The approach curve method for large anode-cathode distances

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Abstract

An important technique used to characterize field emission is the measurement of the emitted current against electric field (IxE). In this work we discuss a procedure for obtaining IxE data based on multiple approach curves. We show that the simulated features obtained for an idealized uniform surface matches available experimental data for small anode-cathode distances, while for large distances the simulation predicts a departure from the linear regime. We also discuss the shape of the approach curves for large anode-cathode distances for a cathode made of carbon nanotubes.

Introduction

Recent achievements in the production of carbon nanotube (CNT) based Field Emission Displays intensified the interest on this material [1]. If further work indeed proves that thinner and larger Field Emission Displays can be fabricated with reliable emission, long lifetime, and low power consumption, [2], it is not unreasonable to expect a considerable impact in the worldwide display business, including the replacement of Liquid Crystal Displays from their hegemonic position in some specific areas, such as large area displays. This belief is based on the intrinsically better image properties of FEDs when compared to other technologies, especially concerning brightness, contrast, color, wide viewing angle, and speed of image formation.

Despite considerable progress, a better understanding of the emission properties of CNT structures produced by the various existing growth techniques [3] is still needed, demanding a continuous effort on field emission characterization techniques. By measuring the emitted current from CNT samples with respect to the applied field (IxE) one can make comparative studies aiming at the optimization of CNT length, diameter, number of nested tubes (in the case of multiwall nanotubes), density, and purification techniques. Another aspect of field emission from CNTs that demands special attention is nanotube burn out, as observed by Wei *et al.* [4]. This phenomenon limits the lifetime of CNTs and may restrict their application. Measurements of the emitted current as a

function of time in combination with long term IxE data gathered for CNT emission in the presence of residual gas may provide a better picture of the lifetime performance issues, in a similar fashion as studied by Dean and Chalamala [5].

The accuracy of the IxE curves depends on the use of a consistent and reproducible measuring technique. The approach curve method (ACM) is a good alternative to the common spacer-based diode characterization (Fig. 1), because it offers the following features: (i) high vacuum conductance between anode and cathode since no spacer is used, allowing a *better* vacuum environment around the sample, (ii) no surface path between anode and cathode since it is a spacer-less method, thus avoiding spacer induced discharges, (iii) self-consistent means for determining the macroscopic field between anode and cathode as it will become clear ahead, (iv) the sample surface remains untouched making it a non-destructive characterization technique, and (v) the size of the anode may be chosen to provide the best accuracy while several points in the same sample can be addressed independently.

Due to the presence of curved electric field lines, the ACM may produce inaccurate results if one inadvertently measures the emitted current for large anode-cathode distances. This is a concern when measuring field emission from CNTs since they can emit considerable currents even for very small macroscopic electric fields, which happens for large anode-cathode distances.

In this paper we calculate the characteristics of the approach curve for small and large anode-cathode distances, and show that the emission area changes and the approach curve becomes non-linear for large distances. We show that for small anode-cathode distances the approach curves apparatus can be modeled as a parallel capacitor, which is supported by experimental data. We also discuss anomalies that arise when large anode-cathode distances are used to characterize CNTs, and consider models that may explain the origin of the observed features.

The approach curve method

The ultimate goal of every field emission measurement is to determine the emitted current density as a function of applied electric field (JxE). To this end, a parallel plate capacitor geometry is normally used, consisting of an emitting surface (cathode) and an electron collector (anode) facing each other. In the approach curve configuration, the anode is usually a truncated cone with its symmetry axis normal to the sample surface and its smaller cap facing the cathode (Fig. 1b). The anode diameter is typically about a tenth of the cathode size, so that several points can be measured on the same sample. A JxE graph is obtained by simply measuring the emitted current for a given cathode-anode distance and several anode voltages.

The voltage applied between the two plates is such that the resulting electric field is large enough to narrow the surface potential barrier of the cathode and allow electrons with energies close to the Fermi level to tunnel through the barrier. In the case of CNTs the emission is facilitated by their small diameter, which results on very high field enhancement factors.

A common field emission data acquisition system, shown in Fig. 1a, uses an insulating spacer of known thickness to set the anode/cathode distance. The presence of a spacer, however, should be avoided since it may lead to electrostatic disturbances due to spacer charging and worsening of vacuum caused by spacer degassing. It is common to observe discharges near spacers, probably induced by gases desorbed from its surface. A spacer-less measuring apparatus (such as the one used in the ACM) uses a micro-manipulator to position the anode parallel to and at a certain distance z from the cathode, without ever coming in contact with the cathode surface. The experimental apparatus used by the authors includes a power supply to provide high voltage between the cathode and the anode, a nano-amperemeter for measuring the emitted current, a ballast resistor for protection against excessive currents, and a data acquisition system for registering the emission curve. It also includes an xy positioning capability to measure several points on the same sample, since the determination of field emission uniformity across the cathode surface is of considerable interest.

