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Hybrid Ionic Conductivity

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Hybrid Ionic Conductivity

A Major Qualifying Project

Submitted to the Faculty of

Worcester Polytechnic Institute

In partial fulfillment of the requirements for the

Degree in Bachelor of Science

in

Mathematical Sciences

By

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Date: 3/25/16

Project Advisors:

Professor Joseph Fehribach, Advisor

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1 Abstract

Hybrid ionic compounds have many potential applications such as in fuel cells or other power sources. This paper covers a study of a system of elliptic partial differential equations and their boundary conditions relating to conductivity of hybrid ionic compounds. It begins with a problem definition which considers the implications of the work function difference within the material. The geometries created assume uniformity in the background material and within the placed particles. All relevant calculations were completed using COMSOL Multiphysics primarily consisting of potential diagrams and current magnitudes. The primary goal of this project was finding optimal arrangements of particles within the background material.

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2 Introduction

Nanoionics is a scientific field of study with many potential applications. This paper focuses on hybrid ionic compounds, a part of nanoionics which examines composites of a bulk material with particles of a different material within it. These have many potential applications such as solid oxide fuel cells (Kim, Virkar, Fung, Mehta, & Singhal, 1999) as they can greatly increase the overall conductivity of the material.

Conductivity is a measure of how easy it is for electrons to move in a given space. One way to determine conductivity is through the work function. The work function of a material is the minimum energy needed to move an electron from its surface to a point in a vacuum directly outside the surface, defined as $W = -e\phi - E_F$ where e is charge of an electron, ϕ electrostatic potential in the vacuum, and E_F Fermi level in the material (Wikipedia, 2016). By applying voltage to the material, one directly controls E_F thus ϕ can be rewritten as $\phi = V - \frac{W}{e}$ where $V = E_F/e$. Note that, for a material with lower or even zero conductivity, less work is required to move an electron off of its surface. The work function, rather than being dependent on the bulk material, is actually dependent on the surface material and the properties of said surface.

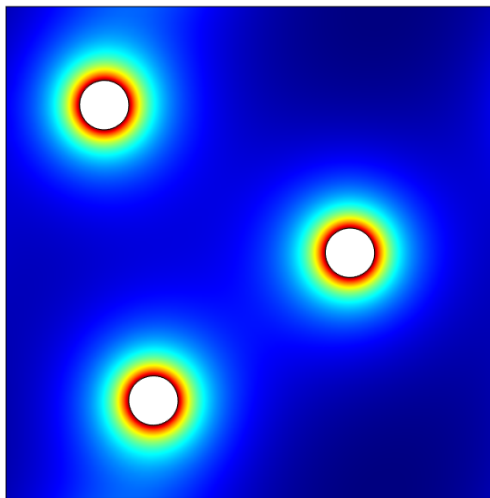


Figure 1: A sample hybrid ionic compound with three particles

For hybrid ionic compounds, substances which contain particles of zero conductivity but are otherwise uniform, the work function is not constant. These are made using special materials of differing work functions. For instance, $Pt/SrZr_{0.9}Y_{0.1}O_{3-\alpha}$ can be used with various volumes of platinum to create one such compound (Matsumoto, Furya, Okada, & Tanji, 1999). As an example, compare the conductivity in the bulk of this material to the area surrounding a single particle (Figure 2). In the area around this non-conducting particle, con-

ductivity increases from the background conductivity to a maximum of $\sigma_b * e^{-u_0}$ at the particle's surface. In other words, due to the differences in work functions between the particle and the bulk material, overall conductivity around the particle increases, and these areas are called *Space Charge Layers*. Furthermore, there exist arrangements of particles where the overall conductivity of the material will increase by creating a path of increased conductivity through the material. This project seeks to find these arrangements and how they are affected by the intrinsic properties of the materials used.

