Scanning Probe Microscopy has been routinely employed as a surface characterization technique for more than 20 years. Tip deconvolution, the longest-standing problem associated with particle image analysis in atomic force microscopy (AFM), can be solved by scanning a pre-characterized nanosphere prior to imaging unknown particles.

### INTRODUCTION

Knowledge of particle size, size distribution, and other particle morphology parameters on the nanometer scale is becoming more important with accelerating developments in the nanotechnology branches of particle technology, toxicology, pharmaceutical, semiconductor, composite, and coating industries. For example, monitoring the presence of particles, powder size, and distribution data is an important aspect of process control. Changes in these aspects and/or the direction of such changes can be quite indicative of events during the manufacturing process, events which can significantly impact the properties and quality of the final product. Tracking such changes can also indicate the point in the manufacturing process at which there is a problem. Particles and particle-size distribution (PSD) significantly contribute to the mechanical strength as well as thermal and electrical properties of the final material. Smart coatings with a great variety of properties can be developed to meet specific requirements of particular applications. Mechanisms of agglomeration, adhesion, and particle-particle interaction in particulate materials need to be understood to solve current challenges in the pharmaceutical industry.

The most common set of morphology parameters listed in Table I. Parameters involving measurements of the third dimension such as height, surface roughness, and volume are possible only with atomic-force microscopy (AFM).

### Table I. The Most Common Set of Morphology Parameters Available for Measurement by Individual Particle Characterization Techniques

<table>
<thead>
<tr>
<th>Morphology Parameters</th>
<th>Optics</th>
<th>TEM/SEM</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size, Radii, Length, Width</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Height</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Perimeter</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Projected Area</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Surface Roughness</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Volume</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### Table II. A Comparison of Resolution and the Most Common Artifacts Associated with Individual Particle Characterization Techniques

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optics</th>
<th>TEM/SEM</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>~150 nm for green light &gt;1 μm for white light</td>
<td>a few Å (TEM) a few nm (FESEM*, secondary electrons) ~0.1 μm (SEM, backscattered electrons)</td>
<td>sub-A (vertical)</td>
</tr>
<tr>
<td>Probe Size, Diameter</td>
<td>1–2 nm</td>
<td>1–30 nm</td>
<td>Tip convolution</td>
</tr>
<tr>
<td>Artifact Associated with a Probe</td>
<td>Chromatic aberration, spherical aberration astigmatism, distortion</td>
<td>Spherical aberration, astigmatism, distortion</td>
<td>Charging if sample is semi- or non-conductive</td>
</tr>
<tr>
<td>Artifact Associated with a Sample</td>
<td>Ambient air</td>
<td>Vacuum, environment controlled</td>
<td>Ambient air liquid, UHV*</td>
</tr>
<tr>
<td>Environmental Requirements</td>
<td>Ambient air</td>
<td>Distractive to sample surface</td>
<td>Non-intrusive</td>
</tr>
<tr>
<td>Artifact Associated with an Interaction</td>
<td>Non-Intrusive</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*FESEM = Field-emission gun scanning-electron microscopy; UHV = ultra-high vacuum
The ability to visualize and directly measure dimensions of a few nanometers is a necessity in nanotechnology. There are few particle analysis techniques capable of delivering morphological information below 100 nm. Ensemble methods, such as dynamic light scattering and gravitational sedimentation techniques, are starting to push the limits of resolution at about the 40 nm to the 100 nm range, respectively.

In certain cases, it is important to ensure that PSD lies within certain limits, making the precision of these measurements more important than their accuracy. Microscopy-based techniques, where counted particles can be visually examined, are usually used for absolute measurement applications. Because the resolution of the measuring technique should be greater than the size of the particles under investigation—in other words, less than 1–100 nm—optical microscopy is excluded (see Table II). However, both AFM and scanning-electron microscopy/transmission-electron microscopy (SEM/TEM) have the required resolution. In fact, AFM is a non-intrusive technique with resolution greater than or comparable to that of an electron microscope. In addition, it is easier to use and involves less sample preparation (see Figure 1). Particles can be measured at ambient condition, while electron microscopy requires vacuum chambers and conductivity of the specimen (see Table II).

