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Force Field Spectroscopy in Three Dimensions

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Abstract. Atomic resolution images in noncontact atomic force microscopy (NC-AFM) reflect planes of constant frequency shift. To draw conclusions on the chemical activity at specific surface sites, however, the force acting between tip and sample should be known locally rather than the frequency shift. This is not an easy translation due to the nonlinear nature of the relationship between the two.

To overcome this problem, several groups have developed an extension to NC-AFM, dynamic force spectroscopy, which allows the precise, distance-dependent measurement of tip–sample forces. The forces are determined from frequency shift vs. distance curves by mathematical analysis. By combining many of these curves in a raster grid, the full three-dimensional surface force field can be probed with atomic resolution as it extends into vacuum. This chapter reviews experiments performed on NiO, NaCl, KBr, and graphite that illustrate the strengths and weaknesses of the different experimental approaches as well as the type of results that can be obtained.

5.1 Introduction

Since its invention in 1986 [1], the success of atomic force microscopy (AFM) roots in its combination of high resolution imaging capabilities and broad versatility, as it is capable of imaging almost any type of surface without the need for tedious sample preparation. Force microscopy relies on the detection of interaction forces between a raster-scanned sharp tip and the investigated surface, with the corresponding signal being recorded as a function of the tip’s lateral position. Typically, finite tip–sample contact areas cause the net interaction to be averaged over the often dozens or even hundreds of atoms involved in the process of contrast formation, with individual atom–atom interactions not explicitly being exploited in conventional AFM imaging modes.

By employing atomically sharp tips in conjunction with the right experimental approach, it is nevertheless possible to measure signals that are dominated by interatomic forces caused by just the tip’s foremost atom. To avoid the above-mentioned averaging effect due to the formation of tip–sample...
contact areas comprising multiple atoms, “dynamic” modes, that is, modes where the tip is oscillated close to the surface, are usually being applied [2,3]. If the tip is scanned in a horizontal raster, the corresponding approach is called dynamic force microscopy (DFM) and enables atomic resolution imaging on many different material classes, including metals [4–6], semiconductors [3,7–10], and insulators [11–14]. Alternatively, dynamic mode operation also allows the measurement of the distance-dependent tip–sample forces (“force distance curves”) at specific lattice sites, which is then referred to as dynamic force spectroscopy (DFS) [15–19]. Recently, combination of the two abilities has culminated in the chemical identification of surface atoms [20]. Moreover, it has been demonstrated how a systematic acquisition of adjacent force distance curves allows to determine three-dimensional (3D) atomic force fields above the sample surface [21,22].

The recent growing interest [23–28] in the force field technique stems from several aspects. From the technical perspective, the availability of 3D atomic-scale force field maps facilitates assessing lateral relaxations of the tip–sample contact occurring during the approach as well as experimental artifacts like piezoelectric drift. From the scientific viewpoint, characterization of the vertical force field allows to calculate the potential energy barriers [23] and landscapes [27].

Experimental access to the spatial variation of the potential energy with sublattice resolution is difficult. Conventional techniques [29] rely on the measurement of the dynamic behavior of test adsorbates by, for example, diffusion experiments and field emission techniques [30]. Direct observation of adatom motion with the field ion microscope [31] or the scanning tunneling microscope [32] is possible, but limited to conducting surfaces. Potential energy barriers can be extracted from those experiments (cf. Fig. 5.1a), but the full spatial characterization of the energy landscape remains a challenge. Ideally, one would measure the site-specific variation of the interaction energy between a test molecule and the substrate. A viable technical solution is the measurement of forces between a single atom-terminated sharp asperity and a flat surface, a basic geometry that is naturally instantiated by scanning probe microscopy techniques (Fig. 5.1b).

An added benefit of this approach is that it also recovers lateral atomic forces [22,24], which has been exploited to determine the lateral force needed to move an atom on a surface [27]. A combination of the simultaneously measured lateral and vertical forces allows to obtain atomic scale force vector fields [33]. Finally, high-precision, low-drift measurements performed at low temperature could successfully probe the 3D force field of graphite with picometer resolution in $x$, $y$, and $z$ and piconewton force resolution [34]. From this dense three-dimensional raster, force maps in all directions could be obtained at all locations within the covered space. This lead in particular to atomically resolved true force images in topview perspective rather than just to vertical $xz$ maps.