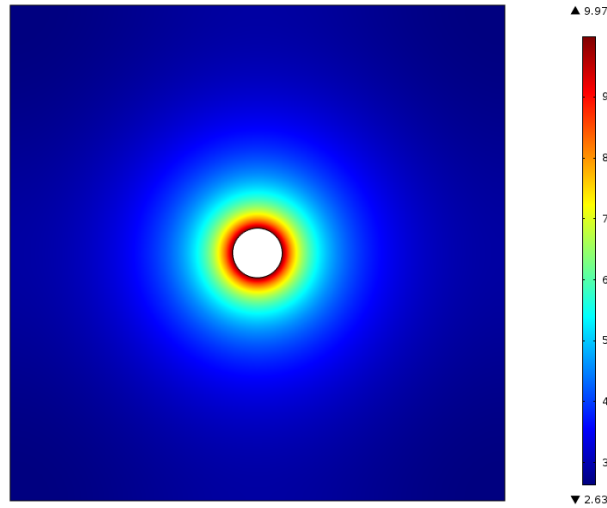


Figure 2: An example compound with a single particle. The scale on the right shows the conductivity for various regions. Conductivity at the surface of the particle (u_0) is 2.3

To better examine these compounds, this paper contains a study on a particular system of partial differential equations, which are derived from electrostatics and Poisson's equation given by $\Delta u = \nabla^2 u = u_{xx} + u_{yy} = f$ (Hackbusch, 1987). Additionally, Laplace's equation is formed by setting $f = 0$. It is clear that these equations are elliptic since $u_{xx} + u_{yy} = u_{xx} + u_{yy} + 0 * u_{xy}$ thus the discriminant < 0 . These equations only depend on spacial dimensions and not time, and thus study steady state problems. The Poisson's equation examined in this paper, however, is nonlinear and is written as $\Delta u = \nabla^2 u = f(u, x, y)$. For this problem, the minimum principle applies which states that if u and its first and second derivatives are continuous in the closure of the domain, u is continuous on the boundary of the domain, and $\Delta u \leq 0$, then u achieves its minimum on the boundary (Logan, 1994). This is a significant result as it allows the solution of the problem to be bounded.

Because of this principle, a solution to this problem is expected. The next section will detail the formation of said problem, as laid out in "PoissonBoltzmann model of space charge layer effects on conductivity in randomly dis-

tributed nanoionic composites” (Fish et al., 2012). Next how the computations were calculated will be discussed. Finally, the results and future suggestions will be given.

3 Problem Definition

For this paper, it is assumed that conductivity is proportional to the charge carrier concentration: $\frac{\sigma}{\sigma_b} = \frac{X}{X_b}$ where the subscript b denotes the value in the bulk of the material, far away from the particles. Furthermore, X is proportional to $e^{-\frac{E}{kT}}$ where E is the energy, k Boltzmann's constant, and T temperature as given by Boltzmann distribution (Wikipedia, 2016). Simplifying this, $\frac{X}{X_b} = e^{-\frac{zFY}{RT}}$ where $z = 1$ is the charge of a charge carrier, F Faraday's constant, Y the local potential relative to the bulk potential, and R the real gas constant. Thus we can write $\frac{\sigma}{\sigma_b} = e^{-u}$ where $u = \frac{FY}{RT}$ is the dimensionless potential.

To better describe the potential, note that $\nabla \cdot E_f = \frac{\rho}{\epsilon}$ where E_f is the electric field, ρ is the free charge density, and ϵ electrical permittivity, which is assumed to be constant. Additionally u can be rewritten as $u = \Psi - \Psi_b$ where Ψ is the electrostatic potential and Ψ_b the potential in the bulk material, which is constant. And since $E_f = -\nabla\Psi$, this can be rewritten as $\Delta u = -\frac{F}{\epsilon RT}\rho$. As the bulk material is electrically neutral, ρ can be described using X_b as $\rho = FX_b(\frac{X}{X_b} - 1)$. Substituting, this becomes $\rho = FX_b(e^{-u} - 1)$ and thus $\Delta u = \frac{1}{2\lambda^2}(1 - e^{-u})$ where λ is the Debye length of the material. The Debye length of this material is given by $\lambda = \frac{\epsilon RT}{2F^2[X]_b}$. This is a constant intrinsic to the material, independent of the particles, and "is the measure of a charge carrier's net electrostatic effect in solution, and how far those electrostatic effects persist" (Wikipedia, 2016). In the context of this problem, with a very large Debye length, a single inserted particle would change the conductivity of the entire domain, even if it was quite small.