IxE curves are obtained from measured IxV curves as follows: at each inter-electrode distance a certain voltage is required to produce a fixed current, which is then plotted against the inter-electrode distance producing Vxd curves. The slope of the Vxd plots is the electric field necessary to yield the desired current. This procedure is repeated for several currents until a smooth IxE plot is generated. This is the ACM. The resulting average macroscopic electric field is very accurate and reproducible. However, good accuracy is only reached after a large amount of emission data is gathered since field emission is normally a very unstable process. This methodology assumes that the Vxd curves are straight lines, which has been confirmed experimentally for a number of systems [6-9]. Figure 2a is an example of IxV curves obtained from CNTs deposited on a metal plate and measured at three cathode-anode distances, demonstrating that the voltage required to yield a constant current decreases with decreasing the anode-cathode distance. Figure 2b shows the resulting Vxd curve, which is a straight line as expected for the case of a flat emitter. The data presented in the figure is just a typical example. A complete analysis of similar samples can be found in Refs. [6-8] where the linearity of the Vxd plot is demonstrated in more detail.

It is worthwhile mentioning two important limitations of virtually every diode-type field emission characterization technique, namely the assumption that the current density is given by the anode current divided by the anode area, and the lack of knowledge about the actual electric field on the cathode surface. Normally the emission is restricted to

spots on the cathode surface, with a total area much smaller than the anode or cathode areas. These spots are evident in photo-emission electron microscopy images of the sample [7]. Other techniques, such as field emission microscopy, can provide atomic resolution of the emission spots on metallic needles and emitters such as CNTs where the nanotube caps can be imaged using this technique [10]. The analysis of the transconductance (dI/dV) following Charbonier-Martin may also provide information about the emission area [11], resulting in effective emission areas much smaller than the total cathode area. Therefore, the actual current density is expected to be a lot higher than its averaged value. As far as the electric field on cathode surface is concerned, it is obtained by assuming an idealized model of the surface since it is strongly dependent on the local surface morphology, which in general is unknown. In practice one assumes an effective macroscopic electric field, which is calculated by dividing the applied voltage by the anode-cathode distance.

For the case of non-flat emitters, such as CNTs, the experimental determination of the work function by means of IxE curves requires the determination of the emitter's geometry (from Transmission Electron Microscopy in the case of CNTs) and the calculation of the field enhancement factor/image charge effect. From an experimental standpoint, it is common to use a practical parameter known as effective work function (W_{eff}), in which the work function and geometrical effects are coupled together, providing a way to compare the emission characteristics of different surfaces from a macroscopic perspective. The parameter W_{eff} may be used for performance analysis but has no intrinsic physical meaning.

The approach curve method range of validity

The ACM implicitly assumes that the anode-cathode system forms an idealized parallel plate capacitor, which is expected to break down for large inter-electrode distances. Thus an upper limit shall exist above which the system can no longer be modeled as a parallel capacitor. In addition, field emission is a process highly sensitive on the local electric field which poses a further constraint on the applicability of the method, since as we shall see the emitting area strongly depends on the anode-cathode spacing. To address these issues, we have used numerical simulations to determine the general shape of an idealized approach curve, where by idealized we mean a flat cathode with a uniform work function throughout the cathode area. Even though in this work we only address the applicability of the ACM for large anode-cathode distances, it is important to mention that the parallel plate assumption made in the ACM also breaks down when the anode is positioned at a distance from the cathode comparable with the characteristic dimensions of the surface roughness.

The finite element method (FEM) was used to model the electric field along the surface of a flat cathode for different anode-cathode separations. We solved the Laplace

equation in cylindrical coordinates and set the boundary conditions by assuming a grounded cathode surface and 100 V in the anode. These values are rather arbitrary and can be adjusted to each particular situation since the solution of the Laplace equation scales linearly with the potential values at Dirichlet boundaries. Because FEM requires a closed boundary for the solution, an artificial cylindrical surface connecting the anode and cathode boundaries was introduced (see Fig. 1b). The electrostatic field in the area of interest should not depend on the particular selection of the artificial boundaries, so we performed a series of FEM calculations using boundaries of different heights and radii to confirm that the results at the cathode surface were accurate. Cylindrical coordinates centered at the middle of the anode were used to solve the Laplace equation.

Figure 3 shows the calculated magnitude of the electric field normal to the cathode surface for different anode-cathode distances. As expected, for small cathode-anode distances the electric field on the cathode is virtually constant at positions just below the anode, similar to the case of an infinite parallel capacitor. The field on the cathode drops fast for locations beyond the anode edges. For large cathode-anode distances, however, the electric field has a maximum at the center of the cathode, while the overall electric field distribution on the cathode is bell shaped. Such behavior indicates the theoretical limit for the application of the ACM, even for a uniform and flat cathode surface. For very large anode/cathode distances the electric field on the cathode can be calculated using the model of a flat conductive surface (cathode) with a metallic sphere (anode) positioned above it. Because of the strong dependence of emission on the electric field the emission sites are restricted to an area immediately below the anode for a small anode-cathode distance, while for large anode-cathode separations the emission sites maybe distributed in an area larger or smaller than the anode area, as discussed ahead.

