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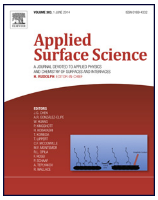

Simulated non-contact atomic force microscopy for GaAs surfaces based on real-space pseudopotentials

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ABSTRACT

We simulate non-contact atomic force microscopy (AFM) with a GaAs(1 1 0) surface using a real-space *ab initio* pseudopotential method. While most *ab initio* simulations include an explicit model for the AFM tip, our method does not introduce the tip modeling step. This approach results in a considerable reduction of computational work, and also provides complete AFM images, which can be directly compared to experiment. By analyzing tip-surface interaction forces in both our results and previous *ab initio* simulations, we find that our method provides very similar force profile to the pure Si tip results. We conclude that our method works well for systems in which the tip is not chemically active.

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1. Introduction

Scanning probe microscopy (SPM) is a powerful technique to explore surface structures and nano-scaled materials [1]. During the last few decades, it has broadened our understanding of not only surface physics and chemistry, but also structure of molecules. The history of SPM began with the invention of the scanning tunneling microscope (STM), which measures quantum tunneling current between a probe and a sample [2]. As the tunneling current is highly sensitive to the tip-sample distance, STM is able to create very high resolution images. While STM has been successful in many applications including conducting and semiconducting materials, it does not always provide direct structural information of the sample as it probes the electronic states close to the fermi level and not the atomic structure. Also, it requires conducting materials for the sample to create tunneling current, which becomes a barrier to the use of STM in insulators.

Atomic force microscopy (AFM) is one mode of SPM that has a few significant advantages over STM. The most important aspect of AFM is its applicability to a wide range of materials as it measures forces acting on a probe from the sample and not a tunneling current. AFM is capable of atomic resolution imaging, which has enabled researchers to reveal many complicated surface structures such as the Si-(1 1 1) 7×7 reconstructed surface [3,4]. Moreover, recent AFM studies have been used to investigate complex nanostructures [5–7]. As a result, it has become the most widely used technique in studying insulating surfaces, nano-structured materials, and biomaterials [8–10].

Although AFM has been applied successfully in studying many surface structures, there can be uncertain and ambiguous results owing to various experimental conditions. As such, the interpretation of experimental AFM images should be examined carefully by coupling with theoretical simulations. However, first-principles based AFM simulations are usually arduous since the force scanning process involves a three-dimensional motion of the tip, *i.e.*, a raster scan and a vertical vibration. The interaction energy has to be calculated for each position with a small spacing in the path of the tip, and accurate energies require a large number of calculations even for a small system [11]. Another difficulty in theoretical simulations may stem from modeling the tip [12,13] since the exact morphology of the tip is unknown.

Recently, an efficient first-principles simulation method for non-contact AFM was proposed by Chan et al. [14]. This method can be used to calculate the tip-surface force without explicit modeling the tip. With the formalism, the force and frequency shift are directly calculated from only the electronic structure of the sample. This not only eliminates the arbitrary model for the tip, but also dramatically reduces the total number of calculations since the three-dimensional motion of the tip is not required. This method has been successfully applied to large surface structures such

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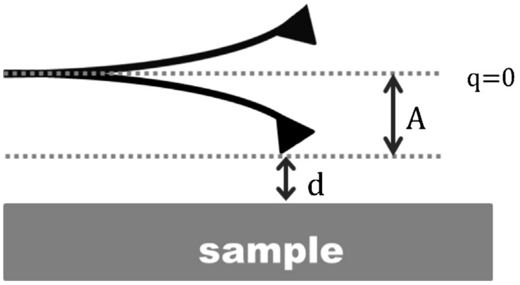

Fig. 1. A simple diagram of the tip motion. $q = 0$ indicates the equilibrium tip-surface position, d is the tip turning point, and A is the oscillation amplitude of the tip.

as Si(1 1 1)-7 × 7 reconstructed surface, Ag/Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$)$R30°$ surface, and Ge/Si(1 0 5)–(1 × 2) surface, and demonstrated qualitatively comparable AFM images.

In spite of the success, some systems may require a careful investigation of the tip. Implicit in the theory of Chan et al. is the assumption of a "chemically inert" tip. In some cases, this assumption may not be valid. For example, AFM measurement for the TiO_2(1 1 0) surface exhibits three qualitatively different contrast modes, and it is not rare to observe the contrast change even within the same AFM experiment [15]. This implies the AFM tip can be contaminated by surface atoms or impurities [12]. In such cases, our method can be used to assess the role of the tip by providing images that are tip independent.

Here we examine non-contact AFM imaging by following a similar approach to Chan et al. [14] based on a real-space implementation of pseudopotentials constructed using density functional theory [16]. Our real-space method is especially useful for partially periodic system such as molecules, wires, surfaces, and interfaces because no artificial periodicity in the non-periodic direction is required [17]. We choose to study the GaAs(1 1 0) surface because it holds a simple structure with no surface reconstruction that has been extensively studied.

