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Theoretical study of field emission by single-wall carbon nanotubes

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Field emission characteristics of various kinds of single-wall carbon nanotubes have been calculated using a combination of methods derived from quantum and electromagnetic theory. The energy distributions of the emitted electrons, obtained for all the nanotubes, confirm the implication of localized states in the emission process. However, the (10,0) nanotube seems to give rise to emission only by a very peaked localized state, whereas the Fermi sea also contributes for the (5,5) nanotubes. Moreover, despite a larger field enhancement, the (5,5) capped nanotube does not allow for currents as large as those emitted by the open-ended one.

Carbon nanotubes as field emitters[1–3] have recently attracted a lot of interest due notably to the very good field-emission stability compared to metallic emitters.[4] Furthermore, currents of the order of 0.1 mA per isolated multiwall carbon nanotube (MWNT) can be obtained.[5] Prototypes of flat panel displays, based on carbon nanotubes, have even been proposed.[6,7] However, the emission mechanisms are still unclear. For example, Bonard *et al.*[8] have experimentally observed clear differences between open and closed MWNT, and Rinzler *et al.*[2] have observed a large current enhancement when the tips of MWNT were opened by laser ablation. Rinzler *et al.* proposed that the emission could take place from an atomic chain unraveling from the end of the tube. However, this hypothesis has not been confirmed by other authors.[9]

Very recently, *ab initio* simulations of single-wall carbon nanotube electron density in a bias field[10] have revealed unusual localized states at the top of the nanotubes. These states are supposed to be responsible for the high currents experimentally observed. Han and Ihm based this conclusion on the fact that the charge accumulated at the end of the nanotube, when a field is applied, leads to a high field enhancement which creates, in terms of Fowler-Nordheim field emission mechanisms, favorable conditions for the emission. However, the implications of these localized states in the emission process have not been checked. Moreover, in the hypothesis of an emission from these localized states, there is no evidence that the field enhancement will play a dominant role in the emission mechanism. Thus, the conclusions pointed out by Han and Ihm[10] relative to the emissiveness of capped and open-ended (5,5) nanotubes are still hypothetical given that emission has not been included in their calculation. In the present work, we have theoretically studied the current received on the anode, from various nanotubes physisorbed on a cathode, in a field emission setup.

In order to study the emission process by various nanotubes, we have used a scattering formalism based on the Lippmann-Schwinger (LS) equation. This formalism has notably been used to study the chemisorption of an adatom on simple metals[11] and to model scanning tunneling microscopy.[12] To our knowledge, its extension to field emission has only been done quite recently.[13] In this formalism, the system is split into two parts: a reference system, corresponding to a metal-biased vacuum-metal (MVM) junction, and a perturbation corresponding to the nanotube. As already described in details in Ref. 13, the wave function of the emitted electron is then computed fully self-consistently by means of the LS equation:

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d^3r' G_0(\mathbf{r},\mathbf{r}';E) V_{\text{eff}}(\mathbf{r}') \psi(\mathbf{r}'), \quad (1)$$

where $\psi_0(\mathbf{r})$ and $G_0(\mathbf{r},\mathbf{r}';E)$, respectively, represent the wave function and the Green's function of the Schrödinger equation for the reference system, $V_{\text{eff}}(\mathbf{r})$ the effective potential of the nanotube, and $\psi(\mathbf{r})$ the wave function of the electron emitted by the nanotube, at energy E, in the actual system (reference system plus perturbation described by V_{eff}). In this method, $\psi(\mathbf{r})$ is computed in direct space, by discretization of Eq. (1) in the region of the nanotube.