Figure 4 shows how the dependence of the electric field on inter-electrode spacing affects the shape of the approach curve under the ideal conditions described before. Three cases were considered: (1) the ideal infinite capacitor, which produces a linear approach curve; (2) the approach curve corresponding to a fixed electric field at the cathode center via solution of the Laplace equation for the geometry of Fig.1(b); (3) similar to (2) but fixing instead the total emitted current. In case (2) we determined the electric field on the flat cathode surface for different cathode-anode distances and for a fixed arbitrary anode voltage φ_{arbt}. The anode voltage V_a required to create a given electric field (E_c = 1 V/μm) at the center of the cathode follows directly from the linearity of the Laplace equation. Figure 4 shows that as the anode-cathode separation increases, the approach curve diverges upwards from a linear behavior. Case (3) is a better approximation to the experimental procedure since the data collection to generate the approach only allows control over the threshold voltage yielding a given emitted current. This threshold voltage and electric field are related through the Fowler-Nordheim (F-N) equation integrated along the cathode:

$$I_{tot} = \int J(V_a, x, y)\, dx\, dy \qquad (1)$$

where I_{tot} is the total current emitted from the cathode and J is the F-N current density at each xy position of the cathode for a given voltage V_a in the anode. In order to determine the voltage V_a required to emit a fixed current, we solve the Laplace equation for an arbitrary anode voltage φ_{arbt} and determine the electric field $E_c(h,x,y)$ on the cathode surface and for different anode-cathode separations h. Hence, we can write the usual F-N expression for the current

$$I_{tot}(h) = \int A.(k.E_c)^2(h,x,y)\, e^{\left(-\frac{B}{k.E_c(h,x,y)}\right)} dx\, dy \qquad (2)$$

where $k(h)$ is a dimensionless parameter. Inverting (2) for a given $I_{tot}(h)$ (we used 10 nA) one can find $k(h)$ and from there the voltage $V_a(h)$:

$$V_a(h) = k(h).\varphi_{arbt}$$

For the anode sizes used in our experimental setup (diameter of 1.25 mm), moving the anode farther than 400 μm from the cathode results in considerable deviation from a parallel capacitor behavior. These general trends are valid for any device/apparatus dimensions as long as they can be reduced to a set up similar to the one described here upon rescaling.

The results shown in Fig. 4 are consistent with the emission measurements performed earlier for anode-cathode distances in the 400 μm range and for different kinds of samples, including CNTs (e.g. [6-8]), even though for CNTs the surface is evidently not flat in a microscopic sense. The results described in [6-8] are consistent with our idealized flat and uniform model cathode since the anode-cathode distance was substantially larger than the asperities of the nanotube sample. In this case the overall CNT cathode emission can be modeled as a flat surface with a very low "effective" work function.

Large anode-cathode gaps and carbon nanotubes

For large anode-cathode distances the picture is not as simple as modeled above and some experimental limitations should be taken into account. Even though theoretically any anode-cathode distance is possible, from a practical standpoint most flat samples (metals and metals with wide bandgap coatings) cannot be measured for anode-cathode gaps in the millimeter range using readily available voltage sources. For instance, as

indicated by experimental data obtained using an anode of 1.25 mm in diameter [8], flat Mo requires an electric field as large as 30 V/μm to emit a current in the 10 nA range. Thus for an anode-cathode separation of 1 mm, voltages as large as tens of kilovolts would be needed to emit 10 nA from a flat Mo cathode. Such a high voltage power supply is normally not available, and even when it is, operating at tens of kilovolts can be an inconvenience. Therefore anode-cathode gaps larger than a few hundred microns are of no interest for the characterization of most flat samples. However, such experimental limitation does not impact CNT characterization since nanotubes can emit currents in the 10 nA range for modest power supplies (in general limited to 3 kV), even when the anode is separated from the cathode by distances as large as few millimeters. So, for the sake of CNT characterization it is very important to understand the behavior of the approach curve at large anode-cathode distances.

CNTs can have a large aspect ratio, as narrow as a few nanometers in diameter and as long as few micrometers. As a result, CNTs tend to align with the applied electric field. CNT samples prepared from powder, as the ones used in Refs. [6,12], are normally embedded in a resin (silver glue). The resulting mixture produces rough cathode surfaces, with mesoscopic bumps (tens to hundreds of microns in size) and non-uniform CNT concentration and distribution. The model introduced in the previous section is not valid for such a complex surface since it is limited to flat and uniform cathodes and does not consider the field alignment, roughness, and non-uniformity described above. Therefore agreement with experimental approach curves obtained from CNT cathodes should not be expected.

Figure 5 shows the approach curve obtained for a single wall nanotubes (SWNT - MER Corporation and other sources) [12] mixed with silver glue paste, that was later spread over the substrate to create a surface as flat as possible. Notice that the approach curve in this case actually bends downward instead of upward, as predicted by our model for a flat sample. The result shown in Fig. 5 was observed for a representative number of samples. Despite the qualitative disagreement between the calculated approach curve in Fig. 4 and the data shown in Fig 5, our simple model may still help to understand the main trends described in Fig. 5, as we now proceed to do.

