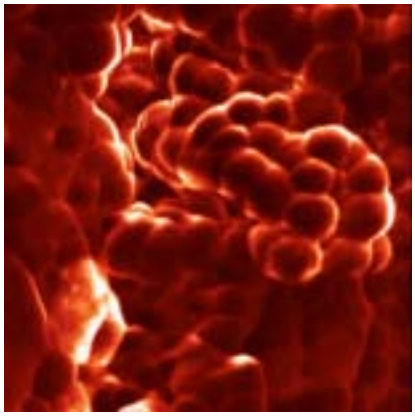
Atomic Force Microscopy for Nanoparticles:

Nanoparticles, a unique subset of the broad field of nanotechnology, include any type of particle with at least one dimension of less than 500 nanometers. Nanoparticles play an important role in a wide variety of fields including advanced materials, pharmaceuticals, and environmental detection and monitoring.

The atomic force microscope (AFM) is ideally suited for characterizing nanoparticles. It offers the capability of 3D visualization and both qualitative and quantitative information on many physical properties including size, morphology, surface texture and roughness. Statistical information, including size, surface area, and volume distributions, can be determined as well. A wide range of particle sizes can be characterized in the same scan, from 1 nanometer to 8 micrometers. In addition, the AFM can characterize nanoparticles in multiple mediums including ambient air, controlled environments, and even liquid dispersions.

Figure 1



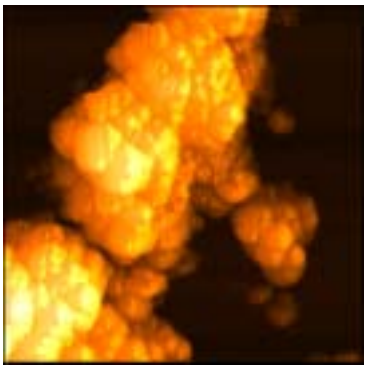
15nm PMMA & LPPP polymer spheres in a crystallized emulator of SDS. (Data courtesy of University of Potsdam, Germany.)

Applications for Nanoparticles

While nanoparticles are important in a diverse set of fields, they can generally be classified as one of two types: engineered or nonengineered.

Engineered nanoparticles are intentionally designed and created with physical properties tailored to meet the needs of specific applications. They can be end products in and of themselves, as in the case of quantum dots or pharmaceutical drugs, or they can be components later incorporated into separate end products, such as carbon black in rubber products[1]. (AFM images of carbon black nanoparticles are shown in Figure 2.) Either way the particle's physical properties are extremely important to their performance and the performance of any product into which they are ultimately incorporated.

Figure 2



Carbon black, commonly used to enhance the properties of manufactured rubber, is clearly visualized using the NANO-R™. Scan size is 2μm x 2μm.

Nonengineered nanoparticles, on the other hand, are unintentionally generated nanoparticles, such as atmospheric nanoparticles created during combustion. With nonengineered nanoparticles, physical properties also play an important role as they determine whether or not ill effects will occur as a result of the presence of these particles.

Depending on the application of interest, nanoparticles may be known by a number of alternative and trade-specific names, including particulate matter, aerosols, colloids, nanocomposites, nanopowders, and nanoceramics.

Figure 3

Some industries with engineered nanoparticles:

- *Pharmaceuticals*
- *Performance chemicals*
- *Chemical mechanical polishing*
- *Quantum dots*
- *Biodetection and labeling*
- *Ceramics*
- *Food products*
- *Cosmetics*

Some industries with nonengineered particles:

- *Environmental detection*
- *Environmental monitoring*
- *Controlled environments*

AFM Capabilities in Nanoparticle Characterization

Qualitative Analysis

Using the AFM, individual particles and groups of particles can be visualized. Visual images are essential in research and development projects and can be critical when troubleshooting quality control issues.

