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Interpreting Laser Diffraction Results for Non-Spherical Particles

David M. Scott

Advanced Particle Sensors

david.scott@particlesci.com

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Abstract

Particle shape is often overlooked in Laser Diffraction measurements, but it affects the diffraction pattern used to determine particle size distribution (PSD). As a result, laser diffraction instruments tend to report bi-modal PSDs for non-spherical particles, even for samples containing a single size class. Therefore a bi-modal result is ambiguous unless shape is considered.

Equipped with only qualitative knowledge of particle shape, the particle analyst can resolve this inherent ambiguity and even use laser diffraction to measure aspect ratio of non-spherical particles. This webinar explains the origin of this effect, describes how to interpret PSD data in such cases, and demonstrates practical applications for measurements of organic crystals, polymer flakes, bacteria, yeast, and clays.

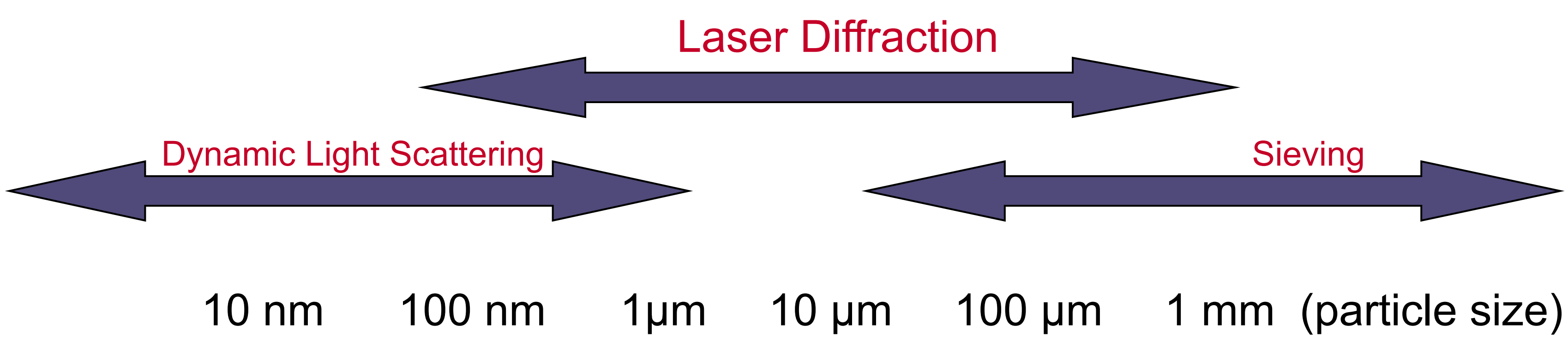
This presentation is based on a conference paper by David M. Scott and Tatsushi Matsuyama, "Laser diffraction of acicular particles: practical applications", at the 2014 International Conference on Optical Particle Characterization (OPC 2014), published in N. Aya et al., Editors, Proceedings of SPIE Vol. 9232 (SPIE, Bellingham, WA 2014), 923210.

Outline

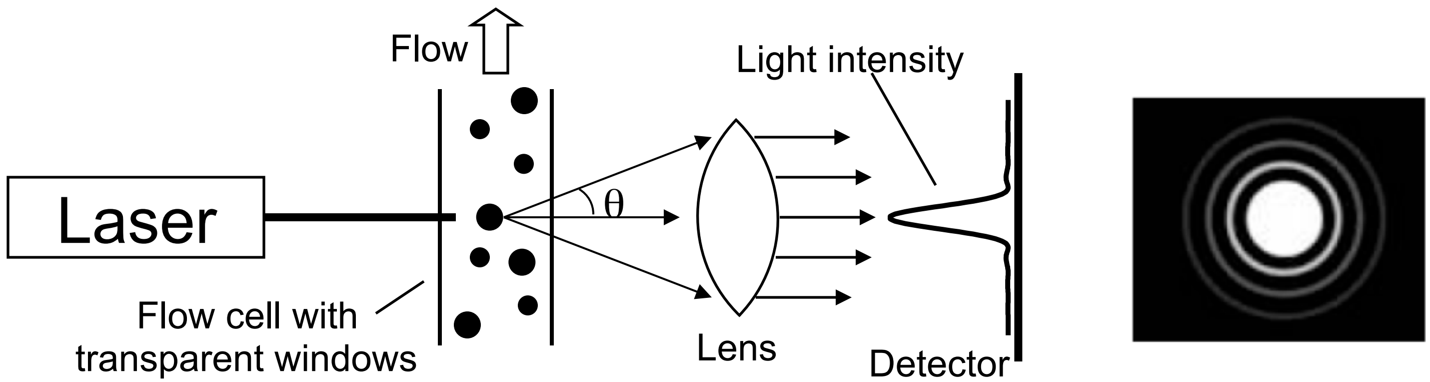
1. Brief Review of Laser Diffraction for Spherical Particles
2. Impact of Shape on Laser Diffraction Results
3. The Measurement Dilemma and Its Resolution
4. Interpreting Results for Non-Spherical Particles
5. Application Examples for Real-World Samples
6. References

Benefits of Laser Diffraction

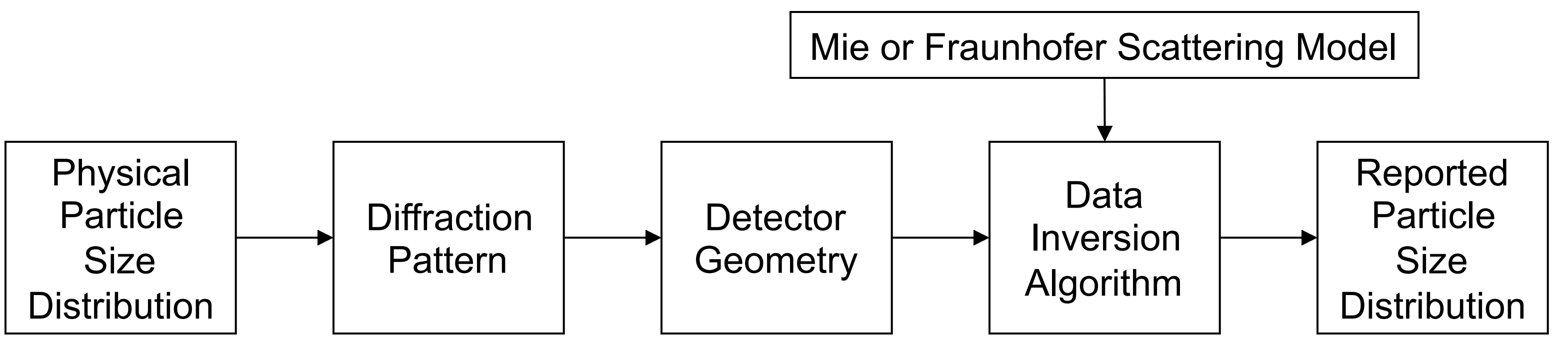
- Fast
- Simple
- Wide range of sizes (less than 100 nm to over 2 mm)
- Requires very little sample (<0.1 g powder, <0.2 mL dispersion)
- Versatile: dispersions, droplets in liquids, sprays, solvents, etc.
- On-line and in-process applications are possible
- Commonly used throughout industry



Laser Diffraction (Spherical Particles)



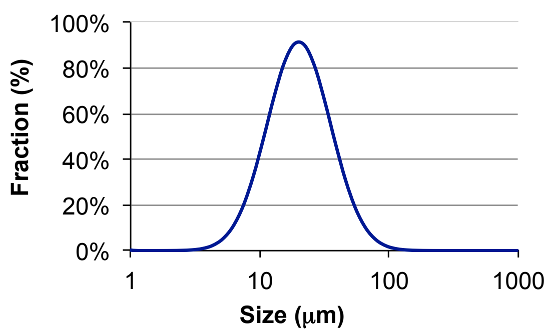
Scott, Industrial Process Sensors (CRC Press, 2008), Fig. 8.12



Detector design and scattering model typically assume that particles are spherical

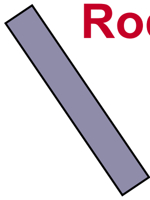
Particle Size Distribution (PSD)

- Samples of interest usually contain a range (distribution) of particle sizes.
- Laser Diffraction size distributions are typically reported on the basis of particle volume.
- PSDs frequently (but not always) approximate a log-normal distribution, which can be described by a median size and a geometric standard deviation.
- Log-Normal distributions shown on a semi-log graph resemble a Normal distribution that is plotted on linear axes.

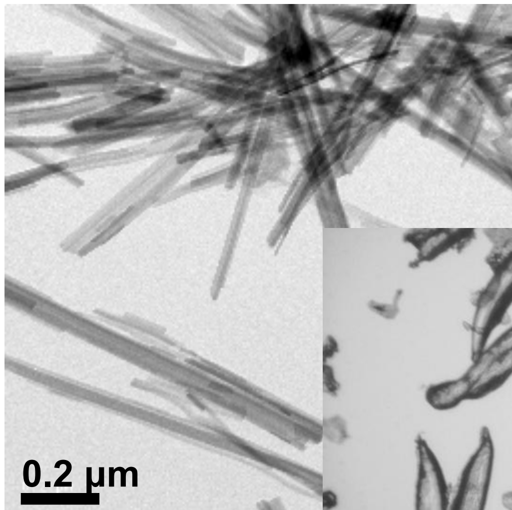


Particles Are Often Non-Spherical !

