

Lower size limit for analysis using light scattering

Figure 2 illustrates that particles somewhat larger than the wavelength of the illumination light will scatter the light principally at very small angles. It also shows that for these particles it is possible to design detectors that provide equal signal current for all the sizes. Note that the height and shape of the scattering peak are essentially constant for sizes over five times the wavelength divided by the refractive index -- in this case $5 * 0.633 / 2.54 = 1.25 \mu\text{m}$.

For particles whose size is similar to or smaller than the wavelength of the illumination light it is not possible to use a similar detector design due to the pronounced peak of scattering (which is dependent on the optical properties of the particle and its surrounding medium). The pronounced peak in the scattering power at about $0.25 \mu\text{m}$ for anatase is also clearly shown.

For particles less than about 50 nm the light scattering is dependent on D^6 . For example, below about $0.25 \mu\text{m}$ for anatase the scattering falls very rapidly. This sharp drop in scattering efficiency is the major reason why laser diffraction units do not provide good results much below about $0.05 \mu\text{m}$. This lower size limit cannot always be achieved and varies with the optical properties of the particle and the surrounding medium.

Fig. 3

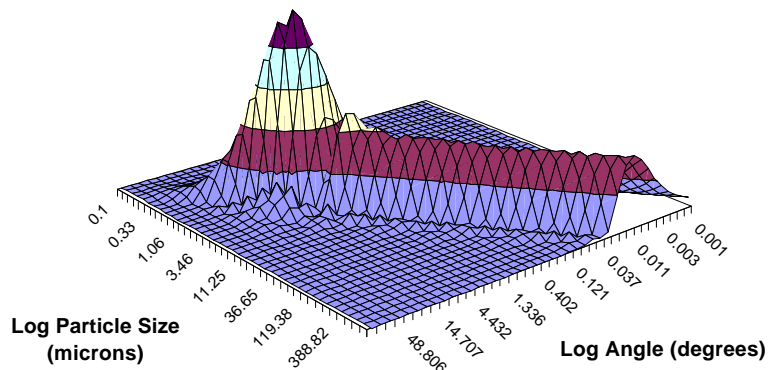


Fig. 3 uses the same Mie theory and scales as Fig. 2 but the material is lactose (RI = 1.533 – 0.01) suspended in *iso*-octane (RI = 1.39).

In Fig. 3 we see that because lactose has a smaller refractive index than anatase the pronounced peak of scattering occurs at a larger particle size (compared with Fig. 2) and that the rapid fall off of scattering due to the D^6 influence also appears at a larger particle size.

If a sample consisted of equal volumes of $0.25 \mu\text{m}$ and $20 \mu\text{m}$ particles, then it would not be possible for a laser diffraction unit to report the volume proportions faithfully *unless* the way that the quantity of light scattered by each size fraction was being correctly predicted. Mie theory provides such correct predictions.

The interaction of a particle with a beam of light results in some of the light being scattered and some being absorbed to heat the particle. The total effect of the particle on the light is termed extinction.

$$\text{Extinction} = \text{Scattering} + \text{Absorption}$$

For spherical particles Mie theory can be used to compute the extinction efficiency as the ratio of the extinction cross section to the geometric cross section. Transparent particles do not absorb light, so the extinction efficiency equals the scattering efficiency. The extinction efficiency, computed as a function of particle size, has pronounced peaks and troughs when the wavelength is near to the particle size. See Figure 4

Fig. 4.

