

## COLLOIDAL AGGREGATION REVISITED: NEW INSIGHTS BASED ON FRACTAL STRUCTURE AND SURFACE-ENHANCED RAMAN SCATTERING

D.A. WEITZ and M.Y. LIN

*Exxon Research and Engineering Co., Route 22 East, Annandale, New Jersey 08801, USA*

and

C.J. SANDROFF

*Bell Communications Research, 600 Mountain Avenue, Murray Hill, New Jersey 07974, USA*

Received 3 September 1984

We have examined both the structure and surface chemistry of gold clusters formed by the kinetic aggregation of colloidal gold particles. The highly disordered, ramified aggregates can be very accurately described as self-similar or fractal objects with a fractal dimension equal to 1.75. Spectroscopic studies performed with surface-enhanced Raman scattering (SERS), clearly indicate that colloidal gold surfaces are highly heterogeneous, consisting both of donor and acceptor sites which can be identified as Au(0) and Au(I), respectively. Aggregation occurs when negatively charged species are displaced from the gold surface by more strongly bound molecular adsorbates, with the rate determined by the nature and concentration of the displacing species. The new insights afforded by the fractal description of the structure of the aggregates and the SERS probe of the chemical nature of the colloid surface should lead to a more complete understanding of the basic mechanisms of colloid aggregation. This potential is illustrated with a quantitative description of the dynamics of aggregate growth measured by dynamic light scattering.

### 1. Introduction

One of the principal, long-term goals of colloid science has been to understand the mechanisms of flocculation and the structure of the resulting aggregates in terms of the microscopic interactions between colloidal particles. In the 130 years since Michael Faraday [1] inaugurated the modern era of colloid science, the problem of colloidal flocculation has attracted a stellar array of both chemists and physicists. Despite a number of classic studies however, major gaps have existed in our fundamental understanding of aggregating colloidal systems. These have centered around two seemingly unrelated problems, one dealing with macroscopic effects, the other with microscopic effects. On the macroscopic side, the large scale structure of colloidal aggre-

gates has not been quantitatively analyzed or characterized. On the microscopic side, very little has been known in detail about the chemistry of colloidal surfaces or the molecular species adsorbed onto them. However, there have recently been two major advances in the study of colloids that, together, address these issues. A remarkably quantitative description of the macroscopic structure of the aggregates is now possible using the concept of self-similar, or fractal structures [2]. At the same time, detailed spectroscopic knowledge of the surface and the adsorbed molecules can often be obtained using the technique of surface-enhanced Raman scattering (SERS) [3–5]. The purpose of this paper is to review these developments, and to show how they can be used to explore some of the very fundamental questions involved in the flocculation of colloidal systems.

The focus of this work is on the behavior of aqueous gold colloids, perhaps the most celebrated and most thoroughly studied system in colloid science. Gold's pre-eminent role among metal sols is due in part to its low reactivity, making it possible to prepare gold suspensions that remain stable against aggregation for long periods of time. Perhaps more important, gold colloids are distinguished by their well-defined optical resonance which is responsible for their characteristic wine-red color. Upon aggregation, this resonance is markedly shifted, giving a simple, qualitative indication of the degree of flocculation in the suspension.

After Faraday's pioneering work [1], gold colloids became the subject of several classic investigations. The explanation for the color of gold sols, put forth by Gustav Mie [6] early in this century, was a major success of his theory of light scattering from small dielectric or metal particles. At about the same time, studies of the aggregation of gold colloids by Zsigmondy [7] lead Von Smoluchowski [8] to develop his rate equation approach to diffusion dominated aggregation. While not developed explicitly for gold colloids, the theory of colloidal particle interactions and colloidal stability developed in the 1930's and 1940's by Derjaguin and Landau and Verwey and Overbeek (DLVO) [9] forms the basis of any discussion of the interaction energies between colloidal gold particles. Gold colloids were also one of the first systems studied by Turkevich [10] in his pioneering work using the newly developed electron microscope in the 1950's. Indeed, because it sticks so well to many proteins, colloidal gold has become a widely used marker material for biophysical studies using an electron microscope [11]. It thus seems fitting that gold colloids have also played a central role in the recent advances in our understanding of colloidal aggregation.

