Computer simulation of scanning tunneling spectroscopy of supported carbon nanotube aggregates

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Abstract. Among the various techniques to investigate carbon nanotubes scanning tunneling microscopy (STM) is one of the most promising since it gives access to both the atomic and electronic structures (STS). The interpretation of the experimental data remains delicate, however. We performed dynamical quantum-mechanical calculations aimed at understanding what controls the current-voltage characteristics in the STM investigation of different arrangements of nanotubes. The calculated STS spectra are directly comparable to experimental data. The theory allowed us to identify one component of pure geometrical origin responsible for an asymmetry of I-V curve, as often observed experimentally above a carbon nanotube. It is emphasized that this asymmetry strongly depends on the shape of the tip, and this may change during the experiment.

INTRODUCTION

A single wall carbon nanotube (SWCNT) consists of one cylindrical shell of graphene sheet with typical diameter of the order of $1\,nm$. A regular, multi-shell structure found experimentally is the "rope" or "raft" [1] of CNTs, which is built by placing side by side the CNTs at the van der Waals distance. To be investigated by STM the CNTs have to be supported on an atomically flat substrate, most frequently Au, or highly oriented pyrolitic graphite (HOPG). The complex structure of the system [2], through which the tunneling takes place makes the interpretation of the STS data delicate. The value of the tunneling gap [3] between the tip and the CNT does influence the STS results. If this gap is reduced below a certain limit switching from tunneling to point contact occurs [4]. Our wave packet dynamical code [2] is used to explore the way the current flows through a CNT in STM configuration.

TUNNEL CURRENT CALCULATION

The tunneling problem is studied in the framework of the two dimensional (2D) potential scattering theory [5]. The current density is determined by calculating the scattering of wave packets (WPs) incident on the barrier potential [2]. We study three tunneling situations. *i)* An STM tunnel junction with no CNT present, *ii)* one SWNT of 1 nm diameter in the STM junction, and *iii)* a raft modeled by three SWNTs. The effective surfaces [2] of the three model barriers are shown in *Fig. 1 inset.*

Fig. 1 shows WP transmission probabilities $P(\theta)$ for zero STM bias as the function of the incidence angle θ, the angle of the wave vector $\vec{k}_0 = (k_{x0}, k_{z0})$ of the initial WP relative to the normal direction. For each barrier the angular dependent transmission was calculated for WPs incident from the support ($P_+(\theta)$, tip positive) and for those incident from the tip ($P_-(\theta)$, tip negative). Incident WP energy is $E = E_F = 5\,eV$. For WPs incident from the support tunneling probability is decreasing with increasing angle because of the decreasing normal momentum of the WP. For WPs incident from the tip, the tunneling probability is influenced by the vortices [5] of the probability current density caused by multiple internal reflections inside the tip. This effect produces a plateau in the $P_-(\theta)$ functions with a shallow minimum around normal incidence. Hence the form of P_- is mainly determined by the particular tip geometry. The $P_+(\theta)$ functions for the raft model have a diffraction grating like characteristic with a strong peak around the normal incidence and smaller shoulders around $30-40°$ caused by the interference between the resonant states on the individual tubes.

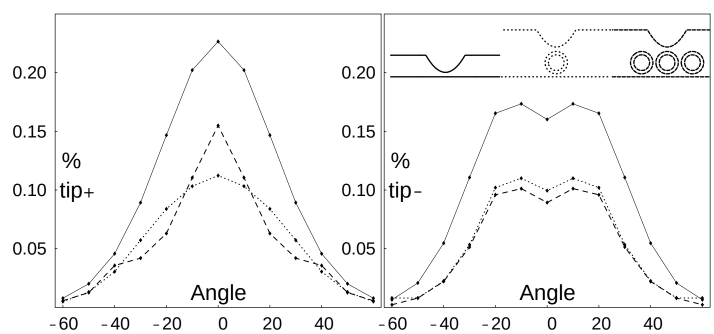

FIGURE 1. Angular dependent wave packet transmission probabilities for different numbers of nanotubes and for different tip polarities. Solid, dotted, and dashed line are for an STM tunnel junction with no nanotube, one nanotube, and a raft model of three nanotubes, respectively. Effective surfaces of the three model potentials are shown in the inset. 100% means the total transmission.

