Materials Today Physics 2 (2017) 35–39

Contents lists available at ScienceDirect

Materials Today Physics

journal homepage: https://www.journals.elsevier.com/materials-today-physics

Insights into van der Waals interaction between nanotubes and planar surfaces

Xiaorong Hou [a, 1], Weiqiang Lv [a, 1], Xian Jian [a, 1], Kechun Wen [a], Yinghua Niu [a], Minda Zou [a], Xingzhi Zhou [a], Weidong He [a, b, c, *]

[a] School of Energy Science and Engineering, University of Electronic Science and Technology of China (UESTC), Chengdu 611731, PR China
[b] Interdisciplinary Program in Materials Science, Vanderbilt University, Nashville, TN 37234-0106, USA
[c] Vanderbilt Institute of Nanoscale Science and Engineering, Vanderbilt University, Nashville, TN 37234-0106, USA

ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form
24 June 2017
Accepted 29 June 2017

Keywords:
Atomic force microscopy
Tip
Carbon nanotube
van der Waals interaction

ABSTRACT

Advanced microscopic technology opens up the opportunity of investigating the microstructure of novel materials and devices. In particular, high-resolution Atomic Force Microscopy (AFM) allows for the atomistic observation of materials for a variety of applications. To improve the imaging capability, several tip morphologies have been proposed to be employed in the AFM field. Among such morphologies, the carbon nanotube (CNT) has drawn extensive attention in recent years due to its high resolution and mechanical strength in imaging conditions. However, the exact theoretical basis for employing the nanotube in advanced AFM remains elusive up to this point. Here, we explore the theoretical basis for employing the nanotube morphology in advanced AFM. To do so, van der Waals (vdW) interaction between the nanotube and a planar disc, a key factor for achieving high imaging sensitivity, is evaluated. The results unanimously verify that nanotube morphology has unprecedented advantages over traditional cone-shaped AFM tips.

1. Introduction

Intrinsic surface states determine physicochemical properties of materials [1,2]. Resolving the feature of materials interface is a major research focus in condensed matter physics and materials science. Scanning probe microscopy (SPM) such as atomic force microscopy (AFM) is a technique employed frequently to study the surface structure at the nanoscale [3]. AFM is operated in three modes, which are contact mode, tapping mode and non-contact mode, respectively. The non-contact mode is often employed to probe electric, magnetic, and/or atomic forces of materials. In this mode, the AFM images are constructed by scanning the tip hovering ~5 nm–15 nm above the sample surface. AFM tips in non-contact mode are often applied with small oscillation so that the van der Waals (vdW) forces can be detected by recording the change of the physical characteristics of oscillating cantilevers, such as amplitude, phase and frequency [4–6]. The resolution of topographic images depends on the sensitivity of detecting variation in attractive vdW interaction since vdW interaction typically dominates the tip-sample interaction regardless of AFM work modes [7,8]. In the AFM test process, lessening the probe-tip blunting and maintaining the morphology of imaging tips are important considerations. Over the past decade, considerable efforts have been made to develop several types of novel AFM tips. In 1996, Dai et al. first introduced carbon nanotube (CNT) tips for SPM to improve the average resolution [9], and Akita et al. acquired a two orders of magnitude enhancement of AFM imaging resolution by using CNT tips as compared with the best Si tips [10]. CNTs have almost no wear [11] and exhibit pronounced mechanical properties such as high Young's modulus. In particular, CNTs are made up of graphene cylinders with length larger than 1 μm and diameters in the range of the 1 nm–20 nm for multiwalled CNTs (MWCNTs), and these features make CNT an excellent candidate for AFM tips with stable tip geometry [12,13]. The high imaging resolution by using CNT tips are considered typically to arise from the aforementioned unique morphologies and properties. Indeed, AFM imaging by using CNT tips is based on the tip-sample interaction which is similar to that of traditional conical tips [11,13]. Hence, comparison between tip-

* Corresponding author. School of Energy Science and Engineering, University of Electronic Science and Technology of China (UESTC), Chengdu 611731, PR China.
E-mail addresses: weidong.he@uestc.edu.cn, weidong.he@vanderbilt.edu (W. He).
[1] These three authors contribute equally to this work.

http://dx.doi.org/10.1016/j.mtphys.2017.06.004
2542-5293/

sample interactions for CNT tips and those for Si conical tips should be made to illustrate quantitatively the merits of CNT AFM tips. Such efforts are expected to facilitate the rational design of high-imaging-resolution/sensitivity CNT tips with optimized geometry. In this report, we investigate into vdW tip-sample interactions between a CNT and a probe planar disc and reveal the theoretical basis for understanding the high probing/imaging sensitivity of advanced AFM employing a nanotube morphology.

2. Models and calculation method

To derive the vdW interaction between a carbon nanotube and a planar sample disc, a geometrical model is built, as shown in Fig. 1a. A conventional cone tip with a disc sample is shown in Fig. 1b.

