Thermal blooming effect on particle sizing with photon correlation spectroscopy

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Photon correlation spectroscopy autocorrelation spectra were measured for gold nanocrystal superlattice colloids under several intensities of an incident laser beam. Thermal blooming in the colloid shifted the correlation spectra toward smaller times. A second cumulant term in the fitting curve proved effective to correct for the thermal blooming effect to yield the correct particle size. © 1999 Optical Society of America

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1. Introduction

Passage of a laser beam through a colloidal medium can result in both absorption and scattering of the light by colloidal particles. Scattering light from a colloidal system provides valuable information about the size and state of aggregation of the particles in the colloid. Photon correlation spectroscopy (PCS), also known as dynamic light scattering, has proved to be a useful method for measuring the size of particles in colloidal solution.[1] The diffusion coefficient, which is related to the hydrodynamic radius of particles, can be measured through the decay of the heterodyne- or homodyne-detected autocorrelation function.

Absorption occurs when the energy of the incident light matches an absorption band of the colloidal particles. Strong absorption induces local heating in the path of the laser beam, which in turn causes a change in the optical index of refraction of the medium and a divergence of the beam. When this diverging beam is projected onto a screen, a broad interference ring pattern appears. This phenomenon, normally called thermal blooming or thermal lensing, has been known for several decades.[2] When the incident beam is close to a free surface, regular or even chaotic oscillation of the ring pattern can occur, depending on both the intensity of the laser beam and its distance away from the surface.[3] To prevent divergence of laser beams through absorbing media, phase conjugation methods have been developed.[4]

Whereas size measurements of particles by PCS in nonabsorbing colloids is a straightforward and often-used technique, similar size measurements in absorbing colloids is problematic and hence uncommon because of the uncertainties incurred by thermal blooming. If the colloid is absorbing, low incident intensities can be used with the aim to minimize thermal blooming, but then low scattering intensities foster difficulties of their own. Other than this imperfect remedy, we know of no other methods reported in the literature for extracting size information from PCS in the presence of thermal blooming.

Here we report PCS measurements on absorbing gold nanocrystal superlattice (NCS) colloids that show that thermal blooming drastically decreases the effective correlation time; hence the particle size inferred from these measurements would be incorrectly too small. However, thermal blooming also causes an extra, second cumulant term in time in the scattering light-intensity autocorrelation function. We show that this term can be accounted for to allow for accurate PCS size measurements in the presence of thermal blooming.

2. Experiments and Results

The sample that we used was a gold NCS colloid recently synthesized in our laboratory. Details of the synthetic procedure can be found in a recent paper.[5] Here we merely outline some of the major steps. First, nanoparticles of gold with an average size of 6.7 nm were synthesized in a didodecyldi-

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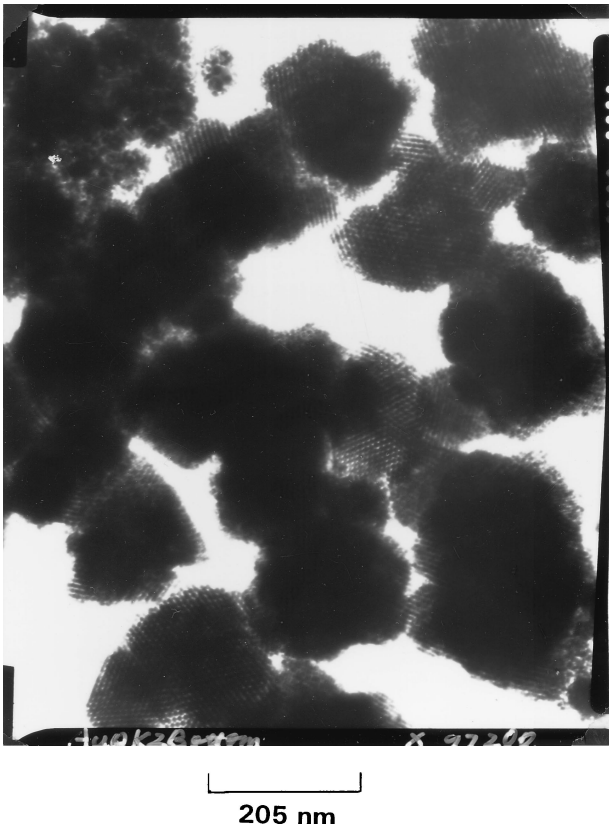

Fig. 1. TEM image of gold NCS's synthesized in didodecyldimethylammonium bromide–water–toluene inverse micelles.

