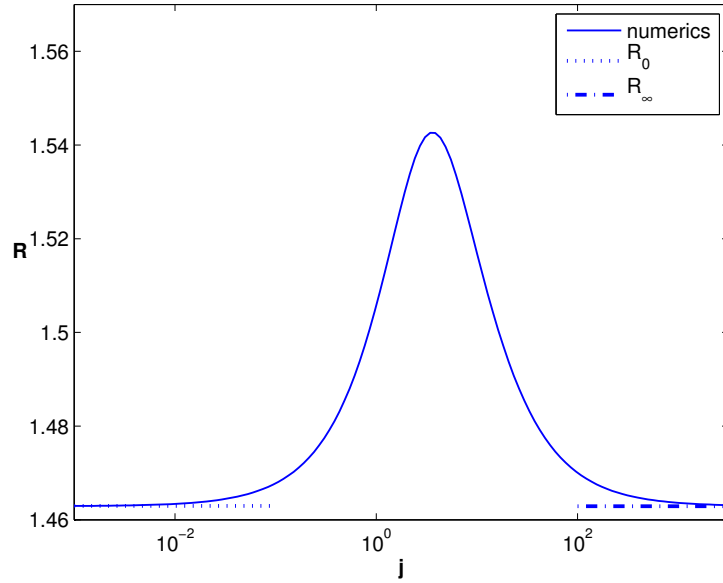


Figure 2.15: Resistance R plotted against electron flux j with parameter values $\alpha = 0.683578$ and $\nu = 0.55342$.

the effective resistance of the layer increases as the electron flux increases. However, for values lying below the curve, we will have $R_0 > R_\infty$. In particular, this will inevitably occur if we let $\nu \rightarrow 0$ with α held fixed, in agreement with the analysis of Section 2.3.5. Finally, for specially chosen parameter values lying on the solid curve, the limiting resistances at small and large values of j should be equal. This prediction is validated in figure 2.15, where, having chosen parameter values that satisfy (2.4.2) and (2.4.4), we find that the numerical solution gives the result $R_0 = R_\infty$.

2.4.2 Monotonicity of the resistance function

2.4.2.1 Introduction

In figure 2.12 we illustrated that, when ν is small, the resistance R is typically a monotonic decreasing function of the electron flux j . However, the analysis of Section 2.4.1 shows that, for larger values of ν , the large-electron flux resistance R_∞ may exceed the small-electron flux limit R_0 , so that the trend may be reversed. Figure 2.15 demonstrates the even more interesting and unexpected possibility that R may be a non-monotonic function of j at intermediate values of ν .

In Sections 2.3.2 and 2.3.3, we found the constant values approached by R as $j \rightarrow 0$ and as $j \rightarrow \infty$ respectively. Below we will revisit these asymptotic analyses to determine the first-order variations in j and hence the *direction* in which R approaches each of its

limiting values. This will enable us to ascertain the generic forms that the resistance-versus-flux curve may take, and which regions of (α, ν) parameter space correspond to each possible form.

2.4.2.2 Small electron flux: $j \ll 1$

Continuing the small- j expansion from Section 2.3.2 to first order, we use (2.3.11) and (2.3.4) to obtain the relation

$$R_1 = -\nu^2 R_0^2 + 2 \int_0^1 u_0(x) u_1(x) dx, \quad (2.4.7)$$

and we recall that $\chi^3 = j/2\nu^2 \ll 1$. Our aim here is to determine the parameter values that give $R_1 = 0$ and therefore delineate the regions of parameter space in which $R(j)$ is an increasing or a decreasing function as $j \rightarrow 0$.

It transpires that the transition where R_1 goes through 0 is at $\alpha = 1$. For simplicity, we therefore use the benefit of hindsight to assume that $\alpha = 1$ (i.e. $\Phi_0 = 0$ and $C_0 \in (0, \pi^2)$) and verify that $R_1 = 0$. With $\alpha = 1$, we have

$$u_0(x) = \frac{\cos(\sqrt{C_0}(x - 1/2))}{\cos(\sqrt{C_0}/2)}. \quad (2.4.8)$$

In particular, we note for future reference the reflectional symmetry of $u_0(x)$ about $x = 1/2$.

The governing equation for the first-order correction $u_1(x)$ is

$$u_1'' + C_0 u_1 = (x - C_1) u_0, \quad (2.4.9)$$

with boundary conditions

$$u_1(0) = \nu^2 R_0, \quad 2u_0'(0)u_1'(0) = (1 - 2\nu^2 C_0) R_0 - C_1, \quad (2.4.10)$$

$$u_1(1) = 0, \quad 2u_0'(1)u_1'(1) = 1 - C_1, \quad (2.4.11)$$

when $\alpha = 1$, where we make use of (2.3.8). Multiplying (2.4.9) by $u_0(x)$ and integrating over the domain gives

$$\int_0^1 u_1'' u_0 dx + C_0 \int_0^1 u_1 u_0 dx = \int_0^1 (x - C_1) u_0^2 dx. \quad (2.4.12)$$

If we take the first term on the left hand side, integrate by parts, and use $u_0'' = -C_0 u_0$, we find

$$\int_0^1 (x - C_1) u_0^2 dx = [u_0 u_1' - u_0' u_1]_0^1. \quad (2.4.13)$$

Now the equations (2.3.7) and (2.4.8) and boundary conditions (2.4.10) enable us to obtain the relation

$$\int_0^1 (x - C_1) u_0^2 dx = \frac{(2C_1 - 1)}{2\sqrt{C_0}} \cot(\sqrt{C_0}/2). \quad (2.4.14)$$

Then by exploiting the symmetry of $u_0(x)$ pointed out above, we note

$$\int_0^1 \left(x - \frac{1}{2}\right) u_0^2 dx = 0, \quad (2.4.15)$$

that we use to write (2.4.14) as

$$\left(C_1 - \frac{1}{2}\right) \left(\frac{1}{\sqrt{C_0}} \cot(\sqrt{C_0}/2) + \int_0^1 u_0^2 dx\right) = 0, \quad (2.4.16)$$

and therefore deduce that $C_1 = 1/2$.

Hence the general solution of (2.4.9) can be written in the form

$$u_1(x) = P(x) + Au_0(x) + Bu'_0(x), \quad (2.4.17)$$

where A and B are integration constants and $P(x)$ is a particular solution to (2.4.9), which may be chosen to be antisymmetric about $x = 1/2$. By evaluating $u_1(x)$ at $x = 0$ and $x = 1$, making use of (2.4.10)–(2.4.11) and again using symmetry arguments, we deduce that

$$\frac{u_1(0) + u_1(1)}{2} = A = \frac{\nu^2 R_0}{2}. \quad (2.4.18)$$

Finally, multiplying (2.4.17) by u_0 , integrating across the domain, noting the symmetries of the terms in the integrand and making use of (2.3.11) to leading-order, we find that

$$2 \int_0^1 u_0(x) u_1(x) dx = 2A \int_0^1 u_0(x)^2 dx = \nu^2 R_0^2. \quad (2.4.19)$$

Substitution into (2.4.7) reveals that $R_1 = 0$ (in this case when $\alpha = 1$). We infer that the resistance is an increasing function of j when $j \ll 1$ provided $\alpha < 1$, as in figure 2.15. However, if $\alpha > 1$ then R will be a decreasing function of j when $j \ll 1$.

2.4.2.3 Large electron flux: $j \gg 1$

At the opposite limit of large electron flux, we continue the analysis started in Section 2.3.3 to obtain the approximations

$$\phi \sim \frac{j}{\alpha}(1 - x) + \frac{\alpha}{2\nu^2}(1 - x^2) + \dots, \quad (2.4.20a)$$

$$n \sim \alpha + (1 - \alpha)e^{-j(1-x)/\alpha} - \frac{\alpha}{\nu^2}(1 - \alpha)(1 - x)e^{-j(1-x)/\alpha} + \frac{\alpha^3}{\nu^2 j}(e^{-j(1-x)/\alpha} - x) + \dots \quad (2.4.20b)$$

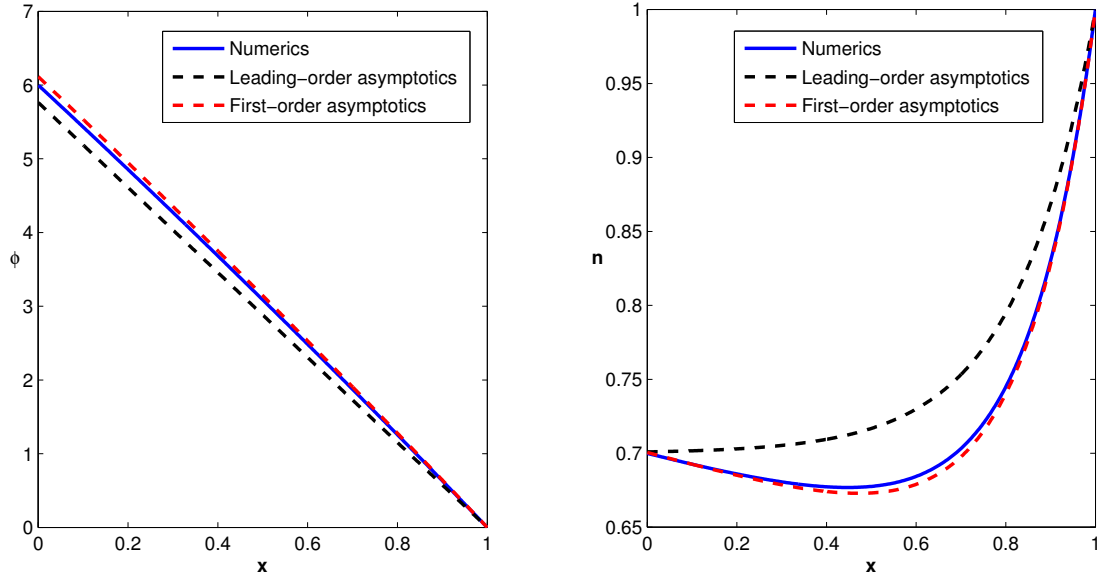


Figure 2.16: Electric potential ϕ and electron density n plotted against position x with parameter values $\nu = 1$ and $\alpha = 0.7$. The numerical solution is found by specifying $\Phi = 6$ to determine $j \approx 4.03$. The asymptotic solutions are found by specifying $j = 4.03$ where the leading-order asymptotics give $\Phi \approx 5.8$ and the first-order asymptotics give $\Phi \approx 6.1$. We plot the leading order expressions from Section 2.3.3 as well as the expressions (2.4.20).

as $j \rightarrow \infty$. We plot the solutions (2.4.20) in figure 2.16. Improved agreement of the first-order approximation with the numerical solution at a moderate value of electron flux is evident. The corresponding electric potential is given by

$$\Phi \sim \frac{j}{\alpha} + \frac{\alpha}{2\nu^2} + \dots, \quad (2.4.21)$$

and hence the resistance may be expanded in the form

$$R \sim \frac{1}{\alpha} + \frac{1}{j} \left(\log \alpha + \frac{\alpha}{2\nu^2} \right) + \dots \quad \text{as } j \rightarrow \infty. \quad (2.4.22)$$

The direction in which R tends to its limiting value $1/\alpha$ is determined by the coefficient of $1/j$ in this expansion. If $\alpha > 1$ then this coefficient is necessarily positive and R must therefore approach $1/\alpha$ from above. The same qualitative behaviour will occur if $\alpha < 1$ and $\nu^2 < -\alpha/2 \log \alpha$. However, if $\alpha < 1$ and $\nu^2 > -\alpha/2 \log \alpha$ then the resistance *increases* towards $1/\alpha$ as $j \rightarrow \infty$.

2.4.2.4 Summary

Our analysis reveals that the behaviour of the resistance R as a function of the electron flux j can follow one of four possible behaviours, illustrated schematically in figure 2.17.

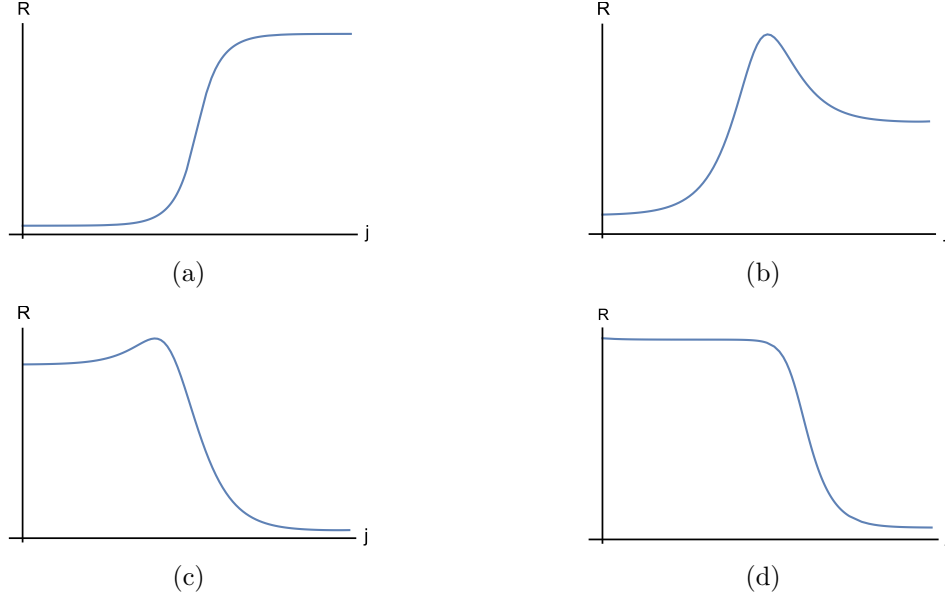


Figure 2.17: Schematic showing the four possible qualitative behaviours of the resistance R as a function of the electron flux j . The legends (a)–(d) refer to the regions of the (α, ν) parameter labelled in figure 2.14 in which each behaviour occurs: (a) R is a monotonic increasing function of j ; (b) R is a non-monotonic function of j and $R_\infty > R_0$; (c) R is a non-monotonic function of j and $R_0 > R_\infty$; (d) R is a monotonic decreasing function of j .

The region of (α, ν) parameter space where each behaviour occurs is labelled (a)–(d) in figure 2.14. In (a) the resistance increases monotonically with j , while in (d) it decreases monotonically. Between these two extremes, the behaviour is non-monotonic, with R decreasing as $j \rightarrow 0$ and as $j \rightarrow \infty$ and, therefore, achieving its maximum value at an intermediate value of j . In this case, the limiting values R_0 as $j \rightarrow 0$ and R_∞ as $j \rightarrow \infty$ may satisfy either $R_0 < R_\infty$ (b) or $R_0 > R_\infty$ (c).

2.5 Discussion and conclusions

In this chapter we analyse a mathematical model for steady electron transport through a glass layer residing between two electrodes. Our key modelling assumptions are that the charge is predominantly carried by electrons, the electron flow is one dimensional and governed by drift and diffusion, and the electron densities on either side of the glass layer are known. For given values of the physical parameters, the model determines either the electron flux as a function of the applied potential difference or *vice versa*. The effective resistance R of the layer is then defined as the ratio of the jump in total potential (combining the electric and chemical potentials) to the corresponding electron flux j .

Via detailed asymptotic analysis, we show that R approaches constant values as j tends to zero and to infinity and therefore behaves like a normal resistor in these regimes. In the limit of small electron flux, the electron density and potential vary consistently across the layer and the limiting resistance R_0 is related to the parameters α and ν by (2.3.7) and (2.3.12). However, for large electron flux, the charge is approximately uniform across the layer except in a boundary layer at the downstream interface, where it varies rapidly. The potential in this limit varies linearly with distance, and the layer acts like a simple resistor with limiting resistance $R_\infty = 1/\alpha$.

We also analyse the limit $\nu \rightarrow 0$, corresponding to the Debye length being much smaller than a typical device length-scale, as is likely to be the case in practice. In this regime, we find that the charge is small outside Debye layers which exist at both interfaces. This layered type solution is often found in the literature; although when considering problems of greater complexity that contain surface recombination [82] or multiple charge carriers [32, 79] additional transition layers are sometimes found in the solution structure, this does not manifest itself in any other parameter regimes we have explored. Although there is not in general a simple explicit formula for the resistance in this case, we identify successive asymptotic regions in which (i) R is approximately constant for small j , (ii) decreases like $j^{-1/2}$ for intermediate values and then (iii) finally approaches a different constant value as $j \rightarrow \infty$. The limiting values for small and large electron flux are consistent with the values R_0 and R_∞ that we found previously in §2.3.2 and 2.3.3 respectively.

When ν is small, we find that R_0 exceeds R_∞ by a large factor of order ν^{-2} . However, for larger values of ν , it is possible for R_0 to be equal to or less than R_∞ . For general values of the parameters ν and α , we find that R may increase or decrease as a function of j or, more surprisingly, achieve a maximum value at some intermediate value of j . The four possible generic behaviours of the function $R(j)$ are shown schematically in figure 2.17, and the regions of (α, ν) parameter space where each occurs are shown in figure 2.14.

In this chapter we have discovered that the resistance of a poorly conducting material, when situated between two relatively good conductors, exhibits many interesting phenomena. However, some of our assumptions may need to be revisited to improve the realism of our model. For example, in practice the glass layer may be far from uniform, with thickness variations from 10 – 1000nm. This issue is addressed in Chapter 3 where we extend our model to two dimensions and consider different glass layer geometries. Furthermore, when the glass layer is as thin as 10nm it is possible that quantum tunnelling effects will start to play a significant role. The inclusion of quantum mechanical effects into our mathematical model is investigated in Chapter 4. Finally, we have assumed in

this chapter that the electron density at the silicon-glass interface is known. In practice it is determined by the electrochemical coupling between the glass and the silicon emitter, and this will be examined further in Chapter 5.

Chapter 3

Two-dimensional modelling

3.1 Introduction

In Chapter 2 we analysed a one-dimensional model for electron flow through the glass layer present at the front side of a screen-printed crystalline silicon solar cell. The model provides a good starting point for understanding the electronic properties of the front contact. However, as stated in Chapter 2, the glass layer can vary from ~ 10 nm - 1000nm [64, 65, 103] and we expect the current to short circuit at thinner regions of the glass. This feature will be investigated both numerically and through asymptotic calculations in the present chapter.

To investigate the short circuiting through thinner regions we will extend the drift-diffusion model presented in Chapter 2 to two dimensions; when considering the two-dimensional extension it is generally necessary to solve numerically. One of the first 2D schemes was devised by Slotboom [91] who reformulated the charge densities in terms of the quasi-fermi levels and solved the resulting system of equations using Gummel iteration [45] and the finite difference method. As found in Chapter 2, and previously in a number of studies, [16, 17, 19, 24, 32, 42, 67, 69, 70, 79, 82], large gradients in the electric potential and electron density are often present near interfaces in semiconductor and electrochemical devices, and therefore the use of non-uniform meshes for finite difference methods has been proposed [92]. For non-uniform meshes the finite element method is more suitable and has been employed in a large number of studies, for example [3] and more recently in [25, 101]. A good review of the numerical methods used previously is given by Snowden [93].

In this chapter we investigate the 2D extension to the mathematical model outlined in Chapter 2. In §3.2 we formulate the model and outline the quantitative and qualitative outputs we wish to determine. Two different mapping techniques to transform the domain to a rectangle are given in §3.3. We then devise and validate a new spectral method based upon the work of Birkisson and Driscoll [21] to solve our 2D model numerically in §3.4.

We find in §3.5 that the current short-circuits through the thinnest regions of the glass layer, as expected. This enables us to determine limiting asymptotic expressions for the average current density for two different canonical glass layer profiles in §3.6, before drawing our conclusions in §3.7.

3.2 Mathematical model

3.2.1 Formulation of the problem

We consider two-dimensional conduction of electrons driven by an applied potential difference $(-\Phi)$ through a symmetric, periodic glass layer of wave-length $\bar{L}$ that has varying thickness, $h(x)$. The glass layer has average thickness H and minimum thickness $h_{\min}$.

We focus on a system where the electron density either side of the glass layer is equal. This corresponds to the situation where a glass layer separates a silver crystallite from the silver electrode (i.e. an Ag-glass-Ag system), and depending on the material properties of the glass could correspond to the situation where a glass layer separates the silicon emitter from the silver electrode (i.e. an Si-glass-Ag system). We want to investigate the short circuiting of the current through thinner regions of the glass layer. We therefore consider two different generic cases for the variation of the thickness of the glass layer:

- The radius of curvature, a , of the silver electrode is much larger than the minimum thickness of the glass layer $h_{\min}$, which implies the thickness of the glass layer varies slowly, see figure 3.1(a).
- The radius of curvature $a = O(h_{\min})$ so that the domain appears wedge-like and the thickness of the glass layer varies quickly, see figure 3.1(b).

In the latter case we will find it convenient to characterise the domain using the apparent angle, β , which the wedge makes with the horizontal.

3.2.2 Nondimensional model

The two-dimensional generalisation of (2.2.7)–(2.2.9) gives the governing equations

$$\nabla \cdot \mathbf{j} = 0, \tag{3.2.1}$$

$$\mathbf{j} = -n\nabla\phi - \nabla n, \tag{3.2.2}$$

$$\nu^2 \nabla^2 \phi = -n, \tag{3.2.3}$$

and the boundary conditions

$$\begin{aligned}
\phi(x, h(x)) &= 0, & n(x, h(x)) &= 1, & \phi(x, 0) &= \Phi, & n(x, 0) &= 1, \\
[\phi_x]_{x=L/2} &= 0, & [n_x]_{x=L/2} &= 0, & [\phi_x]_{x=-L/2} &= 0, & [n_x]_{x=-L/2} &= 0, \\
[\phi]_{x=L/2} &= 0, & [n]_{x=L/2} &= 0, & [\phi]_{x=-L/2} &= 0, & [n]_{x=-L/2} &= 0.
\end{aligned} \tag{3.2.4}$$

where we assume periodic boundary conditions in the x -direction. A schematic of an example domain and the boundary conditions is given in figure 3.2. The dimensionless

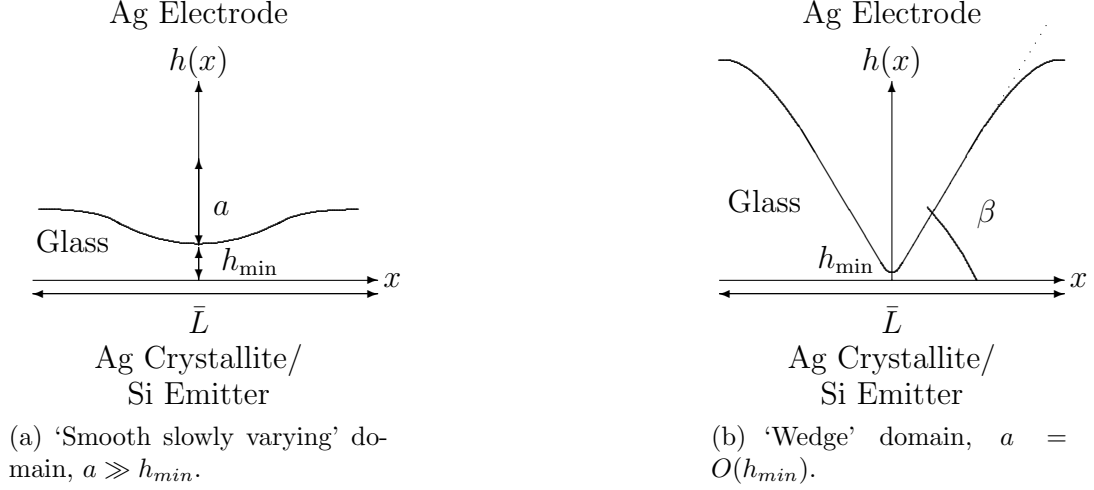


Figure 3.1: The two different domain shapes that are investigated; $h_{\min}$ = minimum glass thickness, a = radius of curvature of the top surface and β = angle from horizontal.

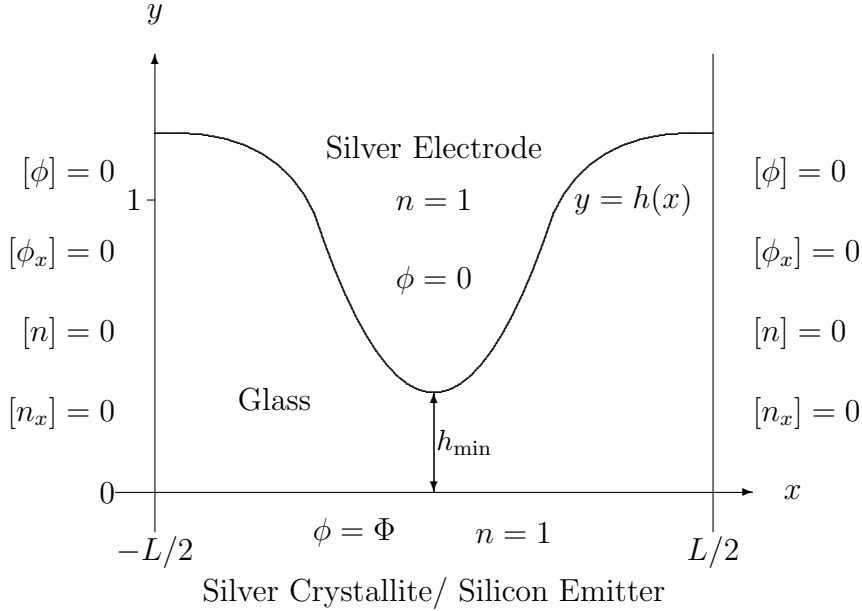


Figure 3.2: Schematic of an example physical domain and boundary conditions.

parameters are

$$L = \frac{\bar{L}}{H}, \quad \nu = \frac{H_D}{H} = \sqrt{\frac{\epsilon k_B T}{q^2 H^2 n_1}}, \quad (3.2.5)$$

where L is the nondimensional length of the glass layer and can be thought of as the aspect ratio ($L : 1$) and H is the average thickness of the glass layer. In this two-dimensional model the scaled Debye length, ν , is the ratio of the Debye length H_D to the average thickness of the glass layer H . We expect the Debye length to be small compared with the average glass layer thickness, and hence the parameter ν to be small and it is in this case that we expect short-circuiting effects to be especially evident. In this chapter we only study the case where the electron density is equal either side of the glass layer and therefore the parameter α (present in Chapter 2) is set to 1. Exactly the same methodology carried out in this chapter could be followed for different values of α . We only consider cases where $\Phi > 0$ since this corresponds to electron flow into the silver electrode.

3.2.3 Model outputs

From the solution of the mathematical model there are a number of different quantities we will calculate to gain greater insight into electron transport across the glass layer. Firstly, we will determine the average current density through the glass layer which is given by

$$Q = \frac{1}{L} \int_{-L/2}^{L/2} \left[-n \frac{\partial \phi}{\partial y} - \frac{\partial n}{\partial y} \right]_{y=0} dx; \quad (3.2.6)$$

the total current is given by QL . To investigate qualitatively the short circuiting of the current through thinner glass layer regions we calculate: (i) the electron trajectories through the glass layer; (ii) the normalised cumulative current

$$Cc(x) = \frac{2}{QL} \int_0^x \left[-n \frac{\partial \phi}{\partial y} - \frac{\partial n}{\partial y} \right]_{y=0} dx. \quad (3.2.7)$$

We only consider half of the domain due to the assumed symmetry of the top surface $y = h(x)$. The deviation of the function $Cc(x)$ from linear indicates focusing of the current.

Finally, the two-dimensional extension of the effective contact resistance defined in (2.2.12) is

$$R = \frac{\Phi}{Q}. \quad (3.2.8)$$

3.3 Transformation to rectangular domain

3.3.1 Introduction

In this chapter we solve (3.2.1)–(3.2.4) using a spectral numerical method. The numerical solution is facilitated by mapping the domain to a rectangle. In this section we outline two alternative mapping techniques: a hodograph formulation, particularly suitable for investigating the slowly varying domain, shown in figure 3.1(a), and a conformal map formulation [15], ideal for investigating the wedge domain, shown in figure 3.1(b).

3.3.2 Hodograph transformation

Equation (3.2.1) implies the existence of a streamfunction $\tau(x, y)$ such that

$$\mathbf{j} = (\tau_y, -\tau_x), \quad (3.3.1)$$

and therefore we can write

$$\tau_y = -n\phi_x - n_x, \quad \tau_x = n\phi_y + n_y, \quad (3.3.2)$$

The introduction of the electrochemical potential $v = \phi + \log n$, see (1.7.1), enables us to write (3.2.2) as

$$\tau_y = -nv_x, \quad \tau_x = nv_y. \quad (3.3.3)$$

Now by considering the boundary conditions (3.2.4), we observe that the change of independent variables from $(x, y) \rightarrow (v, \tau)$, maps the solution domain onto the rectangle $(v, \tau) \in [0, \Phi] \times [-QL/2, QL/2]$.

The Jacobian of the transformation is given by

$$\tilde{J} = \frac{\partial(v, \tau)}{\partial(x, y)} = v_x\tau_y - v_y\tau_x, \quad (3.3.4)$$

and the inverse by

$$\frac{1}{\tilde{J}} = x_v y_\tau - x_\tau y_v. \quad (3.3.5)$$

Making use of (3.3.3) we can write (3.3.4) as

$$\tilde{J} = -n|\nabla v|^2 = -\frac{|\nabla \tau|^2}{n}. \quad (3.3.6)$$

Therefore for a given physical domain with an applied potential difference ($\Phi > 0$) we expect $\tilde{J} < 0$. We note that for $\tilde{J} = 0$, $|\tau| = 0$, meaning there is a stagnation point for

the electron flow in the domain. Additionally, by making use of the chain rule and (3.3.5) we find

$$\begin{pmatrix} v_x & v_y \\ \tau_x & \tau_y \end{pmatrix} = \tilde{J} \begin{pmatrix} y_\tau & -x_\tau \\ -y_v & x_v \end{pmatrix}. \quad (3.3.7)$$

The relation (3.3.7) enables us to invert (3.3.3) and find that

$$x_v = -ny_\tau, \quad y_v = nx_\tau, \quad (3.3.8)$$

and hence

$$\frac{1}{\tilde{J}} = x_v y_\tau - x_\tau y_v = -n \left(ny_\tau^2 + \frac{y_v^2}{n} \right). \quad (3.3.9)$$

To formulate our problem in the Hodograph plane we want to write (3.2.3) in terms of v and τ . We use the chain rule to find that

$$\begin{aligned} \phi_{xx} + \phi_{yy} &= (v_{xx} + v_{yy}) \frac{\partial \phi}{\partial v} + (\tau_{xx} + \tau_{yy}) \frac{\partial \phi}{\partial \tau} + (v_x^2 + v_y^2) \frac{\partial^2 \phi}{\partial v^2} + \\ &2(v_x \tau_x + v_y \tau_y) \frac{\partial^2 \phi}{\partial v \partial \tau} + (\tau_x^2 + \tau_y^2) \frac{\partial^2 \phi}{\partial \tau^2}. \end{aligned} \quad (3.3.10)$$

Differentiating the relation $v = \phi + \log n$, we obtain the two equations

$$\frac{\partial n}{\partial \tau} = -n \frac{\partial \phi}{\partial \tau}, \quad \frac{\partial n}{\partial v} = n - n \frac{\partial \phi}{\partial v}, \quad (3.3.11)$$

which we use with (3.3.2), (3.3.3) and (3.3.4) to give

$$\tau_{xx} + \tau_{yy} = \tilde{J} n \frac{\partial \phi}{\partial \tau}, \quad v_{xx} + v_{yy} = \frac{\tilde{J}}{n} \left(1 - \frac{\partial \phi}{\partial v} \right). \quad (3.3.12)$$

Substituting (3.3.12) into (3.3.10) with further use of (3.3.3), (3.3.4) and (3.3.11) gives

$$\phi_{xx} + \phi_{yy} = -\tilde{J} \left(\left(\frac{\phi_v}{n} \right)_v + (n \phi_\tau)_\tau \right). \quad (3.3.13)$$

Eliminating $\tilde{J}$ from (3.3.13) using (3.3.9) and subsequently substituting (3.3.13) into (3.2.3) gives

$$\left(\frac{\phi_v}{n} \right)_v + (n \phi_\tau)_\tau = \frac{n^3}{\nu^2} \left(ny_\tau^2 + \frac{y_v^2}{n} \right) \quad (3.3.14)$$

Finally, eliminating ϕ from (3.3.14) using (3.3.11) and eliminating x from (3.3.8) we find the governing equations in the hodograph plane:

$$\left(\frac{y_v}{n} \right)_v + (ny_\tau)_\tau = 0, \quad (3.3.15)$$

$$n_{vv} + n_v - \frac{2n_v^2}{n} + n^2 n_{\tau\tau} = \frac{n^3}{\nu^2} \left(ny_\tau^2 + \frac{y_v^2}{n} \right), \quad (3.3.16)$$

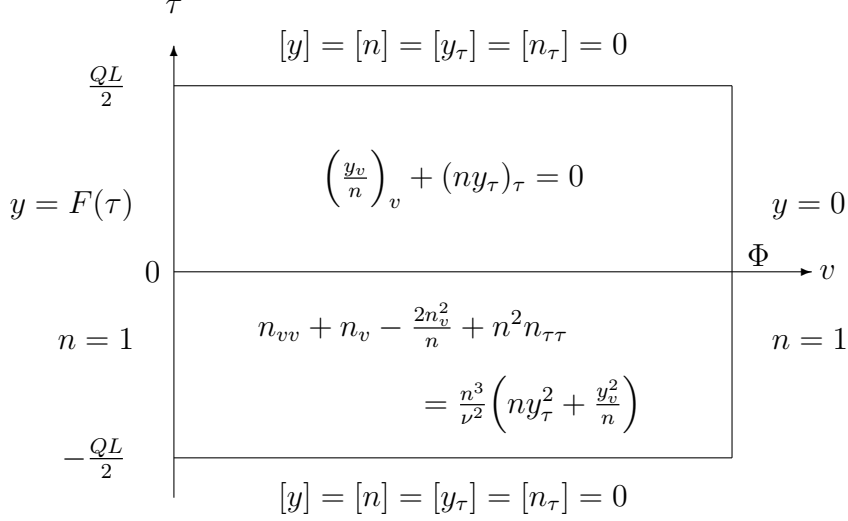


Figure 3.3: Schematic of hodograph plane domain and boundary conditions

with boundary conditions

$$n(0, \tau) = 1, \quad n(\Phi, \tau) = 1, \quad y(0, \tau) = F(\tau), \quad y(\Phi, \tau) = 0 \quad (3.3.17)$$

$$[n_\tau]_{\tau=-QL/2} = 0, \quad [n_\tau]_{\tau=QL/2} = 0, \quad [y_\tau]_{\tau=-QL/2} = 0, \quad [y_\tau]_{\tau=QL/2} = 0, \quad (3.3.18)$$

$$[n]_{\tau=-QL/2} = 0, \quad [n]_{\tau=QL/2} = 0, \quad [y]_{\tau=-QL/2} = 0, \quad [y]_{\tau=QL/2} = 0, \quad (3.3.19)$$

A schematic of the hodograph plane and boundary conditions is shown in figure 3.3. We note that in this formulation, we have to specify QL in order to solve (3.3.15)–(3.3.19), and thus the method has become semi-inverse in nature since we have to then find the length of the domain L . We also input the function $y(0, \tau) = F(\tau)$ that determines indirectly the shape of the top surface $y = h(x)$ in the physical plane.

We obtain ϕ from the relation $\phi = v - \log n$, and to plot our results in the physical plane we calculate $x(v, \tau)$ using:

$$x(v, \tau) = - \int_{-QL/2}^{\tau} \frac{y_v(v, \tau')}{n(v, \tau')} \, d\tau'. \quad (3.3.20)$$

The length of the physical domain is found using

$$L(v) = - \int_{-QL/2}^{QL/2} \frac{y_v(v, \tau)}{n(v, \tau)} \, d\tau; \quad (3.3.21)$$

L should be independent of v and any variation in L over the range of v is due to numerical error. The electron trajectories are easily found as curves of constant τ . Finally, the cumulative current is found by inverting the function $x(\Phi, \tau)$ to determine $\tau(x, 0)$.

3.3.3 Conformal mapping

3.3.3.1 Transformed problem

As an alternative to the hodograph transformation described above, suppose instead that the rectangle $\tilde{r} = [-\tilde{l}/2, \tilde{l}/2] \times [0, \eta^*]$ is mapped onto the physical domain of interest $\{(x, y) : 0 \leq y \leq h(x); -L/2 \leq x \leq L/2\}$ by a conformal transformation. We change variables from $(x, y) \rightarrow (z, \bar{z})$ where $z = x + iy$ and (3.2.1)–(3.2.3) become

$$4 \frac{\partial^2 n}{\partial z \partial \bar{z}} + 2 \left(\frac{\partial n}{\partial z} \frac{\partial \phi}{\partial \bar{z}} + \frac{\partial n}{\partial \bar{z}} \frac{\partial \phi}{\partial z} \right) - \frac{n^2}{\nu^2} = 0, \quad (3.3.22)$$

$$4\nu^2 \frac{\partial^2 \phi}{\partial z \partial \bar{z}} + n = 0. \quad (3.3.23)$$

We then map to the transformed plane by applying

$$z = f(\zeta), \quad \bar{z} = f(\bar{\zeta}), \quad (3.3.24)$$

to (3.3.23)–(3.3.22) to find

$$4 \frac{\partial^2 n}{\partial \zeta \partial \bar{\zeta}} + 2 \left(\frac{\partial n}{\partial \zeta} \frac{\partial \phi}{\partial \bar{\zeta}} + \frac{\partial n}{\partial \bar{\zeta}} \frac{\partial \phi}{\partial \zeta} \right) - G(\zeta) \frac{n^2}{\nu^2} = 0, \quad (3.3.25)$$

$$4\nu^2 \frac{\partial^2 \phi}{\partial \zeta \partial \bar{\zeta}} + G(\zeta)n = 0, \quad (3.3.26)$$

where $G(\zeta) = |f'(\zeta)|^2$. By introducing $\zeta = \xi + i\eta$ we find the governing equations in the transformed frame:

$$\frac{\partial^2 n}{\partial \xi^2} + \frac{\partial^2 n}{\partial \eta^2} + \frac{\partial n}{\partial \xi} \frac{\partial \phi}{\partial \xi} + \frac{\partial n}{\partial \eta} \frac{\partial \phi}{\partial \eta} - G(\xi, \eta) \frac{n^2}{\nu^2} = 0, \quad (3.3.27)$$

$$\nu^2 \left(\frac{\partial^2 \phi}{\partial \xi^2} + \frac{\partial^2 \phi}{\partial \eta^2} \right) + G(\xi, \eta)n = 0, \quad (3.3.28)$$

while the boundary conditions (3.2.4) become

$$\begin{aligned} \phi(\xi, 0) &= \Phi, & n(\xi, 0) &= 1, & \phi(\xi, \eta^*) &= 0, & n(\xi, \eta^*) &= 1 \\ [\phi_\xi]_{\xi=\tilde{l}/2} &= 0, & [n_\xi]_{\xi=\tilde{l}/2} &= 0, & [\phi_\xi]_{\xi=-\tilde{l}/2} &= 0, & [n_\xi]_{\xi=-\tilde{l}/2} &= 0, \\ [\phi]_{\xi=\tilde{l}/2} &= 0, & [n]_{\xi=\tilde{l}/2} &= 0, & [\phi]_{\xi=-\tilde{l}/2} &= 0, & [n]_{\xi=-\tilde{l}/2} &= 0. \end{aligned} \quad (3.3.29)$$

A schematic of the domain and boundary conditions is shown in figure 3.4. Calculation of the average current density in the transformed frame is achieved by first writing (3.2.6) in terms of $(z, \bar{z})$.

$$Q = \frac{\text{Im}}{L} \left\{ \int_{-L/2}^{L/2} \left[2 \left(n \frac{\partial \phi}{\partial z} + \frac{\partial n}{\partial z} \right) \right]_{z=\bar{z}} dz \right\}. \quad (3.3.30)$$

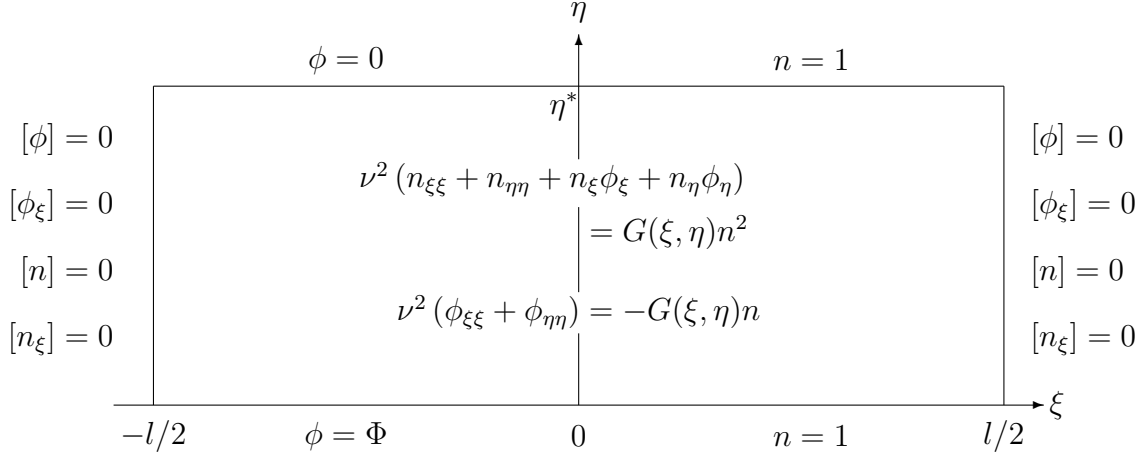


Figure 3.4: Schematic of conformally mapped domain and boundary conditions.

If we then apply the transformation (3.3.24) and introduce the variables (ξ, η) we find

$$Q = \frac{1}{L} \int_{-\tilde{l}/2}^{\tilde{l}/2} \left[-n \frac{\partial \phi}{\partial \eta} - \frac{\partial n}{\partial \eta} \right]_{\eta=0} d\xi. \quad (3.3.31)$$

To obtain the electron trajectories we must solve the equations analagous to

$$\frac{dx}{dt} = - \left(n \frac{\partial \phi}{\partial x} + \frac{\partial n}{\partial x} \right), \quad \frac{dy}{dt} = - \left(n \frac{\partial \phi}{\partial y} + \frac{\partial n}{\partial y} \right), \quad (3.3.32)$$

in the transformed frame. Writing (3.3.32) in terms of $(z, \bar{z})$, using (3.3.24) and then finally introducing (ξ, η) , we find

$$\frac{d\xi}{dt} = - \frac{1}{G(\xi, \eta)} \left(n \frac{\partial \phi}{\partial \xi} + \frac{\partial n}{\partial \xi} \right), \quad \frac{d\eta}{dt} = - \frac{1}{G(\xi, \eta)} \left(n \frac{\partial \phi}{\partial \eta} + \frac{\partial n}{\partial \eta} \right). \quad (3.3.33)$$

The term $G(\xi, \eta)$ merely scales the equations (3.3.33) and therefore has no effect on the path the electrons take. The electron trajectories are therefore found by solving

$$\frac{d\xi}{dt} = - \left(n \frac{\partial \phi}{\partial \xi} + \frac{\partial n}{\partial \xi} \right), \quad \frac{d\eta}{dt} = - \left(n \frac{\partial \phi}{\partial \eta} + \frac{\partial n}{\partial \eta} \right), \quad (3.3.34)$$

using the overloaded `ode45` function in `Chebfun` and the solution is then mapped back to the physical domain. Finally, the cumulative current plots can be produced by noting the relation

$$Cc(x) = \frac{2}{QL} \int_0^x \left[-n \frac{\partial \phi}{\partial \eta} - \frac{\partial n}{\partial \eta} \right]_{\eta=0} \frac{\partial \xi}{\partial x} dx, \quad (3.3.35)$$

and using the overloaded `cumsum` command in `Chebfun`.

3.3.3.2 Mapping function

For a given physical domain a numerical conformal map can be constructed by making use of the Schwarz-Christoffel transformation. However, to explore domains with a wedge-like geometry, we use the following mapping function, see Hale & Tee [46],

$$f(\zeta) = \frac{L}{\pi} \arcsin \left(\frac{\tanh(\varepsilon/2) \operatorname{sn}(2K\zeta/L)}{\operatorname{dn}(2K\zeta/L)} \right), \quad (3.3.36)$$

where K denotes the complete elliptic integral of the first kind; sn and dn are Jacobi elliptic functions. The suppressed argument m of $K(m)$, $\operatorname{sn}(u|m)$ and $\operatorname{dn}(u|m)$ is defined by

$$m = \operatorname{sech}^2(\varepsilon/2). \quad (3.3.37)$$

Hence the map (3.3.36) depends on one parameter ε in addition to the length L of the periodic domain. Using this mapping, the length of the rectangle $\tilde{r}$ is equivalent to the length of the physical domain of interest, $\tilde{l} \equiv L$.

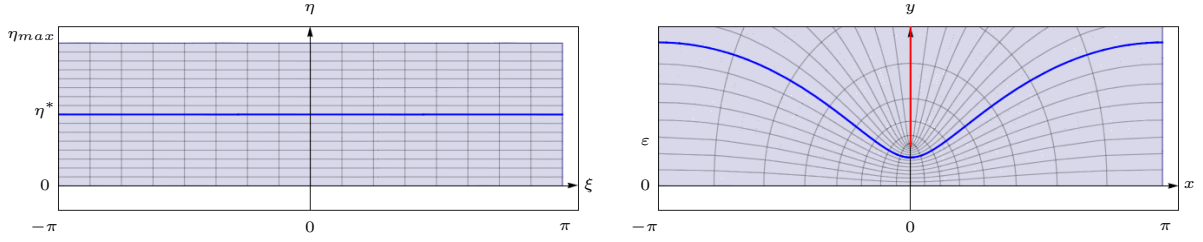


Figure 3.5: The conformal map (3.3.36) with $L = 2\pi$ and $\varepsilon = 0.5$, maps the ζ -plane on the left to the z plane on the right.

The function $f(\zeta)$ is univalent on the rectangle $\tilde{r} = [-L/2, L/2] \times [0, \eta^*]$ provided $\eta^* < \eta_{\max}$, where

$$\eta_{\max} = \frac{L}{2} \frac{K(1-m)}{K(m)}. \quad (3.3.38)$$

As shown in figure 3.5, the function (3.3.36) maps the rectangle $[-L/2, L/2] \times [0, \eta_{\max}]$ in the ζ -plane to a strip $[-L/2, L/2] \times [0, \infty]$ in the z -plane, minus a branch cut from $i\varepsilon L/(2\pi)$ to $i\infty$. For $\eta^* < \eta_{\max}$, the line $\operatorname{Im}(\zeta) = \eta^*$ is mapped to a periodic curved upper surface that is wrapped around the branch cut. The height η^* of the rectangular domain $\tilde{r}$ is chosen to ensure that the nondimensional average thickness of the glass layer is equal to 1, that is,

$$\text{Area} = -\frac{1}{2} \operatorname{Im} \left[\int_{-L/2}^{L/2} f(\xi - i\eta^*) f'(\xi + i\eta^*) d\xi \right] + \frac{L}{2} y_{\max} \equiv L, \quad (3.3.39)$$

where $y_{\max}$ is the maximum value that y takes in the z plane.

