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Electric Field Model and Discrete Event Simulation of Periodically Poled Ferroelectric Templates

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Abstract

An electric field model for ferroelectric templates examines a novel lithography technique which is used in the growth of nanowires. In ferroelectric lithography silver is selectively deposited at the 180 degree domain boundaries of ferroelectric substrates. Current understanding of nanowire production does not have a well-documented explanation of both desired domain boundary wires and undesired interstitial growth. To assist, a model of the electric fields near the surface of ferroelectric templates was created, specifically focusing on periodically poled lithium niobate (PPLN). This model was then utilized to determine how various surface imperfections and material attributes, such as screening properties, affected the electric field and therefore nanowire growth. To test this model a discrete event simulation of the paths of multiple particles was compared to scanning electron microscopy (SEM) images from actual depositions of $AgNO_3$ on PPLN samples. The results and methodology are given here to improve silver nanowires synthesis for use in applications such as surface enhanced Raman spectroscopy and disinfection.

Keywords: Ferroelectric Template, Discrete Event Simulation, Surface Enhanced Raman Spectroscopy

1. Background

Raman spectroscopy is capable of identification of materials and structures at the thousands of molecules scale. As a result there are an enormous amount of applications across fields ranging from art, and forensics, to semiconductor research, and pharmaceuticals. The technique does not harm the material and is relatively inexpensive in comparison with other imaging techniques of similar capabilities. Surface enhanced Raman spectroscopy (SERS) enables an enhancement over standard Raman spectroscopy (up to a factor of 10^{11})[1]. SERS utilizes the same physical effects as standard Raman spectroscopy but enhances how much Raman scattering there is by using nanosize coinage metal particles to amplify the electric field of the incident laser light to the surface of the material in question. These molecules are typically metals; silver and gold are used most frequently.

The UNCA Surface and Nanoscience Laboratory (ASANLab) is currently working on a novel method of synthesising silver nanowires for use in surface enhanced Raman spectroscopy. This method utilizes the domain boundaries of ferroelectric templates which have been measured to have anomalously large electric fields[2]. Ferroelectrics are materials that have an innate electric field. In the case of lithium niobate, used by ASANLab, the electric fields are a result of the asymmetry of one atom within the material's crystalline structure. The specific ferroelectric templates used in this synthesis process are uniquely poled though and the orientation of the crystalline structure determines the orientation of the electric field. To have a particular electric field the ferroelectric is poled by applying an electric field to it. This causes the crystalline structure to reorient itself and therefore align the innate electric field with the poling electric field. The model created here assumes periodic poling, poling that alternates between positive and negative electric fields on a set period. Since it is the crystalline structure itself causing the electric fields the material can be considered to have a volume charge density directly comparable to the structure and material properties of the ferroelectric. This is used to represent the periodically poled ferroelectric by its charge density as seen in figure 1.

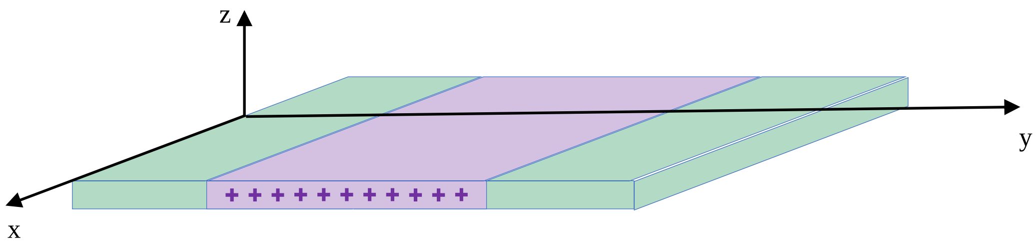

Figure 1. The orientation of the ferroelectric and its alternating charge density

The electric field about ferroelectric templates is not from only the innate electric field, however. There is also an electric field from screening charges, charges that have been brought in by the innate electric field. These screening charges can come from within the material, free electrons, for example, or they can come from outside, such as ions in the air. In this model it is assumed that the screening charges are all from either within the material or outside the material, not both. The charge density of the screening charges is treated as equal but opposite to the charge density of the ferroelectric. The equations themselves will represent the ferroelectric and the screening charges as two planes of charge.

