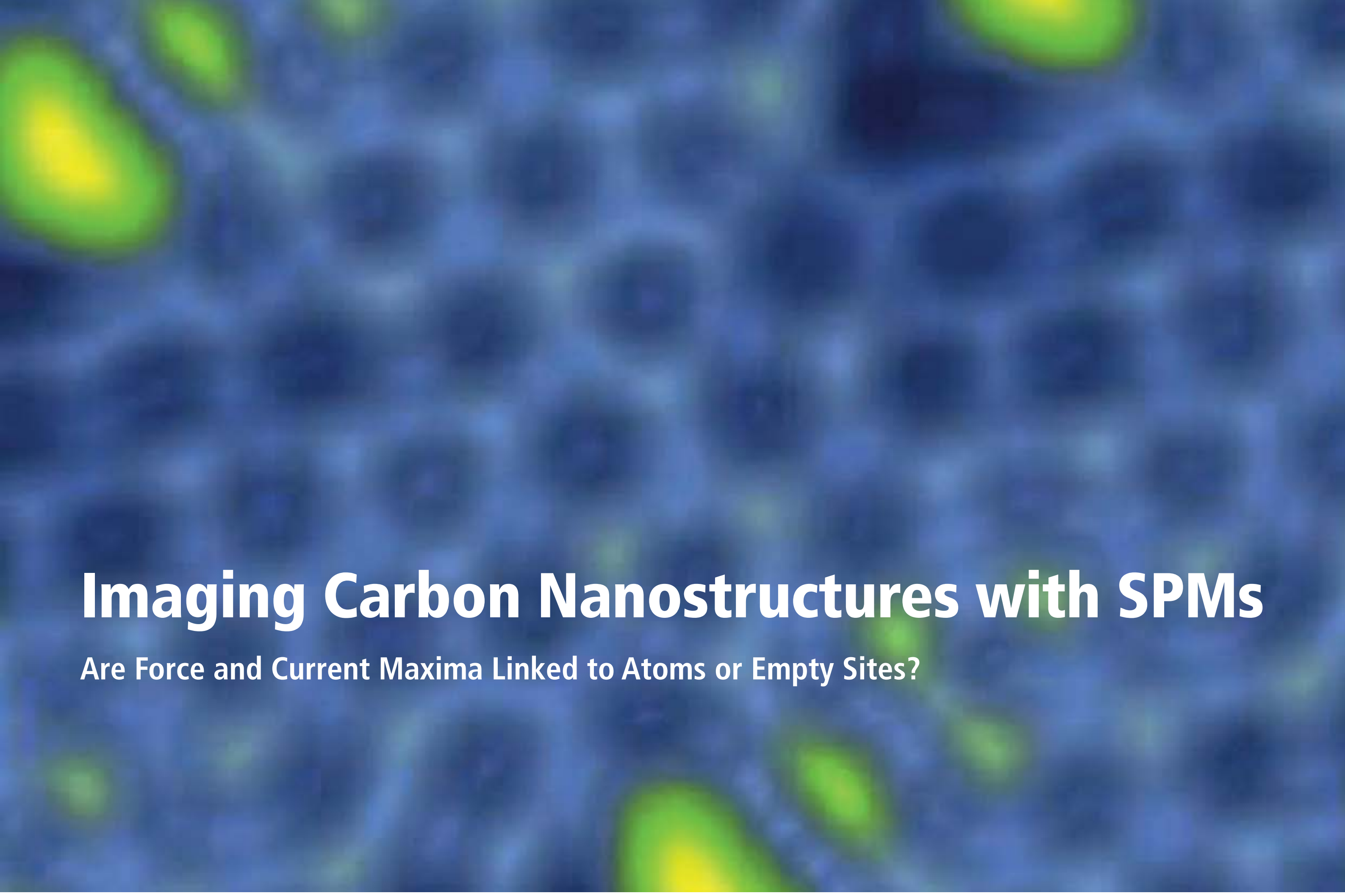

Imaging Carbon Nanostructures with SPMs

Are Force and Current Maxima Linked to Atoms or Empty Sites?

The unique mechanical and electronic properties of fullerenes, nanotubes, graphene and carbon nanoribbons make them very promising materials for nanotechnological applications. First-principles calculations of forces and currents between a tip and carbon nanostructures show that the rich variety of image patterns found in atomic-scale AFM and STM measurements can be rationalized in terms of the chemical reactivity of the tip and the distance range explored in the experiments.

