FORCES FROM CHARGED CHAINS ON DIELECTRIC AND CONDUCTING ATOMIC FORCE MICROSCOPY SENSORS

Thesis Submitted in Partial Fulfillment of the Jay and Jeanie Schottenstein Honors Program

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INTRODUCTION

We consider a charged linear chain probed by an atomic force microscope (AFM). The goal of this thesis is to present a mathematical method for determining the charge of the chain from the AFM force-vs-separation curve. Similar work has already been done for charged rings.[1 2] The AFM is a commonly used tool for measuring the properties of nanoparticles. Indeed, there have been previous instances where the AFM was used to measure the charge of a particle[3 4]. Here, we study objects that can be modeled as long linear chains of charge. Several important molecules are long cylinders[5 6], including viruses and nanotubes. These can be approximated as long lines for the purposes of mathematical modeling. In this paper, we calculate the force-vs-separation curve for linear molecules being probed with either conducting or dielectric AFM tips. If the force-separation curve corresponding to the molecule is measured, then it can be compared to the equations derived here to deduce the charge density of the molecule.

DESCRIPTION OF THE SYSTEM

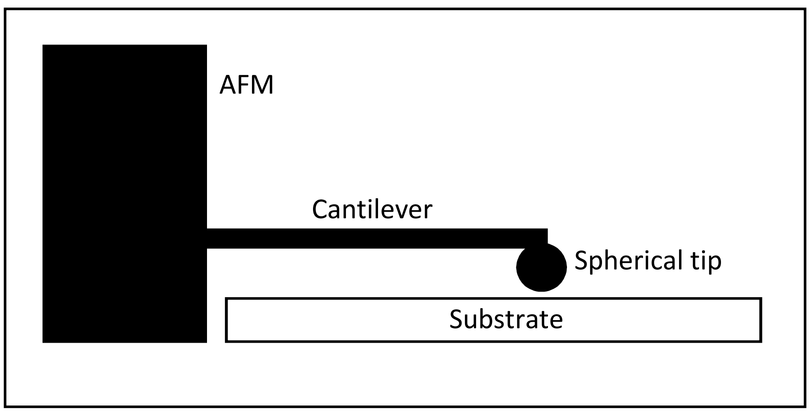

Figure 1. A diagram of the AFM. The substrate can be raised or lowered, adjusting the distance between the tip and the substrate. This diagram is out of scale, as the tip is really proportionally much smaller than this.

As the substrate is raised and lowered, the cantilever bends ever so slightly. The AFM is able to measure this effect and determine the force that is being imparted to the probe. However, in order to understand the forces here we need to look closer at the tip and the molecule.

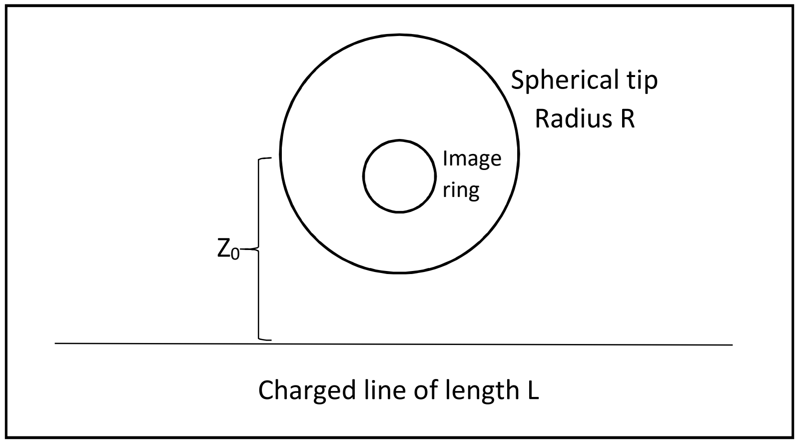

Figure 2. A diagram of the charges. The molecule of length L is separated from the center of the sphere by a distance z_0. The molecule induces a ring of image charge.

The image charge forms a perfect 2 dimensional circle on the plane that contains the line and center of the sphere. However, the charge density is not uniform, even though the charge density on the line of charge is. The top of this circle is at the center of the sphere, and its radius depends on z_0, the distance from the line of charge to the center of the sphere. If the sphere is made of a conducting material, then the image charges are only concentrated on the edge of the ring. However, if the sphere is dielectric, then the image charge is distributed throughout the ring. The model assumes that the length of the line, L, is much greater than the radius of the sphere, R.