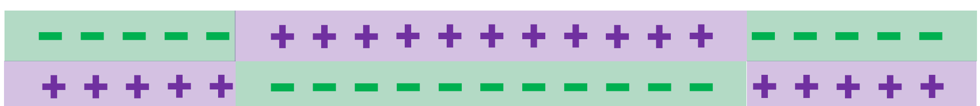

Figure 2. A cross section of the ferroelectric domains and the screening charge domains through the x-y plane

2. An Equation for the Field

The electric field of a ferroelectric template is found by treating each individual domain as a stack of two sheets or planks of charge. One plank is the charge from the material configuration and the other is from the resulting screening charges. The electric field of each plank can be found by treating them as many lines of charge glued together so that we might add the electric fields of all of these lines and therefore find the electric field of the planks of charges. This provides an equation for the electric field of a single domain. As many as desired can then be added together, each following one the opposite of the previous to change the polling between each domain.

Gauss's Law gives equation (1) as the electric field of a line lying on the x axis, where λ is the linear charge density and (y, z) is a point in the y z plane.

$$\vec{E}_{line}(y,z) = \frac{\lambda}{2\pi\epsilon_0(y^2+z^2)}\langle y, z\rangle \tag{1}$$

Letting the boundaries between domains be parallel with the x axis, then the lines of charge will be parallel with the domain boundaries running infinitely in the x and -x directions. It is then possible to integrate from a to b along the y axis (horizontal) to get equation (2) the electric field of a sheet or plank made out of lines of charge

$$\vec{E}_{plank}(y,z) = \frac{\lambda}{4\pi\epsilon_0}\langle Ln\left(\frac{(y-a)^2+z^2}{(y-b)^2+z^2}\right), ArcTan\left(\frac{y-a}{z}\right) - ArcTan\left(\frac{y-b}{z}\right)\rangle \tag{2}$$

This is the electric field at a point (y, z) from a sheet of charge going from $y = a$ to $y = b$ at height $z = 0$. Figure (3) shows us the electric field of this result.

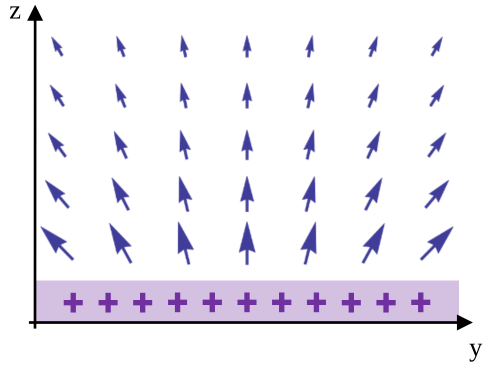

Figure 3. A vector plot of the electric field of a single plank of charge

Now that the electric field of a single plank is represented by equation (2) the innate field of an entire simple periodic ferroelectric template can be represented by making a series of all of the domains. This provides equations (3) and (4) where N is the number of total domains and w is the width of the domains. Equation (3) represents the z component of the field while equation (4) represents the y component.

$$\vec{E}_z(y,z) = \frac{\lambda}{4\pi\epsilon_0}\sum_{n=0}^{N-1}(-1)^n\left(ArcTan\left(\frac{y-nw}{z}\right) - ArcTan\left(\frac{y-(n+1)w}{z}\right)\right) \tag{3}$$

$$\vec{E}_y(y,z) = \frac{\lambda}{4\pi\epsilon_0}\sum_{n=0}^{N}(-1)^n Ln\left(\frac{(y-nw)^2+z^2}{(y-(n+1)w)^2+z^2}\right) \tag{4}$$

The total electric field about a periodically poled ferroelectric template is from the innate electric field and the electric field of the screening charges. The electric field for the screening charges should be the same as the innate electric field except for two very important differences; i) the screening charges have opposite charge; ii) the screening charges are at a slightly different height and therefore will be at a slightly different distance from the positive test charge. The resulting total electric field is therefore represented by equations (5) and (6).