Thanks to the rotational invariance of the reference system, $\psi_0(\mathbf{r})$ is expressed as plane waves in the cathode and the anode, and in the biased vacuum as

$$\psi_0(\mathbf{r}) = e^{i\mathbf{k}_t\cdot\boldsymbol{\rho}}[AC^+(z) + BC^-(z)], \quad (2)$$

where $\mathbf{k}_t$ is the wave vector parallel to the surface, $\boldsymbol{\rho} = (x,y)$, $C^{\pm}(z) = \sqrt{3}e^{i\pi/6}[\text{Ai}(-\xi) \pm i\,\text{Bi}(-\xi)]$, with $\xi = [(2m/\hbar^2)^2 F]^{1/3}[z-(E-W/F)]$ and where Ai and Bi represent the Airy functions, F the applied field, and W the work function. G_0 is then constructed as in Ref. 12. Finally, the wave function of the emitted electron is the solution of the linear system:

$$\sum_{j=1}^{N} [\delta_{ij} - G_0(\mathbf{r}_i,\mathbf{r}_j;E) V_{\text{eff}}(\mathbf{r}_j)\Delta_j]\psi(\mathbf{r}_j) = \psi_0(\mathbf{r}_i), \quad (3)$$

where N is the number of discretization meshes for the nanotube and Δ_j the volume of mesh number j. In the present simulations, the anode and the cathode infinite plane surfaces are 20 nm apart.[22] A nanotube, with a length of the order of 1 nm, is physisorbed on the cathode. The applied field range from 0.15 to 0.3 V/Å which corresponds roughly to an applied potential difference between the two ends of the nanotube ranging from 1.5 to 3 V.

The effective potential of the nanotube is split into two parts: $V_{\text{eff}}(\mathbf{r}) = V_{\text{mol}}(\mathbf{r}) + V_{\text{pol}}(\mathbf{r})$. $V_{\text{mol}}(\mathbf{r})$ corresponds to the effective potential of the molecule, in absence of an applied field, computed using a pseudopotential plus linear combina-

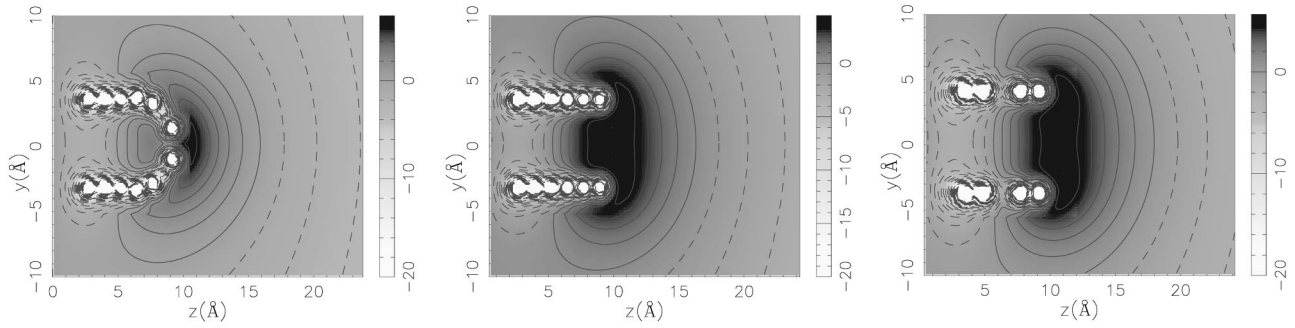

FIG. 1. Effective potential in the vicinity of a capped (5,5) nanotube (left image), an open (5,5) nanotube (central image), and an open (10,0) nanotube (right image). The core potential is cut at −20 eV so as to keep images clear.

tion of atomic orbitals technique.[14,15] $V_{\mathrm{pol}}(\mathbf{r})$ corresponds to the additional potential induced by the applied field. To compute it, we use the natural discretization grid provided by the carbon atoms and use a dipolar approximation by expressing the polarization vector $\mathbf{P}(\mathbf{r})$ as

$$\mathbf{P}(\mathbf{r}) = \epsilon_0 \overleftrightarrow{\chi}(\mathbf{r})\mathbf{E}(\mathbf{r}) = \epsilon_0 \sum_{i=1}^{N_{\mathrm{at}}} \overleftrightarrow{\alpha}_i \delta(\mathbf{r}-\mathbf{r}_i)\mathbf{E}(\mathbf{r}).$$

