Pushing Resolution Limits of Functional Imaging to Probe Atomic Scale Properties

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PERSPECTIVE

ABSTRACT Recent advances in probing properties at very high spatial resolution are enabling remarkable progress in understanding local physical and chemical phenomena. Additionally, these observations raise questions as to the ultimate limit of resolution in what are considered continuum properties. As complex property probes achieve increasingly high spatial resolution, they approach the transition between continuum and atomistic descriptions of properties. The recent observations imply that further advances are imminent.

The past decade has witnessed exciting advances in nanoscience that span topics as diverse as computational logic, biosensors for proteomics, room temperature quantum dots, and nanoparticle toxicity. The ability (or inability) to probe properties at the nanometer/molecular scale limits almost every endeavor involving nanotechnology from fundamental science to manufacturing. While the scientific community has been able to characterize structure at the atomic level for many decades with electrons, photons, X-rays, neutrons, and so forth, it was the advent of scanning probe microscopy that enabled access to local properties. This Perspective discusses the potential of scanning probe microscopy for obtaining information on complex properties of nanometer-scale systems. The ability to probe these diverse properties with atomic-scale spatial resolution will contribute to tremendous advances in chemistry, physics, and materials science.

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It has been over 20 years since the invention of scanning tunneling microscopy (STM)[1] and atomic force microscopy (AFM),[2] and these revolutionary approaches to examining atoms and molecules are widely used. In the intervening years, a vast array of scanning probes have been developed, many of which address local properties. A series of examples are presented here that illustrate the current state of the field and suggest that extremely high spatial resolution, sometimes at the atomic level, of a wide range of properties is possible. If realized, the unanticipated spatial resolution of such diverse properties would enable tremendous advances in chemistry, physics, and materials science. Note that this Perspective is by no means a complete review and readers are referred to reviews in the literature (cited herein) for further information.

The scanning probe tools are based on the interaction between a small tip and a surface, illustrated in Figure 1 for the AFM configuration. This interaction is inherently complex, containing simultaneous contributions from electrostatic, magnetic, mechanical, and atomic bonding forces, which operate over a range of tip−surface separations. In traditional applications, instrumental conditions are set such that one or another contribution dominates the interaction, greatly simplifying the situation. However, when probing in a single interaction regime, the tip−sample interaction contains a great deal of information. The challenge is to extract this information in a quantitative manner with the highest possible spatial resolution. Strategies to isolate complex properties include modulating signals between the sample and tip, utilizing multiple frequencies, independently varying gradients across samples, and so on. Figure 1 suggests some of these configurations.

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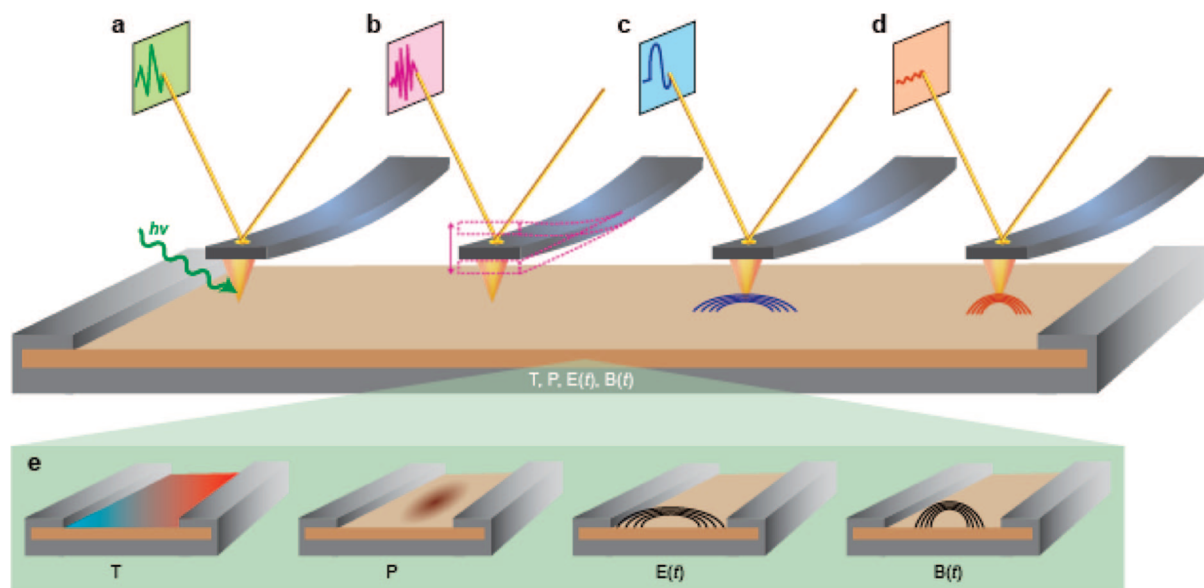