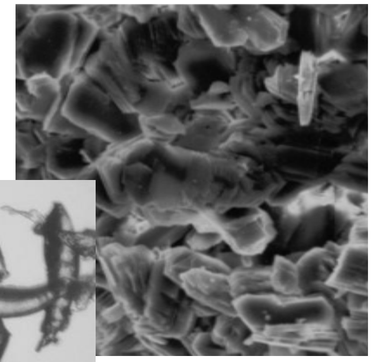
Rods



Sepiolite (clay)

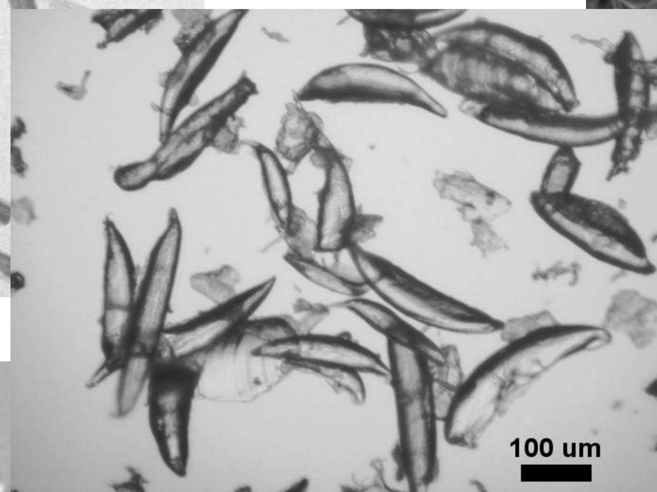


Kaolinite (clay)



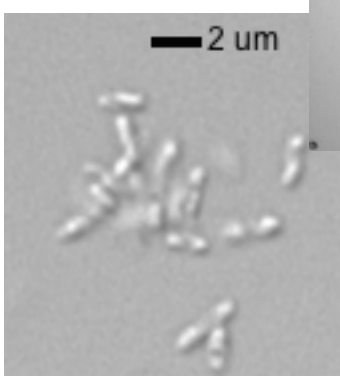
Credit:USGS

Disks



Polymer flakes

Ellipsoids



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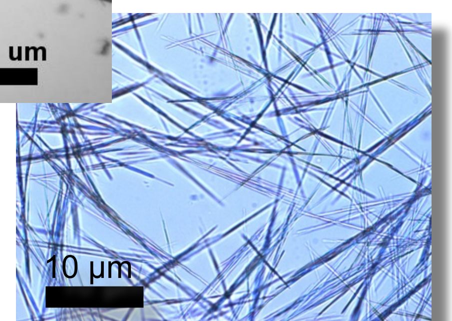
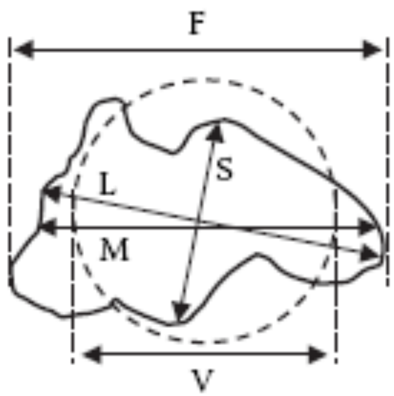


Crystallized amino acid

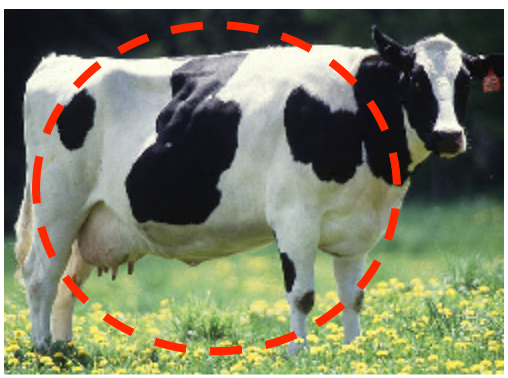
Sizing a Non-Spherical Particle



Scott, Industrial Process Sensors (CRC Press, 2008), Fig. 8.1

Various definitions of particle size :

- Feret's diameter (F)
- Minor axis of the projection (S)
- Martin's diameter (M)
- Equivalent Sphere Diameter, ESD (V)
- etc.



Credit: cow photo from USDA.gov

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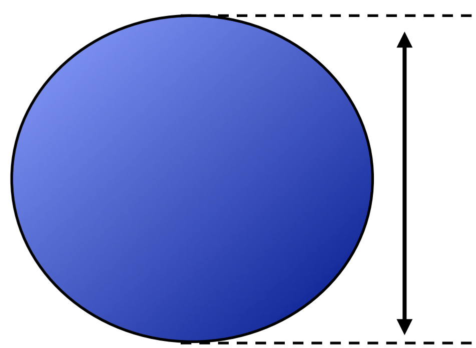
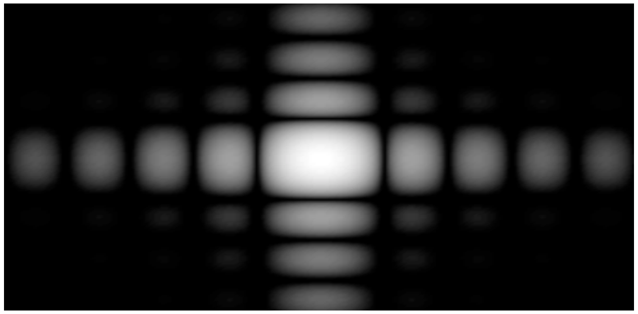


Many applications "assume the spherical cow", or the ESD (diameter of the sphere with equivalent volume).

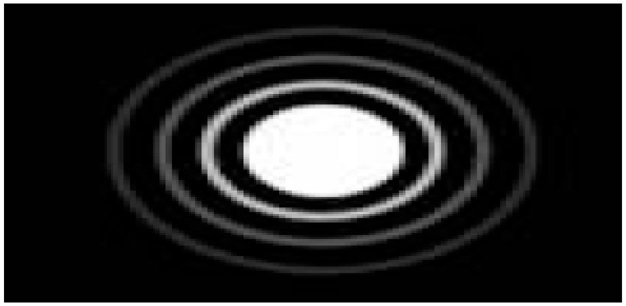
Diffraction from Rods and Spheroids

Rectangle (rods)



Credit: Adapted from an image by Christophe Finot

Ellipse (spheroids, disks)



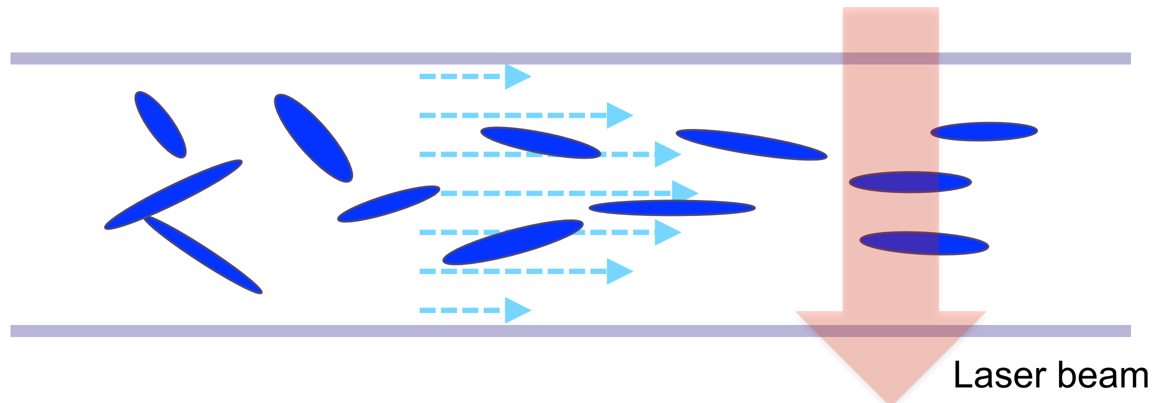
Sphere

Unlike diffraction from a sphere, for rods and disks the intensity depends on the azimuthal angle as well as the polar angle.

Diffraction equations are given by Matsuyama et al. (2000) and Takano et al. (2012)