This leads to

$$V_{\mathrm{pol}}(\mathbf{r}) = \sum_{i=1}^{N_{\mathrm{at}}} \mathbf{H}(\mathbf{r},\mathbf{r}_i)\overleftrightarrow{\alpha}_i \mathbf{E}(\mathbf{r}_i), \tag{4}$$

where $\mathbf{H}(\mathbf{r},\mathbf{r}_i) = -\nabla_{\mathbf{r}_i} G_0^{(EM)}(\mathbf{r},\mathbf{r}_i)$, with $G_0^{(EM)}$ the Green's function associated to the Laplacian operator with limit conditions corresponding to the reference system (MVM junction), $\overleftrightarrow{\alpha}_i$ the anisotropic polarizability tensor for the carbon atom centered at $\mathbf{r}_i$ (Ref. 16), and $\mathbf{E}(\mathbf{r}_i)$ the local electric field at $\mathbf{r}_i$. $\mathbf{E}(\mathbf{r}_i)$ is itself obtained through the analog of the Lippmann-Schwinger equation for the electric field:

$$\mathbf{E}(\mathbf{r}_i) = \mathbf{E}_0(\mathbf{r}_i) + \sum_{j=1}^{N_{\mathrm{at}}} \overleftrightarrow{S}_0(\mathbf{r}_i,\mathbf{r}_j)\overleftrightarrow{\alpha}(\mathbf{r}_j)\mathbf{E}(\mathbf{r}_j), \tag{5}$$

with $\overleftrightarrow{S}_0(\mathbf{r},\mathbf{r}') = \nabla_{\mathbf{r}}\nabla_{\mathbf{r}'} G_0^{(EM)}(\mathbf{r},\mathbf{r}')$ and i ranging from 1 to N_{at}. The explicit expression of $G_0^{(EM)}$ can be found in Ref. 16. This self-consistent equation is simply a linear system of $3N_{\mathrm{at}}$ unknowns, namely the components of the N_{at} vectors $\mathbf{E}(\mathbf{r}_i)$, which can be solved by standard dense matrix solvers.

Thanks to this formalism, we have been able to investigate the emissive properties of three different structures: a (5,5) nanotube capped by a half-C_{60}, and (5,5) and (10,0) open-ended nanotubes with unpassivated dangling bonds. Our aim is to compare the emissive properties of these structures and to determine the implications of the structure and of possible localized states on the emission process. The polarization potentials of these three nanotubes for an applied field of 0.15 V/Å are presented in Fig. 1. These images correspond to a two-dimensional view in the plane $x=0$. The physisorption distance of the nanotubes on the tungsten surface was set to 2.6 Å, with no current-limiting mechanism due to the nature of the contact between the nanotube and the cathode being taken into account. A very large response of the nanotubes with the applied fields can clearly be seen on these figures. This can be attributed to the fact that the high polarizability of this material[17] leads to the occurrence of a large tunnel barrier at the top of the nanotubes (already observed in Ref. 18). The main difference which can be noticed between the different structures, is the penetration depth of this barrier inside the nanotubes. For the capped nanotube, the barrier does not penetrate deeply inside the nanotube and is well localized on the top of the cap. Conversely, the geometry of open-ended structures leads to a large penetration of the barrier inside the nanotube. As this barrier also extends outside, this leads to a wider barrier in the case of open nanotubes. This can also clearly be seen in Fig. 2, where the induced field along the z axis ($x=0$ and $y=0$) is represented for the three previous nanotubes. The major noticeable difference appears again between capped and open-ended nanotubes. The (5,5) capped nanotube presents a large field enhancement on its top, with a maximum value of the order of 1 V/Å and a minimum of the order of −2 V/Å. Conversely, for the open-ended structures, the field enhancement is not so large and its minimum and maximum values are, respectively, only about −1.2 and 0.6 V/Å. Naively, one could conclude on the basis of the Fowler-Nordheim field emission model that the capped nanotubes are better emitters than the open-ended one. However, as we are going to see in the next paragraph, this conclusion is not supported by our simulations.