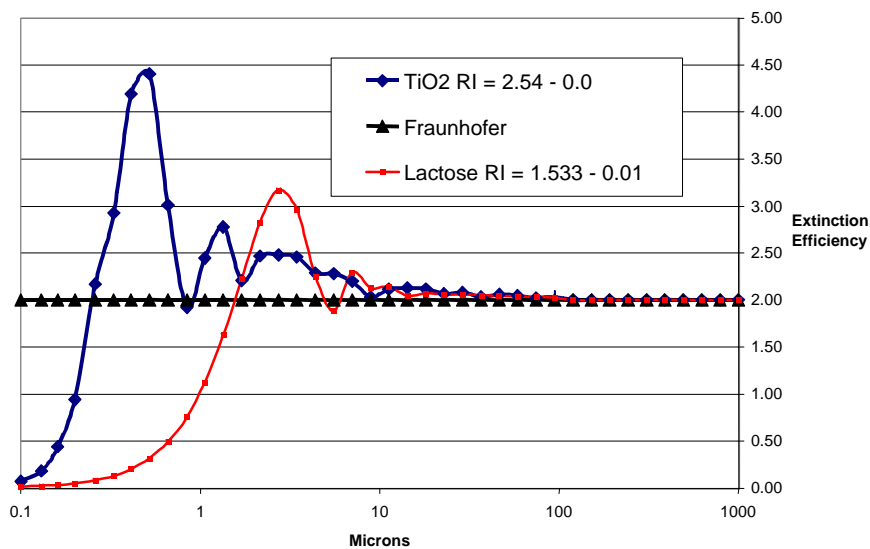


Fig. 4 Extinction efficiency (by Mie theory. Wavelength = 633nm) as a function of particle size for the materials noted. Also shown is the extinction efficiency computed using the Fraunhofer approximation.

Large particles and the Fraunhofer approximation

For very large particles the extinction efficiency asymptotically approaches the value 2 and thus Fraunhofer theory may be used. The value of 2 seems odd, since a flowerpot sitting in a window blocks out light proportional to one times its cross-sectional area. This paradox is fully explained in Ref.2, which explains that the window and the flowerpot are close together (with near field geometry). However for a large particle observed at a distance (in far field geometry) the extinction efficiency is twice its cross-sectional area.

The equations developed by Fraunhofer do not require, or in any way use, any knowledge of the material's refractive index. Since finding or establishing appropriate refractive index values for the material under study requires additional investment of time and effort the concept that the refractive index need not be worried about is very seductive. Thus seduction results in the

Fraunhofer approximation continuing to be employed in particle size circumstances where it is wholly inappropriate. For fine particles, results derived using the Fraunhofer approximation are rarely correct and often are very misleading.

Fig. 5

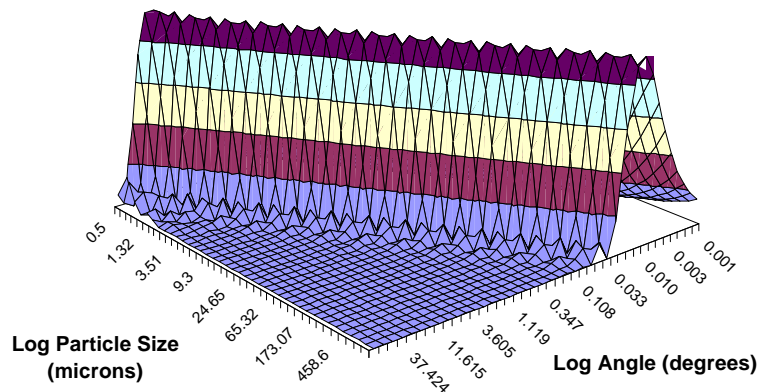


Fig. 5 Scattering energy calculated using the Fraunhofer approximation over an angle range of 0.001 degrees to 90 degrees for a range of sizes between 0.5 μm and 1000 μm and again weighted to illustrate theoretically optimum detector geometry.

The Fraunhofer approximation is calculated for the scattering produced from a small circular hole in a thin metal plate. Using Babinet's principal the scattering patterns produced are the same as for a thin opaque disk in an infinite transparent medium. Scattering patterns beyond 90-degrees are not predicted by the Fraunhofer equations, and as we shall see at angles greater than about 2-degrees errors are observed.