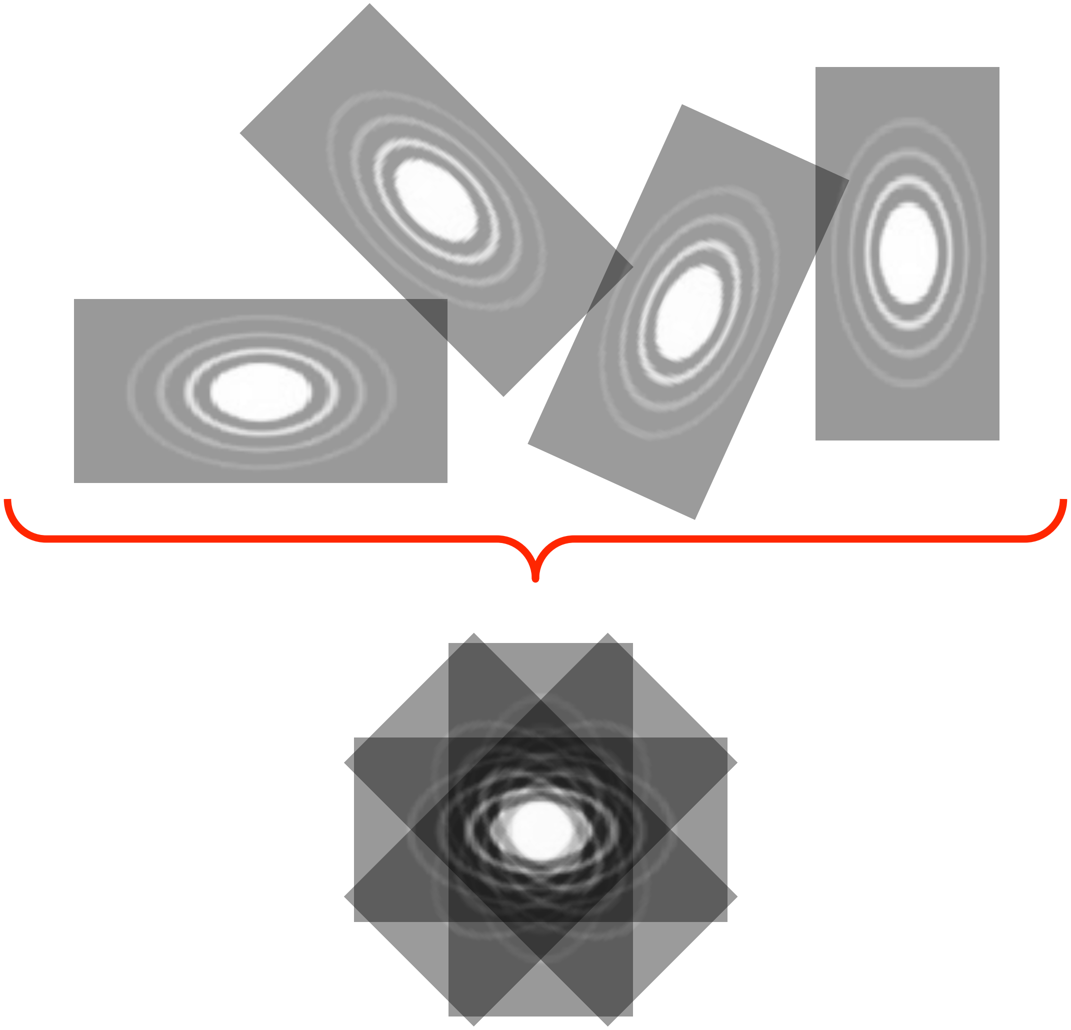
Alignment in Laminar Flow

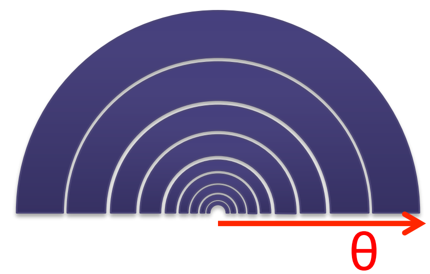
- Flow Cells typically operate in laminar flow regime (with Re << 2000)
- Velocity across the flow cell has parabolic profile



- The flow aligns the particles (Jeffery 1922) perpendicular to the laser beam, but not necessarily in the same direction.

Integration over Many Particles



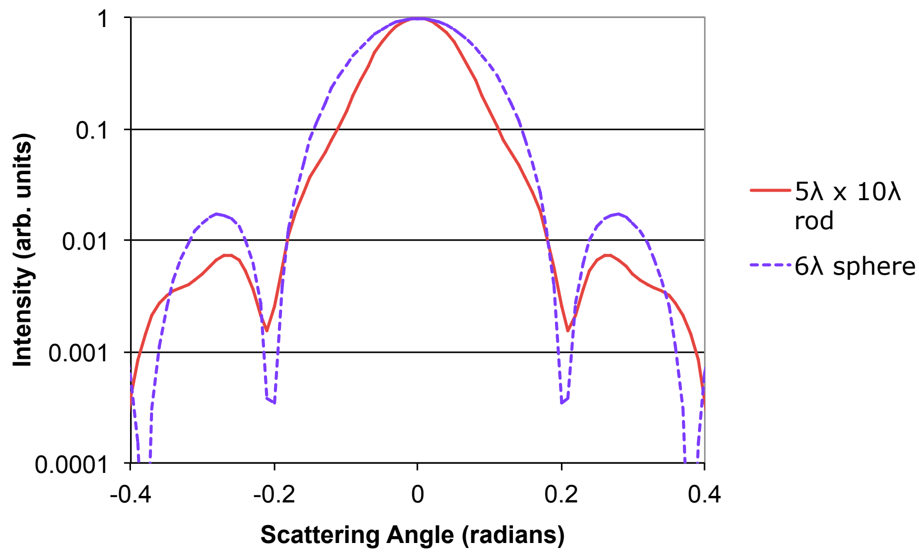


The resulting diffraction pattern (light intensity versus scattering angle θ) is a mixture of contributions from the major and minor axes of the particle.

The Result

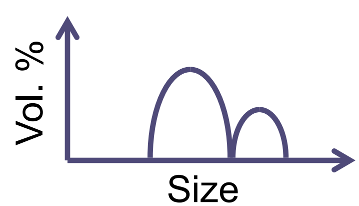
The observed diffraction signal (intensity versus scattering angle) cannot be described by diffraction from a single sphere.

Diffraction pattern



In general, the instrument reports a bi-modal distribution:

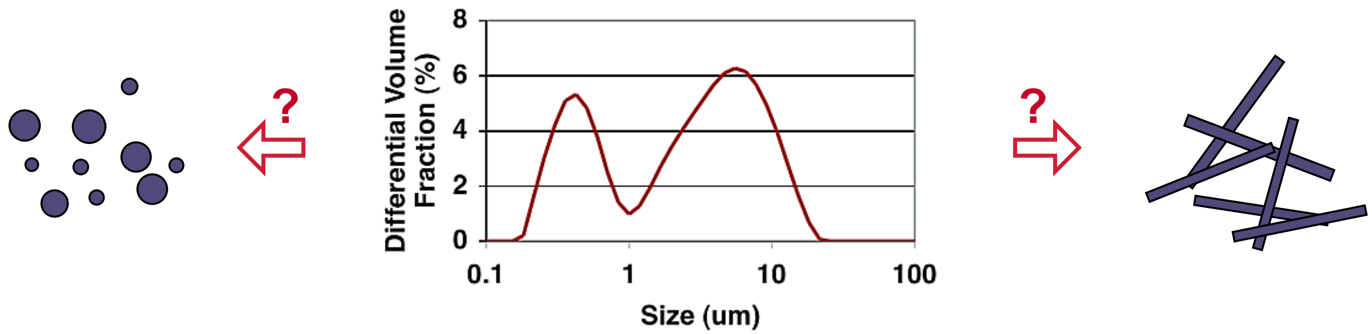
PSD



The Measurement Dilemma

Given a bi-modal or multi-modal result for an unknown material:

- Does the PSD signify that there are different size classes (e.g. primary and aggregate) of quasi-spherical particles?



- Or, does the apparent PSD indicate that non-spherical particles are present?
- How do we interpret PSD results for non-spherical particles?

Resolving Ambiguity

To solve the dilemma, we only need to know whether or not the particles are approximately spherical.

This information may be known *a priori* (e.g. from crystal habit or particle formation considerations), but it is most often determined by imaging:

- Optical microscopy
- Dynamic Image Analysis
- Scanning Electron Microscopy

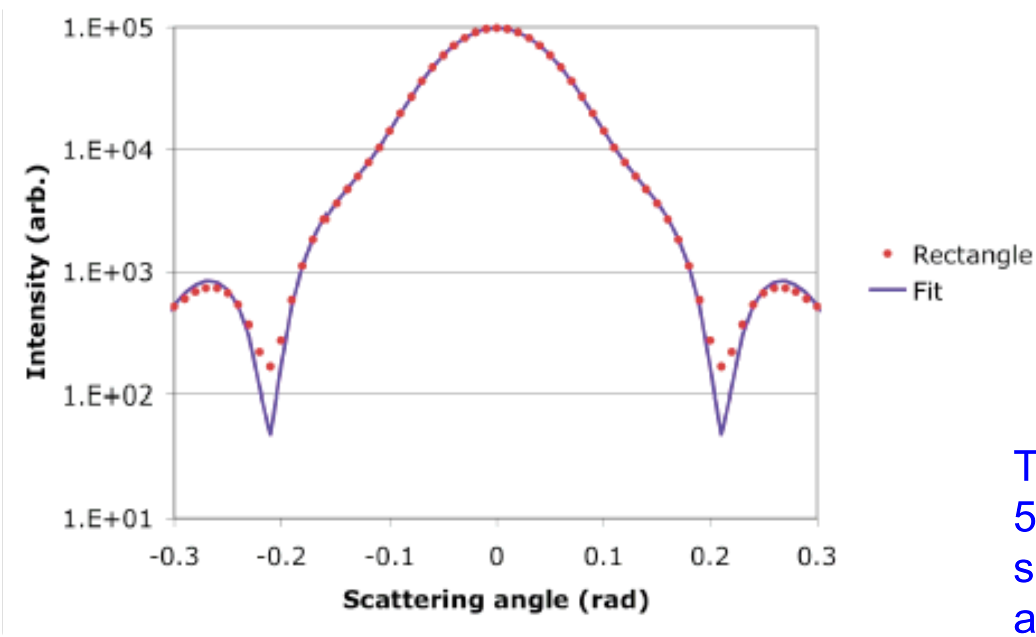
If the particles are approximately spherical, the PSD may be reported as usual.

Interpreting PSD Results for Non-Spherical Particles

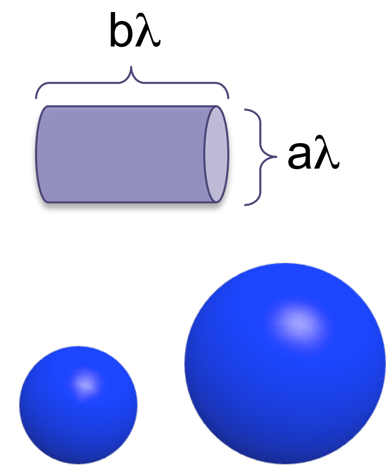
The Approach – Diffraction Equivalence

Since the diffraction signal cannot be described by diffraction from a single sphere, try a mixture of 2 sizes!