Probe artifacts in the case of optical and electron microscopy, such as aberration, astigmatism, and distortion, are well known, studied, and mostly compensated for in the commercially available microscope. Note that theoretical resolution in TEM cannot be obtained, primarily due to the spherical aberration of the lens. A tip artifact or a tip dilation, the phenomenon specific to AFM, manifests itself in a broadening of the lateral dimensions of the surface topography. Interestingly, the vertical resolution of AFM is not affected by the finite size of the probe. In mathematics, this problem is known as tip deconvolution. Imaging very sharp vertical surfaces (those with high relief) is influenced by the sharpness of the tip. Only a tip with sufficient sharpness and aspect ratio can properly image a given vertical or horizontal profile. Some profiles can be steeper or

![Image](https://via.placeholder.com/150)

Figure 2. (a) An AFM image, 14×14 μm, and (b) an SEM picture of the same sample with the array of narrow spikes that show that pillars have a finite rectangular shape at the top.

![Image](https://via.placeholder.com/150)

Figure 3. (a) A three-dimensional (3-D) view of 102 nm sphere, scan size 300 nm×300 nm and (b) a 3-D view of the reconstructed tip obtained from a measured image of a sphere of known diameter.

![Image](https://via.placeholder.com/150)

Figure 4. (a) The height line profile drawn across the center of the tip. The image of the reconstructed tip is obtained from an AFM image of 102 nm square. (b) Markers on the image indicate the points where the measurements are taken. The solid lines on the height profile are for left angle measurements, the dotted lines are for the tip diameter, and the dashed ones are for right angle measurements.

![Image](https://via.placeholder.com/150)

Figure 5. (a) The three-dimensional view of the tip reconstruction obtained on 28 nm colloidal gold spheres. (b) The height line profile is drawn across the center of the tip. Markers on the image indicate the points where the measurements are taken. The solid line on the height profile is for the diameter measurement, left angle measurements are in the dotted lines, and the dashed lines are for the right angle measurements.
sharper than any tip can be expected to image without artifact. False images are generated that reflect the convolution of the tip geometry and the geometry of the object being imaged, rather than the object surface. Mathematical methods of tip deconvolution can be employed for image restoration.\textsuperscript{3,4} The effectiveness of these methods depends on the specific characteristics of the sample and of the probe tip. A known tip implies a known sample; if this is the case, then the morphological subtraction\textsuperscript{3,4} or envelope method\textsuperscript{3} can be used. If the sample is unknown, then the method of blind reconstruction can be utilized.\textsuperscript{3,6}

It has been shown that the combination of erosion with blind reconstruction can produce the most optimum deconvolution results on a known sample.\textsuperscript{4} The major obstacle in AFM, a tip artifact associated with the finite size of the probe, can be compensated for by using a deconvolution method before performing analytical measurements. (Note that all AFM images shown in this paper are obtained on Nano-Rp\textsuperscript{TM}; Nanoflat substrates are used for the sample preparation; and AFM image analysis is performed in NanoRule +\textsuperscript{TM} particle analysis software.)

See the sidebar for details on particle characterization.

**TIP RECONSTRUCTION ON A PARTICLE SAMPLE**

It is possible to reconstruct tip geometry on both known and unknown samples. This article will focus on known samples. To refer to a sample as “known” implies that the size and geometry of particles used as tip characterizers can be independently verified. From a mathematical perspective, it is important to be aware of errors associated with a known sample. Naturally, it is desirable to have a minimum of such errors. The errors in the estimate of characterizer dimensions propagate to comparable errors in the reconstructed tip shape. The characterizer should be stable at the nanoscale with dimensional errors that are small compared to the tip size. Commercially available probes have tip diameters at about 20–30 nm. However, there are some special probes with tip diameters as small as 1 nm.

Patterned silicon wafers are routinely used for dimensional calibration of AFM. National Institute of Standards and Technology traceable gratings are available from VLSI Standards, Inc., of San Jose, California. The grid consists of an array of alternating bars and spaces with uniform pitch in both X and Y directions. The uncertainty associated with the pitch size is comparable to the size of the probe. The reported value is on the order of 20 nm for a 2.99 \( \mu \)m pitch. Note that the size of the square impression is about 1.5 \( \mu \)m \( \times \) 1.5 \( \mu \)m. The calibration grating consisting of an array of sharp tips, with strict symmetry on tip sides, small cone angle (less than 20\(^\circ\)), and small curvature radius of the tips (less than 10 nm) is a very good candidate for determination of stylus shape parameters\textsuperscript{11}

The capabilities of atomic-force microscopy (AFM) in both qualitative and quantitative particle characterization are described elsewhere.\textsuperscript{3} Table I shows the most common morphology parameters required in particle characterization. The ability to measure the width of the feature is critical because it contributes to all morphology parameters. If the diameter of the probe is larger or comparable to the diameter of the particle, then the broadening effect in measuring lateral dimension can be clearly seen (Figures Aa and Ab). In turn, area, perimeter, surface roughness, and volume measurements all are affected differently, while actual particle size is the same in both cases.