$$\vec{E}_z(y,z) = \frac{\lambda}{4\pi\epsilon_0}\sum_{n=0}^{N-1}\left((-1)^n\left(ArcTan\left(\frac{y-nw}{z}\right) - ArcTan\left(\frac{y-(n+1)w}{z}\right)\right) - (-1)^n\left(ArcTan\left(\frac{y-nw}{z+d}\right) - ArcTan\left(\frac{y-(n+1)w}{z+d}\right)\right)\right) \tag{5}$$

$$\vec{E}_y(y,z) = \frac{\lambda}{4\pi\epsilon_0}\sum_{n=0}^{N}\left((-1)^n Ln\left(\frac{(y-nw)^2+z^2}{(y-(n+1)w)^2+z^2}\right) - (-1)^n Ln\left(\frac{(y-nw)^2+z^2}{(y-(n+1)w)^2+z^2}\right)\right) \tag{6}$$

3. The Electric Field of a Ferroelectric Template

Figure (4) shows the electric field at a variety of heights above the template. The field gets smaller as the height increases just as expected. What might not be expected is the electric field close to the domain boundaries. As stated earlier a large spike is seen about the domain boundaries that goes in both the negative and the positive directions. The key to this behavior comes from the height difference of the material and the screening charges.

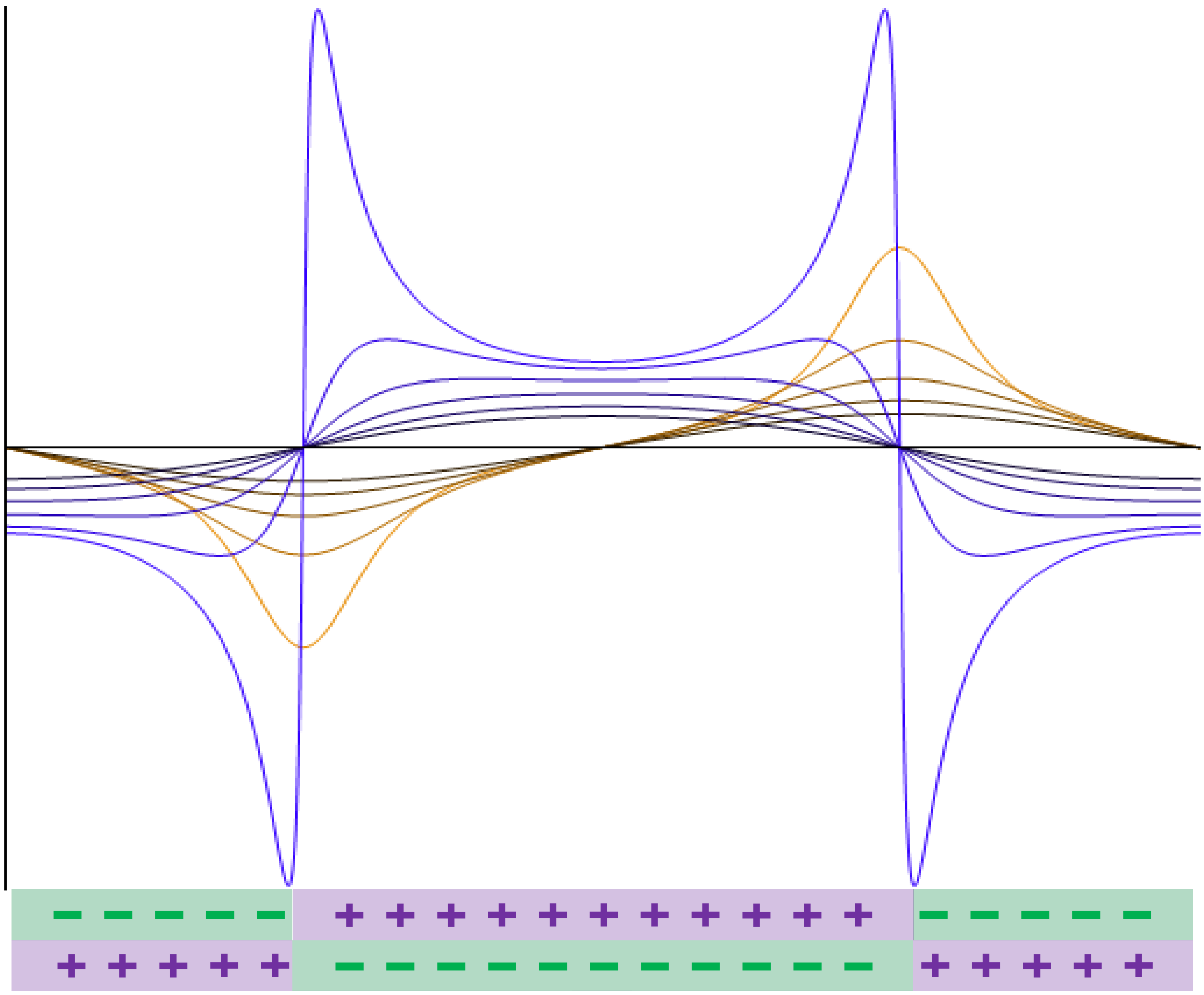

Figure 4. Electric field of a ferroelectric template at various heights

Figure 4 The y and z components of the electric field of a ferroelectric template and its screening charges at several different heights above the template. The **orange** functions are the **horizontal (y)** component while the **blue** are the **vertical (z)**. The functions are darker the higher they go. The lowest (brightest) height is the only height that has smaller distance to the template than the separation of the screening charges and the ferroelectric itself.