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The Experimental Puzzle: Honeycomb versus Hexagonal Images

The simple honeycomb structure shared by these materials represents both a perfect testing ground and a fundamental challenge for STM and AFM with true atomic resolution (FM-AFM). Graphite can be imaged with atomic resolution even in ambient conditions but, after 25 years of research, there is no consensus yet whether the maxima in the atomic-scale images correspond to atoms or to the hollow sites. The first STM images of the graphite(0001) surface did not display the expected honeycomb pattern but a hexagonal arrangement of bright spots (fig. 1) [1]. The accepted interpretation relies on a subtle electronic effect [2]. The Bernal stacking makes the two surface atoms inequivalent. C_α atoms, with a nearest neighbor right below in the second layer, do not contribute significantly to the density of states (DOS) close to the Fermi level and only the C_β atoms are imaged as bright spots at low bias voltages. Although a honeycomb pattern should be recovered for larger biases, the experimental evidence accumulated [3], shows that STM images with a hexagonal pattern are overwhelmingly recorded over a broad range of bias voltages and distance operation conditions. The situation gets even more confusing when one realizes that images with hexagonal symmetry can be also linked with maxima at the hollow sites in the center of the hexagons.

The situation is also puzzling in FM-AFM, as we have experimental results from world-class groups showing either a hexagonal or a honeycomb array of bright spots [4–7]. STM and AFM experiments on graphite are difficult to interpret as carbon planes can be easily pulled out by the interaction with the tip, resulting in local contact for relatively far distances. Single wall carbon nanotubes (SWCNT), much stiffer in the normal direction, offer an excellent alternative to determine the variation of forces and currents with distance. FM-AFM images on SWCNT using semiconductor tips [6] only reach clear atomic contrast at small tip-sample distances. Force spectroscopy data on different sites show maximum attractive forces that are a factor of 10 smaller than those typical for semiconductor surfaces. Therefore, a van der Waals (vdW) tip-CNT interaction has been assumed and the bright spots in the images have been interpreted as hollow sites.

Force Contrast: The Role of Tip Reactivity

Understanding this puzzling situation requires a theoretical analysis that identifies unambiguously the interaction responsible for the atomic contrast in low-dimensional carbon materials and that can reconcile the apparently contradictory experimental results. To that end, we have carried out an extensive

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set of first principles calculations to map out the tip-sample interaction and the electronic currents between several tip apexes with different chemical reactivity and both a (17,0) SWCNT (with a radius close to the one used in the experiments) and a graphite(0001) surface [8]. For an accurate representation of the interaction, we combine density functional theory (DFT) calculations using the PBE exchange-correlation functional for the short-range (SR) chemical force with a semi-empirical atomistic approach for the vdW interaction [8].

The pattern that emerges from these calculations is that the tip reactivity plays a crucial role in the determination of the nature of the atomic contrast but this is always controlled by the SR chemical interaction and not by the vdW. These conclusions are illustrated by the force versus distance curves calculated on top of a carbon atom and on the hollow site for two representative cases: a Si tip with a dimer at the apex (fig. 1d) and a W tip (fig. 1e). With rather inert tips, the total force is attractive mainly due to the vdW contribution, but this interaction does not yield itself atomic contrast. SR interactions are basically repulsive (essentially the Pauli repulsion between electronic clouds) and force maxima correspond to the positions with lower electronic density like the hollow sites, resulting in a hexagonal pattern. For very reactive tips, particularly metallic ones, the SR attractive interaction dominates the total force and gives a honeycomb contrast with maximal forces on the atoms (fig. 1e). This enhanced tip-sample interaction is due to the high reactivity of the dangling bond in the outermost apex atom, that makes a change in the hybridization of the carbon atom on the nanotube (from sp^2 to sp^3) energetically favorable, resulting in the formation of a chemical bond. Beyond the force maximum, the interaction on the top site decreases due to the strong Pauli repulsion and there is a crossing of the force curves that results in force maxima on the hollow sites. Thus, our results predict a reversal of the FM-AFM image contrast for very close distances when metallic tips are used.

Can the Current be Larger on the Hollow Sites?

Having shown that the AFM contrast with metallic tips does depend on the tip-sample distance, the question that naturally arises is whether the trans-