2. AFM theory

True atomic resolution in AFM can be obtained by the frequency modulation operating mode in an ultra-high vacuum environment [4,18]. With these conditions, the morphology of the atomic structure is captured by a small frequency change of the oscillating tip. The theory of motion for the tip has been reported in many previous studies [19–24]. A common approach is to assume the system is a one-dimensional oscillator with an additional force that depends on the tip-surface distance. Fig. 1 shows the schematic of the tip motion. The tip oscillates with the resonance frequency f_0, which is a material-dependent parameter. In most experiments, the amplitude of the motion of the tip is larger than a typical tip-surface interaction distance [25]. In this case, the frequency change can be considered to be a small perturbation. By following the Hamilton-Jacobi formalism, a general expression for the frequency shift can be written [19,26]:

$$\begin{aligned}\Delta f &= -\frac{f_0}{2k_0A^2} < F_{ts} z > = -\frac{f_0^2}{k_0 A}\int_0^{\frac{1}{f_0}} F_{ts}(d + A - A\cos(2\pi f_0 t))\cos(2\pi f_0 t)\mathrm{d}t \\ &= \frac{f_0}{k_0\pi A^2}\int_{-A}^{A} F_{ts}(d + A - q)\frac{q}{\sqrt{A^2 - q^2}}\mathrm{d}q \\ &= \frac{f_0}{k_0\pi A^2}\int_{-A}^{A} -\frac{\partial F_{ts}(d + A - q)}{\partial q}\sqrt{A^2 - q^2}\mathrm{d}q \qquad (1)\end{aligned}$$

where F_{ts}, f_0, k_0, A, and d are the tip-surface force, resonance frequency, spring constant, oscillating amplitude, and distance from the surface to the tip turning point, respectively.

Most nc-AFM simulations compute the tip-surface force by calculating the gradient of the tip-surface total energy with respect to the tip-surface distance. If the electronic influence of the surface on the tip is treated as a small perturbation, the tip-surface interaction energy can be written as

$$E_{ts}(\mathbf{r}) = \int |\phi(\mathbf{r}' - \mathbf{r})|^2 V_{ts}(\mathbf{r}')\mathrm{d}\mathbf{r}', \qquad (2)$$

where $\mathbf{r}$, V_{ts}, and ϕ are the position of the tip, the potential on the tip generated by surface atoms, and the electronic state of the tip, respectively [14]. We assume the tip does not affect surface structure as expected in the limit of a small perturbation. F_{ts} can be described by expanding the potential to the first-order around the tip position $\mathbf{r}$:

$$\begin{aligned}F_{ts} &= -\nabla E_{ts}(\mathbf{r}) \simeq -\nabla V_{ts}(\mathbf{r}) - \nabla[\nabla V_{ts}(\mathbf{r})\int |\phi(\mathbf{r}' - \mathbf{r})|^2(\mathbf{r}' - \mathbf{r})\mathrm{d}\mathbf{r}'] \\ &= -\nabla V_{ts}(\mathbf{r}) - \nabla[\nabla V_{ts}(\mathbf{r})\cdot\mathbf{p}] = -\nabla V_{ts}(\mathbf{r}) - \alpha\nabla(|\nabla V_{ts}(\mathbf{r})|^2), \qquad (3)\end{aligned}$$

where $\mathbf{p}$ is the polarization of the tip, assumed to have a linear relation to ∇V_{ts} by α, the polarizability of the tip material. The first term is a monopole caused by the electrons of the tip, which is canceled by the ionic potential of the tip if the tip is neutral. In this setting, the force acting on the tip is now proportional to the dipole interaction,

$$F_{ts}(\mathbf{r}) \approx -\alpha\nabla(|\nabla V_{ts}(\mathbf{r})|^2). \qquad (4)$$

The tip-surface potential is obtained by the hartree and the ionic potential from DFT calculations: $V_{ts} = V_{hart} + V_{ion}$. The exchange-correlation potential is not included in V_{ts} because the tip is treated as a classical object.

The calculated tip-surface force from Eq. (4) can be inserted to Eq. (1) to compute the frequency shift. Since V_{ts} decays very fast in vacuum, the most relevant integration region is only a couple of angstroms near the tip-surface turning point (d in Fig. 1). Therefore, the integration region in Eq. (1) can be reduced from $(-A, A)$ to $(-A, -A+2\Delta)$, with Δ chosen to be small compared to A.

3. Computational details

All calculations were performed with real-space pseudopotentials with the local density approximation for the exchange-correlation functional from Ceperley and Alder [27]. The Kohn-Sham equation is solved on a grid using a high-order finite difference method [28,29]. The convergence of the total energy is controlled by the grid spacing, which was taken to be 0.35 a.u. We applied the grid spacing of 0.25 a.u. for composing AFM images in order to increase the resolution. We used Troullier-Martins pseudopotentials [30] with a partial core-correction for the Ga atom. The parameters used to generate the pseudopotentials were from previous work by Kim and Chelikowsky for vacancies in the GaAs surface [31]. With these pseudopotentials, we obtained a lattice parameter of 5.59 Å, which agrees within 1% of the experimental value [32].

Our simulation cell for the GaAs(1 1 0) surface contains a 1 × 2 surface unit with five atomic layers that corresponds to the slab thickness of 17.79 Å, and 21 Å of a vacuum was inserted. In order to passivate the dangling bonds on the opposite side of the surface, we generated hydrogen-like pseudopotentials with a $1s^{0.75}$ and $1s^{1.25}$ ionic configuration for Ga and As atom, respectively [33]. The $\vec{k}$-points were generated by a Monkhorst-Pack scheme [34] with a 4 × 3 mesh. Geometry optimization was performed until the force

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