MATHEMATICAL DERIVATION

I. Metallic sphere

The first step is to derive the value and position of the image charge in the presence of a conducting sphere. For a point charge in the presence of such a sphere, the formula was derived by Lord Kelvin and can be found in elementary electrostatics textbooks[7]. Here we first assume that the sphere is grounded, so there is no counter charge in the center of the sphere. To find the entire charge distribution, simply add up the image of each section of the line.

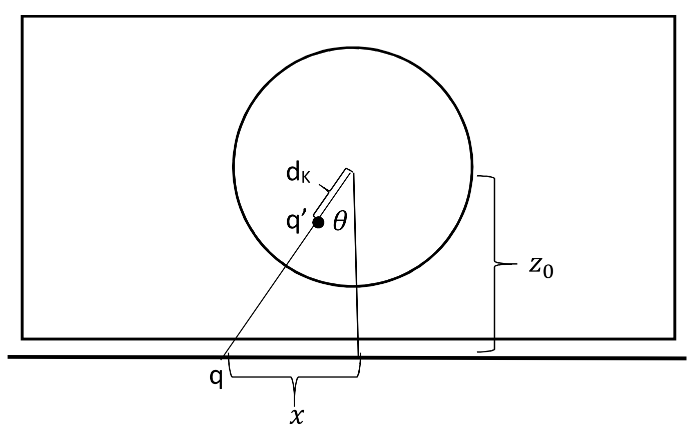

Figure 3. Each point charge q on the charged line produces an image charge q' somewhere along the line connecting it with the center of the sphere. The distance between the image charge and the center of the sphere is r', which is a function of x.

$$\frac{dq}{dx} = \lambda \to \frac{dq'}{dx} = -\frac{\lambda R}{\sqrt{z_0^2 + x^2}} \qquad r(x) = \sqrt{z_0^2 + x^2} \to d_K(x) = \frac{R^2 \cos(\theta)}{z_0}$$

The charge density of the line of charge is λ. The angular density and angular position of the image charge was derived using Kelvin's equations. If the line were to have infinite length, then the image charge at the center of the sphere would diverge. However, real molecules are not infinite, so the image charge will be finite. Also, $r = k\cos(\theta)$ forms a circle of diameter k, so the image charge is circular.

Now that the image charge is known, we compute the force. In order to do this, we approximate the line as infinite, leaving a much simpler expression for the electric field. Also, the force now points in the z direction, which is the only force the AFM can measure anyway. The distance to the line is given by:

$$z(x) = z_0 - d_K(x)\frac{z_0}{\sqrt{z_0^2 + x^2}}$$

$$F = \int_{-L/2}^{L/2} \left(\frac{\lambda}{2\pi\epsilon_0 z(x)}\right)\left(\frac{dq}{dx}\right)_x d\theta = \frac{1}{2}\int_0^{L/2} \left(\frac{\lambda}{2\pi\epsilon_0 z(x)}\right)\left(\frac{dq}{dx}\right)_x d\theta$$

Before solving the integral, we convert to dimensionless quantities:

$$\eta = z_0/R \qquad \beta = L/R \qquad \xi = x/R \qquad \Phi = \pi\epsilon_0 F/\lambda^2$$

$$\Phi = \frac{-1}{\eta}\int_0^{\beta/2} \frac{\sqrt{\eta^2 + \xi^2}}{\eta^2 + \xi^2 - 1} d\xi = \frac{-1}{\eta}\left[\tan^{-1}\frac{\left(\frac{\beta}{\sqrt{(\eta-1)^2(\beta^2 + 4\eta^2)}}\right)}{\sqrt{\eta^2 - 1}} + \ln\left(\frac{\beta + \sqrt{\beta^2 + 4\eta^2}}{2\eta}\right)\right]$$

Taking the limit as $\beta \gg \eta$, we can simplify this force to:

$$\Phi = \frac{-1}{\eta}\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} + \ln(\beta) - \ln(\eta)\right]$$

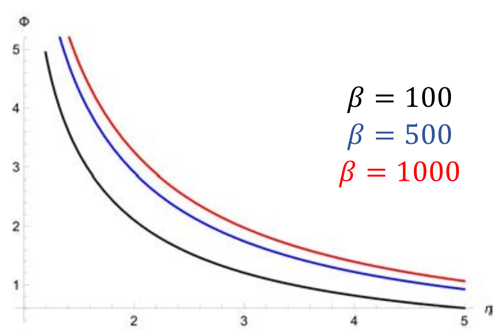

Figure 4: A plot of the force as a function of distance for different length lines of charge.