As previously discussed the electric field of the screening charge is very similar to the innate electric field. Mathematically the screening field can be written in terms of the innate field (equation (7)).

$$\vec{E}_{screen}(y,z) = -\vec{E}_{innate}(y,z+d) \tag{7}$$

Which provides equations (5) and (6) for the total field. It can then be seen from that equation that the total electric field is the difference of the electric field between two heights. This is precisely what causes the spikes to emerge.

Closer to the surface of the ferroelectric the innate electric field becomes larger and changes more suddenly. Further from the surface it becomes smoother and reduces in magnitude. With this in mind a point is observed some distance away from a sheet. If the sheet is moved slightly further away from the point then the magnitude and direction of the electric field will change the same as if the charge had been moved slightly further away instead. Meaning the electric field will become smoother and reduce in magnitude when the sheet is moved away from the point. Hence, for the total electric field, when the difference between two heights is looked at, the largest difference happens at the edges of the domains where the change in sharpness is most pronounced. This difference can be seen in figure 5

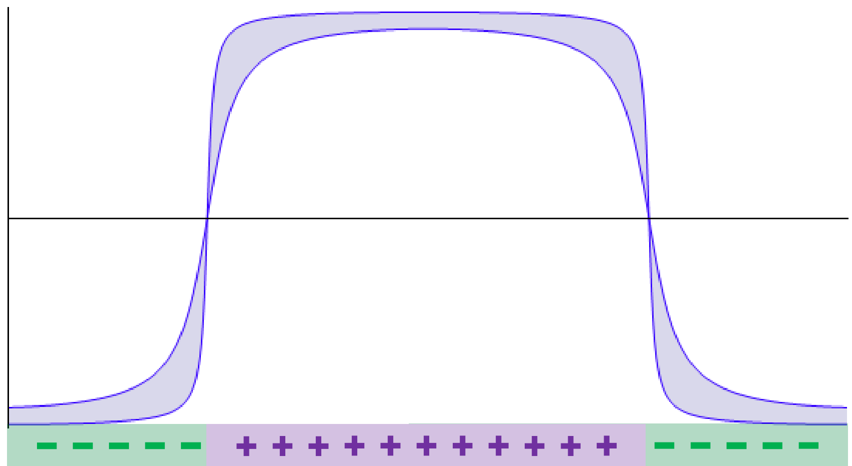

Figure 5. Vertical component of electric field of periodically poled domains at 2 similar heights

Figure 5 This is the vertical (z) component of the electric field of a ferroelectric template at two similar heights. The shaded region is the separation, or difference, of the two different functions.