One size (a) represents the particle diameter, and the other (b) represents the length (scaling to wavelength simplifies the math).



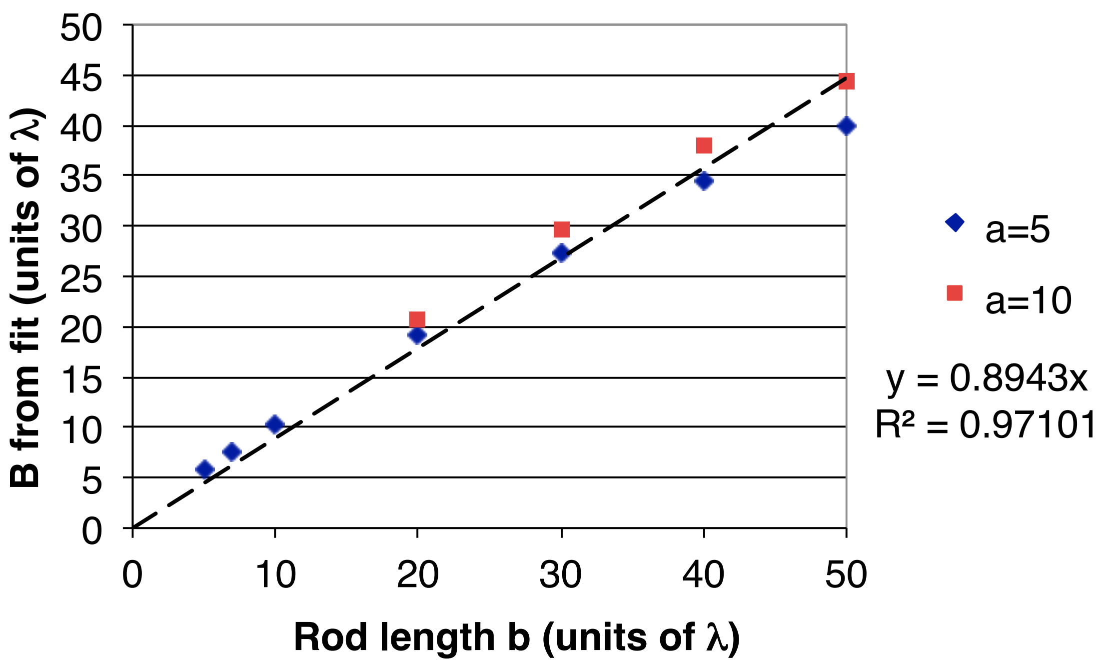
5 λ x 10 λ rectangle

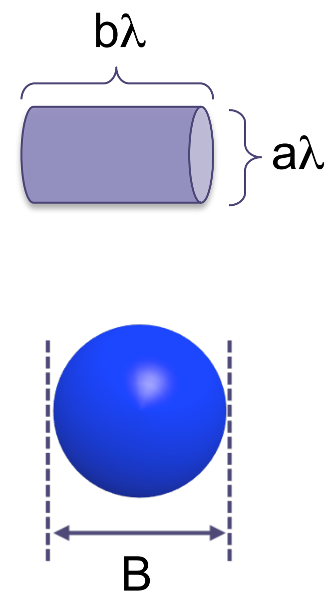


The diffraction pattern of a 5 λ x 10 λ rod is nearly the same as the pattern from a mixture of 6.1λ and 10.4λ spheres.

Interpreting Particle Length

The previous calculation of equivalent diffraction has been repeated for a number of rods of various lengths (bλ).



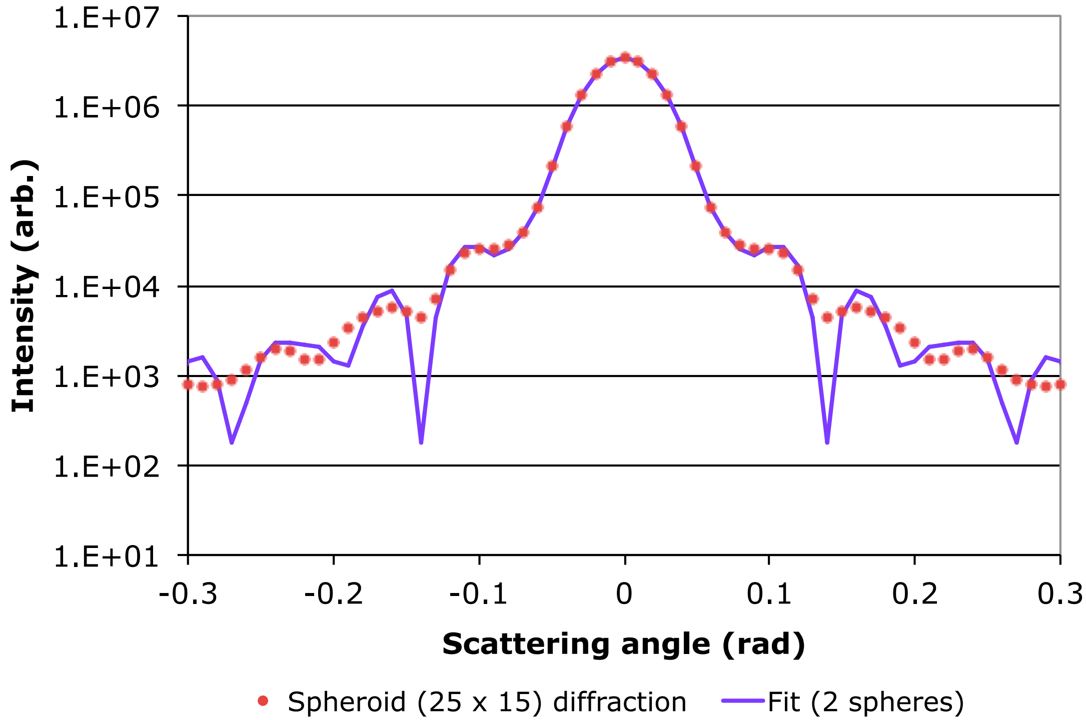


Numerical results show the diameter of the large sphere (B) is about 10% smaller than the actual rod length (b).

Diffraction Equivalence for Spheroids

The diffraction pattern from a spheroid can also be represented as the combined diffraction from two spheres.

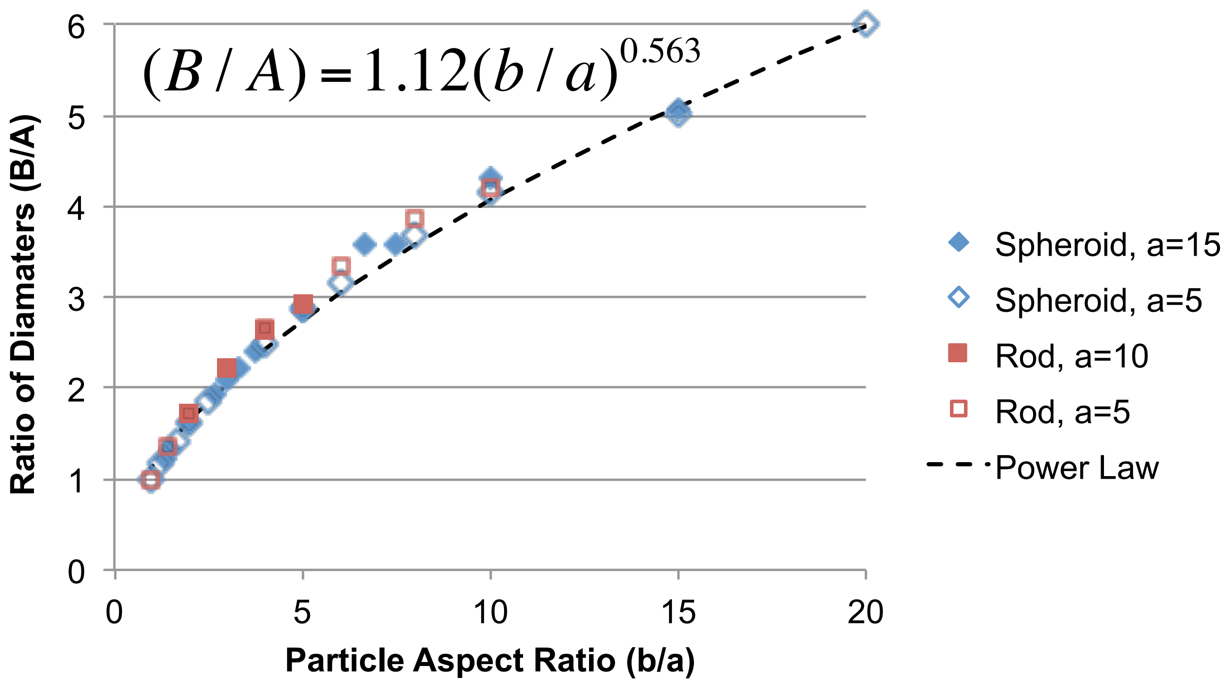
Note: Side lobes cannot be fit accurately with only 2 spheres. Matsuyama et al. (2000) showed a size distribution is needed .