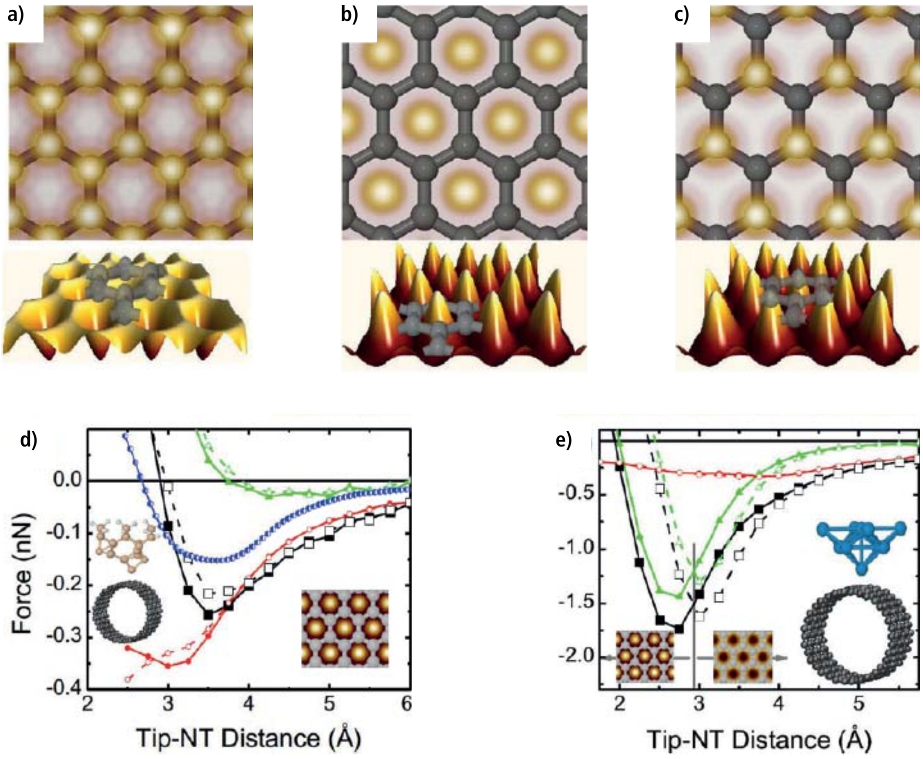

Fig. 1: Topographic STM (AFM) images reflect the displacement of the tip to keep the current (force) constant while scanning over the surface. Bright spots correspond to positions with the largest currents (forces) and, thus, to the highest retraction (largest tip-sample distance). (a) Maximal currents (forces) on the carbon atoms produce a honeycomb pattern of bright spots matching the underlying atomic structure. A hexagonal pattern is consistent with current (force) maxima either on three of the six atoms in the ring (c) or on the hollow sites (b).Tips with different chemical reactivity provide these different contrasts. (d) Total force (black) for a dimer-terminated Si tip and a (17,0) SWCNT. Open (solid) symbols correspond to the tip on a carbon atom (hollow site). The vdW interaction (red, circles) gives a common attractive background that sets the absolute force values close to the experiment [6] (blue circles) but the short-range interaction (green, triangles) provides the atomic scale contrast in the near-contact regime, with force maxima on the hollow site (inset). (e) Reactive tips, like a W tip, change locally the carbon sp2 hybridization and provide force maxima on the atoms in the attractive regime.

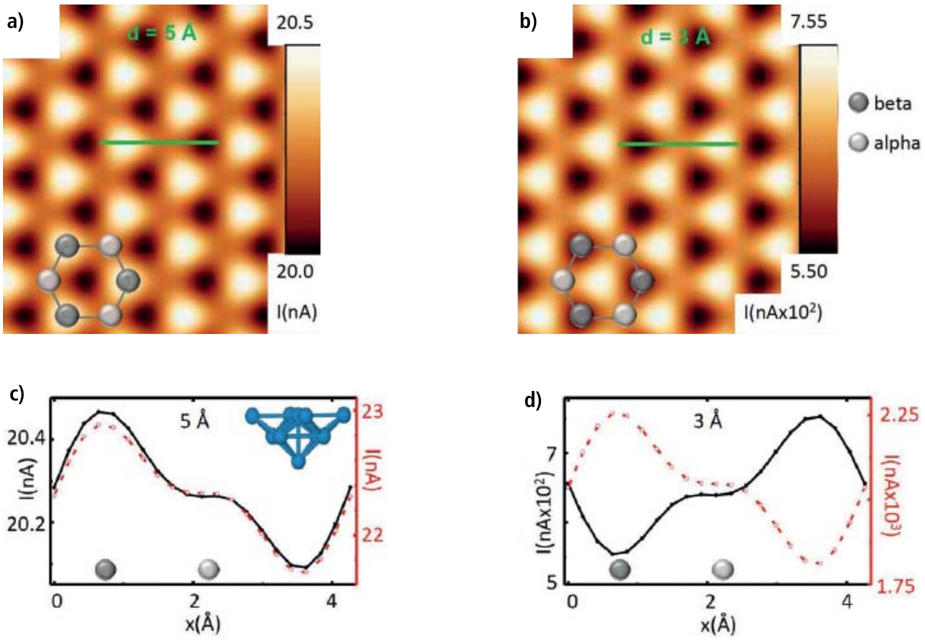

Fig. 2: Calculated constant height STM images on graphite(0001) (V=–300 mV), including multiple scattering effects, for a tip-surface distance of (a) 5 Å and (b) 3 Å. Both images display a hexagonal pattern but with maxima on either C_β atoms or hollow sites. (c-d) Line profiles, taken along the green line, show that multiple scattering contributions, not included in the common perturbative approaches (red), are needed to capture the contrast inversion found in the exact solution (black).