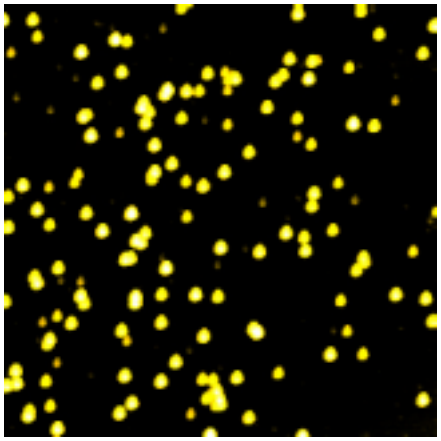
Unlike other microscopy techniques, the AFM offers visualization in three dimensions. TEM provides images that are merely 2D projections, while generating 3D images from light microscopy and SEM are nonstandard and require rigorous calibration to a known standard.

In Figure 4, 73μm NIST traceable microspheres are shown in both perspective view and top view. 3D information is incorporated in both views. In the perspective view, the 3D nature of the image is obvious. In the top view, the intensity of the color reflects the height of the particle.

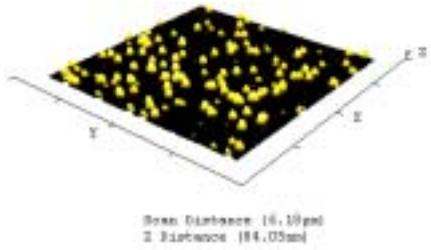
In material sensing mode, the AFM can distinguish between different materials, providing spatial distribution information on composite materials with otherwise uninformative topographies. In Figure 5, material inhomogeneity can be seen on a topographically flat organic film. Nanocomposites can be similar analyzed for dispersion of particulate matter.

Figure 4

(a) 2D topography image



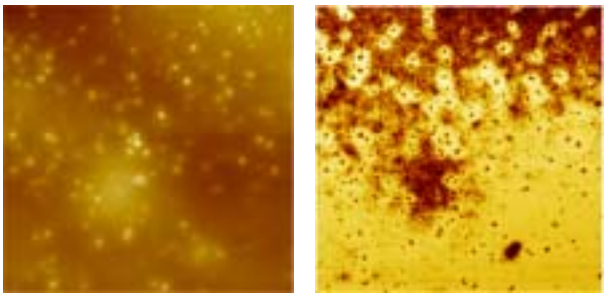
(b) 3D topography image



NIST traceable polystyrene microspheres from Duke Scientific scanned with the NANO-R™. Mean Ø of microspheres is 73nm. Scan size is 6μm x 6μm.

Figure 5

(a) Topographical scan ***(b) Material sensing scan***



Inhomogeneities in organic film on polymer substrate. Using material sensing mode on the NANO-R™ allows observation of material inhomogeneities in nanocomposites with relatively flat topographies.

Quantitative Analysis

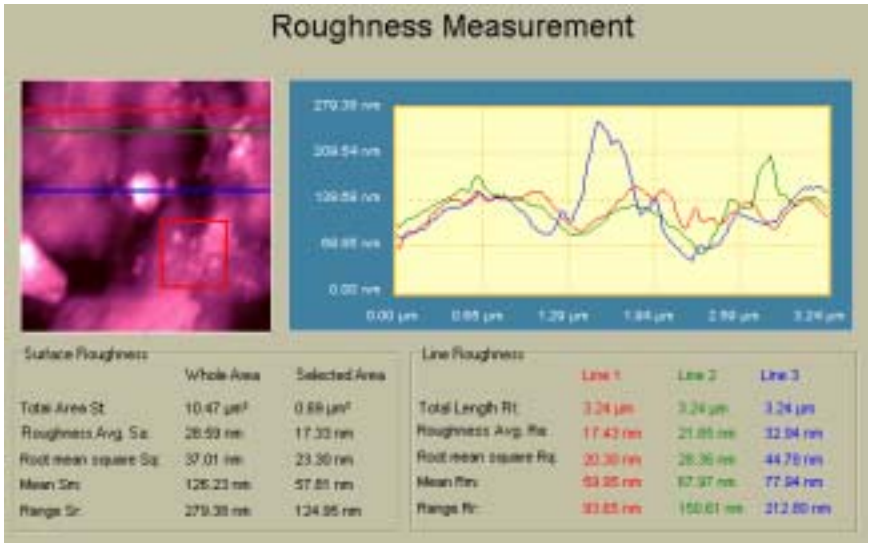
Software-based imaging processing of AFM data can generate quantitative information on both individual nanoparticles and groups of nanoparticles.