The currents emitted by the three simulated nanotubes, as a function of energy, are presented in Fig. 3. Despite its

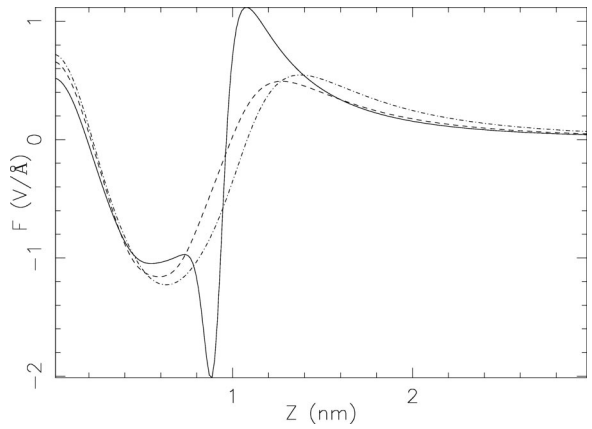

FIG. 2. Induced field (without the applied field) observed along the nanotube axis ($x=0$, $y=0$) for a capped (5,5) nanotube (solid line), an open (5,5) nanotube (dashed line), and an open (10,0) nanotube (dash-dotted line).

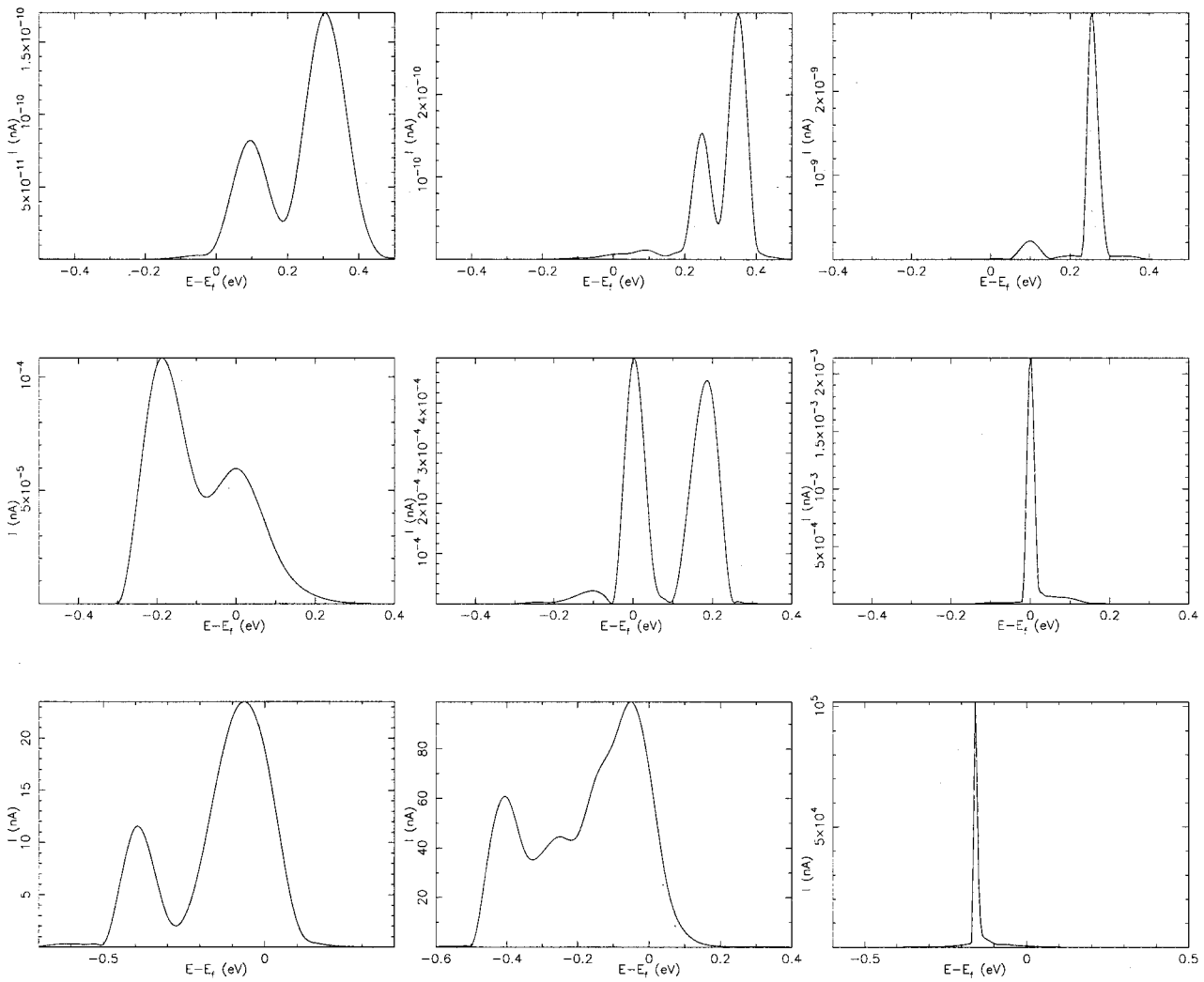

FIG. 3. Energy distribution of electrons emitted from a capped (5,5) nanotube (left images), an open (5,5) nanotube (central images), and an open (10,0) nanotube (right images). From top to bottom, the applied field is 0.15, 0.20, and 0.30 V/Å.

larger field enhancement factor, the (5,5) capped nanotube does not exhibit a larger current than the open-ended one. Hence, the field enhancement factor seems to be less important than the influence of localized states. Indeed, for all the nanotubes and all the applied fields, the occurrence of more or less sharp peaks can be noticed. Such a multipeaks spectrum typically corresponds to an emission from spatially localized states with well-defined energies. However, it is not possible to exclude an emission from the Fermi sea since, for weak fields hence low emitted currents, an emission can occur above the Fermi level, from the tail of the energy distribution. Thus, the emission from carbon nanotubes may have a double origin. This hypothesis seems to be confirmed for the (5,5) nanotubes by the evolution of the peaks with the applied field. One can clearly notice that one of the peaks is kept centered at the Fermi level for 0.20 and 0.3 V/Å, whereas other peaks move above and below the Fermi level. This means that the peak located above or well centered on the Fermi level originates from the Fermi sea, while the others originate from localized states. This dependence of the localization of these last peaks with the applied field can be interpreted in terms of a penetration of the field inside the nanotube tip. It clearly proves the spatial localization of the corresponding states as already shown experimentally with nanotips.[19,20] However this dependence seems to be complex considering that the observed evolution of the peaks positions cannot be simply related with the potential energy variations at the top of the nanotubes.