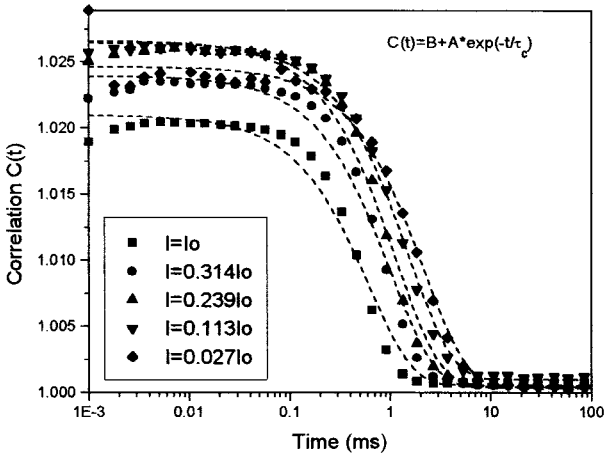

Fig. 2. Correlation function of gold NCS colloid under several intensities of the incident laser beam. Points, experimental data; dashed curves, fitting curves with an exponential decay function as shown in Eq. (1).

methylammonium bromide–water–toluene inverse micelle system. Dodecanethiol was then added to the colloid to modify the particle surface, followed by an ethanol washing process. The collected precipitates were then redissolved into toluene. A brief reflux heating completely redissolved the precipitates. After one day of sitting on the benchtop, the 6.7-nm gold nanoparticles spontaneously formed superlattice structures and precipitated to the bottom of the vial. Figure 1 shows a TEM image of such NCS structures. Supercrystal sizes range from 180 to 300 nm.

We could break apart the loose NCS aggregates at the bottom of the vial by simply shaking the colloid for several seconds. PCS was performed on the shaken sample at room temperature with a 488-nm argon laser. The gold colloid has an absorption band that includes this wavelength. The power output of the laser was 50 mW. Scattered light was collected by a FW130 photomultiplier tube at a 30° angle. The signal from the photomultiplier tube was amplified, discriminated, and passed to a commercial correaltor where the homodyne-detected correlation function was calculated. Correlation functions were collected at several light intensities by addition of different filters in the incident beam. Figure 2 shows the decay curves for five intensities. At the lowest intensity the thermal blooming ring pattern was very small. As we continuously increased the intensity of incident beam, the thermal blooming became large. Meanwhile, as shown in Fig. 2, the correlation decay curve shifted toward the smaller time region.

If the diffusion caused by Brownian motion was the only reason for the scattered light to become less correlated, the correlation decay could be described by a simple exponential curve:

$$C(t) = B + A \exp(-t/\tau_c). \tag{1}$$

In Eq. (1), B is the background or noise level, A is related to both the incident beam's transverse coherence and the scattered transverse coherence across the photocathode, and τ_c is the correlation time. The correlation time τ_c is given by

$$\tau_c = (2Dq^2)^{-1}, \tag{2}$$

where D is the particle diffusion coefficient given by $D = k_B T/3\pi\eta d$, in which η is the viscosity of the solvent toluene, k_B is the Boltzmann constant, T is the absolute temperature, and d is the average diameter of the colloidal particles. q is the scattering wave vector, given by $q = 4\pi n \sin(\theta/2)/\lambda$, where λ is the wavelength of the laser, θ is the scattering angle, and n is the index of refraction of the solvent. Fitting the data by use of single exponential decay [Eq. (1)] shows that only the decay curve under a low-intensity beam obeys the simple exponential function (dashed curves in Fig. 2). Under high intensity, it deviates drastically from the exponential curve. Furthermore, the correlation time from the fit, plotted in Fig. 3, decreases by more than a factor of 3 as the thermal blooming increases. Thus sizes inferred from these fits would also have a range of a factor of 3, which is clearly unacceptable.