Prolate spheroid

Estimating Aspect Ratio

Calculations for rods and spheroids show that the aspect ratio (b/a) and the corresponding ratio (B/A) of spheres giving equivalent diffraction appear to be related by a universal curve:



Given (B/A), the aspect ratio is estimated as $(b/a) = 0.893(B/A)^{1.776}$

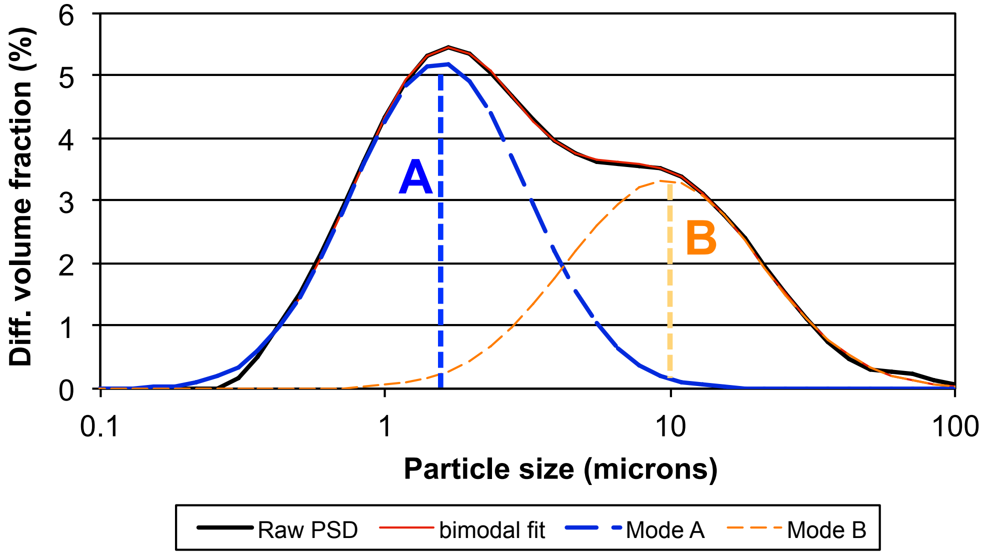
Deconvolution (Fitting)

- Diffraction from mono-sized rods and spheroids can be approximated by combining two or more spheres.
- A range of sphere sizes is required to approximate diffraction from polydisperse samples.
- In most cases, bi-lognormal distributions can be fitted to the observed data, thus deconvolving the length and width contributions.
- Median sizes (a and b) of the two component distributions are related to the median values of the minor and major axes (A and B) of the subject particles.

Bi-Log-Normal Distribution

Bi-Log-Normal distribution is characterized by TWO logarithmic median sizes, TWO logarithmic standard deviations, and the relative contributions of both size components.

This example shows a bi-log-normal distribution fitted to data:

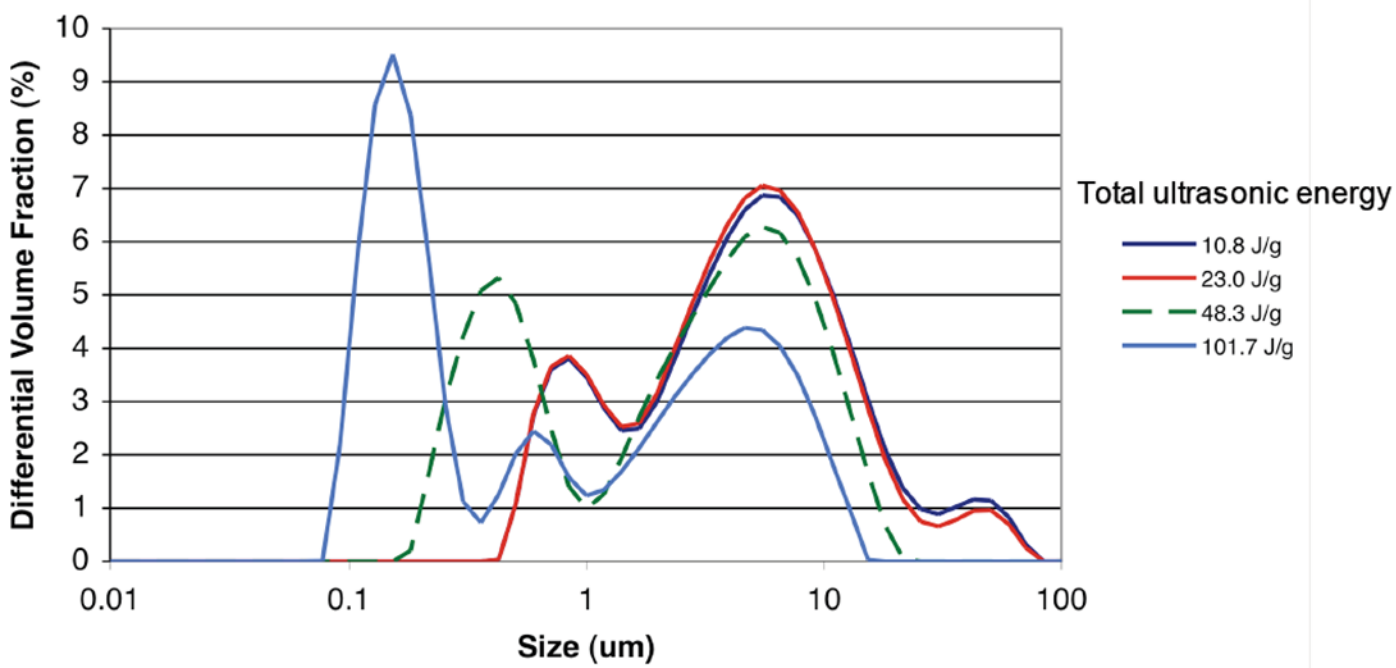


Note: Median size A and B can be approximated directly (without fitting) from the positions of the peaks.

Examples: Rod-Like Particles

Sepiolite

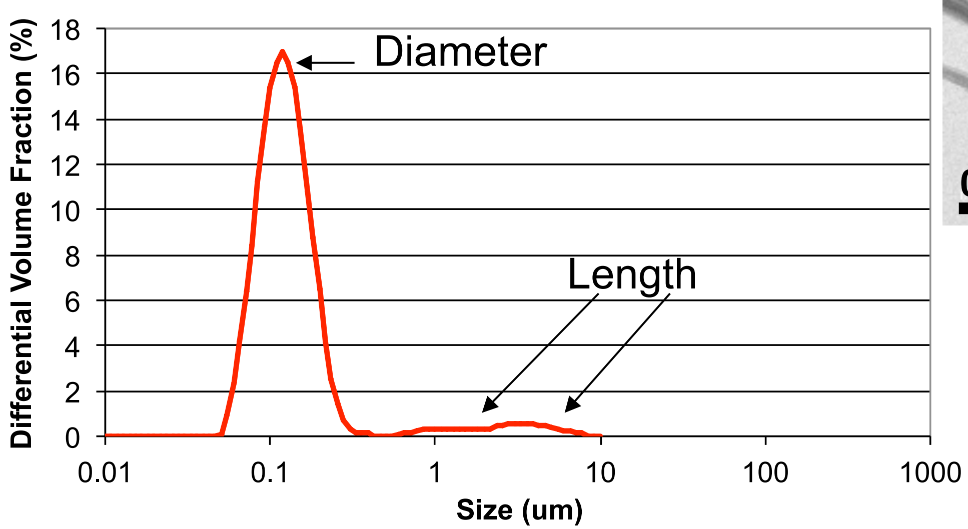
- Sepiolite is a magnesium silicate clay with fibrous structure, used to reinforce materials (e.g. nanocomposites)
- High power sonication disperses the fibers
- Peak associated with the fiber diameter becomes more prevalent as fibers become more dispersed

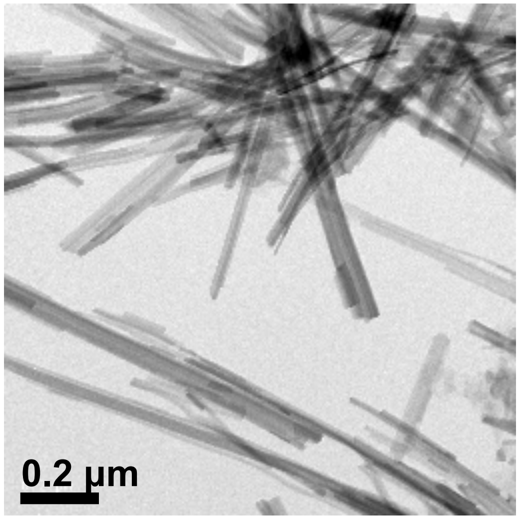


Sepiolite (Dispersed)

PSD of well-dispersed sepiolite is dominated by the peak associated with diameter

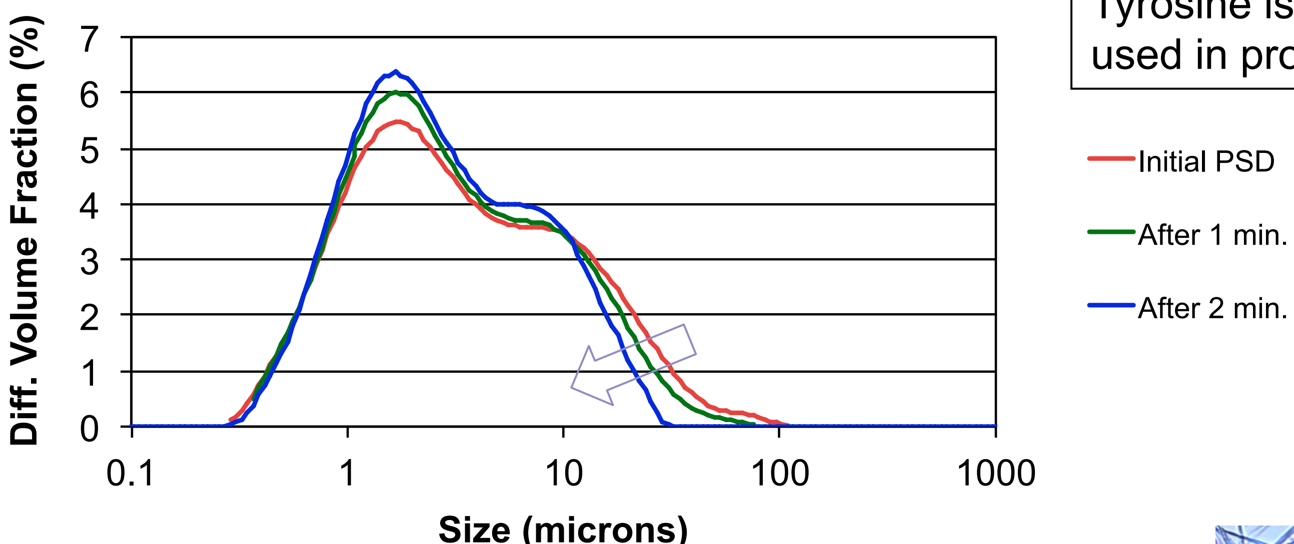
Note: Diffraction theory predicts this effect for infinitely long rods (Bohren & Huffman 1998)