To consider wedge-like shapes we let ε be small so the geometry approaches that of a rounded wedge which narrowly avoids intersecting the lower surface $y = 0$ at $x = 0$, see figure 3.6. In the limit as $\varepsilon \rightarrow 0$, we find that

$$\eta_{\max} \sim \frac{\pi L}{4 \log(8/\varepsilon)}, \quad z = f(\zeta) \sim \frac{\varepsilon L}{2\pi} \sinh \left(\frac{2\zeta \log(8/\varepsilon)}{L} \right). \quad (3.3.40)$$

The parameters η^* and ε may thus be related to the asymptotic minimum layer thickness $h_{\min}$ and wedge angle β using the formulae

$$\eta^* = \frac{\beta L}{2 \log(8/\varepsilon)}, \quad \varepsilon = \frac{2\pi h_{\min}}{L \sin \beta}, \quad (3.3.41)$$

and the local geometry is that of a hyperbola, with

$$y^2 \cos^2 \beta - x^2 \sin^2 \beta = h_{\min}^2 \cos^2 \beta. \quad (3.3.42)$$

Using the relations (3.3.41) we can create a conformal map from the rectangular ζ plane to the wedge shaped z plane where the wedge has a given angle from the horizontal β and a given minimum thickness $h_{\min}$. The length of the domain L is specified by (3.3.39).

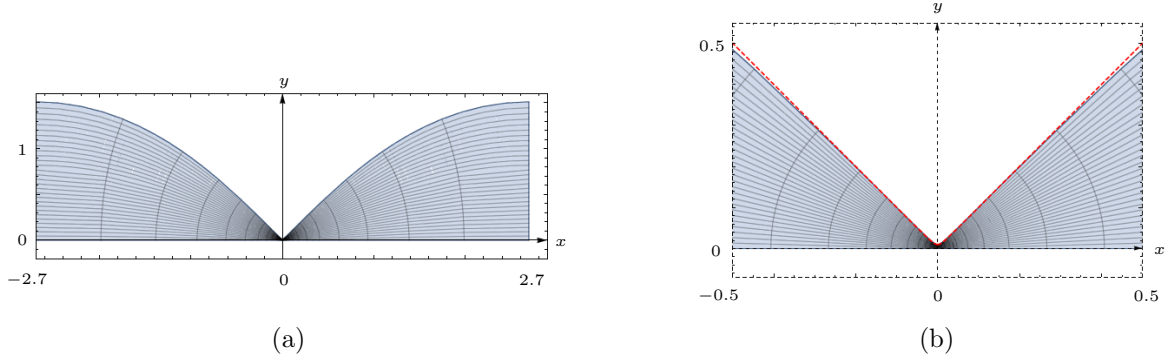


Figure 3.6: The conformal map (3.3.36) with $L \approx 5.39$, $\varepsilon \approx 0.0165$ and $\eta^* \approx 0.342$. In a) we plot the whole domain in the z plane, where the values of η^* and ε are set using (3.3.41) to make $\beta = \pi/4$ and $h_{\min} = 0.01$. In b) we show the local geometry at the wedge tip, where the red dashed line is given by (3.3.42).

3.3.4 Summary

We have formulated two different techniques for mapping the governing equations to a rectangular domain. These approaches each have advantages and disadvantages and are appropriate for treating different domains. The conformal map formulation is straightforward to apply and, if an analytic map can be found, allows easy manipulation of the

domain shape. Of course in general the Schwarz-Christoffel toolbox can be used to obtain numerical mapping functions for any given domain shape, although this adds computational effort. The calculation of the electron trajectories and cumulative current also requires significant additional numerical calculations. In contrast, the hodograph plane formulation makes it easy to determine these desired quantities. In theory, the hodograph plane formulation allows the treatment of a wide range of domain shapes. However, to easily produce a given domain *a priori* knowledge of the appropriate $y = F(\tau)$ is needed.

3.4 Numerical method

3.4.1 Introduction

Via either of the transformations described in Section 3.3, we may henceforth assume that the transformed model is posed on a rectangular domain. The numerical method we will use is a 2D spectral method. The basis of solving differential equations using spectral methods is to take discrete data on a grid, interpolate this data with a global function and then evaluate the derivative of the interpolating function on the grid. Given a periodic problem one would typically use trigonometric interpolants on equispaced points, and given a non-periodic problem it is commonplace to use Chebyshev polynomial interpolants on Chebyshev spaced points [96]. Both formulations laid out in §3.3 are periodic in one direction and non-periodic in the other, and we will therefore choose the appropriate interpolants in each direction accordingly.

3.4.2 Demonstration of implementation

We will give a detailed description of how the numerical method is implemented on the conformally mapped problem, (3.3.28)–(3.3.29); this numerical method can be applied to analogous nonlinear elliptic equations in a rectangle and therefore exactly the same methodology is used for the hodograph plane formulation. To apply Newton's method we calculate the Fréchet derivatives of the governing equations with respect to the two unknowns ϕ and n :

$$\frac{\partial(3.3.28)}{\partial\phi} : \nu^2 \left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} \right), \quad (3.4.1)$$

$$\frac{\partial(3.3.28)}{\partial n} : G(\xi, \eta), \quad (3.4.2)$$

$$\frac{\partial(3.3.27)}{\partial\phi} : \frac{\partial n}{\partial\xi} \frac{\partial}{\partial\xi} + \frac{\partial n}{\partial\eta} \frac{\partial}{\partial\eta}, \quad (3.4.3)$$

$$\frac{\partial(3.3.27)}{\partial n} : \frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} + \frac{\partial\phi}{\partial\xi} \frac{\partial}{\partial\xi} + \frac{\partial\phi}{\partial\eta} \frac{\partial}{\partial\eta} - \frac{2n}{\nu^2} G(\xi, \eta). \quad (3.4.4)$$

Given an approximation (ϕ_k, n_k) to the solution, we therefore calculate an improved approximation $(\phi_{k+1}, n_{k+1}) = (\phi_k, n_k) + \gamma_k(\hat{u}_k^\phi, \hat{u}_k^n)$, where $\hat{u}_k^\phi, \hat{u}_k^n$ are the updates and γ_k is a damping parameter that increases the chance of an initial guess converging to a solution [21]. The updates satisfy the linear partial differential equations

$$\begin{aligned} & \left(\nu^2 \left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} \right) \frac{G(\xi, \eta)}{\frac{\partial n_k}{\partial \xi} \frac{\partial}{\partial \xi} + \frac{\partial n_k}{\partial \eta} \frac{\partial}{\partial \eta}} \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \frac{\partial \phi_k}{\partial \xi} \frac{\partial}{\partial \xi} + \frac{\partial \phi_k}{\partial \eta} \frac{\partial}{\partial \eta} - \frac{2n_k}{\nu^2} G(\xi, \eta) \right) \begin{pmatrix} \hat{u}_k^\phi \\ \hat{u}_k^n \end{pmatrix} \\ &= - \begin{pmatrix} \nu^2 \left(\frac{\partial^2 \phi_k}{\partial \xi^2} + \frac{\partial^2 \phi_k}{\partial \eta^2} \right) + G(\xi, \eta) n_k, \\ \frac{\partial^2 n_k}{\partial \xi^2} + \frac{\partial^2 n_k}{\partial \eta^2} + \frac{\partial n_k}{\partial \xi} \frac{\partial \phi_k}{\partial \xi} + \frac{\partial n_k}{\partial \eta} \frac{\partial \phi_k}{\partial \eta} - G(\xi, \eta) \frac{n_k^2}{\nu^2} \end{pmatrix}. \end{aligned} \quad (3.4.5)$$

We ensure that the initial guess (ϕ_0, n_0) satisfies the boundary conditions in the η direction so we can specify homogenous boundary conditions for the update $\hat{u}$. We also specify periodic boundary conditions in the ξ direction, i.e.

$$\begin{aligned} \hat{u}^\phi(\xi, 0) &= 0, \quad \hat{u}^\phi(\xi, \eta^*) = 0, \quad \hat{u}^n(\xi, 0) = 0, \quad \hat{u}^n(\xi, \eta^*) = 0, \\ [\hat{u}_\xi^\phi]_{\xi=-L/2} &= 0, \quad [\hat{u}_\xi^\phi]_{\xi=L/2} = 0, \quad [\hat{u}_\xi^n]_{\xi=-L/2} = 0, \quad [\hat{u}_\xi^n]_{\xi=L/2} = 0, \\ [\hat{u}^\phi]_{\xi=-L/2} &= 0, \quad [\hat{u}^\phi]_{\xi=L/2} = 0, \quad [\hat{u}^n]_{\xi=-L/2} = 0, \quad [\hat{u}^n]_{\xi=L/2} = 0. \end{aligned} \quad (3.4.6)$$

The successive approximations are calculated repeatedly until the update $||\hat{u}_k|| < 10^{-5}$.

To solve (3.4.5), (3.4.6) numerically, we convert the variables $\phi_k, n_k, \hat{u}_k^\phi, \hat{u}_k^n$ and $G(\xi, \eta)$ from 2D continuous objects into vectors on the domain discretised with equispaced points in the periodic ξ direction and Chebyshev spaced points in the non-periodic η direction. To turn the 2D grid into a vector, we index from the bottom left hand corner as illustrated in figure 3.7.

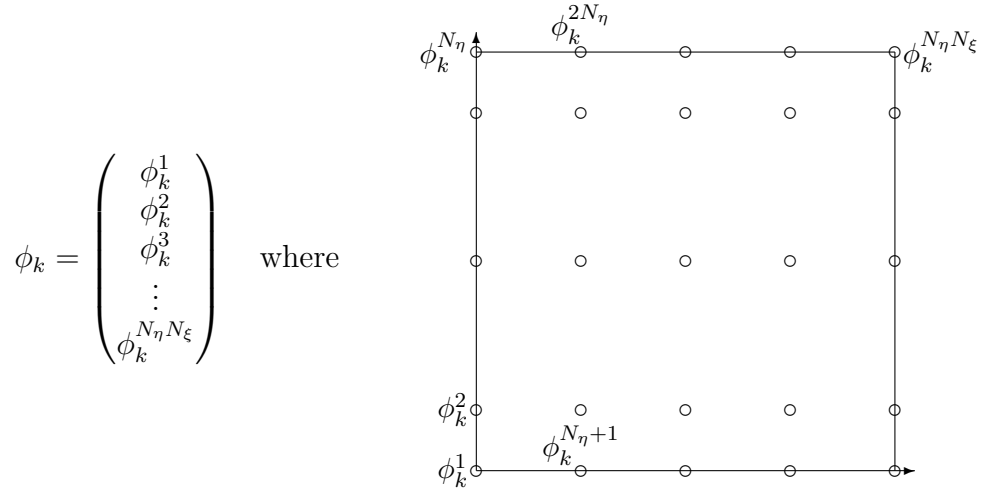


Figure 3.7: N_ξ, N_η , are the number of points in the ξ and η direction respectively.

To write the system (3.4.5) as a matrix equation we introduce the notation:

$$D_\xi^n : \quad \text{the } n\text{th order differentiation matrix in the } \xi \text{ direction,} \quad (3.4.7)$$

$$\begin{aligned} d[n_k] : \quad & \text{a square diagonal matrix with the variable } n_k \text{ on its} \\ & \text{diagonal.} \end{aligned} \quad (3.4.8)$$

We make use of the Schwarz-Christoffel toolbox [38] and take the differentiation matrices from the MATLAB dmsuite [107], where D_ξ^n is a Fourier differentiation matrix and D_η^n is a Chebyshev differentiation matrix. Using this notation, (3.4.5) becomes

$$\begin{aligned} & \begin{pmatrix} \nu^2 (D_\xi^2 + D_\eta^2) & d[G(\xi, \eta)] \\ d[D_\xi^1 n_k] D_\xi^1 + d[D_\eta^1 n_k] D_\eta^1 & D_\xi^2 + D_\eta^2 + d[D_\xi^1 \phi_k] D_\xi^1 + d[D_\eta^1 \phi_k] D_\eta^1 - d\left[\frac{2n_k}{\nu^2} \cdot G(\xi, \eta)\right] \end{pmatrix} \begin{pmatrix} \hat{u}_k^\phi \\ \hat{u}_k^n \end{pmatrix} \\ & = - \begin{pmatrix} \nu^2 (D_\xi^2 \phi_k + D_\eta^2 \phi_k) + G(\xi, \eta) \cdot n_k, \\ D_\xi^2 n_k + D_\eta^2 n_k + D_\xi^1 n_k \cdot D_\xi^1 \phi_k + D_\eta^1 n_k \cdot D_\eta^1 \phi_k - G(\xi, \eta) \cdot \frac{n_k \cdot n_k}{\nu^2} \end{pmatrix}. \end{aligned} \quad (3.4.9)$$

where $\cdot$ denotes element-wise multiplication, and the boundary conditions are

$$\hat{u}^\phi(\xi, 0) = 0, \quad \hat{u}^\phi(\xi, \eta^*) = 0, \quad \hat{u}^n(\xi, 0) = 0, \quad \hat{u}^n(\xi, \eta^*) = 0. \quad (3.4.10)$$

Boundary conditions in the ξ -direction are not needed as we use Fourier differentiation matrices that assume periodicity. To apply the boundary conditions (3.4.10) we replace rows in the matrices in (3.4.9) so that the relevant elements of $\hat{u}_k^\phi$ and $\hat{u}_k^n$ are selected and set to zero. We first solve the problem in 1D using **Chebfun** and then extend this into the second dimension to create the initial guess. The system (3.4.9) is then solved using damped Newton iteration where the damping parameter γ_k is calculated using the algorithm given in the appendix of [21].

Finally, to obtain the variables ϕ and n in the transformed frame we first interpolate the periodic points to Chebyshev points using `fourint.m` [107] and then use **Chebfun** to create **chebfun** objects of ϕ and n . This enables us to access the wide range of functionality built into **Chebfun** for further analysis of the results.

3.4.3 Validation

3.4.3.1 Taylor testing

A method to confirm the correctness of the linearisation is the Taylor remainder convergence test (Taylor test) [20, 40]. The Taylor test uses Taylor's theorem to define the first-order Taylor remainder as

$$\mathcal{T}_1(k) = \|\mathcal{F}(\mathcal{U} + k\tilde{\mathcal{U}}) - \mathcal{F}(\mathcal{U})\| \rightarrow 0 \quad \text{at} \quad O(k), \quad (3.4.11)$$

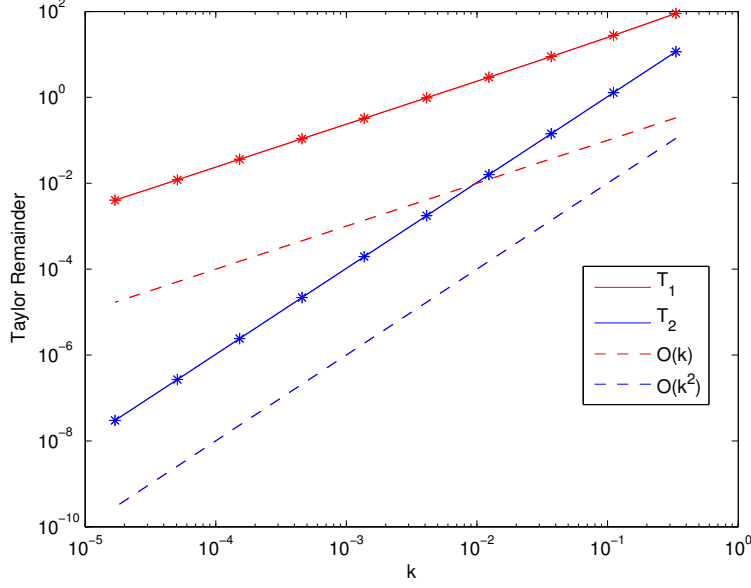


Figure 3.8: Taylor test for the conformal map formulation.

where $\mathcal{F}$ is a given operator, $\mathcal{U}$ is the argument and $\tilde{\mathcal{U}}$ is a perturbation to the argument. Additionally, the second-order Taylor remainder is given by

$$\mathcal{T}_2(k) = \|\mathcal{F}(\mathcal{U} + k\tilde{\mathcal{U}}) - \mathcal{F}(\mathcal{U}) - k\mathcal{F}'(\mathcal{U})\tilde{\mathcal{U}}\| \rightarrow 0 \quad \text{at} \quad O(k^2), \quad (3.4.12)$$

where $\mathcal{F}'(\mathcal{U})$ is the Fréchet derivative of $\mathcal{F}$ at $\mathcal{U}$. In relation to the implementation outlined in §3.4.2, $\mathcal{F}(\mathcal{U})$ refers to the matrix on the left hand side of (3.4.5), $\mathcal{F}'(\mathcal{U})$ to the matrix on the right hand side of (3.4.5) and $\mathcal{U} = (\phi_k, n_k)$.

To test our conformal map formulation we calculate $\mathcal{T}_1$ and $\mathcal{T}_2$ where $G(\xi, \eta) = 1$, $\nu = 1$, $\eta^* = 2$, $L = 2\pi$ and we use the test function

$$\mathcal{U} = (\sin[\xi] \cos[\pi\eta/2] + 2, \sin[\xi] \cos[\pi\eta/2] + 2). \quad (3.4.13)$$

The results are plotted in figure 3.8, where it is evident $\mathcal{T}_2 \sim O(k^2)$ as $k \rightarrow 0$. Similarly, we calculate $\mathcal{T}_1$ and $\mathcal{T}_2$ in the hodograph plane formulation where $\nu = 1$, $QL = 2\pi$, $\Phi = 1$ and we use the test function

$$\mathcal{U} = (\sin[\tau] \cos[\pi v/2] + 2, \sin[\tau] \cos[\pi v/2] + 2). \quad (3.4.14)$$

In figure 3.9 we show that $\mathcal{T}_2 \sim O(k^2)$ as $k \rightarrow 0$. The quadratic convergence of $\mathcal{T}_2$ for both methods assures us that our linearisation is correct.

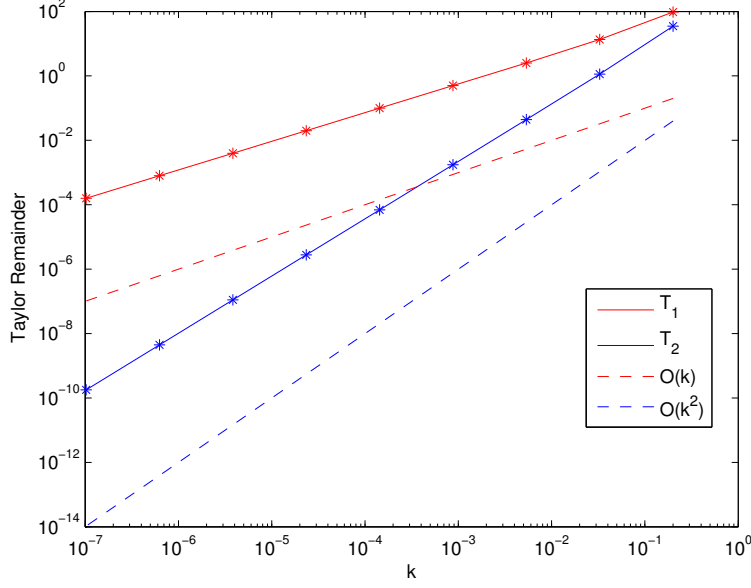


Figure 3.9: Taylor test for the hodograph plane formulation.

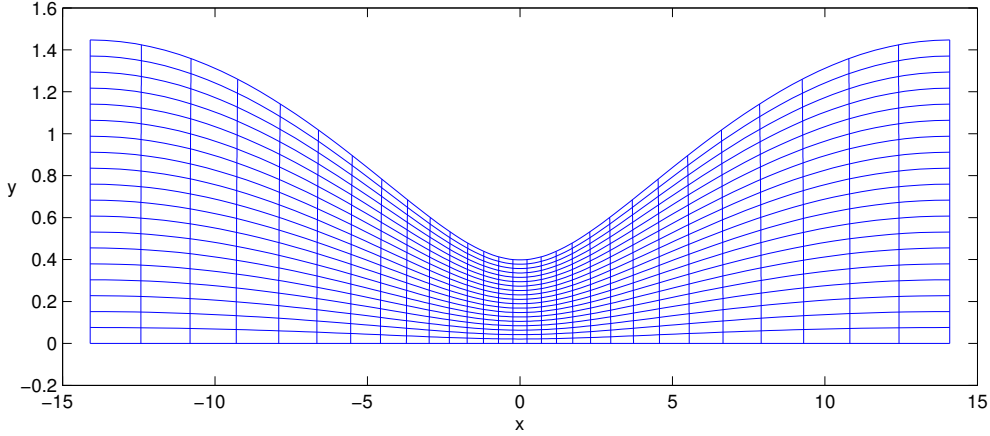


Figure 3.10: Domain used for validation.

3.4.3.2 Spectral convergence test

We now investigate the convergence for both the conformal map formulation and the hodograph plane formulation for the same test problem. The domain considered is produced using (3.3.36) with $L \approx 28.2$, $\varepsilon = 0.57$, and $\eta^* = 0.84$ and is shown in figure 3.10. We also let $\Phi = 1$ and $\nu = 0.2$ in our numerical test. We are able to use the results from the conformal map formulation to determine the inputs to the hodograph plane formulation. We use (3.3.31) to determine QL and the function $y = F(\tau)$ is obtained numerically by using the functionality of **Chebfun**.

To examine the convergence of the numerical method we fix the number of points

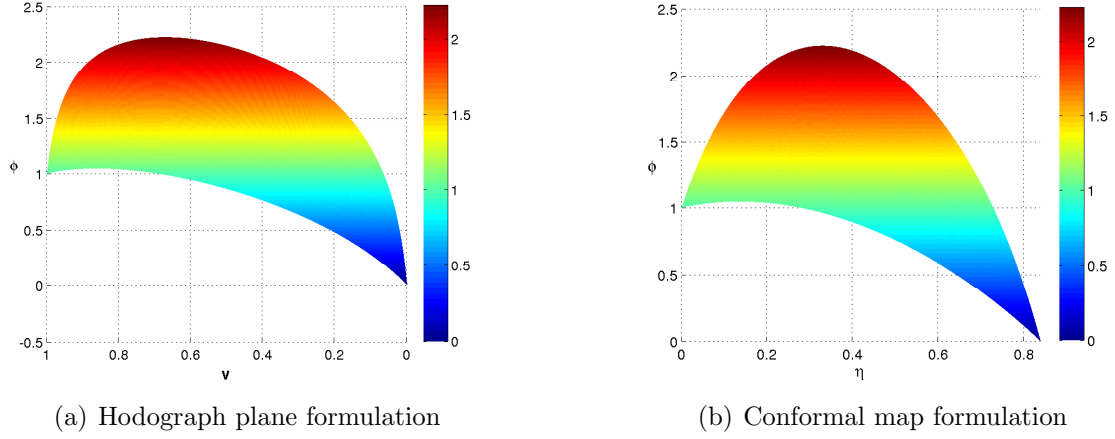


Figure 3.11: Electric potential ϕ in transformed domains for parameters $L \approx 28.2$, $\Phi = 1$, $\nu = 0.2$ and the physical domain given by figure 3.10.

in one direction and vary the number of points in the other and then observe how the integrated quantity Q converges by considering the quantities

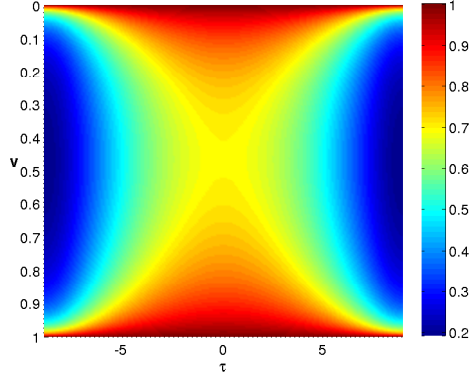
$$\Delta Q^{N_\xi} = |Q^{N_\xi+4} - Q^{N_\xi}|, \quad \Delta Q^{N_\eta} = |Q^{N_\eta+4} - Q^{N_\eta}|, \quad (3.4.15)$$

for the conformal map approach, and

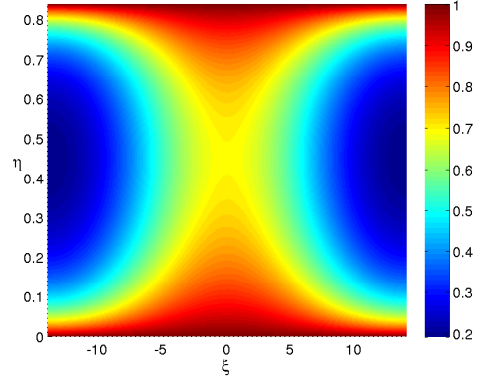
$$\Delta Q^{N_v} = |Q^{N_v+4} - Q^{N_v}|, \quad \Delta Q^{N_\psi} = |Q^{N_\psi+4} - Q^{N_\psi}|. \quad (3.4.16)$$

for the hodograph approach.

Tables 3.1(a)–3.1(d) show the results of our convergence tests and clearly demonstrate that both numerical methods rapidly converge to the same solution. We observe that the error decreases exponentially with the number of discretisation points, as expected for a spectral method. It is evident that fewer points are required in the conformal map formulation than the hodograph plane formulation to achieve the same accuracy. We believe that this occurs because the solutions for ϕ and n are smoother in the conformal mapping plane than in the hodograph plane. In figures 3.11 and 3.12 we demonstrate the different structures for ϕ and n in the transformed domains. Figure 3.11 shows that steeper gradients in ϕ are present in the v -direction in the hodograph plane formulation than in the η direction in the conformal map formulation. Similarly, figure 3.12 shows that there are steeper gradients in n in the τ -direction in the hodograph plane formulation than in the ξ direction in the conformal map formulation. The presence of the steeper gradients means that more points are needed to obtain a fully resolved solution. Additionally, we find in the hodograph plane formulation the numerical method is sensitive to sharp gradients in the function $y(0, \tau) = F(\tau)$.



(a) Hodograph plane formulation



(b) Conformal map formulation

Figure 3.12: Electron density n in transformed domains for parameters $L \approx 28.2$, $\Phi = 1$, $\nu = 0.2$ and the physical domain given by figure 3.10.

Table 3.1: Convergence Tests

(a) Convergence of conformal map formulation in ξ direction, where $N_\eta = 31$.

N_ξ	Q^{N_ξ}	ΔQ^{N_ξ}
4	0.63598	8.5×10^{-5}
8	0.63607	5.7×10^{-8}

(b) Convergence of conformal map formulation in η direction, where $N_\xi = 12$.

N_η	Q^{N_η}	ΔQ^{N_η}
7	0.46937	1.6×10^{-1}
11	0.62815	7.6×10^{-3}
15	0.63574	3.2×10^{-4}
19	0.63605	1.2×10^{-5}
23	0.63607	4.4×10^{-7}
27	0.63607	1.5×10^{-8}

(c) Convergence of hodograph plane formulation in v direction, where $N_\tau = 32$.

N_v	Q^{N_v}	ΔQ^{N_v}
17	0.63110	4.5×10^{-3}
21	0.63561	4.0×10^{-4}
25	0.63600	5.0×10^{-5}
29	0.63606	7.0×10^{-6}
33	0.63606	1.1×10^{-6}
37	0.63607	2.1×10^{-7}
41	0.63607	4.7×10^{-8}

(d) Convergence of hodograph plane formulation in τ direction, where $N_v = 45$.

N_τ	Q^{N_τ}	ΔQ^{N_τ}
4	0.57976	5.1×10^{-2}
8	0.63071	4.8×10^{-3}
12	0.63554	4.7×10^{-4}
16	0.63601	4.7×10^{-5}
20	0.63606	4.8×10^{-6}
24	0.63607	4.8×10^{-7}
28	0.63607	4.9×10^{-8}

3.4.4 Discussion

In this section we have demonstrated the implementation of a new numerical recipe that can be used to solve for the electron density and electric potential in both the conformal

mapping and the hodograph plane formulations. The linearisation for the Newton iteration and the exponential convergence of the numerical method has been validated for both implementations. The agreement that we find between the different implementations for the solution of the same problem gives high confidence in both methods.

The solution of problems with moderately small values of ν are efficiently solved by our numerical recipe with the spectral method coping well with the boundary layers present at the interfaces. However, in the limit where $\nu \rightarrow 0$ the problem becomes increasingly stiff and these boundary layers, that we characterised in 1D in §2.3.5, become incredibly sharp so that a large number of grid points are required to resolve them. Increasing the number of grid points increases the computation time and the memory required to converge to a solution.

Even though the hodograph plane formulation intuitively appears to be a more natural coordinate system for the problem, we find that the mapping introduces sharp gradients in the solution structure of ϕ and n and therefore actually adds to the numerical difficulty. On the other hand, as discussed in §3.3.4, the hodograph plane formulation has the advantage of easy calculation of the trajectories and cumulative current when compared with the conformal map formulation.

For solution on an arbitrary domain we have been unable so far to produce an efficient iterative procedure to find the corresponding $y = F(\tau)$ in the hodograph plane formulation and therefore recommend the use of the conformal map formulation with a numerical Schwarz-Christoffel map. When considering slowly varying domains the hodograph plane formulation is the most suited as we can make use of asymptotic calculations, outlined in Section 3.6.1, to specify an appropriate $y = F(\tau)$. The conformal map formulation with the analytic mapping function (3.3.36) is better for solving in wedge-like domains.

3.5 Example numerical solutions

3.5.1 Smooth domain

We consider the domain shown in figure 3.13 where $h_{\min} = 0.06$, $L \approx 31.4$, the radius of curvature at $h_{\min}$ is $a \approx 1.7$ and

$$F(\tau) = h_{\min} \sec^2 \left(\frac{\tau}{\Phi} \sqrt{\frac{h_{\min}}{2a}} \right) \quad (3.5.1)$$

in the central region, where the edges are patched to polynomials (this choice will be justified below in Section 3.6.1). For illustration, we set $\Phi = 1$ and $\nu = 0.1$, since we expect the normalised Debye length to be small in practice. In figure 3.14 we plot the numerical solutions for ϕ and n . We observe boundary layers at the two surfaces

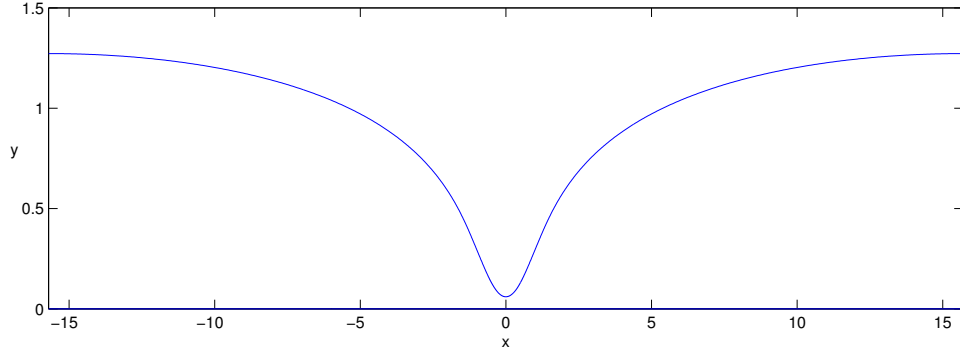


Figure 3.13: Example slowly varying domain used; $h_{\min} = 0.06$ and the radius of curvature at the minimum is $a \approx 1.7$.

of the glass layer away from the minimum $h = h_{\min}$. Near the minimum, however, we see that $n \approx 1$ while ϕ varies approximately linearly across the layer. Both of these structures were found in Chapter 2 in limiting one-dimensional solutions, see §2.3.5 and §2.3.3 respectively. The presence of the large electron density in the central region means we expect the majority of the current to be collected there. This is visible in figure 3.15 where the electron trajectories are plotted with equal current between each pair of trajectories, and are largely concentrated around $h = h_{\min}$. Also figure 3.15(b) displays the quasi-1D nature of the solution near $h = h_{\min}$, as the electron trajectories have little x -variation. This quasi-1D behaviour is due to the slowly varying top surface: note the different axes scalings in figure 3.13.

The effective resistance of the domain in figure 3.13 with $\nu = 0.1$ and $\Phi = 1$ is $R = 1.35$. On the other hand, with $\nu = 0.1$ and $\Phi = 1$, a uniform glass layer with the same average thickness has an effective resistance $R = 5.30$. Therefore the short circuiting causes a reduction in the net resistance by a factor of approximately 4.

3.5.2 Wedge-like domain

We will now analyse a wedge domain where we let $\Phi = 1$, $\nu = 0.05$, $h_{\min} = 0.01$, $L \approx 5.4$ and $\beta = \pi/4$. The corresponding parameter values in the mapping function (3.3.36) are $\varepsilon \approx 0.016$ and $\eta^* \approx 0.34$. The domain is shown in figure 3.16.

In figure 3.17 the numerical solutions for ϕ and n are plotted. These figures exhibit the same general features as figures 3.14(a) and 3.14(b), with a boundary layer structure away from $h = h_{\min}$ and a region of high current density near $h = h_{\min}$. The short circuiting of the current through the thinner region is demonstrated by plotting the cumulative current distribution in figure 3.18. We observe that over 80% of the current is collected within a neighbourhood $[-0.25, 0.25]$ of $x = 0$. In figure 3.18 we include the corresponding curve for a glass layer with constant thickness for a reference. In general, the more concave the

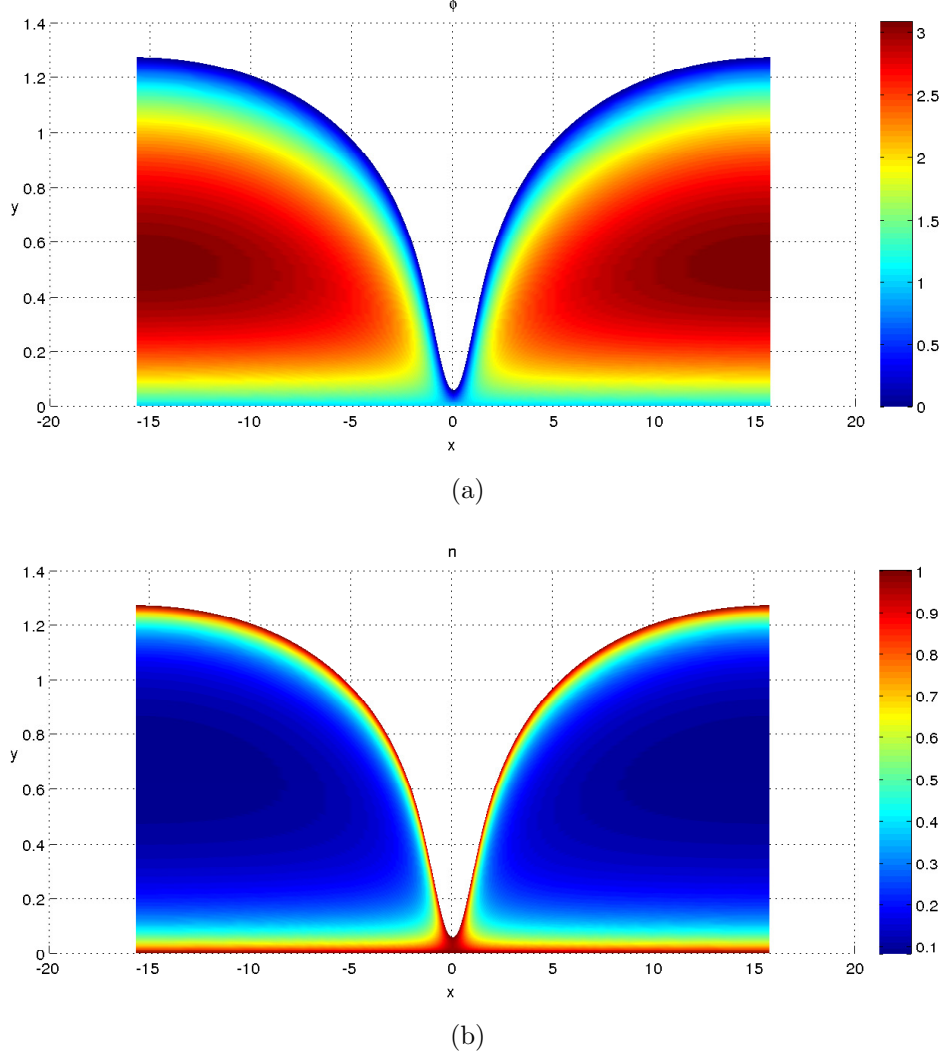
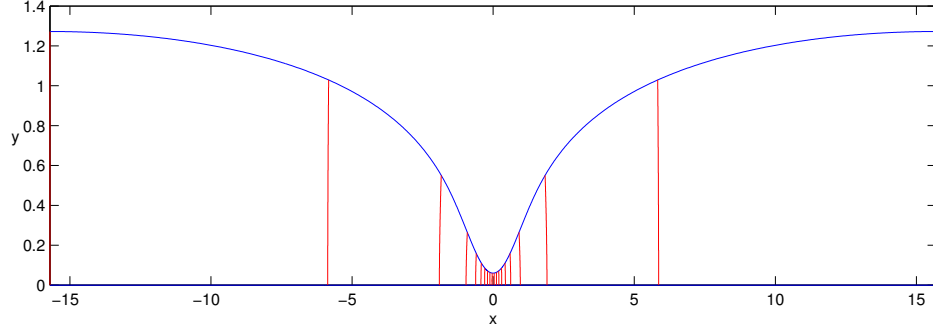
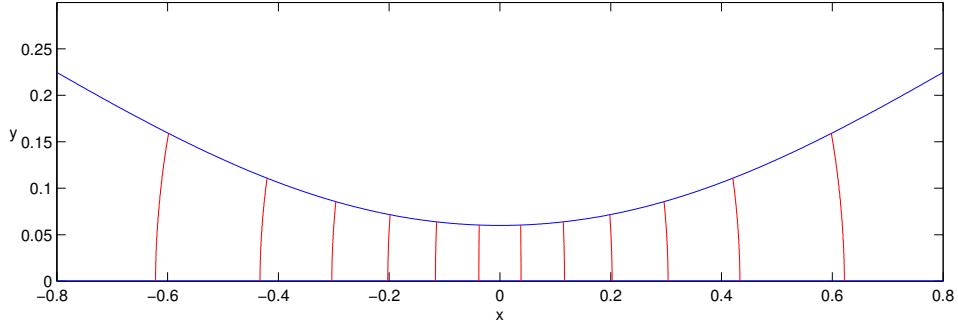


Figure 3.14: Electric potential ϕ and electron density n plotted against position x and y with parameter values $\nu = 0.1$, $\Phi = 1$, $L \approx 31.4$ and $Q = 0.74$.

normalised cumulative current is, the more the current is short circuiting through the region around $h = h_{\min}$. Finally, the effective resistance for domain shown in figure 3.16, with $\Phi = 1$ and $\nu = 0.05$, is $R = 0.6$. For comparison, with the same values for Φ and ν , the resistance of a uniform glass layer with the same average thickness is $R = 15.0$. This example illustrates the dramatic effect that nonuniform thickness may have on the net resistance: here the short circuiting of the current causes a reduction in the resistance by a factor of 25. The increased difference between these values when compared with those in §3.5.1 is mainly due to the smaller values of $h_{\min}$ and ν used.



(a) Full domain electron trajectories



(b) Central region electron trajectories

Figure 3.15: Electron trajectories through the glass layer. An equal current is carried between each pair of adjacent trajectories.

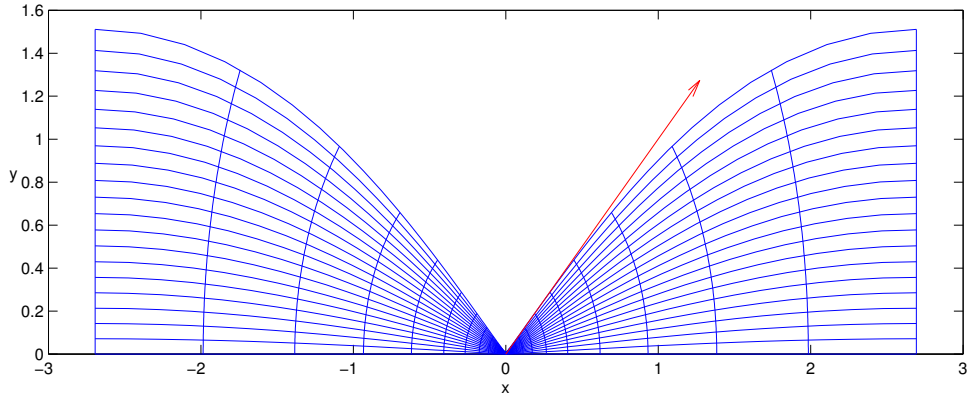


Figure 3.16: Example wedge domain used, $h_{\min} = 0.01$, $L \approx 5.4$, $\varepsilon \approx 0.016$, $\eta^* \approx 0.34$ and the red arrow indicates the angle $\beta = \pi/4$.

3.5.3 Summary

We have considered some example cases and found that short circuiting through the thinner regions of the glass layer causes a significant reduction in resistance when compared with a constant thickness domain. This behaviour motivates us to seek asymptotic ex-

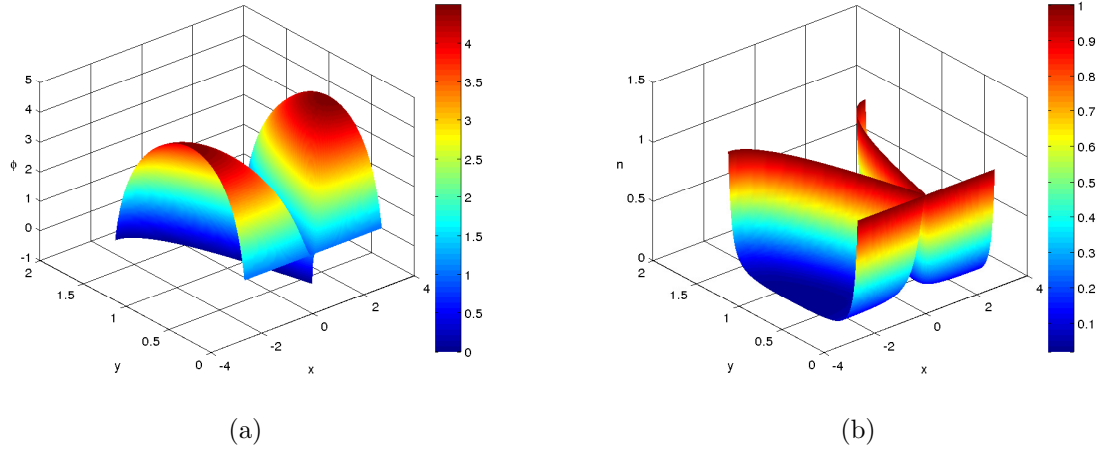


Figure 3.17: Electric potential ϕ and electron density n plotted against position x and y with parameter values $\nu = 0.05$, $\Phi = 1$ and $Q = 1.70$.

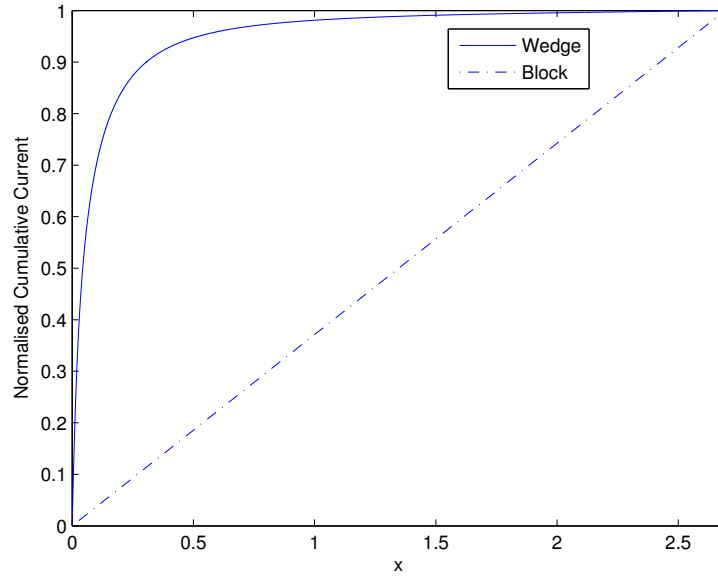


Figure 3.18: Normalised cumulative current, (3.2.7), plotted against horizontal position x . 'Wedge' is the normalised cumulative current for the domain shown in figure 3.16, and 'Block' is the corresponding curve for a glass layer with constant thickness.

pressions for the average current density as the minimum thickness $h_{\min} \rightarrow 0$. We will see that the solution structure depends crucially on whether the local behaviour is “slowly varying” or “wedge-like”.

3.6 Asymptotic analysis

3.6.1 Slowly varying domain

We now calculate an approximation to the average current density in the limit $h_{\min} \rightarrow 0$ where the local radius of curvature, $a \gg h_{\min}$. It follows that the thickness profile near the local minimum is indeed slowly varying and is approximated by a parabola

$$h(x) \sim h_{\min} + \frac{x^2}{2a} \quad (3.6.1)$$

with local aspect ratio $\delta_2 = (h_{\min}/2a)^{1/2} \ll 1$. We focus on this region by performing the rescalings

$$y = h_{\min} Y \quad x = (2ah_{\min})^{1/2} X. \quad (3.6.2)$$

The electron flux takes the form $\mathbf{j} = h_{\min}^{-1}(\delta_2 I, J)$ and, to lowest order in δ_2 , the problem (3.2.1)–(3.2.4) is quasi-one-dimensional, i.e.

$$J_Y = 0, \quad J = -n\phi_Y - n_Y, \quad (\nu/h_{\min})^2 \phi_{YY} = -n, \quad (3.6.3)$$

subject to the boundary conditions

$$\begin{aligned} \phi &= \Phi, & n &= 1 & \text{at } Y &= 0, \\ \phi &= 0, & n &= 1 & \text{at } Y &= 1 + X^2. \end{aligned} \quad (3.6.4)$$

The problem now depends on X only parametrically, and the transformations

$$\hat{Y} = \frac{Y}{1 + X^2}, \quad \hat{J} = (1 + X^2)J, \quad \hat{\nu} = \frac{\nu}{h_{\min}(1 + X^2)}, \quad (3.6.5)$$

reduce (3.6.3)–(3.6.4) to the corresponding purely one-dimensional problem

$$\frac{d\hat{J}}{d\hat{Y}} = 0, \quad \hat{J} = -n \frac{d\phi}{d\hat{Y}} - \frac{dn}{d\hat{Y}}, \quad \hat{\nu}^2 \frac{d^2\phi}{d\hat{Y}^2} = -n, \quad (3.6.6)$$

$$\phi(0) = \Phi, \quad n(0) = 1 \quad \phi(1) = 0, \quad n(1) = 1, \quad (3.6.7)$$

which corresponds to the model (2.2.7)–(2.2.9) in Chapter 2 with $\alpha = 1$. From Chapter 2, we recall that the electron flux $j_{1D} = j_{1D}(\nu, \Phi, \alpha)$ and we therefore denote the solution for the current in this one-dimensional problem by $\hat{J} = j_{1D}(\hat{\nu}, \Phi, 1)$.