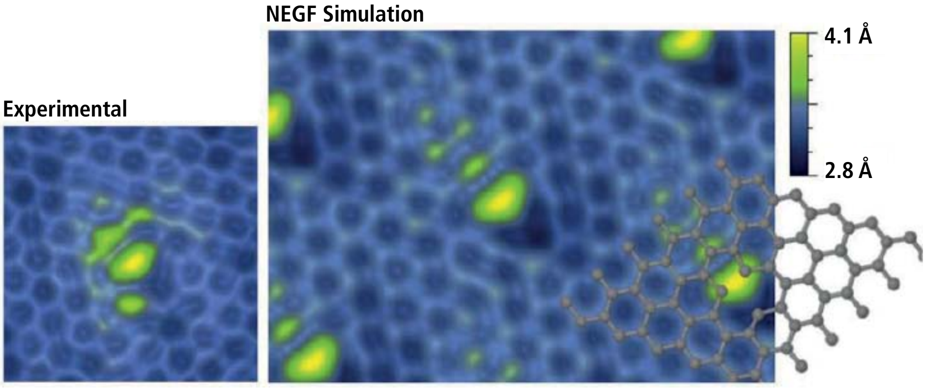

Fig. 3: Identification of a single carbon vacancy in the graphene/Pt(111) system. Experimental and calculated constant current STM images at V=+100 mV with the atomic model obtained from DFT calculations on a 6x6 unit cell superimposed. A non-equilibrium Green's function (NEGF) formalism with an idealized Pt apex with a single dz^2 orbital to represent the microscope tip has been used for the STM calculations. This model produces atomically resolved images in good agreement with the Moire patterns observed in the experiments [10].

port properties are also affected and conflicting STM images on graphite could be explained in terms of the operation conditions. We have carried out simulations of the current between a W tip and a graphene bilayer [8]. We map the first-principles hamiltonian onto a local orbital basis and use a non-equilibrium Green's function (NEGF) formalism that includes multiple scattering effects to all orders [9]. The critical importance of these effects in the evolution of the contrast can be clearly seen in the constant-height profiles (fig. 2) for a bias voltage of –300 mV (filled states). At typical tunneling distances, we reproduce the classical result: the C_β sites, yielding larger currents, correspond to the bright spots in the STM images. In the near-contact regime, multiple scattering effects make the large current on top of the carbon atoms to deviate from the exponential growth predicted by perturbative approaches (like Tersoff-Hamann or Bardeen Theory) and to saturate [9]. Therefore, at distances smaller than 4 Å, the hollow sites become the brighter spots, leading to a contrast inversion. Given the large normal compliance of graphite and the large tip-sample vdW forces for the typical STM tips (as no particular effort is put in sharpening them), we think that most of the STM experiments, even if nominally far from the surface, are probing this near-contact regime.

Unraveling the Structure of Defects on Graphene on Metal Surfaces (Pt(111))

After proving that we can have current maxima on the hollow sites, one may wonder whether STM would be able to reveal the presence of single-atom vacancies in these materials. We have studied this problem for a graphene layer grown on top of a Pt(111) surface [10]. Single C vacancies have been introduced by irradiating the surface with 140 eV Ar$^+$ ions. Contrary to the case of the graphite surface, we cannot directly identify in the STM images (fig. 3) the point defects generated by Ar sputtering with the threefold patterns predicted for single C vacancies on a free-standing graphene layer. Even in graphene/Pt(111), one of the weakest interacting graphene-metal systems, the interaction becomes stronger in the presence of defects and modify their structure. DFT calculations and STM simulations, using the same NEGF formalism mentioned above, help to unravel their nature. The comparison between theory and experiment (fig. 3) identifies the defects as single vacancies and correlates the main features in the image with the structure of the vacancy. In particular the heart-shaped, elongated protrusion corresponds to the C-C dimer formed to saturate two of the three dangling bonds left after the removal of the C atom.

Conclusions

This work shows that both DFT simulations and NEGF transport calculations are really powerful tools to unravel the contrast mechanisms in SPM imaging. When combined with STM/AFM instruments that record simultaneously the force and the current (which are already available commercially), they promise to pave the way for the atomic-scale characterization of the structure, chemical reactivity and nanotribological properties of complex oxides and organic systems.

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