For individual particles, size information (length, width, and height) and other physical properties (such as morphology and surface texture) can be measured. In Figure 6, surface roughness data generated from a scan of a wood fiber is shown.[2]

Statistics on groups of particles can also be measured through image analysis and data processing. Commonly desired ensemble statistics include particle counts, particle size distribution, surface area distribution and volume distribution. With knowledge of the material density, mass distribution can also be easily calculated. Image processing of an AFM image are shown in Figure 7. A scan of colloidal gold and the particle size distribution calculated by image processing is shown in Figure 8.

Whenever data from single-particle techniques is processed to provide statistical information, the concern over statistical significance exists. It is easy to attain greater statistical in AFM by combining data from multiple scans to obtain information on the larger population.

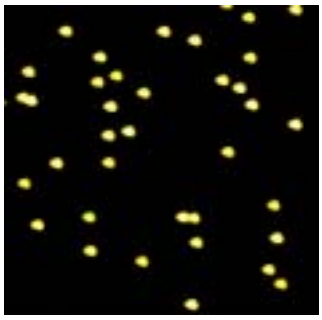
Figure 6



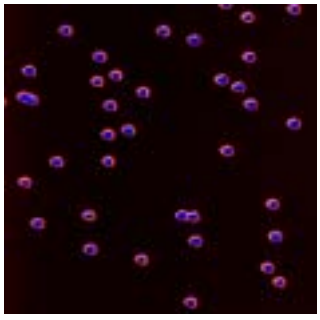
A wood fiber scanned with an AFM to measure roughness. Paper products containing such wood fibers can vary in quality based on the physical properties of the fibers.

Figure 7

(a) Original NANO-R image

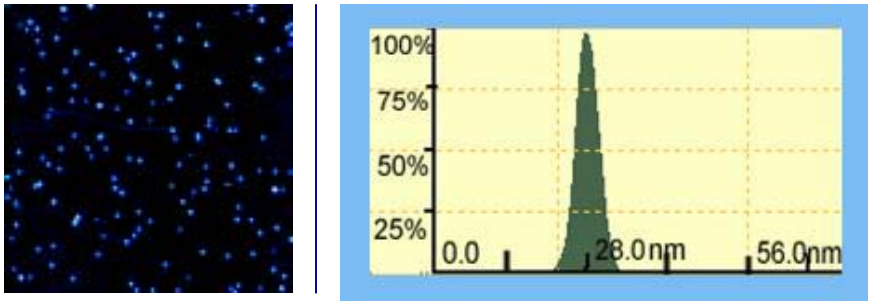


(b) Particle boundaries determined by image processing



Polystyrene microspheres with mean diameter of 102nm. (a): Topographical scan image. (b): Image processing used to determine boundaries of individual particles. Ensemble data can be further processed to provide statistical information such as particle size distribution.

Figure 8



Scan of colloidal gold and associated particle size distribution. Mean Ø = 28nm.

Mediums

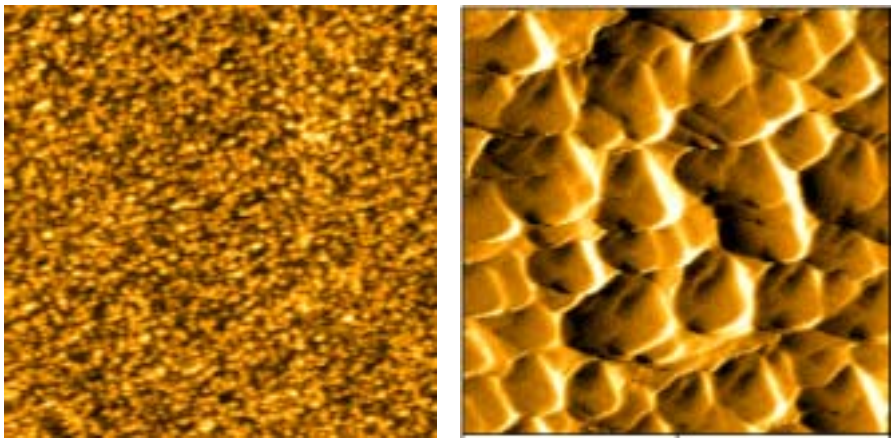
AFM can be performed in liquid or gas mediums. In contrast, TEM and SEM generally require high-vacuum conditions, which can alter the particles being examined. For example, with combustion-generated nanoparticles, a major component of the particles are volatile components that evaporate at low pressure.