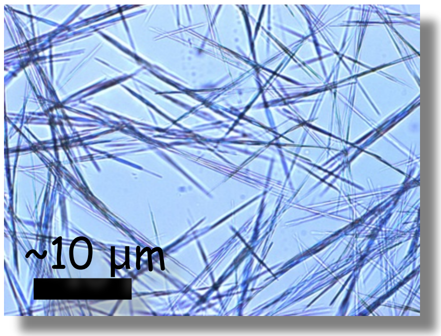
Sonication energy: 300 J/g

Tyrosine Crystals



Tyrosine crystals in methanol

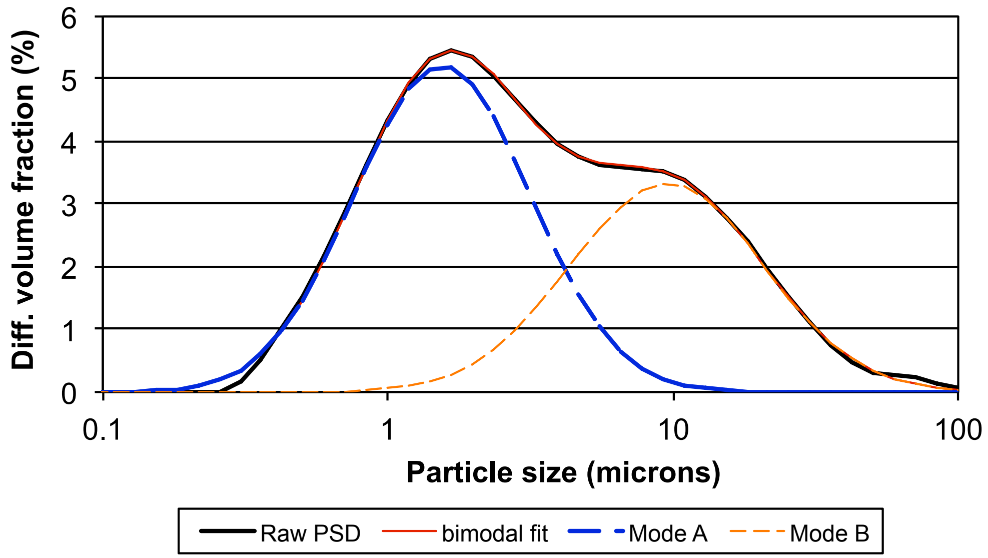
Tyrosine is an amino acid used in protein synthesis



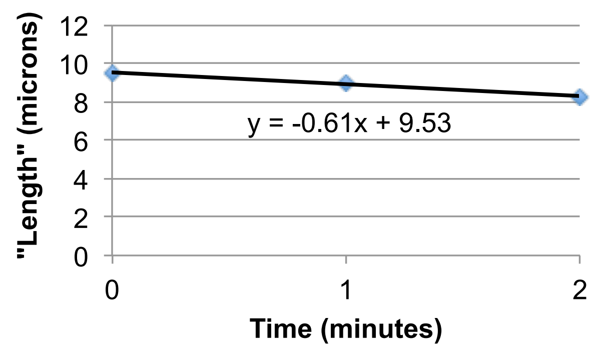
Crystals are broken by the pump during recirculation (note the reduction in the coarse tail of the distribution over time). No sonication was used in this example.

Deconvolution of Crystal Data

Bi-modal deconvolution is used to determine the approximate crystal length as a function of time:

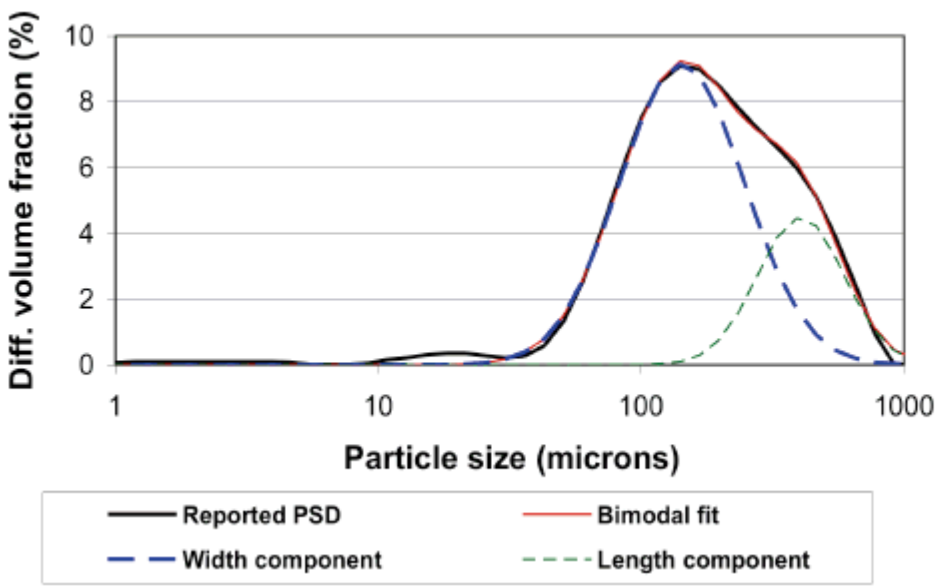


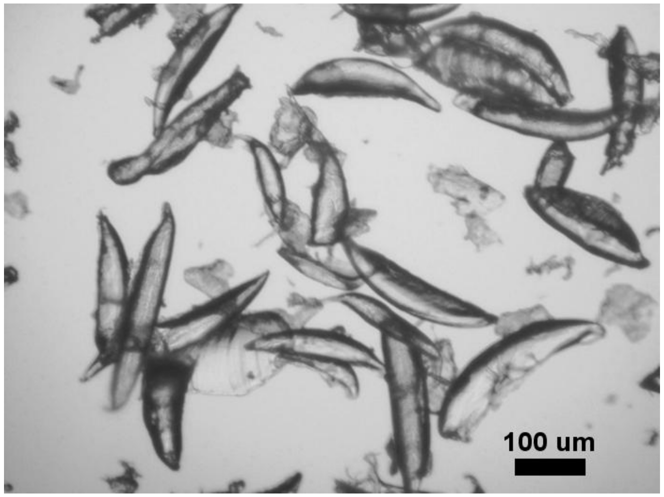
The median crystal length decreases about 0.6 microns per minute during recirculation



Example: Ellipsoidal Particles

Polymer Flakes

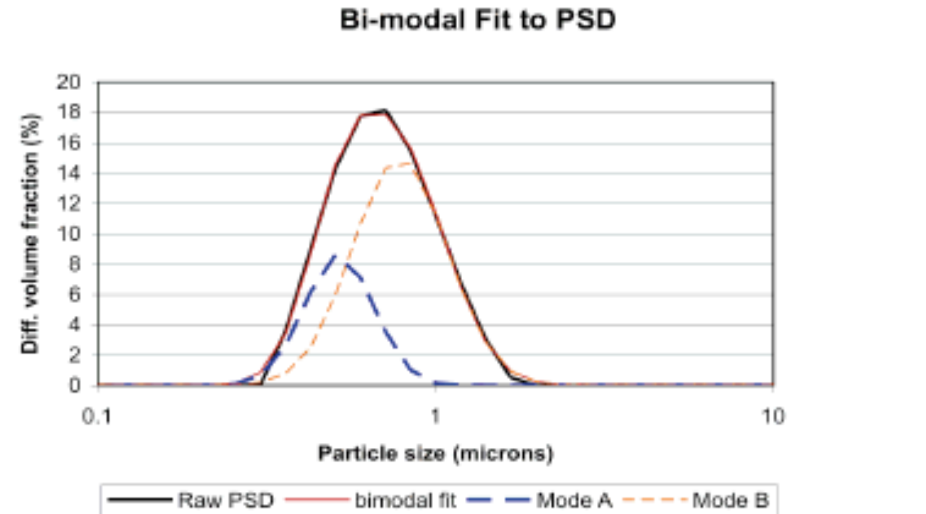




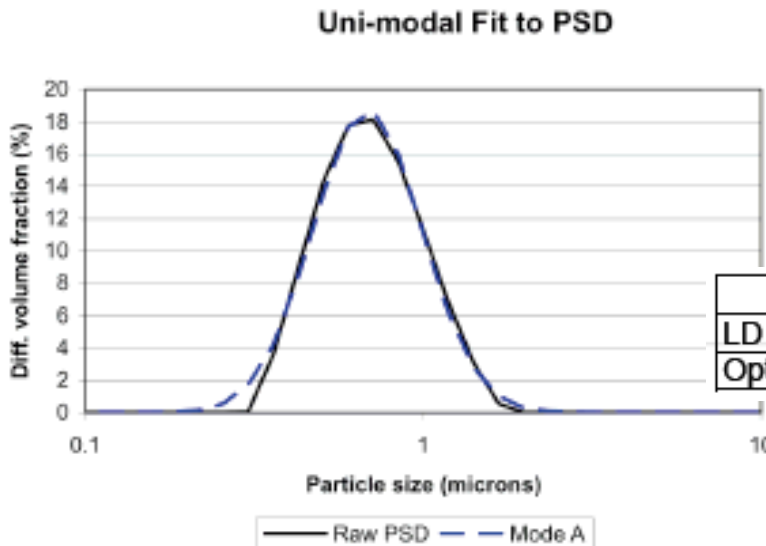
- Median of distribution corresponding to width is 143 μm
- Median of distribution corresponding to length is 406 μm

