Nucleation of Gold Nanoparticle Superclusters from Solution

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Measurements of the solubility curve of a quasi-monodisperse gold nanoparticle solution are given. Temperature quenches from the one-phase to the two-phase regime yielded superclusters of the nanoparticle solid phase with sizes that depended on the quench depth. Classical nucleation theory was used to describe these sizes using a value of the surface tension for the nanoparticle solid phase of 0.042 $\mathrm{erg/cm^2}$. This value is consistent with molecule size scaling of the surface tension. In total these results show that suspensions of nanoparticles act like molecular solutions.

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Recent advances in synthetic chemistry have given rise to a wide variety of nanoparticles with a high degree of both chemical and physical uniformity [1–5]. These nanoparticles, also called nanoclusters of atoms, often have nonbulk properties due to either or both finite size effects and the large fraction of surface matter. The novel, size dependent properties combined with the uniformity suggest that nanoparticles can be understood and manipulated as large, nearly stoichiometric molecules [6,7]. Because of this, nanoparticles and their assemblies have great promise as a basis for a wide variety of new materials with unprecedented properties and hence have seen considerable attention in the recent literature.

Nanoparticles are usually surface ligated with any of a variety of organic compounds and these ligands cause colloids of the nanoparticles to be stable against irreversible aggregation. Often these colloids act as solutions with the nanoparticles displaying reversible temperature and solvent dependent solubility [8]. In many cases when the nanoparticles are highly uniform, the precipitating solid is a two- or three-dimensional superlattice of the nanoparticles. Thus there is strong analogy to the phase behavior of molecular solutions, and it is then reasonable to ask what controls the phase behavior of nanoparticle solutions and what is the nature of nucleation and growth of the insoluble phase? Such questions are not only of inherent intellectual interest but are also very useful, for with an understanding of this science, we will be able to control the self-assembly of nanoparticles into superlattices, ramified aggregates, gels, and films on surfaces. There are recent studies of the growth of clusters of the solid precipitate phase from solutions destabilized by either ligand exchange [9] or synthesis in a poor solvent [10]. Still lacking are phase diagram measurements and nucleation studies.

For an endothermic dissolution process, an increase in temperature increases the solubility. With a certain solvent and a certain concentration, the system will stay in the one-phase region when the temperature is higher than the phase transition temperature. Conversely, below the phase transition temperature, the system would be found in the two-phase region with a solid, precipitated phase in equilibrium with a dissolved phase. We therefore expect that when a one-phase gold nanoparticle colloidal solution is temperature quenched below a solubility phase boundary, the nanoparticles will nucleate and aggregate to form precipitates of superclusters of nanoparticles in equilibrium with the remaining dissolved, colloidal phase. We use the term ‘‘supercluster’’ for a cluster of nanoparticles to differentiate it from the term ‘‘nanocluster’’ which has been used to describe a single nanoparticle. For a monodispersed nanoparticle system, we expect that the phase boundary would be distinct and well defined and the superclusters of nanoparticles would possibly be long-distance ordered superlattices.

In this Letter we report measurements of the phase diagram of a gold nanoparticle solution. We then temperature quench the one-phase, homogeneous solution into the two-phase regime and study the nucleation of the solid phase.

The gold nanoparticles were made via the solvated metal atom dispersion digestive ripening method. The detailed synthetic procedure has been described in previous papers by our group [5,11,12]. Briefly, the method involves a sealed, evacuated (4×10^{-3} Torr) reactor submerged in liquid nitrogen. Gold and acetone were coevaporated and deposited on the wall of the vessel. After the liquid nitrogen was removed, the gold-acetone matrix melted and mixed with dodecanethiol and *t*-butyl toluene at the bottom of the reactor. Acetone was then evaporated from the prepared product mixture. Digestive ripening involved refluxing the gold/*t*-butyl toluene/dodecanethiol colloid at 190 °C under an inert atmosphere for 1.5 hours. The digestive ripening step takes the polydisperse system of nanoparticles and narrows the distribution to a quasi-monodisperse situation. The gold nanoparticles produced by this method were soluble in *t*-butyl toluene. The resulting sample was a dark wine red colloidal solution at room temperature. These particles are essentially the same as those prepared in our laboratory by the inverse micelle method [5].

