

1 The Need for ASAT

[T]he limits, to which our thoughts are confin'd, are small in respect of the vast extent of Nature it self; some parts of it are too large to be comprehended, and some too little to be perceived. And from thence it must follow, that not having a full sensation of the Object, we must be very lame and imperfect in our conceptions about it, and in all the proportions which we build upon it.

Robert Hooke in *Micrographia* 1665 [1]

1.1 The Role of Microscopy in the Development of Human Knowledge

As a species, humans have done well. We can feed and shelter ourselves, cure many diseases, and map the human proteome. We can fly to the moon and find the Higgs boson. Of course, it hasn't always been this way. It took time for humanity to develop the knowledge we benefit from today. Have you ever stopped to ponder how this knowledge was gained? We studied the world around us. We used our eyes to see things and help us make things. Vision is perhaps the most essential asset to humans in the development of knowledge: as our vision goes, so goes our learning. Improved vision certainly leads to improved information.

Consider the work of Tycho Brahe (1546–1601) as an example. According to Wikipedia, Brahe decided that better instrumentation for celestial observation would lead to better understanding of our cosmos. At the time, human knowledge included understanding of the planets, the sun, and stars, but the prevailing theory of the cosmos was the geocentric model of Ptolemy. Copernicus had “revolutionized” our understanding of the cosmos with his heliocentric model in 1543, though many still believed in the Ptolemaic system. The relationships and origins of the celestial bodies were not understood. By insisting on improved instruments and systematically applying high-quality (for the time) sextants and quadrants to observation of our cosmic surroundings, patterns emerged, and eventually a global context for our planet was devised. Brahe's successor, Johannes Kepler was then able to solve the motion of the planets in elliptical orbits around the sun, which became the foundation of Newton's theory of gravity. Thus, higher-quality observations led directly to radically different and irrefutable changes to our understanding of our cosmos. Brahe was the last of the great

astronomers who relied on the unaided eye. Telescopes were introduced in the seventeenth century and further opened our understanding of the cosmos.

What, then, has been the role of microscopy in the development of human knowledge? The unaided human eye can resolve about 100 micrometers, about the width of a human hair. As our intellect developed as a species, our eyes gathered information about our surroundings, and we gained knowledge. We developed communication skills and archival storage mechanisms to preserve knowledge. Ultimately, we were limited, however, by the quality of our vision.

Consider, as an example, the black plague and how our vision limited our ability to gain knowledge about this scourge. In 1350, the black plague or “great death” was spreading north from the eastern Mediterranean Sea through Europe. Otherwise healthy adults in the prime of life were falling ill and dying in a matter of weeks. By 1353, 50 percent of Europe’s population had died. People and governments felt helpless to do anything. The explanations offered at the time included bad air, earthquakes, astrological forces, and poisoning of the wells by “Jews, friars, foreigners, pilgrims, lepers, and Romani.” People with skin conditions such as acne and psoriasis were exterminated as a hopeful prophylaxis. A report to the king of France from the medical faculty in Paris in the late fourteenth century blamed the heavens in the form of a conjunction of three planets that occurred in 1345.

It is easy to believe that these were silly thoughts, but when you have no information about the cause and no concept of the origin of the disease, it is almost impossible to get it right. The best source of possible information about the disease, the human eye, was inadequate to resolve the bacteria that were the cause. It was three hundred years later that light microscopes were invented in Europe, principally by Antonie van Leeuwenhoek. Gradually, the microscopes improved, and with them so did human knowledge of our microscopic world. Eventually humans learned that bacteria in the guts of fleas that traveled on rats were the cause of the plague. The point, of course, is that, lacking any substantive information about the relevant length scale on which the disease operated, even very smart people were reduced to wild conjecture. Information is the key to unlocking understanding. This story illustrates a crucial fact: the length scales of human knowledge throughout history are directly tied to the microscopies available at the time. The converse of large length scales also is true, as illustrated by our earlier recounting of Tycho Brahe’s work.

By the nineteenth century, bacteria in our water and our gut had been identified, yeast in our food was understood, cells in our bodies were observed, and the microstructure of metals was being studied. These advances led to new fields of science including bacteriology, food science, cellular biology, and metallurgy. In the twentieth century, microscopies reached all the way to the atom in resolving power. The field ion microscope produced images of atoms in 1955. In subsequent decades, so too did the transmission electron microscope and the scanning tunneling microscope. Semiconductor devices were developed, computers and smartphones flourished, and aerospace travel came of age. Our modern life is a direct product of knowledge gained from microscopes. As shown in Figure 1.1, human knowledge has progressed through the centuries with the length scale of our knowledge as determined by the availability