Three possible explanations for the approach curve obtained for the CNT sample were considered: (i) nanotube burn or degassing, (ii) nanotube alignment with the electric field, and (iii) large scale roughness on the cathode surface.

The generation of an approach curve may take an hour or more, depending on the number of anode-cathode distances measured. For long term emission data acquisition, structural changes in the cathode might take place either due to CNT burn-out or degassing, perhaps leading to the behavior shown in Fig. 5. In order to rule out this possibility, the authors performed a sequence of 3 approach curves (approaching,

distancing and approaching) for a single characteristic point on the sample, and all three curves showed a shape similar to Fig. 5 [13]. The independence of the shape of the approach curve with time indicates that the phenomenon underlying Fig. 5 is purely geometric and neither degassing nor burning as considered in hypothesis (i) are leading cause.

Hypothesis (ii) is based on the fact that CNTs align with even small external electric fields [14]. Figure 6 shows the calculated electric field on the cathode surface for different anode-cathode separations, under the constraint that the total emitted current is constant. As before, these results are for a flat and uniform cathode. Notice that the value of the electric field at positions far from the cathode center increases considerably as the anode-cathode gap increases. Although the off-center electric field for large anode-cathode gap is not high enough to significantly increment the total emitted current, it may be high enough to align the CNTs with the electric field [14]. As a result, the field enhancement at the aligned CNTs increases, leading to a larger number of emission sites located in the region outside the disk immediately below the anode. Such scenario would result in a diminished Vxd slope, since a smaller macroscopic electric field would be required to produce the same current as the anode is moved away from the cathode. To be true, this hypothesis relies on the assumption that the CNTs return to their pre-external field orientation as the anode-cathode gap gets smaller (reversible alignment). Wei et al. [14] observed that nanotube alignment at low fields could be reverted by removing the field. However, following their observations, when the emitted current is high enough the alignment becomes permanent due to structural changes. Therefore the confirmation or not of this hypothesis still depends on further studies involving the reproducibility of Fig. 5 for small and large emitted currents.

The presence of macroscopic structures such as bumps and ridges on the sample surface disrupts the field close to the surface. In fact, one should not expect a linear behavior for the approach curve when the anode surface gets close to the crest of a bump on the cathode. However, to justify such a large scale downward bend in the approach curve as observed in Fig. 5 the bumps would need to be in the sub-millimeter to millimeter range, which is far too big for the SWNT samples measured. Therefore we discard this hypothesis.

Using our simplified flat and uniform cathode model we have calculated the current density on the cathode for different anode-cathode separations under the constraint that the total emitted current is constant, as shown in Fig. 7. For this idealized case, the emission area reduces as the anode-cathode gap increases, in contrast with hypothesis (ii) which depends on the increase of the number of emission sites as the anode-cathode separation is incremented. This incompatibility points to the limiting assumptions of the model, more specifically sample uniformity, and suggests follow-up experiments.

The calculations and data presented here show that for large anode-cathode gaps, the parallel plate capacitor assumption of the ACM breaks down as evidenced by the increase of the electric field on the cathode surface in the region outside the disk immediately below the anode. Our calculations also indicate that the strong non-linear behavior measured for CNT cathodes may be used to investigate the uniformity and distribution of emission sites across the cathode surface.

Conclusions

For the apparatus described in this paper which is commonly used to generate approach curves, field emission for small anode-cathode separations smaller than the anode diameter can be accurately modeled as a parallel plate capacitor where the emitted current comes mainly from areas immediately below the anode. This is true as long as the anode-cathode separation is considerably larger than the typical roughness of the sample surfaces. For large anode-cathode separations larger than the anode diameter, the approach curve deviates from the linear behavior and bends upwards, while the emission area reduces. This is valid under the assumption that the cathode is flat and that the surface properties are uniform across the cathode surface. These assumptions do not hold if the emitters are CNTs. In this case, the approach curve also deviates from the linear behavior, but bends downwards instead. We discussed several hypotheses to explain the non-linear behavior observed experimentally for CNTs: (i) tube burning and degassing, (ii) alignment of CNTs with the applied electric field for those CNTs in the region outside the disk immediately below the anode, and (iii) presence of bumps localized below the anode. While data and sample conditions seem to rule out hypotheses (i) and (iii), hypothesis (ii) is plausible at this point. If confirmed by future investigation on the relation between the non-linear behavior of the approach curve for CNTs and off-center CNT emission, this model may lead to a new procedure to determine CNT cathode uniformity and distribution of emission sites.