Figure 1 shows a TEM image of the nanoparticles. The size of the gold core measured from the TEM image is 4.9 ± 0.5 nm in diameter. The nanoparticles are ligated with dodecanethiol with a total length of 1.7 nm. The concentration of the gold stock colloidal solution was 0.68 mg/ml. Dynamic light scattering measurements (see below) found a mean hydrodynamic diameter of 8.4 ± 1.0 nm. This is in very good agreement with the TEM value when twice the ligand length is added, *viz.* 8.3 ± 0.5 nm.

t-butyl toluene is a good solvent for the gold nanoparticles at room temperature such that the solutions are essentially opaque to visible light. To shift the phase transition temperature to an accessible temperature above room temperature and at dilutions to yield optically transparent solutions, we mixed the gold nanoparticles in *t*-butyl toluene with 2-butanone, a poor solvent that is miscible with *t*-butyl toluene. The mixing ratio was 40 microliters of the stock gold/*t*-butyl toluene solution in 960 microliters of 2-butanone. Mixing was done at 65 °C where the resulting system is one phase, as described below, and kept there for the brief time before they were quenched to lower temperatures.

The phase diagram, i.e., solubility curve (saturated nanoparticle concentration versus temperature) was determined by measuring the concentration of the gold nanoparticle solution above the precipitate with which it is in equilibrium as a function of temperature. The supernatant concentration was measured by ultraviolet to visible range absorption calibrated against a known sample. To ensure that all the superclusters of the precipitate were at the bottom of the test tube, the solutions were centrifuged at 300 g at the quenched temperature for 15 minutes. This time is about an order of magnitude greater than the settling time indicated by the Stokes drag calculation of terminal velocities for the superclusters. Moreover, subsequent ultraviolet to visible range measurements at longer centrifuge times showed no further spectrum change indicating that all the precipitate was at the bottom. Figure 2 shows a plot of the phase diagram. The temperature dependence is rather modest, a 15% change over a temperature range of 35 °C.

Quenches from the one-phase to the two-phase regime were made by moving the sample in its container at 65 °Cto a lower temperature, temperature-controlled sample holder. Then the light scattering measurement was started (see below). We report here quenches for a concentration of 0.027 mg/ml. The sample container was a round glass test tube with a 10 mm diameter. The volume of the sample in the test tube was 1 ml. A test experiment with the same volume in the same container using a polystyrene microsphere suspension showed that the characteristic time ($1/e$) of the temperature quench was 100 seconds.

Quenches into the two-phase regime caused the formation of superclusters of nanoparticles on the order of a few hundred nanometers in size. An obvious shifting to the red of the plasmon absorption band in the ultraviolet to visible range absorption spectrum was found with the size-

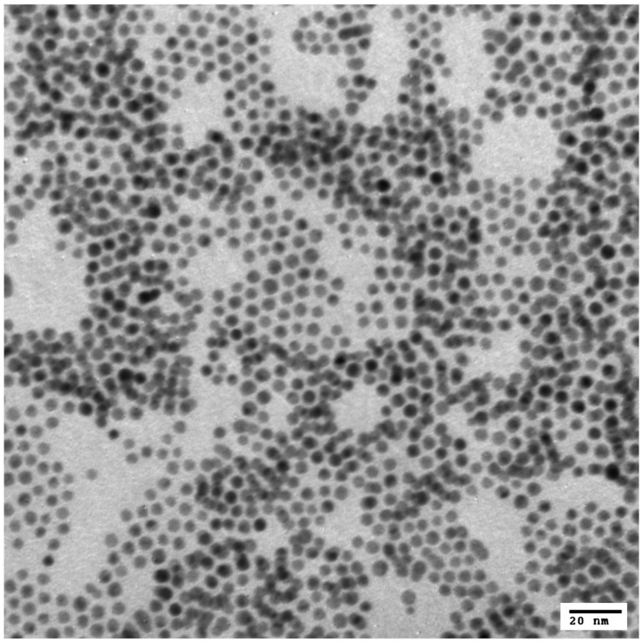

FIG. 1. TEM picture of dodecanethiol ligated gold nanoparticles prepared in *t*-butyl toluene.