The domain for the problem (Ω) is a unit cell with a number of particles contained within its bounds. Here, the unit cell is a rectangle with equal sides (ie a square) with constant σ_0 . For the calculations, σ is scaled by σ_b , or in other words, the obtained values of σ correspond to $\sigma_b = 1$. Additionally, within the particles the conductivity is 0. It is assumed that this arrangement within the cell is repeated in a grid-like pattern many times in every direction. Therefore, potential (u) is continuous and differentiable, or periodic, across the boundaries of the cell.

To examine how effective a given geometry is at conducting, it is necessary to examine voltage (V). V is assumed to satisfy $\nabla \cdot (\sigma \nabla(V)) = 0$ where σ is defined by e^{-u} where u is calculated from the first equation. As this is linear, V can be defined to be 0 at $y = 0$, and 1 at $y = 1$. Summarizing, the equations and boundary conditions are as follows:

PDE:

$$\Delta u = \frac{1}{2\lambda^2}(1 - e^{-u}) \quad \text{on } \Omega \quad (1)$$

$$\nabla \cdot (\sigma \nabla(V)) = 0 \quad \text{on } \Omega \quad (2)$$

BC:

$$\begin{aligned}
 &u \text{ is periodic across } x = 0 \text{ and } x = 1 \\
 &u \text{ is periodic across } y = 0 \text{ and } y = 1 \\
 &u = u_0 \text{ on the inner boundary} \\
 &V \text{ is periodic across } x = 0 \text{ and } x = 1 \\
 &V(x, 0) = 0 \\
 &V(x, 1) = 1
 \end{aligned}$$

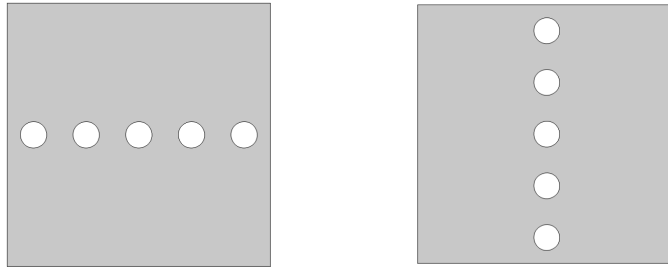
These equations are independent of time. Since u is periodic across the boundaries, it and its derivatives must be continuous on Ω and $0 \geq 1 - e^{-u} \geq 1 - eu_0$ so (1) must have a unique solution. And because V is linear with σ calculated from (1), (2) has a unique solution as well.

The simplest case was considered first: a single circular particle inscribed in the center of the cell with $u_0 = -2.3$. After choosing the radius of the circle (R) and the value of (λ) , the following line integral was calculated on the top boundary:

$$\int_b^a -u \frac{dV}{dy} \tag{3}$$

By evaluating this, the current through the material can be calculated and the thus effective conductivity can be inferred. From this, reasonable ranges of λ can be found as λ too small or too large are not worth studying.

Next, five particles were used with $R = .05$ and the arrangement of them within the square was varied (Figure 3). This allows for a more thorough analysis of the effects of these particles to the background material and how their effects blend with one another in the arrangements. The same line integral was calculated to find the best possible variation of particles for selected λ and u_0 values. Finding the optimal arrangements can be used in potential applications of these kinds of compounds.



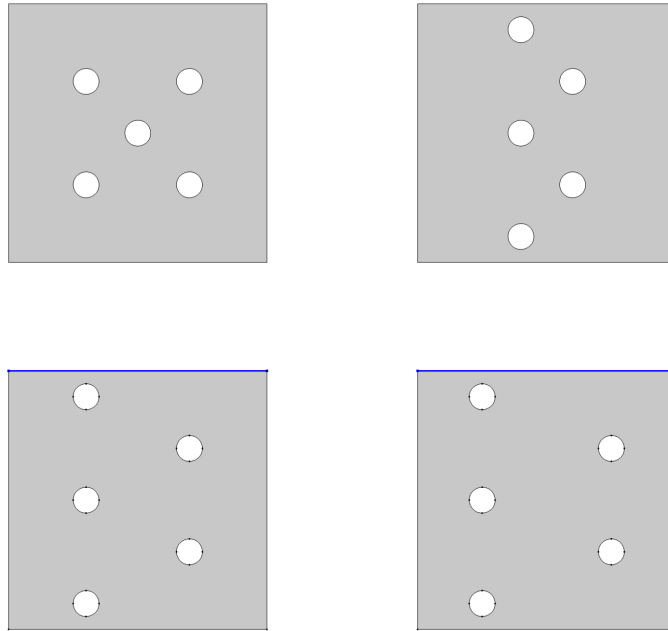


Figure 3: Arrangements of particles for the five particle calculations. The first two place all 5 along the center line of the cell, horizontally and vertically. The third places all the particle close to the center of the cell. The last 3 place the particle in two lines of varying distances, each being .1, .2, and .25 away from the center line respectively.