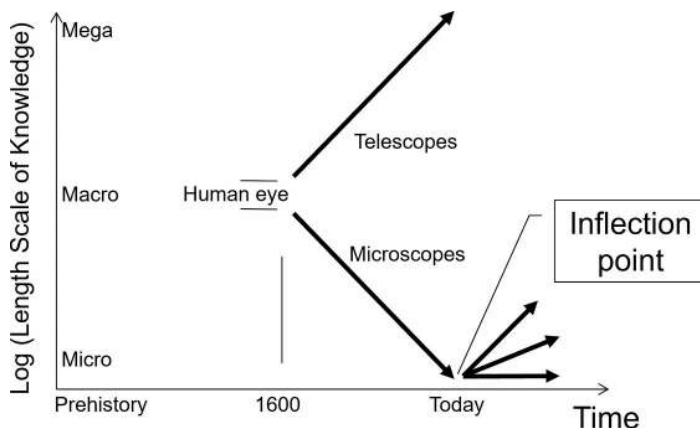


Figure 1.1 The evolution of the length scales of human knowledge through microscopy and telescope. We are at an inflection point on the small side where we have reached the atomic scale. Note that our knowledge of the subatomic scale does not rely on microscopes: smashing apart the building blocks of nature, atoms, to find out what they are made of is a distinct endeavor and is not the subject of this book.

of microscopes (and telescopes) that can resolve such scales. With each new microscopy advance come advances in science that improve the human condition. Microscopes are, arguably, humanity’s most valuable tool. In 2003, one of us (TFK) had the pleasure of attending a lecture titled “Wheel, Fire, Microscope” given by Joe Pesché [2]. His point was that microscopy stands with the greatest fundamental developments of humanity.

The history of microscopy has been the quest to learn more and more about less and less. After the inflection point shown in Figure 1.1, this quest will be to learn more and more about more and more. Atomic-Scale Analytical Tomography (ASAT) is a vehicle toward this end.

1.2 What Is ASAT?

As a concept, ASAT means observing and cataloguing every atom in its place. That is, ASAT is an experimental discipline that delivers the position and chemical identity of every atom in a volume with atomic-scale and isotopic precision [3], [4] for a given moment in time. Note that this description implies that vacancies are inherently evident in the data. Consider the significance of some of the terms in this definition. The size of the volume is most relevant. It should be evident to any materials scientist that ASAT data on volumes of say, 1,000 atoms (about $(2 \text{ nm})^3$), while impressive, would severely limit the applications space of the technique. The number of microstructural features that are fully contained in 1,000-atom volumes is very limited. If ASAT volumes reach a billion atoms (about $(200 \text{ nm})^3$), then clearly much larger structures will have been accessed. For example, a 10,000-atom volume

would suffice to detect one dopant atom in the channel of a 14 nm node transistor, 1,000,000 atoms will capture the entire doped region of the channel of the transistor, 30,000,000 atoms will capture all the active components of the transistor structure, and about a billion atoms will capture the interconnections the volume contains. If there is a failure in a transistor, understanding the origins of the problem is facilitated by having the entire structure.

The preceding analysis presumes that the captured volume is centered on the feature of interest. When the captured volume is not perfectly centered, as can be the case, then even larger analysis volumes are required to subtend the feature of interest. So, larger analysis volumes are important also for breadth of view.

You might argue, correctly, that for a century we have had diffraction-based techniques that deliver high-precision atom positions. But diffraction-based techniques work on a collective of atoms and deliver an average. These collective techniques are no longer good enough when structures are being engineered at the single-atom level.

1.3 What Is the Importance of ASAT?

How could ASAT technology impact our scientific and technological endeavors? An answer to this question will be given by illustration of some applications-driven needs in this section.

Today, a single atom in a structure can make the difference between success and failure. For example, the electrical properties of active components in electronic devices made of nanotubes vary markedly with inclusion, or not, of a single atom [5]–[7]. In addition, the properties of many materials, such as photovoltaic cells, are controlled by their defect populations. Therefore, characterization tools, such as ASAT, that would detect and identify single atoms and vacancies are critical to lay the scientific foundation for the development of future materials. When every atom counts, you must count every atom.

An intriguing application, and the most difficult to experimentally attain, is the complete characterization of the point defect populations and the solute environment around each point defect. This application demands both 100% detection efficiency for all types of atoms and a 3-D real-space resolution sufficient to position each atom with sub-nanometer-scale precision. If the positions of all the atoms are accurately known, including interstitials, then any missing atoms are vacancies or voids. Once the individual vacancies are mapped, the solute atoms around each vacancy can be determined. This would enable vacancy–solute interactions to be investigated, which is particularly important for a fundamental understanding of diffusion and kinetics studies, especially under extreme conditions.