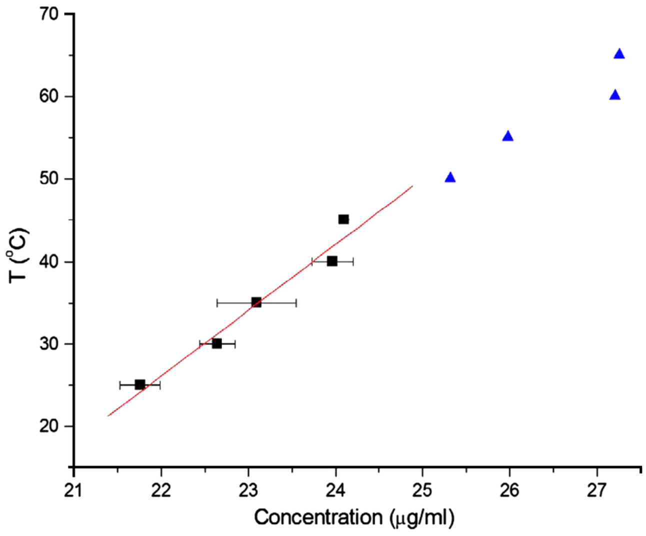

FIG. 2 (color online). Phase diagram of gold nanoparticles in 4% *t*-butyl toluene +96% 2-butanone. The data marked by square points were measured after 15-minute centrifuging, linearly fitted with the straight line. The triangle points were measured, without centrifuging, 30 minutes after the quench and may have less accuracy.

increasing in formation of the superclusters. To obtain the size of superclusters quantitatively, the nanoparticle superclusters were investigated using dynamic light scattering (DLS). The light source was a 10 mW He-Ne laser with a wave length of $\lambda = 632.8$ nm. A multiple tau digital correlator was used to measure the correlation function of the scattering light. The scattering angle was fixed at 90 degrees in all the experiments. DLS measures the intensity-intensity autocorrelation function of the scattering light. From this the mean radius R of the superclusters can be determined given the temperature and the viscosity of the medium for which we took that of 2-butanone. Attempts to measure supercluster size with TEM were foiled because during TEM slide preparation, the bad solvent (2-butanone) evaporated faster than the good solvent (*t*-butyl toluene) so that the superclusters redissolved on the TEM grid.

The *in situ* measurement with DLS of the quenched solutions showed that the size of the nanoparticle superclusters came to a constant size within the sample temperature equilibration time. That implies the nucleation and growth process was faster than 100 sec. After that, the size kept constant for about 1 h. This implies that the nanoparticle superclusters had stopped growing. The scattered intensity also stopped evolving on the same time scale to imply that the nanoparticle superclusters were not gravitationally settling. This is supported by terminal velocity calculations using the Stokes drag, supercluster sizes measured via DLS, and the viscosity of 2-butanone.

Figure 3 shows the size of the nanoparticle superclusters as a function of quench depth. Figure 3 shows that the supercluster size decreases with deeper quenches. This is a classic result known for both ionic and molecular solutions: deep quenches cause fine precipitates.

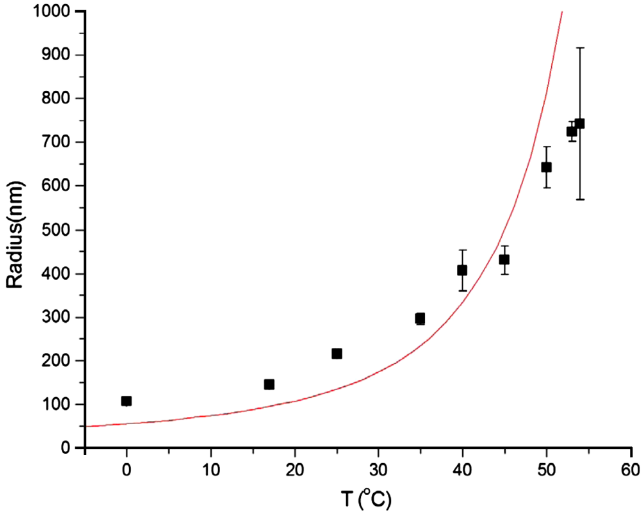

FIG. 3 (color online). The sizes of superclusters formed with different quench temperatures, quenched from 65 °C. The line is the best fit to the nucleation theory described in the text with a single fit variable, the surface tension of the solid phase with a value of 0.042 erg/cm^2.

