Polydisperse Mixture of Gold Nano-Particles

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ABSTRACT

Gold colloids synthesized in water media, usually from direct reduction of a salt ($KAuCl_4$), always exhibit a size distribution, which may be characterized by TEM or SEM measurements. These are in essence polydisperse systems with a dispersion that cannot be established just by observing the extinction spectra. One of the most crucial aspects on the synthesis of nanoparticles has to do with the particle size and the degree of dispersion; most applications require specific (almost mono-disperse) particle sizes. The optical properties of metallic particles are directly related to its dielectric function (or complex refraction index). In metals presenting electronic inter-band transitions (as in the case of Au), the dielectric constant is an unknown function of the particle size. This effect gains importance, as the size of the particle gets smaller. This is a preliminary work connecting the extinction spectra of metallic colloids to its size distribution.

Keywords: Gold colloids, polydisperse system, plasmon resonance, dielectric function

POLYDISPERSE MIXTURES

We assume a mixture of spherical particles with a continuous distribution of size normalized as

$$\int_0^{\infty} p(I)\,dI = 1 \qquad (1)$$

where I is the diameter of the sphere and p(I) a continuous density function. The extinction cross section of a single metallic sphere is a function of the size, I, and of the wavelength, λ:

$$C = C(I, \lambda) \qquad (2)$$

and the extinction cross-section displayed by a polydisperse mixture is given by:

$$Cm = Cm(\lambda, p(I); I) = \int_0^{\infty} p(I) C(\lambda, I) dI \qquad (3)$$

In deriving the previous equation we have assumed the spectrum per each sphere to be additive. If the mixture is statistically narrow [1], a perturbation expansion may be performed and the cross section for the mixture may be modeled as:

$$Cm(\lambda, p(I); I) = C(\lambda, I_0) + \eta C'(\lambda, I_0) + \text{higher order terms} \qquad (4)$$

where I_0 represents the first moment of the distribution, namely the size of the most abundant component, $C(\lambda, I_0)$ is the cross section of such a component, η is a "small parameter" associated with the variance of the size distribution function,

$$\eta = [\int_0^{\infty} I^2 p(I) dI - I_0^2] / I_0^2 \qquad (5)$$

and $C'(\lambda, I_0)$ is the first correction term due to mixing.

SINGLE PARTICLE

The previous approach requires an excellent relationship for the extinction efficiency of a single spherical particle as well as a parametric equation for the correction term. Mie's equation [2] gives a good fitting of the extinction efficiency of spherical particles. The theory was developed for a single particle, assuming the dielectric constant to be independent of the particle size [3].

The extinction coefficient C_{ext} is related to the Mie scattering coefficients a_n and b_n through

$$C_{ext} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)[Re(a_n + b_n] \qquad (6)$$

where $x = \pi I n_0/\omega$, n_0 is the refractive index of the host medium, ω is the wavelength of the incident light *in vacuo*. a_n and b_n are the scattering coefficients, which are functions of the particle diameter, I, and of the wavelength in terms of Ricatti-Bessel functions. For particles with diameters less than 100 [nm], only the first three terms in equation (6), are usually needed. In the case of gold, an excellent agreement is obtained for particle sizes higher than 40nm. The discrepancy for smaller sizes is due to the unknown dependency of the dielectric constant with size. Figure 1 shows a preliminary correction to the dielectric constant of gold due to size. These curves were obtained by numerically manipulating absorption data of commercial colloids.

