UTILIZING THE COULOMB FORCE ON A CARBON NANOTUBE TO ENHANCE THE RESOLUTION OF ELECTROSTATIC FORCE MICROSCOPE

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Various sources, which affect the resolution of the electrostatic force microscope, are discussed. In addition to an overall hump due to the finite distribution of charges, we find that the electrostatic force versus lateral position plot shows better resolution in certain scanning directions, and in some others it may even exhibit misleadingly different amplitudes from different positions with the same magnitude of charge. Since the electric field measured experimentally is outside of the sample, we need to solve an integral equation to determine the charge distribution. But due to the finite resolution of the probe, the problem can be much simplified by discretizing the space and ending up with the simple process of inverting a matrix. The influence by the image charges from the conducting substrate is automatically taken care of. We describe analytic/numerical calculations for the charge distribution on the nanotube and its atomic force with a conducting surface or a charged cluster. Implication caused by the tilt of the nanotube is also discussed.

Keywords: Electrostatic force microscopy; carbon nanotube; scanning probe microscopy.

1. Introduction

Carbon nanotubes (CNTs), aside from their well-defined cylindrical shape and small radii, exhibit unprecedented elastic properties and are both electrically conducting and chemically stable. Therefore, it is natural for people¹–⁶ in the area of scanning force microscopy to try to improve the resolution by affixing a single CNT to the conventional conic tip. In this paper we concentrate on the electrostatic force microscope (EFM) and discuss the factors that affect and eventually limit its resolving power. Analytic/numerical calculations will be derived for the charge distribution on the CNT surface and its electrostatic force with a conducting surface or a charged area on the sample.

It is known that we can build a system of lenses that magnifies as many times as we want, but still could not see two points that are too close together because of the

¹For experimental details.
limitation of geometric optics.\textsuperscript{7} It is then legitimate to ask, after experimentalists\textsuperscript{6} have improved the resolution on topography by more than ten folds (\(\sim 5\) nm, see Ref. 6), why the new EFM failed to resolve charged defects within \(\approx 50\) nm and whether this limitation is intrinsic.

Since the development of the CNT tip, there have not been enough experiments to clarify the origin of this bad resolution. Various sources are under inspection, e.g.,

- Due to the interface roughness, image charges in the heavily doped semiconducting substrate have a broader distribution than that of the charged defects, but for the sake of charging we cannot replace the substrate by an insulator or insert too thick an insulating spacer.
- Surface roughness of the sample, i.e., its topography, causes spatial variation on the defect number within the same range of electrostatic force from the probe.
- Defect density in the amorphous sample is limited so that a large area of defects is unavoidably involved for each charging process (while the electric bias has to be strong enough to produce a successful charging).
- \textit{(Trapping-energy dependent)} field-enhanced charge diffusion.

\section{Results and Discussion}

Firstly, it is important to realize that resolution may vary with different scanning directions. This is important because in reality the distance between neighboring rows of scan is always finite. A bad choice could lead to bad resolution for all successive scans. For instance, in Fig. 1 three different scanning directions are taken. The thick gray line apparently has the worst resolution, while the thick black line can even mislead us to interpret the different amplitudes as being from charges of different magnitudes. Another observation is the overall hump due to finite distribution of charges. These features derive from the convolution of charges and need to be heeded when analyzing the EFM data.

The size of a probe is crucial and is exemplified by the electrostatic potential energy profiles in Fig. 2. A point charge and a finite segment with the same charge are used to sample a one-dimensional array of point charges. Clearly the variation becomes less distinct when we increase the size of the probe. For a probe with structures, e.g., the new EFM consists of a lever, a cone, and finally the cylindrical and hemispherical parts of a CNT, the effective size depends on probe/sample separation \(d\). This is clearly shown in the empirical force/distance relation in Ref. 6 which exhibits distinct behavior in different regimes of \(d\).

Take a simple point probe. It is impossible to determine the charge density by the potential profile at some fixed \(d\) outside the sample since the integral equation involved has no unique solution. But due to the finite resolution of the EFM, we can discretize and approximate the sample/substrate by two (or more) parallel \(N \times N\) square lattices. The equation then becomes solvable and involves simply the standard numerical process of inverting a matrix. Here the input is the \(z\)-component
Fig. 1. Electrostatic force versus the lateral position of the probe. Defect charges are placed on a square lattice in the central $9 \times 9$ positions. The thin (thick gray) line scans along the $(1, 0)$ direction and at integer (half-integer) $y$'s, while the thick black line is along the $30^\circ$ lines.

Fig. 2. Electrostatic energy versus the lateral position of the probe. The sample consists of an infinite array of point charges with their spacing as our length unit. The thin line uses a point charge as the probe, while the thick line uses a segment of length 0.5 and with the same charge.

of the electric field that we measure by an EFM, and it is just as sufficient as the electric potential.\footnote{Constrained by the Maxwell's equations, the $z$-component of electric field is just as capable in uniquely determining the charge profile as the electric potential.} By the way, in order to match the number of unknowns, we shall need data from at least two (or more) different $d$'s. In principle, the more layers, the better the approximation.