Figure 1. Accessing properties through multiple modulations in scanning probe microscopy, including (a) coupling light into the tip−sample junction, (b) deflection of the cantilever to access information about the direct properties of the sample, (c) electric field modulation, and (d) magnetic field modulation. (e) The parameters of the sample can also be modulated, including temperature, pressure, and the electric and magnetic fields with lateral gradients.

For the sake of discussion, it is useful to categorize scanning probes (somewhat arbitrarily) according to complexity: direct, first-, second-, and third-order. Direct properties are those that arise from STM and noncontact AFM (nc-AFM) configurations, in that these extract properties from the original signal. First-order complexity comes from extracting nonmechanical properties from the mechanical response of an oscillating cantilever, that is, electrostatic and magnetic force microscopy. Second-order complexity refers to the use of modulating signals at the tip−sample junction. Exploiting the frequency dependence, lateral sample perturbations, or the interdependence of multiple properties is referred to as third-order complexity.

Properties from STM and AFM. Since direct properties stem from STM and AFM, it is not surprising that they have inherently high spatial resolution and lead to elegant fundamental results. Davis and colleagues demonstrate an interesting slant in imaging electronic properties with atomic resolution.[3] In some superconducting oxides, the conductivity arises from the removal of oxygen, which significantly alters the correlated states. In strongly correlated electron systems, the density of states (DOS) may not be symmetric with respect to the Fermi energy. The local asymmetry in state density is manifested in tunneling spectra (*I*/*V* curves) and is detectable with STM. The ratio of differential conductance at positive and negative bias is used to map the degree of symmetry. Figure 2a shows a conductance ratio map of $Ca_{1.88}Na_{0.12}CuO_2Cl_2$. With great attention to experimental noise reduction and consideration of potential artifacts, atomic resolution is achieved in conductance ratio maps and correlated with topographic STM images. The similarity of the DOS symmetry maps on compounds with obvious differences in atomic structure led the authors to associate the symmetry variations with an electronic cluster glass in the underlying Cu−O plane.

Charge density waves are an interesting example of correlated electron interactions that result in local variations in electronic properties. Almost at its invention, STM was used to image charge density waves at room temperature in chalcogenides[4] and continues to be used on a wider range of compounds. Recently, the phase transitions responsible for the appearance of charge density waves have been observed in real space on oxide surfaces.[5,6] Again taking advantage of the fact that STM is sensitive to variations in state densities, it can be used to distinguish between the atomic structure and the spatial variations in charge. Figure 2b illustrates this phenomenon on $K_{0.3}MoO_3$ using temperature-dependent STM acquired below the phase transition, at which point the lattice and charge density wave structures separate. The STM contrast includes both atomic topography and charge density variations. The two periodicities are separated using a Fourier transform to identify the components due to the atomic structure and those due to the charge density wave and superimposes these on a reconstructed image (inset of Figure 2b). Thus, spatial maps of the charge (the property) are separated from and compared to those of the atomic structure.