Above (figure 4) is a plot of the force for different size molecules. This function depends on the length of the molecule and is also scaled by the charge density. It can be difficult to separate those two dependencies using experimental data. Therefore, we define:

$$\Psi(\eta) = \eta(\Phi + \ln(\beta)) = -\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

$$\psi(\eta) = (1 - \eta)\left(\Phi + \frac{\ln(\beta)}{\eta}\right) = \frac{\eta - 1}{\eta}\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

If the experimentalist plots these quantities as a function of separation, there will be curves with particular shapes (figure 5), scaled by the charge density and shifted up by a constant which depends logarithmically on the length of the molecule. This will allow for both quantities to be measured by fitting. The first curve is simpler, but the second is constructed not to diverge, which may prove helpful for some applications. Fortunately, these functions, as well as the original force, are scaled by the charge density squared, allowing for greater accuracy in the measurement of the density itself. Additionally, ψ has a maximum at $\eta = 1.64$, which can be helpful for calibration. Finally, if the length of the molecule is known through other means, then the added constant can also be used to deduce the density, further improving accuracy.

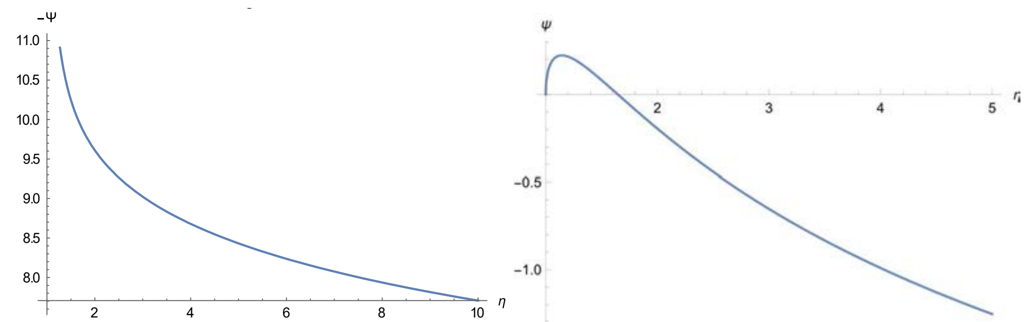

Figure 5. Plots of Ψ (left) and ψ (right), which are the same for a line of any length.

II. Insulated Conducting Sphere

The previous discussion assumed that the spherical tip was grounded. However, if the sphere is insulated, there is an additional charge interacting with the line of charge. Aside from the Kelvin charge, which was derived in part one, there is a simple point charge at the center of the sphere. Since the sphere is charge neutral, and there is a charged region, there must be an equal and opposite charge somewhere else on the sphere. It is known that excess charge on a conducting sphere can be treated as if it is all concentrated at the center, consistent with the requirement that the sphere be an equipotential. Thus, the second force is simply that of a point charge a distance η away from the line of charge. The value of the point charge is:

$$Q_{center} = -Q_{Kelvin} = -2\lambda \int_0^{\frac{\beta}{2}} \frac{d\xi}{\sqrt{\eta^2 + \xi^2}} = 2\lambda \sinh^{-1}\left(\frac{\beta}{2\eta}\right)$$

Now the total dimensionless force can be written as:

$$\Phi = \Phi_{Kelvin} - \frac{\pi\epsilon_0}{\lambda^2}\frac{\lambda}{2\pi\epsilon_0\eta}Q_{center}$$

$$\Phi = \frac{1}{\eta}\left[\ln(\eta) - \ln(\beta) - \frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} + \sinh^{-1}\left(\frac{\beta}{2\eta}\right)\right]$$