In Fig. 1a, two cylindrical coordinate systems are built by setting the origin points at the centers of the CNT bottom surface and the upper surface of the sample, respectively. The longitudinal x-axis and y-axis are along the central axis of the CNT and the disc, respectively. Let P_1 be any point in ω, and P_2 be any point in Ω. Then we get $P_1(b\cdot cos\vartheta, b\cdot sin\vartheta, x)$ and $P_2(a\cdot cos\varphi, a\cdot sin\varphi, y)$, where b and a are radial distances for P_1 and P_2, and ϑ and φ are angular coordinates of P_1 and P_2, respectively. We then have $0 \le \vartheta \le 2\pi$, $r \le b \le R, d \le x \le d + L\ 0 \le \varphi \le 2\pi, 0 \le a \le A$, and $-h \le y \le 0$. The volume element in ω is denoted as $\partial\omega = b\partial\vartheta\partial b\partial x$, and the volume element in Ω is $\partial\Omega = a\partial\varphi\partial a\partial y$. The separation between P_1 and P_2 is calculated by Eq. (1),

$$|P_1P_2|^2 = (x-y)^2 + a^2 + b^2 - 2ab\cos(\vartheta - \varphi) \quad (1)$$

and the vdW interaction between volume element P_1 and P_2 is calculated by Eq. (2) [14,15].

$$vdW = \iint \frac{\lambda q_1 q_2}{|P_1P_2|^6}\partial\omega\partial\Omega \quad (2)$$

where q_1 and q_2 are the atomic concentrations of the tip and the sample, respectively, and λ is the vdW constant. For the calculation of vdW interaction, we set $\lambda q_1 q_2 = 1$ and all vdW interactions calculated in this study have a unit of $\lambda q_1 q_2$. So only the geometrical factor of the AFM tips is discussed regardless of the tip materials. By integrating all the volume in Ω and all the volume in ω as given in Eq. (3), we can evaluate the vdW between the CNT tube and the sample disc.

$$\mathrm{vd}W_{tube} = \int_{-h}^{0}\int_{d}^{d+L}\int_{r}^{R}\int_{0}^{A}\int_{0}^{2\pi}\int_{0}^{2\pi} \frac{\lambda q_1 q_2}{\left((x-y)^2 + a^2 + b^2 - 2ab\cos(\vartheta-\varphi)\right)^3} ab\partial\varphi\partial\vartheta\partial a\partial b\partial x\partial y \quad (3)$$

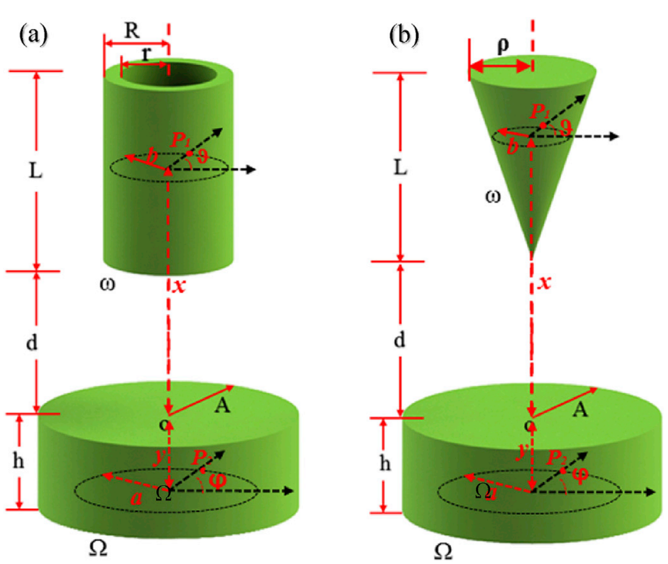

Fig. 1. (a) A geometrical schematic of a carbon nanotube AFM tip with a disc sample; (b) A geometrical sketch of a conventional AFM tip with a disc sample. ω stands for the CNT tip or the cone tip, and Ω is the sample disc. Both CNT and cone tips have the same length of L, and the same separation of d between the tip and the sample. The sample discs both have a radius of A and a height of h. The CNT tip has an inner radius of r and an outer radius of R. The cone tip has an upper surface with a radius of ρ, $\rho^2 = 3(R^2 - r^2)$.

A similar method is employed to calculate the vdW interaction between the cone tip and the sample disc. The details of the numeric integration as well as the integration for the vdW interaction between cone tips and samples are provided in the Supporting Information.

3. Results and discussion

CNTs with various radii, wall thicknesses and lengths can be synthesized to be employed as AFM tips [13,16,17]. Fig. 2 shows the effect of inner (r) and outer (R) radii of CNTs on the vdW interaction between the tip and the sample disc. As shown in Fig. 2a, at a fixed R, vdW interaction decreases with increasing r for a CNT tip. For instance, As R is 12 nm, the vdW interaction decreases from 14 to 2.5 with increasing r from 0 nm (carbon cylinder) to 11 nm (single wall carbon nanotube with 1 nm wall thickness). As R is 20 nm, the vdW interaction decreases from 40 for a carbon cylinder to 4 for a single wall carbon nanotube. The results indicate that the CNT is more sensitive to an increase in the wall thickness of CNT at a given outer radius of CNT tips. Thus, with the same outer diameter, multi-walled CNT is superior to single wall CNT AFM tips based on the superior tip force sensitivity. At fixed r, vdW interaction increases significantly as the tip outer radius increases for both CNT tips and cone tips, as shown in Fig. 2a and b. However, as the outer tip radius increases, the lateral resolution of the AFM imaging decreases dramatically [18,19]. An optimized size of the AFM tip must be selected to balance the sensitivity with resolution. To compare the vdW interaction of cone tips with CNT tips, the length and volume for the cone tip are kept the same as the CNT tip, that is, $\rho^2 = 3(R^2 - r^2)$. It can be found from Fig. 2b that the vdW interaction between the cone tip and the sample is much weaker than that of the CNT tip with the same parameters. For instance, as R is 12 nm, vdW interaction is 14 for CNT and only 0.08 for cone tip as $r = 0$. vdW interaction is 2.5 for CNT and only 0.01 for cone tips as $r = 9$ nm. Therefore, the force sensitivity of CNT tips is much higher than that of conventional cone tips. Fig. 2c–d shows vdW interaction *versus* r with different tip lengths (L). As shown in Fig. 2c, compared to the change of inner radii, the impact of the length of the CNT tip on vdW interaction between a CNT tip and a sample