Fig. 2 shows the incidence energy dependence of the transmission probability of WPs with normal incidence through an STM tunnel junction with no CNT present

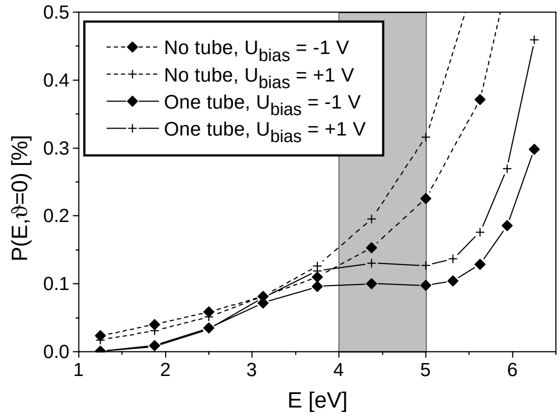

FIGURE 2. Energy dependent transmission of a wave packet incident from the normal direction for tip positive and negative $1\,V$ bias potential. Full (broken) lines are for one (zero) nanotube. The zero of the energy scale is always fixed to the band bottom of the *launching side* of the wave packet. On this energy scale always the states between $E = 4\,eV$ and $E = 5\,eV$ (shaded region on the figure) contribute to the tunnel current at zero temperature.

and through a CNT in the tunnel junction for positive and negative $1\,V$ biases. To model the non vanishing bias an electrostatic potential was added to the jellium potential. The tip, the CNT, and the support are assumed to be perfect conductors. The transmission for the STM tunnel junction with no CNT present follows an exponential like energy dependence characteristic of plane - plane tunneling. The presence of CNT, however, causes a plateau to appear between 3.8 and $5\,eV$. This plateau is a sign of resonant tunneling [2] caused by the two tunnel interfaces.

To estimate the tunnel current flowing through the real 3D junction we assumed that the the perpendicular-to-the-calculation-plane angle dependence of the transmission is like that of a plane-plane system and the tunneling channel is of cylindrical shape. $I(U_{bias})$ curves for the STM tunnel junction with no CNT present, for one CNT in the junction, and for three CNTs calculated with the assumption of a free electron like dispersion relation are shown in *Fig. 3 (a)*. All $I(U_{bias})$ curves of *Fig. 3 (a)* show some degree of asymmetry. These asymmetries are better displayed in the $I(U_{bias}) + I(-U_{bias})$ graphs of *Fig. 3 (b)*. The asymmetry of the tunnel gaps with CNTs are increasing with U_{bias} and has a much larger value than that of the STM junction with no CNT present. These asymmetries are of pure geometrical origin because of the free electron like DOS assumption. In our model the particular tip shape influences the structure of the probability current vortices produced in the tip and this effect is expected to influence the negative side of the STS curve when positive polarity means tunneling from sample to tip. In those STS measurements where larger tunneling current values were used during establishing the position of the STM tip before the feedback loop is switched off a point contact can occur between the CNT and its support. In this case unusual features are expected on the positive side of the STS spectrum while the negative side will

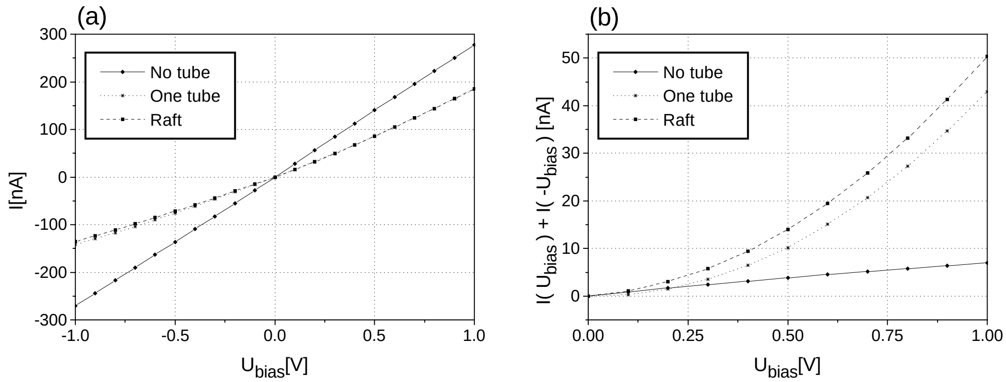

FIGURE 3. *a)* Tunnel current as the function of STM bias for an STM junction with no nanotube, one nanotube and for a nanotube raft. *b)* Tunnel current asymmetries for the curves in Fig. *(a)*.

not differ in shape from symmetric spectra but the magnitude of the tunneling current will increase significantly. These expectations are fulfilled by the experimental data [6]. The absolute values of our calculated currents are higher than those in STS measurements. This is mainly because in STM experiments the tunneling gap is determined in topographic mode. An $1\,nA$ current is expected at say $0.1\,V$ bias at gap of $0.4\,nm$. If U_{bias} is increased without modifying the gap value it would result a strong increase of the tunneling current. To avoid saturation of the tunneling current at bias values exceeding, say $1\,V$, when performing spectroscopy larger tunneling gap values are used than during topographic imaging.

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