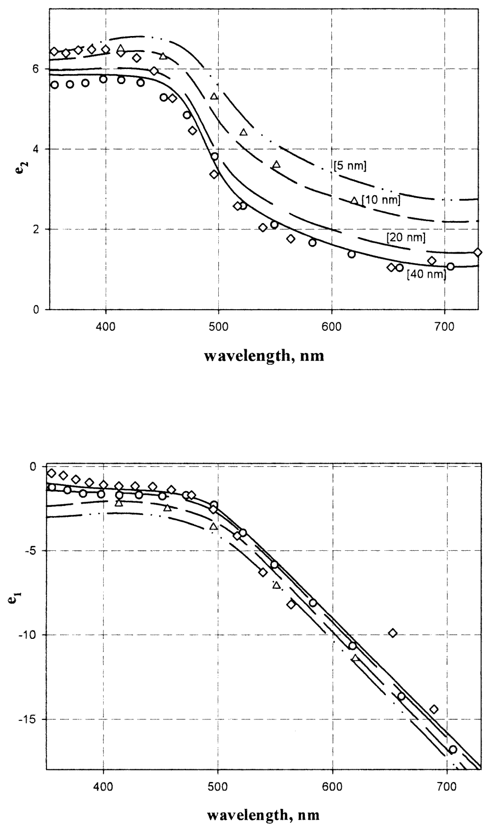

Figure 1: Components of the dielectric function of Au particles vs. wavelength for various particle sizes. The solid line (40nm), short dash (20nm), long dash (10nm), and dash-dot-dot (5nm) are our calculations. The triangles are from Kreibig, U., 1977, for 5nm [4]. Diamonds [Palik E., 1998[5]] and circles [Johnson P., and R. Christy, 1972 [6]] are values reported for bulk gold.

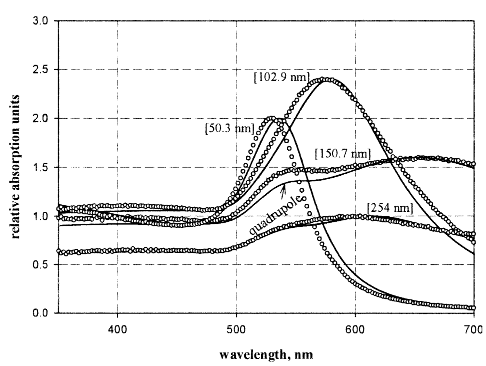

Figure 2: Extinction spectra for colloids of different mean sizes. The solid lines are simulations using Mie's equation and the open circles are absorption measurements.

As particles get smaller, the interband contribution is unknown and affects substantially the dielectric properties of the metal. Several authors have attempted to model this effect for gold particles (see Kreibig U., and M. Vollmer, 1995 [7], for a review) but studies were performed, as in Figure 1, analyzing the extinction spectra of colloids. Single particle experiments are needed to have better representation of this phenomenon. Figure 2 shows the fit to the extinction spectra of commercial gold colloids by using this modified dielectric constant. Observe that the position of the maximum absorption is directly related [8] to the mean size of the particles. It is also interesting to observe how well the model predicts the contribution of quadrupole effects. Our experimental data were obtained from commercial colloids which have narrow size distributions, but important enough to explain any deviations from Mie's model.

We have used Mie's model to follow the growth kinetics of Au in a very fast process [9] and the maximum peak in the extinction spectrum (plasmon or dipole contribution) was used to characterize the size as a function of time. In Figure 3, we summarize this dependence as well as that of the quadrupole effect.

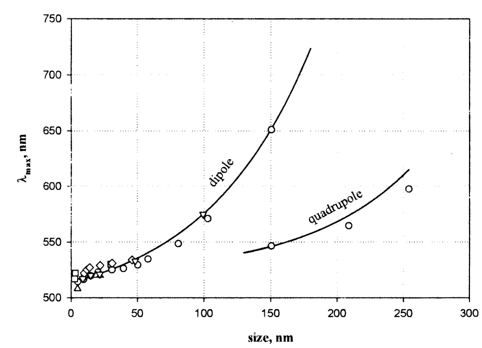

Figure 3. Position of the maximum absorption peak, versus particle size. The solid lines are simulations using Mie's equation and the symbols are absorption measurements. Experimental data is shown as: squares [Galleto, P., et al., 1999 [10]], triangles up [Logunov, S.T., et al., 1997 [11]], triangles down [Stephan, L., and M. A. El-Sayed, 1999 [8]], diamonds [Sau, T.K., et al., 2001 [12]], and circles [Viera, O., 2002 [13]].

Fortunately even for poly-disperse mixtures the maximum peak still represents the mean size, and the mixing effect affect mainly the tails of the spectrum. To give a visual idea of the proposed work, in Figure 4, we present the simulated extinction spectrum for a modisperse gold colloid of size 75nm compared to mixtures with normalized variances of 0.13 and 0.23. The distribution was simulated adopting a lognormal distribution of sizes and the extinction spectra were generated numerically.