The last 5 years have seen exciting advances in the understanding of AFM at atomic resolution.[7−9] In the case of nc-AFM, a tip is oscillated with precise control so close to a surface that bonding forces are

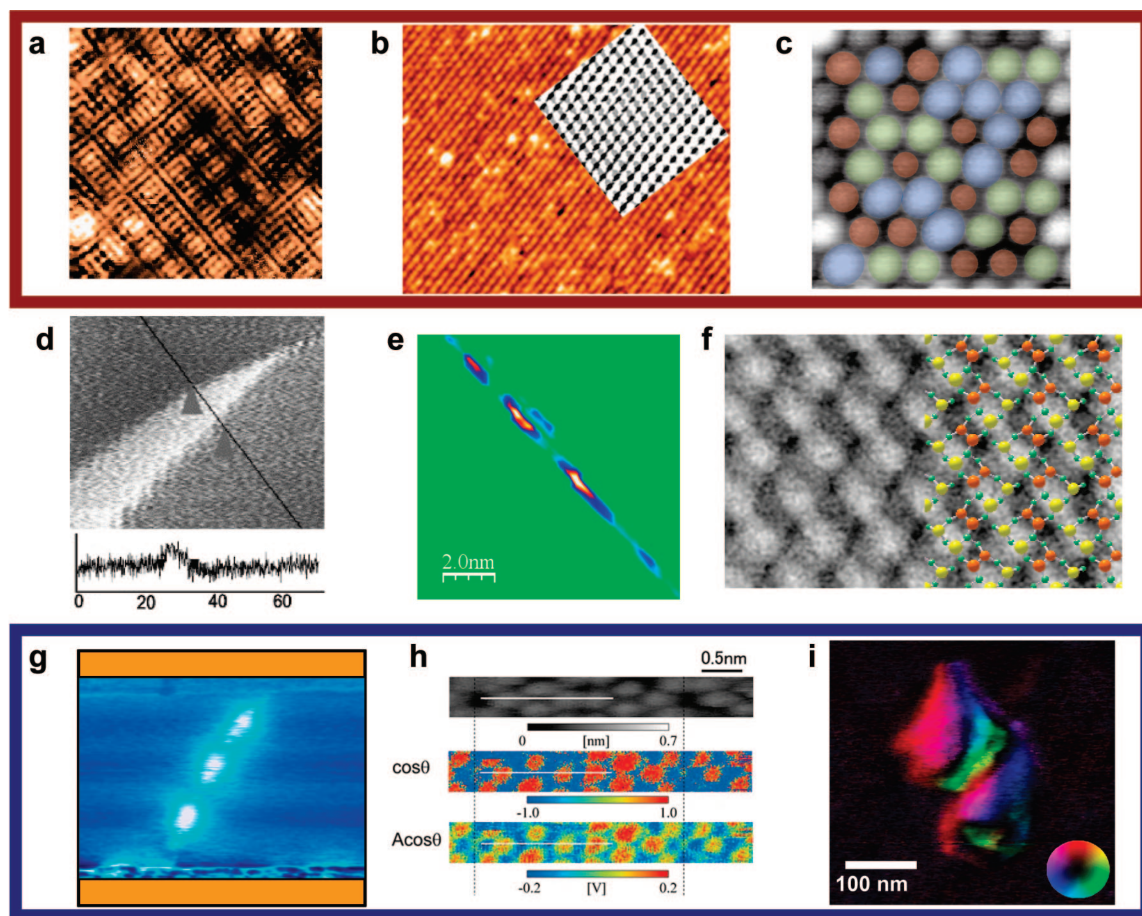

Figure 2. Characterization of spatially resolved properties: (a) 12 nm × 12 nm map of the conductance asymmetry at ±150 mV on $Ca_{1.88}Na_{0.12}CuO_2Cl_2$, a superconductor. The bright contrast indicates high symmetry in density of states; dark contrast indicates asymmetry. Reprinted with permission from ref 3, copyright 2003 by AAAS (www.sciencemag.org); (b) 17 nm × 15 nm STM image (V_s = +1.5 V, I_t = 0.2 nA, W tip) of $K_{0.3}MoO_3$ (20$\bar{1}$) containing both atomic structure and charge density. The reconstruction from reverse Fourier transform filtering of the two periodicities of the atomic structure and charge density waves. Reprinted with permission from ref 6, copyright 2007 by The American Physical Society. (c) 4.3 nm × 4.3 nm nc-AFM image of Si(111) with atoms color-coded for chemical force in force spectroscopy; blue, green, and red correspond to forces calibrated and associated with Sn, Pb, and Si atoms, respectively. Reprinted with permission from ref 10, copyright 2007 by Macmillan Publishers Ltd. (www.nature.com). (d) MFM image of the magnetic domain structure of a permalloy thin film taken with an FIB-milled tip coated with a CoCr thin film. The marker distance is 7 nm. Reprinted with permission from ref 31, copyright 2003 by Elsevier (www.elsevier.com/locate/tsf). (e) 10 nm × 10 nm conductance map of a HfO thin film containing electronic defects that result in leakage current. Previously unpublished data by M. Brukman and D. Bonnell. (f) 6.5 nm × 4 nm electrostatic potential image of the Ge(105)-(1 × 2) surface superimposed with the atomic model. Bright (dark) color indicates high (low) potential, that is, repulsive (attractive) for electrons. A 1.5 kHz voltage with 250 mV amplitude was applied to the sample. Reprinted with permission from ref 23, copyright 2004 by The American Physical Society. (g) Scanning impedance image of a single-wall carbon nanotube connected to two electrodes with an ac bias across the nanotube, as current is recorded as a function of tip position. Reprinted with permission from ref 32, copyright 2002 by The American Physical Society. (h) Scanning nonlinear dielectric spectroscopy of the Si(111)-(7 × 7) surface in which the topographic structure is obtained from the first harmonic in capacitance and the polarization of the adatoms is obtained from the second harmonic. Upward dipole is red; downward dipole is blue. Reprinted with permission from ref 24, copyright 2007 by The American Physical Society. (i) Vector PFM map of local electromechanical property (maximum is 7.5 pm/V) of protein microfibrils on human tooth enamel. Color indicates the orientation of the electromechanical response vector, while the intensity provides the magnitude (color wheel diagram). Reprinted with permission from ref 29, 2006 by Elsevier (www.elsevier.com/locate/ultramic).