E Coli

RMS error 0.128

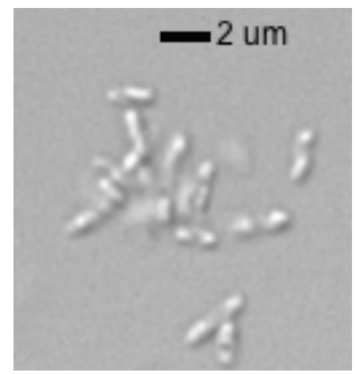


RMS error 0.267



Best fit to PSD is obtained with two size modes

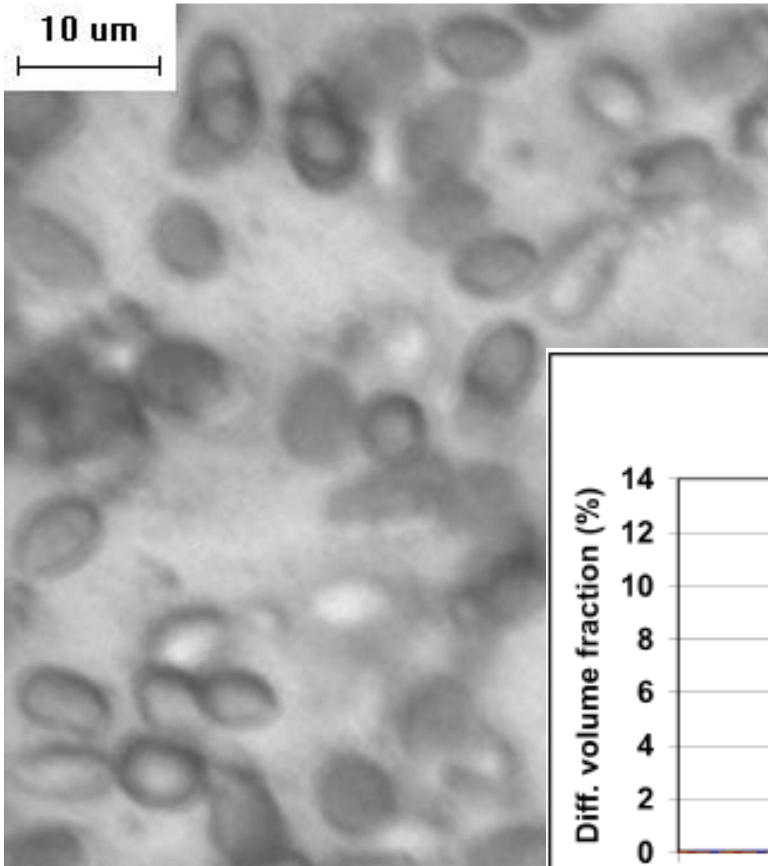
Ratio of the two modes is 1.5, consistent with direct microscopic observation



	Length (um)	Width (um)	Aspect Ratio
LD deconvolution	0.78	0.52	1.50
Optical Microscopy	0.94	0.63	1.49

RI = 1.397+0.01i (Balaev et al. 2002)

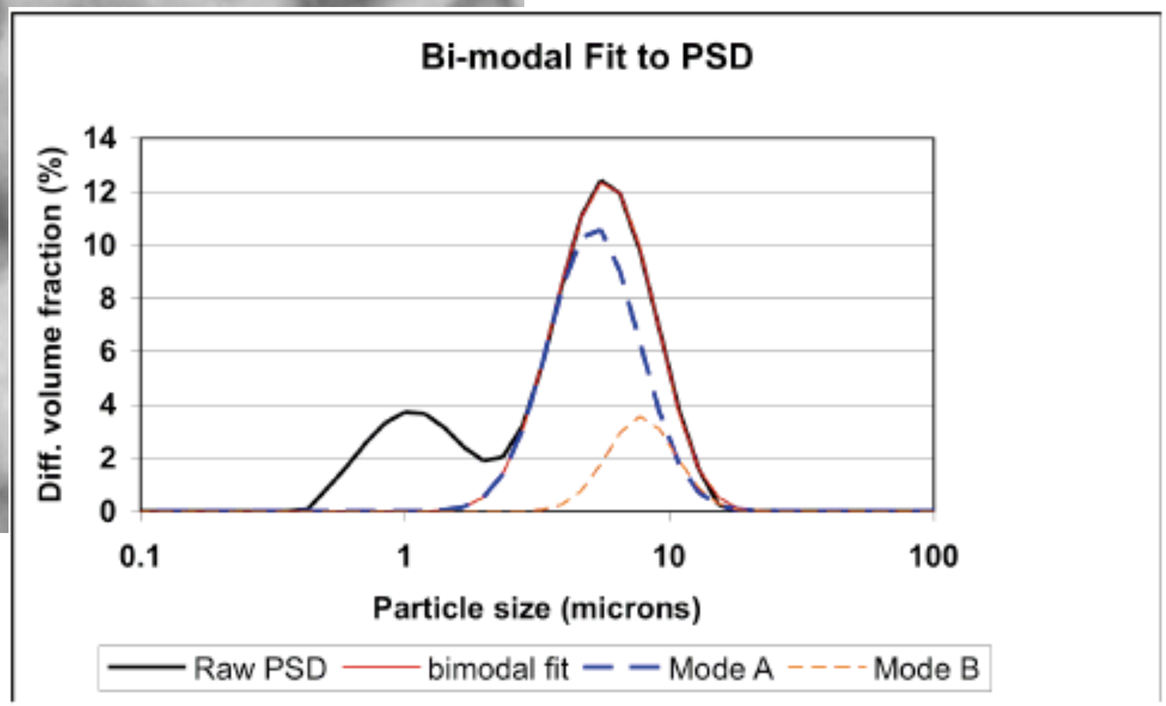
Yeast



Deconvolution of coarse peak yields 5.2 x 7.8 µm, close to observed size

Origin of PSD peak at 1 µm is unclear (scattering from cell wall??)