Imagine the complexity of first-wall nuclear materials and reactor internals with nonequilibrium concentrations of vacancies, interstitials, multigenerational daughter-product isotopes, nanoclusters, precipitates, grain boundaries, and so on. These structures evolve in real time at the atomic scale. Any strategy for developing materials for

these applications will require far more information than is available in today's microscopes. ASAT would address this complexity head-on.

The tendency for solute atoms to cluster together in the solid solution and then mediate the nucleation of second phases, or to change physical properties such as strength in materials has received considerable attention as an important phenomenon [8]–[10]. This area has developed significantly because Atom Probe Tomography (APT) has been the only technique that can directly find and chemically identify small individual solute clusters in real space [11], [12]. Yet, there are imperfections in APT data (trajectory aberrations) that ultimately place limits on the precision of these results. Also, for solute atom clusters containing fewer than about five atoms or so, the influence of the detection efficiency becomes greater [11], [13].

Diffraction studies of the structure of amorphous materials have given us a broad understanding of the relative positions of the atoms that comprise them. However, as smaller volumes are probed, it has been found that this global averaging of the relative interatomic positions does not hold on the smaller scales [14]–[17]. This variation in local atomic structure may be responsible for understanding of important properties. In principle, element-specific radial distribution functions can be derived from ASAT data about any point in a volume [18]. Variations in the local radial distribution function would be readily calculated with ASAT and may reveal new insights into this important class of materials.

Once ASAT becomes established, there will be no (materials) secrets anymore. Reverse engineering of even the smallest structures will become possible. In other words, a competitive analysis will not be limited by lack of knowledge of a structure down to its atomic scale.

1.4 Integrated Computational Materials Engineering (ICME)

We begin, however, with a note of caution by pointing out that knowing the identity and position of all atoms in a material is usually a means and not an end in itself. Almost always, this microstructural information is sought with a view to discerning the material's properties and behavior. True ASAT of real-world microstructures would provide an unprecedented understanding of existing materials and, perhaps more importantly, enable the design and development of new materials. ASAT would in fact be a key enabler of ICME (integrated computational materials engineering)-based approaches because it would establish the essential underpinning data for the atomic-scale modeling and simulation. It might enable an entirely new branch of microscopy where structure might be directly related to properties at the atomic level. This paradigm shift from “structural microscopy” to “structure-properties microscopy” could ultimately blur the line between characterization and measurement.

We propose, therefore, that there is a very real nexus between the states of knowledge in structure–property relationships, and microscopy science and technology. In terms of the former, it is noteworthy that the field of computational materials science is making great strides with increasingly sophisticated materials modeling and

simulation possible over a wide range of length scales. These strides forward are crucial for microscopy science and technology, since these computational platforms must become the target destination of the hard-won 3-D atomistic information resolved by the microscope. Interdisciplinary collaboration raises the prospect for realizing materials informatics and ICME [19], [20], since atomic identities and locations can serve as inputs and physical properties will become the computed outputs. It is in this context that ASAT holds true promise as the ultimate microscopy. The experimental determination of atom positions and identities may outpace computational materials science now, but these fields will naturally share a common ground and generate synergies that result only when they are combined.

These new microscopies will certainly lead to new scientific findings and discoveries. As with all new fields of microscopy, history has shown that the full impact of the development cannot be completely anticipated at its time of inception.

1.5 Looking Forward

No scientific technique is all things to all people. All have limitations that should be understood. It is healthy for us to recognize and advertise up-front the limitations of a technique. The challenge is to expand the applicability and accuracy of techniques. In this book, we try to explore objectively the strengths and limitations of both electron microscopy and atom probe tomography with a view to establishing synergies that have yet to appear.

Atomic-scale tomography is a term that has been used by diverse groups to mean different things. At its core, it means that the location of every atom in a volume has been determined in three-dimensional space with high precision. This definition should apply to any type of material, whether it is a pure element or a complex alloy. When implemented in TEM, the volume has typically been small: thousands of atoms. A definition that came from the atom probe community in Kelly et al. [3] includes a billion atoms. Such “large” volumes are important, as they open the universe of applications to a much broader array of materials and structures. The term was expanded to atomic-scale analytical tomography [4] to explicitly call out the fact that analytical information (chemical bonding/electronic structure, diffraction information, etc.) can and should be an integral component of atomic-scale microscopy.

The remainder of the book is dedicated to exploring realistic means for achieving ASAT in the next decade or sooner. Erwin Müller, the father of atomic-scale imaging, once said that “It seems as if the evasive atoms still hide from the curious eye of the casual sightseer and reveal themselves rewardingly only to the serious researcher” [21], [22]. We hope to change that and see ASAT capabilities, maybe not in every kitchen but at least in every research center. In this sense, the atomic age is upon us.