Dry particles can be scanned in both ambient air and under controlled environments, such as nitrogen or argon gas. Liquid dispersions of particles can also be scanned, provided the dispersant is not corrosive to the probe tip.

Particles dispersed in a solid matrix can also be analyzed by topographical or material sensing scans of cross-sections of the composite material. Such a technique is useful for investigating spatial dispersion in nanocomposites. Precipitates in a nickel aluminum alloy are shown in Figure 9.

Figure 9

(a) Scan size: 27μm x 27μm ***(b) Scan size: 3μm x 3μm***



Ni_3Al precipitates in a nickel aluminum alloy. (a): 27 μm x 27μm topography image. (b): 3μm x 3μm shading image.

Range

In many industries, the ability to scan from the nanometer range into the micron range is important. With AFM, particles anywhere from 1nm to 8μm in height can be measured in a single scan.

It is important to note that AFM scanning is done physically with a probe time in constant or intermediate contact. Therefore, particles must be pushed against a 2D surface during the scan. With the NANO-R™, the maximum 2D scan range for a single scan is 80μm x 80μm. Multiple scans can be performed, however, to provide greater statistical accuracy.

Figure 10

Key attributes of AFM for characterization of nanoparticles:

- *Qualitative analysis*
  - *3D visualization*
  - *Material sensing*
- *Quantitative analysis*
  - *Size*
  - *Morphology*
  - *Surface texture/roughness parameters*
  - *Statistical information*
    - *Particle counting*
    - *Size distribution*
    - *Surface area distribution*
    - *Volume and mass distributions*
    - *Spatial distribution*
- *Mediums*
  - *Gas*
    - *Ambient air*
    - *Controlled environments*
  - *Liquid dispersions*
  - *Solid dispersions*
- *Range*
  - *Particle size: 1nm to 8μm*
  - *Scan range: up to 80μm*

Common Particle Analysis Techniques

Given the wide variety of applications that use particles, it makes sense that there are many different ways to analyze and characterize particles. The following is a partial list of commercially available techniques employed in particle measurement:

- Acoustic Attenuation Spectroscopy
- Aerosol Mass Spectroscopy (Aerosol MS)
- Cascade Impaction
- Condensation Nucleus Counter (CNC)
- Differential Mobility Analysis (DMA)
- Dynamic Light Scattering (DLS) or Photon Correlation Spectroscopy (PCS) or Quasi-elastic Light Scattering (QELS)
- Electrical Zone Sensing (Coulter Counting)
- Electroacoustic Spectroscopy
- Electrokinetic Sonic Amplitude
- Gas Absorption Surface Area Analysis (e.g. BET)
- Laser Doppler Velocimetry (LDV)
- Laser Light Diffraction or Static Light Scattering
- Light Microscopy or Optical Imaging
- Microelectrophoresis
- Scanning Electron Microscopy (SEM)
- Sedimentation (Gravitational & Centrifugal)
- Sieving
- Tapered Element Oscillating Microbalance (TEOM)
- Transmission Electron Microscopy (TEM)
- X-ray Diffraction (XRD)

Ensemble vs. Single-Particle Techniques

Particle analysis techniques can generally be classified as ensemble or single-particle techniques.

With ensemble techniques, a signal from an individual particle cannot be isolated. Instead, ensemble techniques receive signals from multiple particles simultaneously. Laser light diffraction is a commonly employed ensemble technique.

In contrast with ensemble techniques, single-particle techniques isolate and identify signals from individual particles. Statistical information for groups of particles can be obtained by processing data from many different individual particles. A common example of a single-particle technique is optical imaging combined with image processing to measure and analyze particles.