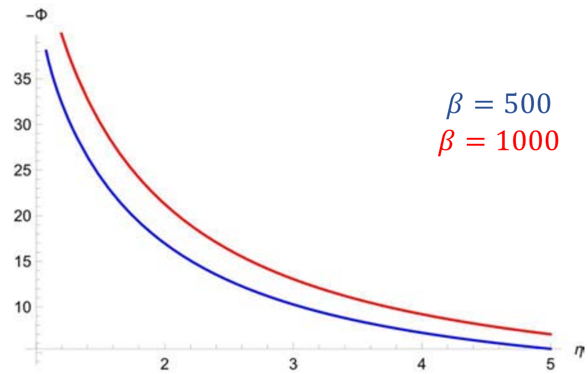

Figure 6: A plot of the force aa a function of distance for lines of different length

Above (figure 6) is a plot of the force for different size molecules. It has the same drawbacks as before. Now we define the functions Ψ and ψ slightly differently, accounting for the extra term in the force.

$$\Psi(\eta) = \eta\left(\Phi + \ln(\beta) - \sinh^{-1}\left(\frac{\beta}{2\eta}\right)\right) = -\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

$$\psi(\eta) = (1 - \eta)\left(\Phi + \frac{\ln(\beta) - \sinh^{-1}(\beta/2\eta)}{\eta}\right) = \frac{\eta - 1}{\eta}\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

These functions will produce the same graphs as before (figure 5). However, if one wants to manipulate the data as little as possible, one can define φ for the isolated sphere. This graph (figure 7) produces a clear maximum. The maximum is nearly constant at $\eta = 1.22$ for $\beta > 100$. Of course, there are many other possible functions besides those explored here, each with their own possible uses.

$$\varphi = \Phi(\eta + 1) = \frac{(\eta - 1)}{\eta}\left[\ln(\eta) - \ln(\beta) - \frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} + \sinh^{-1}\left(\frac{\beta}{2\eta}\right)\right]$$

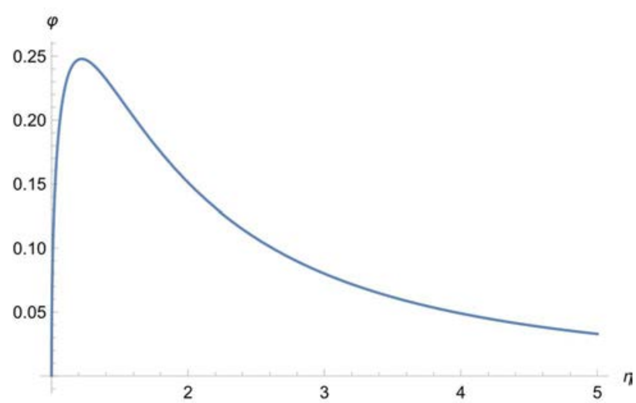

Figure 7: A plot of the φ function for an isolated conducting sphere.

III. Dielectric Sphere

The previous analysis holds for a metallic sphere or AFM tip. However, most AFM tips are made of dielectric materials. In order to account for that, we use a theory developed by Lindell[8], which accounts for the effects of the dielectric. The image charge of a point charge outside a sphere will have two components. The Kelvin charge remains almost unchanged; it is just multiplied by a constant which depends on the material. The second charge is a linear distribution that spans from the center of the sphere to the point of the Kelvin charge. This charge is the same sign as the real charge, and opposite to the Kelvin charge. In this section we will analyze this second charge distribution, which is unique to a dielectric material. Here, ρ is the distance from the center of the sphere, d_K is the same Kelvin distance as in the previous section, and ϵ is the dielectric constant of the material.

The image charge distribution corrosponding to a single charge, as given by Lindell, is:

$$\lambda'(\rho) = \frac{\epsilon - 1}{(\epsilon + 1)^2} \frac{Q}{R} \left(\frac{\rho}{d_K}\right)^{-\epsilon/(\epsilon+1)}$$

Now, we must apply this to a line of charge. It will give a two dimensional distribution of charge within the circle created by the Kelvin charge. For the duration of the paper, we will work in polar coordinates in order to make the calculations simpler. Here, z depends on 2 variables because the image charge is 2 dimensional, rather than forming a one dimensional curve.

$$\frac{dq}{d\theta} = \lambda z_0 \sec^2(\theta) \qquad r(\theta) = z_0 \sec(\theta) \qquad z(\rho, \theta) = z_0 - \rho\cos(\theta)$$