4 Computations

COMSOL Multiphysics 5.0 was used for the calculations. From the Model Wizard, two Poisson equations were created and the solver set to stationary. For the geometry, a square with sides of length 1 was created with its bottom left corner at the origin. Next the circles were formed which represented the particles and were placed appropriately in the square. Finally, a difference between the square and the circles formed the final domain of the problem. The boundary conditions were set up as usual, with the periodic conditions specified as continuity and Dirichlet conditions for u_0 and the non-periodic conditions of V . The default solver was used for the computations (note that for COMSOL 5.0 a nonlinear solver is assumed for nonlinear problems).

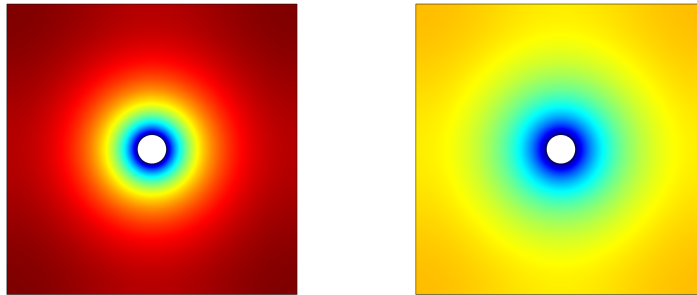
5 Results

For the single particle simulations, the following table summarizes the results:

R/λ	.25	7	14	20
.0001	1.2897	9.2537	9.7772	9.8761
.001	1.4679	9.5237	9.8506	9.9099
.01	1.8239	9.5857	9.7588	9.7892
.05	1.8239	9.5857	9.7588	9.7892
.1	2.1683	9.2608	9.3318	9.3496
.15	2.4543	8.5735	8.6365	8.6473
.2	2.6562	7.6977	7.7357	7.7422
.25	2.7424	6.671	6.693	6.6967
.3	2.6978	5.5577	5.5697	5.5717

Table 1: Table summarizing the result of the single particle iterations. The left-hand side, R , is the radius of the particle. The top, λ is the Debye length of the material. The values of the table are the result of the line integral discussed in Section 2 to find effective current.

Holding λ constant and varying R gives some interesting results. As R is increased, the current increases before decreasing to 0. As expected, $e^{2.3} \approx 9.97$ is an upper bound of this table. As λ is increased, the amount the current increases from $R = .0001$ to its maximum value is greatly diminished. For instance, at $\lambda = 20$, the current increases by < 0.1 from $R = .0001$ to $R = .001$. As λ is lowered, the amount the potential increases is greatly lowered. This is because, as λ is increased, the space charge layer the particle produces is very large to begin with, and if λ is small, the SCL is very small (view the heat graphs for a visual of the field). Increasing the value of R when λ is large will only lower overall conductivity due to this. Therefore, for each Debye length there is some optimal particle radius which depends on the Debye length of the material. For the λ presented here and for the selected R values, $R = .25, .01, .001, .001$ are optimal. Finally, as the effects of large λ are extreme, they will not be examined further as they are not realistic in their effects.



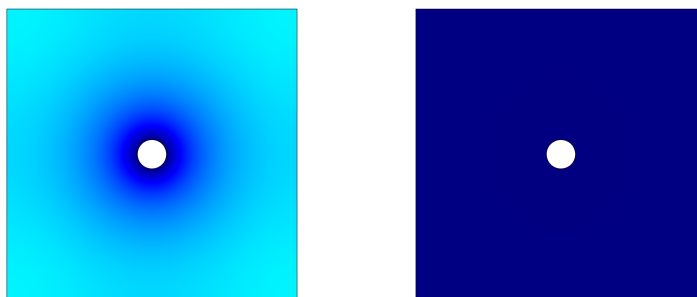


Figure 4: Particle effectiveness for different λ . The λ values from top right to bottom left are .25, 7, 14, 20. $R = .05$ is fixed. The color scaling on all of these is the same. This shows that when λ is large, a single particle completely changes the conductivity of the cell to be closer to u_0 .