In general, morphological information, such as shape and aspect ratio, as well as surface information, such as texture and roughness parameters, cannot be obtained using ensemble techniques. Only single-particle techniques which look at individual particles can supply such information. Physical parameters for each particle in a set of particles are recorded to generate a statistical distribution for the entire set of particles.

Which Technique is "The Best"?

Obviously, there is not one single "best technique" for *all* situations. Determining the best technique for a particular situation requires knowledge of the particles being analyzed, the ultimate application of the particles, and the limitations of techniques being considered.

Depending on the application of interest, a number of techniques can be used to analyze and characterize nanoparticles. In industries where aerosols play an important role, tools such as the Differential Mobility Analyzer (DMA) are commonplace. With fine powders, light scattering techniques are common.

The table on page 6 describes some common particle analysis techniques and their benefits and drawbacks in comparison with the AFM.

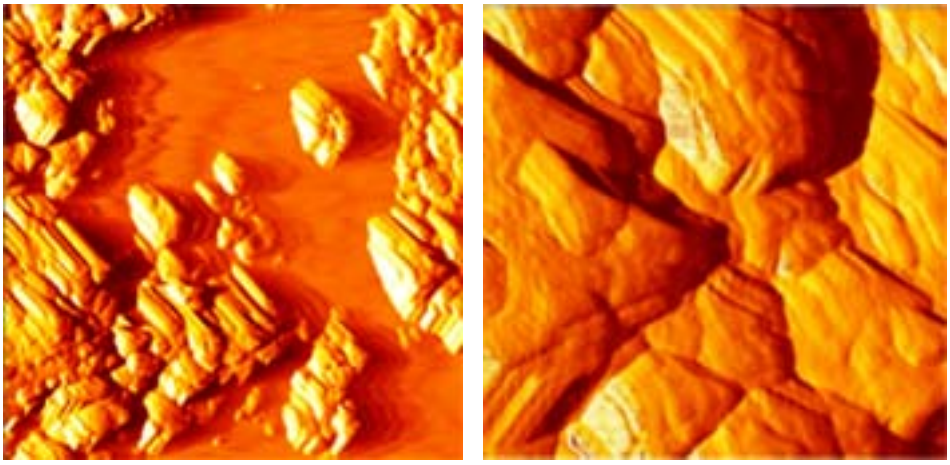
Technique	Common Applications	Characteristics	Comparison with AFM
Laser Light Diffraction	*Powders*	• *Ensemble technique* • *Commonly used in chemical and pharmaceutical industries* • *Fraunhofer and Mie light scattering are the basic principles of operation* • *Typical range: 1μm to 1000μm*	• *Morphological information limited to aspect ratio* • *No surface information* • *Imaging of individual particles impossible* • *Range excludes particles <1μm, but, unlike AFM, can measure particles with much larger diameters (>10μm)*
Dynamic Light Scattering	*Powders*	• *Ensemble technique* • *Also commonly used in chemical and pharmaceutical industries* • *Relies on Brownian motion of particles in a liquid medium to determine particle size* • *Typical range: 50nm to 1μm*	• *Morphological information limited to aspect ratio* • *No surface information* • *Imaging of individual particles impossible* • *Sample must be dispersed in liquid, which can alter particle characteristics* • *Range is comparable to AFM, but fails to span the gap to measure in the 1μm to 10μm range*
Sedimentation	*Powders*	• *Ensemble technique* • *Level of obscuration of visual light or X-ray signal determines particle size distribution* • *Typical range: >0.1μm*	• *No morphological information* • *No surface information* • *Imaging of individual particles impossible* • *Range excludes particles <100nm* • *Sample must be dispersed in liquid*
Coulter Counting	*Powders*	• *Single particle technique* • *Established technique for particle counting* • *Provides measurement based on volume displacement* • *Typical range: >0.5μm*	• *No morphological information* • *No surface information* • *Imaging of individual particles impossible* • *Range excludes particles <0.5μm* • *Sample must be dispersed in electrolytic liquid*
DMA + CNC	*Aerosols*	• *Ensemble technique* • *DMA creates monodisperse stream of particle; relies on mass-based charge to isolate particles within a specified size range* • *CNC grows small particles to a size large enough to detect with other techniques, such as light scattering* • *Typical range: >10nm*	• *No morphological information* • *No surface information* • *Imaging of individual particles impossible* • *CNC alters particles before they are measured*
Light Microscopy	*Powders and Aerosols*	• *Single particle technique* • *Typical range: >1μm*	• *Resolution limited by light wavelength; range excludes particles <1μm*
SEM	*Powders and Aerosols*	• *Single particle technique* • *Compositional information can be obtained with EDS.* • *Typical range: 50nm to 1cm*	• *Sample preparation can be complex* • *Generally must be performed at vacuum* • *Costly equipment*
TEM	*Powders and Aerosols*	• *Single particle technique* • *Compositional and crystallographic information can also be obtained.* • *Typical range: 5nm to 500μm*	• *Since e-beam is transmitted through sample, image is 2D projection of sample* • *Sample preparation can be very complex* • *Must be performed under vacuum* • *Costly equipment*