Electrostatic forces acting on the conic tip of conventional EFM have been modeled by Belaidi et al.\footnote{Constrained by the Maxwell's equations, the $z$-component of electric field is just as capable in uniquely determining the charge profile as the electric potential.} by an equivalent charge distribution. Generalization to the CNT case is straightforward and has been done by one of us, Tseng.\footnote{Constrained by the Maxwell's equations, the $z$-component of electric field is just as capable in uniquely determining the charge profile as the electric potential.} The predicted force-separation relation for a metal surface agrees qualitatively with the experiments. For comparison, we shall lay out exact analytic formulations which...
Fig. 3. Multiply both sides of Eq. (2) by $P_\ell$ and integrate over appropriate $\theta$ ranges. Assign $\ell = 0, \ldots, 5$ to $[0, \pi/2]$, and $\ell = 6, \ldots, 9$ to $[\pi/2, \pi)$. This enables us to solve for $a_n$ with $n = 0, \ldots, 9$. With these ten $a_n$, the potential/charge-density on the surface of CNT are plotted in thin/thick lines as a function of $\cos \theta$. Both the equal potential $V_0$ and the radius $R$ have been set to unity for simplicity.

enable systematic numerical evaluations. First, denote the radius of CNT by $R$ and approximate its enclosed end by a hemisphere. Then, assign the origin at the center of the hemisphere. For simplicity, assume that the CNT is perpendicular to the sample surface. Laplace equation requires the potential outside CNT in spherical coordinates be expressed in terms of the Legendre polynomials: 

$$V(r, \theta) = \sum_{n=0}^{\infty} a_n \frac{R^n}{r^{n+1}} P_n(\cos \theta).$$

(1)

There is no $\phi$ dependence because of the azimuthal symmetry. Now approximate the CNT as a continuous metal, i.e., neglecting the detail zig-zag or arm-chair configuration. For an isolated charged CNT the potential on its surface is constant, which gives us the boundary conditions to solve for $a_n$:

$$V_0 = \begin{cases} V(R, \theta) = \sum_{n=0}^{\infty} a_n \frac{R^n}{r^{n+1}} P_n(\cos \theta), & \text{for } \theta \in [0, \frac{\pi}{2}], \\ V(R, \sin \theta) = \sum_{n=0}^{\infty} a_n \frac{R^n}{\sin \theta} \sin^{n+1} \theta \cdot P_n(\cos \theta), & \text{for } \theta \in \left[\frac{\pi}{2}, \pi\right]. \end{cases}$$

(2)

bTechnically, it is ill-advised to discretize $\theta$ because the resulting $a_n$ oscillate in sign and diverge with $n$. A better approach is to multiply both sides of Eq. (2) by $P_\ell$ and integrate over appropriate $\theta$ ranges. Then assign $\ell$ some large number of integers and solve for the same number of $a_n$. It is found that avoiding even $\ell$'s, which render $\int_0^1 P_\ell(x)dx = 0$ unless $\ell = 0$, reproduces better the equal potential on the hemisphere. If two more $\ell$'s are assigned to $[0, \pi/2]$ without discarding the even $\ell$, the equal potential on the cylindrical part of CNT is reproduced better (see Fig. 3).
Since there is no electric field inside the CNT, its surface charge density is then

$$\sigma(r, \theta) = \begin{cases} 
\frac{1}{4\pi} \sum_{n=0} \frac{(n + 1)a_n}{R^{n+2}} \cdot P_n(\cos \theta), & \text{for } \theta \in \left[0, \frac{\pi}{2}\right], \\
\frac{1}{4\pi} \sum_{n=0} \frac{(n + 1)a_n}{R^{n+2}} \sin^{n+1} \theta \cdot P_n(\cos \theta), & \text{for } \theta \in \left[\frac{\pi}{2}, \pi\right].
\end{cases}$$

For calibration, experimentalists\textsuperscript{6} apply the AFM to a conducting slab connected between them by a bias. The electrostatic potential from the image charge\textsuperscript{10} is easy to include — just subtract the bias \(V_0\) in Eq. (2) by the same \(V(r, \eta)\) in Eq. (1) with

$$r = \sqrt{(2d)^2 + R^2 - 4dR \cos \theta},$$
$$\cos \eta = \frac{2d - R \cos \theta}{\sqrt{(2d)^2 + R^2 - 4dR \cos \theta}},$$

for \(\theta\) less than \(\pi/2\), and replace the \(R\) in Eq. (4) when it is greater. Similarly for an insulator, depending on the size of the charged area, we just look up the potential form generated by a point charge or a charged finite disk,\textsuperscript{10} and subtract it from the left-hand-side of Eq. (2). In either case the coefficients \(a_n\) can be obtained to give a new charge distribution on the CNT surface and the force-distance relation.

In real experiments, it is hard to foretell which side of the conic tip the CNT will be attached to. Therefore, the CNT is normally not perpendicular to the sample surface and the tilting angle can be large. In this case, the loss of azimuthal symmetry will force us to adopt the full solution of the Laplace equation involving the associated Legendre polynomials.\textsuperscript{10} In principle, the above procedures can still be followed except calculations becomes involved. In practice, due to the large aspect ratio of CNT, we expect the equivalent charge distribution devised by Belaidi \textit{et al.}\textsuperscript{8} to remain a good approximation.

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References