accessed. In this regime, differences in short-range forces can be used to map atomic structure as long as the tip terminates in a single atom with a stable configuration. This is enabled by optimized force feedback strategies (frequency modulation) and stiff cantilever or tuning fork configurations. The tip–surface interaction is a complicated combination of bonding forces. Sugimoto *et al.*[10] exploit these interactions and take this analysis to the next level, using force differences between atomic sites for chemical identification. They first compare force–distance curves over various atoms on binary alloys to quantify force ratios of different atoms, in this case for Si:Pb and Si:Sn. This information is then used to interpret variations in force on more complex surfaces. Figure 2c illustrates how local chemical

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force variations are used to identify Pb (green), Sn (blue), and Si (red) atoms. The atoms cannot be distinguished by topographic structure alone, thus necessitating force spectroscopy. Hence, mapping a "chemical" property provides information not evident from the physical structure.

Properties from First-Order Complexity. Almost immediately after the invention of AFM, it was understood that long-range interactions could be detected with cantilever-based systems (first-order complexity), leading to electrostatic force microscopy (EFM) and magnetic force microscopy (MFM). Variants of these approaches utilize electrically conducting or magnetic tips to detect variations of force with the consequences to cantilever oscillations and map variations in local properties. Although the interactions are complex and include local and macroscopic effects, careful analytical models and experimental controls enable these properties to be deconvolved and evaluated. These techniques are powerful, but the spatial resolution is intrinsically lower than the atomic level since the measurement is usually made 50−200 nm above the surface. However, spatial resolution much beyond expectations has been realized. For example, improvements in tip optimization for MFM have enabled significant advances in spatial resolution.[11−15] The strategy is to minimize the area of magnetic material at the tip end to allow operation much closer to the surface while decreasing the lateral extent of tip magnetic fields. This is accomplished with a variety of electrodeposition and focused ion beam processing. Figure 2d shows spatial resolution approaching 5 nm using this idea.[16] In this case, an electron-beam-deposited needle tip was used to probe a permalloy thin film with defined magnetic domain structures. Magnetic field variation over a distance of 15 nm is clearly resolved, in addition to features as small as 7 nm; one might extrapolate even a smaller "minimum detectable size" from these data.