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2 History of Atomic-Scale Microscopy

We can trace our microscopic understanding of reality to the advent of microscopy in the 1600s, a pivotal point in the origins of modern science. With the invention of light microscopy, most notably as practiced by Antonie van Leeuwenhoek, imaging at successively finer length scales became possible. Through continuous improvement, the limits of the light microscope were approached, although innovation has continued to push beyond the diffraction limit of about 200 nm. In the 1930s, the resolution of the transmission electron microscope surpassed that of the light microscope [1]. Today we are able to resolve single atoms with, not one, but three distinct microscopy techniques: atom-probe field ion microscopy, electron microscopy, and scanning probe microscopy. If there was ever any doubt about the value of pushing to ever-finer resolution, we can take solace in the words of Jean Perrin in 1926. At the time, the concept of imaging atoms seemed remote to most scientists. In his Nobel Prize acceptance speech [2], he noted the importance of seeing atoms:

[C]ertain scholars considered that since the appearances on our scale were finally the only important ones for us, there was no point in seeking what might exist in an inaccessible domain. I find it very difficult to understand this point of view since what is inaccessible today may become accessible tomorrow (as has happened by the invention of the microscope), and because coherent assumptions on what is still invisible may increase our understanding of the visible.

Thus, the history of efforts to resolve atoms may inform scientists in other realms: what may seem impossible today could be routine in the near future. This book portrays a vision that will be an advance in microscopy. The goal may be difficult to realize today, but we are making steady progress toward it. A mere two decades ago, atomic-scale tomography was a dream. Now, it is a concrete objective. In this chapter, we consider the history of the atom and the microscopies that have led us to this dream.

2.1 The Concept of Atoms

The history of the concept of atoms begins with the Greek atomists, Leucippus and Democritus, in the fifth century BCE. Leucippus and Democritus foresaw, through deductive reasoning, that matter must ultimately be made up of building blocks. They conceived that matter consisted of “atoms and the void.” Indeed, they saw that, although matter appears to be a continuum, it can be sliced. If an object could be

sliced into two pieces, then these in turn could be sliced into two pieces each, and so on. This progression then poses the question, “Is it possible to slice matter in half an infinite number of times?” These philosophers then deduced that the answer must be no. Thus, two millennia before von Laue demonstrated the existence of atoms [3]–[7], leading Greek intellects could foresee them as the basic building blocks of matter. Such is the power of deductive reasoning. It is thus also fitting that the word for these indivisible objects, at least in many western languages, has its origins in the Greek language. Indeed, atom comes from the Greek “a” meaning “not,” and “tomos” meaning “to divide” (i.e., atom means “indivisible”).

2.2 Atomic-Scale Tomography Is the Ultimate

Human knowledge extends to structures on a scale much finer than atoms, so a proton-scale or quark-scale microscope would seem to be the ultimate.¹ However, we argue that an atomic-scale microscope is the ultimate for the following reason: *the smallest building block for both synthetic and natural structures is the atom*. Indeed, both humans and nature engineer structures with atoms, not quarks or other subatomic particles. Protons and quarks are constituents of atoms, just as sand and clay are the constituents of red bricks.² There is a finite number of known types of atomic building blocks ($< 10^3$ stable isotopes). Given all the evidence we have at this juncture, all building blocks (atoms) of a specific type (e.g., all ^{54}Cr atoms) are identical, and so it is only necessary to discover their structure once. It is the assembly of the building blocks that makes a unique structure, such as the one illustrated in Figure 2.1.

Thus, we argue that a microscope that determines the position and identity of every atom (i.e., building block) in a structure with high precision and for large volumes would be the ultimate microscope. In this book, we further consider how this device could be built, and we ponder the answer to the equally important follow-up questions: What could be achieved with it, whom would it impact, and how?

2.3 The Development of Atomic Theory

Experimental evidence for the existence of atoms developed gradually over several centuries, beginning in the Middle Ages. An excellent, nontechnical review of this history was given by Oliver Sacks [8]. Empirical observations such as electrolysis of water, which produced exactly twice as much gas on the cathode as on the anode, hinted at the discrete nature of the makeup of materials. Scientists of the eighteenth and nineteenth centuries honed notions of atomic structure: Robert Boyle, who hypothesized that matter consisted of atoms and clusters of atoms in motion in the *Skeptical*

¹ We use the word “ultimate” in the sense of one of its definitions: the last in a progression.

² This analogy is not perfect, since we know that all bricks for construction are not identical down to the finest detail.