Fraunhofer predicts the extinction efficiency to be 2 for all sizes of particles. For large particles, the general form of the scattering pattern predicted by Fraunhofer, is very similar to that rigorously predicted by Mie. Figure 6 shows that the Fraunhofer approximation and the rigorous solution offered by Mie are in good agreement both in amplitude and in pattern up to about 2-degrees. At angles above about 2-degrees, for this size of particle, there is a difference but by this point the intensity has reduced by 10^5 and thus is not significant in this case.

Fig. 6.

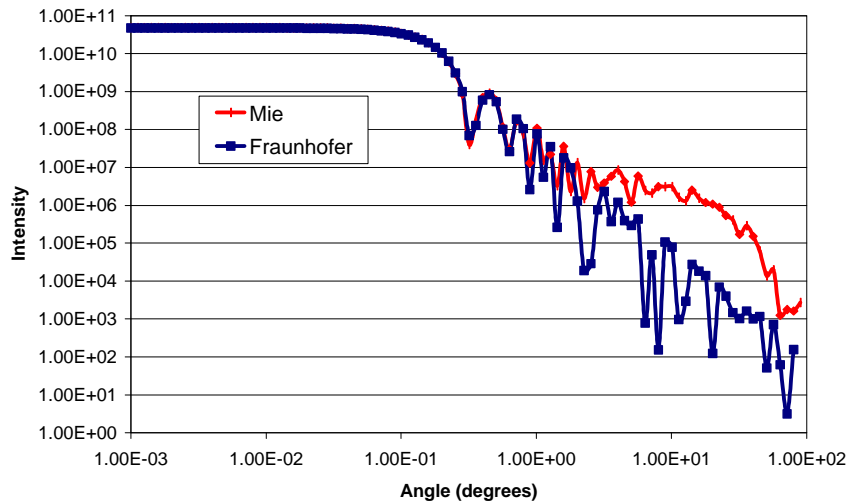


Fig. 6 Scattering intensity against angle from 0.001 degrees to 90 degrees for a 100 μm particle of latex (RI = 1.59 – 0.0), comparing Mie theory to the Fraunhofer approximation.

Fig. 7.

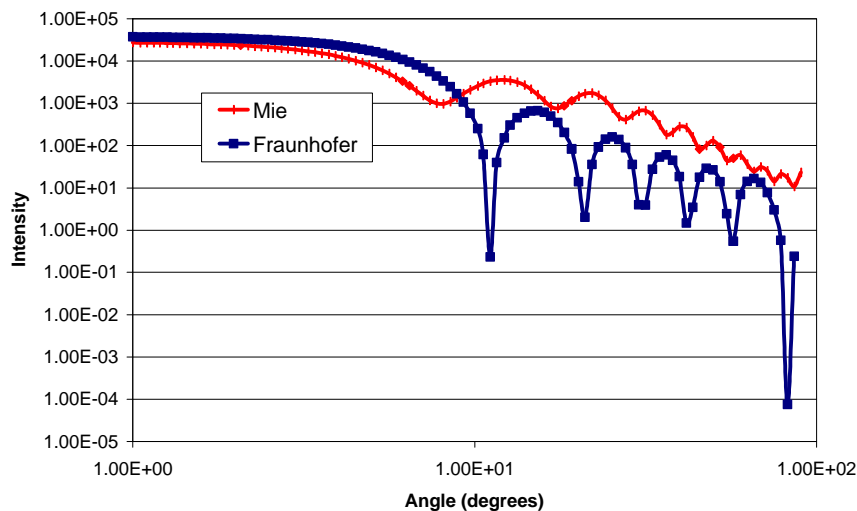


Fig. 7 Scattering intensity against angle over a range of 1 degree to 90 degrees for a 3 μm particle of latex (RI = 1.59 – 0.0).

However, Figure 7 shows that for a 3 μm latex particle even the angular position of the first minimum is different. Fraunhofer predicts a pronounced second peak of scattering near 90 degrees. This is due to the light passing through the particle creating an additional constructive interference with the light diffracted around the edge of the particle. Again the differences occur above about 2-degrees. Thus use of the Fraunhofer approximation would cause not only an error in the particle size reported but also in a mis-interpretation of the second peak of scattering as a quantity of smaller particles that are not, in fact, present.