The particle sample is the same in both Figure Aa and Ab. The examined sample consists of 102 nm polystyrene spheres (Duke Scientific, Fremont, California) deposited substrate.

Figure B illustrates the way in which three different types of tips used for the simulation can alter topographical AFM data of the spheres.\textsuperscript{8} Shown are three simulated images and the corresponding height profiles for four latex spheres with radii 56, 68, 91, and 102 nm, respectively. The image size in parts a, c, and e is always 3,000 nm \( \times \) 500 nm. Three different types of tips have been used for the simulation: (a) ideal tip (assumed as delta function), (c) conical tip with 6 nm apex radius and 50\(^\circ\) total opening angle, and (e) tip with 50 nm apex radius and 50\(^\circ\) total opening angle. The corresponding height profiles across the centers of the spheres are displayed in parts b, d, and f, respectively. The

![Particle Characterization](image-url)
influence of the tip geometry on the measured topography of the latex spheres (especially its apparent width) is clearly visible. This is a phenomenon of tip convolution.

To circumvent this type of problem, the authors use half of the measured height of the particles as a true measure for the sphere radius. Note that the height is not affected by the size of the probe.

For an exact determination of the sphere radii, one must consider elastic deformation under the influence of attractive adhesive forces, compressibility due to the interaction with the styli, and the possibility of particle conformation on the surface. The amount of elastic deformation was calculated by U. Schwartz. The calculated deformation gives the range of 0.5–0.9 nm. The largest deformation of 0.9 nm was estimated for a 220 nm latex sphere and is less than 0.4%. Scanning-electron microscopy images of polystyrene spheres of 100 nm and colloidal gold of 28 nm do not reveal any evidence that particles are being deformed on the substrate. The compressibility comparison on colloidal gold spheres and the tobacco mosaic virus has been reposted by J. Vasenka. The study suggests that colloidal gold particles are incompressible and can be independently characterized through electron microscopy. This characteristic makes colloidal gold particles a good candidate for tip geometry characterization. Some particles may collapse into a pancake-like shape or retain their spherical shape depending on rigidity of the particle and substrate surface free energy. However, the authors are not aware of any reported data on latex or colloidal gold spheres suggesting the possibility of conformation on the surface.

The narrowness of the size distribution curve for the nominal size value is critical to AFM particle characterization analysis. There are several manufacturers producing spherical particles with a nominal size below 100 nm. Usually spherical shape and size is independently measured with transmission-electron microscopy or photon correlation spectroscopy (PCS). The standard deviation varies between 4.5–7.2 nm, which is 5–16%, with a mean diameter of 100 nm and 50 nm, respectively. The specification for particles with a 20 nm diameter is 21 nm ± 1.5 nm, calibrated with PCS (Duke Scientific, Inc.). In the case of colloidal gold particles, the reported coefficient of variation for a mean diameter of 4.79 nm is 11.1%, for 20.51 nm–5.4%, and for 30.7 nm–3.9% (Ted Pella, Inc., Redding, California).

In addition, it has been suggested that fullerenes may be used as uniform spheres for tip characterization. The outer diameter of carbon-60 is 10.18 Å.

The study suggests that the use of polystyrene sphere. The calculated deformation gives the range of 0.5–0.9 nm. The outer diameter of carbon-60 is 10.18 Å. The closing image mentioned and the complicated shape (NT-MDT, Moscow). However, the lack of specifications for the parameters mentioned makes the problem more complicated. Figure 2 shows an AFM image of the pillars in comparison to the SEM image. Both AFM and SEM data agree that the spikes appear to have variations in shape and size. The use of single spherical particles has been proposed for tip characterization for several reasons.