By applying the transformations carried out above on (3.2.6), we deduce that the average current density of the layer in the limit $\delta_2 \rightarrow 0$ is approximated by

$$Q \sim \frac{1}{L} \sqrt{\frac{2a}{h_{\min}}} \int_{-\infty}^{\infty} j_{1D} \left(\frac{\nu}{h_{\min}(1 + X^2)}, \Phi, 1 \right) \frac{dX}{1 + X^2}. \quad (3.6.8)$$

The function $j_{1D}(\hat{\nu}, \Phi)$ is, in general, determined numerically; however we found various analytic approximations in limiting cases in Chapter 2. In particular, in Section 2.3.4 we found that, in the limit $\hat{\nu} \rightarrow \infty$, the layer acts as a resistor with

$$\phi \sim \Phi(1 - \hat{Y}), \quad n \sim 1, \quad j_{1D} \sim \Phi. \quad (3.6.9)$$

If $h_{\min} \ll \nu$, i.e. the minimum thickness is smaller than the Debye length, we may therefore use $j_{1D} \approx \Phi$ to approximate (3.6.8) as

$$Q \sim \frac{\pi\Phi}{L} \sqrt{\frac{2a}{h_{\min}}}. \quad (3.6.10)$$

Now we wish to test the approximation (3.6.10) against our numerical results. As noted in Section 3.3.4, the hodograph formulation is most suited when *a priori* knowledge of an appropriate $y = F(\tau)$ is known. Here we can use the asymptotic behaviour of the solution 3.6.9 to determine the corresponding local behaviour of $F(\tau)$ near the minimum thickness, namely we find

$$\tau \sim \frac{\Phi}{\delta_2} \int_0^X \frac{d\tilde{X}}{1 + \tilde{X}^2}, \quad (3.6.11)$$

which we use along with the relation $y = h_{\min}(1 + X^2)$ to determine

$$F(\tau) \sim h_{\min} \sec^2 \left(\frac{\delta_2 \tau}{\Phi} \right). \quad (3.6.12)$$

Note that we expect $\tau = O(1/\delta_2)$ as $\delta_2 \rightarrow 0$. Evidently (3.6.12) breaks down as $\delta_2 \tau \rightarrow \Phi\pi/2$ and $X \rightarrow \pm\infty$. In any case, the numerical scheme requires $F(\tau)$ to be periodic, which we achieve by patching the edges of (3.6.12) to suitable polynomials. A selection of domains used for comparison to our asymptotic expression are shown in figure 3.19, where, in a similar manner to the conformal map formulation, the average thickness of the glass layer is taken to be 1 for each domain.

In figure 3.20 we demonstrate that the asymptotic expression (3.6.10) gives a good approximation to the results of numerical simulations for the average current density Q as $\delta_2 \rightarrow 0$. This analysis accentuates how short circuiting through any thin spots in the glass layer may dominate the overall flux. However, the approximation (3.6.10) rests on the assumption that $h_{\min} \ll a$, and will therefore fail if the curvature of the glass surface is too large in the neighbourhood of the minimum. To describe the local behaviour in such sharp “wedge-like” domains, a different asymptotic approach is required, as will be demonstrated below.

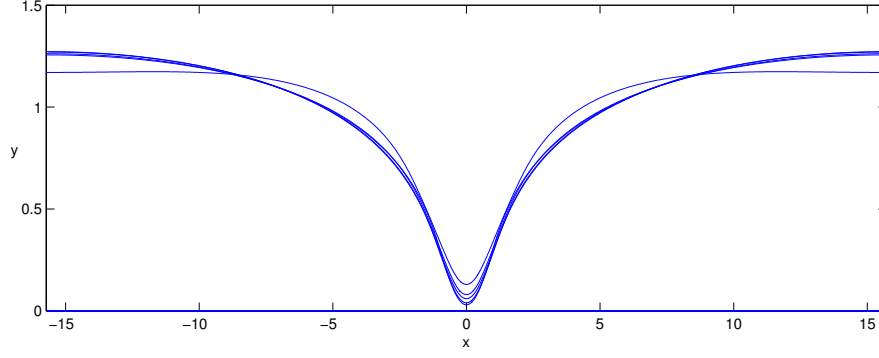


Figure 3.19: Slowly varying domains considered where $L \approx 31.4$, $h_{\min} \in [0.03, 0.13]$ and $a \in \approx [1.6, 1.8]$.

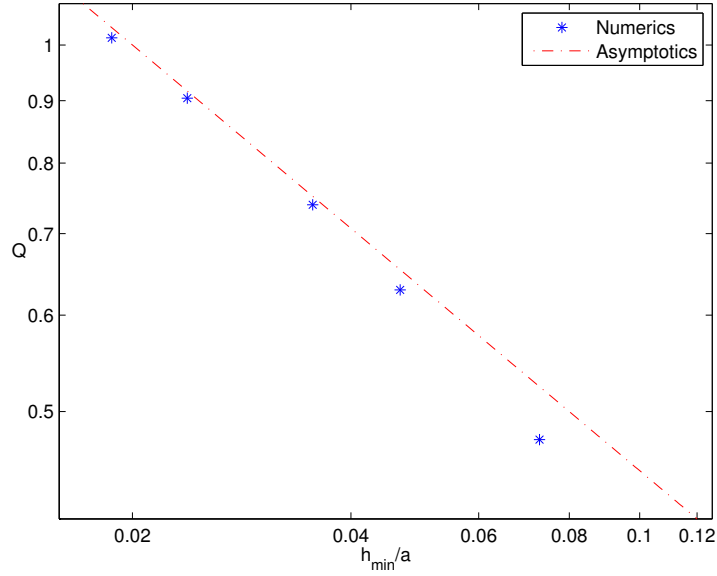


Figure 3.20: Average current density Q plotted against glass layer minimum thickness $h_{\min}/a$, where $\Phi = 1$, $\nu = 0.1$, $L \approx 31.4$ and $h_{\min}/a \in \approx [0.019, 0.073]$. The asterisks show the results of numerical simulations; the dot-dashed curve shows the asymptotic expression (3.6.10).

3.6.2 Wedge-like domain

3.6.2.1 Introduction

In this section we investigate the behaviour of the average current density in a wedge-like domain, with $a = O(h_{\min})$ as $h_{\min} \rightarrow 0$. If we naively set $h_{\min} = 0$, we are left with the “outer” problem illustrated in figure 3.21(a): the glass layer thickness reaches zero with a corner singularity at (without loss of generality) $x = 0$. The problem is regularised over a small region in which $(x, y) = h_{\min}(\tilde{x}, \tilde{y})$, as illustrated in figure 3.21(b). In this “inner”

problem, the glass layer has unit minimum thickness and approaches a wedge shape as $(\tilde{x}, \tilde{y}) \rightarrow \infty$. In the next sections we analyse the inner and outer problems and match them asymptotically to obtain an approximation for the net flux through the layer.

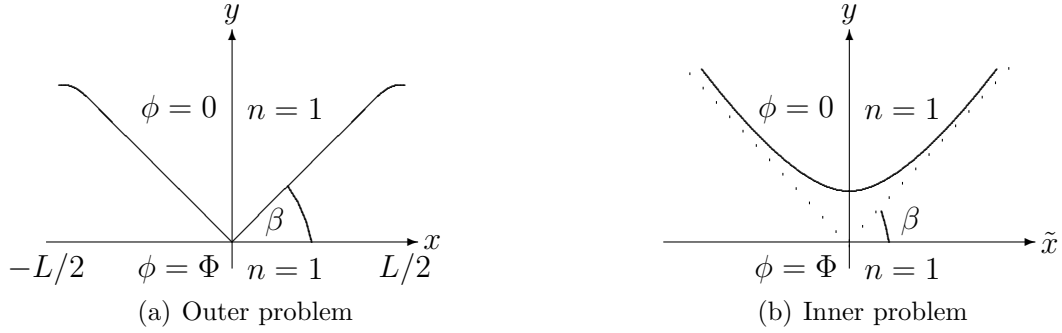


Figure 3.21: Schematics of outer and inner problems.

3.6.2.2 Outer problem

The outer problem, namely the full governing equations (3.2.1)–(3.2.3) with the boundary conditions shown in figure 3.21(a), requires numerical solution in general. For matching purposes, we only require the asymptotic behaviour of the solution approaching the wedge tip. To find this we first formulate (3.2.1)–(3.2.3) in plane polar coordinates (r, θ)

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial n}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 n}{\partial \theta^2} + \frac{1}{r^2} \frac{\partial n}{\partial \theta} \frac{\partial \phi}{\partial \theta} + \frac{\partial n}{\partial r} \frac{\partial \phi}{\partial r} = \frac{n^2}{\nu^2}, \quad (3.6.13)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} + \frac{n}{\nu^2} = 0, \quad (3.6.14)$$

and then consider the limit $r \rightarrow 0$. Taking (3.6.13)–(3.6.14), considering the limit $r \rightarrow 0$, and making the ansatz

$$\phi \sim \hat{\phi}_0(\theta) + r^2 \hat{\phi}_1(\theta) + \dots, \quad (3.6.15)$$

$$n \sim \hat{n}_0(\theta) + r^2 \hat{n}_1(\theta) + \dots, \quad (3.6.16)$$

we find to leading order our governing equations are

$$\frac{\partial^2 \hat{n}_0}{\partial \theta^2} + \frac{\partial \hat{n}_0}{\partial \theta} \frac{\partial \hat{\phi}_0}{\partial \theta} = 0, \quad (3.6.17)$$

$$\frac{\partial^2 \hat{\phi}_0}{\partial \theta^2} = 0, \quad (3.6.18)$$

with boundary conditions

$$\hat{\phi}_0(r, \beta) = 0, \quad \hat{n}_0(r, \beta) = 1, \quad \hat{\phi}_0(r, 0) = \Phi, \quad \hat{n}_0(r, 0) = 1. \quad (3.6.19)$$

The solution to this outer problem in the limit $r \rightarrow 0$ is then found to be

$$\phi \sim \Phi \left(1 - \frac{\theta}{\beta} \right) + O(r^2), \quad n \sim 1 + O(r^2), \quad (3.6.20)$$

where

$$\mathbf{j} \sim \frac{\Phi}{\beta r} \mathbf{e}_\theta + O(r). \quad (3.6.21)$$

3.6.2.3 Inner problem

In the inner problem we scale $(x, y) = h_{\min}(\tilde{x}, \tilde{y})$ and let $h_{\min} \rightarrow 0$ while expanding the solution as

$$n \sim \tilde{n}_0 + h_{\min}^2 \tilde{n}_1 + \dots, \quad \phi \sim \tilde{\phi}_0 + h_{\min}^2 \tilde{\phi}_1 + \dots. \quad (3.6.22)$$

In the limit $h_{\min} \rightarrow 0$, $h_{\min}/\nu \ll 1$ and we therefore find that $\tilde{n}_0 = 1$ and $\tilde{\phi}_0$ satisfies Laplace's equation

$$\frac{\partial^2 \tilde{\phi}_0}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{\phi}_0}{\partial \tilde{y}^2} = 0, \quad (3.6.23)$$

subject to the boundary conditions shown in figure 3.21(b). In principle, this problem is easily solved by conformal mapping. Assuming that the inner geometry shown in figure 3.21(b) is the image of a strip $0 \leq \text{Im}(\tilde{\zeta}) \leq 1$ under the conformal map

$$\tilde{z} = \tilde{x} + i\tilde{y} = \tilde{f}(\tilde{\zeta}) = \tilde{f}(\tilde{\xi} + i\tilde{\eta}), \quad (3.6.24)$$

then the solution in the strip is given by

$$\tilde{\phi}_0 = \Phi(1 - \tilde{\eta}). \quad (3.6.25)$$

Here we have assumed that $\tilde{f}$ maps the real line to itself and also fixes the points 0, i and ∞ . For example, the locally hyperbolic upper surface described by (3.3.42) corresponds to the mapping function

$$\tilde{f}(\tilde{\zeta}) = \frac{\sinh(\beta \tilde{\zeta})}{\sin \beta}. \quad (3.6.26)$$

To test our asymptotic calculations we make use of the mapping (3.6.26) and consider the numerical solution of the electron density and electric potential in the vicinity of the wedge tip for the problem where $\beta = \pi/4$, $h_{\min} = 0.01$, $L \approx 5.4$, $\nu = 0.05$, $\Phi = 1$ and $Q \approx 1.70$. In figure 3.22 we see that the numerical solution for the electron density n agrees with the asymptotic prediction $n \sim 1$. Figure 3.23 shows the reasonable agreement between the asymptotic and numerical solutions for the electric potential.

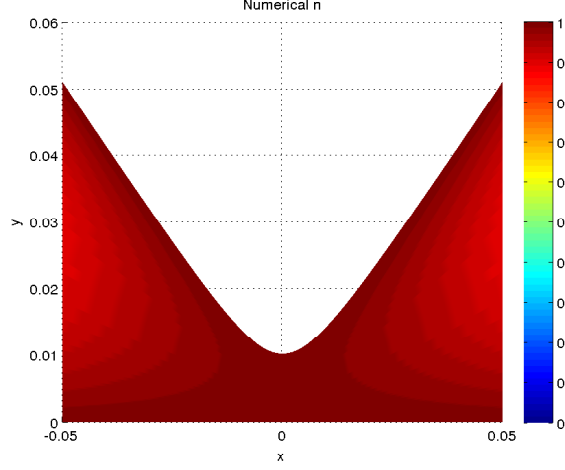


Figure 3.22: Numerical solution for the electron density n plotted against position x and y where $\beta = \pi/4$, $h_{\min} = 0.01$, $L \approx 5.4$, $\nu = 0.05$, $\Phi = 1$ and $Q \approx 1.70$.

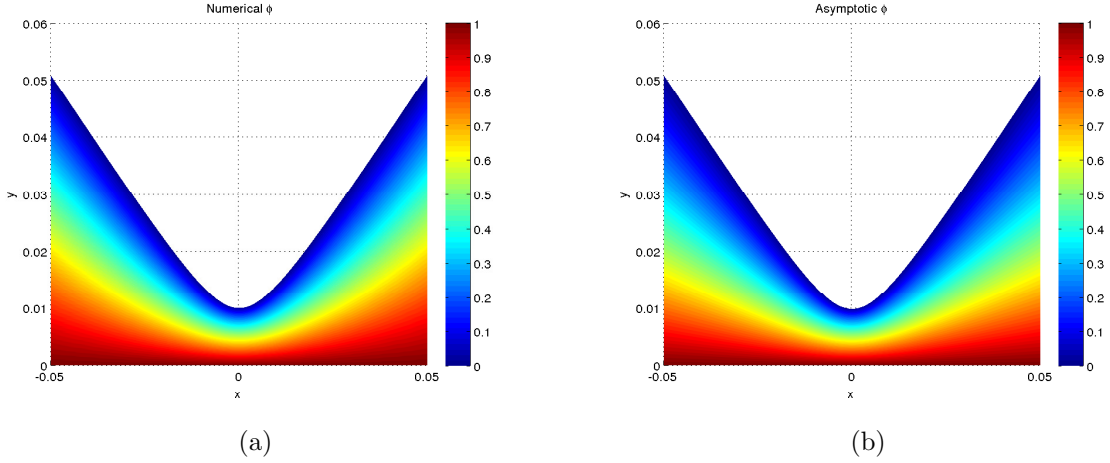


Figure 3.23: Numerical and asymptotic solutions for electric potential ϕ plotted against position x and y where $\beta = \pi/4$, $h_{\min} = 0.01$, $L \approx 5.4$, $\nu = 0.05$, $\Phi = 1$ and $Q \approx 1.70$. The asymptotic solution is found using the expression (3.6.25) and the mapping (3.6.26).

3.6.2.4 Average current density approximation

Now we find the leading-order average current density through the layer by integrating over the inner and outer regions. Assuming symmetry about the y -axis, we have

$$Q = \frac{2}{L} \left(\underbrace{\int_{\lambda}^{L/2} \left[-n \frac{\partial \phi}{\partial y} - \frac{\partial n}{\partial y} \right]_{y=0} dx}_{I_{\text{out}}} + \underbrace{\int_0^{\lambda/h_{\min}} \left[-\tilde{n} \frac{\partial \tilde{\phi}}{\partial \tilde{y}} - \frac{\partial \tilde{n}}{\partial \tilde{y}} \right]_{\tilde{y}=0} d\tilde{x}}_{I_{\text{in}}} \right), \quad (3.6.27)$$

where λ is assumed to satisfy $h_{\min} \ll \lambda \ll 1$, and I_{out} , I_{in} are the contributions from the outer and inner regions respectively. We know from (3.6.21) that the outer integral I_{out}

diverges logarithmically as $\lambda \rightarrow 0$ and, by subtracting the singular part, we obtain

$$I_{\text{out}} \sim \int_0^{L/2} \left[-n \frac{\partial \phi}{\partial y} - \frac{\partial n}{\partial y} - \frac{\Phi}{\beta x} \right]_{y=0} dx + \frac{\Phi}{\beta} \log \left(\frac{L}{2\lambda} \right). \quad (3.6.28)$$

For the inner contribution, we may perform the integral in the $\tilde{\zeta}$ -plane to obtain

$$I_{\text{in}} = \int_0^{\tilde{\xi}^*} \left[-\tilde{n} \frac{\partial \tilde{\phi}}{\partial \tilde{\eta}} - \frac{\partial \tilde{n}}{\partial \tilde{\eta}} \right]_{\tilde{\eta}=0} d\tilde{\xi} \sim \Phi \tilde{\xi}^*, \quad (3.6.29)$$

where $\tilde{\xi}^*$ is the point on the $\tilde{\xi}$ -axis corresponding to $\tilde{x} = \lambda/h_{\min}$, i.e.

$$\tilde{f}(\tilde{\xi}^*) = \frac{\lambda}{h_{\min}}. \quad (3.6.30)$$

Now, from the wedge geometry, we must have $\tilde{f}(\tilde{\zeta}) \sim b e^{\beta \tilde{\zeta}}$ as $\tilde{\zeta} \rightarrow \infty$, where b is a real constant that depends on the detailed inner geometry; for example, for the mapping function (3.6.26) inverting the relation (3.6.30) and considering the limit $h_{\min} \rightarrow 0$ gives $b = 1/(2 \sin \beta)$. Hence the leading-order inner integral is given by

$$I_{\text{in}} \sim \frac{\Phi}{\beta} \log \left(\frac{\lambda}{b h_{\min}} \right) + O(h_{\min}^2). \quad (3.6.31)$$

Finally, by substituting (3.6.28) and (3.6.31) into (3.6.27), we obtain the following approximation for the average flux:

$$Q \sim \frac{2\Phi}{\beta L} \log \left(\frac{L}{h_{\min}} \right) + K_2, \quad (3.6.32)$$

where the order-one constant K_2 is given by

$$K_2 = \frac{2}{L} \int_0^L \left[-n \frac{\partial \phi}{\partial y} - \frac{\partial n}{\partial y} - \frac{\Phi}{\beta x} \right]_{y=0} dx - \frac{2\Phi}{\beta L} \log(2b). \quad (3.6.33)$$

3.6.2.5 Comparison between asymptotics and numerics

To validate our asymptotics we perform a sequence of simulations that fix the constant K_2 . We therefore consider a range of domains with the same β and L , as shown in figure 3.24, and take $\nu = 0.1$ and $\Phi = 1$ in each simulation. The consequence of fixing K_2 is that we must relax our condition that the average thickness is 1. The results are plotted in the linear-log plot in figure 3.25 where it is evident the asymptotic expression (3.6.32) gives a very good approximation for the average current density Q as $h_{\min}/L \rightarrow 0$. In principle, one could calculate K_2 by solving the outer problem but we curve-fit to find $K_2 \approx -0.87$ for this particular geometry. Similarly to §3.6.1 the analysis demonstrates how the overall flux is dominated by short circuiting through thinner regions.

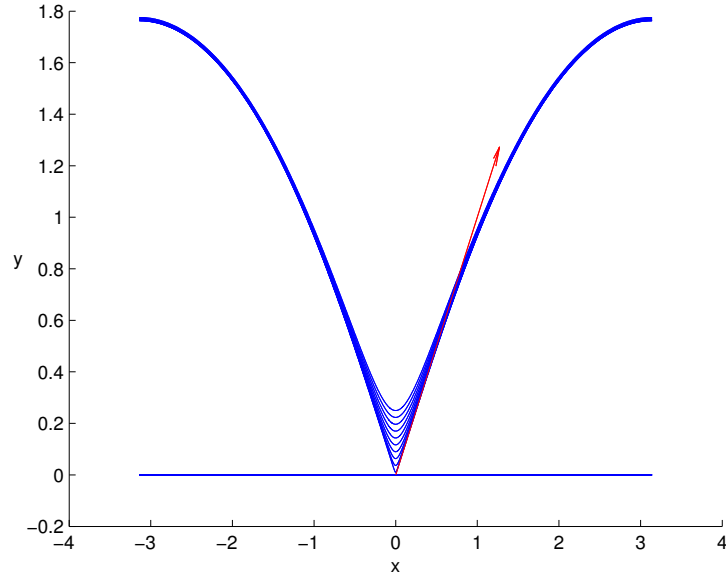


Figure 3.24: Wedge domains considered where $h_{\min} \in [0.01, 0.25]$, $L = 2\pi$ and the red arrow indicates the angle $\beta = \pi/4$.

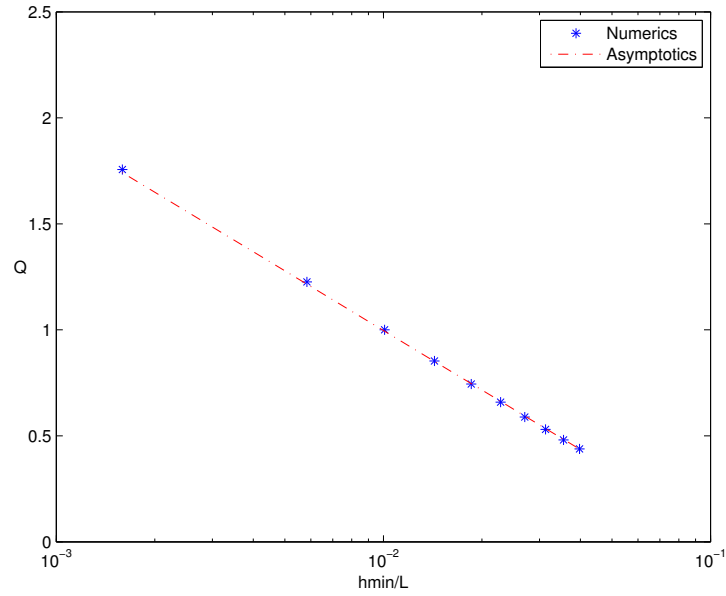


Figure 3.25: Average current density Q plotted against glass layer minimum thickness $h_{\min}$, where $\beta = \pi/4$, $\Phi = 1$, $\nu = 0.1$, $L = 2\pi$ and $h_{\min} \in [0.01, 0.25]$. The asterisks show the results of numerical simulations; the dot-dashed curve shows the asymptotic expression (3.6.32) where we fit to find for this geometry $K_2 \approx -0.87$.

3.7 Conclusions

In this chapter we extend to two dimensions the mathematical model from Chapter 2 for steady electron transport through a glass layer between two electrodes. We maintain many of the same modelling assumptions: that the charge is predominantly carried by electrons, that the electron flow is governed by drift and diffusion, and that the electron densities are known either side of the glass layer. The analysis focuses on the short-circuiting of current through thinner regions of the glass layer, and we present a spectral numerical method to solve the model once it has been mapped onto a rectangular domain.

We make use of two different mapping techniques; the appropriate approach to use in a given situation depends on the geometry under consideration and the questions one wishes to answer. In both cases, we demonstrate the capability of the numerical method through its exponentially rapid convergence and its ability to produce insightful results such as the electron trajectories and the normalised cumulative current. In considering nonuniform domains, the numerical results demonstrate how the current short-circuits through thinner regions of the glass. Consequently, the effective resistance is significantly lower than comparable domains with constant glass layer thickness.

We use the numerical simulations to inform asymptotic calculations conducted on domains with small minimum thickness $h_{\min}$. We consider two canonical local geometries. First we suppose that the thickness profile is smooth, and the local layer thickness is therefore “slowly varying” as $h_{\min} \rightarrow 0$. In this limit, we find that the current through the layer diverges like $Q \propto (a/h_{\min})^{1/2}$, where $a \gg h_{\min}$ is the local radius of curvature. The second regime considered is where $a = O(h_{\min})$, so that the local behaviour of the surface is “wedge-like”. In this latter case, we find it convenient to characterise the domain using the apparent angle, β , which the wedge makes with the horizontal, and find a weaker logarithmic divergence of the current, $Q \propto -1/\beta \log(h_{\min})$, as $h_{\min} \rightarrow 0$. Both predictions are found to agree well with full numerical calculations.

The importance of the short-circuiting effects enables us to conclude that the resistance of the glass layer and therefore the effective contact resistance is determined by the number and breadth of regions of the glass layer where the glass layer thickness is much smaller than the Debye length and not the average thickness of the glass layer.

Chapter 4

Density gradient theory

4.1 Introduction

In Chapter 3 we extended the model presented in Chapter 2 to consider short circuiting through the thinner regions of the glass layer. The thickness of the glass layer in the thin regions can be as small as 10nm. At the 10nm length scale it is possible that quantum mechanical effects will have an affect on the resistance of the glass layer and the electron density distribution in the glass layer [77]. In this chapter we investigate two different methods for including quantum mechanical effects into charge transport models: (i) density gradient confinement theory (DGC) and (ii) density gradient tunnelling theory (DGT); see §1.8 for more details. DGC theory is the lowest-order quantum correction to the drift diffusion equations and therefore is only strictly applicable when quantum effects are a small perturbation to the system, but, is often used to describe situations where quantum mechanical effects are significant [1, 6, 10, 12, 13, 35, 99]. The less widely used DGT theory is used when modelling the ballistic dominated quantum mechanical tunnelling that is known to take place on length scales $\approx 1\text{--}3\text{nm}$ [6].

In §4.2 we use DGC theory to introduce quantum mechanical effects into the one-dimensional model of electron flow across a glass layer outlined in Chapter 2. We find that the quantum mechanical effects change the distribution of the electron density in the glass layer but the effects are unmeasurable on the macroscopic scale. In §4.3 we investigate DGT theory for modelling charge transport in metal-insulator-metal devices by first summarising and second extending the work of Ancona [4]. We find that DGT theory produces physically reasonable results and perform an asymptotic analysis to characterise the solution structure of the electron density within the insulator. Finally, in §4.4 we summarise our findings and compare the two methods for including quantum mechanical effects.

4.2 Density gradient confinement theory

4.2.1 Nondimensional model

To apply DGC theory to our one-dimensional mathematical model of electron flow through a glass layer we include a longer-range interaction term (that henceforth we refer to as the quantum term) in (2.2.7). As discussed in §1.8, this term is formulated by assuming that the non-locality of quantum mechanics can be approximated by letting the energy densities of the electron and hole gases depend on the spatial gradients of the charged particle densities. Including the longer-range interaction term from (1.8.1a) into (2.2.4) and nondimensionalising with the scalings introduced in (2.2.6) we find that the governing equations become

$$\frac{dj}{dx} = 0, \quad (4.2.1)$$

$$j = -n \frac{d\phi}{dx} - \frac{dn}{dx} + \delta_3^2 n \frac{d}{dx} \left(\frac{1}{\sqrt{n}} \frac{d^2 \sqrt{n}}{dx^2} \right), \quad (4.2.2)$$

$$\nu^2 \frac{d^2 \phi}{dx^2} = -n. \quad (4.2.3)$$

The addition of the higher-order quantum term means that we also add an additional ‘quantum boundary condition’ into (2.2.9) to obtain the following

$$n(0) = \alpha, \quad \phi(0) = \Phi, \quad n(1) = 1, \quad \phi(1) = 0, \quad \frac{1}{\sqrt{n}} \frac{d^2 \sqrt{n}}{dx^2} \Big|_{x=0,1} = 0. \quad (4.2.4)$$

The physical reasoning for the additional boundary condition is given in §1.8. The resistance is calculated using (2.2.12), and the dimensionless parameters α and ν are those defined in (2.2.10), whilst the dimensionless quantum parameter δ_3 is given by

$$\delta_3 = \frac{\hbar}{\sqrt{2m_n r_n k_B T H^2}}. \quad (4.2.5)$$

The quantum parameter δ_3 is the scaled electron quantum length. The electron quantum length defines the length scale over which quantum mechanical behaviour arises and is of the order of the wavelength associated with an electron (the de Broglie wavelength) [6].

To estimate the value of δ_3 , we assume Planck’s constant $\hbar$ is $1.04 \times 10^{-34} \text{m}^2 \text{kg s}^{-1}$, Boltzmann’s constant k_B is $1.38 \times 10^{-23} \text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$, the absolute temperature T is 300K, the statistical factor r_n is 3, as is often found in “high” temperature experiments [5], and the thickness of the glass layer is in the range $H \in (10^{-8} \text{m}, 10^{-6} \text{m})$. The mass of a free electron, $9.11 \times 10^{-31} \text{kg}$, is a suitable approximation for the effective electron mass m_n in the glass layer as the estimated effective electron mass in silicon [95] and the various estimated values for silicon dioxide [102] are all of the order of the mass

of a free electron. We therefore conclude that the dimensionless quantum parameter $\delta_3 \in (10^{-3}, 10^{-1})$. By assuming the absolute permittivity ϵ of the glass is that of silicon dioxide ($3.45 \times 10^{-11} \text{Fm}^{-1}$) we find the important ratio δ_3/ν is given by

$$\frac{\delta_3^2}{\nu^2} \approx 9 \times 10^{-26} \text{m}^3 \times n_1, \quad (4.2.6)$$

where in Chapter 2 we estimated that $n_1 \in (10^{20} \text{m}^{-3}, 10^{28} \text{m}^{-3})$. Taking into account the calculations carried out above we assume $\delta_3 \ll 1$ and $\delta_3 \lesssim O(\nu)$ in all following calculations.

4.2.2 Numerical solution

To obtain a numerical solution we substitute (4.2.2) into (4.2.1) enabling us to rewrite the governing equations and boundary conditions (4.2.1)–(4.2.4) as

$$n'' = -n'\phi' + \frac{n^2}{\nu^2} + \frac{\delta_3^2}{2} \left(-\frac{2n'^4}{n^3} + \frac{5n'^2 n''}{n^2} - 2\frac{n'^2 + n' n'''}{n} + n'''' \right), \quad (4.2.7)$$

$$\nu^2 \phi'' = -n, \quad (4.2.8)$$

$$n(0) = \alpha, \quad \phi(0) = \Phi, \quad n(1) = 1, \quad \phi(1) = 0, \quad \frac{2nn'' - n'^2}{4n^2} \Big|_{x=0,1} = 0. \quad (4.2.9)$$

We find the numerical solution is facilitated by introducing

$$\bar{u} = \log n, \quad (4.2.10)$$

to make the governing equations

$$\nu^2 \phi'' = -e^{\bar{u}}, \quad 0 = \phi' \bar{u}' - \frac{e^{\bar{u}}}{\nu^2} + \bar{u}'' + \bar{u}'^2 - \frac{\delta_3^2}{2} (\bar{u}'^2 \bar{u}'' + 2\bar{u}' \bar{u}''' + \bar{u}''^2 + \bar{u}^{iv}), \quad (4.2.11)$$

and the boundary conditions

$$\bar{u}(0) = \log \alpha, \quad \phi(0) = \Phi, \quad \bar{u}(1) = 0, \quad \phi(1) = 0, \quad \frac{1}{4}(\bar{u}'^2 + 2\bar{u}'') \Big|_{x=0,1} = 0. \quad (4.2.12)$$

We calculate j by reversing the substitution (4.2.10), taking (4.2.2) and rearranging to find

$$\frac{j}{n} = -\frac{d}{dx} \left(\phi + \log n + \frac{1}{\sqrt{n}} \frac{d^2 \sqrt{n}}{dn^2} \right), \quad (4.2.13)$$

integrating over the domain, and finally applying the boundary conditions (4.2.4) to give

$$j = \frac{\Phi + \log \alpha}{\int_0^1 \frac{dx}{n(x)}}. \quad (4.2.14)$$

The evaluation of the integral in (4.2.14) and the numerical solution of (4.2.11)–(4.2.12) is performed using the spectral software package **Chebfun**. The numerical results are plotted below after we have performed the corresponding asymptotic analysis.

4.2.3 Resistance

In this section we investigate the effect the quantum term has on the resistance of the glass layer when $\delta_3 \ll 1$ and $\delta_3 \lesssim O(\nu)$ in the different asymptotic regions explored in §2.3.

In the regions where $\nu \geq O(1)$ and in the regions where $j \gg 1$ it is straightforward to show that the leading-order problem remains unchanged with the introduction of the quantum term. This means that the leading-order expressions for the resistance of the glass layer in these regions

$$\begin{aligned}
R &\sim R_0(\alpha, \nu), & \text{where } \nu &= O(1), j \ll 1, \\
R &\sim \frac{\alpha - 1}{\alpha \log \alpha}, & \text{where } \nu &\gg 1, j \ll 1, \\
R &\sim \frac{(\Phi + \log \alpha)(1 - e^\Phi)}{\Phi(1 - \alpha e^\Phi)}, & \text{where } \nu &\gg 1, \Phi = O(1), \\
R &\sim \frac{1}{\alpha}, & \text{where } \nu &\geq O(1), j \gg 1, \\
R &\sim \frac{2\sqrt{2}}{3\nu\sqrt{j}} \left[\left(1 + \frac{\nu^2 j}{2\alpha^2}\right)^{3/2} - \left(\frac{\nu^2 j}{2\alpha^2}\right)^{3/2} \right], & \text{where } \nu &\ll 1, \nu\sqrt{j} = O(1),
\end{aligned}$$

still hold. In the small Debye length limit where $\delta_3 = O(\nu) \ll 1$ the quantum term enters at leading order in the boundary layers at the interfaces, however, in §4.2.3.1 below we demonstrate that since the outer problem and its matching conditions remain unchanged, the leading-order outer solution remains unchanged.

4.2.3.1 Small Debye length: $\delta_3 = O(\nu) \ll 1, \nu\sqrt{j} \ll O(1)$

In the small Debye length limit, where $\nu \rightarrow 0, \delta_3 \rightarrow 0, \nu\sqrt{j} \ll O(1)$ and $\delta_3 = O(\nu)$, we hypothesise that $j = O(\nu^2)$ as in §2.3.5 and expect that $n = O(\nu^2)$ away from the boundaries. Near the boundaries there are boundary layers in order to satisfy the $O(1)$ boundary conditions for n at $x = 0$ and $x = 1$.

The leading-order equations away from the boundaries are (2.3.28) and therefore if we make the substitution $\phi = 2 \log(U/\nu)$ the general solution takes the same form as (2.3.29) and is given by

$$U = a_1 \text{Ai}(\chi x - \bar{w}) + b_1 \text{Bi}(\chi x - \bar{w}), \quad (4.2.15)$$

where a_1, b_1 and $\bar{w}$ are integration constants. The general solution of the leading-order outer problem is unchanged by the introduction of the quantum term, however, the quantum term is present at leading order in the the Debye layer and therefore will alter the solution profile of ϕ and n in the Debye layer. We now demonstrate that since the

far field behaviour of the inner solution is unchanged by the introduction of the quantum term the boundary conditions applied to the outer problem are unchanged. Therefore the key macroscopic quantity of resistance is unchanged by the introduction of the quantum term.

We first consider the boundary layer at $x = 0$ and make the rescaling $x = \nu X_0$ before letting $\nu \rightarrow 0$ so that (4.2.2) and (4.2.3) become

$$0 = -n\phi_{X_0} - n_{X_0} + \frac{\delta_3^2}{\nu^2} n \frac{d}{dX_0} \left(\frac{\sqrt{n}_{X_0 X_0}}{\sqrt{n}} \right), \quad (4.2.16)$$

$$\phi_{X_0 X_0} = -n. \quad (4.2.17)$$

Integrating (4.2.16) we find

$$d = -\phi - \log n + \frac{\delta_3^2}{\nu^2} \frac{\sqrt{n}_{X_0 X_0}}{\sqrt{n}}, \quad (4.2.18)$$

where d is a constant of integration. By using the boundary conditions (4.2.4) we find $d = -\Phi + \log \alpha$ and therefore

$$-\Phi + \log \alpha = -\phi - \log n + \frac{\delta_3^2}{\nu^2} \frac{\sqrt{n}_{X_0 X_0}}{\sqrt{n}}. \quad (4.2.19)$$

To match with the outer Airy solution (4.2.15) in the limit $X_0 \rightarrow \infty$ we must have ϕ and n of the form

$$\phi \sim d_1 + 2 \log X_0, \quad (4.2.20a)$$

$$n \sim \frac{2}{X_0^2}, \quad (4.2.20b)$$

where d_1 is a constant. Finally, substituting (4.2.20) into (4.2.19) to determine d_1 we find in the limit $X_0 \rightarrow \infty$

$$\phi \sim \Phi + \log \left(\frac{\alpha}{2} \right) + 2 \log X_0, \quad (4.2.21a)$$

$$n \sim \frac{2}{X_0^2}. \quad (4.2.21b)$$

To consider the boundary layer at $x = 1$ we make the substitution $x = 1 - \nu X_1$, and follow a similar method, to find, in the limit $X_1 \rightarrow \infty$ that

$$\phi \sim -\log 2 + 2 \log X_1, \quad (4.2.22a)$$

$$n \sim \frac{2}{X_1^2}. \quad (4.2.22b)$$

By matching (4.2.15) with (4.2.21) and (4.2.22) we obtain the system of equations

$$a_1 \text{Ai}(-\bar{w}) + b_1 \text{Bi}(-\bar{w}) = 0, \quad (4.2.23a)$$

$$a_1 \text{Ai}(\chi - \bar{w}) + b_1 \text{Bi}(\chi - \bar{w}) = 0, \quad (4.2.23b)$$

$$\chi \{a_1 \text{Ai}'(-\bar{w}) + b_1 \text{Bi}'(-\bar{w})\} = e^{\Phi/2} \sqrt{\frac{\alpha}{2}}, \quad (4.2.23c)$$

$$\chi \{a_1 \text{Ai}'(\chi - \bar{w}) + b_1 \text{Bi}'(\chi - \bar{w})\} = -\frac{1}{\sqrt{2}}. \quad (4.2.23d)$$

Equations (4.2.23) are identical to the system (2.3.30) presented in Chapter 2 and therefore $a_1 \equiv a_0$, $b_1 \equiv b_0$ and $\bar{w} \equiv w$. Thus the leading-order outer problems are equivalent in the drift diffusion and DGC models, with the result that the quantum term does not alter the electron flux. Moreover, the asymptotic expressions for resistance in the limit $\nu \rightarrow 0$ found in Chapter 2 ((2.3.38) and (2.3.40)) are also valid for the DGC equations where $\delta_3 = O(\nu) \ll 1$.

In figure 4.1 we plot the solution of the DGC system (4.2.11)–(4.2.12) where $\Phi = 0.0507$, $\nu = 0.01$, $\alpha = 1$ and $\delta_3 = 0.01$. These parameter values are chosen for illustrative purposes. We also plot the solution of the DD system (2.2.7)–(2.2.9) with the same values of Φ , ν and α for comparison. We demonstrate that the outer asymptotic solution for ϕ and n (found by making use of (2.3.28) and (4.2.15), and solving the system (4.2.23) to determine a_1 , b_1 , $\bar{w}$ and Φ) gives a good approximation to both numerical solutions away from the boundaries, and that the DD electron flux (j^{DD}) is approximately the same as the DGC electron flux (j^{DGC}).

4.2.3.2 Comparison between asymptotics and numerics

In figure 4.2 we plot the resistance R versus the electron flux j with parameter values $\nu = 0.01$, $\alpha = 1$ and $\delta_3 = 0.01$. The red solid curve shows the DD numerical solution and the green solid curve shows the DGC numerical solution, both obtained using **Chebfun**. We find that the leading-order expressions for resistance calculated in Chapter 2 give a good approximation to the DGC numerical solution up to $j \approx 10^2$, where the numerics fail due to the increasing stiffness of the problem. In addition, up to $j \approx 10^2$ the DGC numerical solution and DD numerical solution show excellent agreement. As $j \rightarrow \infty$ our asymptotic analysis informs us that the DGC numerical solution should continue to follow the DD numerical solution and therefore we conclude the addition of the quantum term causes a negligible effect on the resistance of the glass layer.

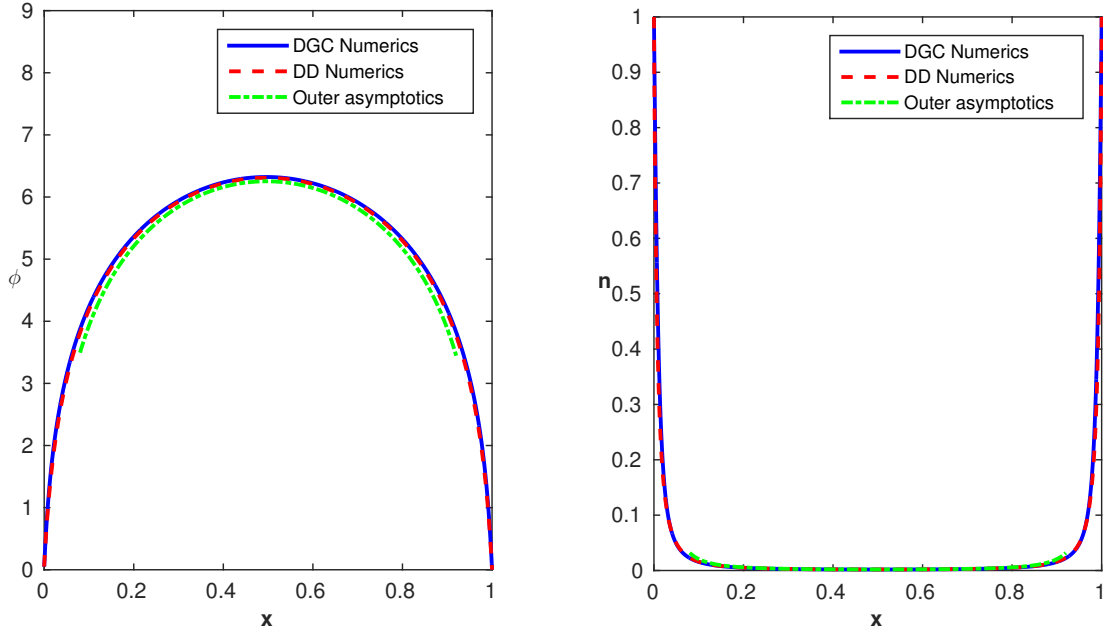


Figure 4.1: Electric potential ϕ and electron density n plotted against position x where $\nu = 0.01$, $\alpha = 1$ and $\delta_3 = 0.01$. The numerical solutions are found by specifying $\Phi = 0.0507$ to determine $j^{DGC} \approx j^{DD} \approx 0.0002$. The asymptotic solution is found by specifying $j = 0.0002$ to determine $\Phi \approx 0.0507$.

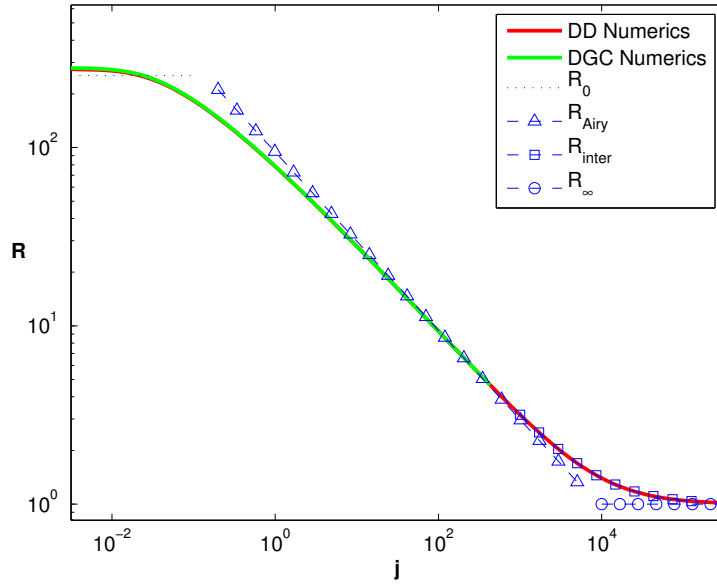


Figure 4.2: Resistance R plotted against electron flux j with $\nu = 0.01$, $\alpha = 1$ and $\delta_3 = 0.01$: numerical solution (solid red); small- j estimate (2.3.13) (dotted); $j \gtrsim 1$ approximation (2.3.40) (triangles); intermediate approximation (2.3.46) (squares); large- j limit (2.3.18) (circles).

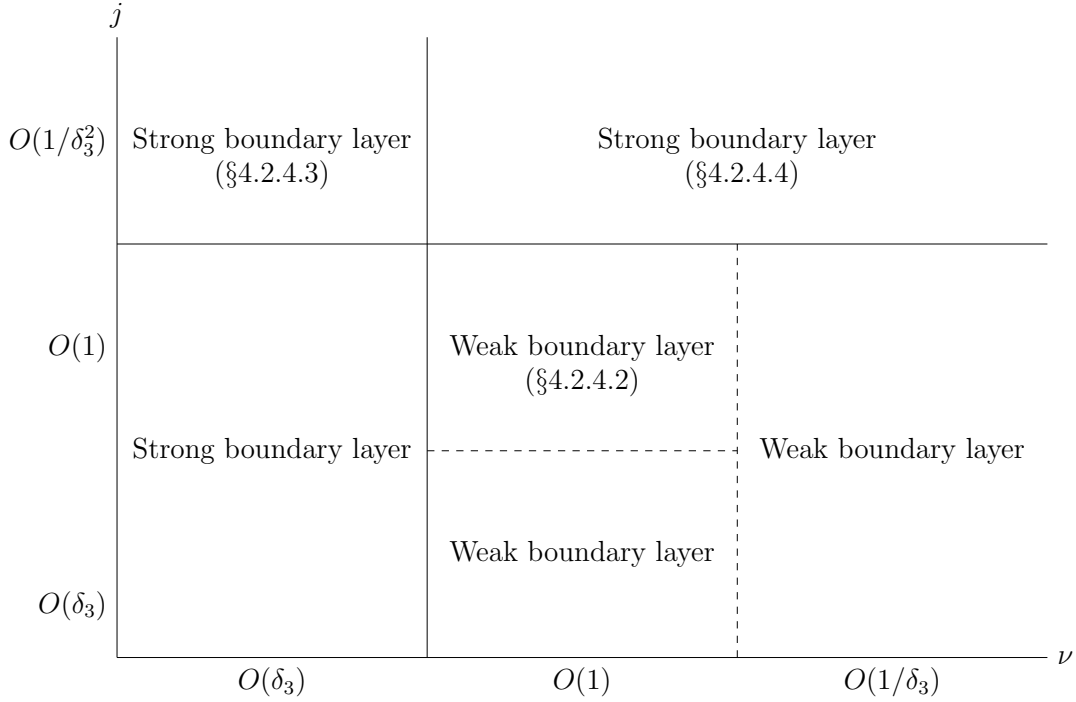


Figure 4.3: Diagram showing the type of boundary layer present in various different asymptotic regimes.

4.2.4 Quantum boundary layers

4.2.4.1 Overview

The inclusion of the higher order quantum term into (4.2.2) means that additional boundary conditions are required. The outer solution does not in general satisfy these additional boundary conditions and we therefore expect to see the presence of quantum boundary layers in the solution profiles of the electric potential ϕ and electron density n . In this section, we determine the structure of the quantum boundary layers as j and ν vary where $\delta_3 \ll 1$ and $\delta_3 \leq O(\nu)$. Figure 4.3 gives a summary of the results of this section, showing the type of quantum boundary layer in the various asymptotic regimes explored. The label ‘Weak boundary layer’ refers to regions where the quantum term does not have an order-one effect on ϕ or n . In contrast, the ‘Strong boundary layer’ label refers to regions where the quantum term does cause an order-one change in the profile of ϕ or n . The strong boundary layer occurs where the scaled Debye length $\sim$ quantum parameter or where there is an appreciable electron flux in the boundary layer. In the region where $\nu = O(\delta_3)$ and $j \lesssim O(1)$, the profiles of ϕ and n in the boundary layer are found by solving (4.2.17) and (4.2.19). We will not investigate this region further in this chapter.