The nanoparticle supercluster sizes R can be compared to the prediction of classical nucleation theory. In a supersaturated metastable system homogeneous nucleation theory describes embryonic nuclei of the precipitate which form by monomer-monomer aggregation. If these nuclei are smaller than the critical nucleation size, they will dissolve. Only the nuclei larger than the critical nucleation size will continue to grow. The theory gives the number density n^* of growable nuclei as [13]

$$n^* = n_0 \exp\left\{\frac{-16\pi v^2 \gamma^3}{3k_B^3 T^3[\ln(C/C^*)]^2}\right\}, \tag{1}$$

where $n_0$is the initial number density of monomers, v is the volume occupied by one monomer in the supercluster, not in solution, γ is the surface tension of supercluster, k_B is Boltzmann's constant, $T$is the temperature, C is the solution concentration, and C^* is the equilibrium solubility of monomers at the given temperature.

In our system the monomers are the individual nanoparticles, and the precipitate is the nanoparticle superclusters. The initial number density of monomers can be calculated from the solution mass concentration

$$n_0 = \frac{C}{\rho v}, \tag{2}$$

where ρ is the mass density of the nanoparticle supercluster.

LaMer and Dinegar gave a growth model by assuming a short nucleation burst followed by diffusional growth of the nuclei [14]. In that model, the growth of each nucleus is influenced only by the monomers in an impermeable spherical shell, centered on the nucleus, with the volume $1/n^*$. Once all the excess monomers, the difference between the original solution concentration C and solubilityC^*, e.g., $(C - C^*)$, are exhausted, the superclusters with number density n^* have grown to their maximum size V,

$$V = \frac{4\pi}{3} R^3 = \frac{C - C^*}{n^* \rho}. \tag{3}$$

Combining Eqs. (1)–(3), we have

$$\frac{4\pi}{3} R^3 = v\left(1 - \frac{C^*}{C}\right) \exp\left\{\frac{16\pi v^2 \gamma^3}{3k_B^3 T^3[\ln(C/C^*)]^2}\right\}. \tag{4}$$

The solubility curve C^* was measured and is given in Fig. 2. All of the other quantities in Eq. (4) are experimentally measurable except the surface tension γ. The measured radii of Fig. 3 were fitted with Eq. (4) with the surface tension as the single fit parameter. Figure 3 shows an excellent fit can be obtained with a surface tension of 0.042 erg/cm^2.

The fit of nucleation theory to the nanoparticle supercluster size data is successful in two aspects. First, the functionality of decreasing supercluster size with increasing quench depth is obtained. Second, the fit parameter gamma represents a new quantity: the surface tension of a solid phase of aggregated nanoparticles, most likely a superlattice. From atomic and molecular perspectives, the value we obtain from our fit is quite small, nearly 3 orders of magnitude smaller than those found for atomic and molecular liquids and solids which are typically in the range 10 to 30 $\mathrm{erg/cm^2}$. However, nanoparticle solids are new materials composed of large nanoparticle "molecules". The surface tension of a hard sphere condensed phase is entirely entropic, and one would expect entropy to be the dominant contribution to the surface tension for the weakly interacting nanoparticle molecules where the interactions are on the order of the thermal energy, kT [15]. The entropic surface tension for a close packed fcc lattice is given by [16]

$$\gamma = 0.61 k_B T/\sigma^2, \tag{5}$$

where σ is the diameter of the "molecule". Above we described the monomer diameter as 8.4 ± 1.0 nm. Then we find, at room T, $\gamma = 0.033 \pm 0.08\ \mathrm{erg/cm^2}$, which has surprising consistency with the fit value.

In conclusion we have shown that a nanoparticle solution displays a temperature dependent solubility curve. Temperature quenches from the one-phase to the two-phase regime described by the solubility curve yields superclusters of the nanoparticle solid phase. Classical nucleation theory can describe the size of the nanoparticle superclusters as a function of quench depth with a very small but reasonable surface tension for the nanoparticle solid phase. In total these results show that suspensions of quasi-monodisperse nanoparticles act like molecular solutions.

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