A model of the interaction of ionic tips with ionic surfaces for interpretation of scanning force microscope images

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Scanning force microscopy (SFM) is an increasingly popular tool in surface studies. With the promise of lateral as well as vertical atomic resolution, its use is sure to become widespread in fields such as catalysis and crystal growth. However, the interpretation of the observed images is still unclear and therefore theoretical models are very important for an understanding of the imaging mechanism. We present a review of our recent calculations on the interaction between ionic tips and ionic surfaces and its effects on the scanning process. Our theoretical model of the SFM experiment combines an atomistic treatment of the interaction between a crystalline sample and the nanoasperity at the end of the tip with a semiemipirical treatment of the mesoscopic van der Waals attraction between tip and surface and the macroscopic parameter of cantilever deflection. These static calculations based on total energy minimisation were used to determine the surface and tip geometries and energy as a function of tip height at each point of a scan. Scanlines of the perfect (001) surfaces of LiF and MgO were studied at different constant vertical forces exerted on the tip with and without jump to contact. Although scanlines showing lattice periodicity were obtained in some cases, the calculations demonstrate that the tip–surface interaction is a collective phenomenon with the tip probing several rows of surface ions. The calculations demonstrated a wide range of deformations of the tip and sample during a surface scan, and the (often reversible) interchange of material between the tip and sample. The conditions required for the resolution of point defects as well as the mechanism of friction are discussed.

Keywords: alkali halides; magnesium oxide; surfaces; point defects; atomistic modelling; tip–surface interaction; scanning force microscope imaging

1. Introduction

The force between two samples in contact arises from both microscopic and
mesoscopic interactions and depends on the shape and constitution of the samples, the surrounding media, and the surface micro-structure as revealed by extensive studies using surface apparatus (SFA) (see, for example, refs. [1–7]). Unlike SFA, the scanning force microscope (SFM) is capable of measuring the force between a sharp tip and a sample with high spatial resolution along the surface. Several recent reviews of the technique can be found in refs. [8–15]. The SFM has been used to measure the force dependence on the distance between the tip and surface, which is called force spectroscopy, and the tip position as it scans the surface continuously along some trajectory. The latter information can be proposed [14] and presented in the form of three-dimensional topographic maps which can be interpreted as a surface image. Simultaneously, one can measure variations in the friction force between the tip and sample as a function of tip position [16–19]. In some cases, both topographical and friction force images demonstrate atomic periodicity (see, for example, refs. [19–22]). It is indeed very tempting to interpret atom sized features periodically arranged in these images as individual atoms or molecules.

The SFM perhaps finds its greatest utility in the study of insulators, where scanning tunnelling microscopy is usually not an option. Ionic and ionic–covalent materials comprise one of the largest classes of insulators and have wide applications in surface science and catalysis. Furthermore, the most widely used SFM tips have Si$_3$N$_4$ or SiO$_2$ surfaces, which are also fairly ionic materials. One of the most fascinating goals of the further development of SFM is the observation and study of individual surface structures of atomic dimensions, such as steps, kinks and point defects. Detailed knowledge of microscopic structures of these surface features and their modifications due to chemical and physical processes is vital for our understanding of catalytic and many other surface processes. Several SFM images interpreted as presenting defects at ionic surfaces have already been reported [20,23–25]. Modifications of the surface structure during photo-induced decomposition of alkali halides have been studied using SFM [26].

It is the aim of this paper to discuss the interpretation of the SFM images of ionic surfaces on the basis of the results of atomistic modelling of the tip–surface interaction and surface scanning. We believe that atomistic modelling including the effects of both mesoscopic and microscopic forces in a realistic way are an important part of the understanding and utilisation of SFM, particularly in UHV experiments.

The long-range mesoscopic forces [3,11] between tips and surfaces include the van der Waals attraction of the macroscopic tip to the sample [27–31], a capillary force when imaging in liquid or air due to the presence of fluid films at the surface (see, for example, ref. [32]), and an electrostatic force due to patch charges and the surface charging after cleavage [11]. In intimate contact, the repulsive and attractive short-range forces between a smaller number of tip and sample atoms in the contact area play a decisive role in regulating the force equilibrium. In order to have a convenient terminology, we will refer to these latter forces as comprising the chemical interaction force between the tip and sample. The chemical forces which