4.2.4.2 Weak boundary layers

In figure 4.3 several asymptotic regions are labelled ‘Weak boundary layer’. For illustrative purposes we analyse the regime where $\nu = O(1)$, $j = O(1)$. We first consider the boundary at $x = 0$, and, making the rescaling $x = \delta_3 X_2$, we find to leading order

$$0 = -n \frac{d\phi}{dX_2} - \frac{dn}{dX_2} + n \frac{d}{dX_2} \left(\frac{1}{\sqrt{n}} \frac{d^2 \sqrt{n}}{dX_2^2} \right), \quad (4.2.24)$$

$$\frac{d^2 \phi}{dX_2^2} = 0. \quad (4.2.25)$$

Making use of the boundary conditions (4.2.4) we find in the boundary layer

$$\phi \sim \Phi, \quad n \sim \alpha. \quad (4.2.26)$$

Similar analysis can be performed at the boundary $x = 1$ to find the leading-order solutions

$$\phi \sim 0, \quad n \sim 1. \quad (4.2.27)$$

The constant solutions found in the boundary layers means that to leading-order the solution profiles of ϕ and n are unchanged, as shown in figure 4.4. In the large Debye length limit and the small electron flux limit the constant boundary layer solutions are also found. We demonstrate the excellent agreement between the DD numerical solution and the DGC numerical solution in the large Debye length limit and the small electron flux limit in figures 4.5 and 4.6 respectively.

4.2.4.3 Large electron flux: $j \gg 1$, $\delta_3 \ll 1$, $\nu \gtrsim O(1)$

In the large electron flux limit, the leading-order solution for n (2.3.15b) found in Chapter 2 satisfies the quantum boundary condition at $x = 0$ and therefore we focus on the boundary layer at $x = 1$. We begin by making the following rescalings

$$x = 1 + \delta_3^{4/3} X_3, \quad \phi = \delta_3^{-2/3} \varphi, \quad j = \delta_3^{-2} \mathcal{J}. \quad (4.2.28)$$

Substituting 4.2.28 into (4.2.2)–(4.2.3), we find to leading order that

$$\mathcal{J} = -n \varphi_{X_3} + n \left(\frac{\sqrt{n}_{X_3 X_3}}{\sqrt{n}} \right)_{X_3}, \quad (4.2.29)$$

$$\varphi_{X_3 X_3} = 0. \quad (4.2.30)$$

Solving (4.2.30) and matching to the outer solution (2.3.15a), found in Chapter 2, we determine that

$$\varphi = -\frac{\mathcal{J}}{\alpha} X_3. \quad (4.2.31)$$

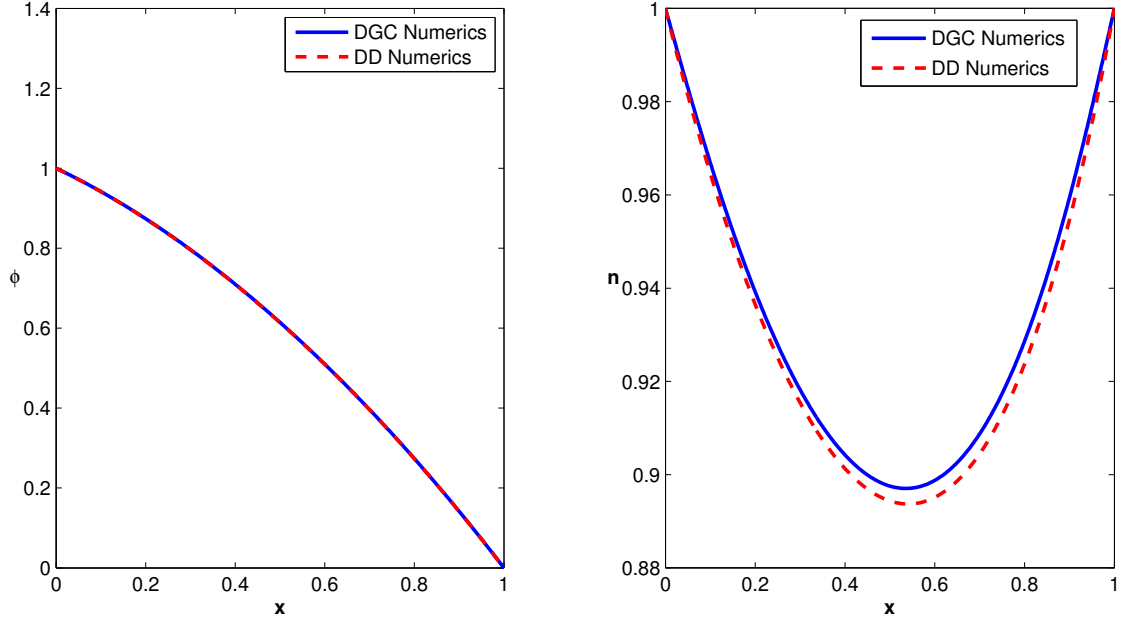


Figure 4.4: Electric potential ϕ and electron density n plotted against position x where $\Phi = 1$, $\nu = 1$, $\alpha = 1$, $\delta_3 = 0.1$ and $j^{DGC} \approx j^{DD} \approx 0.93$.

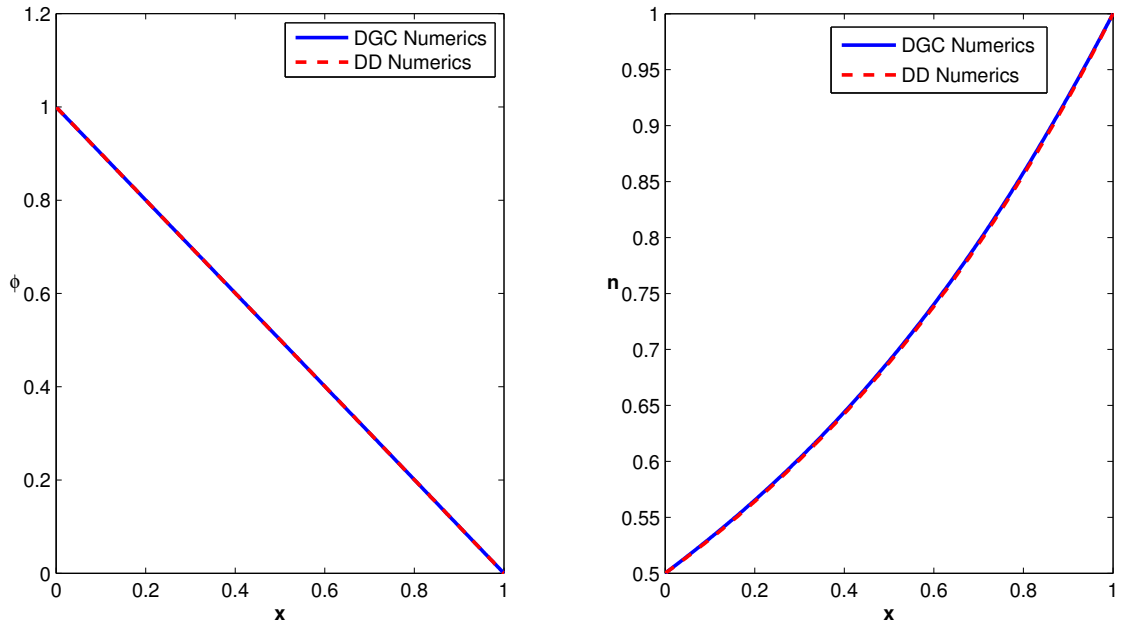


Figure 4.5: Electric potential ϕ and electron density n plotted against position x where $\Phi = 1$, $\nu = 10$, $\alpha = 0.5$, $\delta_3 = 0.1$ and $j^{DGC} \approx j^{DD} \approx 0.21$.

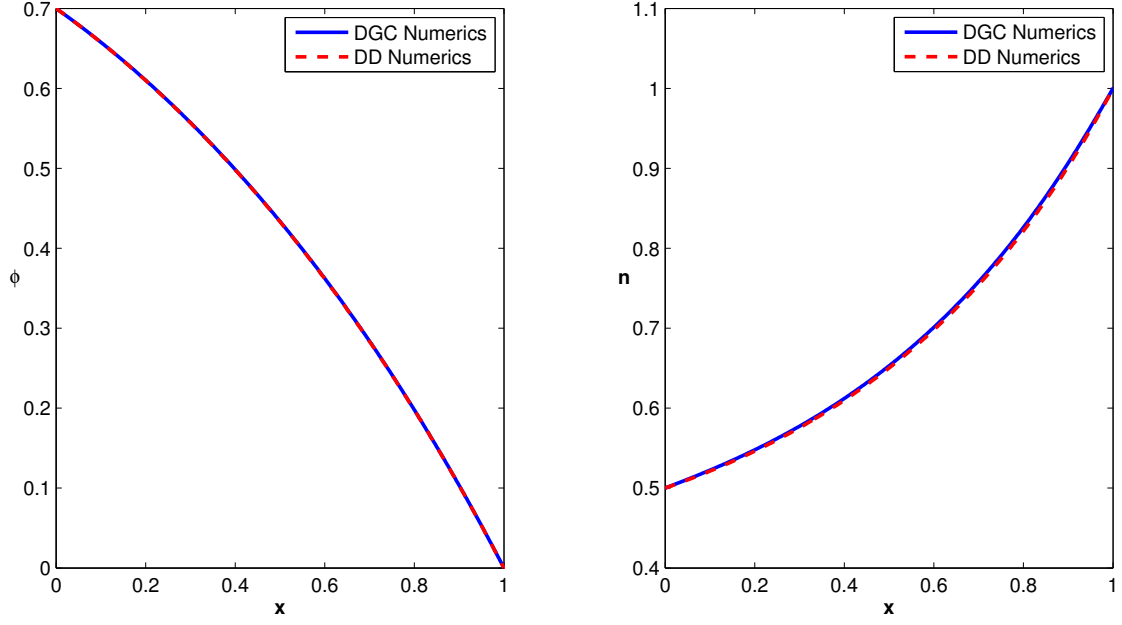


Figure 4.6: Electric potential ϕ and electron density n plotted against position x where $\Phi = 0.7$, $\nu = 1$, $\alpha = 0.5$, $\delta_3 = 0.1$ and $j^{DGC} \approx j^{DD} \approx 0.0045$.

We use the expression (4.2.31) to find

$$\mathcal{J} = n \frac{\mathcal{J}}{\alpha} + n \left(\frac{\sqrt{n} X_3 X_3}{\sqrt{n}} \right)_{X_3}. \quad (4.2.32)$$

We normalise by letting $X_3 = (\alpha/\mathcal{J})^{1/3} \mathcal{X}$ and $n = \alpha \mathcal{N}$ so that (4.2.32) becomes

$$1 = \mathcal{N} + \mathcal{N} \left(\frac{\sqrt{\mathcal{N}} \mathcal{X} \mathcal{X}}{\sqrt{\mathcal{N}}} \right)_{\mathcal{X}}, \quad (4.2.33)$$

where

$$\mathcal{N} \rightarrow 1 \quad \text{as} \quad \mathcal{X} \rightarrow -\infty, \quad \mathcal{N}|_{\mathcal{X}=0} = \frac{1}{\alpha}, \quad \frac{1}{\mathcal{N}} \sqrt{\mathcal{N}} \mathcal{X} \mathcal{X}|_{\mathcal{X}=0} = 0. \quad (4.2.34)$$

We solve (4.2.33)–(4.2.34) numerically by shooting from $\mathcal{X} = -\infty$ to $\mathcal{X} = 0$. To determine an initial condition for the shooting method we linearise (4.2.33) as $\mathcal{N} = 1 + \bar{\mathcal{N}}$ to find

$$\frac{1}{2} \bar{\mathcal{N}}_{\mathcal{X} \mathcal{X} \mathcal{X}} + \bar{\mathcal{N}} \sim 0, \quad (4.2.35)$$

and therefore

$$\bar{\mathcal{N}} \sim e^{\mathcal{X}/2^{2/3}} \left[d_2 \cos \left(\sqrt{3}/2^{2/3} \mathcal{X} \right) + d_3 \sin \left(\sqrt{3}/2^{2/3} \mathcal{X} \right) \right], \quad (4.2.36)$$

where d_2 and d_3 are constants. The equation (4.2.33) for $\mathcal{N}$ is translationally invariant in $\mathcal{X}$ and so we write (4.2.36) as

$$\bar{\mathcal{N}} \sim e^{\hat{\mathcal{X}}/2^{2/3}} \left[d_4 \cos \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) \right], \quad (4.2.37)$$

where d_4 is a constant and $\hat{\mathcal{X}}$ is a translation of $\mathcal{X}$ given by $\hat{\mathcal{X}} = \mathcal{X} - \mathcal{X}^*$. We now formulate the shooting problem (4.2.33)–(4.2.34) as

$$1 = \mathcal{N} + \mathcal{N} \left(\frac{\sqrt{\mathcal{N}}_{\hat{\mathcal{X}}\hat{\mathcal{X}}}}{\sqrt{\mathcal{N}}} \right)_{\hat{\mathcal{X}}}, \quad (4.2.38)$$

where we shoot from $\hat{\mathcal{X}} = -\hat{\mathcal{X}}_{\text{Init}}$, where $\hat{\mathcal{X}}_{\text{Init}} \gg 1$, with initial conditions

$$\mathcal{N} = 1 + e^{\hat{\mathcal{X}}/2^{2/3}} \left[d_4 \cos \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) \right] \quad \text{at} \quad \hat{\mathcal{X}} = -\hat{\mathcal{X}}_{\text{Init}}, \quad (4.2.39)$$

$$\mathcal{N}_{\hat{\mathcal{X}}} = \frac{d_4 e^{\hat{\mathcal{X}}/2^{2/3}}}{2^{2/3}} \left[\cos \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) - \sqrt{3} \sin \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) \right] \quad \text{at} \quad \hat{\mathcal{X}} = -\hat{\mathcal{X}}_{\text{Init}}, \quad (4.2.40)$$

$$\mathcal{N}_{\hat{\mathcal{X}}\hat{\mathcal{X}}} = -\frac{d_4 e^{\hat{\mathcal{X}}/2^{2/3}}}{2^{1/3}} \left[\cos \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) + \sqrt{3} \sin \left(\sqrt{3}/2^{2/3} \hat{\mathcal{X}} \right) \right] \quad \text{at} \quad \hat{\mathcal{X}} = -\hat{\mathcal{X}}_{\text{Init}}. \quad (4.2.41)$$

We shoot until the condition

$$\frac{1}{\mathcal{N}} \sqrt{\mathcal{N}}_{\hat{\mathcal{X}}\hat{\mathcal{X}}} |_{\hat{\mathcal{X}}=\mathcal{X}^*} = 0 \quad (4.2.42)$$

is satisfied to determine $\mathcal{X}^*$ and therefore find

$$\mathcal{N} |_{\hat{\mathcal{X}}=\mathcal{X}^*} = \frac{1}{\alpha}. \quad (4.2.43)$$

The value of d_4 chosen is thus determined by α with the numerically computed relationship between α and d_4 plotted in figure 4.7.

In the limit $\alpha \rightarrow 1$ the initial condition (4.2.39) is valid throughout the domain. To determine $\mathcal{X}^*$ in the limit $\alpha \rightarrow 1$ we substitute (4.2.41) into (4.2.42) to find

$$\mathcal{X}^* \rightarrow -\frac{7 \cdot 2^{2/3} \pi}{6\sqrt{3}} \quad \text{as} \quad \alpha \rightarrow 1. \quad (4.2.44)$$

The relation between α and d_4 in the limit $\alpha \rightarrow 1$ is then obtained using (4.2.39), (4.2.43) and (4.2.44) to find

$$d_4 \sim \frac{2}{\sqrt{3}} \left(1 - \frac{1}{\alpha} \right) e^{7\pi/(6\sqrt{3})} \quad \text{as} \quad \alpha \rightarrow 1. \quad (4.2.45)$$

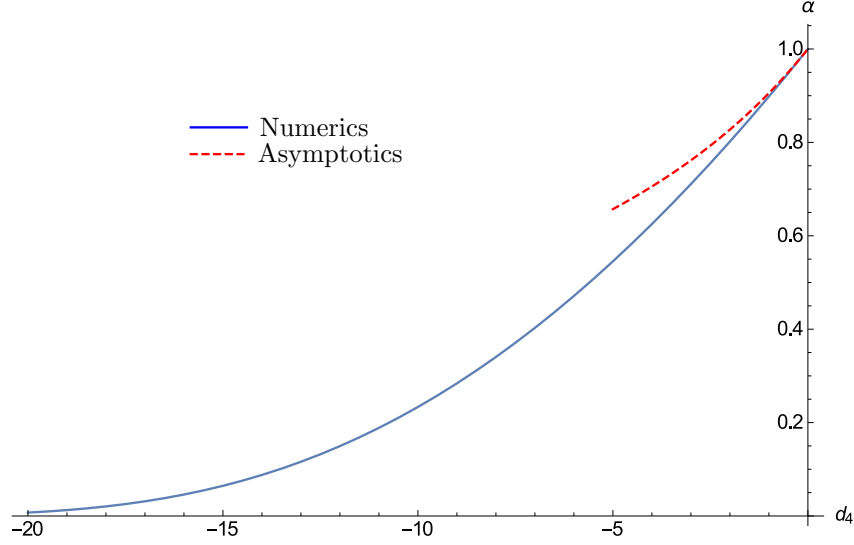


Figure 4.7: α plotted against d_4 .

We plot the asymptotic relation (4.2.45) in figure 4.7 as a dashed curve and see good agreement with the numerical solution in the limit $\alpha \rightarrow 1$.

In figure 4.8 we demonstrate the good agreement between the full numerical solution and the solution of the shooting problem in the boundary layer. It is striking that the quantum term has made a profound qualitative difference to the solution structure in the boundary layer, leading to significant oscillations in the electron density profile. Nevertheless, we reiterate that both the outer solution and the overall electron flux are not significantly affected.

4.2.4.4 Distinguished limit: $\delta_3 = O(\nu) \ll 1$, $\nu\sqrt{j} = O(1)$

We now consider the distinguished limit where $\nu\sqrt{j} = O(1)$ and $\delta_3 = O(\nu) \ll 1$. The key difference from §4.2.4.3 is that in this section $\nu \ll 1$.

In the regime where $\nu\sqrt{j} = O(1)$ and $\delta_3 = O(\nu) \ll 1$ we find a weak boundary layer at $x = 0$ where ϕ and n take the constant solutions (4.2.26). To investigate the boundary at $x = 1$ we make the following scalings

$$x = 1 + \nu^{4/3}X_4, \quad \phi = \nu^{-2/3}\hat{\phi}, \quad j = \nu^{-2}\tilde{J}, \quad \delta_3 = \sqrt{D}\nu, \quad (4.2.46)$$

where D is an order-one constant. Substituting (4.2.46) into (4.2.2)–(4.2.3) we find to leading-order

$$\tilde{J} = -n\hat{\phi}_{X_4} + Dn \left(\frac{\sqrt{n}_{X_4X_4}}{\sqrt{n}} \right)_{X_4}, \quad (4.2.47)$$

$$\hat{\phi}_{X_4X_4} = 0. \quad (4.2.48)$$

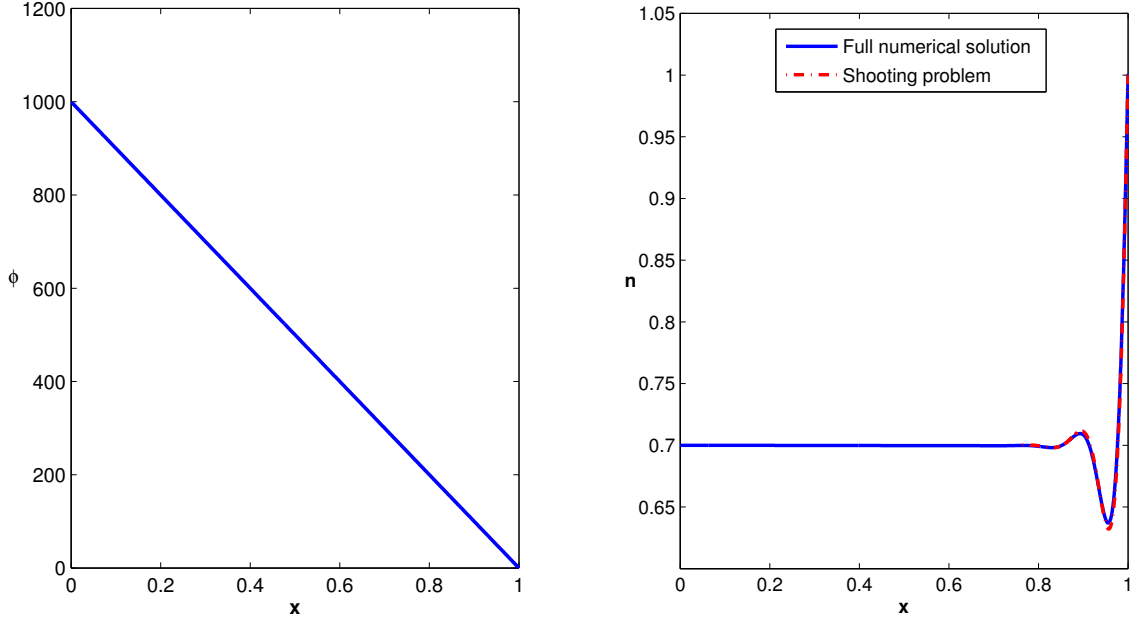


Figure 4.8: Electric potential ϕ and electron density n plotted against position x where $\Phi = 1000$, $\nu = 1$, $\alpha = 0.7$, $\delta_3 = 0.1$ and $j^{DGC} \approx 700$.

Solving (4.2.48) and matching to the outer solution (2.3.44), found in Chapter 2, we find

$$\hat{\phi} = -\sqrt{2\tilde{\mathcal{J}}} \left(1 + \frac{\tilde{\mathcal{J}}}{2\alpha^2}\right)^{1/2} X_4. \quad (4.2.49)$$

Substituting (4.2.49) into (4.2.47) we obtain the equation

$$\tilde{\mathcal{J}} = n\sqrt{2\tilde{\mathcal{J}}} \left(1 + \frac{\tilde{\mathcal{J}}}{2\alpha^2}\right)^{1/2} + Dn \left(\frac{\sqrt{n}X_4X_4}{\sqrt{n}}\right)_{X_4}. \quad (4.2.50)$$

We let

$$n = \sqrt{\frac{\tilde{\mathcal{J}}}{2}} \left(1 + \frac{\tilde{\mathcal{J}}}{2\alpha^2}\right)^{-1/2} \hat{\mathcal{N}}, \quad X_4 = \left(\frac{D}{\sqrt{2\tilde{\mathcal{J}}}} \left(1 + \frac{\tilde{\mathcal{J}}}{2\alpha^2}\right)^{-1/2}\right)^{1/3} \mathcal{X}_2, \quad (4.2.51)$$

to obtain an equivalent shooting problem to the one outlined in (4.2.33)–(4.2.34)

$$1 = \hat{\mathcal{N}} + \hat{\mathcal{N}} \left(\frac{\sqrt{\hat{\mathcal{N}}}\mathcal{X}_2\mathcal{X}_2}{\sqrt{\hat{\mathcal{N}}}}\right)_{\mathcal{X}_2}, \quad (4.2.52)$$

with boundary conditions

$$\hat{\mathcal{N}} \rightarrow 1 \quad \text{as} \quad \mathcal{X}_2 \rightarrow -\infty, \quad \hat{\mathcal{N}}|_{\mathcal{X}_2=0} = \sqrt{\frac{2}{\tilde{\mathcal{J}}}} \left(1 + \frac{\tilde{\mathcal{J}}}{2\alpha^2}\right)^{1/2}, \quad \frac{1}{\hat{\mathcal{N}}} \sqrt{\hat{\mathcal{N}}}\mathcal{X}_2\mathcal{X}_2|_{\mathcal{X}_2=0} = 0. \quad (4.2.53)$$

The only difference between the shooting problem (4.2.52)–(4.2.53) and the shooting problem (4.2.33)–(4.2.34) is the scalings on the variables n and x . In figure 4.9 we demonstrate the reasonable agreement between the full numerical solution and the shooting problem in the boundary layer at $x = 1$. The shooting problem numerical solution will converge to the full numerical solution as ν and $\delta_3 \rightarrow 0$

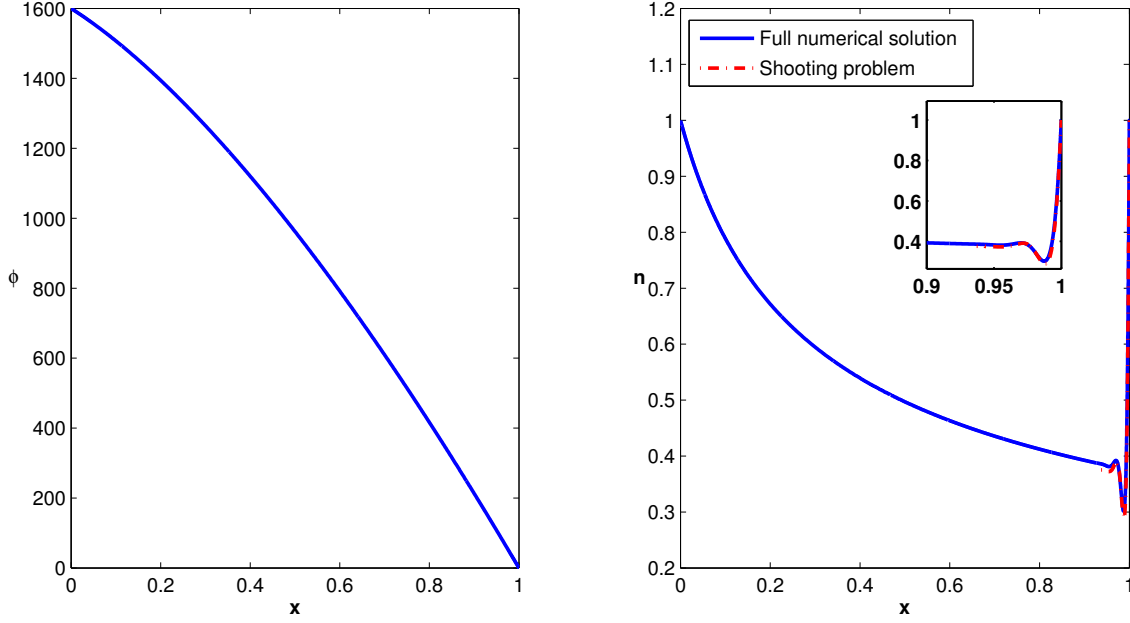


Figure 4.9: Electric potential ϕ and electron density n plotted against position x where $\Phi = 1600$, $\nu = 0.02$, $\alpha = 1$, $\delta_3 = 0.02$ and $j^{DGC} \approx j^{DD} \approx 820$.

4.2.5 Summary

We have investigated the use of DGC theory to include quantum mechanical effects into our DD model of electron flow across a glass layer. DGC theory differs from the classical DD model through the addition of a quantum term. We have found that the introduction of the quantum term leaves the leading-order outer problem unchanged in all parameter regimes explored. The resistance in each of the parameter regimes is therefore unchanged and the asymptotic expressions we found in Chapter 2 still hold. This means that if the glass layer thickness $\gtrsim 10$ nm it is reasonable to assume that quantum effects do not play an important role in determining the contact resistance of a solar cell.

The introduction of the higher order quantum term means that additional boundary conditions are required. We find that there are corresponding quantum boundary layers at the interfaces. However, if the quantum parameter $\delta_3 \ll \nu$ and the electron flux j is not appreciable in the boundary layer, then the quantum boundary layers are weak

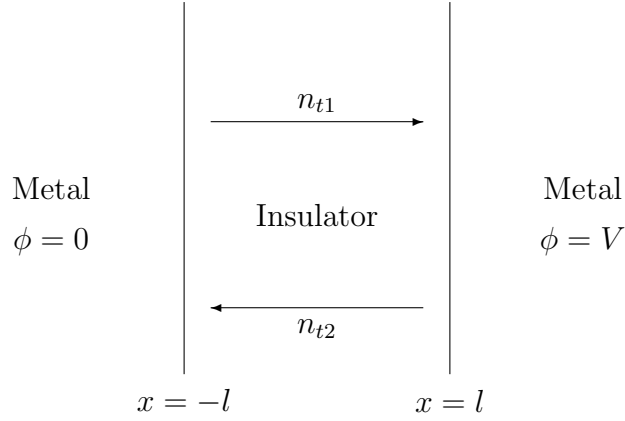


Figure 4.10: Schematic of the metal-insulator-metal device

boundary layers and do not affect the solution structure of the electric potential ϕ or the electron density n to leading order. If the quantum parameter $\delta_3 = O(\nu)$ we find a strong boundary layer where the profile of ϕ and n is altered to leading order. The most interesting phenomena to occur due to the addition of the quantum term is when $j = O(1/\delta_3^2)$ and the electron flux plays an important role in the boundary layer. Here, we find oscillatory variations in the distribution of n . We are unaware of the oscillatory behaviour being reported in other studies that make use of the density gradient confinement theory. However, when using non-equilibrium Green's function methods this oscillatory behaviour is often observed [6] and is attributed to Friedel oscillations that are the quantum mechanical analogue of electrical charge screening [47]. It would be interesting to try to verify these observations experimentally, but, since the effect of the introduction of the quantum term is unmeasurable on the macroscopic scale this would be a difficult task.

4.3 Density gradient tunnelling theory

4.3.1 Introduction

In this section, by summarising and then extending the work of Ancona [4], we investigate the density gradient tunnelling (DGT) theory for modelling charge transport in very small devices (1–3nm). The DGT theory is a continuum alternative to microscopic quantum transport theories for modelling quantum tunnelling.

4.3.2 Model formulation

A schematic of the device is shown in figure 4.10. To formulate the mathematical model for charge transport through an insulator with metal contacts we begin by taking the

system (1.8.3) (where inertia is considered an important effect and n_t is the tunnelling electron density) and make the following assumptions:

- Only electron tunnelling is important and therefore hole tunnelling is neglected.
- The system is in steady state and the electron tunnelling is one-dimensional.
- Diffusion is neglected within the insulator.

We thus arrive at the following system of equations¹:

$$\frac{d^2\phi}{dx^2} = \frac{qn_t}{\epsilon_I}, \quad (4.3.1)$$

$$\frac{dJ}{dx} = 0, \quad (4.3.2)$$

$$\frac{d}{dx} \left(\phi + \frac{\hbar^2}{2m_n r_n q} \frac{1}{\sqrt{n_t}} \frac{d^2 \sqrt{n_t}}{dx^2} - \frac{m_n}{2q} v_n^2 \right) \equiv \frac{d\Psi}{dx} = 0, \quad (4.3.3)$$

where ϵ_I is the absolute permittivity of the insulator and Ψ is the kinetic electrochemical potential. The quantity Ψ will be constant throughout the insulator and dependent on which electrode the electrons originate from. To resolve the contradiction that $d\Psi/dx = 0$ and Ψ takes different values on each electrode Ancona [4] defined 2 distinct electron subpopulations inside the the insulator (shown in figure 4.10):

- One population moving from left to right: electron subpopulation 1 with density n_{t1} .
- One population moving from right to left: electron subpopulation 2 with density n_{t2} .

The two subpopulations of electrons satisfy ‘upstream’ and ‘downstream’ boundary conditions respectively. We now summarise the boundary conditions applied; more details are given in [8]. At the upstream electrode a constant tunnelling electron density is specified along with an additional boundary condition to ensure continuity of the kinetic electrochemical potential across the metal-insulator interface:

$$n_{t1} = n_M, \quad \theta_{MB} = \frac{\hbar^2}{2m_n r_n q} \frac{1}{\sqrt{n_{t1}}} \frac{d^2 \sqrt{n_{t1}}}{dx^2} - \frac{m_n}{2q} v_{1n}^2 \quad \text{at } x = -l \quad (4.3.4a)$$

$$n_{t2} = n_M, \quad \theta_{MB} = \frac{\hbar^2}{2m_n r_n q} \frac{1}{\sqrt{n_{t2}}} \frac{d^2 \sqrt{n_{t2}}}{dx^2} - \frac{m_n}{2q} v_{2n}^2 \quad \text{at } x = l, \quad (4.3.4b)$$

where θ_{MB} is the ‘Schottky barrier height’ and is given by $\theta_{MB} = 1/q(W_{\text{electrode}} + \chi_{\text{ins}})$, $W_{\text{electrode}}$ is the workfunction of the metal electrode and χ_{ins} is the electron affinity of the

¹Ancona [4] uses the opposite sign convention for the electric potential.

insulator. In general, the Schottky barrier height will be different at each electrode but that is not the case here as we are considering identical contacts. The constant n_M is the tunnelling electron density at the insulator side of the metal-insulator interface. The exact size of n_M is unknown but is expected to be small [4].

At the downstream electrode we use the following boundary conditions formulated by Ancona [4]:

$$\frac{dn_{t1}}{dx} = 0 \quad \text{at } x = l, \quad (4.3.5a)$$

$$\frac{dn_{t2}}{dx} = 0 \quad \text{at } x = -l. \quad (4.3.5b)$$

Ancona attributes the boundary conditions (4.3.5) to ‘elastic capture’ of the tunnelling electrons at the downstream contact [6]. The boundary conditions are completed by the potential difference applied across the insulator

$$\phi = 0 \quad \text{at } x = -l, \quad (4.3.6a)$$

$$\phi = V \quad \text{at } x = l. \quad (4.3.6b)$$

The current density of each subpopulation is constant and determined by the density and velocity of the tunnelling electrons at the downstream contact:

$$J_1 = -\gamma n_{t1} \quad \text{at } x = l, \quad (4.3.7a)$$

$$J_2 = \gamma n_{t2} \quad \text{at } x = -l, \quad (4.3.7b)$$

where γ is the average velocity of the electron subpopulation at the downstream electrode and is used as a fitting parameter. The total current density is found by simple addition of the current density of each subpopulation:

$$J = J_1 + J_2. \quad (4.3.8)$$

Integrating (4.3.3) and making use of the boundary conditions (4.3.4), (4.3.6) we obtain the system of equations

$$\frac{d^2\phi}{dx^2} = \frac{q(n_{t1} + n_{t2})}{\epsilon_I}, \quad (4.3.9a)$$

$$\frac{dJ_1}{dx} = 0, \quad (4.3.9b)$$

$$\frac{dJ_2}{dx} = 0, \quad (4.3.9c)$$

$$-\phi - \theta_{MB} + \frac{\hbar^2}{2m_n r_n q} \frac{1}{\sqrt{n_{t1}}} \frac{d^2 \sqrt{n_{t1}}}{dx^2} - \frac{m_n}{2q} v_{1n}^2 = 0, \quad (4.3.9d)$$

$$-\phi - (\theta_{MB} - V) + \frac{\hbar^2}{2m_n r_n q} \frac{1}{\sqrt{n_{t2}}} \frac{d^2 \sqrt{n_{t2}}}{dx^2} - \frac{m_n}{2q} v_{2n}^2 = 0, \quad (4.3.9e)$$

with boundary conditions

$$\phi = 0, \quad n_{t1} = n_M, \quad \frac{dn_{t2}}{dx} = 0, \quad \text{at } x = -l, \quad (4.3.10a)$$

$$\phi = V, \quad n_{t2} = n_M, \quad \frac{dn_{t1}}{dx} = 0, \quad \text{at } x = l, \quad (4.3.10b)$$

where the total current density $J = J_1 + J_2$ is determined using

$$J_1 = -\gamma n_{t1} \quad \text{at } x = l, \quad (4.3.11)$$

$$J_2 = \gamma n_{t2} \quad \text{at } x = -l. \quad (4.3.12)$$

The system (4.3.9a)–(4.3.12) is an eighth order system with eight boundary conditions and therefore it is reasonable to expect there to be a unique solution.

By definition, the total current density J is the electron velocity v_n multiplied by the tunnelling electron density n_t and therefore the electron velocities v_{1n} , v_{2n} are eliminated from (4.3.9) using

$$v_{1n} = \frac{J_1}{n_{t1}}, \quad v_{2n} = \frac{J_2}{n_{t2}}. \quad (4.3.13)$$

where the current densities J_1 and J_2 are constant.

We now introduce the following nondimensional variables

$$\phi = -\frac{\gamma^2 m_n}{2q} \phi^*, \quad \theta_{MB} = \frac{\gamma^2 m_n}{2q} \theta_{MB}^*, \quad n_{t1} = n_M n_{t1}^*, \quad n_{t2} = n_M n_{t2}^*, \quad (4.3.14a)$$

$$x = lx^*, \quad V = -\frac{\gamma^2 m_n}{2q} \bar{V}, \quad J_1 = \gamma n_M J_1^*, \quad J_2 = \gamma n_M J_2^*. \quad (4.3.14b)$$

Substituting (4.3.14) into (4.3.9) and dropping the starred notation we obtain

$$\nu_{QM}^2 \frac{d^2 \phi}{dx^2} = -(n_{t1} + n_{t2}), \quad (4.3.15a)$$

$$-(\phi + \theta_{MB}) + \frac{B}{\sqrt{n_{t1}}} \frac{d^2 \sqrt{n_{t1}}}{dx^2} - \frac{J_1^2}{n_{t1}^2} = 0, \quad (4.3.15b)$$

$$-\phi - (\theta_{MB} + \bar{V}) + \frac{B}{\sqrt{n_{t2}}} \frac{d^2 \sqrt{n_{t2}}}{dx^2} - \frac{J_2^2}{n_{t2}^2} = 0. \quad (4.3.15c)$$

The boundary conditions (4.3.10) become

$$\phi = 0, \quad n_{t1} = 1, \quad \frac{dn_{t2}}{dx} = 0, \quad \text{at } x = -1, \quad (4.3.16a)$$

$$\phi = -\bar{V}, \quad n_{t2} = 1, \quad \frac{dn_{t1}}{dx} = 0, \quad \text{at } x = 1, \quad (4.3.16b)$$

where the total current density $J = J_1 + J_2$ is found using

$$J_1 = -n_{t1} \quad \text{at } x = 1, \quad (4.3.17a)$$

$$J_2 = n_{t2} \quad \text{at } x = -1. \quad (4.3.17b)$$

The dimensionless parameters are

$$\nu_{QM} = \sqrt{\frac{\epsilon_I \gamma^2 m_n}{2q^2 l^2 n_M}}, \quad B = \frac{\hbar^2}{l^2 \gamma^2 m_n^2 r_n}. \quad (4.3.18)$$

To estimate the size of B we let m_n be the mass of a free electron $9.11 \times 10^{-31} \text{kg}$, $l = 1.75 \text{nm}$, $r_n = 1$, $\hbar = 1.04 \times 10^{-34} \text{m}^2 \text{kgs}^{-1}$, and $\gamma = 10^6 \text{m s}^{-1}$, to find $B = O(10^{-3})$. The size of γ is chosen to ensure $\gamma^2 m_n / (2q) = O(1) \text{ Volt}$; Ancona [4] matched numerical solutions of (4.3.15)–(4.3.16) to experiments to determine $\gamma = O(10^6) \text{m s}^{-1}$. The value $r_n = 1$ corresponds to the relevant low electron density limit [4]. The parameter $\nu_{QM} \gg 1$ due to the small device length l and the expected low tunnelling electron density n_M . We exploit the largeness of ν_{QM} to obtain the following approximation to the electric potential

$$\phi \sim -\frac{\bar{V}}{2}(x+1). \quad (4.3.19)$$

Substituting (4.3.19) into (4.3.15b)–(4.3.15c) and letting $\sqrt{n_{t1}} = s_1$, $\sqrt{n_{t2}} = s_2$ we obtain the equations

$$\frac{1}{2}(x - z_1) + \frac{B}{\bar{V} s_1} \frac{d^2 s_1}{dx^2} - \frac{J_1^2}{\bar{V} s_1^4} = 0, \quad (4.3.20a)$$

$$\frac{1}{2}(x - z_2) + \frac{B}{\bar{V} s_2} \frac{d^2 s_2}{dx^2} - \frac{J_2^2}{\bar{V} s_2^4} = 0, \quad (4.3.20b)$$

where

$$z_1 = (2\theta_{MB}/\bar{V} - 1), \quad (4.3.21)$$

$$z_2 = (2\theta_{MB}/\bar{V} + 1), \quad (4.3.22)$$

The boundary conditions now take the form

$$s_1 = 1, \quad \frac{ds_2}{dx} = 0, \quad J_2 = s_2^2 \quad \text{at } x = -1, \quad (4.3.23a)$$

$$s_2 = 1, \quad \frac{ds_1}{dx} = 0, \quad J_1 = -s_1^2 \quad \text{at } x = 1. \quad (4.3.23b)$$

The system (4.3.20)–(4.3.23) is the nondimensional analogue of the model (4.2), (3.2c) and (3.4) in Ancona [4]. We now exploit the smallness of the parameter B to conduct asymptotic analysis on the system (4.3.20)–(4.3.23). This allows us to determine the current densities J_1 , J_2 in terms of the parameters B , $\bar{V}$ and θ_{MB} . We find that for physical parameter values of θ_{MB} and $\bar{V}$, $z_2 > 1$ and therefore electron subpopulation s_2 always has the same qualitative behaviour. In contrast, $z_1 > 1$ when $\bar{V} < \theta_{MB}$ and $z_1 \in (-1, 1)$ when $\bar{V} > \theta_{MB}$, and we find the solution profile of s_1 has very different qualitative behaviour in the two cases.

4.3.3 Normal tunnelling: $B \ll 1$, $\bar{V} = O(1)$, $\bar{V} < \theta_{MB}$

Considering the regime where $B \ll 1$, $\bar{V} = O(1)$ and $\bar{V} < \theta_{MB}$, known as the normal tunnelling regime, we find that $z_1, z_2 > 1$. Therefore the first terms in equations (4.3.20) are negative throughout the domain $x \in [-1, 1]$. We therefore solve (4.3.20)–(4.3.23) asymptotically by matching a WKB outer solution to an inner boundary layer problem.

4.3.3.1 Numerical solution

To find the numerical solution for s_1 we begin by letting

$$s_1 = \frac{\sqrt{-J_1}}{\sqrt[4]{\bar{V}}} \omega. \quad (4.3.24)$$

Substituting (4.3.24) into (4.3.20)–(4.3.23) we obtain the shooting problem

$$\frac{B}{\bar{V}} \omega'' = \frac{1}{\omega^3} - \frac{(x - z_1)}{2} \omega, \quad (4.3.25)$$

where

$$\omega'(1) = 0, \quad \omega(1) = \bar{V}^{1/4}, \quad J_1 = -\frac{\sqrt{\bar{V}}}{\omega(-1)^2}. \quad (4.3.26)$$

A numerical solution is found to the system (4.3.25)–(4.3.26) by using `ode45` in MATLAB where the conditions specified at $x = 1$ for ω are used as initial conditions for the differential equation (4.3.25). We then shoot to $x = -1$ where we use the final condition in (4.3.26) to determine the value of J_1 . The numerical solution for s_2 is found by solving an analogous shooting problem.

4.3.3.2 Electron subpopulation 1

We first consider electron subpopulation 1 where we expect the current density J_1 to be negative and exponentially small in the parameter B . We therefore let $J_1 = -\varepsilon_1^2$, where $\varepsilon_1 \ll 1$, to obtain the system

$$Bs_1'' - \frac{\varepsilon_1^4}{s_1^3} = \frac{\bar{V}}{2}(z_1 - x)s_1, \quad (4.3.27a)$$

$$s_1(-1) = 1, \quad s_1'(1) = 0, \quad s_1(1) = \varepsilon_1. \quad (4.3.27b)$$

Near $x = 1$ (4.3.27b) informs us that $s_1 = O(\varepsilon_1)$ and we therefore solve for a boundary layer in this region. We let $s_1 = \varepsilon_1 S$ and $x = 1 - \sqrt{B}X_5$ to find the system (4.3.27) becomes

$$S_{X_5 X_5} - \frac{1}{S^3} = \frac{\bar{V}}{2}(z_1 - 1 + \sqrt{B}X_5)S, \quad (4.3.28a)$$

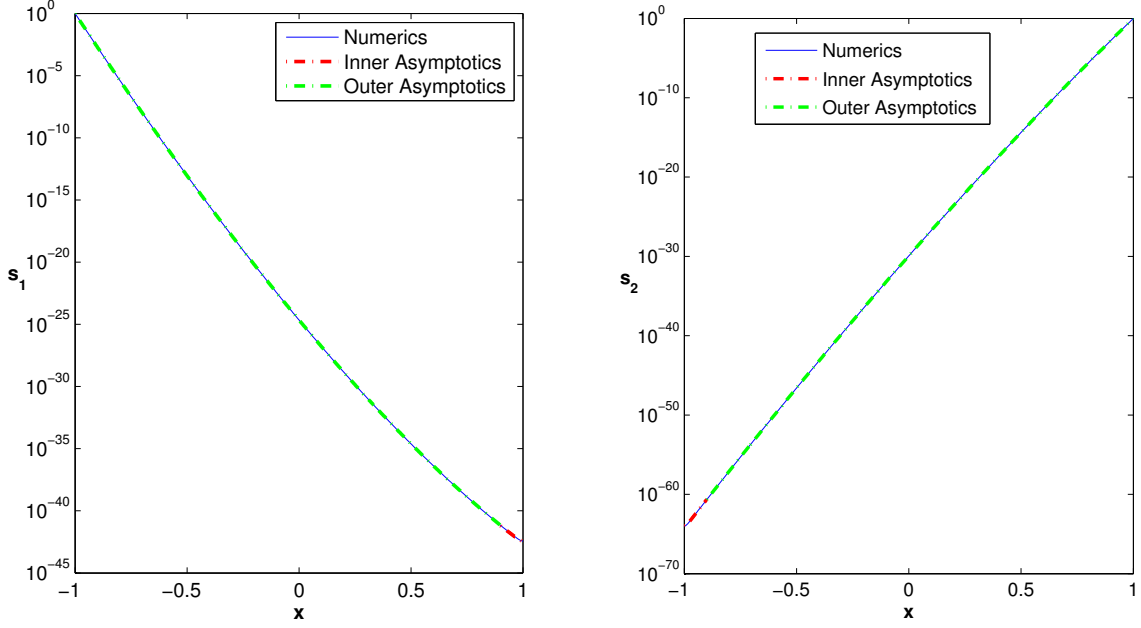


Figure 4.11: Square rooted electron subpopulation 1 and square rooted electron subpopulation 2 plotted against position x where $B = 10^{-3}$, $\bar{V} = 3$, $\theta_{MB} = 4$, $z_1 = 5/3$, $z_2 = 11/3$, $J_1 \approx -1.40 \times 10^{-85}$, $J_2 \approx 9.89 \times 10^{-129}$ and $J \approx -1.40 \times 10^{-85}$. We recall that $\bar{V}$, θ_{MB} , z_1 are related through (4.3.21) and $\bar{V}$, θ_{MB} , z_2 are related through (4.3.22).

$$S(0) = 1, \quad S_{X_5}(0) = 0. \quad (4.3.28b)$$

We let $m = \sqrt{\bar{V}/2(z_1 - 1)}$ and expand S as $S \sim S_0 + \sqrt{B}S_1 + \dots$ to obtain the leading order system in the boundary layer:

$$\frac{d^2 S_0}{dX_5^2} = \frac{1}{S_0^3} + m^2 S_0. \quad (4.3.29a)$$

$$S_0(0) = 1, \quad \frac{dS_0(0)}{dX_5} = 0. \quad (4.3.29b)$$

Multiplying (4.3.29a) by dS_0/dX_5 , integrating, and applying the boundary conditions (4.3.29b) we find

$$\frac{dS_0}{dX_5} = \frac{m}{S_0} \sqrt{\left(S_0^2 + \frac{1}{m^2}\right)(S_0^2 - 1)}. \quad (4.3.30)$$

We separate variables, integrate, and apply the boundary conditions (4.3.29b) again to obtain

$$S_0 = \sqrt{\cosh^2(mX_5) + \frac{1}{m^2} \sinh^2(mX_5)}. \quad (4.3.31)$$

To determine the outer solution away from the boundary layer at $x = 1$ we apply the WKB method. We therefore assume an asymptotic expansion of s_1 in the form

$s_1 \sim A(x, B)e^{f(x)/\sqrt{B}}$ that we substitute into (4.3.27a) to find

$$\frac{\bar{V}}{2}(x - z_1)Ae^{f/\sqrt{B}} + Be^{f/\sqrt{B}} \left(A'' + \frac{2A'f'}{\sqrt{B}} + \frac{A}{\sqrt{B}}f'' + \frac{Af'^2}{B} \right) - \varepsilon_1^4 A^{-3} e^{-3f/\sqrt{B}} = 0. \quad (4.3.32)$$

Substituting the expansion $A \sim A_0 + \sqrt{B}A_1 + \dots$ into (4.3.32) we find to leading order

$$f = \pm \frac{\sqrt{2\bar{V}}}{3}(z_1 - x)^{3/2}, \quad (4.3.33)$$

and to $O(\sqrt{B})$

$$A_0 = \frac{C_4}{(z_1 - x)^{1/4}}, \quad (4.3.34)$$

where C_4 is a constant to be determined. We therefore have two linearly independent solutions for s_1 :

$$s_1 \sim \frac{C_4}{(z_1 - x)^{1/4}} \exp \left[\pm \frac{\sqrt{2\bar{V}}}{3\sqrt{B}}(z_1 - x)^{3/2} \right]. \quad (4.3.35)$$

By applying the boundary condition $s_1(-1) = 1$ we find the appropriate exponentially decaying solution is given by

$$s_1 \sim \left(\frac{z_1 + 1}{z_1 - x} \right)^{1/4} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}}((z_1 + 1)^{3/2} - (z_1 - x)^{3/2}) \right]. \quad (4.3.36)$$

We now determine the value of ε_1 and therefore J_1 by matching the inner solution (4.3.31) to the outer solution (4.3.36). Considering (4.3.31) in the limit $X_5 \rightarrow \infty$ we find

$$S_0 \sim \frac{\sqrt{m^2 + 1}}{2K} e^{mX_5}, \quad (4.3.37)$$

and writing (4.3.36) in terms of the inner variables S_0, X_5 we find

$$\varepsilon_1 S_0 \sim \left(\frac{z_1 + 1}{z_1 - 1} \right)^{1/4} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}}((z_1 + 1)^{3/2} - (z_1 - 1)^{3/2}) \right] e^{mX_5}. \quad (4.3.38)$$

Solving the equations (4.3.37)–(4.3.38) for ε_1 we find

$$\varepsilon_1 \sim \frac{2m}{\sqrt{m^2 + 1}} \left(\frac{z_1 + 1}{z_1 - 1} \right)^{1/4} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}}((z_1 + 1)^{3/2} - (z_1 - 1)^{3/2}) \right] \quad (4.3.39)$$

and therefore reintroducing the variable θ_{MB} we find

$$J_1 \sim -\frac{8\bar{V}\sqrt{\frac{\theta_{MB}}{\bar{V}}\left(\frac{\theta_{MB}}{\bar{V}} - 1\right)}}{2 + 2\theta_{MB} - \bar{V}} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}} \left(\left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} - 2 \right)^{3/2} \right) \right]. \quad (4.3.40)$$

We take $B = 10^{-3}$, $\bar{V} = 3$ and $\theta_{MB} = 4$ to find the asymptotic expression (4.3.40) gives $J_1 \sim -1.41 \times 10^{-85}$ that has excellent agreement with the numerically calculated $J_1 \approx -1.40 \times 10^{-85}$. In figure 4.11 we demonstrate the excellent agreement between the expressions (4.3.31), (4.3.36) and the numerical solution.