Sample Preparation

Nanoparticles typically fall into one of two categories when it comes to sample preparation. The first category is nanoparticles rigidly attached to a solid structure. The second category is nanoparticles with weak adhesion to the substrate, such as dispersions of nanoparticles in liquid or dry mediums.

Figure 12

(a) Scan size: 21μm x 21μm *(b) Scan size: 3μm x 3μm*



Calcium phosphate (CaP) nanocrystals on Tempfix scanned with the NANO-R.

A good example of the first category is nanoparticles imbedded a solid matrix, as in the case of nanocomposites or nanoprecipitates[3]. In such cases, typically a cross-section of the composite material is scanned to determine such properties as average particle size and spatial distribution.

Examples of nanoparticles in the second category are quantum dots, diesel soot particles, carbon black, and colloidal suspensions.[4] Sample preparation for the second category of nanoparticles can be more complicated than for the first category. Because the AFM works by scanning a mechanical probe across a flat surface, any structure being imaged must have greater affinity to the flat surface than to probe tip. When nanoparticles do attach to the probe, the resulting images typically show reduced resolution. Streaking may occur if nanoparticles are not rigidly attached to the flat surface. To avoid such artifacts, close contact or vibrating mode is strongly recommended for such samples.

In certain cases it is necessary to affix nanoparticles in liquid or dry mediums to a sticky substrate. A cheap and easy way to do this is the use of double-sided sticky tape or other similar methods commonly used by microscopists. More refined techniques include the use of mica, "Tacky Dot" slides, and TempFix. Calcium phosphate nanocrystals mounted on TempFix can be seen in Figure 12. Information on mica use is readily available in technical literature.[5] Use of "Tacky Dot" slides and TempFix are well described in PNI's Application Note "Atomic Force Microscopy for Nanostructures."

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[1] J.B. Donnet, T.K. Wang, J.C.M. Peng, and S. Rebouillat, *Carbon Fibers, 3rd edition,* New York, NY, Marcel Dekker, 1998.

[2] L. Boras and P. Gatenholm, "Surface Composition and Morphology of CTMP Fibers," *Holxforschung*, Vol. 53, No. 2,1999,188-194.

[3] F. Li, S.V. Prikhodko, A.J. Ardell, and D. Kim, "Proceeding of the International Conf. On Solid-Solid Phase Transformations. '99 (JIMIC-3)," (Edited by M. Koiwa, K. Otsuka, and T. Miyazaki) *The Japan Institute of Metals*, 1999, 545.

[4] M. Mucalo, C. Bullen, M. Manely-Harris, and T.McIntire, "Arabinogalactan from the Western larch tree: a new, purified and highly water-soluble polysaccharide-based protecting agent for maintaining precious metal nanoparticles in colloidal suspention," *Journal of Material Science*, 37, 2002, 493-504.

[5] J. Vasenka, S. Manne, R. Giberson, T. Marsh, and E. Henderson, "Colloidal Gold Particles as an Incompressible AFM Imaging Standard for Assessing the Compressibility of Biomolecules," *Biophysical Journal*, Vol. 65, 1993, 992-997.