Properties from Second-Order Complexity. Second-order complexity in probes involves modulating a field between the tip and sample to extract information resident in harmonics of the response function. When the tip is in contact and modulated with an electrical signal, this results in scanning conductance, scanning capacitance microscopy (SCM), scanning spreading resistance microscopy (SSRM), and so forth.[17] Here, the spatial resolution is assumed to be limited by tip contact area; given the dimensions of tips, the resolution should be 10−30 nm. Recently, lateral resolution approaching 1 nm has been achieved in capacitance at localized electronic states on a SiO_2 surface.[18] Spatial resolution of $<$5 nm was demonstrated for resistance in InGaAs quantum wells and 1−3 nm for resistance on p- and n-MOS devices.[19−21] Figure 2e shows an example of conductance through defects on a HfO film on Si.[22] The spatial resolution is less than 1 nm with an estimated tip contact diameter of ∼10 nm. The reduction of the apparent tip−surface interaction dimension from the contact diameter by a factor of ∼8−10 implies the operation of a field-focusing mechanism. The focusing arises from the fact that the stress distribution underneath the tip−sample junction is not uniform, and that a region half the size of the contact zone experiences 50% greater stress than the nominal load. This stress gradient, in conjunction with the presence of a pressure-dependent phase transition, produces a local region of higher conductivity in the sample. The limits of spatial resolution that might be achieved through this mechanism have not yet been determined.

With the tip above the surface, detecting the first harmonic of the response to the modulated electric field yields the well-known surface potential or Kelvin force microscopy. Surface potential variations have been used to map phases in composite materials, behavior in differently terminated self-assembled monolayers, voltage drops at interfaces in operating electronic devices, ferroelectric domains, in addition to other uses, and will continue to find wide application. The recent observation of atomic resolution surface potential takes this approach to an entirely new level. Figure 2f shows the surface potential of Ge (105)-(1 × 2).[23] By comparing STM, nc-AFM, and theoretical calculations, Hasegawa and colleagues developed an atomic model for this complex surface structure that involves interactions among dangling bonds. The atomic resolution surface potential provides strong evidence of charge transfer between dangling bonds. The bright contrast is associated with the rebonded atoms (marked yellow in the model), while so-called normal dimers (orange) exhibit lower potential. The implications of this result are significant: work function, electron affinity, and ioniza-

tion potential are related to surface potential and may be accessible at the atomic level.

Multiple Modulations for Higher Order Properties. The capacitance of a tip–sample junction contains a considerable amount of information that can be extracted in a number of ways, depending on the sample. For example, in low dimensional samples (*i.e.*, nanowires, tubes, dots), the density of states becomes a very strongly varying function of voltage, in some cases approaching singularities. This results in a second-order electrostatic effect that can be accessed in the second harmonic of the force response. Strong spatial variations in electronic structure, such as those that occur at atomic defects, also influence local capacitance. In the absence of geometric constraint or inhomogeneity, the capacitance reflects the local dielectric function, which itself contains higher order terms.

We have at our disposal any number of combinations of modulations to the tip–sample junction and across the sample to pinpoint the property of interest. The simultaneous imposition of high- and low-frequency electrical signals to the tip–surface junction has been used to extract dielectric properties of nanofibers. As noted above, direct measure of the second harmonic of an electric tip–surface modulation could extract density of states variations out of a Coulombic background signal. A time-varying bias across a sample with an interface (diode), boundary or defect and a static tip–surface bias, referred to as scanning impedance microscopy, provides an additional order of information about the sample properties. In this configuration, both the amplitude and the phase of the response are related to the sample rather than to the cantilever. Figure 2g shows a scanning impedance image of a single-walled carbon nanotube containing several defects. An ac signal is imposed through the nanotube, and the image records the current through the tube as a function of the position of a dc-biased tip. In this image, high contrast is associated with scattering centers at the defects. The tip bias dependence of this image is used to determine the valence band energy at the individual defects. Furthermore, imposing variations in frequency of the signal across the sample provides access to dynamic processes.