4.3.3.3 Electron subpopulation 2

Now considering electron subpopulation 2 we follow an analogous procedure to determine in the boundary layer near $x = -1$

$$\hat{S}_0 = \sqrt{\cosh^2(\hat{m}X_6) + \frac{1}{\hat{m}^2} \sinh^2(\hat{m}X_6)}, \quad (4.3.41)$$

where $\hat{S}_0 = s_2/\varepsilon_2$, $\hat{m} = \sqrt{\bar{V}/2(z_2 + 1)}$ and $X_6 = (x + 1)/\sqrt{B}$. In addition, a similar WKB approach to above gives the outer solution to be

$$s_2 \sim \left(\frac{z_2 - 1}{z_2 - x} \right)^{1/4} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}} ((z_2 - x)^{3/2} - (z_2 - 1)^{3/2}) \right]. \quad (4.3.42)$$

In figure 4.11 we show the excellent agreement between the expressions (4.3.41), (4.3.42) and the numerical solution.

$$\varepsilon_2 \sim \frac{2\hat{m}}{\sqrt{\hat{m}^2 + 1}} \left(\frac{z_2 - 1}{z_2 + 1} \right)^{1/4} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}} ((z_2 + 1)^{3/2} - (z_2 - 1)^{3/2}) \right], \quad (4.3.43)$$

and therefore

$$J_2 \sim \frac{4\bar{V} \left(\frac{\theta_{MB}}{\bar{V}} \left(\frac{\theta_{MB}}{\bar{V}} + 1 \right) \right)}{1 + \theta_{MB} + \bar{V}} \exp \left[-\frac{2\sqrt{2\bar{V}}}{3\sqrt{B}} \left(\left(\frac{2\theta_{MB}}{\bar{V}} + 2 \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} \right) \right]. \quad (4.3.44)$$

We take $B = 10^{-3}$, $\bar{V} = 3$ and $\theta_{MB} = 4$ to find the asymptotic expression (4.3.44) gives $J_2 \sim 9.89 \times 10^{-129}$ that has excellent agreement with the numerically calculated $J_2 \approx 9.89 \times 10^{-129}$.

4.3.3.4 Total current density

The total current density is $J = J_1 + J_2$, where we have determined in §4.3.3.2 and §4.3.3.3 that J_1 and J_2 are exponentially small in the parameter B . Moreover, examining the exponents of (4.3.40) and (4.3.44) we see that $|J_2| \ll |J_1|$ since if $\bar{V} < \theta_{MB}$

$$\left(\frac{2\theta_{MB}}{\bar{V}} + 2 \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} < \left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} - 2 \right)^{3/2}, \quad (4.3.45)$$

and therefore $J \sim J_1$ meaning the total current density

$$J \sim -\frac{8\bar{V} \sqrt{\frac{\theta_{MB}}{\bar{V}} \left(\frac{\theta_{MB}}{\bar{V}} - 1 \right)}}{2 + 2\theta_{MB} - \bar{V}} \exp \left[-\frac{\sqrt{2\bar{V}}}{3\sqrt{B}} \left(\left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} - 2 \right)^{3/2} \right) \right], \quad (4.3.46)$$

where $\bar{V} < \theta_{MB}$. Examining figure 4.12 it is evident that the asymptotic expression (4.3.46) has excellent agreement with the numerically calculated J .

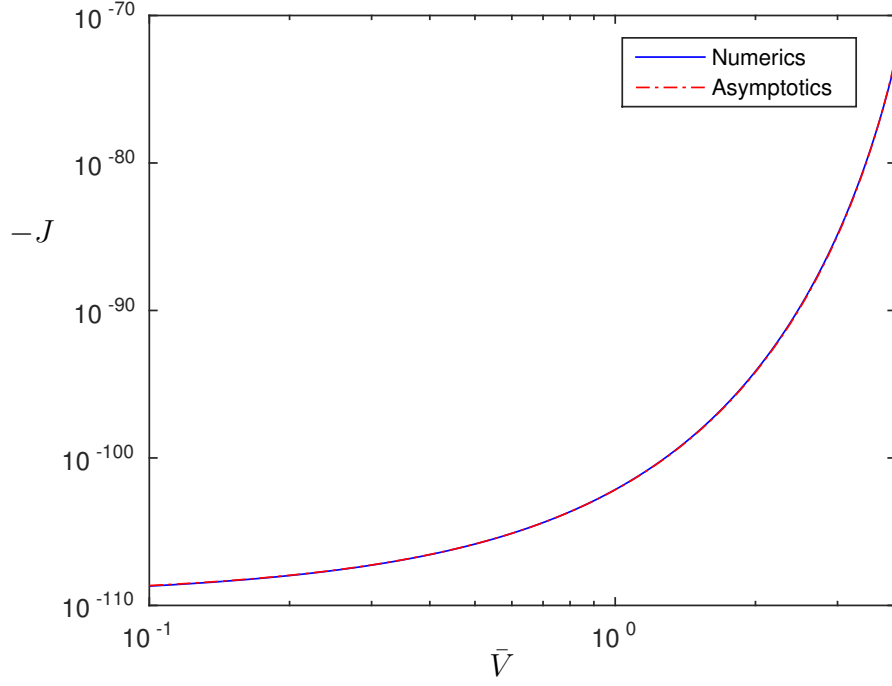


Figure 4.12: Current density ($-J$) plotted against applied potential difference $\bar{V}$ where $B = 10^{-3}$ and $\theta_{MB} = 4$. The asymptotic solution is given by (4.3.46) and the numerical solution is found by solving the system (4.3.25)–(4.3.26) in MATLAB.

4.3.3.5 Summary

By conducting asymptotic analysis on the system (4.3.20)–(4.3.23) in the regime where $B \ll 1$, $\bar{V} = O(1)$ and $\bar{V} < \theta_{MB}$ we have determined explicit leading-order solutions for the current densities J_1 , J_2 that enabled us to determine that $|J_2| \ll |J_1|$ and therefore obtain an explicit solution for the total current density J (4.3.46).

Analysing (4.3.46), we find that the DGT theory produces physically reasonable results, since increasing the length of the insulator (decreasing B) and also increasing the barrier height θ_{MB} results in the current density decreasing exponentially and increasing the applied potential difference $\bar{V}$ results in the current density increasing exponentially, which are well-known features of quantum mechanical tunnelling [90]. Finally, we note that Ancona [4] did find the outer WKB solutions (4.3.36), (4.3.42) but did not solve the inner boundary layer problem and therefore did not obtain our accurate approximation to the total current density.

4.3.4 Fowler-Nordheim tunnelling: $B \ll 1$, $\bar{V} = O(1)$, $\bar{V} > \theta_{MB}$

When $B \ll 1$, $\bar{V} = O(1)$ and $\bar{V} > \theta_{MB}$, known as the Fowler-Nordheim tunnelling regime, we make use of (4.3.21) and (4.3.22) to find $z_1 \in (-1, 1)$ and $z_2 > 1$. The ranges of z_1 , z_2 mean that the solution given for J_2 in (4.3.44) still holds when $\bar{V} > \theta_{MB}$ but

the solution for J_1 (4.3.40) is no longer valid. This is because when $z_1 \in (-1, 1)$ the sign of the first term in (4.3.20a) changes within the domain leading to different qualitative behaviour in the two regions $-1 < x < z_1$ and $z_1 < x < 1$. In particular, we find in the region $z_1 < x < 1$ an oscillatory solution structure for s_1 that was not found in §4.3.3.2.

4.3.4.1 Numerical solution

In figure 4.13 we show a solution of the shooting problem (4.3.25)–(4.3.26). Examining figure 4.13 we see the presence of two distinct regions where the qualitative behaviour of ω differs. In the region $-1 < x < z_1$ there is an exponentially decaying solution that we investigate in §4.3.4.3. In the region $z_1 < x < 1$ there is oscillatory behaviour that is orders of magnitude smaller than the solution in the region $-1 < x < z_1$, we investigate this region in §4.3.4.2. The two different asymptotic solutions found are matched together in §4.3.4.4.

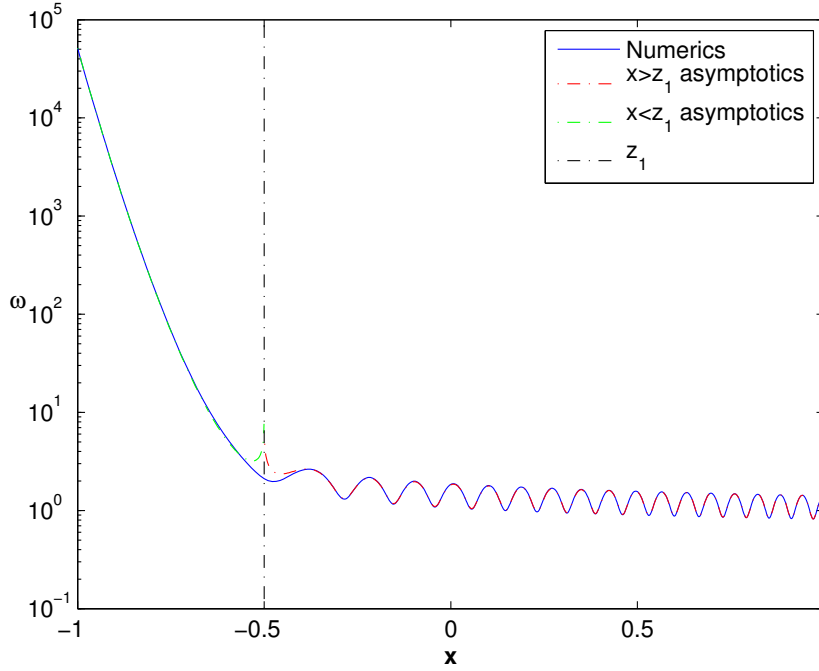


Figure 4.13: The scaled square rooted electron subpopulation ω plotted against position x where $B = 10^{-3}$, $\bar{V} = 4$, $\theta_{MB} = 1$, $z_1 = -1/2$ and $J_1 \approx -7.60 \times 10^{-10}$. We recall that $\bar{V}$, θ_{MB} , z_1 are related through (4.3.21). The black dashed line indicates the value of z_1 , the red dashed line is the expression (4.3.68) and the green dashed line is the expression (4.3.71) where $K_3 \approx 1.28$.

4.3.4.2 Oscillatory solution: $z_1 < x < 1$

We use the method of multiple scales to solve in the region $z_1 < x < 1$ where we hypothesise that the oscillatory behaviour occurs over a short length scale. We find it convenient to start from the formulation (4.3.25)–(4.3.26) where we introduce the short length scale X (not to be confused with the variable X used in Chapter 2) and the long length scale τ (not to be confused with the variable τ used in Chapter 3) by letting

$$\omega = \frac{2^{1/4}}{(x - z_1)^{1/4}} W(X, x), \quad \text{where} \quad X = \frac{\sqrt{V}(x - z_1)^{3/2}}{\sqrt{B}}, \quad \tau = \frac{3}{2} \log(x - z_1). \quad (4.3.47)$$

We use the result

$$\begin{aligned} \frac{d^2 \omega}{dx^2} = & \frac{2^{1/4}}{(x - z_1)^{1/4}} \left\{ W_{XX} \left(\frac{dX}{dx} \right)^2 + 2W_{X\tau} \frac{dX}{dx} \frac{d\tau}{dx} + W_{\tau\tau} \left(\frac{d\tau}{dx} \right)^2 \right. \\ & - \frac{1}{2(x - z_1)} \left(W_X \frac{dX}{dx} + W_\tau \frac{d\tau}{dx} \right) + \left(W_X \frac{d^2 X}{dx^2} + W_\tau \frac{d^2 \tau}{dx^2} \right) \\ & \left. + \frac{5}{16} (x - z_1)^{-2} W \right\}, \end{aligned} \quad (4.3.48)$$

to deduce that substituting (4.3.47) into (4.3.25) gives the governing equation

$$\begin{aligned} W_{XX} + 2\sqrt{\frac{B}{V}}(x - z_1)^{-3/2} W_{\tau X} + \frac{B}{V} W_{\tau\tau} (x - z_1)^{-3} - \frac{B}{V} W_\tau (x - z_1)^{-3} \\ - \frac{5}{36} \frac{B}{V} (x - z_1)^{-2} W = \frac{2}{9} \left(\frac{1}{W^3} - W \right). \end{aligned} \quad (4.3.49)$$

Expanding W as

$$W \sim W_0 + \sqrt{\frac{B}{V}} e^{-\tau} W_1 + O(B), \quad (4.3.50)$$

and substituting into (4.3.49) we find to leading order

$$W_{0XX} = \frac{2}{9} \left(\frac{1}{W_0^3} - W_0 \right), \quad (4.3.51)$$

and to $O(\sqrt{B})$

$$W_{1XX} + \frac{2}{9} \left(1 + \frac{3}{W_0^4} \right) W_1 = -2W_{0\tau X}. \quad (4.3.52)$$

Multiplying (4.3.51) by W_{0X} and integrating we find

$$W_{0X}^2 = \frac{2}{9W_0^2} \left(\frac{1}{A(\tau)^2} + A(\tau)^2 - W_0^2 - \frac{1}{W_0^2} \right), \quad (4.3.53)$$

where $A(\tau)$ is a variable that only depends on the long length scale τ . The variable $A(\tau)$ is the maximum of W_0 and $1/A(\tau)$ is the minimum of W_0 over the short length scale

X . Considering a single branch of W_0 , so that $W_0 \in [1/A(\tau), A(\tau)]$, we take the positive square root without loss of generality to find

$$W_{0X} = \frac{\sqrt{2}}{3W_0} \sqrt{(A(\tau)^2 - W_0^2)(W_0^2 - 1/A(\tau)^2)}. \quad (4.3.54)$$

Taking (4.3.54), separating the variables, and integrating, we obtain

$$W_0 = \frac{1}{\sqrt{2}A(\tau)} \sqrt{A(\tau)^4 + 1 + (A(\tau)^4 - 1) \sin \left[\frac{2\sqrt{2}}{3}(X - C_3(\tau)) \right]}, \quad (4.3.55)$$

where $C_3(\tau)$ is a variable that only depends on the long length scale τ .

To find the dependence of A on τ and therefore the solvability condition we consider the $O(\sqrt{B})$ equation (4.3.52). It is evident that W_{0X} solves the homogeneous problem for W_1 and we therefore substitute $W_1 = VW_0$ into (4.3.52) and use (4.3.51) to find

$$\frac{d}{dX} [W_{0X}^2 V_X] = -2W_{0X}W_{0\tau X}. \quad (4.3.56)$$

The variables W_0 and W_1 are periodic over the short length scale X and therefore V will be periodic over the short length scale X . Hence, we deduce the solvability condition

$$\int_0^\lambda W_{0X}W_{0\tau X} dX = 0, \quad (4.3.57)$$

where λ is the length of one wavelength of the periodic solution on the short length scale X . Integrating (4.3.57) by parts and making use of (4.3.51) we find

$$\int_0^\lambda W_{0X}W_{0\tau X} dX = [W_{0\tau}W_{0X}]_0^\lambda - \frac{2}{9} \frac{d}{d\tau} \int_0^\lambda -\frac{1}{W_0^2} - \frac{W_0^2}{2} dX. \quad (4.3.58)$$

By using (4.3.53) we find

$$\int_0^\lambda W_{0X}W_{0\tau X} dX = [W_{0\tau}W_{0X}]_0^\lambda - \int_0^\lambda W_{0X}W_{0\tau X} + \frac{2}{9} \frac{dA(\tau)}{d\tau} \left(A(\tau) - \frac{1}{A(\tau)^3} \right) \lambda = 0. \quad (4.3.59)$$

The first two terms on the right-hand side of (4.3.59) are zero due to the periodicity of W_0 and therefore since $A > 1$ by definition we deduce that

$$\frac{dA}{d\tau} = 0. \quad (4.3.60)$$

Moreover, we hypothesise that $dC_3/d\tau = 0$ and therefore A and C_3 are constants that we determine from the initial conditions.

Making use of

$$\frac{d\omega}{dx} = \left(W_X \frac{dX}{dx} + W_\tau \frac{d\tau}{dx} \right) \frac{2^{1/4}}{(x - z_1)^{1/4}} - \frac{2^{1/4}}{4} (x - z_1)^{-5/4} W, \quad (4.3.61)$$

we write the initial conditions (4.3.26) as

$$W_X = \frac{\sqrt{B}}{\sqrt{\bar{V}}(1-z_1)^{3/2}} \left(\frac{W}{6} - W_\tau \right), \quad W = \frac{(1-z_1)^{1/4} \bar{V}^{1/4}}{2^{1/4}}, \quad (4.3.62)$$

$$\text{at } X = X^* = \frac{\sqrt{\bar{V}}(1-z_1)^{3/2}}{\sqrt{B}} \quad \text{and} \quad \tau = \tau^* = \frac{3}{2} \log(1-z_1). \quad (4.3.63)$$

Taking (4.3.62) to leading order in W we find

$$W_{0X} = 0 \quad \text{at } X = X^* \quad \text{and} \quad \tau = \tau^*, \quad (4.3.64)$$

$$W_0 = \frac{(1-z_1)^{1/4} \bar{V}^{1/4}}{2^{1/4}} \quad \text{at } X = X^* \quad \text{and} \quad \tau = \tau^*. \quad (4.3.65)$$

Applying the initial condition (4.3.64) to (4.3.55) we find $C_3 = X^* \pm 3\pi/(4\sqrt{2})$. We take $C_3 = X^* + 3\pi/(4\sqrt{2})$ without loss of generality to find

$$W_0 = \frac{1}{\sqrt{2}A} \sqrt{A^4 + 1 - (A^4 - 1) \cos \left[\frac{2\sqrt{2}}{3}(X - X^*) \right]}. \quad (4.3.66)$$

Finally, using the remaining initial condition (4.3.65) we determine

$$A = \frac{2^{1/4}}{\bar{V}^{1/4}(1-z_1)^{1/4}} \quad (4.3.67)$$

and therefore

$$\omega \sim \frac{\left\{ 2 + \bar{V}(1-z_1) + (\bar{V}(1-z_1) - 2) \cos \left[\frac{2\sqrt{2\bar{V}}}{3\sqrt{B}} ((x-z_1)^{3/2} - (1-z_1)^{3/2}) \right] \right\}^{1/2}}{\sqrt{2}(1-z_1)^{1/4} \bar{V}^{1/4} (x-z_1)^{1/4}}, \quad (4.3.68)$$

in the region $z_1 < x < 1$. In figure 4.13 we demonstrate that (4.3.68) has excellent agreement with the numerical solution for $x > z_1$.

The asymptotic expression (4.3.68) shows that the amplitude of the oscillating solution is dependent on the quantity $\bar{V}(1-z_1)$. Making use of (4.3.68) we determine an approximation to the amplitude of the oscillations at $x = 1$

$$A_{\text{Final}} \sim \left| \frac{(2\bar{V}(1-z_1))^{1/2} - 2}{2\sqrt{2}(1-z_1)^{1/2} \bar{V}^{1/4}} \right|. \quad (4.3.69)$$

The asymptotic expression (4.3.69) enables us to determine, for a given barrier height θ_{MB} , how the amplitude of the oscillations at $x = 1$ changes as $\bar{V}$ is varied. An example is shown in figure 4.14 where we demonstrate the excellent agreement between the numerically calculated amplitude at $x = 1$ and the expression (4.3.69). Numerical error in the calculation of A_{Final} is the cause of the noisy appearance of the numerical solution. Full details of how A_{Final} is calculated numerically are given in Appendix B. .

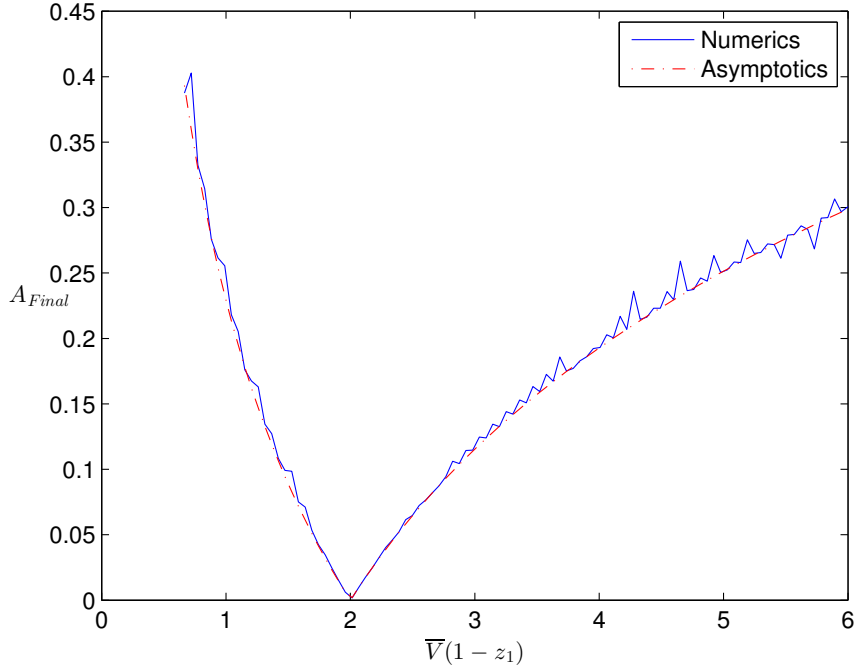


Figure 4.14: The amplitude at $x = 1$, A_{Final} , plotted against $\bar{V}(1 - z_1)$ where $B = 10^{-4}$, $\theta_{MB} = 1$, $\bar{V} \in [4/3, 4]$ and $z_1 \in [-1/2, 1/2]$. We recall that $\bar{V}$, θ_{MB} , z_1 are related through (4.3.21).

4.3.4.3 Exponential solution: $-1 < x < z_1$

In the region $-1 < x < z_1$ our numerical solution informs us that $\omega \gg 1$ and therefore

$$\frac{B}{\bar{V}} \omega'' \sim -\frac{(x - z_1)}{2} \omega. \quad (4.3.70)$$

Solving (4.3.70) in the limit $B \rightarrow 0$ we find in the region $-1 < x < z_1$

$$\omega \sim \frac{K_3}{(z_1 - x)^{1/4} \bar{V}^{1/12}} \exp\left(\frac{\sqrt{2\bar{V}}}{3\sqrt{B}}(z_1 - x)^{3/2}\right), \quad (4.3.71)$$

where K_3 is a constant. The expression (4.3.71) is shown to agree well with the numerical solution in figure 4.13.

Taking (4.3.71), using (4.3.26) and reintroducing the variable θ_{MB} we find

$$J_1 \sim -\frac{\sqrt{2\theta_{MB}} \bar{V}^{1/6}}{K_3^2} \exp\left(-\frac{8\theta_{MB}^{3/2}}{3\sqrt{B\bar{V}}}\right). \quad (4.3.72)$$

We determine the constant K_3 numerically in §4.3.4.4 by matching (4.3.68) and (4.3.71).

4.3.4.4 Matching region: $x \approx z_1$

To determine the constant K_3 we consider the region $x \approx z_1$ and apply the scalings

$$x = z_1 + B^{1/3}\xi, \quad \omega = B^{-1/12}v, \quad (4.3.73)$$

to find

$$\frac{v_{\xi\xi}}{\bar{V}} = \frac{1}{v^3} - \frac{\xi v}{2}. \quad (4.3.74)$$

We solve (4.3.74) numerically with the matching conditions as $\xi \rightarrow \infty$ (using (4.3.68))

$$v \sim \frac{\left\{ 2 + \bar{V}(1 - z_1) + (\bar{V}(1 - z_1) - 2) \cos \left[\frac{2\sqrt{2\bar{V}}}{3} \xi^{3/2} - \frac{2\sqrt{2\bar{V}}}{3\sqrt{B}} (1 - z_1)^{3/2} \right] \right\}^{1/2}}{\sqrt{2}(1 - z_1)^{1/4} \bar{V}^{1/4} \xi^{1/4} B^{1/12}}, \quad (4.3.75)$$

and as $\xi \rightarrow -\infty$ (using (4.3.71))

$$v \sim \frac{K_3}{|\xi|^{1/4} \bar{V}^{1/12}} \exp \left(\frac{\sqrt{2\bar{V}}}{3} |\xi|^{3/2} \right). \quad (4.3.76)$$

Solving (4.3.74)–(4.3.76) allows us to determine the constant K_3 that will depend on z_1 as well as B and $\bar{V}$ through the argument of $\cos$ in (4.3.75). For a fixed value of z_1 the constant K_3 will depend on the remainder $r \in [0, 2\pi]$, where

$$\frac{2\sqrt{2\bar{V}}}{3\sqrt{B}} (1 - z_1)^{3/2} = 2k\pi + r \quad \text{for } k \in \mathbb{Z} \gg 1. \quad (4.3.77)$$

In figure 4.15 we take $z_1 = -1/2$ and demonstrate the validity of the relation (4.3.77) for 3 values of k . We observe that the value of K_3 is independent of k provided it is sufficiently large.

4.3.4.5 Total current density

In the regime where $B \ll 1$, $\bar{V} = O(1)$, $\bar{V} > \theta_{MB}$ we have found the asymptotic expression (4.3.72) for J_1 whilst J_2 is given by the asymptotic expression (4.3.44) found in §4.3.3.3. Letting $B = 10^{-3}$, $\bar{V} = 2$, $\theta_{MB} = 1$ and finding $K_3 \approx 1.27$ using the method outlined in §4.3.4.4 the expression (4.3.72) gives $J_1 \sim -4.84 \times 10^{-19}$ and (4.3.44) gives $J_2 \sim 2.52 \times 10^{-77}$ that have excellent agreement with the numerically calculated values $J_1 \approx -4.84 \times 10^{-19}$ and $J_2 \approx 2.53 \times 10^{-77}$. By analysing the exponents in (4.3.44) and (4.3.72) we find for $\bar{V} > \theta_{MB}$

$$\frac{8\theta_{MB}^{3/2}}{3\bar{V}} < \frac{2\sqrt{2\bar{V}}}{3} \left(\left(\frac{2\theta_{MB}}{\bar{V}} + 2 \right)^{3/2} - \left(\frac{2\theta_{MB}}{\bar{V}} \right)^{3/2} \right) \quad (4.3.78)$$

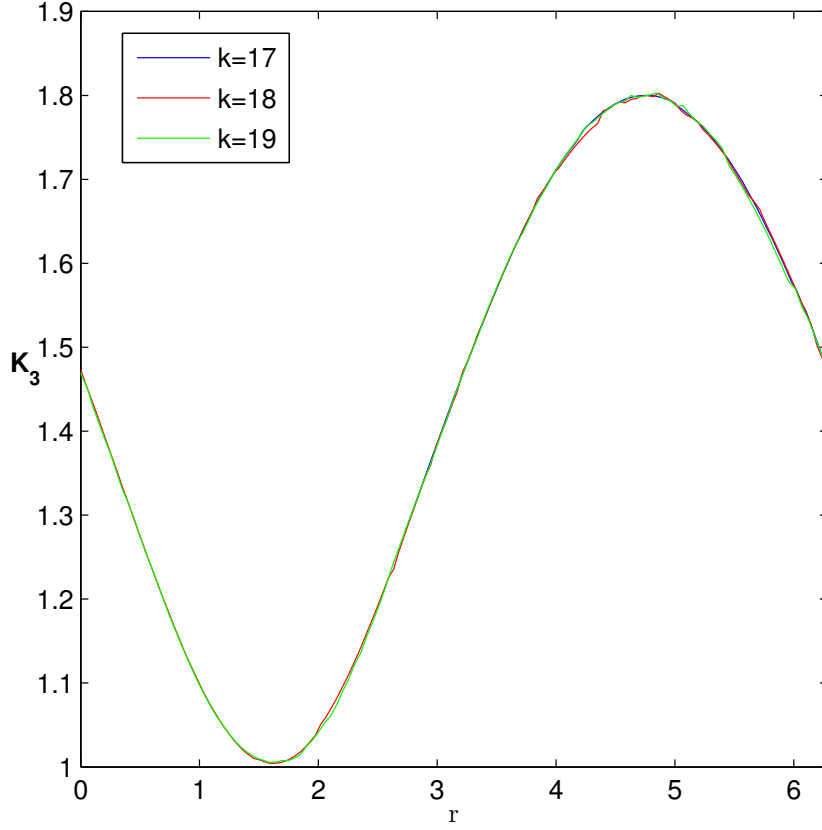


Figure 4.15: The constant K_3 plotted against the remainder r where $z_1 = -1/2$ and $k = 17, 18, 19$.

and therefore similarly to §4.3.3 $|J_2| \ll |J_1|$ making the total current density

$$J \sim J_1 \sim -\frac{\sqrt{2\theta_{MB}}\bar{V}^{1/6}}{K_3^2(z_1, r)} \exp\left(-\frac{8\theta_{MB}^{3/2}}{3\sqrt{B\bar{V}}}\right), \quad (4.3.79)$$

where $B \ll 1$, $\bar{V} = O(1)$ and $\bar{V} > \theta_{MB}$. In figure 4.16 we demonstrate the validity of the relation (4.3.79) by comparing to the numerical solution. In figure 4.16 oscillatory variation in the current density is evident that is well predicted by the asymptotic expression (4.3.79). A physical interpretation of these oscillations could be that the wave-like nature of electrons in quantum mechanics leads to some resonant effects.

4.3.4.6 Summary

In the regime where $B \ll 1$, $\bar{V} = O(1)$ and $\bar{V} > \theta_{MB}$ we have determined that electron subpopulation 2 has the same qualitative behaviour as is present in §4.3.3 and therefore the asymptotic expression for J_2 found in §4.3.3 still holds. On the other hand, electron

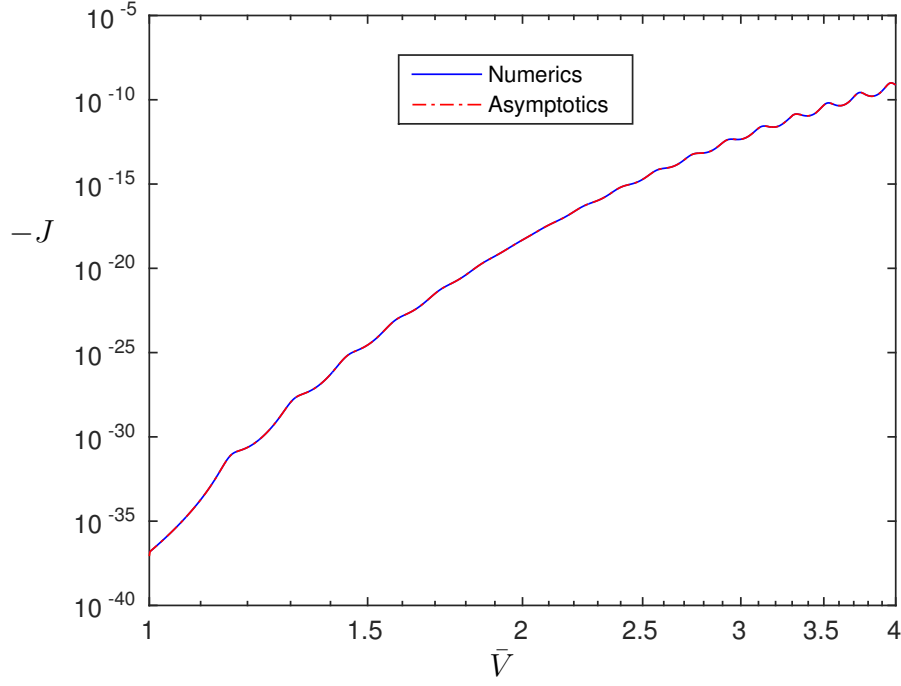


Figure 4.16: Current density ($-J$) plotted against applied potential difference $\bar{V}$ where $B = 10^{-3}$ and $\theta_{MB} = 1$. The asymptotic solution is given by (4.3.79) and the numerical solution is found by solving the system (4.3.25)–(4.3.26) in MATLAB.

subpopulation 1 has different qualitative behaviour with the presence of an exponentially decaying solution and an oscillatory solution in differing regions of the domain. The oscillatory solution is many orders of magnitude smaller than the exponential solution and therefore carrying out a naive boundary value problem procedure (as done by Ancona [4, 6]) does not observe this behaviour. The oscillatory behaviour is often found when using non-equilibrium Green's function methods to model tunnelling and is attributed to the quantum mechanical charge screening effect known as Friedel oscillations [6, 55]. We have used asymptotic methods to fully characterise the oscillatory solution and to determine an explicit solution for the total current density J . The explicit solution for J (4.3.79) contains a prefactor K_3 that we have outlined a procedure for finding. We find that there is also oscillatory behaviour in the current density that we attribute to resonant effects present due to the wave-like behaviour of electrons in quantum mechanics.

Setting $\bar{V} = \theta_{MB}$ ($z_1 = 1$), the two asymptotic expressions for current density (4.3.46) and (4.3.79) found where $\bar{V} < \theta_{MB}$ and $\bar{V} > \theta_{MB}$, respectively, will not agree. Hence, to determine the asymptotic expression for current density where $\bar{V} = \theta_{MB}$ the local asymptotic problem where $\bar{V} \approx \theta_{MB}$ ($z_1 \approx 1$) must be solved.

Similarly to §4.3.3 the expression (4.3.46) is a physically reasonable result, since increasing the length of the insulator (decreasing B) and also increasing the barrier height θ_{MB} results in the current density decreasing exponentially and increasing the applied

potential difference $\bar{V}$ results in the current density increasing exponentially.

4.4 Discussion and conclusions

In this chapter, we have investigated two different approaches for modelling quantum mechanical effects. The DGC theory approach involves the addition of a quantum term into the drift diffusion equations. As the DGC theory is the lowest order quantum correction it is technically only mathematically valid when the quantum term is a small perturbation to the system. This means that in our boundary layer analysis in §4.2.4 when the quantum term is present to leading order it is questionable whether it is legitimate to neglect further higher-order terms. In this chapter we have not investigated the validity of the DGC equations but instead (like many in device research [6]) have used the model and analysed the results for our system.

Naively, it appears the DGC theory is most applicable when considering current flow on length scales $\geq 10\text{nm}$. The lack of inertial effects in the DGC theory means that when applying it to length scales $O(1)\text{nm}$ it can be considered little more than a curve fitting technique [6]. The DGT theory neglects scattering and includes inertial effects making it most applicable to length scales $O(1)\text{nm}$. The model that is most relevant to an ‘intermediate’ situation will depend on the size of many relevant parameters whose exact value is often known by no-one.

We analysed a mathematical model based upon DGC theory to determine if quantum mechanical effects are important when considering electron flow across the glass layer present at the front contact of a silicon solar cell. We found that the inclusion of quantum mechanical effects changes the distribution of electron density in the glass layer but is unmeasurable on the macroscopic scale. In particular, the quantum term leads to oscillatory behaviour in the solution profile of the electron density. We also investigated the DGT theory by extending the work of Ancona [4]. Our reformulation of the boundary value problem into an initial value problem enables easy numerical solution and allows us to observe otherwise unreported oscillatory behaviour in the solution profile of the square rooted electron density. Furthermore, through asymptotic analysis we were able to fully characterise these oscillations and obtain approximate analytic expressions for the total current density. We found the approximate expressions for total current density to be physically reasonable and comparable to those from more complicated microscopic quantum transport theories [90].

As noted above, in our investigations of the two different theories we found oscillatory behaviour to be present in the solution structure of the electron density in both cases. Oscillatory behaviour of the electron density is found when using the nonequilibrium Green’s

function method to model quantum mechanical tunnelling and is attributed to quantum mechanical electric charge screening (Friedel oscillations) [6, 55]. Friedel oscillations is therefore a possible physical interpretation of this oscillatory behaviour. However, the origin of these oscillations is different in the two cases. The introduction of the quantum term in DGC theory led to the oscillations in §4.2 whilst the oscillations arose in §4.3.4 when the inertial term was present at leading order. An interesting extension to the analysis carried out in this chapter would be to consider a mathematical model involving a combination of these two theories.

In summary, we conclude that the incorporation of quantum effects is not likely to be necessary to explain the contact resistance in situations of physical interest to silicon solar cell manufacturers.

Chapter 5

Investigation into the silicon emitter-glass interface boundary condition

5.1 Introduction

In Chapter 2, when considering the silicon emitter-glass-silver electrode system we took the electron density at the silicon-glass interface to be a known constant. In this chapter we examine the validity of this original simplified boundary condition by extending the model presented in Chapter 2 to include current flow through the silicon.

In §5.2–5.4 by extending the model presented in Chapter 2, we formulate a model for current flow through the Si-glass-Ag system. In §5.5 we solve the model numerically and demonstrate that the inclusion of holes in the silicon has negligible effect. In §5.6 by solving in the silicon in the small Debye length limit we derive effective boundary conditions on the silicon-glass interface. Finally, in §5.7 we discuss how to incorporate the effective boundary conditions into the one-dimensional and two-dimensional models investigated in Chapters 2 and 3, respectively.

5.2 Formulation of the problem

By extending the drift diffusion model in Chapter 2 we consider one-dimensional conduction through a Si-glass-Ag system. We apply the Ideal boundary conditions at the glass-silver interface and assume the silicon is in equilibrium away from the silicon-glass interface. The silicon is taken to be doped n-type silicon, as is usual for the emitter of a silicon solar cell [74]. A schematic of the device under consideration is given in figure 5.1; the silicon is contained in $-L_{\text{Si}} < x < 0$ and the glass layer in $0 < x < H$.

To formulate the equations within the silicon we take the model (1.6.10)–(1.6.14) and make the following assumptions

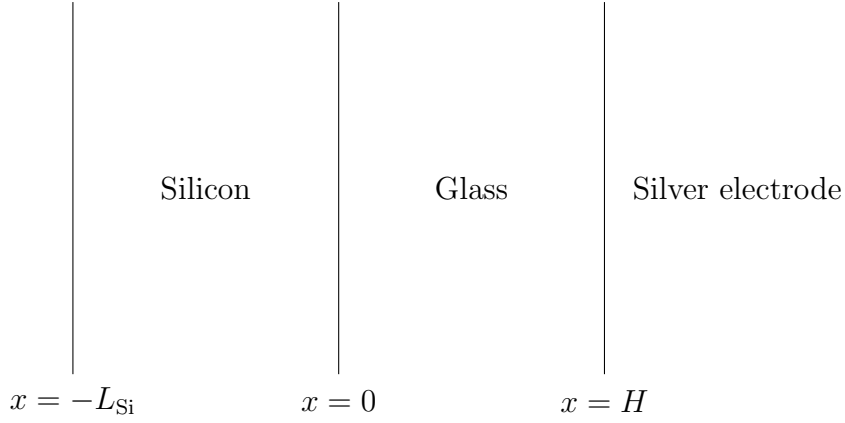


Figure 5.1: Schematic of the Si-glass-Ag system

- There is no generation within the silicon.
- The recombination in the silicon is assumed to take place via traps (Shockley-Read-Hall recombination). In Shockley-Read-Hall recombination the electron is thermally emitted [74].
- The silicon is doped with donor impurities with the doping constant throughout.
- The system is in quasi-steady state.
- The mobilities of the electrons and holes in the silicon are equal.

We therefore arrive at the following system of equations in the region $-L_{\text{Si}} < x < 0$

$$\frac{d}{dx}(j_p - j_n) = 0, \quad (5.2.1)$$

$$\frac{dj_n}{dx} = -\frac{np - \hat{n}_i^2}{T_1 n + T_1 p + T_2}, \quad (5.2.2)$$

$$\frac{d^2 \phi}{dx^2} = \frac{q}{\epsilon_{\text{Si}}}(n - p - N_D), \quad (5.2.3)$$

$$j_n = \hat{\mu} \left(-n \frac{d\phi}{dx} + \frac{k_B T}{q} \frac{dn}{dx} \right), \quad (5.2.4)$$

$$j_p = -\hat{\mu} \left(p \frac{d\phi}{dx} + \frac{k_B T}{q} \frac{dp}{dx} \right), \quad (5.2.5)$$

where ϵ_{Si} is the absolute permittivity of silicon, $\hat{\mu}$ is the mobility of charge carriers in the silicon and T_1 and T_2 are recombination constants. Within the glass in region $0 < x < H$

we take the equations (2.2.7)–(2.2.8) as they were presented in Chapter 2

$$\frac{dj_n}{dx} = 0, \quad (5.2.6)$$

$$\frac{d^2\phi}{dx^2} = \frac{qn}{\epsilon}, \quad (5.2.7)$$

$$j_n = \mu \left(-n \frac{d\phi}{dx} + \frac{k_B T}{q} \frac{dn}{dx} \right). \quad (5.2.8)$$

In practice, there is positively doped silicon abutting the negatively doped silicon, however, since we only wish to investigate the silicon-glass interface we make the assumption that the n-type silicon is in equilibrium away from the interface and also apply an electric potential difference over the device to give

$$\phi = -\Phi + \tilde{\Phi}, \quad n = N_D, \quad p = \frac{\hat{n}_i^2}{N_D}, \quad \text{at } x = -L_{\text{Si}}, \quad (5.2.9)$$

where $\hat{n}_i$ is the intrinsic electron density of silicon and $\tilde{\Phi}$ is given by

$$\tilde{\Phi} = -\frac{1}{q} (\hat{\chi}_n + W_{\text{Ag}}). \quad (5.2.10)$$

Here, $\hat{\chi}_n$ is the electron affinity of silicon. We make the following assumptions for the jump conditions at the silicon-glass interface

- There is continuity of electric potential and electric displacement

$$\phi|_{x=0-} = \phi|_{x=0+}, \quad \epsilon_{\text{Si}} \frac{d\phi}{dx}|_{x=0-} = \epsilon \frac{d\phi}{dx}|_{x=0+}. \quad (5.2.11)$$

- There is continuity of electric current and there exists electron-hole recombination at the interface

$$j|_{0-} - j_p|_{0-} = j|_{0+}, \quad j_p|_{0-} = T_3(np - \hat{n}_i^2), \quad (5.2.12)$$

where T_3 is the electron-hole recombination rate.

- The discontinuity in the conduction bands present at the silicon-glass contact is realised by an effective discontinuity in the electron density. The jump in electron density is found by assuming the Fermi levels are aligned [43]:

$$n|_{0-} = \gamma_n n|_{0+}, \quad \text{where } \gamma_n = \frac{\hat{g}_c}{\bar{g}_c} \exp \left(-\frac{\hat{\chi}_n - \bar{\chi}_n}{k_B T} \right). \quad (5.2.13)$$

Here $\hat{g}_c$ is the conduction band density of states in the silicon.