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Fig. 1 – Two diode configurations for field emission measurements: (a) using a spacer, (b) spacer-less. In the approach curve method (ACM) configuration (b) is used, because the anode-cathode gap is variable and the absence of the spacer results in less desorbed gas buildup and dielectric breakdown events. Configuration (b) allows measurements at several points on the sample (e.g. P1, P2, and P3, as indicated). The dashed lines in Fig. 1b show the boundaries considered for the finite element method calculation.

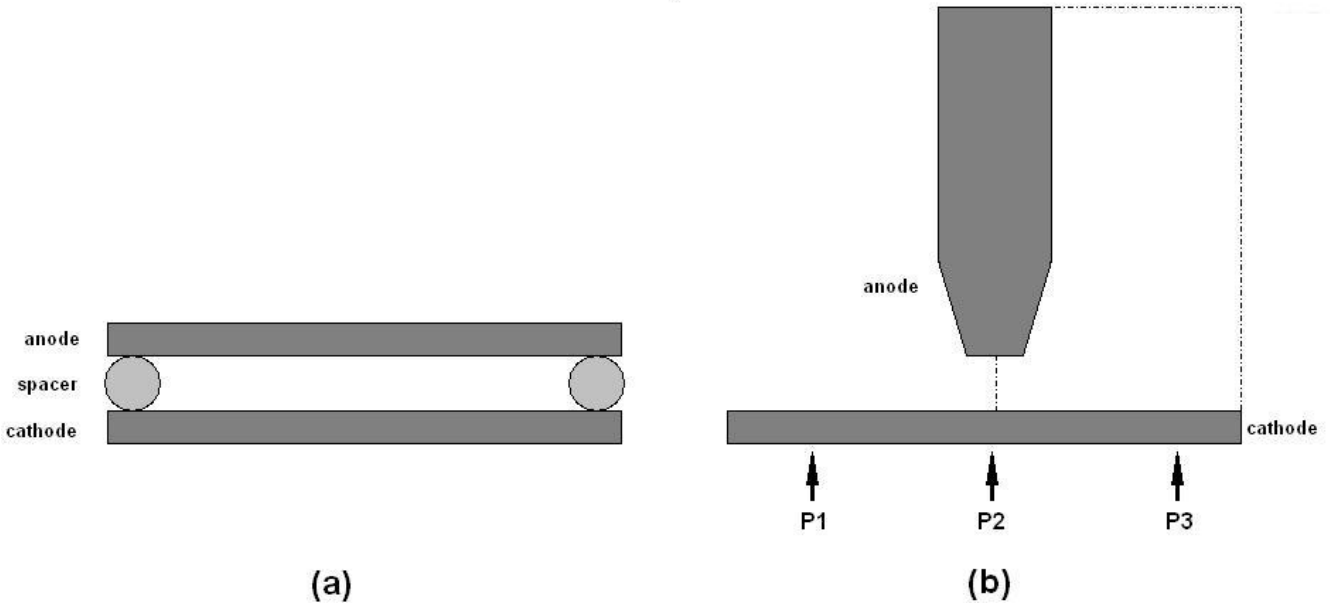

Fig.2 – (a) Schematic description of the approach curve method (ACM): by defining an arbitrary threshold current, one can obtain the voltage necessary to produce that current for different anode-cathode distances; (b) by plotting these voltages with respect to the anode-cathode gap, the electric field necessary to produce the threshold current can be determined.