Putting all of this together, the charge density inside the circle is given by:

$$\sigma(\rho, \theta) = \frac{\epsilon - 1}{(\epsilon + 1)^2} \frac{\lambda z_0 \sec^2(\theta)}{R} \left(\frac{\rho}{d_K(\theta)}\right)^{-\frac{\epsilon}{\epsilon+1}}$$

Again, we assume the electric field of an infinite line of charge. Converting to dimensionless quantities, $s = \rho/d_K$ and the integral for the force is given by:

$$\Phi = \frac{1}{\eta} \frac{\epsilon - 1}{(\epsilon + 1)^2} \int_0^{\frac{\pi}{2}} \int_0^1 \left(\frac{s^{\frac{-\epsilon}{\epsilon+1}} \sec(\theta)}{1 - \frac{s}{\eta^2} \cos^2(\theta)} \right) ds d\theta$$

This integral diverges because the secant diverges at $\pi/2$. In order to deal with it, we create two integrals. The first is our original integral minus the secant multiplied by a constant. This integral does not diverge because the two terms are equal and opposite at the problematic point. The second integral adds back the term that was subtracted before. It would diverge if the line was actually infinite, but we will be able to treat it as a function of the length of the line.

$$\Phi = \frac{1}{\eta} \frac{\epsilon - 1}{(\epsilon + 1)^2} \left[\int_0^{\frac{\pi}{2}} \int_0^1 \left(\frac{s^{-\frac{\epsilon}{\epsilon+1}} \sec(\theta)}{1 - \frac{\rho}{\eta^2} \cos^2(\theta)} - s^{\frac{-\epsilon}{\epsilon+1}} \sec(\theta) \right) ds d\theta + \int_0^{\frac{\pi}{2}} \int_0^1 s^{-\epsilon/(\epsilon+1)} \sec(\theta)\, ds d\theta \right]$$

$$\Phi_{\text{A}} = \frac{1}{\eta}\frac{\epsilon - 1}{(\epsilon + 1)^2}\int_0^{\frac{\pi}{2}}\int_0^1 \left(\frac{s^{-\frac{\epsilon}{\epsilon+1}}\sec(\theta)}{1 - \frac{s}{\eta^2}\cos^2(\theta)} - s^{\frac{-\epsilon}{\epsilon+1}}\sec(\theta) \right) ds d\theta$$

$$= \frac{1}{\eta}\frac{\epsilon - 1}{(\epsilon + 1)^2}\left[\frac{1}{4\eta^2} \left(\frac{8(1+\epsilon)\sqrt{\eta^2 - 1}\cos^{-1}\left(\frac{\sqrt{\eta^2 - 1}}{\eta}\right) Hypergeometric2F1\left(1, \frac{2+\epsilon}{1+\epsilon}, \frac{5+3\epsilon}{2+2\epsilon}, \frac{1}{\eta^2}\right)}{3+\epsilon} \right.\right.$$

$$\left.\left. - 2^{\frac{\epsilon-1}{\epsilon+1}}\sqrt{\pi}\,\Gamma\left(\frac{3+\epsilon}{1+\epsilon}\right) HypergeometricPFQRegularized\left(\left\{1, \frac{2+\epsilon}{1+\epsilon}, \frac{2+\epsilon}{1+\epsilon}\right\}, \left\{\frac{5+3\epsilon}{2+2\epsilon}, \frac{3+2\epsilon}{1+\epsilon}\right\}, \frac{1}{\eta^2}\right) \right) \right]$$

$$\Phi_B = \frac{1}{\eta}\frac{\epsilon - 1}{(\epsilon + 1)^2}\int_0^{\frac{\pi}{2}}\int_0^1 s^{-\frac{\epsilon}{\epsilon+1}}\sec(\theta)\, ds d\theta$$

$$\Phi_B = \frac{1}{\eta}\frac{\epsilon - 1}{(\epsilon + 1)}\left[\ln\left(cos\left(\frac{\theta_{max}}{2}\right) + sin\left(\frac{\theta_{max}}{2}\right)\right) - \ln\left(cos\left(\frac{\theta_{max}}{2}\right) - sin\left(\frac{\theta_{max}}{2}\right)\right)\right]$$

$$\Phi_B = \frac{1}{\eta}\frac{\epsilon - 1}{\epsilon + 1}\left[\frac{\ln(2)}{2} - \ln\left(cos\left(\frac{\theta_{max}}{2}\right) - sin\left(\frac{\theta_{max}}{2}\right)\right)\right]$$

$$\theta_{max} = \tan^{-1}(\beta/2\eta)$$

Below (figure 8) is a plot of the Lindell Force for different values of β, ignoring the ϵ coefficient. It turns out that Φ_A is two orders of magnitude smaller than Φ_B, so it can be ignored in most applications. However, for metamaterials with a negative value for ϵ, it is possible that Φ_A could become important.