We complete the system by applying the Ideal boundary condition (1.7.3) for the electron density at the glass-silver interface and specifying the electric potential

$$\phi = 0, \quad n = n_1 = \bar{g}_c \exp \left(-\frac{\bar{\chi}_n + W_{\text{Ag}}}{k_B T} \right), \quad \text{at } x = L. \quad (5.2.14)$$

5.3 Nondimensionalisation

For the nondimensionalisation we scale the length and charge carrier densities differently in each region. In the silicon ($-L_{\text{Si}} < x < 0$) we let

$$n = N_D n^*, \quad p = \frac{\hat{n}_i^2}{N_D} p^*, \quad x = L_{\text{Si}} x^*, \quad (5.3.1)$$

whilst in the glass ($0 < x < H$) we apply the same scalings for the length and electron density as in §2.2.2:

$$x = H x^*, \quad n = n_1 n^*. \quad (5.3.2)$$

We scale all the electric potentials with the thermal voltage $k_B T/q$, the electron flux with $\mu k_B T n_1 / (qH)$ and the hole flux with $\mu k_B T \hat{n}_i^2 / (qL_{\text{Si}} N_D)$. We include a minus sign in our scalings of the electric potential ϕ and electric potential difference Φ as well as dropping the standard subscript n for the electron flux for consistency with Chapters 2–4. The remaining scalings thus take the form

$$\phi = -\frac{k_B T}{q} \phi^*, \quad \tilde{\Phi} = \frac{k_B T}{q} \tilde{\Psi}, \quad \Phi = -\frac{k_B T}{q} \Phi^*, \quad j_n = \frac{\mu k_B T n_1}{qH} j^*, \quad j_p = \frac{\mu k_B T \hat{n}_i^2}{qH N_D} j_p^*. \quad (5.3.3)$$

The dimensionless parameters that emerge from the scalings we have applied are

$$\begin{aligned} K &= \frac{n_i}{N_D}, \quad L_1 = \frac{H}{L_{\text{Si}}}, \quad \nu = \sqrt{\frac{\epsilon k_B T}{q^2 H^2 n_1}}, \quad \bar{T}_1 = \frac{\mu k_B T T_1 n_1 N_D}{qH L_{\text{Si}} n_i^2}, \quad \bar{T}_2 = \frac{T_2}{T_1 N_D}, \\ \Sigma &= \frac{\epsilon_{\text{Si}}}{\epsilon}, \quad \bar{C} = \frac{N_D}{n_1}, \quad M = \frac{\mu}{\hat{\mu}}, \quad \bar{T}_3 = \frac{T_3 H N_D q}{\mu k_B T}, \quad \tilde{\Psi} = \frac{q \tilde{\Phi}}{k_B T}, \\ \lambda &= \sqrt{\frac{\epsilon_{\text{Si}} k_B T}{q^2 L_{\text{Si}}^2 N_D}}, \quad \gamma_n = \frac{\hat{g}_c}{\bar{g}_c} \exp\left(-\frac{\hat{\chi}_n - \bar{\chi}_n}{k_B T}\right) = \frac{\hat{g}_c}{n_1} \exp\left(\frac{q V_{bi}}{k_B T}\right). \end{aligned}$$

The important parameters to consider are: γ the ratio between the electron density in the silicon and the electron density in the glass, λ the scaled Debye length in the silicon, and ν the scaled Debye length in the glass that is identical to the variable defined in (2.2.10). The high level of doping present in the silicon emitter of a solar cell means λ will be small in practice, an estimate of the size of λ is given in (5.4.1).

Applying the scalings (5.3.1)–(5.3.3) to the system (5.2.1)–(5.2.14) and dropping the

starred notation we obtain the governing equations

$$\left. \begin{aligned} \frac{d}{dx}(K^2 \bar{C} j_p - j) &= 0 \\ \bar{T}_1 \frac{dj}{dx} &= -\frac{np - 1}{n + K_n^2 p + \bar{T}_2} \\ \lambda^2 \frac{d^2 \phi}{dx^2} &= -(n - K^2 p - 1) \\ \frac{M}{L_1 \bar{C}} j &= -n \frac{d\phi}{dx} - \frac{dn}{dx} \\ \frac{M}{L_1} j_p &= p \frac{d\phi}{dx} - \frac{dp}{dx} \end{aligned} \right\} \quad \text{in } -1 < x < 0, \quad (5.3.4)$$

$$\left. \begin{aligned} \frac{dj}{dx} &= 0 \\ \nu^2 \frac{d^2 \phi}{dx^2} &= -n \\ j &= -n \frac{d\phi}{dx} - \frac{dn}{dx} \end{aligned} \right\} \quad \text{in } 0 < x < 1, \quad (5.3.5)$$

the jump conditions

$$\phi|_{0-} = \phi|_{0+}, \quad \Sigma L_1 \frac{d\phi}{dx}|_{0-} = \frac{d\phi}{dx}|_{0+}, \quad n|_{0-} = \frac{\gamma_n}{\bar{C}} n|_{0+}, \quad (5.3.6)$$

$$j|_{0-} - \bar{C} K^2 j_p|_{0-} = j|_{0+}, \quad j_p|_{0-} = \bar{T}_3 (np - 1), \quad (5.3.7)$$

and the boundary conditions

$$\left. \begin{aligned} \phi &= \Phi + \tilde{\Psi} \\ n &= 1 \\ p &= 1 \end{aligned} \right\} \quad \text{at } x = -1, \quad \left. \begin{aligned} \phi &= 0 \\ n &= 1 \end{aligned} \right\} \quad \text{at } x = 1. \quad (5.3.8)$$

When solving the system (5.3.4)–(5.3.8) we specify the electric potential difference Φ and determine the total charge carrier flux $\mathcal{Q}$ using

$$\mathcal{Q} = \int_{-1}^0 (K^2 \bar{C} j_p - j) dx = \int_0^1 j dx. \quad (5.3.9)$$

The effective resistance of the Si-glass-Ag system is given by the total potential difference V_{tot} over the total charge carrier flux:

$$R = \frac{V_{\text{tot}}}{\mathcal{Q}} = \frac{\Phi + \tilde{\Psi} + \log(\bar{C}/\gamma_n)}{\mathcal{Q}}. \quad (5.3.10)$$

The definition of resistance (5.3.10) differs from the one originally given in Chapter 2 (2.2.12), as the built in potential (that is the electric potential difference between the anode and cathode of the device in equilibrium) is given by $(-\tilde{\Psi} - \log(\bar{C}/\gamma_n))$ rather than $(-\log \alpha)$. Subtracting the built in potential from the applied electric potential difference ensures that at zero total potential difference $V_{\text{tot}} = 0$ there is zero total charge carrier flux $\mathcal{Q} = 0$. If holes are neglected, the total charge carrier flux is equivalent to the electron flux.

5.4 Nondimensional parameter estimation

We now obtain estimates for the nondimensional parameters. Boltzmann's constant, k_B , is $1.38 \times 10^{-23} \text{m}^2 \text{kgs}^{-2} \text{K}^{-1}$ and charge on an electron, q , is $1.6 \times 10^{-19} \text{C}$ with other parameter sizes contained in Table 5.1. The parameters ϵ_{Si} , $\hat{\mu}$, $\hat{g}_c$, $\hat{\chi}_n$, $\hat{n}_i$, W_{Ag} , $\tilde{\Phi}$ are those found in Sze & Ng [95], whilst we take the values of L_{Si} and N_D for a typical solar cell n-type emitter from Nelson [74]. The reasoning behind the parameter estimate for $\bar{\chi}_n$ is given in §2.2.1. The values for the recombination constants T_1 and T_2 are those taken in [78].

We assume the absolute permittivity of the glass ϵ is that of silicon dioxide. We assume the mobility of the electrons in the glass μ is much less than the mobility of electrons in silicon i.e. $\mu \ll \hat{\mu}$. As discussed in §2.2.2 we expect $n_1 \in (10^{20} \text{m}^{-3}, 10^{28} \text{m}^{-3})$ and therefore for illustration purposes let $n_1 \approx 10^{24} \text{m}^{-3}$. We estimate the thickness of the glass layer $H \approx 5 \times 10^{-7} \text{m}$ and let the absolute temperature T be room temperature. These estimates lead to the following approximate parameter sizes:

$$\begin{aligned} K &\approx 9.7 \times 10^{-10}, & L_1 &\approx 1, & \nu &\approx 10^{-2}, & \bar{T}_1 &\approx 10^{19}, \\ \bar{T}_2 &\approx 1.6 \times 10^{-15}, & \Sigma &\approx 3.04, & \bar{C} &\approx 10, & M &\ll 1, \\ \gamma_n &\approx 10^{-3}, & \tilde{\Psi} &\approx -9.66, & \lambda &\approx 2.6 \times 10^{-3} \end{aligned} \quad (5.4.1)$$

We take the final dimensionless parameter $\bar{T}_3 \approx O(1)$ as the completely unknown parameter T_3 makes any estimate difficult. The possibly surprising smallness of the parameter γ_n arises from our assumption in §2.2.1 that the electron affinity of the glass layer has been manipulated by the industrialists so that $|\bar{\chi}_n| \gtrsim W_{Ag}$. There is lots of potential variation in these parameter values and therefore these estimates must be taken with caution.

The very small value of K and very large value of $\bar{T}_1$ found lead us to hypothesise that to leading-order we can neglect holes in the silicon. If we neglect holes in the silicon, the governing equations from system (5.3.4)–(5.3.8) become

$$\left. \begin{aligned} \frac{dj}{dx} &= 0 \\ \lambda^2 \frac{d^2\phi}{dx^2} &= 1 - n \\ \frac{M}{L_1 \bar{C}} j &= -n \frac{d\phi}{dx} - \frac{dn}{dx} \end{aligned} \right\} \quad \text{in } -1 < x < 0, \quad (5.4.2)$$

$$\left. \begin{aligned} \frac{dj}{dx} &= 0 \\ \nu^2 \frac{d^2\phi}{dx^2} &= -n \\ j &= -n \frac{d\phi}{dx} - \frac{dn}{dx} \end{aligned} \right\} \quad \text{in } 0 < x < 1, \quad (5.4.3)$$

ϵ_{Si}	$1.05 \times 10^{-10} \text{ Fm}^{-1}$
ϵ	$3.45 \times 10^{-11} \text{ Fm}^{-1}$
T	$300K$
L_{Si}	$5 \times 10^{-7} \text{ m}$
H	$5 \times 10^{-7} \text{ m}$
N_D	10^{25} m^{-3}
$\hat{n}_i$	$9.7 \times 10^{15} \text{ m}^3$
$\hat{\mu}$	$1.5 \times 10^{-2} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
μ	$\ll 1.5 \times 10^{-2} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
T_1	$2.7 \times 10^{-7} \text{ s}^{-1}$
T_2	$4.3 \times 10^3 \text{ s}^{-1} \text{ m}^{-3}$
$\hat{g}_c$	$3 \times 10^{25} \text{ m}^{-3}$
$\hat{\chi}_n$	-4.05 eV
W_{Ag}	4.3 eV
$\tilde{\Phi}$	-0.25 V
$\bar{\chi}_n$	$\lesssim -4.3 \text{ eV}$
n_1	$(10^{20} \text{ m}^{-3}, 10^{28} \text{ m}^{-3})$

Table 5.1: Physical parameter values.

with jump conditions

$$\begin{aligned} \phi|_{0-} &= \phi|_{0+}, \quad \Sigma L_1 \frac{d\phi}{dx}|_{0-} = \frac{d\phi}{dx}|_{0+}, \quad n|_{0-} = \frac{\gamma_n}{\bar{C}} n|_{0+}, \\ j|_{0-} &= j|_{0+}, \end{aligned} \quad (5.4.4)$$

and boundary conditions

$$\left. \begin{aligned} \phi &= \Phi + \tilde{\Psi} \\ n &= 1 \end{aligned} \right\} \quad \text{at } x = -1, \quad \left. \begin{aligned} \phi &= 0 \\ n &= 1 \end{aligned} \right\} \quad \text{at } x = 1, \quad (5.4.5)$$

We verify our hypothesis numerically in §5.5 below.

5.5 Numerical solution

We numerically solve the two systems (5.3.4)–(5.3.8) (including holes in the silicon) and (5.4.2)–(5.4.5) (neglecting holes in the silicon) by following the method outlined by Foster et al. [43]. The method involves transforming all the governing equations to the same interval $(0, 1)$ and solving with the software package **Chebfun**. We outline the procedure by considering system (5.4.2)–(5.4.5) with exactly the same methodology followed when solving system (5.3.4)–(5.3.8). The transformation is carried out by making the following

change of variables on (5.4.2)–(5.4.5)

$$\left. \begin{aligned} x &= -z \\ j(x) &= \hat{j}(z) \\ n(x) &= \hat{n}(z) \\ \phi(x) &= \hat{\phi}(z) \end{aligned} \right\} \quad \text{in} \quad -1 < x < 0, \quad (5.5.1)$$

$$\left. \begin{aligned} x &= z \\ j(x) &= \tilde{j}(z) \\ n(x) &= \tilde{n}(z) \\ \phi(x) &= \tilde{\phi}(z) \end{aligned} \right\} \quad \text{in} \quad 0 < x < 1. \quad (5.5.2)$$

The governing equations are now posed on the region $0 < z < 1$ and given by

$$\begin{aligned} \frac{d\hat{j}}{dz} &= 0, & \lambda^2 \frac{d^2 \hat{\phi}}{dz^2} &= 1 - \hat{n}, \\ \frac{M}{L_1 \bar{C}} \hat{j} &= \hat{n} \frac{d\hat{\phi}}{dz} + \frac{d\hat{n}}{dz}, & \frac{d\tilde{j}}{dz} &= 0, \\ \nu^2 \frac{d^2 \tilde{\phi}}{dz^2} &= -\tilde{n}, & \tilde{j} &= -\tilde{n} \frac{d\tilde{n}}{dz} - \frac{d\tilde{n}}{dz}. \end{aligned} \quad (5.5.3)$$

The boundary conditions are

$$\left. \begin{aligned} \hat{\phi} - \tilde{\phi} &= 0 \\ -\Sigma L_1 \frac{d\hat{\phi}}{dz} &= \frac{d\tilde{\phi}}{dz} \\ \hat{n} &= \frac{\gamma_n}{\bar{C}} \tilde{n} \\ \hat{j} &= \tilde{j} \end{aligned} \right\} \quad \text{at} \quad z = 0, \quad \left. \begin{aligned} \hat{\phi} &= \Phi + \tilde{\Psi} \\ \hat{n} &= 1 \\ \tilde{\phi} &= 0 \\ \tilde{n} &= 1 \end{aligned} \right\} \quad \text{at} \quad z = 1. \quad (5.5.4)$$

Equations (5.5.3)–(5.5.4) comprise a sixth order system with eight boundary conditions. To solve, we specify the electric potential difference Φ and determine the electron fluxes given by $\tilde{j}$ and $\hat{j}$.

In (5.4.1) we found that for physically realistic parameter values our nondimensional parameters take extreme values which make the systems (5.3.4)–(5.3.8) and (5.4.2)–(5.4.5) difficult to solve numerically, even using **Chebfun** that is well suited for stiff problems. To test our no holes hypothesis we therefore pick three different sets of nondimensional parameter values that are equivalent to letting $n_1 = 10^{24} m^{-3}$, $M = 10^{-1}$, $\Phi = 11$, fixing $\bar{T}_3 = 1$, using the parameter values from Table 5.1 and considering the silicon to be doped to different levels.

1. Parameter values where the doping in the silicon is $N_D \approx 10^{24}m^{-3}$:

$$\begin{aligned} K &= 10^{-8}, & L_1 &= 1, & \nu &= 10^{-2}, & \bar{T}_1 &= 10^{18}, & \bar{T}_2 &= 10^{-14}, & \Sigma &= 3.04, \\ \bar{C} &= 1, & M &= 10^{-1}, & \gamma_n &= 10^{-3}, & \tilde{\Psi} &= -9.66, & \bar{T}_3 &= 1, & \Phi &= 11, \\ \lambda &= 8.2 \times 10^{-3}. \end{aligned} \tag{5.5.5}$$

2. Parameter values where the doping in the silicon is $N_D \approx 10^{23}m^{-3}$:

$$\begin{aligned} K &= 10^{-7}, & L_1 &= 1, & \nu &= 10^{-2}, & \bar{T}_1 &= 10^{17}, & \bar{T}_2 &= 10^{-13}, & \Sigma &= 3.04, \\ \bar{C} &= 10^{-1}, & M &= 10^{-1}, & \gamma_n &= 10^{-3}, & \tilde{\Psi} &= -9.66, & \bar{T}_3 &= 1, & \Phi &= 11, \\ \lambda &= 2.6 \times 10^{-2}. \end{aligned} \tag{5.5.6}$$

3. Parameter values where the doping in the silicon is $N_D \approx 10^{22}m^{-3}$:

$$\begin{aligned} K &= 10^{-6}, & L_1 &= 1, & \nu &= 10^{-2}, & \bar{T}_1 &= 10^{16}, & \bar{T}_2 &= 10^{-12}, & \Sigma &= 3.04, \\ \bar{C} &= 10^{-2}, & M &= 10^{-1}, & \gamma_n &= 10^{-3}, & \tilde{\Psi} &= -9.66, & \bar{T}_3 &= 1, & \Phi &= 11, \\ \lambda &= 8.2 \times 10^{-2}. \end{aligned} \tag{5.5.7}$$

In figures 5.2–5.4 we find excellent agreement between the numerical solution profiles of the electric potential ϕ and electron density n when solving systems (5.3.4)–(5.3.8) (including holes in the silicon) and (5.4.2)–(5.4.5) (neglecting holes in the silicon). Moreover, we find the two systems give the same value for total charge carrier flux $\mathcal{Q}$ for each set of parameter values considered. The excellent agreement between the numerical solutions of (5.3.4)–(5.3.8) and (5.4.2)–(5.4.5) found (even when considering a low doping of $N_D = 10^{22}m^{-3}$) means we neglect the holes in the silicon henceforth.

5.6 Derivation of effective boundary conditions

In §5.5 we numerically validated the assumption that the motion of holes in the silicon can be neglected and therefore reduced the governing equations in the silicon to (5.4.2). In this section we analyse the reduced governing equations in the silicon (5.4.2) along with the jump conditions (5.4.4) and boundary conditions at $x = -1$ (5.4.5) in the physically relevant limit $\lambda \rightarrow 0$ to determine effective boundary conditions at the silicon-glass interface.

Considering (5.4.2) in the limit $\lambda \rightarrow 0$ we find the solution to the leading-order outer problem is

$$n = 1, \quad \phi = \Phi + \tilde{\Psi}. \tag{5.6.1}$$

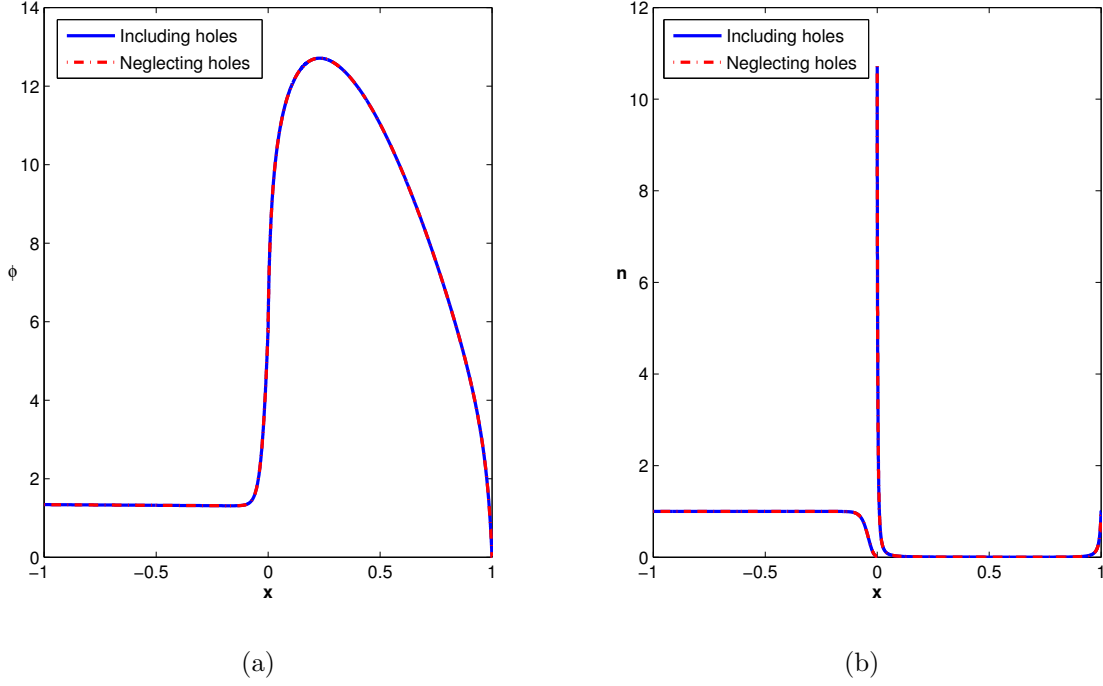


Figure 5.2: Electric potential ϕ and electron density n plotted against position x with all parameter values given in (5.5.5). Solving system (5.3.4)–(5.3.8) (including holes in the silicon) we find total charge carrier flux $\mathcal{Q} \approx 0.036$ and solving system (5.4.2)–(5.4.5) (neglecting holes in the silicon) we find total charge carrier flux $\mathcal{Q} \approx 0.036$.

The numerical solutions presented in figures 5.2–5.4 demonstrate the presence of a boundary layer in ϕ and n near $x = 0$. We solve in the boundary layer by making the rescaling $x = \lambda X_0$ to find (5.4.2) to leading-order is

$$\begin{aligned} \phi_{X_0 X_0} &= 1 - n, \\ n\phi_{X_0} + n_{X_0} &= 0. \end{aligned} \tag{5.6.2}$$

Integrating (5.6.2) and matching to the outer solution (5.6.1) we find

$$\begin{aligned} n &= e^{\Phi + \tilde{\Psi} - \phi}, \\ \phi_{X_0} &= \sqrt{2(\phi + e^{\Phi + \tilde{\Psi} - \phi} - (\Phi + \tilde{\Psi}) - 1)}. \end{aligned} \tag{5.6.3}$$

For consistency with Chapters 2–4 we define $n|_{0+} = \alpha$ and make use of (5.4.4) and (5.6.3) to obtain the effective boundary conditions at the silicon-glass interface in the limit $\lambda \rightarrow 0$:

$$\left. \begin{aligned} \phi &= \Phi + \tilde{\Psi} + \log\left(\frac{\bar{C}}{\gamma_n \alpha}\right) \\ n &= \alpha \\ \frac{d\phi}{dx} &= \frac{\Sigma L_1}{\lambda} \sqrt{2\left(\log\left(\frac{\bar{C}}{\gamma_n \alpha}\right) + \frac{\gamma_n \alpha}{\bar{C}} - 1\right)} \end{aligned} \right\} \text{ at } x = 0. \tag{5.6.4}$$

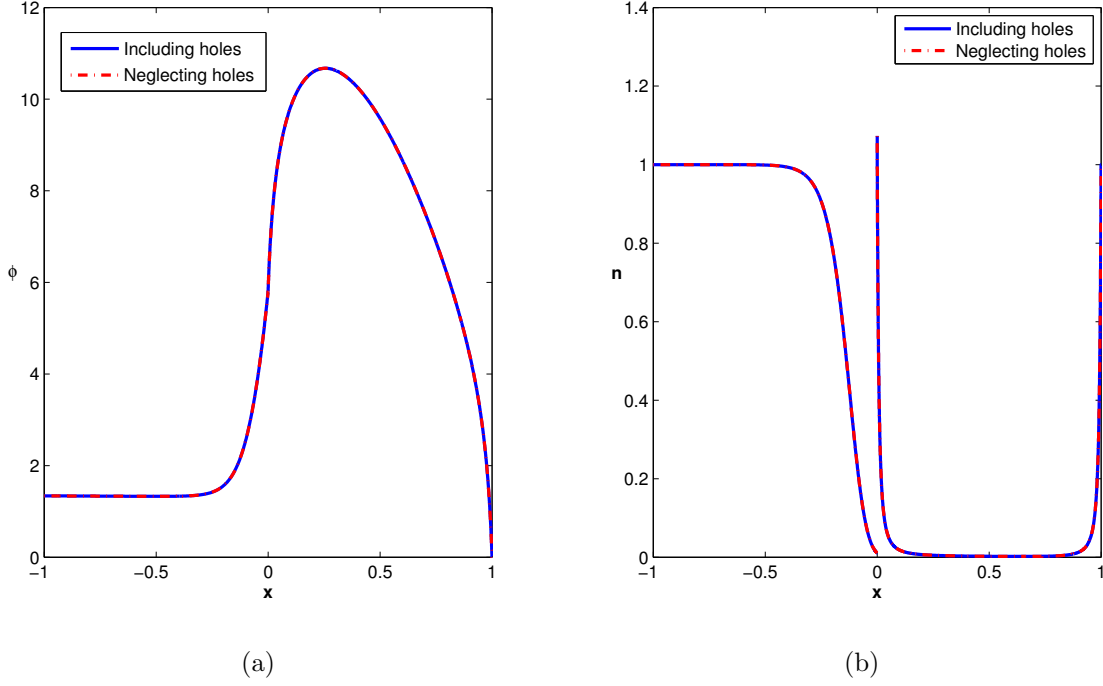


Figure 5.3: Electric potential ϕ and electron density n plotted against position x with all parameter values given in (5.5.6). Solving system (5.3.4)–(5.3.8) (including holes in the silicon) we find total charge carrier flux $\mathcal{Q} \approx 0.023$ and solving system (5.4.2)–(5.4.5) (neglecting holes in the silicon) we find total charge carrier flux $\mathcal{Q} \approx 0.023$.

By deriving effective boundary conditions we have obtained a closed model in the glass region which is given by (5.6.4), the governing equations

$$j = -n \frac{d\phi}{dx} - \frac{dn}{dx}, \quad (5.6.5)$$

$$\nu^2 \frac{d^2\phi}{dx^2} = -n, \quad (5.6.6)$$

and boundary conditions

$$\left. \begin{array}{l} \phi = 0 \\ n = 1 \end{array} \right\} \quad \text{at } x = 1. \quad (5.6.7)$$

The system (5.6.4)–(5.6.7) is a 3rd order system with 5 boundary conditions and two unknowns j and α and so it might reasonably be expected to have a unique solution in which j and α are determined as part of the solution. The three coupled boundary conditions (5.6.4) applied at $x = 0$ take a different form from the two Dirichlet conditions at $x = 0$ given in (2.2.9). The key difference is that in (5.6.4) there is an additional condition on ϕ' that means we do not specify α but solve for α . Furthermore, as shown in figure 5.2, α can take values greater than one. The final difference is that in (5.6.4) the electric potential ϕ specified at the silicon-glass interface is the applied electric potential

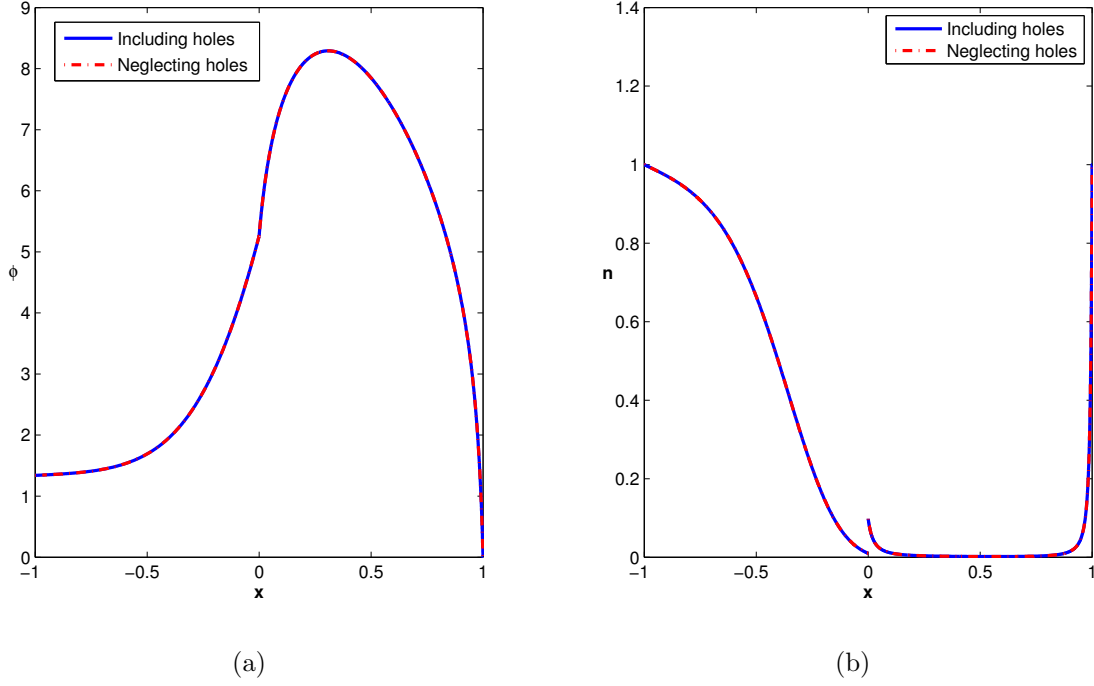


Figure 5.4: Electric potential ϕ and electron density n plotted against position x with all parameter values given in (5.5.7). Solving system (5.3.4)–(5.3.8) (including holes in the silicon) we find total charge carrier $\mathcal{Q} \approx 0.01$ and solving system (5.4.2)–(5.4.5) (neglecting holes in the silicon) we find total charge carrier flux $\mathcal{Q} \approx 0.01$.

difference Φ minus the built in potential $(-\tilde{\Psi} - \log(\bar{C}/\gamma_n))$, whereas, in (2.2.9) the electric potential ϕ at the silicon-glass interface was simply the applied electric potential difference Φ .

It is important to remember the effective boundary conditions (5.6.4) were derived in the limit $\lambda \rightarrow 0$ and lose validity if $\lambda \gtrsim O(1)$ or in the limit $\Phi \rightarrow \infty$ ($j \rightarrow \infty$).

We solve the system (5.6.4)–(5.6.7) numerically using **Chebfun** where we use the bisection method to determine the value of α that satisfies the condition on ϕ' in (5.6.4) up to a percentage error of $O(\nu)$. Similarly to system (5.4.2)–(5.4.5) we specify the applied electric potential difference Φ and determine the electron flux j .

To check the validity of our effective boundary conditions we also solve the system (5.4.2)–(5.4.5) with parameter values

$$\Phi = 11, 16, 21, \quad \bar{C} = 1, \quad \gamma_n = 10^{-3}, \quad \tilde{\Psi} = -9.66, \quad \Sigma = 3.04, \quad (5.6.8)$$

$$M = 10^{-4}, \quad L_1 = 1, \quad \nu = 10^{-2}, \quad \lambda = 8.2 \times 10^{-3}. \quad (5.6.9)$$

and compare the solution within the glass layer. In figures 5.5–5.7 we demonstrate the good agreement between the solution profiles of the electric potential ϕ and the electron density n when solving in the silicon and when making use of the effective boundary

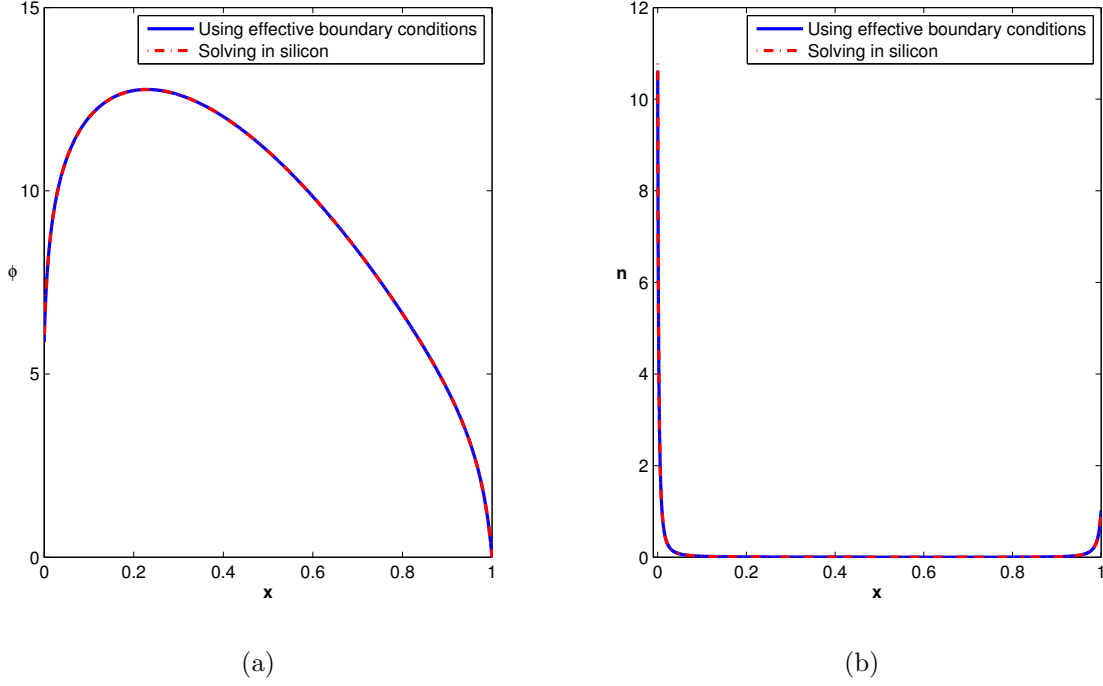


Figure 5.5: Electric potential ϕ and electron density n plotted against position x with $\Phi = 11$, $\bar{C} = 1$, $\gamma_n = 10^{-3}$, $\tilde{\Psi} = -9.66$, $\Sigma = 3.04$, $M = 10^{-4}$, $L_1 = 1$, $\lambda = 8.2 \times 10^{-3}$, and $\nu = 10^{-2}$. Solving system (5.4.2)–(5.4.5) (solving in the silicon) gives $j \approx 0.036$, $\alpha \approx 10.8$, and $\phi(0) \approx 5.9$ and solving system (5.6.4)–(5.6.7) (using effective boundary conditions) gives $j \approx 0.036$, $\alpha \approx 10.6$ and $\phi(0) \approx 5.9$.

conditions (5.6.4). Moreover, we see good agreement between the values of α , $\phi(0)$ and j found. In §5.7 below we discuss how we could incorporate the effective boundary conditions (5.6.4) into the work carried out in Chapters 2–3.

5.7 Application of effective boundary conditions

5.7.1 Introduction

In §5.6 we derived the effective boundary conditions (5.6.4) that should be applied to the silicon-glass interface when considering the Si-glass-Ag system in the physically relevant limit: small Debye length in the silicon $\lambda \ll 1$. These boundary conditions take a different form to those originally specified in Chapter 2. In this section we therefore investigate how the application of the boundary conditions (5.6.4) would change the analysis carried out in Chapter 2. We also discuss how the boundary conditions (5.6.4) could be incorporated into Chapter 3 to investigate the Si-glass-Ag system in two dimensions. In Chapter 4 we found that quantum mechanical effects were not important in explaining contact resistance in situations of physical interest and we therefore do not look to incorporate the

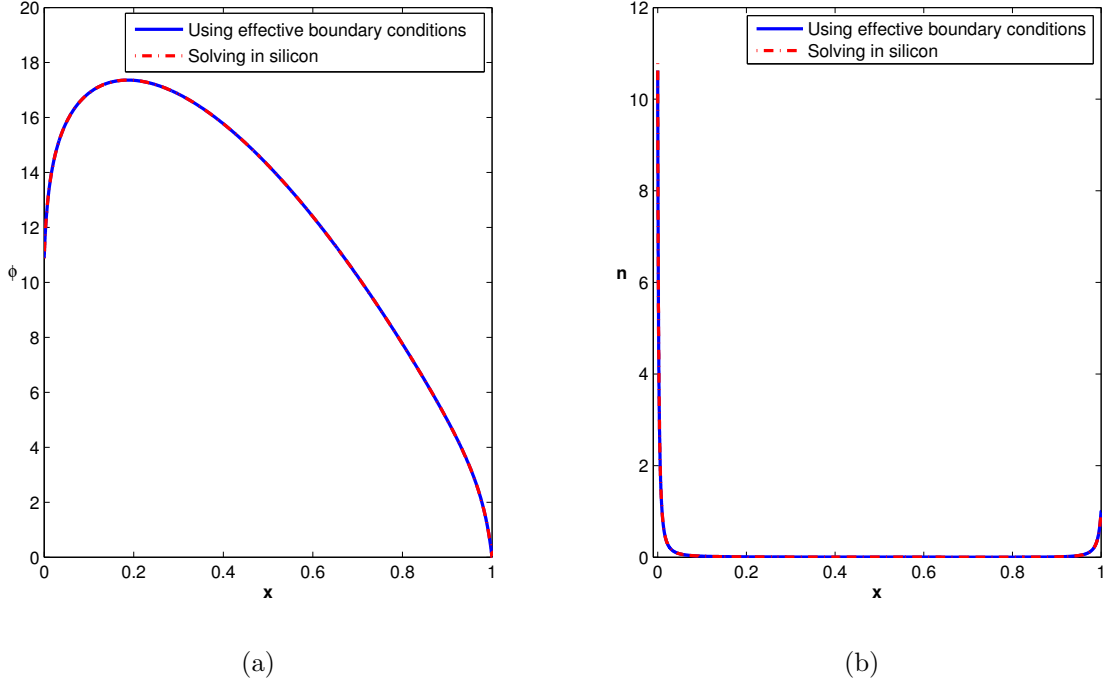


Figure 5.6: Electric potential ϕ and electron density n plotted against position x with $\Phi = 16$, $\bar{C} = 1$, $\gamma_n = 10^{-3}$, $\tilde{\Psi} = -9.66$, $\Sigma = 3.04$, $M = 10^{-4}$, $L_1 = 1$, $\lambda = 8.2 \times 10^{-3}$, and $\nu = 10^{-2}$. Solving system (5.4.2)–(5.4.5) (solving in the silicon) gives $j \approx 0.066$, $\alpha \approx 10.8$, and $\phi(0) \approx 10.9$ and solving system (5.6.4)–(5.6.7) (using effective boundary conditions) gives $j \approx 0.065$, $\alpha \approx 10.6$ and $\phi(0) \approx 10.9$.

boundary conditions (5.6.4) into the density gradient confinement model (4.2.2)–(4.2.3).

5.7.2 Application to 1D problem

The effective boundary conditions (5.6.4) were derived in the physically relevant limit where the Debye length in the silicon is small $\lambda \ll 1$. We therefore investigate how they affect the asymptotic calculations carried out in Chapter 2 in the physically relevant limit where the Debye length in the glass is small $\nu \ll 1$. In this section, as in §2.3.5.2, we take the electron flux j to be known and look to determine the applied potential difference Φ .

Following the methodology in §2.3.5.2 we find the effective boundary conditions (5.6.4) give rise to the following expressions for electric potential ϕ and electron density n in the boundary layer at $x = 0$

$$\phi \sim \Phi + \tilde{\Psi} + 2 \log \left(\sqrt{\frac{\bar{C}}{\gamma_n}} \left(\frac{1}{\sqrt{\alpha}} + \frac{X_0}{\sqrt{2}} \right) \right), \quad n \sim \alpha \left(1 + X_0 \sqrt{\frac{\alpha}{2}} \right)^{-2}. \quad (5.7.1)$$

where we make use of the condition on ϕ' in (5.6.4) to determine that α is given by the

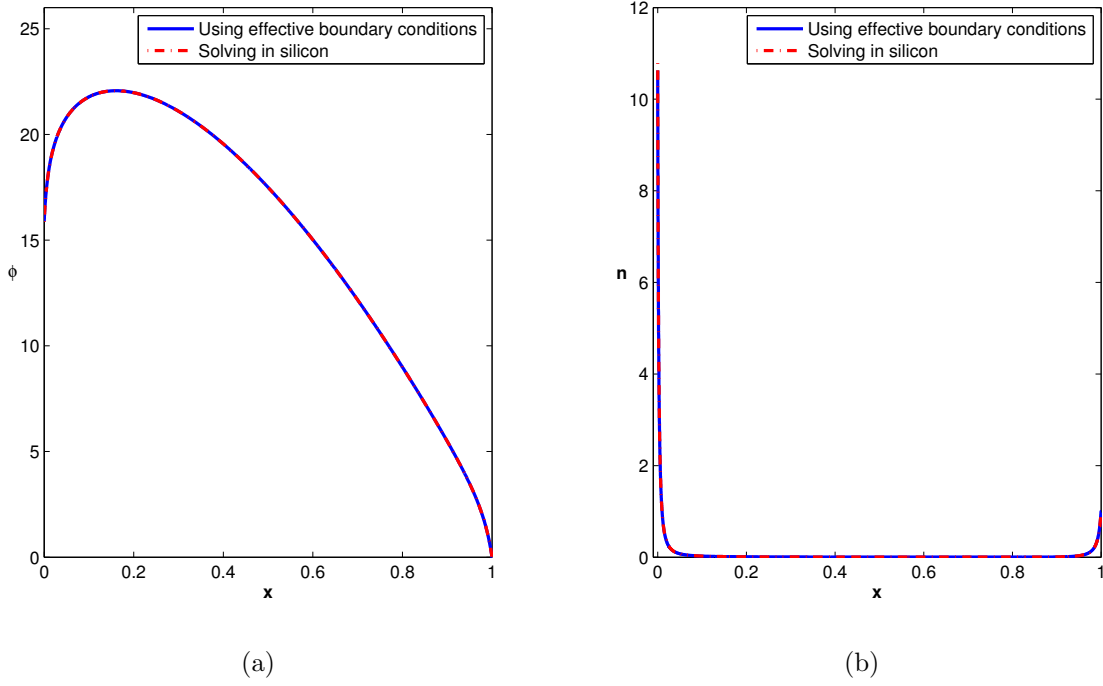


Figure 5.7: Electric potential ϕ and electron density n plotted against position x with $\Phi = 21$, $\bar{C} = 1$, $\gamma_n = 10^{-3}$, $\tilde{\Psi} = -9.66$, $\Sigma = 3.04$, $M = 10^{-4}$, $L_1 = 1$, $\lambda = 8.2 \times 10^{-3}$, and $\nu = 10^{-2}$. Solving system (5.4.2)–(5.4.5) (solving in the silicon) gives $j \approx 0.10$, $\alpha \approx 10.8$, and $\phi(0) \approx 15.9$ and solving system (5.6.4)–(5.6.7) (using effective boundary conditions) gives $j \approx 0.10$, $\alpha \approx 10.6$ and $\phi(0) \approx 15.9$.

solution of the transcendental equation

$$\alpha = \frac{\bar{C}\Sigma}{(1 - \Sigma\gamma_n)} \left[\log \left(\frac{\bar{C}}{\gamma_n \alpha} \right) - 1 \right]. \quad (5.7.2)$$

The expression (5.7.2) shows that α only depends on material parameters and not on the applied potential difference when the Debye length in both the glass and silicon is small. This is evident in the numerical simulations carried out in §5.6 where for various applied potential differences Φ the value of α remained approximately constant. Taking physical parameter values that were estimated in (5.4.1) we find that $\alpha \approx 108$ in the Si-glass-Ag system. Given that $\alpha = 1$ in the Ag-glass-Ag system this is a surprising result and means our original assumption that $\alpha < 1$ is not correct. However, the value of $\alpha > 1$ does not affect any of the asymptotic analysis carried out in Chapter 2.

The leading-order equations away from the boundaries are (2.3.28) and therefore if we make the substitution $\phi = 2 \log(U/\nu)$ the general solution takes the same form as (2.3.29) and is given by

$$U = a_2 \text{Ai}(\chi x - \hat{w}) + b_2 \text{Bi}(\chi x - \hat{w}), \quad (5.7.3)$$

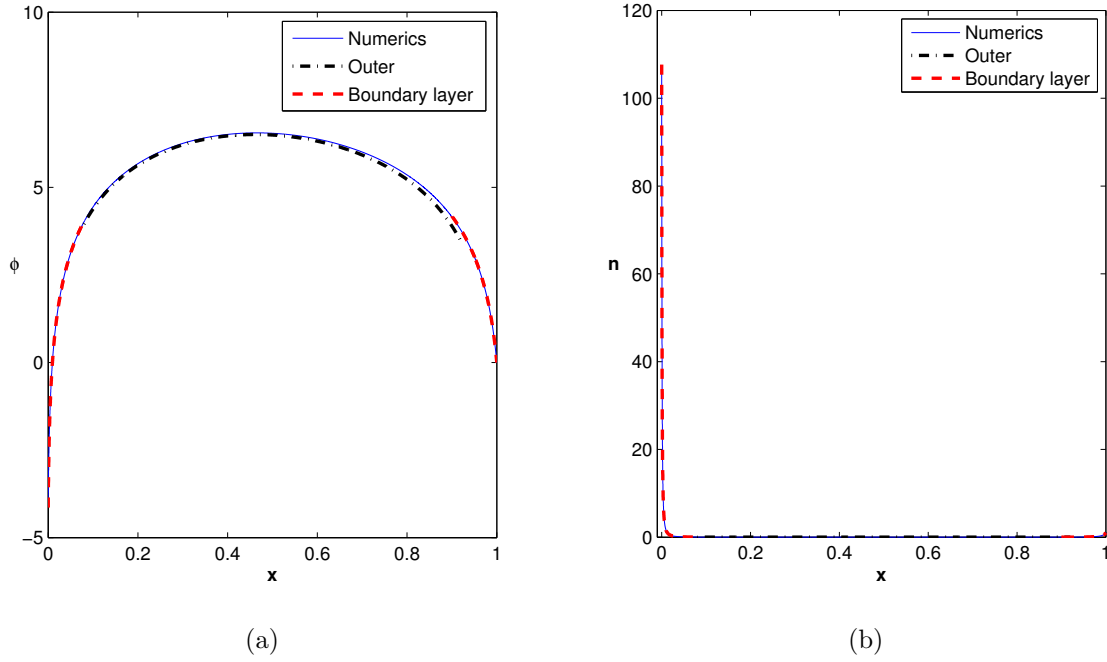


Figure 5.8: Electric potential ϕ and electron density n plotted against position x with $\bar{C} = 10$, $\gamma_n = 10^{-3}$, $\tilde{\Psi} = -9.66$, $\Sigma = 3.04$, $\lambda = 2.6 \times 10^{-3}$, and $\nu = 0.01$. The numerical solution is found by solving system (5.6.4)–(5.6.7) (using effective boundary conditions) with $\Phi = 1$ to determine $j \approx 0.0021$ and $\alpha \approx 108$. The asymptotic solution is found by specifying $j = 0.0021$ to determine $\alpha \approx 108$ and $\Phi \approx 0.99$.

where a_2 , b_2 and $\hat{w}$ are integration constants. The expressions (2.3.27) found in the boundary layer at $x = 1$ are still valid and therefore using (2.3.27), (5.7.1), and following the method in §2.3.5.3 we find the constants a_2 , b_2 and $\hat{w}$ as well as the applied electric potential difference Φ are given by the solution of the following system of four equations:

$$a_2 \text{Ai}(-\hat{w}) + b_2 \text{Bi}(-\hat{w}) = 0, \quad (5.7.4a)$$

$$a_2 \text{Ai}(\chi - \hat{w}) + b_2 \text{Bi}(\chi - \hat{w}) = 0, \quad (5.7.4b)$$

$$\chi \{a_2 \text{Ai}'(-\hat{w}) + b_2 \text{Bi}'(-\hat{w})\} = e^{(\Phi + \tilde{\Psi})/2} \sqrt{\frac{\bar{C}}{2\gamma_n}}, \quad (5.7.4c)$$

$$\chi \{a_2 \text{Ai}'(\chi - \hat{w}) + b_2 \text{Bi}'(\chi - \hat{w})\} = -\frac{1}{\sqrt{2}}, \quad (5.7.4d)$$

remembering $\chi = (j/2\nu^2)^{1/3}$.

In figure 5.8 we demonstrate that the outer asymptotic solution for ϕ and n and the boundary layer expressions (2.3.27) and (5.7.1) give a good approximation to the numerical solution when using the material parameter values estimated in (5.4.1).