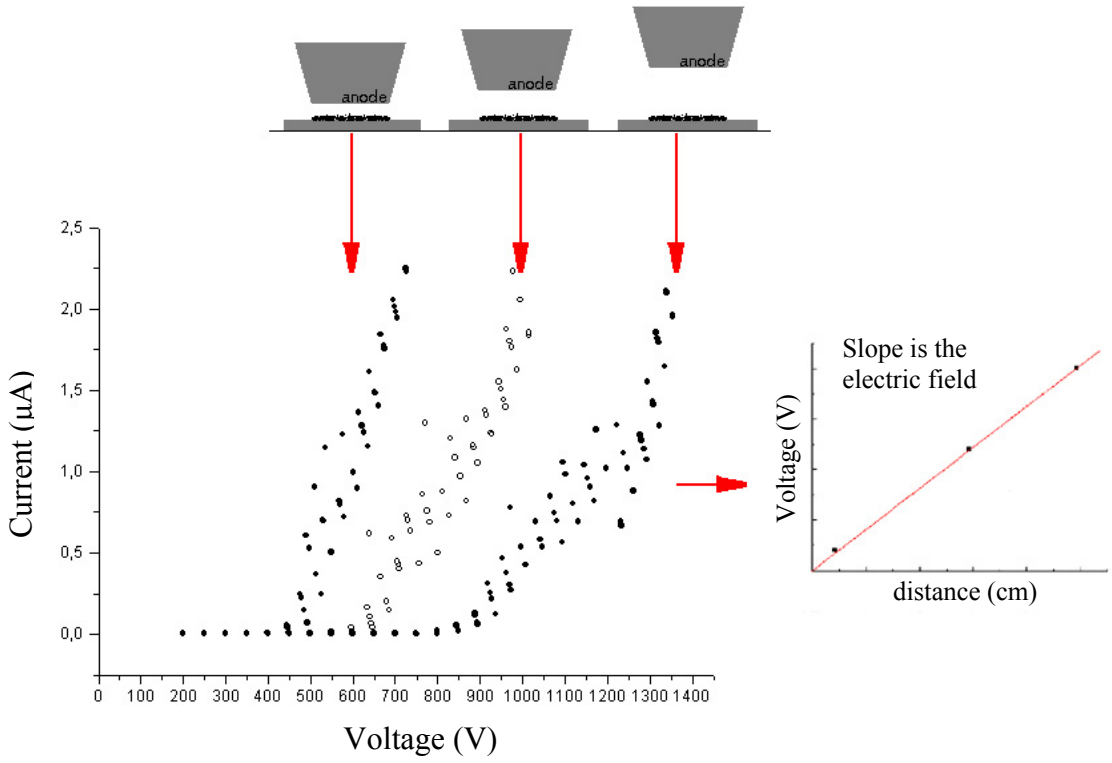

Fig. 3 - Electric field calculated at the surface of the cathode for different anode-cathode distances. Anode diameter is 1.25 mm.

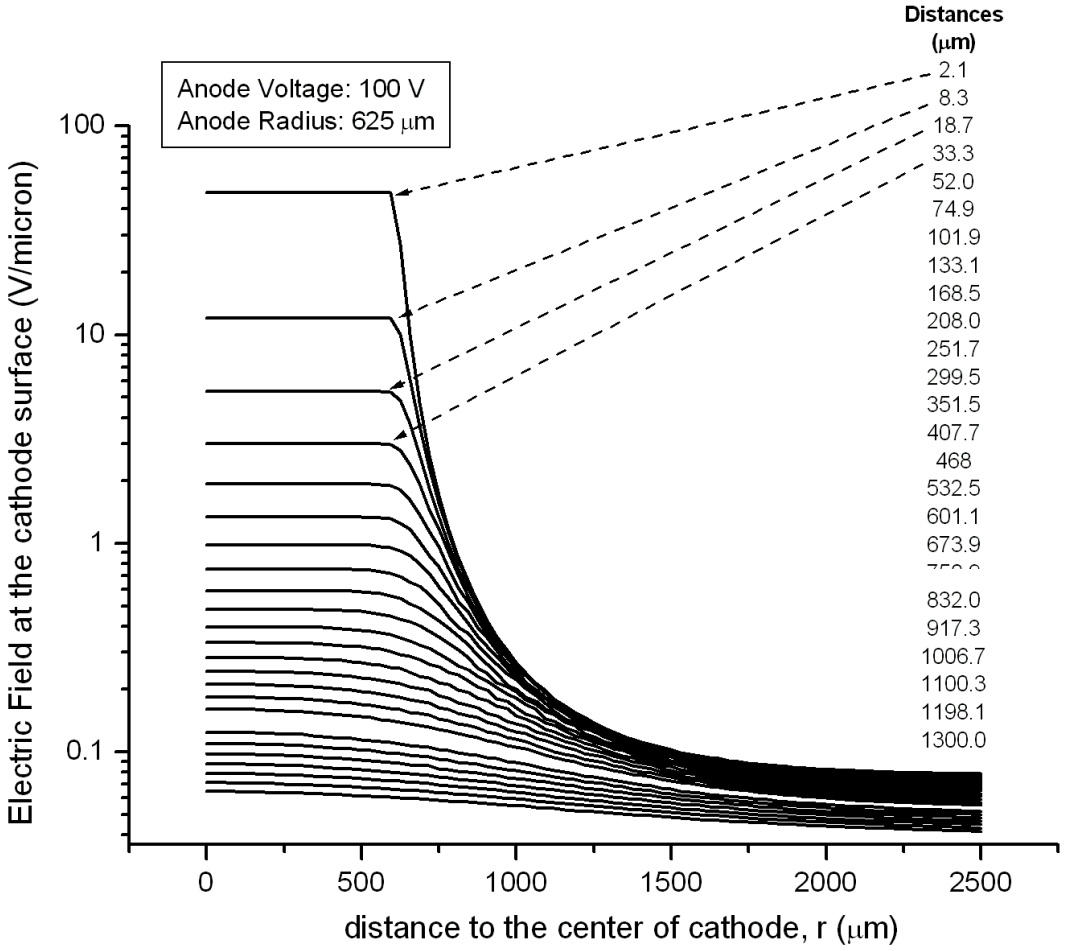

Fig. 4 – Approach curve calculated for a flat and uniform cathode surface. In this simulation we used W=0.05 eV as the effective work function. Solid line: ideal planar capacitor; empty circles: voltage required to maintain constant the total emitted current I_{tot}; filled circles: voltage required to maintain constant the electric field at the center of the cathode.