Using light polarisation is size analysis

Light is an electromagnetic radiation just like television transmissions. The radiation is in the form of electric and magnetic fields at right angles to each other whose amplitude is oscillating at the frequency of transmission. You may note that in some locations television antennas consist of a series of vertical metal rods. If this is the case then the transmission signal is vertically polarised. The metal rods of the antenna couple strongly with the vertically polarised electric vector. If the transmission were horizontally polarised then the antenna rods would be horizontal. Laser light may be randomly, circularly or linearly polarised. Both random and linear polarisation has been employed in laser diffraction instruments. If the laser is vertically polarised then any detector placed in the vertical plane will respond principally to light scattered in the vertical plane. If further detectors are positioned in the horizontal plane then these detectors will respond to the out-of-plane scattered light. Spherical particles whose size is close to the illuminating wavelength show a pronounced polarisation effect, so that when the illuminating beam is vertically polarised much more of the scattered light has vertical polarization than horizontal polarisation. This is illustrated in Fig. 8.

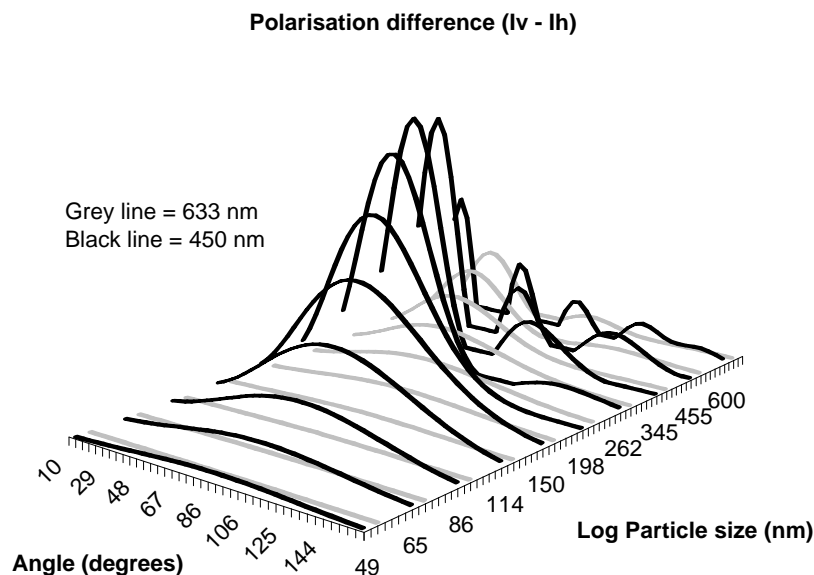


Fig. 8 Difference in Intensity Polarization difference (Int_V-Int_H) plotted for equal volumes of each size of spherical particle 50 to 600 nm over angles from 10 to 160 degrees. Each size shows the polarisation difference calculated by Mie theory for wavelengths of 450 nm (black line) and 633 nm (grey line).

In some implementations of laser diffraction the polarisation difference is extensively utilised in the analysis of particles below 400 nm. Such implementations use a range of wavelengths, such as 450 nm, 600 nm, 750 nm and 900 nm. The curves in Fig. 8 demonstrate that the angles around 90 degrees are the significant ones. Fig. 8, also demonstrates the crucial importance of the shorter wavelength blue light illumination in providing supporting light scattering evidence of the quantity of particles less than 0.4 μm .

Some manufacturers provide several methods of analysis and allow the user to avoid (disable) a method when conditions or materials are outside the range where the method would yield valid results. If measurement of extinction at both blue and red light wavelengths is coupled with high angle light scattering measurements at both blue and red light wavelengths then the particle size and quantity contribution below 0.4 μm can also be precisely determined. This later method has the advantage that it does not need to be disabled. Polarisation difference techniques, used in conjunction with forward (low angle) light scattering, can produce artefacts for some materials and will need to be disabled if this is the case.