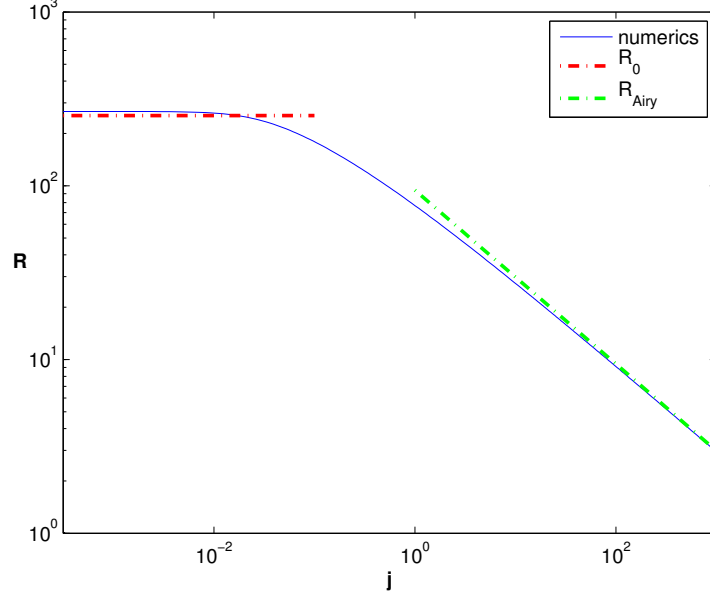


Figure 5.9: Resistance R plotted against electron flux j with $\bar{C} = 1$, $M = 10^{-4}$, $\gamma_n = 10^{-3}$, $\Sigma = 3.04$, $\tilde{\Psi} = -9.66$ and $\nu = 0.01$: numerical solution solving in silicon (solid); small- j estimate (5.7.5) (red dashed); $j \gtrsim 1$ approximation using (5.7.6) (green dashed).

Using (5.7.4) and (5.3.10) we realise that the effective boundary conditions (5.6.4) make the expressions found for resistance in §2.3.5 valid for our new definition of resistance. We therefore find

$$R \sim \frac{1}{4\pi^2\nu^2} \quad \text{where } j \ll \nu^2 \ll 1, \quad (5.7.5)$$

$$R \sim \frac{2\sqrt{2}}{3\nu\sqrt{j}} \quad \text{where } j = O(1), \nu \ll 1, \quad (5.7.6)$$

as found in (2.3.38) and (2.3.40) in Chapter 2. The asymptotic expressions (5.7.5), (5.7.6) are shown to have good agreement with the numerical solution of system (5.4.2)–(5.4.5) in figure 5.9.

In Chapter 2 we found asymptotic expressions for the resistance in the distinguished limit where $\nu\sqrt{j} = O(1)$ and also in the limit where $j \rightarrow \infty$. The effective boundary conditions (5.6.4) are not valid when $\nu\sqrt{j} = O(1)$ or when $j \rightarrow \infty$, and we would therefore need to determine modified effective boundary conditions to derive an asymptotic expression for resistance in these limits. We hypothesise that, as found above in the regimes where $j \ll \nu^2 \ll 1$ and $j = O(1)$, $\nu \ll 1$, in the limits $\nu\sqrt{j} = O(1)$ and $j \rightarrow \infty$ solving in the silicon would lead to the same asymptotic approximations obtained in Chapter 2.

5.7.3 Application to 2D problem

In principle, the effective boundary conditions (5.6.4) could be incorporated into the two-dimensional model analysed in Chapter 3 to investigate the Si-glass-Ag system. This would involve modifying the boundary conditions (3.2.4) to specify at $y = 0$

$$\begin{aligned}\phi(x, 0) &= \Phi + \tilde{\Psi} + \log\left(\frac{\bar{C}}{\gamma_n \alpha(x)}\right), \\ n(x, 0) &= \alpha(x), \\ \frac{d\phi}{dn}(x, 0) &= \frac{\Sigma L_1}{\lambda} \sqrt{2\bar{C}\Sigma \left(\log\left(\frac{\bar{C}}{\gamma_n \alpha(x)}\right) + \frac{\gamma_n \alpha(x)}{\bar{C}} - 1 \right)}.\end{aligned}\tag{5.7.7}$$

The parameter $\alpha(x)$ is then an unknown position dependent variable that must be solved for. The validity of the boundary conditions (5.7.7) would be questionable in the limit where the minimum glass layer thickness $h_{\min} \rightarrow 0$ as then the electron flux $\mathbf{j} \rightarrow \infty$ in the area surrounding $h_{\min}$.

5.8 Discussion and conclusions

In Chapter 2 when considering the Si-glass-Ag system we took the electron density at the silicon-glass interface to be a known constant. In this chapter we investigated the validity of this simplified boundary condition.

When considering the Si-glass-Ag system, we demonstrated that holes in the silicon can safely be neglected. In contrast to the model proposed in Chapter 2, by solving in the silicon, we found that in general coupled boundary conditions should be applied at the silicon-glass interface where the parameter α is not determined but is an additional unknown. Furthermore, we found that depending on the values of different parameters it is possible for $\alpha > 1$. However, in the physically relevant regime where the Debye length in the silicon and glass is small we found that α is specified through the solution of a transcendental equation. Moreover, a redefinition of the resistance R led to the same asymptotic approximations for resistance as were found in Chapter 2 in the small Debye length limit. The inclusion of current flow through the silicon introduces additional nondimensional parameters that can take extreme values making the full system ideal for detailed asymptotic analysis. Such an analysis is beyond the scope of this thesis and will not be considered here.

Overall, as we obtain the same asymptotic expressions for resistance as found in Chapter 2, we believe our original generalised boundary condition of specifying the electron density at the silicon-glass interface was a good starting point for analysis.

Chapter 6

Conclusions

In this chapter we give a summary of our work, discuss the modelling assumptions and how the relaxation of the modelling assumptions could lead to further research and, finally, outline how our results are applicable to contact resistance on the front side of a silicon solar cell.

6.1 Summary

We begin in Chapter 1 by providing a summary of the theory of electronic contacts and outlining what is known about the formation and conduction mechanisms present at the front contact of a silicon solar. In particular, we note that much of the literature focuses on whether silver crystallites embedded in the silicon emitter or small silver precipitates in the glass layer play a leading role in aiding current transport across the contact. Furthermore, we outline the drift diffusion, density gradient confinement and density gradient tunnelling models that we use in this thesis.

In Chapter 2 we formulate a one-dimensional model based upon the drift diffusion equations for electron transport across the glass layer at the front contact of a silicon solar cell. We consider two different possible systems, namely, a glass layer separating either (i) the silicon emitter from a silver electrode (Si-glass-Ag system); (ii) a silver crystallite from the silver electrode (Ag-glass-Ag system). We make the key approximations of ignoring the motion of holes and neglecting the boundary effects at the silicon-glass and glass-silver interfaces, instead simply taking the electron densities either side of the glass layer as known constants. We solve the resulting equations both numerically and by employing asymptotic techniques in various parameter regimes. For example, we analyse the limit of the Debye length being much smaller than the typical device length-scale, as is likely to be the case in practice. The asymptotic analysis allows us to determine that the resistance of the glass layer depends sensitively on the physical parameters, with different approximate explicit relations found in different parameter regimes. We also

obtain the surprising result that, depending on the values of physical parameters, the resistance of the glass layer may be a monotonic increasing, monotonic decreasing, or non-monotonic function of the electron flux.

Chapter 3 extends the model presented in Chapter 2 to two dimensions. Two different mapping techniques are proposed to transform the domain of interest to a rectangle, where the appropriate approach depends on the geometry and the questions to be answered. A new spectral method to solve the two-dimensional model numerically is devised and validated. Our numerical method enables us to obtain quantitative results such as the average current density and resistance of the glass layer as well as qualitative results such as the normalised cumulative current and the trajectories the electrons take through the glass layer. We then are able to determine that, as expected, the current short-circuits through the thinnest regions of the glass layer. The short circuiting of the current enables us to find limiting asymptotic expressions for the average current density for two different generic cases for the variation of the thickness of the glass layer: (i) the glass layer varies slowly (smooth slowly varying domain) (ii) the glass layer varies quickly (wedge-like domain).

Chapter 4 is separated into two sections. In the first section we include quantum effects into the one-dimensional model proposed in Chapter 2 by introducing a longer range interaction term (quantum term) that is a small perturbation to the drift diffusion equations. We find that, when the electron flux is sufficiently large, the introduction of the quantum term leads to oscillatory variations in the distribution of the electron density in a boundary layer. However, the introduction of the quantum term has negligible effect on the resistance of the glass layer. In the second section of Chapter 4 we extend the work of Ancona [4] to investigate the density gradient tunnelling theory for modelling quantum mechanical tunnelling in metal-insulator-metal structures. We use asymptotic methods to obtain explicit leading-order relations for the current density that are comparable to those obtained from more complicated microscopic quantum transport theories. Furthermore, we use asymptotics to characterise otherwise unreported oscillatory variations in the electron density that occur when inertial effects are present to leading order.

To investigate the correct boundary condition to apply at the silicon-glass interface the model presented in Chapter 2 is extended to include current flow through the silicon in Chapter 5. We demonstrate that holes can safely be neglected in the silicon and that in general the electron density at the silicon-glass interface cannot be specified but is an unknown parameter. However, we find in the physically relevant regime where the Debye length is small in both the silicon and glass that the electron density at the silicon-glass interface is specified in terms of the values of material parameters. In addition, in this

regime we find that extending the model presented in Chapter 2 to include current flow through the silicon leaves the asymptotic expressions found for resistance unchanged.

6.2 Discussion and future research

Throughout this thesis we have made a number of simplifying assumptions. In this section we readdress the key assumptions and outline areas for future work.

The drift diffusion and the density gradient confinement models that have been analysed in this thesis are based on the continuum approximation that is questionable on the small scales considered. However, previous authors have applied the drift diffusion equations to consider current flow in devices of size $O(100)\text{nm}$ [42,43,82] and the density gradient confinement model to devices of size $< 100\text{nm}$ [77]. The continuum approximation is relaxed by simulating devices using computationally expensive Monte Carlo numerical experiments [54]. Due to the numerical nature of Monte Carlo methods any analytical progress with these models is impossible making the analysis and interpretation of results difficult.

In Chapter 2 we made the simplifying assumption of neglecting the motion of holes in the glass layer. In Chapter 5 we were reassured of the validity of this assumption as the inclusion of holes in the n-type silicon emitter was found to have negligible effect. However, if we wished to consider a solar cell with a p-type silicon emitter that has a very high density of holes we would have to reconsider the no holes assumption. To investigate the contact resistance of a solar cell with a p-type emitter we could introduce holes into our model of current flow through the glass layer.

We considered the resistance of the glass layer over a large range of applied potential differences in Chapter 2 and could therefore plot current-voltage curves and resistance-current curves. In Chapter 3 we only considered the regime where the scaled applied potential difference was $O(1)$. An interesting extension would be to consider the two dimensional model over a large range of applied potential differences. The asymptotic relations for current density found in Chapter 3 inform us that in the regime where the applied potential difference is $O(1)$ the glass layer acts an Ohmic resistor, however, over a large range of applied potential differences we expect the glass layer to exhibit similar non-ohmic behaviour as was found in Chapter 2.

We considered short circuiting effects in Chapter 3 by extending the model presented in Chapter 2 to two dimensions. The interface of the front contact of a silicon solar cell is a three-dimensional system and therefore it would be interesting to extend the work carried out in Chapter 3 to a third dimension. A three dimensional mapping function would be difficult to find and it is therefore likely that minimal progress could be made

on formulating an analogous numerical method. However, in three dimensions we expect the short circuiting effects to be even more prominent making the system suitable for asymptotic analysis.

In this thesis we have focused on characterising the resistance of the glass layer. Within the glass layer there are often small silver precipitates (nano-Ag colloids) that are thought to aid electron transport [31, 53, 64–66]. An interesting extension to our work would be to include the nano-Ag colloids in the glass layer. This could be achieved through a homogenisation technique, and we anticipate that the effect of the colloids on the glass layer would be similar to that of doping and therefore could make a significant difference to its resistance.

To validate our mathematical model experimental work should be carried out. To isolate the properties of the front contact from the p-n junction we suggest taking a homogenous block of n-type silicon and creating an Ohmic contact on the back surface (by sputtering or other means) and screen printing a silver front contact. The resistance of the prepared sample should be measured over a range of current densities spanning many orders of magnitude and compared with the results of our model. We expect to find regions where the resistance is Ohmic, and therefore does not vary with current density, and regions where the resistance is non-Ohmic, and therefore does vary with current density. The model accurately represents the effective contact resistance for a range of applied electric potential difference, however, it is known the drift diffusion model fails at very high fields and therefore care must be taken when considering large potential differences.

6.3 Application to contact resistance of silicon solar cell

The models analysed in this thesis are highly idealised and contain many unknown parameters. Therefore, it is difficult to arrive at any quantitative conclusions about the contact resistance on the front side of a silicon solar. The key qualitative findings that are of interest to those researching contact resistance on the front side of a silicon solar are outlined below.

- The resistance of the glass layer, and therefore the effective contact resistance, depends sensitively on many different physical parameters. The important parameters are:
 - The mobility of electrons in the glass μ that scales the effective contact resistance linearly.

- The absolute permittivity of the glass ϵ . The effective contact resistance increases as the absolute permittivity decreases.
 - The thickness of the glass layer H . The effective contact resistance increases nonlinearly as the thickness of the glass layer increases.
 - The doping in the silicon N_D , the conduction band density of states of the glass $\bar{g}_c$, and the electron affinity of the glass $\bar{\chi}_n$. In general, the effective contact resistance decreases as the doping in the silicon, the conduction band density of states, and the magnitude of the electron affinity increases. However, if the glass layer is sufficiently thick the effective contact resistance will be independent of these parameters.
- Short-circuiting effects are likely to be important with the majority of current flowing through a region near the glass layer minimum thickness.
 - Quantum mechanical effects are unlikely to be an important conduction mechanism.

Overall, our investigation into the transport mechanisms present at the front side of a silicon solar cell has led to a number of interesting mathematical problems, and our work will also be of interest to adjacent fields since the situation in which a (relatively) poor conductor is positioned between two good conductors arises in many different physical applications, for example in electrochemical thin-films [16, 24, 32], microelectronics [35, 104], electrochromic glass [72] and metal corrosion [101].

Appendix A

Appendix A: Asymptotic expansions of Airy functions

A.1 Introduction

In this appendice we give more detailed descriptions of the asymptotic expansions carried out in Section 2.3.

A.2 $\chi \rightarrow 0$ expansion

By numerically solving the transcendental equation given by the imaginary component of (2.3.35) we determine that $w = O(\chi^{-2})$ as $\chi \rightarrow 0$; see figure 2.10. We therefore apply the ansatz $w = d\chi^{-2}$, where d is a constant, to (2.3.35) to obtain

$$-e^{jR/2} = \frac{\text{Ai}(\chi - d\chi^{-2}) + i \text{Bi}(\chi - d\chi^{-2})}{\text{Ai}(-d\chi^{-2}) + i \text{Bi}(-d\chi^{-2})}. \quad (\text{A.2.1})$$

Expanding the right hand side using the relation [2]

$$\text{Ai}(z) + i \text{Bi}(z) = 2e^{\pi i/3} \text{Ai}(ze^{-2\pi i/3}), \quad (\text{A.2.2})$$

and the expansion [2]

$$\text{Ai}(-z) \sim \frac{1}{\sqrt{\pi}z^{1/4}} \left(\sin(\zeta + \pi/4) \sum_{k=0}^{\infty} (-1)^k D_{2k} \zeta^{-2k} - \cos(\zeta + \pi/4) \sum_{k=0}^{\infty} (-1)^k D_{2k+1} \zeta^{-2k-1} \right) \quad (\text{A.2.3})$$

valid as $z \rightarrow \infty$, where $\zeta = 2/3z^{3/2}$, $D_0 = 1$ and

$$D_k = \frac{\Gamma(3k + 1/2)}{54^k k! \Gamma(k + 1/2)}, \quad (\text{A.2.4})$$

gives

$$-e^{jR/2} \sim e^{i\sqrt{d}} + g(d)\chi^3 + \dots, \quad (\text{A.2.5})$$

where $g(d)$ is some function of d . Evaluating the imaginary component of (A.2.5) to leading order we find

$$\sin \sqrt{d} = 0, \quad (\text{A.2.6})$$

and therefore $d \sim \pi^2$, we have selected the smallest non-zero root. The real component of (A.2.5) gives $R = 0$. To obtain the leading order approximation to the resistance we must determine the next order in d . Equation (A.2.5) informs us that an appropriate ansatz is now $w = \frac{1}{\chi^{-2}}(\pi^2 + \hat{d}\chi^3)$, where $\hat{d}$ is a constant. Repeating the steps outlined above we determine $\hat{d} = 1/2$ and

$$jR \sim \frac{\chi^3}{2\pi^2}. \quad (\text{A.2.7})$$

Continuing this process up to $a = O(\chi^{12})$ we obtain the expressions in (2.3.36) and (2.3.37).

A.3 $\chi \rightarrow \infty$ expansion

The relevant Airy expansions are [2]

$$\text{Ai}(z) \sim \frac{e^{-\zeta}}{2\sqrt{\pi}z^{\frac{1}{4}}} \sum_{k=0}^{\infty} (-1)^k \frac{D_k}{\zeta^k}, \quad (\text{A.3.1})$$

$$\text{Bi}(z) \sim \frac{e^{\zeta}}{\sqrt{\pi}z^{\frac{1}{4}}} \sum_{k=0}^{\infty} \frac{D_k}{\zeta^k}, \quad (\text{A.3.2})$$

as $z \rightarrow \infty$, where ζ and D are the same variables as used in Section A.2.

Appendix B

Appendix B: Numerical calculation of A_{Final}

To calculate the amplitude of the oscillations of ω at $x = 1$ we focus on the region $x \in [z_1, 1]$. We interpolate the local maxima of ω to determine the upper envelope ω_{upp} and the local minima of ω to determine the lower envelope ω_{low} , as shown in figure B.1. The amplitude of the oscillations at $x = 1$ is then estimated by

$$A_{\text{Final}} = \frac{1}{2}(\omega_{\text{upp}}|_{x=1} - \omega_{\text{low}}|_{x=1}). \quad (\text{B.0.1})$$

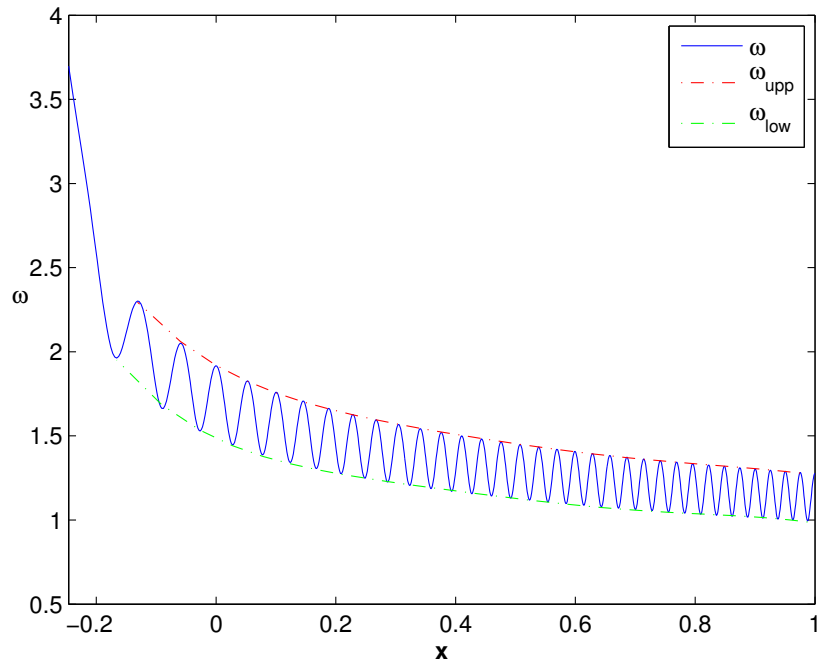


Figure B.1: The scaled square rooted electron subpopulation ω against position x in the region $x \in [z_1, 1]$ where $B = 10^{-4}$, $\bar{V} = 2.65$, $\theta_{MB} = 1$ and $z_1 = -0.25$.

Appendix C

Appendix C: Investigation into Ohmic boundary conditions

C.1 Introduction

In this appendice we show that the qualitative features of an ideal Schottky contact and Ohmic contact are found when applying the Ohmic boundary conditions (1.7.3) at the semiconductor-metal interface. For illustrative purposes we analyse the contact between a n-type semiconductor and metal.

C.2 Mathematical model

C.2.1 Formulation of the problem

We analyse the n-type semiconductor-metal contact by assuming one-dimensional conduction through a layer of n-type semiconductor in contact with a metal electrode. We assume that the semiconductor is in equilibrium away from the contact and impose the Ohmic boundary conditions (1.7.3) at the semiconductor-metal interface. We take the model (1.6.10)–(1.6.14), reduce to one dimension, and make the following assumptions

- The charge is predominantly carried by electrons rather than holes. Considering an n-type silicon-silver contact the electron density has its minimum value at the silicon-silver interface and the hole density its maximum. Substituting values from Table C.1 into (1.7.3) we find that at the interface the electron density $n \approx 10^{21} \text{ m}^{-3}$ and the hole density $p \approx 10^{11} \text{ m}^{-3}$. We therefore ignore the motion of holes henceforth.
- There is no generation or recombination of electrons in the glass.
- The system operates in a quasi-steady state.

- The silicon is doped with donor impurities with the doping constant throughout.
- An electric potential difference Φ is applied across the semiconductor.

We thus arrive at the following system of equations

$$\frac{dj_n}{dx} = 0, \quad (C.2.1)$$

$$j_n = \mu_n \left(-n \frac{d\phi}{dx} + \frac{k_B T}{q} \frac{dn}{dx} \right), \quad (C.2.2)$$

$$\frac{d^2\phi}{dx^2} = \frac{q}{\epsilon}(n - N_D), \quad (C.2.3)$$

The boundary conditions are

$$\phi(0) = -\Phi + V_{bi}, \quad \phi(L_{\text{sem}}) = 0, \quad (C.2.4)$$

$$n(0) = N_D, \quad n(L_{\text{sem}}) = n_m = g_c \exp \left(-\frac{\chi_n + W_{\text{metal}}}{k_B T} \right), \quad (C.2.5)$$

where L_{sem} is the length of the semiconductor layer and

$$V_{bi} = -\frac{1}{q} (\chi_n + W_{\text{metal}}). \quad (C.2.6)$$

The boundary condition $n(0) = N_D$ is the leading-order expression for n when applying (1.7.2) to a n-type semiconductor-metal contact.

C.2.2 Nondimensionalisation

For the nondimensionalisation we scale the electron density with doping (N_D), we take the length scale to be the thickness of the semiconductor layer (L_{sem}), scale the potential and built-in potential with $-k_B T/q$ and scale the electron flux with $\mu_n k_B T N_D / (q L_{\text{sem}})$. The nondimensionalisation then proceeds as follows:

$$\begin{aligned} x &= L_{\text{sem}} x^*, & n &= N_D n^*, & \phi &= -\frac{k_B T}{q} \phi^*, & (C.2.7) \\ \Phi &= -\frac{k_B T}{q} \Phi^*, & V_{bi} &= \frac{k_B T}{q} \Phi_{bi} & j_n &= \frac{k_B T N_D}{q L_{\text{sem}}} j^*. \end{aligned}$$

Substituting (C.2.7) into (C.2.2) and (C.2.3) and dropping the starred notation we obtain

$$\frac{dj}{dx} = 0, \quad (C.2.8)$$

$$j = -n \frac{d\phi}{dx} - \frac{dn}{dx}, \quad (C.2.9)$$

$$\nu^2 \frac{d^2\phi}{dx^2} = 1 - n, \quad (C.2.10)$$

The non-dimensional boundary conditions are

$$n(0) = 1, \quad \phi(0) = \Phi + \Phi_{bi}, \quad n(1) = \alpha_{\text{sem}}, \quad \phi(1) = 0. \quad (\text{C.2.11})$$

The dimensionless parameters are

$$\alpha_{\text{sem}} = \frac{n_m}{N_D}, \quad \Phi_{bi} = \frac{qV_{bi}}{k_B T}, \quad \text{and} \quad \nu = \sqrt{\frac{\epsilon k_B T}{q^2 L_{\text{sem}}^2 N_D}}. \quad (\text{C.2.12})$$

We note that ν is the scaled Debye length in the semiconductor and is equivalent to (1.7.6). The total potential difference across the device is a combination of the electric potential difference, built-in potential difference and the chemical potential difference and is given by

$$V_{\text{tot}} = \Phi + \Phi_{bi} - \log \alpha_{\text{sem}}. \quad (\text{C.2.13})$$

C.3 Numerical results

C.3.1 Numerical method

We solve the system of equations (C.2.8)–(C.2.10) numerically using **Chebfun** where we apply the boundary conditions (C.2.11) and determine j .

C.3.2 Schottky contact

To investigate an ideal Schottky contact we consider a n-type silicon-silver contact and therefore taking values from Table C.1 we find $\Phi_{bi} \approx -9.66$, $\nu \approx 0.008$ and $\alpha_{\text{sem}} \approx 10^{-3}$. We consider the system (C.2.8)–(C.2.11) in zero bias ($V_{\text{tot}} = 0$), forward bias ($V_{\text{tot}} > 0$) and reverse bias ($V_{\text{tot}} < 0$), results shown in figure C.1. All the qualitative features of an ideal Schottky contact are evident in figure C.1. Examining figure C.1(b) we observe the depletion region near the silicon-silver contact at $x = 1$ where the electron density is relatively small. Figure C.1(b) also demonstrates that in forward bias the depletion region decreases in size and in reverse bias the depletion region increases in size. Analysing figure C.1(a) we see the ‘potential barrier’ realised by the steep variation in electric potential that occurs at the silicon-silver interface. Moreover, figure C.1(a) shows that the size of this potential change decreases in forward bias and increases in reverse bias. In figure C.2 we show the current-voltage characteristics of the silicon-silver contact by plotting electron flux j against the total potential difference V_{tot} . We again see all the qualitative features of an ideal Schottky contact. In reverse bias the electron flux is approximately constant and very small. In forward bias the electron flux initially increases rapidly as the total potential difference increases and at high forward biases a linear relation is obtained due to the series resistance of the silicon.

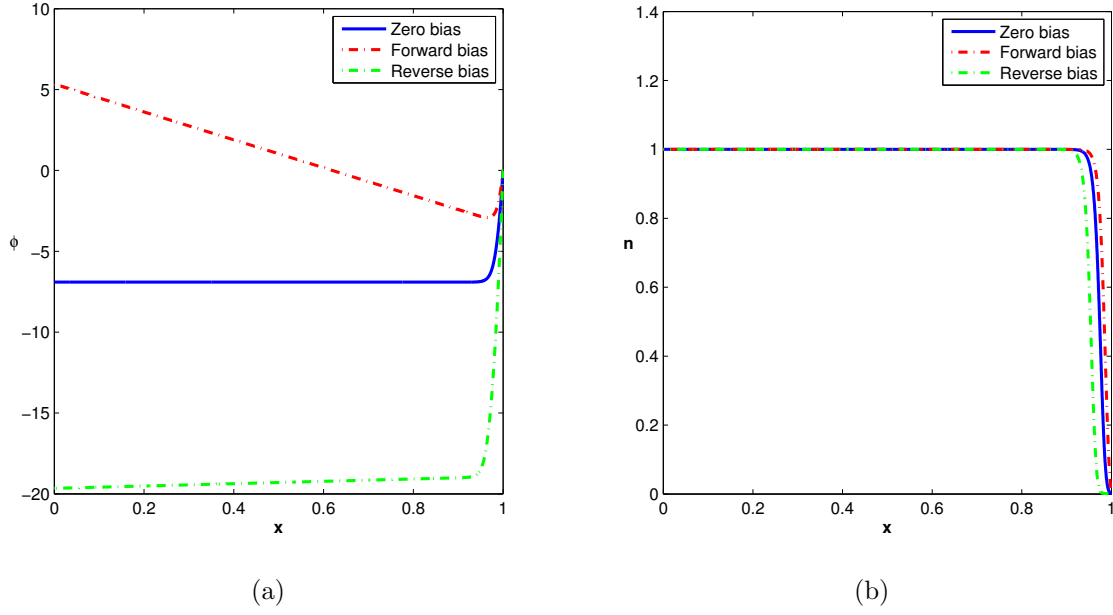


Figure C.1: Electric potential ϕ and electron density n plotted against position x with parameter values $\Phi_{bi} = -9.66$, $\nu = 0.008$, $\alpha_{sem} = 10^{-3}$ for various Φ and j . For the solid blue line $\Phi = \Phi_{bi} + \log \alpha_{sem}$ and $j \approx 0$; for the dashed red line $\Phi = 15$ and $j \approx 8.6$; for the dashed green line $\Phi = -10$ and $j \approx -0.73$.

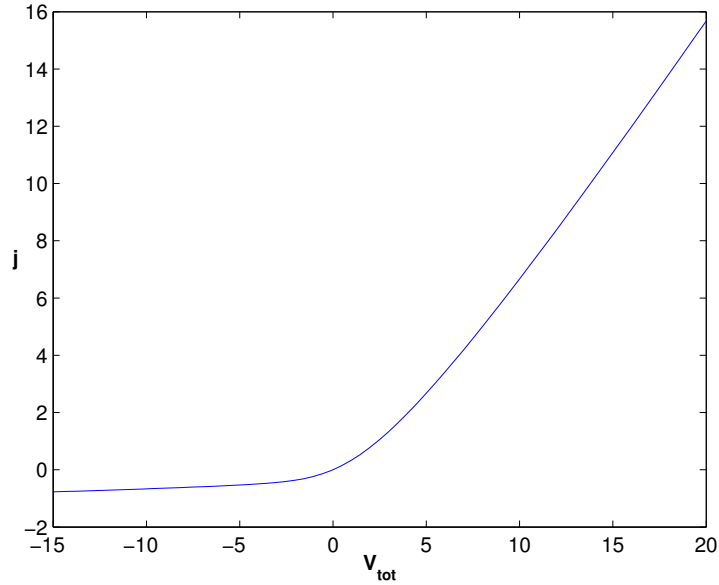


Figure C.2: Electron flux j plotted against total potential difference V_{tot} parameter values $\nu = 0.008$, $\Phi_{bi} = -9.66$ and $\alpha_{sem} = 10^{-3}$.

C.3.3 Ohmic contact

To consider an Ohmic contact between an n-type semiconductor and metal we let $\nu = 0.008$, $\Phi_{bi} = 0$ and $\alpha_{sem} = 10$. Remembering that an Ohmic contact occurs where $(-\chi_n) \gtrsim$

$\hat{\epsilon}$	$1.05 \times 10^{-10} \text{ Fm}^{-1}$
T	300K
k_B	$1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
q	$1.6 \times 10^{-19} \text{ C}$
L_{sem}	$5 \times 10^{-7} \text{ m}$
N_D	10^{24} m^{-3}
n_i	10^{16} m^{-3}
g_c	$3 \times 10^{25} \text{ m}^{-3}$
g_v	$3 \times 10^{25} \text{ m}^{-3}$
W_{metal}	4.3 eV
χ_n	-4.05 eV
χ_p	-5.17 eV

Table C.1: Parameter values taken for n-type silicon-metal contact [95]. We choose a high level of doping N_D as is commonly present in n-type silicon and pick a suitable length scale L_{sem} to analyse the silicon-metal contact.

W_{metal} . Similarly to §C.3.2 we solve the system (C.2.8)–(C.2.11) in zero bias, forward bias and reverse bias, results shown in figure C.3. In figure C.3(b) we see the properties of an Ohmic contact with the accumulation of charge at the contact. Moreover, the electron density profile is unchanged by applying a differing electric potential difference. The linear relationship between electron flux j and total potential difference V_{tot} found in figure C.4 confirms the Ohmic nature of the contact.

C.4 Conclusions

We have investigated the application of the Ohmic boundary conditions (1.7.3) for a semiconductor-metal contact. The boundary conditions (1.7.3) do not depend on the applied potential difference. However, we have found that by applying the boundary conditions (1.7.3) to a n-type semiconductor-metal contact we are able to reproduce all the key qualitative features of an ideal Schottky contact. Furthermore, by choosing appropriate parameter values and applying the boundary conditions (1.7.3) the key features of an Ohmic contact are evident. We therefore believe that to avoid confusion it is suitable to rename the Ohmic boundary conditions (1.7.3) as Ideal boundary conditions. Here, we solved the model (C.2.8)–(C.2.11) numerically, however, we hypothesise that by conducting asymptotic analysis in a similar manner to [79] approximate expressions for the electron flux could be found.

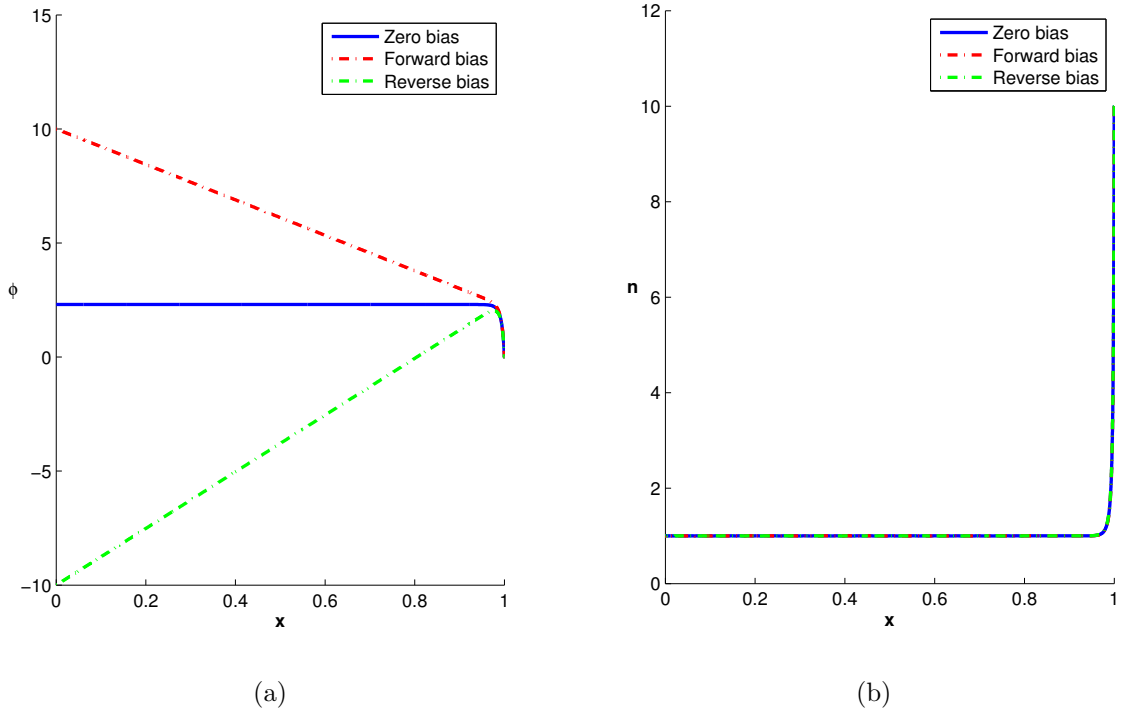


Figure C.3: Electric potential ϕ and electron density n plotted against position x with parameter values $\Phi_{bi} = 0$, $\nu = 0.008$, $\alpha_{sem} = 10$ for various Φ and j . For the solid blue line $\Phi = \log \alpha_{sem}$ and $j \approx 0$; for the dashed red line $\Phi = 10$ and $j \approx 7.77$; for the dashed green line $\Phi = -10$ and $j \approx -12.43$.

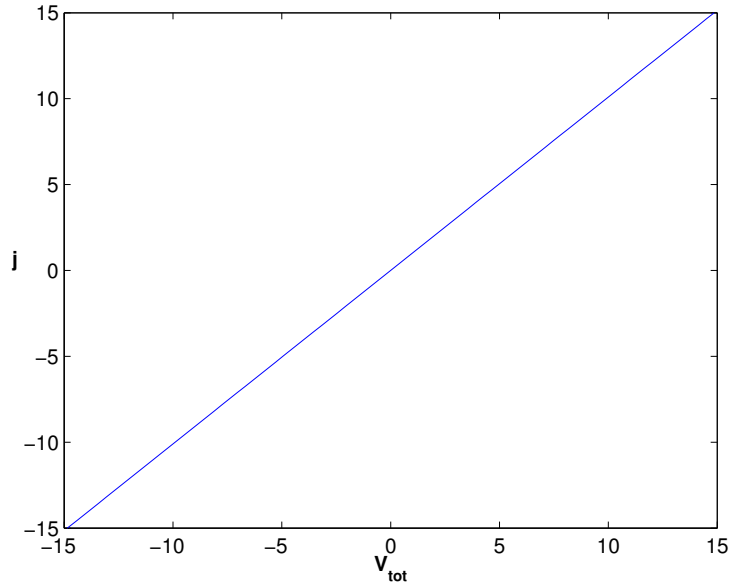


Figure C.4: Electron flux j plotted against total potential difference V_{tot} parameter values $\nu = 0.008$, $\Phi_{bi} = 0$ and $\alpha_{sem} = 10$.

Appendix D

Appendix D: Summary for DuPont (UK) Ltd

In this standalone appendice we summarise our work in non-technical terms for the benefit of DuPont (UK) Ltd. We highlight the key results that are of potential interest to the silicon-crystalline solar cell industry.

D.1 Effective contact resistance

To investigate the effective contact resistance at the front side of a silicon-crystalline solar cell we consider two different possible systems, namely a glass layer separating either (i) a silver crystallite from the silver electrode (Ag-glass-Ag system); (ii) the silicon emitter from the silver electrode (Si-glass-Ag system).

To define the effective contact resistance we introduce the following parameters:

- The electric potential difference across the glass layer, $(-\Phi)$.
- The electron density at the glass-silver electrode interface, n_1 , where

$$n_1 = \bar{g}_c \exp\left(-\frac{\bar{\chi}_n + W_{\text{Ag}}}{k_B T}\right). \quad (\text{D.1.1})$$

Here, $\bar{g}_c$ is the conduction band density of states of the glass, $\bar{\chi}_n$ is the electron affinity of the glass (that we have defined as a negative quantity), W_{Ag} is the workfunction of silver, k_B is Boltzmanns constant and T is the absolute temperature. The results in this document are based on the assumption that $10^{20}\text{m}^{-3} \lesssim n_1 \lesssim 10^{26}\text{m}^{-3}$.

- The electron density at the silicon-glass interface when considering the Si-glass-Ag system and the electron density at the silver crystallite-glass interface when considering the Ag-glass-Ag system, n_0 . In the Ag-glass-Ag system $n_0 = n_1$. In the Si-glass-Ag system we do not have an explicit expression for n_0 , however, we

do know that n_0 increases as the doping in the silicon, N_D , the conduction band density of states $\bar{g}_c$, of the glass, and the magnitude of the electron affinity, $|\bar{\chi}_n|$, of the glass increases.

- The total potential difference across the glass layer, V .
- The current density, J .

We thus define the effective contact resistance as

$$R = \frac{-\Phi + \log(n_0/n_1)}{J} = \frac{V}{J}, \quad (\text{D.1.2})$$

where $\log(n_0/n_1)$ is the chemical potential difference across the glass layer.

D.2 Physical parameters

The resistance of the glass layer, and therefore the effective contact resistance, depends on many different physical parameters. The dependencies that we have identified are

- The effective contact resistance scales linearly with the mobility, μ , of electrons in the glass.
- The effective contact resistance increases with the absolute permittivity, ϵ , of the glass layer.
- The effective contact resistance increases nonlinearly as the thickness, H , of the glass layer increases.
- In general, the effective contact resistance decreases as the doping in the silicon, N_D , the conduction band density of states $\bar{g}_c$, of the glass, and the magnitude of the electron affinity, $|\bar{\chi}_n|$, of the glass increases. However, if the glass layer is sufficiently thick the effective contact resistance becomes independent of these parameters.

All figures in this document are produced by picking values from the parameter ranges outlined in Table D.1.

D.3 Comparison between thick glass layer and thin glass layer

In this section we compare and contrast the qualitative electronic behaviour between a thick glass layer ($\sim 500\text{nm}$) and a thin glass layer ($\sim 10\text{nm}$). We find that much of the

ϵ	$(3.45 \times 10^{-11} \text{ Fm}^{-1}, 1.05 \times 10^{-10} \text{ Fm}^{-1})$
T	300K
k_B	$1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
q	$1.6 \times 10^{-19} \text{ C}$
H	$(10^{-8} \text{ m}, 5 \times 10^{-7} \text{ m})$
n_1	$(10^{20} \text{ m}^{-3}, 10^{26} \text{ m}^{-3})$
n_0	$(10^{18} \text{ m}^{-3}, 10^{26} \text{ m}^{-3})$
μ	$< 2 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$

Table D.1: Parameter values used for plotting figures.

qualitative behaviour is the same in both the Ag-glass-Ag system and the Si-glass-Ag system.

Our model assumes that there is an electric potential difference ($-\Phi$) across the glass layer, that the electrons move by drift and diffusion and that the local electric field depends on the electron density.

D.3.1 Electric potential and electron density

The electric potential ϕ throughout the glass layer will be negative and therefore to aid analysis in all our figures we plot $(-\phi)$ (that is a positive quantity) against position. We refer to $(-\phi)$ as the negative electric potential henceforth. In figures D.1 and D.2 we plot the negative electric potential $(-\phi)$ and the electron density n within a thick glass layer of thickness H_{Thick} for the Ag-glass-Ag system and the Si-glass-Ag system, respectively. We find that in both systems there are steep gradients in the electron density at the glass layer interfaces and that the electron density is very small in the centre of the glass layer. There are also steep gradients in the negative electric potential at the glass layer interfaces. We have found that in the centre of the glass layer $n \approx k_B T / (q^2 H_{\text{Thick}})$, where q is the charge on an electron.

In figures D.3 and D.4 we plot the negative electric potential $(-\phi)$ and the electron density n within a thin glass layer of thickness H_{Thin} for the Ag-glass-Ag system and the Si-glass-Ag system, respectively. The glass layer now behaves in a similar manner to a normal resistor with a linear negative electric potential. Furthermore, the electron density remains high throughout the glass layer when compared with the electron density in the thick glass layer.

As the glass layer thickness decreases from H_{Thick} to H_{Thin} the steep gradients in the negative electric potential and electron density found in figures D.1 and D.2 reduce until the negative electric potential and electron density have profiles similar to those found in figures D.3 and D.4.

D.3.2 Effective contact resistance

The effective contact resistance of the thick glass layer in the Si-glass-Ag system and the Ag-glass-Ag system is

$$R_{\text{Thick}} \approx \frac{q^2 H_{\text{Thick}}^3}{4\pi^2 \mu \epsilon k_B T}. \quad (\text{D.3.1})$$

The effective contact resistance of the thin glass layer in the Ag-glass-Ag system is

$$R_{\text{Thin}} \approx \frac{H_{\text{Thin}}}{\mu n_1}. \quad (\text{D.3.2})$$

The effective contact resistance of the thin glass layer in the Si-glass-Ag system is

$$R_{\text{Thin}} \approx \frac{H_{\text{Thin}}}{\mu n_1} \left(\frac{n_0 - n_1}{n_0 \log(n_0/n_1)} \right). \quad (\text{D.3.3})$$

Increasing the doping of the silicon increases the value of n_0 and therefore decreases the effective contact resistance when the glass layer is thin in the Si-glass-Ag system, on the other hand, when the glass layer is thick the effective contact resistance is independent of n_0 and therefore independent of the doping.

The relations (D.3.1)–(D.3.3) inform us that the effective resistance scales linearly with the glass layer thickness when the glass layer is thin ($R_{\text{Thin}} \propto H_{\text{Thin}}$) and scales nonlinearly with the glass layer thickness when the glass layer is thick ($R_{\text{Thick}} \propto H_{\text{Thick}}^3$).

D.4 Short circuiting effects

The relations (D.3.1)–(D.3.3) confirm that we expect the current to short circuit through thinner regions of the glass layer. This feature is discussed in this section.

To demonstrate the short circuiting of the current we consider the Ag-glass-Ag system with the glass layer thickness profile plotted in figure D.5. For illustrative purposes, we suppose that the electrode has a periodic structure with length L and the glass layer has an average thickness H_{avg} where $L > H_{\text{avg}}$. Here, the average thickness of the glass layer is in the H_{Thick} regime and the minimum thickness of the glass layer (found at $x = 0$) is in the H_{Thin} regime.

The negative electric potential ($-\phi$) and electron density n for a given applied electric potential difference ($-\Phi$) is shown in figure D.6. At thicker regions of the glass layer the negative electric potential and electron density have a profile similar to that shown in figure D.1. In the region around the glass layer minimum the negative electric potential and electron density have a profile similar to that shown in figure D.3.

A key quantity we use to highlight the behaviour of a spatially varying contact is the normalised cumulative current, C_c . We define the normalised cumulative current as the

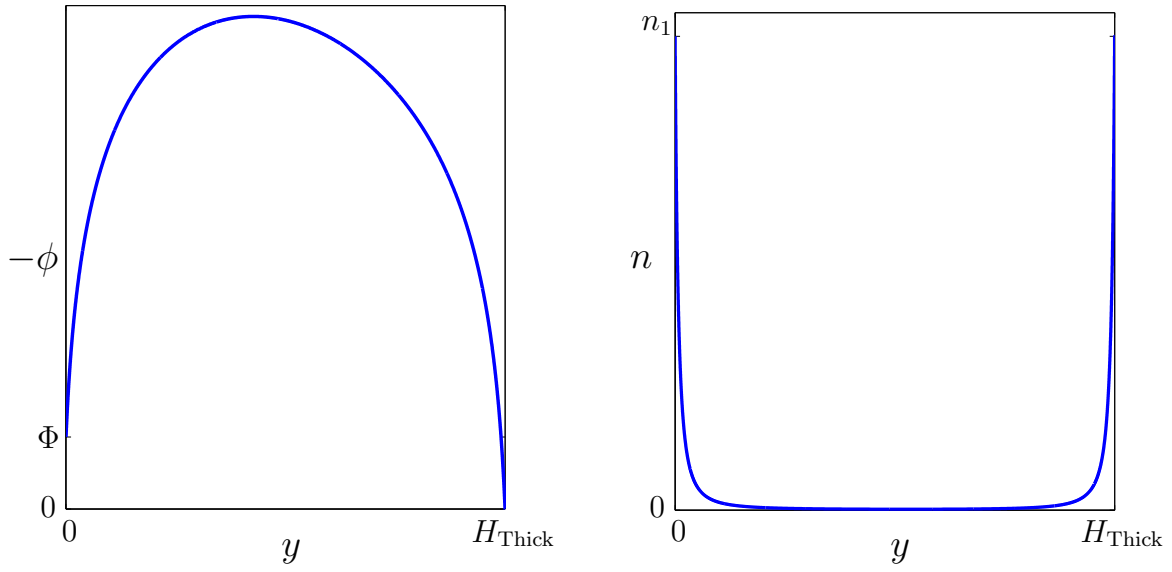


Figure D.1: Negative electric potential ($-\phi$) and electron density n plotted against position y for a thick glass layer separating a silver crystallite from the silver electrode. The applied potential difference is given by $(-\Phi)$, the thickness of the glass layer by H_{Thick} , and the electron density at the glass-silver interfaces by n_1 .