For the five particle iteration, the following figure shows which alignment of the particles is the optimal one.

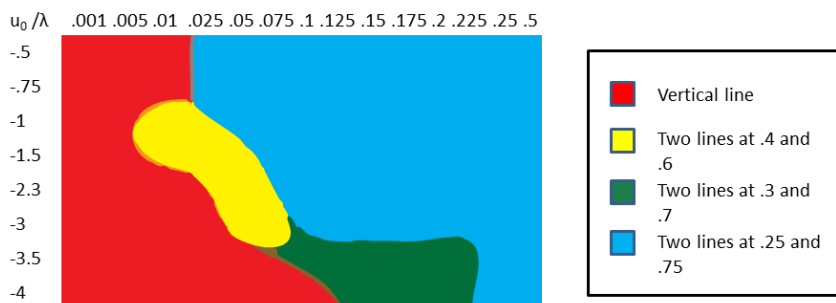


Figure 5: Optimal arrangements for a given u_0 and λ . The left axis is u_0 and the top λ . Each section represents a different arrangement as indicated by the key. The sections between the mono-colored areas indicate areas where one arrangement or another may be optimal.

It is clear that, in general, for small λ a straight line configuration is most effective and for larger λ having a wide spacing of the particles is most effective. However there is a clear divide between them where different spacings of particles become most effective.

Where the straight line configuration is optimal, the effectiveness of an individual particle is quite small (Figure 6). Therefore, grouping the particles closer results in the best conductivity, even if the particles do cause much interference along the meridian of the cell. Having the particles further apart results in a lower overall conductivity since the material lacks a path of increased conductivity for charge to follow. In the areas where spacing the particles far apart is

optimal, the effectiveness of an individual particle is comparatively large. Because of this, spacing the particles reduces the interference they cause on one another and creates a pathway of increased conductivity through the material.

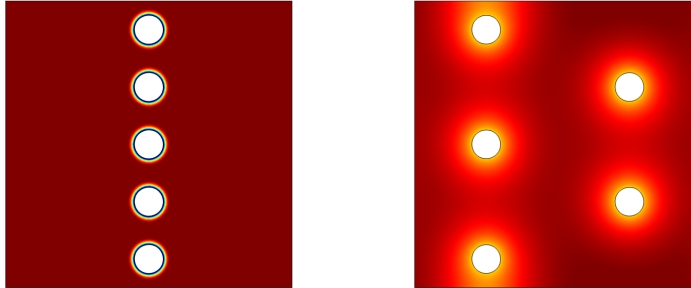


Figure 6: Comparing two different optimal arrangements. The one of the left has ineffective particles so it is necessary to group them close to be effective. On the right, the particles are effective enough to create a larger *SCL* so they must be spaced further apart.

Between these two large areas, both close spacings and divided spacings are optimal. This area is both dependent on ψ_0 and on λ creating the diagonal seen. Take $\psi_0 = 2.3$. Taking λ from .05 to .1 results in a close spacing, but not a straight line, to be most optimal. This is because while each individual particle has a relatively small effect on the conductivity, it is large enough now to where moving the particles apart will reduce the interference they cause while increasing conductivity. Setting $\psi_0 = -4$ results in a larger spacing being optimal between the straight line and the furthest spacing. At this point the particles have an even larger effect, so it is necessary to move them further apart to avoid interference and maximize conductivity.

6 Conclusion

In summary, for small λ generally a vertical line arrangement is optimal, and for large λ , a far spacing of two lines is optimal. For a given λ of a material, there is an optimal radius for the particles to gain maximum conductivity in area immediately surrounding the particle. Using COMSOL Multiphysics, these arrangements and radii have been found for different λ in a two-dimensional case. For future studies, three-dimensional cases should be studied perhaps beginning with the three-dimensional equivalents of the arrangements in this paper. Additionally, a more analytical approach for the solution is suggested, taking the partial differential equations along with the boundary equations and proving that a solution must exist. Finally, taking these results and creating the compound with the arrangements would allow for a complete analysis of the effectiveness of these compounds.

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