The question of the limit of spatial resolution in capacitance-based multiple modulation measurements arises naturally. Whether tips are in contact or not, the same issues that were raised in the context of other probes arise here. The expectation is that continuum properties will not be resolved with atomic dimensions; however, there is no obvious fundamental limitation. For the case of a homogeneous material, the capacitance defines the dielectric constant. Although the dielectric constant is usually thought of in terms of the static term, of course, higher order terms describe a nonlinear electric field response. Extrapolating this to the atomic level, dielectric constant becomes local polarizability of a single dipole.

Cho *et al.* recently took advantage of the fact that some ratios of differential capacitance contain higher order terms that reflect spontaneous polarization (polarizability) while in others the polarization cancels out.[24] They measure the first and second harmonic of the tip–surface function signal simultaneously to obtain topography and dielectric function. The measurement is accomplished with a resonator configured from a tip, encircled on the sample by a metallic ring.[25] Figure 2h shows a segment of the familiar Si(111)-(7 × 7) surface topography that arises from the first harmonic signal and two representations of the second harmonic signal which contains the polarity of the surface dipole. The red contrast indicates a dipole moment pointed upward, while the blue indicates a downward pointing moment. This study controlled variations in tip work function and sample carrier sign, so this is compelling evidence for polarization at the atomic level. Note that this probe exploits the tensorial nature of the properties of solids and is referred to as scanning nonlinear dielectric microscopy.

Polarization plays a large role in organic and inorganic ferroelectric compounds, which have been extensively characterized by piezo force microscopy.[26,27] In this class of materials, there is an additional nonlinear relationship between electric field and mechanical strain that is described by coefficients in higher order tensors. These properties are necessarily direction dependent, as well. Kalinin and colleagues have carefully analyzed the deformation mechanisms in the cantilever and developed a technique to decouple three simultaneous modes of AFM cantilever deflection: out-of-plane bending, lateral torsion, and longitudinal buckling.[28,29] The three modes correspond to sample displacements perpendicular to the sample plane and in-plane either perpendicular to or along the cantilever axis, so isolating these mechanical responses to electrical field variation explicitly probes the direction dependence of the piezoelectric coupling coefficient. The result is a vector map of the piezoelectric coupling coefficient. Since piezo force microscopy is a contact probe and avoiding electrostatic force artifacts requires a relatively large load, the spatial resolution is related to the tip–surface contact area and is usually 30–100 nm. Here the resolution, defined as the half-width of a boundary, is 5 nm. Imaging in liquids further improves spatial resolution by screening ever present long-range electrostatic forces, and 3 nm resolution has been demonstrated.[30]

Prospects in Atomic Resolution and Complexity. The examples illustrated above portend exciting advances along two directions relevant to

probing local phenomena: spatial resolution and complexity. The list of properties that have been imaged at atomic resolution is impressive: DOS asymmetry, charge density, chemical bonding, surface potential, direction, and magnitude of dipole polarization. It is not surprising that those associated with STM achieve these limits; however, it was not so obvious that those extracted from capacitance probes would achieve this resolution. Similarly surprising is the high spatial resolution achieved in continuum property probes: 7 nm for magnetic force, 1−3 nm for capacitance, resistance, conductance, and even for piezoelectric constants.

Equally exciting is the access to increasingly complex properties at this level of spatial resolution. Demonstrations of property coefficients from high-order tensors can be accessed and include direction dependence, suggesting exciting new directions in local characterization. Furthermore, this Perspective has not addressed the exciting potential of advances in scanning superconducting quantum interference device (SQUID) microscopy, spin-resolved transport, combined optical/electrical probes, or optical mechanical probes, all of which approach complex properties.

As we take complex property probes to increasingly higher spatial resolution, we reach the transition between continuum and atomistic descriptions of properties: from dielectric constant to atomic polarizability, from work function to ionization potential, from piezoelectric coupling to single molecule flexoelectricity. These advances can have a transformative impact on the understanding of local phenomena. Rather than standing on a maturity plateau, we are poised at the beginning of a new generation in this field.

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