At the center of the domains there is a small difference that is not hugely significant. As the domain boundary is approached however the change in sharpness makes the difference between the curves significant. A plot of the total charge (6) shows that the curve is indeed the difference seen in figure (5).

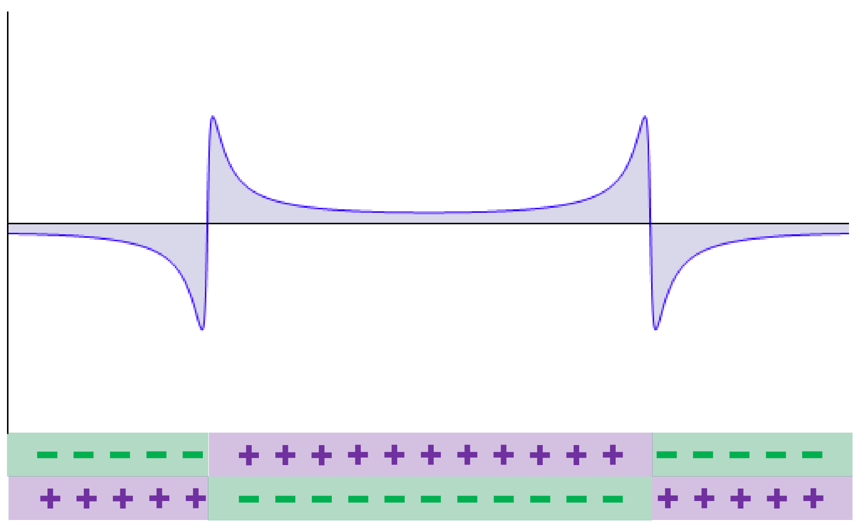

Figure 6. Vertical component of electric field from ferroelectric and resulting screening charges

These unique field characteristics only appear for heights that are significantly smaller than the separation between the material and the screening charges. Beyond these small distances the field is not only weaker, but it transitions much more smoothly between domains. Figure (4) shows the electric field at a variety of heights giving an idea of the sensitive dependence on the height.

4. Effects of Multiple Domains on Center Domain

Periodically poled ferroelectric templates typically have well over a thousand domains. Meaning that if the total electric field from one of these templates was to be written down using equations (5) and (6) it would be quite large and therefore difficult to use, specifically for computer applications. Luckily the effects of each additional term are not very significant. A comparison between 5 domains and 500 domains can be seen in table (1). It shows that at the heights important in nanowire synthesis that 5 domains is a very good approximation of 500 sheets. At heights significantly higher however, it is clear that more than 5 sheets are necessary for a good approximation. The simulations here were all performed at far lower heights.

Table 1. Percent error of 5 sheets to 500 sheets over a range of heights (rows) and widths (columns)

Height	-0.1w	-0.01w	0.01w	0.1w
1d	.34%	.53%	.52%	.27%
21d	1.3%	11.0%	10%	1.0%
41d	2.8%	25.0%	24%	2.2%

5. Discrete Event Simulation of Nanowire Synthesis

The culmination of this research was to test the model by simulating the synthesis of wires and seeing if it predicted the results that are received experimentally. To do this a discrete event simulation of the paths of many particles starting spread out evenly above the ferroelectric was created. The particles would be allowed to follow their path until they either reached the material, or time ran out on the simulation, whichever came first. Their final positions would be logged. This test gives a view of the final positions of particles “raining” down on the template.

The method for this test relied on finding the path of a particle with some initial position. The force on the particle remained constant between ticks in time and time went in discrete increments where the acceleration of each particle was constant between ticks. The equations (8), (9), and (10) were used for each tick where, at some tick n, s_n is the position of the particle, v_n the velocity, and a_n the acceleration. The force used was not only the electric field from the ferroelectric. Early tests that were run with just the ferroelectric field showed that a drag force was necessary. The drag force used in these tests is shown in equation (11). With the addition of this drag force the simulation had completed its requirements for this research and was ready to produce data.