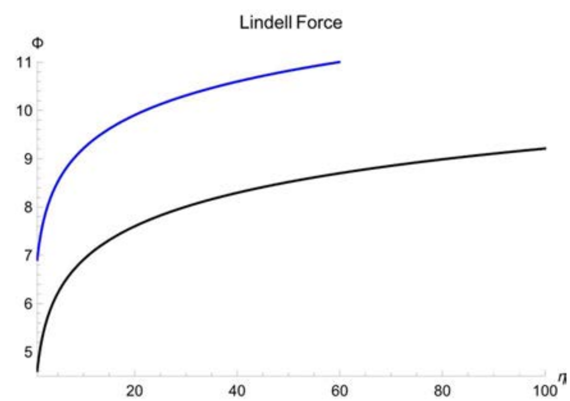

Figure 8. The Lindell Force for a line of $\beta = 100$ (black), and a line of $\beta = 1000$ (blue)

Finally, we calculate the total force curve for a dielectric sphere near a line of charge. This is the sum of the Kelvin force multiplied by $\epsilon - 1/\epsilon + 1$ and the Lindell force.

$$\Phi = \frac{\epsilon - 1}{\epsilon + 1}\frac{1}{\eta}\left[-\ln(\beta) + \ln(\eta) - \frac{\sin^{-1}\left(\frac{1}{\eta}\right)}{\sqrt{\eta^2 - 1}} + \frac{1}{\epsilon + 1}\left[\frac{\ln(2)}{2} - \ln\left(cos\left(\frac{\theta_{max}}{2}\right) - sin\left(\frac{\theta_{max}}{2}\right)\right)\right]\right]$$

Below (figure 9) is a plot of the total force on a dielectric sphere for different values of η and β.

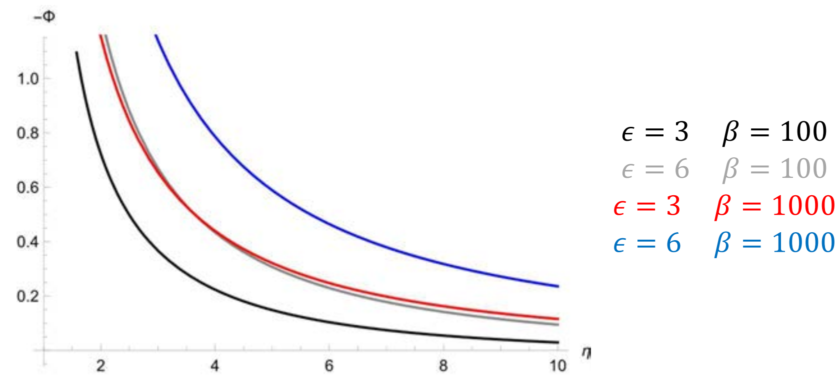

Figure 9: The total force, including the Kelvin and Lindell components.

Once again, the force decreases smoothly with distance and does not have any special features. Again, we could redefine the original functions Ψ and ψ to account for the new terms. These functions would then have the same graphs as those in figure 5.

$$\Psi(\eta) = \eta\left(\Phi + \ln(\beta) - \frac{\Phi_{Lindell}}{\epsilon + 1}\right) = -\frac{\epsilon - 1}{\epsilon + 1}\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

$$\psi(\eta) = (1 - \eta)\left(\Phi + \frac{\ln(\beta)}{\eta} - \frac{\Phi_{Lindell}}{\eta(\epsilon + 1)}\right) = \frac{\eta - 1}{\eta}\left[\frac{\sin^{-1}(1/\eta)}{\sqrt{\eta^2 - 1}} - \ln(\eta)\right]$$