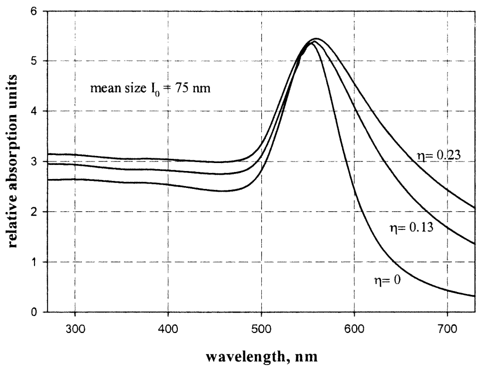

Figure 4: Spectra of polydisperse mixture of particles with mean size 74 nm.

Figure 5 shows a representation of a normalized density function as the variance changes. The curves were generated using a lognormal distribution and serve to represent how dispersed (or narrow) is the size distribution for a particular normalized variance.

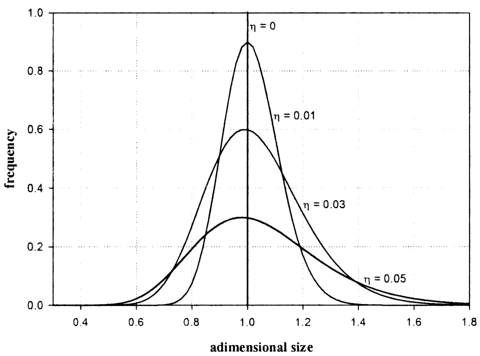

Figure 5: Normalized density distribution function. $p(I/I_0)$ vs. I/I_0

PRELIMINARY RESULTS

We have evaluated $C(\lambda, I_0)$ and $C'(\lambda, I_0)$ for several cases and found that the feasibility of the present approach is strongly influenced by the mean size. For mean sizes smaller than 50 nm, the perturbation expansion may be extended up to normalized variances of 0.08; however for mean sizes around 100nm, the model fails for variances over 0.03. Figure 3 shows the case of a gold colloid with mean size of 30 nm. The solid curves are computed using Mie equation for a polydisperse mixture as described by equation 3, and the dotted lines represent our calculations using the perturbation expansion of equation 4. The single particle spectrum (η =0) is used as a reference.

For variances less than 0.06, both models coincide on the same line; but for more disperse size distributions, the differences are important.

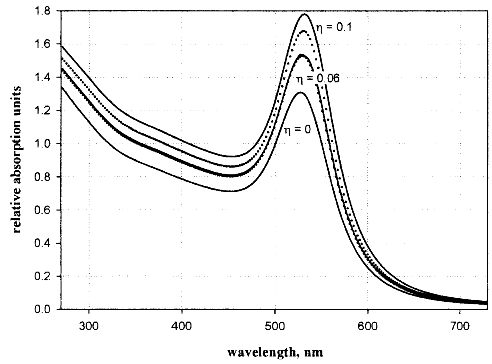

Figure 6: Extinction spectra of gold colloids with mean size of 30 nm. The solid lines are our calculations using Mie model and equation 3. The dotted lines were obtained using the perturbation expansion proposed in equation 4.

As mentioned earlier, the main effect of size dispersion is reflected on the tails of the extinction spectrum. Particle aggregation (or larger particles) will raise the low energy tail of the spectrum, with respect to the single particle case, and will lower the high-energy portion of it. The opposite effect is noticed when the size distribution is due to a high number of small particles. Figure 7 shows the spectra of a gold colloid prepared in our lab following the recipes that are found elsewhere [14]. This colloid with a mean size of ~15nm, was modeled with a variance of 0.0425. With that variance, the low energy part of the measured spectra is perfectly fit with the model, but deviations in the left side are noticeable. The knowledge of a better description for the dielectric function as a function of size could in general help with the representation of the high energy part of the colloid absorption spectra, which is (for small particles) affected by the interband effect.

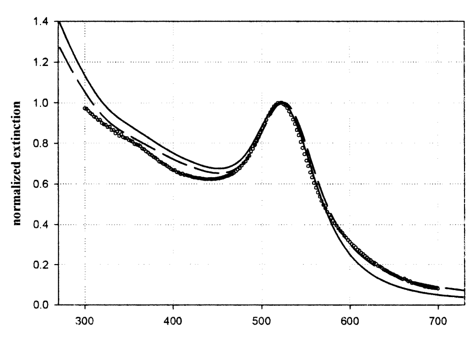

Figure 7: Extinction spectrum for a colloid with mean size 14.9 nm. The small circles are our measurements, the solid line is obtained using Mie's model for a single particle, and the dash line was generated using a variance of 0.0425.

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