Comment on "Limits of the Fractal Dimension for Irreversible Kinetic Aggregation of Gold Colloids"

In a previous Letter by Weitz *et al.*,[1] static light scattering was used to obtain the *in situ* fractal dimension of gold aggregates formed in solution. They asserted that the scattering intensity could be analyzed in the Born approximation for weak scattering. In this approximation the scattered intensity should depend only on Q, the momentum transfer. Such a unique dependence on Q allows a direct interpretation of static scattering in terms of the pair-correlation function.

We have repeated and extended the previous measurements of the angular distribution of light scattered from large "diffusion-limited" gold aggregates to test this weak-scattering assumption. At the concentration and incident wavelength employed by Weitz *et al.*, gold aggregates extinguish more than 80% of the incident light in a 1-cm path-length cell. An additional feature which was previously neglected both experimentally and theoretically is a large depolarization of the incident light for gold aggregates. This depolarization is wavelength (λ) dependent and amounts to nearly 10% of the light at $\lambda = 632$ nm, the incident wavelength used in previous studies.[1] Both of these observations make the applicability of the weak-scattering approximation questionable.

We have determined the angular dependence of the intensity of light scattered from large gold aggregates. At the concentrations (1.6×10^{12} particles/cm,[3] $\lambda = 632$ nm) studied by Weitz *et al.* we find results which agree with theirs. However (see Fig. 1), altering the wavelength to $\lambda = 457$ nm (away from the optical resonance) changes both the angular dependence and absolute value of the intensity (the Rayleigh ratio). In addition, the power-law exponent x, which describes the Q dependence of the intensity, is significantly larger at 457 than at 632 nm. By tenfold dilution of the sample we can demonstrate that this effect is due to multiple scattering. The results of such a dilution are shown in Fig. 1. The intensity no longer follows a power law and the reduced multiple scattering results in an increase in the apparent exponent x. Additionally, the wavelength dependence of the scattering becomes smaller, though still significant. The latter observation rules out simple structural rearrangement as an explanation of our results.

It is clear from our measurements that the apparent power-law scattering observed by Weitz *et al.* is an artifact of intense multiple scattering which has the effect of making the angular distribution of scattered light more isotropic than is observed from the diluted clusters. Thus, the exponent observed from the undiluted samples cannot be directly related to the fractal dimension. In fact, the variation in exponent observed on a change of the wavelength is nearly as large as that claimed by Weitz *et al.* for the scattering differences between diffusion-limited and reaction-limited clusters.

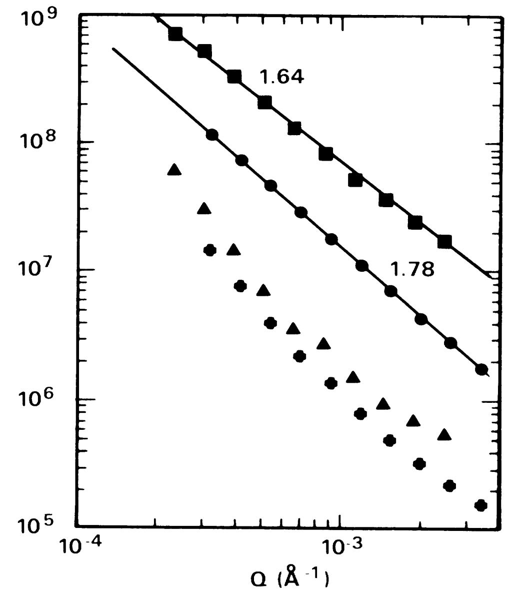

FIG. 1. Static scattered intensity $I(Q)$, corrected for sample absorbance, from gold aggregates as a function of wave vector (Q), wavelength (λ), and dilution. Intensities are shown relative to the instrument calibration standard n-propanol (an ideal dipole scatterer), implying that curves for identical concentrations should superimpose if the Born approximation is satisfied. The scattering exponent x is shown in the figure. The squares represent an undiluted sample (1.6×10^{12} colloids/cm^3) as previously studied (Ref. 1) ($\lambda = 632$ nm, $x = 1.64$). Circles represent the same undiluted aggregates ($\lambda = 457$ nm, $x = 1.78$). Triangles are the aggregates diluted tenfold ($\lambda = 632$ nm, $x > 2$, concentration $\sim 10^{11}$). Crosses are the diluted sample measured at $\lambda = 457$ nm. The effect of resonance enhancement of the scattering is easily observed in the data.

A final interesting observation is that the diluted clusters exhibit nearly the same large depolarization of incident light ($\sim 10\%$) as the undiluted samples, which indicates that scalar scattering theories are inadequate to describe scattering from either metallic sols or large metallic clusters.

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[1]D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, Phys. Rev. Lett. **54**, 1416 (1985).