However, we also define new functions $\widehat{\Psi}$ and $\hat{\psi}$ which manipulate the data less. They are plotted below (figure 10). Both have a well-defined minima or maxima. Again, we could not find an exact solution for the position these features, but they can be evaluated numerically. It is worth noting that these equations are also valid for a grounded conductor. The value of ϵ will just be very high.

$$\widehat{\Psi} = -\eta^2\Phi$$

$$\hat{\psi} = (1 - \eta)\eta\Phi$$

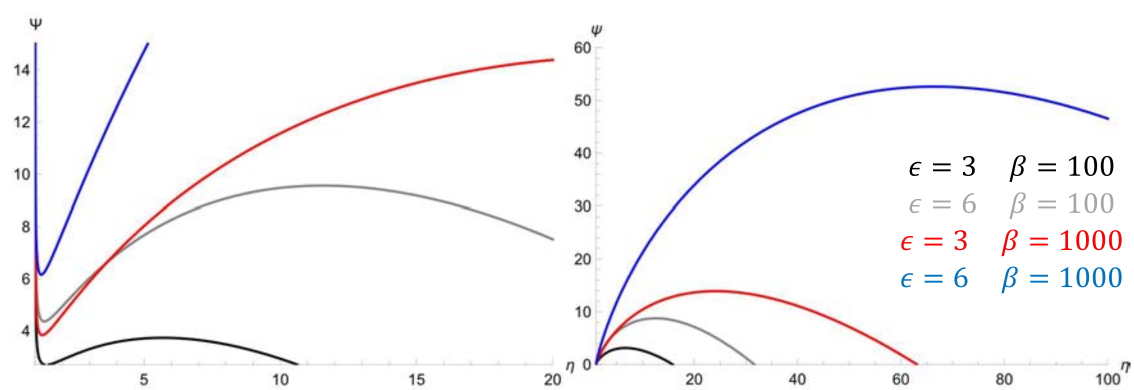

Figure 10: A graph of the functions $\widehat{\Psi}$ (left) and $\widehat{\psi}$ (right) for various values of β and ϵ

CONCLUSION

In this paper we have considered the electrostatic force between a line of charge and a spherical AFM tip. We considered both conducting tips as well as dielectric ones. The mathematical expressions can be used to measure, by fitting, the charge density of the line. These expressions and graphs should prove useful for an experimentalist operating an atomic force microscope.

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[1] Lazarev, D., Zypman F. R. (2016) Determination of charge and size of rings by atomic force microscopy. Journal of Electrostatics, 83, 69-72. Doi: 0.1016/j.elstat.2016.07.008

[2] Eisenberg Y., Zypman F. R. (2019) Ring of charge probed with Atomic Force Microscopy dielectric tip. Journal of Electrostatics, 97, 95-100. doi: 10.1016/j.elstat.2019.01.002

[3] Zypman, F. (2018) Nanoparticle Charge in Fluid from Atomic Force Microscopy Forces within the Nonlinear Poisson-Boltzmann Equation. Journal of Applied Mathematics and Physics, 6, 1315-1323. doi: 10.4236/jamp.2018.66110

[4] Zypman, F., Eppel, S. (2013) Electrostatic Force Curves in Finite-Size-Ion Electrolytes. *Langmuir* 2013, 29, 38, 11908-11914. doi: 10.1021/la402344m

[5] Yang, D., Xie, L., Bobicki, E., Xu, Z., Liu, Q., Zeng, H., (2014) Probing Anisotropic Surface Properties and Interaction Forces of Chrysotile Rods by Atomic Force Microscopy and Rheology. *Langmuir* 2014, 30, 36, 10809-10817. Doi: 10.1021/la5019373

[6] Widjaja, E., Eckerle, D., Sloan, J., & Harris, M. (2006). The Characterization of the Effect of Electric Fields on Tobacco Mosaic Virus (TMV) Alignment using Atomic Force Microscopy (AFM). *Microscopy and Microanalysis, 12*(S02), 626-627. doi:10.1017/S1431927606065640

[7] Pollack, G. L., Stump, D. R. Electromagnetism (2002), Addison Wesley.

[8] Lindell, I. V. (1993). Image theory for electrostatic and magnetostatic problems involving a material sphere. American Journal of Physics 61, 39 (1993); doi: 10.1119/1.17407