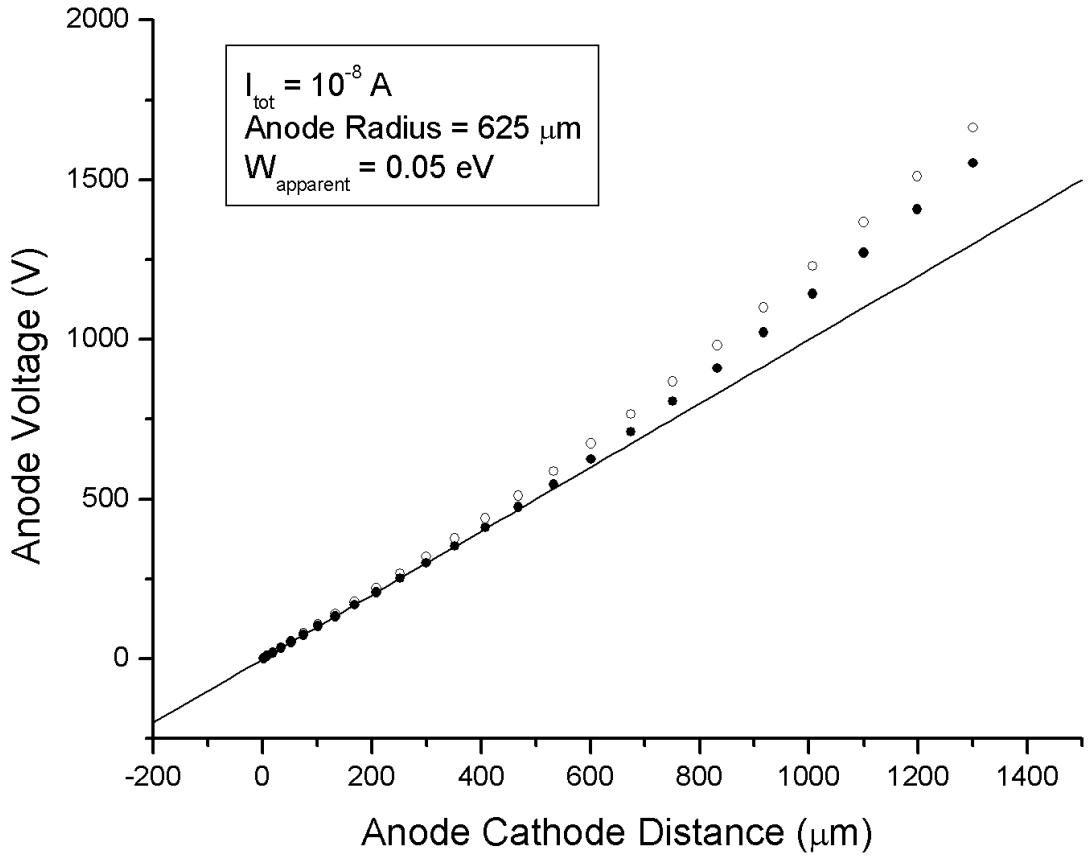

Fig. 5 – Experimental field emission data obtained for a mixture of single wall nanotubes (SWNT) with silver glue, spread over a flat surface. The behavior is qualitatively different from the simulated curves for a flat and uniform cathode shown in Fig. 4.