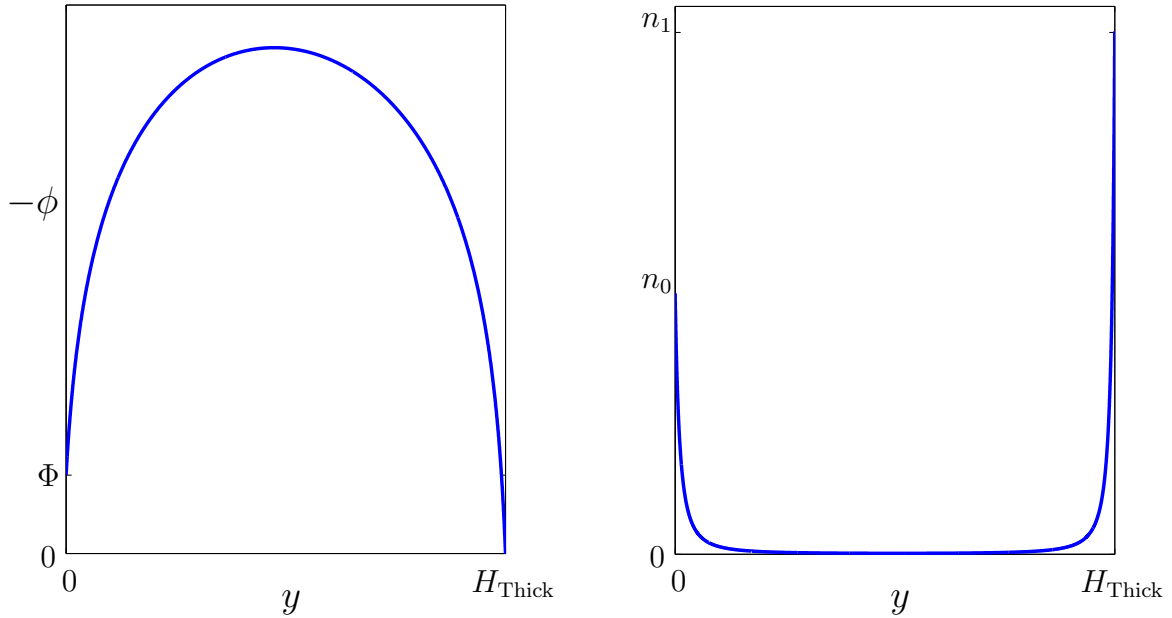


Figure D.2: Negative electric potential ($-\phi$) and electron density n plotted against position y for a thick glass layer separating the silicon emitter from the silver electrode. The applied potential difference is given by $(-\Phi)$, the thickness of the glass layer by H_{Thick} , the electron density at the glass-silver interface by n_1 and the electron density at the silicon-glass interface by n_0 .

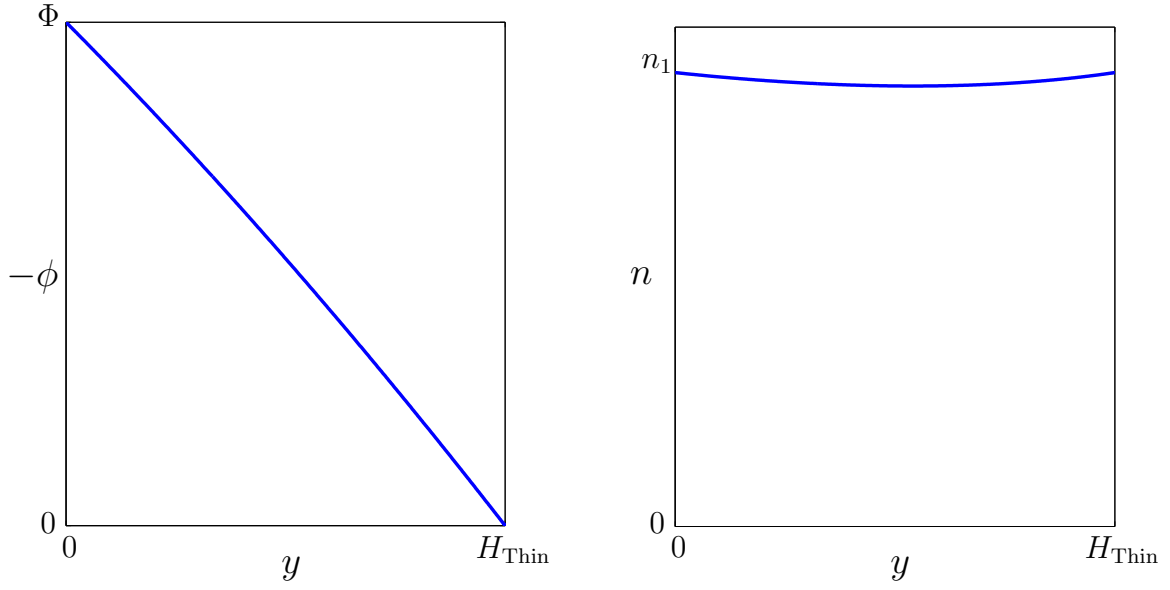


Figure D.3: Negative electric potential ($-\phi$) and electron density n plotted against position y for a thin glass layer separating a silver crystallite from the silver electrode. The applied potential difference is given by $(-\Phi)$, the thickness of the glass layer by H_{Thin} , and the electron density at the glass-silver interfaces by n_1 .

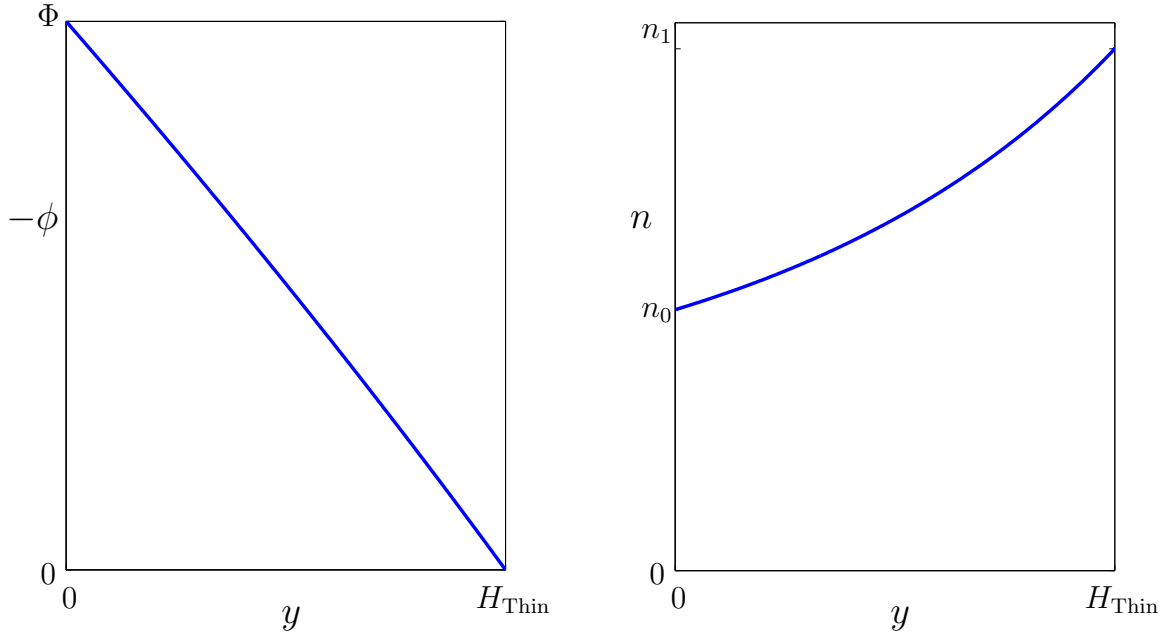


Figure D.4: Negative electric potential ($-\phi$) and electron density n plotted against position y for a thin glass layer separating the silicon emitter from the silver electrode. The applied potential difference is given by $(-\Phi)$, the thickness of the glass layer by H_{Thin} , the electron density at the glass-silver interface by n_1 and the electron density at the silicon-glass interface by n_0 .

fraction of the total current that is contained in a given distance x from the minimum in the glass layer thickness and we note that a uniform thickness glass layer has a linear cumulative current curve. We show the normalised cumulative current for the nonuniform glass layer (shown in figure D.5) in figure D.7. We can see that the line is curved outwards, indicating that the vast majority of the current passes through a region very close to the glass layer minimum. We expect exactly the same short circuiting effects to be present when considering the Si-glass-Ag system.

Since we know the glass layer profile at the front contact of silicon solar cell varies between 10nm-1000nm, we conclude that the effective contact resistance is determined by the number and breadth of regions of the glass layer that are in the H_{Thin} regime and not the average glass layer thickness.

D.5 Electron trajectories

We have investigated the trajectories the electrons take through the glass layer. In figure D.8 we show that when the glass layer varies slowly the electron trajectories go (approximately) straight through the glass layer and when the glass layer varies quickly the electron trajectories have an appreciable curve towards the glass layer minimum.

D.6 Quantum mechanical effects

One question of interest to DuPont is whether quantum mechanical effects alter the effective contact resistance. To answer this question we consider the role that quantum mechanical effects have on the effective contact resistance. We consider the Ag-glass-Ag system where the glass layer thickness is given by H_{Thin} and include quantum mechanical effects.

In figure D.9 we plot the electric potential and electron density within the glass layer when including and when neglecting quantum mechanical effects. We find that the inclusion of the quantum mechanical effects makes a negligible change to the electric potential, and the electron density and therefore has a negligible effect on the resistance of the glass layer. We expect this to also be the case when considering the Si-glass-Ag system.

Overall, we conclude that the incorporation of quantum effects is not likely to be necessary to explain the contact resistance in situations of physical interest to DuPont (UK) Ltd.

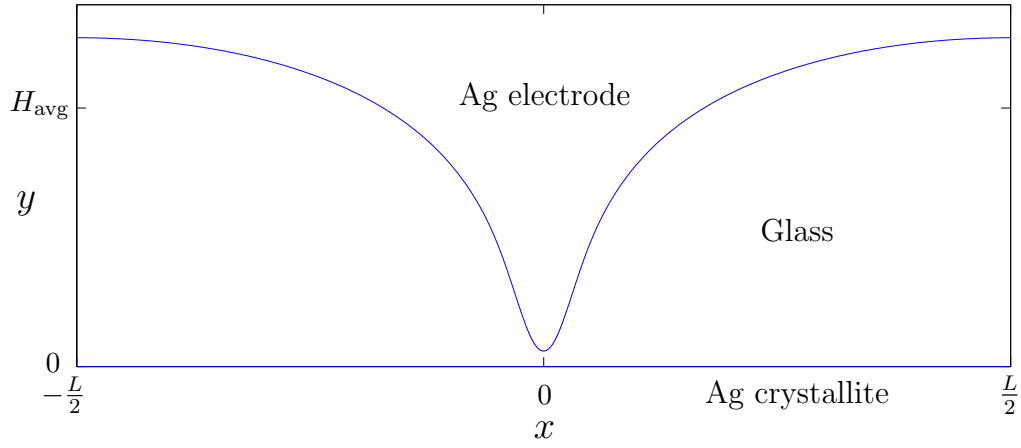
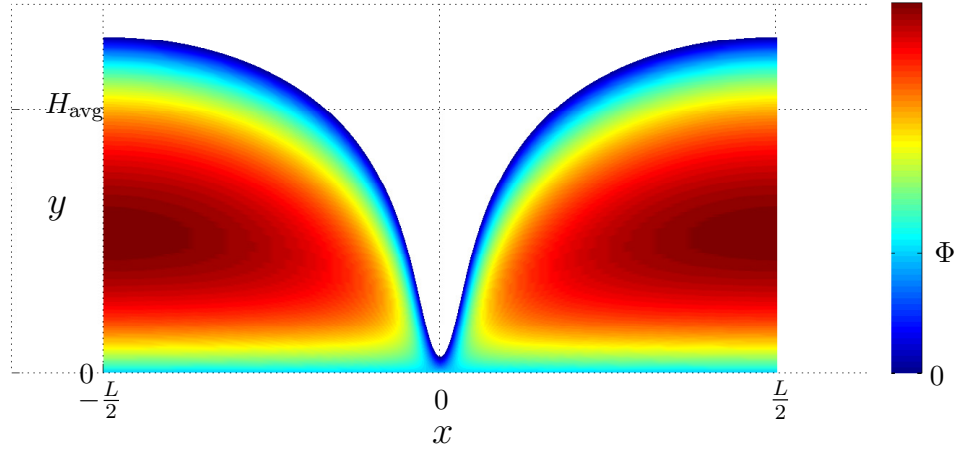


Figure D.5: The glass layer thickness profile.

Negative electric potential ($-\phi$)



Electron density n

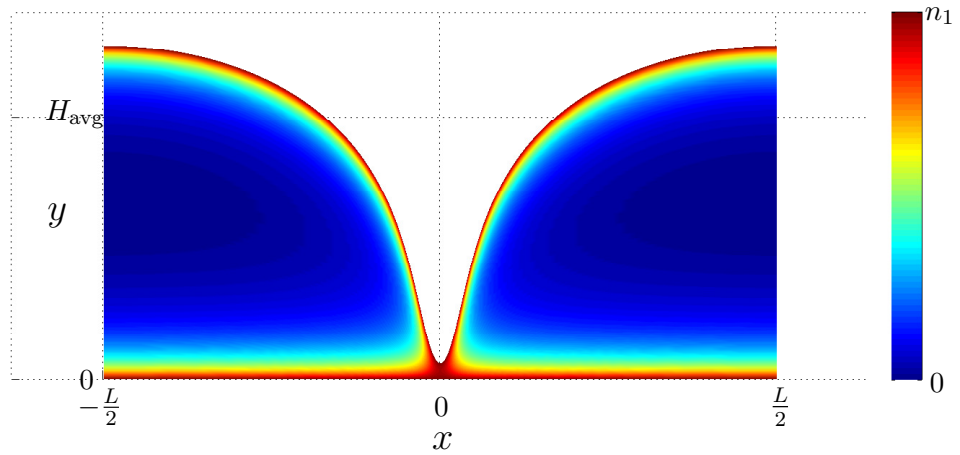


Figure D.6: Negative electric potential ($-\phi$) and electron density n plotted against position x and y . The applied potential difference is given by $(-\Phi)$, the average thickness of the glass layer by H_{avg} , and the electron density at the glass-silver interfaces by n_1 .

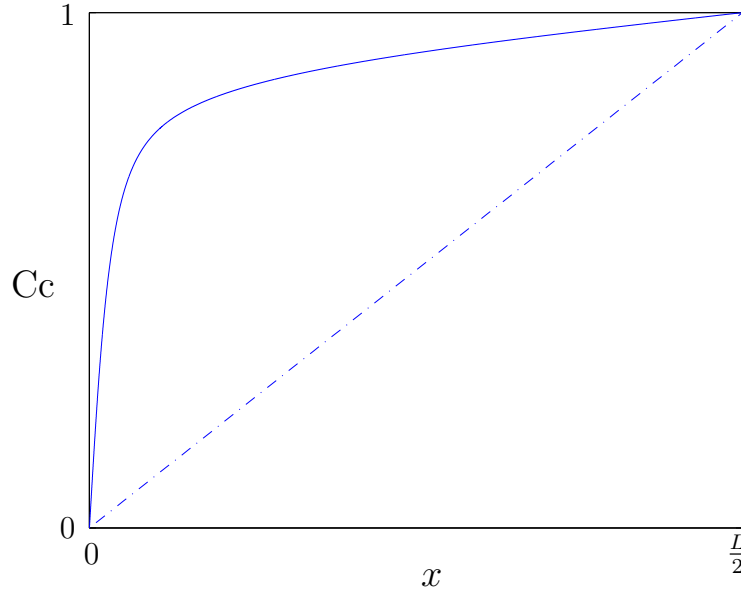


Figure D.7: Normalised cumulative current C_c plotted against horizontal position x . The solid line is the cumulative current curve with the thickness profile shown in figure D.5 and the dot-dashed line is the cumulative current curve for a glass layer with uniform thickness.

D.7 Validation of the mathematical model

To validate our mathematical model the effective contact resistance should be measured over a range of current densities spanning many orders of magnitude and compared with the results of our model, as illustrated in figure D.10. We expect to find regions where the effective contact resistance is Ohmic, and therefore does not vary with current density, and regions where the effective contact resistance is non-Ohmic, and therefore does vary with current density. The model accurately represents the effective contact resistance for a range of applied electric potential difference, however, it is known the drift diffusion model fails at very high fields and therefore care must be taken when considering large potential differences.

D.8 Summary

In summary we have found

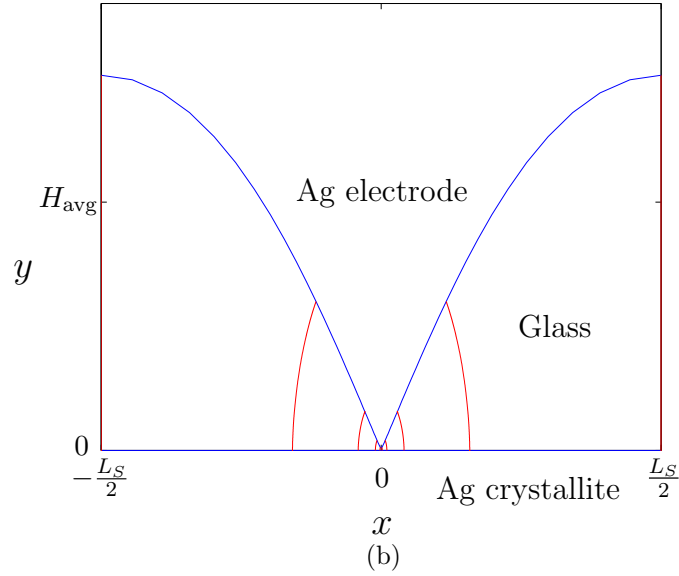
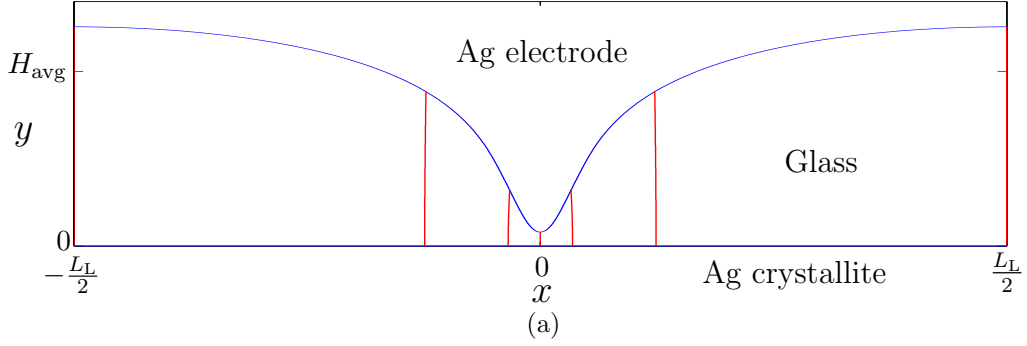


Figure D.8: Figure (a) shows the electron trajectories through a glass layer where the thickness of the glass layer varies slowly ($L_L \gg H_{\text{Avg}}$) and figure (b) shows the electron trajectories through a glass layer where the thickness of the glass layer varies quickly ($L_S \approx H_{\text{Avg}}$).

- The resistance of the glass layer, and therefore the effective contact resistance, depends on many different physical parameters.
- Short-circuiting effects are important with the majority of current flowing through a region near the glass layer minimum thickness.
- Quantum mechanical effects are unlikely to be an important conduction mechanism.

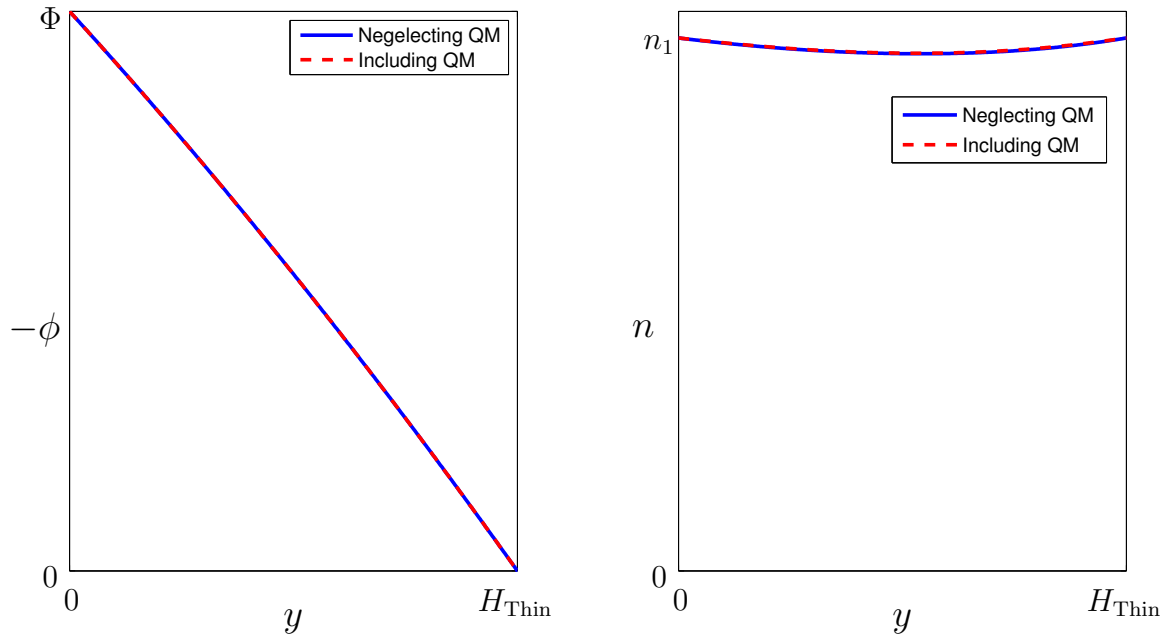


Figure D.9: Negative electric potential ($-\phi$) and electron density n plotted against position x for a thin glass layer separating a silver crystallite from the silver electrode. The applied potential difference is given by $(-\Phi)$, the thickness of the glass layer by H_{Thin} , and the electron density at the glass-silver interfaces by n_1 .

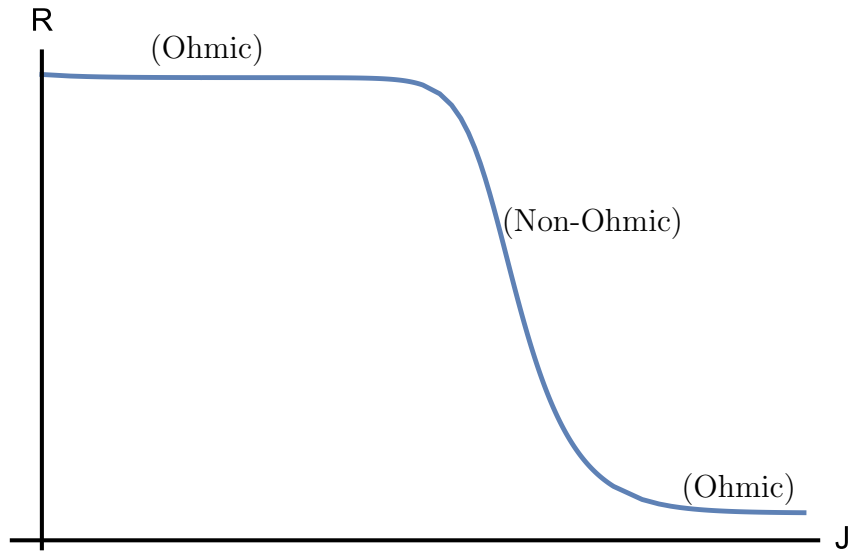


Figure D.10: Effective contact resistance R plotted against current density J .

We therefore recommend that to reduce the effective contact resistance at the front side of a silicon solar cell DuPont (UK) Ltd should focus on creating a paste that maximises the number of regions where the glass layer is in the H_{Thin} regime ($H \approx 10\text{nm}$).

Bibliography

- [1] H. Abebe and E. Cumberbatch. Quantum mechanical effects correction models for inversion charge and current-voltage (IV) characteristics of the MOSFET device. In *Proceedings 2003 Nanotechnology Conference*, pages 218–221, 2003.
- [2] M. Abramowitz and I. Stegun. *Handbook of mathematical functions with formulas, graphs, and mathematical tables*. Dover publications, New York, 1964.
- [3] T. Adachi, A. Yoshii, and T. Sudo. Two-dimensional semiconductor analysis using finite-element method. *IEEE Transactions on Electron Devices*, 26(7):1026–1031, 1979.
- [4] M. G. Ancona. Macroscopic description of quantum-mechanical tunneling. *Physical Review B*, 42(2):1222, 1990.
- [5] M. G. Ancona. Density-gradient analysis of field emission from metals. *Physical Review B*, 46(8):4874, 1992.
- [6] M. G. Ancona. Density-gradient theory: a macroscopic approach to quantum confinement and tunneling in semiconductor devices. *Journal of Computational Electronics*, 10(1-2):65, 2011.
- [7] M. G. Ancona and G. J. Iafrate. Quantum correction to the equation of state of an electron gas in a semiconductor. *Physical Review B*, 39(13):9536, 1989.
- [8] M. G. Ancona and A. Svizhenko. Density-gradient theory of tunneling: Physics and verification in one dimension. *Journal of Applied Physics*, 104(7):073726, 2008.
- [9] M. G. Ancona and H. F. Tiersten. Macroscopic physics of the silicon inversion layer. *Physical Review B*, 35(15):7959–7965, 1987.
- [10] M. G. Ancona, D. Yergeau, Z. Yu, and B. A. Biegel. On Ohmic boundary conditions for density-gradient theory. *Journal of Computational Electronics*, 1(1–2):103–107, 2002.

- [11] M. G. Ancona, Z. Yu, R. W. Dutton, P. J. Voorde, M. Cao, and D. Vook. Density-gradient analysis of MOS tunneling. *IEEE Transactions on Electron Devices*, 47(12):2310–2319, 2000.
- [12] M. G. Ancona, Z. Yu, W. C. Lee, R. W. Dutton, and P. V. Voorde. Density-gradient simulations of quantum effects in ultra-thin-oxide MOS structures. In *SISPAD*, pages 97–100, 1997.
- [13] A. Asenov, G. Slavcheva, A. R. Brown, J. H. Davies, and S. Saini. Increase in the random dopant induced threshold fluctuations and lowering in sub-100 nm MOSFETs due to quantum effects: a 3-D density-gradient simulation study. *IEEE Transactions on Electron Devices*, 48(4):722–729, 2001.
- [14] C. Ballif, D. Huljic, G. Willeke, and A. Hessler-Wyser. Silver thick-film contacts on highly doped n-type silicon emitters: Structural and electronic properties of the interface. *Applied Physics Letters*, 82(12):1878, 2003.
- [15] M. Z. Bazant. Conformal mapping of some non-harmonic functions in transport theory. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, 460:1433–1452, 2004.
- [16] M. Z. Bazant, K. T. Chu, and B. J. Bayly. Current-voltage relations for electrochemical thin films. *SIAM Journal on Applied Mathematics*, 65(5):1463–1484, 2005.
- [17] M. Z. Bazant, K. Thornton, and A. Ajdari. Diffuse-charge dynamics in electrochemical systems. *Physical Review E*, 70(2), 2004.
- [18] C. M. Bender and S.A. Orszag. *Advanced Mathematical Methods for Scientists and Engineers*. Springer-Verlag, New York, 1999.
- [19] P. M. Biesheuvel and M. Z. Bazant. Nonlinear dynamics of capacitive charging and desalination by porous electrodes. *Physical Review E*, 81(3):031502, 2010.
- [20] Á. Birkisson. *Numerical solution of nonlinear boundary value problems for ordinary differential equations in the continuous framework*. PhD thesis, University of Oxford, Oxford, 2013.
- [21] Á. Birkisson and T. A. Driscoll. Automatic Fréchet differentiation for the numerical solution of boundary-value problems. *ACM Transactions on Mathematical Software*, 38(4):26, 2012.

- [22] J . P. Black, C. J. W. Breward, and P. D. Howell. Two-dimensional modeling of electron flow through a poorly conducting layer. *SIAM Journal on Applied Mathematics*, 78(2):289–312, 2015.
- [23] J. P. Black, C. J. W. Breward, P. D. Howell, and R. J. S. Young. Mathematical modeling of contact resistance in silicon photovoltaic cells. *SIAM Journal on Applied Mathematics*, 73(5):1906–1925, 2013.
- [24] A. Bonnefont, F. Argoul, and M. Z. Bazant. Analysis of diffuse-layer effects on time-dependent interfacial kinetics. *Journal of Electroanalytical Chemistry*, 500(1):52–61, 2001.
- [25] D. Brinkman, K. Fellner, P. A. Markowich, and M.-T. Wolfram. A drift–diffusion–reaction model for excitonic photovoltaic bilayers: Asymptotic analysis and a 2D HDG finite element scheme. *Mathematical Models and Methods in Applied Sciences*, 23(05):839–872, 2013.
- [26] E. Cabrera, S. Olibet, J. Glatz-Reichenbach, R. Kopecek, D. Reinke, and G. Schubert. Current transport in thick film Ag metallization: Direct contacts at silicon pyramid tips? *Energy Procedia*, 8:540–545, 2011.
- [27] E. Cabrera, S. Olibet, J. Glatz-Reichenbach, R. Kopecek, D. Reinke, and G. Schubert. Experimental evidence of direct contact formation for the current transport in silver thick film metallized silicon emitters. *Journal of Applied Physics*, 110(11):114511, 2011.
- [28] E. Cabrera, S. Olibet, D. Rudolph, E. Wefringhaus, R. Kopecek, D. Reinke, and G. Schubert. Influence of surface topography on the glass coverage in the contact formation of silver screen-printed Si solar cells. *IEEE Journal of Photovoltaics*, 3(1):102–107, 2013.
- [29] Enrique Cabrera, Sara Olibet, Dominik Rudolph, Per Erik Vullum, Radovan Kopecek, Daniel Reinke, Carmen Herzog, Daniel Schwaderer, and Gunnar Schubert. Impact of excess phosphorus doping and Si crystalline defects on Ag crystallite nucleation and growth in silver screen-printed Si solar cells. *Progress in Photovoltaics: Research and Applications*, 23:367–375, 2013.
- [30] J. Chapman, J. Norbury, C. Please, and G. Richardson. Ions in solutions and protein channels. *Fifth Mathematics in Medicine Study Group, University of Oxford*, 2005.

- [31] L. K. Cheng, L. Liang, and Z. Li. Nano-Ag colloids tunneling mechanism for current conduction in front contact of crystalline si solar cells. In *Proceedings of the 34th IEEE Photovoltaics Specialists Conference (PVSEC)*, pages 2344–2348, Philadelphia, PA, 2009.
- [32] K. T. Chu and M. Z. Bazant. Electrochemical thin films at and above the classical limiting current. *SIAM Journal on Applied Mathematics*, 65(5):1485–1505, 2005.
- [33] I. B. Cooper, K. Tate, J. S. Renshaw, A. F. Carroll, K. R. Mikeska, R. C. Reedy, and A. Rohatgi. Investigation of the mechanism resulting in low resistance Ag thick-film contact to Si solar cells in the context of emitter doping density and contact firing for current-generation Ag paste. *IEEE Journal of Photovoltaics*, 4(1):134–141, 2014.
- [34] C. R. Crowell and M. Begulwala. Recombination velocity effects on current diffusion and IMREF in Schottky barriers. *Solid-state electronics*, 14:1149–1157, 1971.
- [35] E. Cumberbatch, S. Uno, and H. Abebe. Nano-scale MOSFET device modelling with quantum mechanical effects. *European Journal of Applied Mathematics*, 17(4):465–489, 2006.
- [36] P. Damle, A. W. Ghosh, and S. Datta. First-principles analysis of molecular conduction using quantum chemistry software. *Chemical physics*, 281(2):171–187, 2002.
- [37] P. S. Damle, A. W. Ghosh, and S. Datta. Unified description of molecular conduction: From molecules to metallic wires. *Physical Review B*, 64(20):201403, 2001.
- [38] T. A. Driscoll. Algorithm 843: improvements to the Schwarz-Christoffel toolbox for MATLAB. *ACM Transactions on Mathematical Software (TOMS)*, 31(2):239–251, 2005.
- [39] M. Eberstein, J. Slim, K. Reinhardt, and U. Partsch. Kinetic aspects of the contact formation by glass containing silver pastes. In *27th European Photovoltaic Solar Energy Conference and Exhibition*, pages 840–844, Frankfurt, Germany, 2012.
- [40] P. E. Farrell, D. A. Ham, S. W. Funke, and M. E. Rognes. Automated derivation of the adjoint of high-level transient finite element programs. *SIAM Journal on Scientific Computing*, 35(4):C369–C393, 2013.
- [41] P. Ferrada, R. Harney, E. Wefringhaus, U. Jaeger, A. Wolf, D. Biro, M. Weiss, and J. Lossen. Characterization of height-selective emitters. *Energy Procedia*, 8:220, 2011.

- [42] J. M. Foster, J. Kirkpatrick, and G. Richardson. Asymptotic and numerical prediction of current-voltage curves for an organic bilayer solar cell under varying illumination and comparison to the Shockley equivalent circuit. *Journal of Applied Physics*, 114(10):104501, 2013.
- [43] J. M. Foster, H. J. Snaith, T. Leijtens, and G. Richardson. A model for the operation of perovskite based hybrid solar cells: Formulation, analysis, and comparison to experiment. *SIAM Journal on Applied Mathematics*, 74(6):1935–1966, 2014.
- [44] G. Grupp, B. Daniel, G. Emanuel, R. Preu, F. Schittlhelm, and G. Willeke. Analysis of silver thick-film contact formation on industrial silicon solar cells. In *Proceedings of the 31st IEEE Photovoltaics Specialists Conference (PVSEC)*, pages 1289–1292, Orlando, Florida, 2005.
- [45] H. K. Gummel. A self-consistent iterative scheme for one-dimensional steady state transistor calculations. *IEEE transactions on Electron Devices*, 11(10):455–465, 1964.
- [46] N. Hale and T. W. Tee. Conformal maps to multiply slit domains and applications. *SIAM Journal on Scientific Computing*, 31(4):3195–3215, 2009.
- [47] W. A. Harrison. *Solid state theory*. Courier Corporation, 1970.
- [48] M. Hilali, M. Al-Jassium, B. To, H. Moutinho, A. Rohatgi, and S. Asher. Understanding the formation and temperature dependence of thick-film ag contacts on high-sheet-resistance Si emitters for solar cells. *Journal of the Electrochemical Society*, 152(10):G742–G749, 2005.
- [49] M. M. Hilali, K. Nakayashiki, C. Khadlilkar, R. C. Reedy, Robert C., A. Rohatgi, A. Shaikh, S. Kim, and S. Sridharan. Effect of Ag particle size in thick-film Ag paste on the electrical and physical properties of screen printed contacts and silicon solar cells. *Journal of the Electrochemical Society*, 153(1):A5–A11, 2006.
- [50] R. Hoenig, M. Duerrschnabel, W. van Mierlo, Z. Aabdin, J. Bernhard, J. Biskupek, O. Eibl, U. Kaiser, J. Wilde, F. Clement, and D. Biro. The nature of screen printed front side silver contacts - results of the project mikrosol. *Energy Procedia*, 43:27–36, 2013.
- [51] K.-K. Hong, S.-B. Cho, J. S. You, J.-W. Jeong, S.-M. Bea, and J.-Y. Huh. Mechanism for the formation of Ag crystallites in the Ag thick-film contacts of crystalline Si solar cells. *Solar Energy Materials and Solar Cells*, 93(6):898–904, 2009.

- [52] J.-Y. Huh, K.-K. Hong, S.-B. Cho, S.-K. Park, B.-C. Lee, and K. Okamoto. Effect of oxygen partial pressure on Ag crystallite formation at screen-printed Pb-free Ag contacts of Si solar cells. *Materials Chemistry and Physics*, 131(1-2):113, 2011.
- [53] A. S. Ionkin, B. M. Fish, Z. R. Li, M. Lewittes, P. D. Soper, J. G. Pepin, and A. F. Carroll. Screen-printed silver pastes with metallic nano-zinc and nano-zinc alloys for crystalline silicon photovoltaic cells. *Applied Materials and Interfaces*, 3(2):606–611, 2011.
- [54] C. Jacoboni and P. Lugli. *The Monte Carlo method for semiconductor device simulation*, volume 3. Springer, 1989.
- [55] B. A. Janta-Polczynski, J. I. Cerdá, G. Éthier-Majcher, K. Piyakis, and A. Rochefort. Parallel scanning tunneling microscopy imaging of low dimensional nanostructures. *Journal of Applied Physics*, 104(2):023702, 2008.
- [56] M.-I. Jeong, S.-E. Park, D.-H. Kim, J.-S. Lee, Y.-C. Park, K.-S. Ahn, and C.-J. Choi. Transmission electron microscope study of screen-printed Ag contacts on crystalline Si solar cells. *Journal of the Electrochemical Society*, 157(10):H934–H936, 2010.
- [57] C.-S. Jiang, Z. G. Li, H. R. Moutinho, L. Liang, A. Ionkin, and M. M. Al-Jassim. Real-space microscopic electrical imaging of n^+ -p junction beneath front-side Ag contact of multicrystalline Si solar cells. *Journal of Applied Physics*, 111(8):083704, 2012.
- [58] A. Khanna, P. K. Basu, A. Filipovic, V. Shanmugam, C. Schmiga, A. G. Aberle, and T. Mueller. Influence of random pyramid surface texture on silver screen-printed contact formation for monocrystalline silicon wafer solar cells. *Solar Energy Materials and Solar Cells*, 132:589–596, 2015.
- [59] S. J. Kim, S. Y. Kim, J. M. Park, J. N. Heo, J. H. Lee, S. M. Lee, D. H. Kim, W. T. Kim, K. R. Lim, D. Kim, S. C. Park, H. K. Kim, M. C. Song, J. Park, S. S. Jee, and E.-S. Lee. Exploiting metallic glasses for 19.6% efficient back contact solar cell. *Applied Physics Letters*, 101(6):064106, 2012.
- [60] S. Kontermann, R. Preu, and G. Willeke. Calculating the specific contact resistance from the nanostructure at the interface of silver thick film contacts on n-type silicon. *Applied Physics Letters*, 99(11):111905, 2011.

- [61] S. Kontermann, A. Ruf, and R. Preu. Atomistic simulations of the silicon surface structure at the interface of silver thick film contacts on n-type silicon. *Materials Research Society Symposium Proceedings*, 1323:131–136, 2011.
- [62] S. Kontermann, G. Willeke, and J. Bauer. Electronic properties of nanoscale silver crystals at the interface of silver thick film contacts on n-type silicon. *Applied Physics Letters*, 97(19):191910, 2010.
- [63] G. Kulushich, B. Bazer-Bachi, T. Takahashi, H. Iida, R. Zapf-Gottwick, and J. H. Werner. Contact formation on 100 Ω /sq emitter by screen printed silver paste. *Energy Procedia*, 27:485, 2012.
- [64] Z. G. Li, L. Liang, and L. K. Cheng. Electron microscopy study of front-side Ag contact in crystalline Si solar cells. *Journal of Applied Physics*, 105(6):066102, 2009.
- [65] Z. G. Li, L. Liang, A. S. Ionkin, B. M. Fish, M. E. Lewittes, L. K. Cheng, and K. R. Mikeska. Microstructural comparison of silicon solar cells’ front-side Ag contact and the evolution of current conduction mechanisms. *Journal of Applied Physics*, 110(7):074304, 2011.
- [66] C.-H. Lin, S.-Y. Tsai, S.-P. Hsu, and M.-H. Hsieh. Investigation of Ag-bulk/glassy-phase/Si heterostructures of printed Ag contacts on crystalline Si solar cells. *Solar Energy Materials and Solar Cells*, 92(9):1011–1015, 2008.
- [67] P. A. Markowich. A singular perturbation analysis of the fundamental semiconductor device equations. *SIAM Journal on Applied Mathematics*, 44(5):896–928, 1984.
- [68] P. A. Markowich. *The Stationary Semiconductor Device Equations*. Springer Verlag, New York, 1986.
- [69] P. A. Markowich, C. A. Ringhofer, and C. Schmeiser. An asymptotic analysis of one-dimensional models of semiconductor devices. *IMA Journal of Applied Mathematics*, 37(1):1–24, 1986.
- [70] P. A. Markowich and C. S. Schmeiser. Uniform asymptotic representation of solutions of the basic semiconductor-device equations. *IMA Journal of Applied Mathematics*, 36(1):43–57, 1986.
- [71] D. Meier and D. Schroder. Contact resistance: Its measurement and relative importance to power loss in a solar cell. *IEEE Transactions on Electron Devices*, 61(5):647–653, 1984.

- [72] R. J. Mortimer. Electrochromic materials. *Chemical Society Reviews*, 26(3):147–156, 1997.
- [73] W. D. Murphy, J. A. Manzanares, S. Mafé, and H. Reiss. A numerical study of the equilibrium and nonequilibrium diffuse double layer in electrochemical cells. *The Journal of Physical Chemistry*, 96(24):9983–9991, 1992.
- [74] J. Nelson. *The physics of solar cells*. Imperial College Press London, London, 2003.
- [75] S. Olibet, D. Rudolph, E. Cabrera, J. Hoornstra, A. J. Carr, A. W. Weeber, Y. Fu, and R. Kopecek. What makes a high-performing screen-printed Ag contact? realities and idealities from microscopical insight. In *22nd Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes*, Colorado, USA, 2012.
- [76] R. Pinnau. A note on boundary conditions for quantum hydrodynamic equations. *Applied mathematics letters*, 12(5):77–82, 1999.
- [77] R. Pinnau. A review on the quantum drift diffusion model. *Transport Theory and Statistical Physics*, 31(4-6):367–395, 2002.
- [78] C. P. Please. *Some mathematical problems of semiconductor devices*. PhD thesis, University of Oxford, Oxford, UK, 1978.
- [79] C. P. Please. An analysis of semiconductor p-n junctions. *IMA Journal of Applied Mathematics*, 28(3):301–318, 1982.
- [80] D. Pysch, A. Mette, A. Filipovic, and S. W. Glunz. Comprehensive analysis of advanced solar cell contacts consisting of printed fine-line seed layers thickened by silver plating. *Progress in Photovoltaics: Research and Applications*, 17(2):101, 2009.
- [81] Y. Ren, Y. Yang, T. Bao, C. Fan, and G. Chen. Investigation of the effect of forming gas annealing on front silver electrodes of c-Si solar cells. *Surface and Interface Analysis*, 44(7):856–862, 2012.
- [82] G. Richardson, C. P. Please, J. M. Foster, and J. Kirkpatrick. Asymptotic solution of a model for bilayer organic diodes and solar cells. *SIAM Journal on Applied Mathematics*, 72(6):1792–1817, 2012.
- [83] N. Sano, A. Hiroki, and K. Matsuzawa. Device modeling and simulations toward sub-10 nm semiconductor devices. *IEEE Transactions on Nanotechnology*, 1(1):63–71, 2002.

- [84] D. Scharfetter and H. Gummel. Large-signal analysis of a silicon read diode oscillator. *IEEE Transactions on Electron Devices*, 16(1):64–77, 1969.
- [85] C. Schmeiser and H. Steinrück. A new approach to the modeling of pnpn structures. *Solid-State Electronics*, 34(1):57–62, 1991.
- [86] G. Schubert. *Thick Film Metallisation of Crystalline Silicon Solar Cells*. PhD thesis, University of Konstanz, 2006.
- [87] G. Schubert, J. Horzel, R. Kopecek, F. Huster, and P. Fath. Silver thick film contact formation on lowly doped phosphorous emitters. In *Proceedings of the 20th European Photovoltaic Solar Energy Conference (EU PVSEC '05)*, page 934, Barcelona, Spain, 2005.
- [88] G. Schubert, F. Huster, and P. Fath. Physical understanding of printed thick-film front contacts of crystalline Si solar cells—review of existing models and recent developments. *Solar Energy Materials and Solar Cells*, 90(18-19):3399–3406, 2006.
- [89] V. Shanmugam, J. Cunnusamy, A. Khanna, P. Kanti Basu, Y. Zhang, C. Chen, A. F. Stassen, M. B. Boreland, T. Mueller, B. Hoex, and A. G. Aberle. Electrical and microstructural analysis of contact formation on lightly doped phosphorus emitters using thick-film Ag screen printing pastes. *IEEE Journal of Photovoltaics*, 4(1):168, 2014.
- [90] J. G. Simmons. Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film. *Journal of Applied Physics*, 34(6):1793, 1963.
- [91] J. W. Slotboom. Iteratics scheme for 1- and 2- dimensional DC-transistor simulation. *Electronics Letters*, 5(26):677–678, 1969.
- [92] J. W. Slotboom. Computer-aided two-dimensional analysis of bipolar transistors. *Electron Devices, IEEE transactions on*, 20(8):669–679, 1973.
- [93] C. M. Snowden. Semiconductor device modelling. *Reports on Progress in Physics*, 48(2):223–275, 1985.
- [94] solarbuzz. *Solar PV Industry Targets 100 GW Annual Deployment in 2018*. <http://www.solarbuzz.com/news/recent-findings/solar-pv-industry-targets-100-gw-annual-deployment-2018-according-npd-solarbuzz>. Accessed August 2014.

- [95] S. M. Sze and K. K. Ng. *Physics of semiconductor devices*. John Wiley & Sons, 2006.
- [96] L. N. Trefethen. *Spectral methods in MATLAB*. SIAM, Philadelphia, 2000.
- [97] L. N. Trefethen. *Approximation Theory and Approximation Practice*. SIAM, Philadelphia, 2013.
- [98] L. N. Trefethen et al. *Chebfun Version 5.0*, 2014. <http://www.chebfun.org>.
- [99] S. Uno, H. Abebe, and E. Cumberbatch. Analytical description of inversion-layer quantum effects using the density gradient model and singular perturbation theory. *Japanese Journal of Applied Physics*, 46(12R):7648, 2007.
- [100] M. van Soestbergen, P. M. Biesheuvel, and M. Z. Bazant. Diffuse-charge effects on the transient response of electrochemical cells. *Physical Review E*, 81(2), 2010.
- [101] M. van Soestbergen, A. Mavinkurve, R. T. H. Rongen, K. M. B. Jansen, L. J. Ernst, and G. Q. Zhang. Theory of aluminum metallization corrosion in microelectronics. *Electrochimica Acta*, 55(19):5459, 2010.
- [102] J. F. Verwey, E. A. Amerasekera, and J. Bisschop. The physics of SiO₂ layers. *Reports on Progress in Physics*, 53(10):1297–1331, 1990.
- [103] J. D. Walker, S. Seyedmohammadi, Y. Yang, and C. Khadlilkar. Front surface crystalline silicon contacts formed via thick film silver pastes. In *Photovoltaic Specialists Conference (PVSC), 2011 37th IEEE*, pages 2212–2215, 2011.
- [104] M. Ward, F. Odeh, and D. Cohen. Asymptotic methods for metal oxide semiconductor field effect transistor modeling. *SIAM Journal on Applied Mathematics*, 50(4):1099–1125, 1990.
- [105] M. Ward, L. Reyna, and F. Odeh. Multiple steady state solutions in a multi-junction structure. *Applied Mathematics Letters*, 2(4):395–400, 1989.
- [106] J. R. Watling, A. R. Brown, and A. Asenov. Can the density gradient approach describe the source-drain tunnelling in decanano double-gate MOSFETs? *Journal of Computational Electronics*, 1(1):289–293, 2002.
- [107] J. A. C. Weideman and S. C. Reddy. A MATLAB differentiation matrix suite. *ACM Transactions on Mathematical Software (TOMS)*, 26(4):465–519, 2000.