# Rotational Diffusion and Results from DLS Measurements

DLS measurements of some colloidal gold samples show the main peak at the expected size, but often a small peak at small sizes is also obtained. The following intensity particle size distribution (PSD) received were taken both in the backscattering configuration and at 90 degrees. Both measurements show a main peak in the PSD at about 40 nm and smaller peak at about 2 nm:
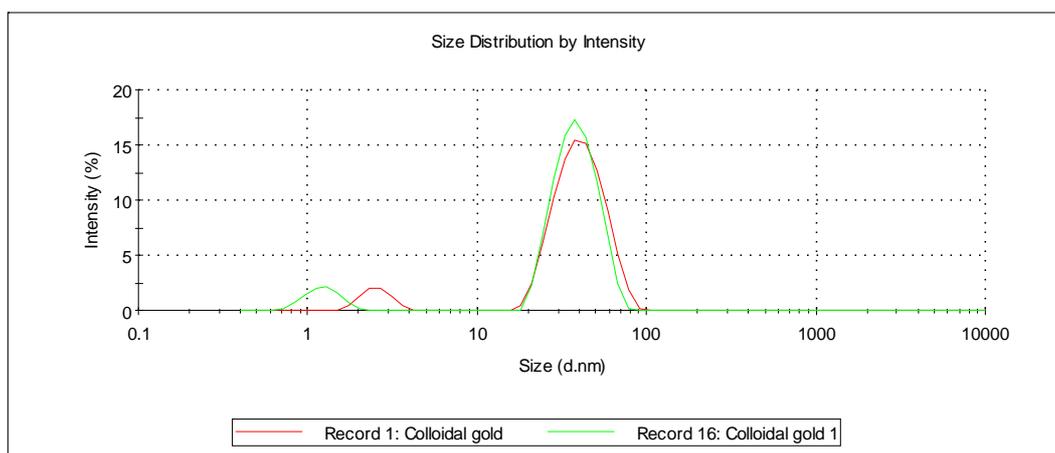
I will discuss some of the results contained in the file a little later in this e-mail. However, I want to start by discussing what the peak at small sizes is in some of the measurements. This is something we have found in the past with samples such as colloidal gold or colloidal silver or quantum dots. We have shown this to be due to rotational diffusion of the particles. Dynamic light scattering measures time dependent fluctuations in the scattering intensity in order to determine the **translational** diffusion coefficient. Normally, the **rotational** component occurs on such a rapid timescale that we do not see it. However, with material such as colloidal gold, rotational diffusion can be measured and manifests itself as a peak at small sizes.

This ability to measure the rotational component in some colloidal gold samples is due to the strange refractive index properties of colloidal gold - the refractive index of colloidal gold is 0.2 at a wavelength of 633nm (see the following references from www.luxpop.com) and because of the birefringent nature of the material (see http://www.answers.com/topic/birefringence?cat=technology for more discussion of birefrigence). This birefringence occurs due to one of 2 reasons..........either the particles are non-spherical or they are non-isotropically scattering due to their crystal structure.

First set of refs:
At a wavelength of 633 nm (1.959 eV), the index of refraction of gold is n = 0.20, k = 3.32.

Note that for thin films the index can vary depending on deposition parameters.
References:
[1] L. G. Shulz, "The optical constants of silver, gold, copper and aluminum. 1) the absorption coefficient k and 2) the index of refraction n," *J. Opt. Soc. Am.* , Vol. 44, No. 5, pp. 357-362 and 362-368,
[2] M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. W. Alexander, Jr., and C. A. Ward, "Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared," *Appl. Opt.* , Vol. 22, No. 7, 1 April 1983, pp. 1099-1119 (Molutevich et al).
Second set of refs:
At a wavelength of 633 nm (1.959 eV), the index of refraction of gold is n = 0.197, k = 3.0908.

Note that for thin films the index can vary greatly depending on deposition parameters.
References:
[1] E. D. Palik, "Handbook of Optical Constants of Solids, " Academic Press.

What this means is that the colloidal gold sample preparation which shows the peak at small sizes is different to ones where only 1 peak is obtained. The difference is due to the reasons discussed above...........either the particles are non-spherical or the crystal structure is different resulting in birefringence in the scattering. The way in which we have proved this in the past with other samples showing similar results is to measure them at 2 different angles - in the Zetasizer Nano series we could use 90 and 173° respectively. The relaxation time of translational diffusion is angular dependent. The relaxation time of rotational diffusion is not.

Here is an example of a colloidal gold sample measured at 90° (green line) and 173° (red line). The main peak shows angular dependence and it is well know that for translational diffusion, the relaxation time of the DLS autocorrelation function is given by qD where q is the scattering vector and D is the translational diffusion coefficient. We have also performed de-polarised light scattering measurements to further prove the small peak is due to rotational diffusion.

Relaxation times distribution