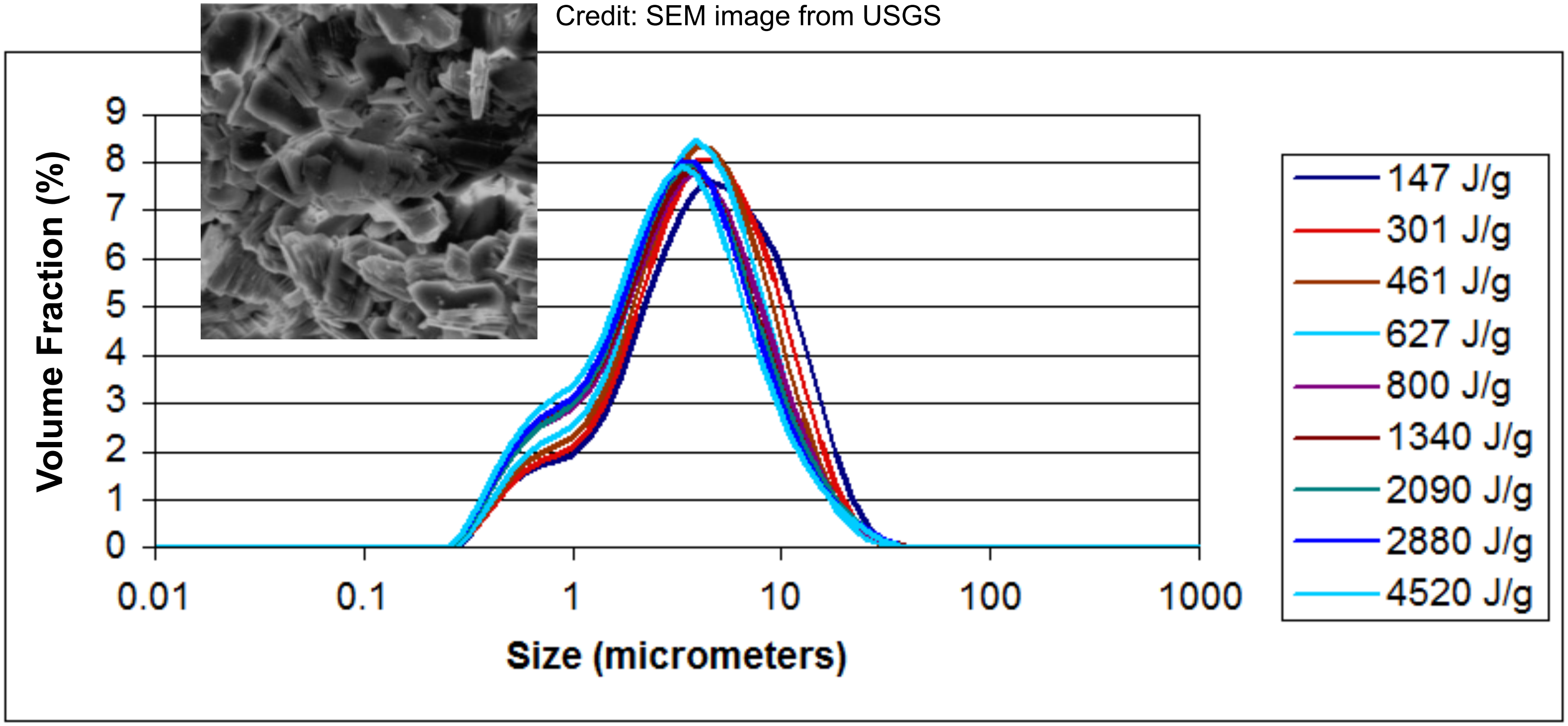
Assume RI=1.52+0.01i



Examples: Plate-Like Particles

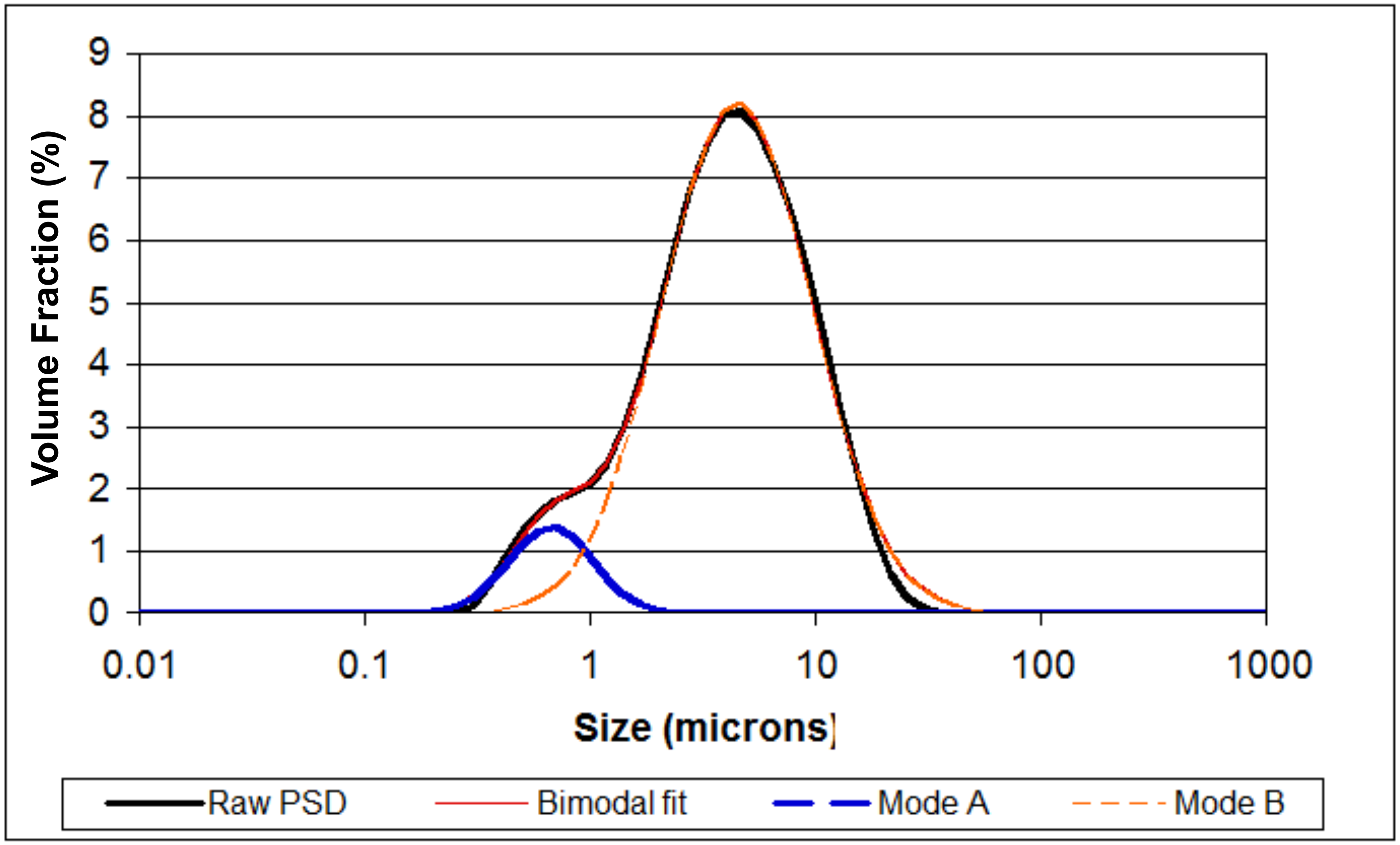
Dispersion of Kaolinite

Credit: SEM image from USGS



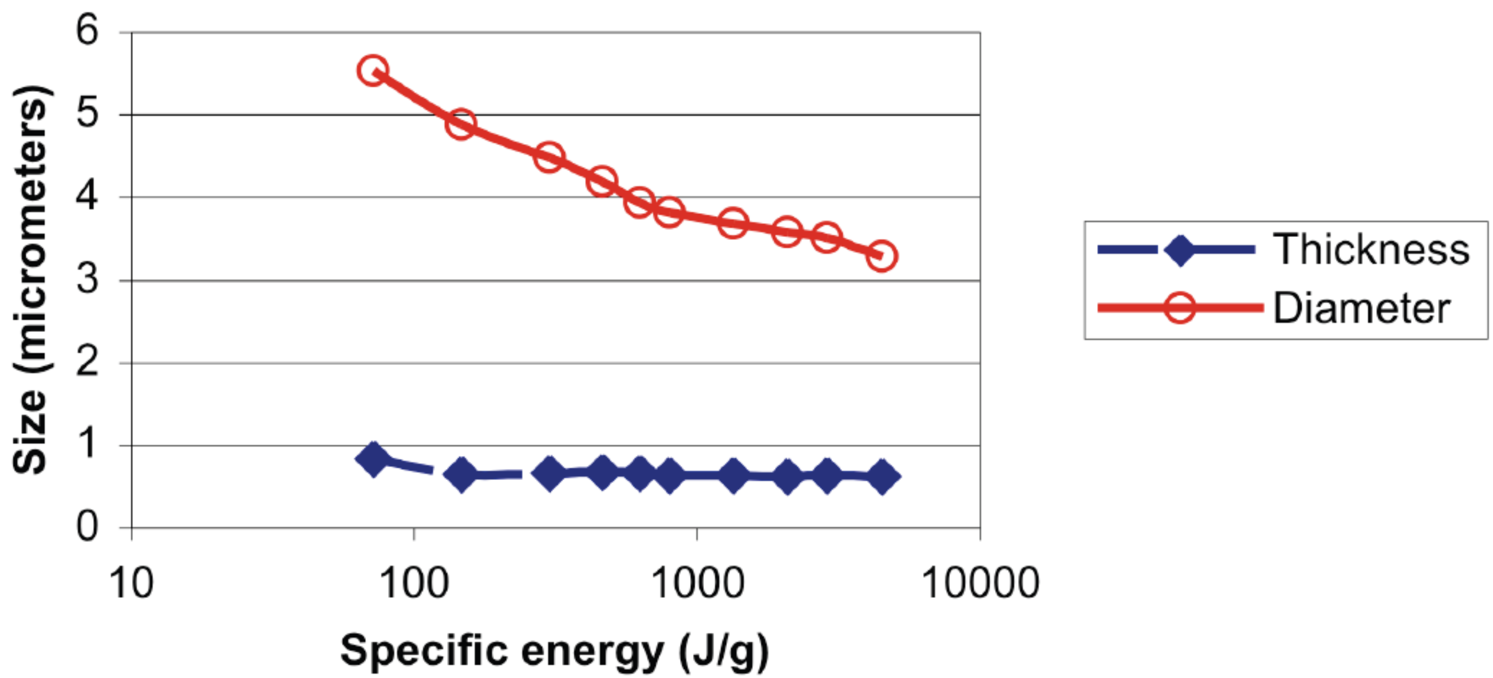
- Kaolinite was dispersed in an organic solvent with a high shear mixer
- Samples were drawn at regular intervals of time
- Power number of the rotor was used to estimate the total specific energy for each sample

Deconvolution of Kaolinite PSD



Example of deconvolution of ESD PSD obtained with kaolinite

Dispersion of Kaolinite



- Results of deconvolving the ESD PSD data at each specific energy
- Component due to diameter decreases in size: plates are breaking
- Component due to thickness remains constant: there appears to be little exfoliation of the plates above 100 J/g

Conclusions

- Laser Diffraction typically gives bi-modal results for non-spherical particles, especially for (b/a)>1.5.
- Interpretation of multi-modal PSDs requires *a priori* knowledge of particle shape, but detailed information is not necessary to monitor particle size and aspect ratio.
- Bi-lognormal distributions can be fit to PSD data for a variety of industrial particles, yielding approximate distributions of particle length and width (or width and thickness).
- A universal curve has been discovered that shows the true aspect ratio varies as a power of the ratio of diameters (B/A).
- Finally, deconvolution of apparent PSD allows us to estimate aspect ratio and true dimensions of non-spherical particles.

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Credits

- Cow image from USDA.gov is in the public domain.
- Rectangular diffraction pattern is adapted from an image by Christophe Finot and used under license CC-BY-SA shown at https://creativecommons.org/licenses/by-sa/1.0/legalcode
- Kaolinite image from from United States Geological Survey (Bulletin 1614, 1985) is in the public domain