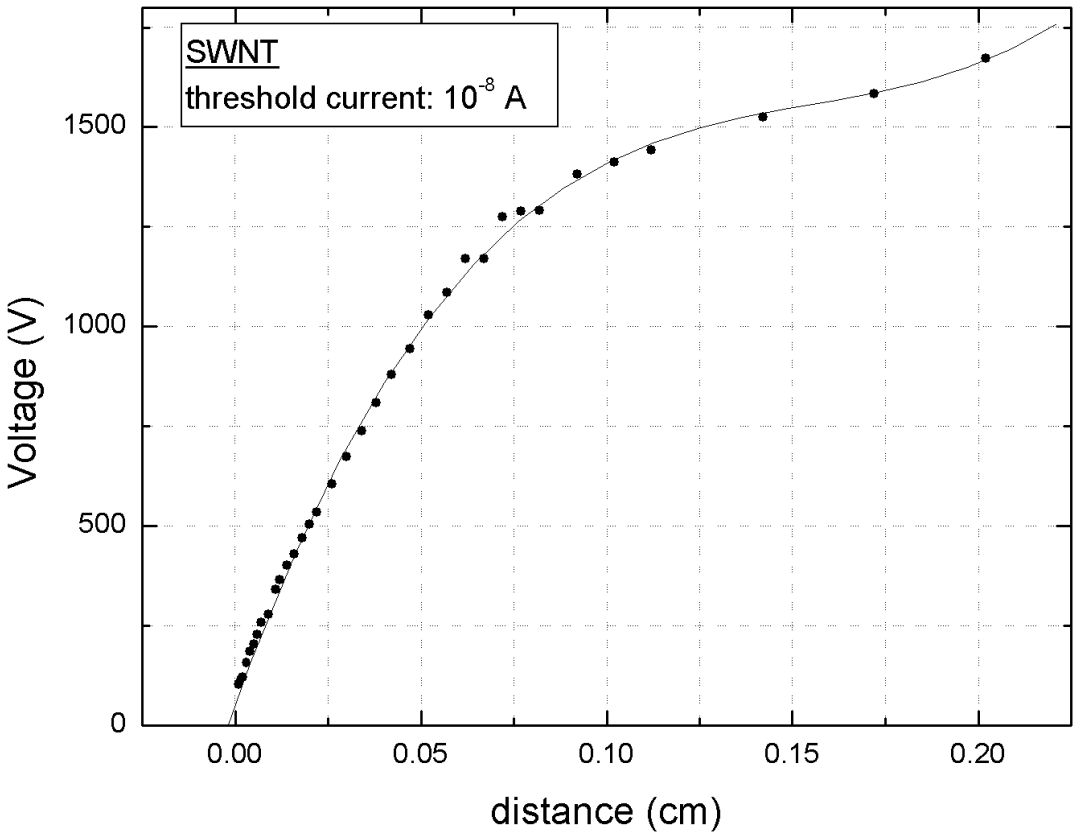

Fig. 6 – Electric field distribution on a flat cathode surface for different anode-cathode separations, calculated under the constraint that the emitted current is the same for all separations. Notice that the electric field increases noticeably outside the disk corresponding to the projection of the anode area onto the cathode surface (*i.e.*, r > 625 m).

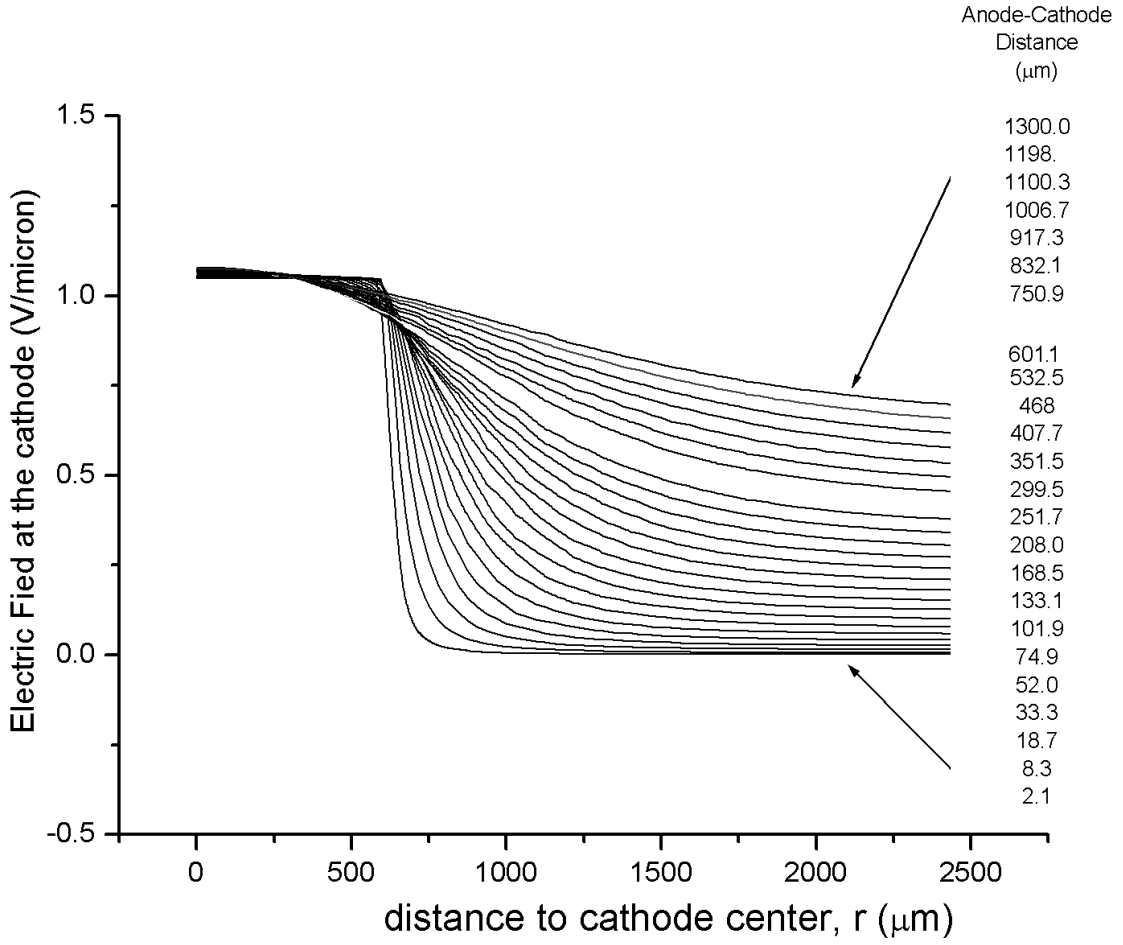

Fig. 7 – Uniform current density distribution for a flat and uniform cathode. The emission area reduces as the anode-cathode gap increases.