The high degree of symmetry, manufacturability, consistent uncertainties on the scale of 1–3 nm, noncompressibility, negligible elastic deformation, and conformation on the substrate make colloidal gold and polystyrene particles favorable candidates for tip geometry checkers. Figure 3 shows one example of a three-dimensional view of a tip reconstructed from an AFM image of a 102 ± 3 nm polystyrene sphere.

The reconstructed tip appears to be asymmetrical in shape with a tip radius of ~38 nm, a left angle of 65°, and a right angle of 50° (Figure 4). The reconstructed tip obtained on scanning 28 nm colloidal gold spheres (Ted Pella, Inc., Redding, California) is shown on Figure 5. The tip has a radius of ~2 nm, a left angle of 58°, and a right angle of 46°. The reconstructed tip is outer bound on the part of the tip which contacts the particle during the scan. This happens due to the fact that dilation and erosion operators are not strict inverses of one another for an arbitrary tip. The closing operation tends to smooth the edge from the outside. The tip’s outer bound estimate is the more important one because it leads to a lower bound estimate of the sample surface.

SURFACE RECONSTRUCTION

Once the geometry of the tip is estimated, it is possible to reconstruct the surface topography. Figure 6 shows AFM images of the particles before and after reconstruction. Ideally, if a tip is perfectly reconstructed, the reconstructed sample surface will be an outer bound that contains an actual sample. This outer bound will be equal to the true sample surface at those points where the tip actually touched, and it will be larger at points where the tip was unable to touch. Notice that the true particle surface is a cylinder with a hemisphere cap. That is, it contains vertical sidewalls where the tip was not able to touch. This is one of the reasons that these reconstructed samples seem dilated (compare Figures 5e, computer-simulated tip dilation, and Figure 6, tip dilation on measured and reconstructed surfaces).

AFM RESOLUTION ON PARTICLES

The conventional definition of resolution in the field of light and electron microscopy is based on the Lord Rayleigh criterion: when the maximum intensity of an Airy disc coincides with the first minimum of the second, then two points can be distinguished.
sets the resolution limit as $d/2$, as shown in Figure 7. The Rayleigh criterion can be applied to three-dimensional images of AFM. Here, the intensity peaks are analogous to height line profiles. Let us assume “$r$” is tip radii, “$R$” is sphere radii, and “$h$” is the height difference between the top of the sphere and the lowest point in a line profile drawn between two spheres. $H$ is the distance that actually can be measured on the height profile. These line profile measurements should be performed on deconvoluted surfaces to compensate for tip artifact.

The easiest case, that in which particles are far apart, is shown in Figure 8a. The particles are clearly resolved, and the probe goes all the way down between two particles. Criterion “$h$” measures the height difference between the top of the sphere and the lowest point in the line profile drawn between two adjacent spheres. In this case, $h = 2R$ (Figure 8b). In Figure 8c, the spheres touch each other and it is assumed that there is no interaction. The height line profile is shown in Figure 8d. The height of the sphere remains the same, while the ability of the probe to go between the particles will be limited by the finite diameter of the probe. If we assume the ideal case, in which the probe is represented by delta-function, then $h = R$. If the finite size of the probe and the upper-lower bounds of the tip reconstruction are taken into account, then separation, $t$, between two spheres will be smaller. This can be shown, if the size of the probe is equal to the diameter of the sphere, $h = 0.26R$. If the diameter of the sphere is one-half of the diameter of the probe, then $h = 0.39R$. If $r = 0.2R$—the most realistic case for $50$ nm radius spheres—then $h = 0.54R = 27$ nm. This criteria could be considered the spatial resolving limit for AFM. To summarize: $h = R - ((2R + r)^{1/2} - r)$; $h = 0.26$—corresponds to $r = R$; $h = 0.54$—resolution criteria, $r = 0.2R$; $h = R$, probe-delta functions, $r = 0$.

CONCLUSION

In this work, tip deconvolution and image restoration are done on known, pre-characterized manufacturable spheres from a commercial vendor, rather than an arbitrary unknown surface or mathematically modeled structure. This is a practical, innovative solution to the long-standing problem of tip deconvolution.

References


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|Figure 8. Left-hand images show probe gliding over two spheres. The size of probe is smaller than the diameter of particles. In (a) and (b) the particles are far apart. In (c) and (d) the particles are touching. | Figure 8. Left-hand images show probe gliding over two spheres. The size of probe is smaller than the diameter of particles. In (a) and (b) the particles are far apart. In (c) and (d) the particles are touching. |