We believe that this deviation is a result of thermal heating owing to the laser beam, which creates a temperature gradient along the radial direction of the beam. Particles inside the scattering volume there-

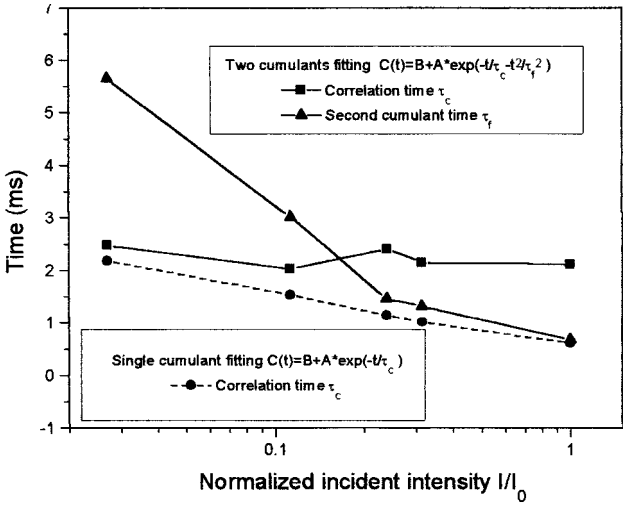

Fig. 3. Comparison of the decay times obtained by a single exponential fitting curve and two-cumulant fitting curves. Single exponential fit, circles with dashed curve; two-cumulant fit, first cumulant decay time τ_c (squares with solid curve) and second cumulant decay time τ_f (triangles with solid curve).

fore have a translational motion that is due to thermophoresis as well as to the random Brownian motion. A second cumulant term was introduced in the correlation function to account for this translational motion[6]:

$$C(t) = B + A \exp(-t/\tau_c - t^2/\tau_f^2), \qquad (3)$$

where τ_c and τ_f are the first and second cumulant decay times, respectively. Figure 4 shows that using this form of correlation function greatly improves the fitting in the thermal blooming region. The values of τ_c and τ_f obtained under different light intensities are plotted in Fig. 3 (filled squares, triangles, and circles with solid curves). The most interesting thing to notice is that only the second cumulant decay

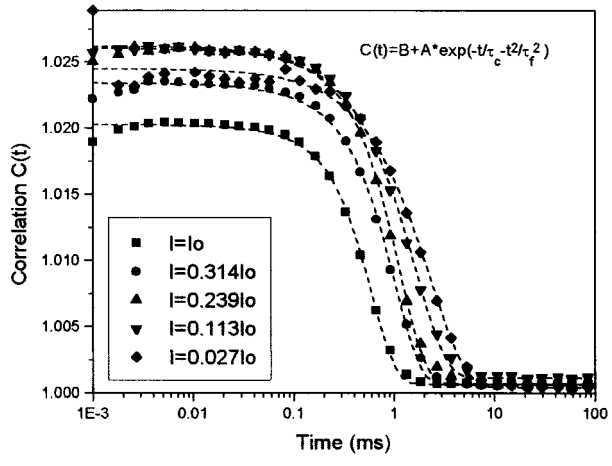

Fig. 4. The same experimental data as in Fig. 2 but fitted with a two-cumulant decay function as shown in Eq. (3).

time τ_f changes with light intensity, whereas the first cumulant time τ_c (correlation decay time) remains relatively unchanged for different intensities of the beam, in strong contrast to τ_c obtained from the fits to Eq. (1). Thus we conclude that by use of the two-cumulant fit the particle size can be accurately determined even in the thermal blooming region. Higher-order cumulant terms were also used to fit the correlation functions; however, their contributions were quite small compared with that of the second cumulant term and therefore were ignored. The supercrystal size deduced from the fit to Eq. (2) is 318 nm, slightly larger than the average TEM size. This small discrepancy between the PCS measurements and the TEM measurements probably has two causes. First, light scattering strongly weighs the large-sized part of the size distribution and, second, the colloid might still have a small degree of aggregation.

3. Conclusion

In conclusion, we measured the correlation function of a gold NCS colloid under several laser intensities. We found that correlation functions shifted toward smaller time as we increased the intensity of the incident beam. A second cumulant term was introduced in the correlation function to yield the particle size independently of the incident intensity.

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