$$\vec{s}_n = \vec{s}_{n-1} + \vec{v}_n dt \tag{8}$$

$$\vec{v}_n = \vec{v}_{n-1} + \vec{a}_n dt \tag{9}$$

$$\vec{a}_n = \frac{1}{m}\vec{E}(\vec{s}_n) + \frac{1}{m}\vec{F}_{drag}(\vec{v}_n) \tag{10}$$

$$\vec{F}_{drag}(\vec{v}) = -\frac{1}{2}\vec{v} \tag{11}$$

As this research was for general periodically poled ferroelectric templates specific constants were not available. The constants of most importance (the screening charge separation and the starting height) were chosen to be on the same order of the material used by ASANLab all other constants should not have incredible impact on the general observed behavior.

Figure (7) shows the position of each point over the full time interval. It is easy to see that within positive domains the charges are repelled completely and the negative domains pull charges in. To a certain extent this is the observed behavior. SEM measurement of nanowire synthesis on PPLN has shown that there is interstitial growth within every other domain, and significantly less interstitial growth in the remaining in-between domains. On the other hand, the histogram in figure (8) predicts that there should be wire growth on every other domain boundary instead of every domain boundary as has been observed in experiments[3].

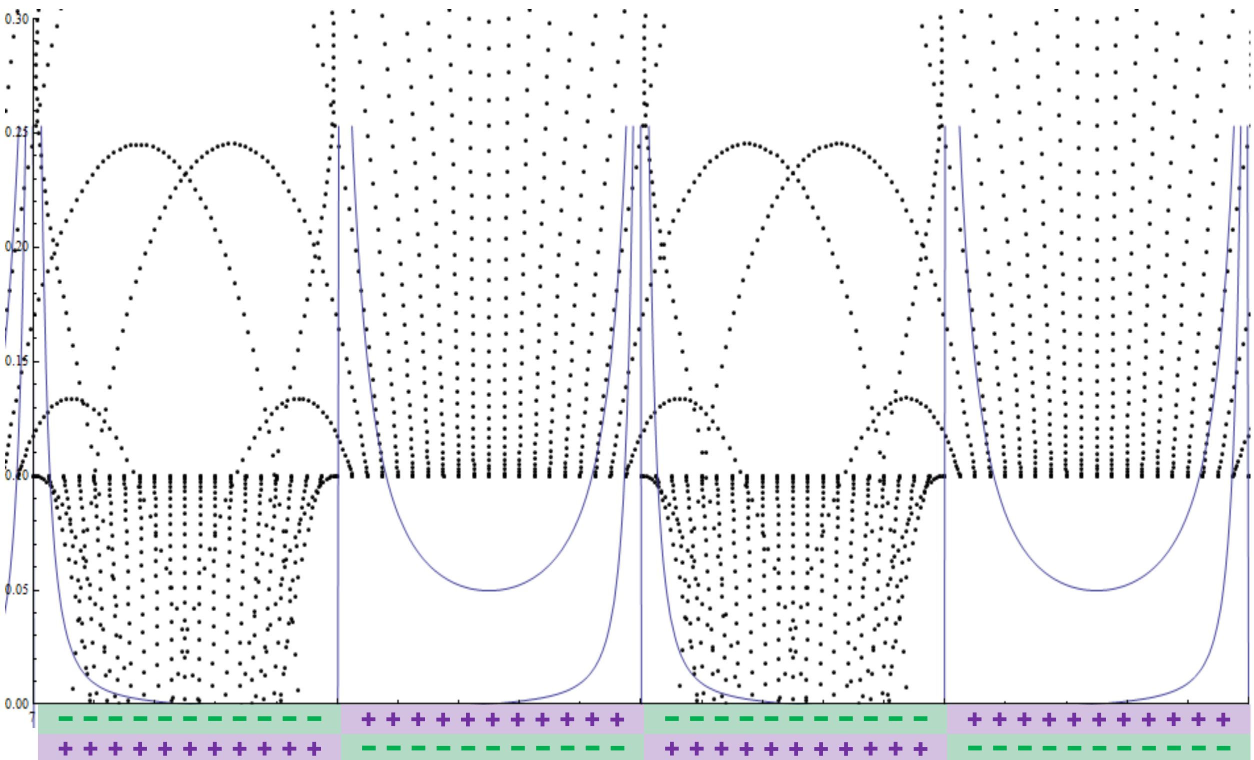

Figure 7. Resulting paths of discrete step simulation with charges placed at 1d

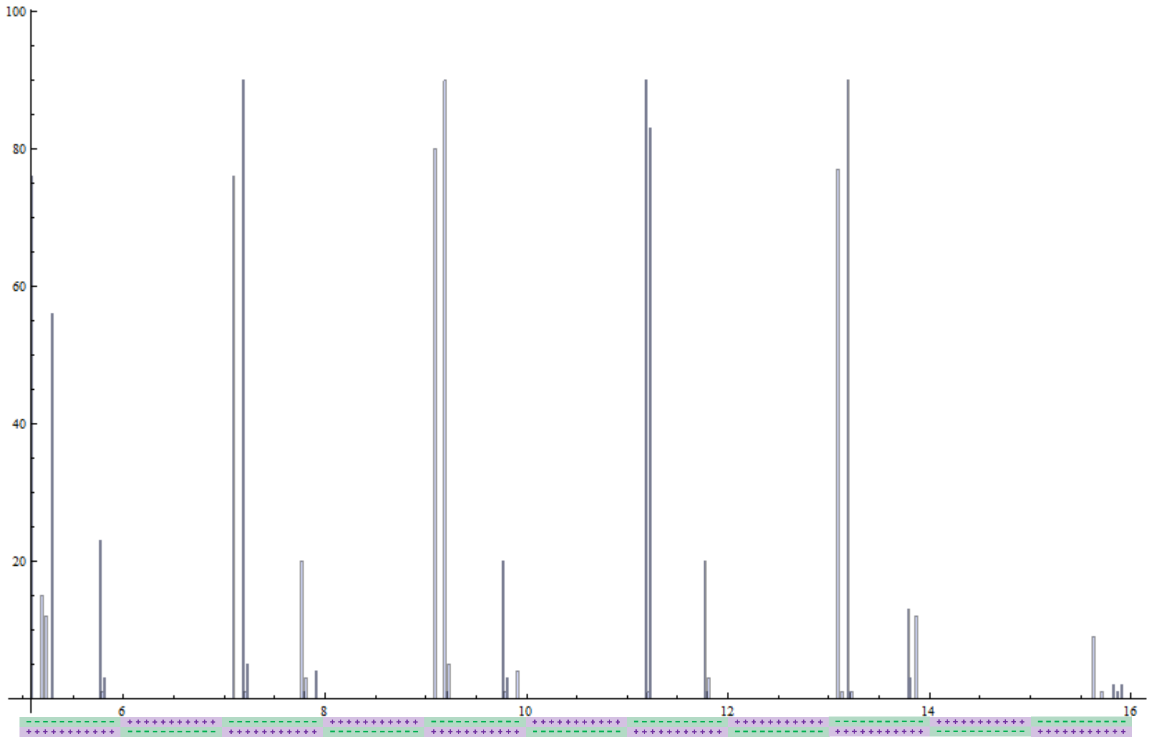

Figure 8. Histogram of ending positions of 1000 particles starting at 1d

6. Conclusion and Future Work

The derivation of this model shows some useful insight into the anomalously large electric fields at the domain boundaries. It also provides a good framework for any future work regarding ferroelectric templates and their electric fields. The field model in conjunction with the discrete event simulation should be a good stepping stone for testing nanowire synthesis. The simulation could be especially useful for interstitial growth tests as more insight is shed into the processes at work. While the simulation has promise, both it and the model will need to be refined for further work. The model itself is sound, however much better testing could be done by using experimental values for the constants. More accurate predictions using the simulation would require adding in better transport properties which would possibly require more knowledge about the synthesis process itself.

Applying transport properties, adding in more complex topography to the ferroelectric templates, and using experimentally measured constants would all be parts of future work. Future work might be focused on anything from testing possible synthesis methods, to determining the effects of changing fundamental material properties such as the domain width or screening charge separation.

7. Acknowledgements

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8. References

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