This shift of the main peak position is also observed for the (10,0) nanotube. However there are large differences with the corresponding figures for the (5,5) nanotubes. The energy distributions obtained for the (10,0) nanotube at 0.20 and 0.30 V/Å exhibit a single, sharp, and very intense peak. Actually, the half maximum is around 0.2 eV for the capped (5,5) nanotube, around 0.1 eV for the open-ended (5,5) nanotube, and around 0.05 eV for the (10,0) nanotubes. This fairly agrees with the experimental results of Fransen *et al.*,[21] since these authors observed large differences between the width at half maximum for different samples. They even concluded that the energy distributions with the sharper peaks correspond to semiconducting nanotubes and the others to metallic ones. Considering the small length of the nanotubes used for these simulations (typically 1 nm), it is not possible to talk about metallic or semiconducting properties for these (5,5) and (10,0) open-ended nanotubes. Nonetheless, the large difference between the two energy distributions clearly prove the importance of the nanotube structure in the emission mechanism, compared to the field

enhancement factor, that may even be overestimated in this study, considering the limited lengths of the simulated nanotubes, as pointed out by Han and Ihm.[10]

In conclusion, we have simulated the electron emission by various nanotubes, taking into account the MVM junction. We find that, contrary to the Fowler-Nordheim model, the field enhancement factor is not the main parameter driving the emission from the nanotubes, since the capped (5,5) nanotube does not give rise to currents higher than for the open one. We confirm that localized states are mainly responsible for the high currents observed with open-ended nanotubes, so that the detailed structure of the nanotubes plays an important role. However, we have also pointed out differences between the (5,5) nanotubes, for which the Fermi sea contribution cannot be neglected, and the (10,0) nanotube, which tends to emit only from a very sharp localized state.

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