We have structured this review as follows. After a brief description of the experimental techniques, we introduce the idea of self-similar structures and discuss some of their unique physical properties. When these notions are applied to the structure of colloidal gold aggregates, we are able to deduce that the clusters are indeed fractal. We show that the structure and long-range

symmetry of the aggregates can be quantitatively characterized by their fractal dimension, shedding light on possible mechanisms by which the aggregates are formed. Following this is a short theoretical section where we try to summarize some of the current ideas in the field of aggregation, with special emphasis on the kinetic models now in favor for describing the growth of fractal objects. We then discuss our experimental SERS results, which probe the chemical nature of the gold surface and its adsorbates and lead us to conclude that colloidal gold surfaces are surprisingly heterogeneous. In the following section, the new characterization of the gold aggregate structure and surface are combined to gain new insight into the fundamental mechanisms of aggregation. Our emphasis is on the dynamics of aggregation and the influence of the surface adsorbates and fractal structure on these kinetic processes. Finally, we conclude with a section that discusses some of the major questions that have yet to be resolved. We show how these new techniques may help in their resolution, leading to a much deeper and broader understanding of the basic mechanisms of colloid aggregation.

## 2. Experimental techniques

The aqueous gold sol used in these experiments was prepared from a modified recipe described by Turkevich et al. [12]. We added 5 cm<sup>3</sup> of a 10<sup>-3</sup> M solution of sodium tetrachloroaurate to 90 cm<sup>3</sup> of triply distilled, deionized water and heated the resulting solution to 90°C for 15 min. While stirring vigorously, we rapidly added 5 cm<sup>3</sup> of a reducing solution, composed of 0.5% (by weight) sodium citrate. The solution was maintained at 90°C for 30 min during which time color changes from gray to blue to purple were seen before the sol assumed the wine-red hue typical of gold particles much smaller than the wavelength of light. After heating, the solution was cooled in an ice bath. This procedure reliably provided us with gold suspensions which behaved in a highly reproducible manner in a wide variety of experimental tests [13]. As determined from transmission electron microscope (TEM) images, the sol consisted of polycrystalline gold particles, roughly spherical in shape, with an average diameter of  $\sim 14.5 \pm 1.5$  nm. Assuming all the gold in the solution was reduced, the concentration of particles was  $\sim 10^{12}$  cm<sup>-3</sup>. Aggregation was initiated by a variety of means, but in each case, we added one part in ten of the aggregating agent to the freshly prepared colloid solution so as to maintain the particle concentration at a fixed value.

The primary technique for the study of the structure of the aggregate clusters was with the use of TEM micrographs [14,15]. The samples were prepared using a carbon-coated TEM grid which was placed in an air glow discharge for several minutes. The resulting hydrophilic grid was readily wet by the aqueous sol, several  $\mu$ l of which was placed on the grid and allowed to dry.

The drying process caused the three-dimensional structure of the colloidal aggregates to collapse so that the TEM images represent a two-dimensional projection of the clusters.

Surface and kinetic studies of the colloid were performed using light scattering techniques. The SERS spectra were obtained with excitation in the red, using about 80 mW from the 647.1 nm line of a Kr<sup>+</sup> laser. Quasielastic light scattering was done with the 632.8 nm line of a HeNe laser. The autocorrelation function of the scattered light was measured with a digital correlator that had 128 real time channels. Since the colloid scatters quite intensely, high quality data were collected in a few seconds, and thus measurements could be made sufficiently frequently to follow the dynamics of the fastest aggregation. The data were analyzed by calculating the initial logarithmic derivative, or first cumulant of the autocorrelation function [16]. Despite the fact that the autocorrelation functions are highly non-exponential, reflecting the wide distribution in cluster sizes, the first cumulant can be used to obtain an accurate measure of a mass-weighted mean of the cluster size distribution [17], allowing the aggregation dynamics to be followed.

### 3. Fractal structure of colloidal aggregates

A key feature of the modern description of the structure of highly disordered materials is the use of self-similarity or scale invariance [2,18]. A self-similar structure has the property that its basic appearance remains unchanged when the object is viewed on a dilated length scale. Such an object, possessing no characteristic or intrinsic length scale, but exhibiting this dilation symmetry is often called a fractal.

A structure which exhibits scale invariance can be quantitatively characterized in a number of ways. One of the most direct is to consider how some physical property scales with the size of the object. Mass is a particularly appropriate parameter for the study of colloidal aggregates. Circles of radius  $R$  are drawn around some point and the mass,  $M$ , within each circle is measured. A fractal will exhibit scaling behavior, so that

$$M \sim R^{d_f}, \quad (1)$$

where  $d_f$  is defined as the fractal dimension, and quantitatively characterizes the long-range dilation symmetry. For the trivial case of a solid object,  $d_f = d$ , where  $d$  is the Euclidean dimension of space. However, for all cases of interest here,  $d_f < d$ , and is typically not an integer.

An alternate way of characterizing a scale invariant structure is to consider its average mass-mass correlation function,  $c(r)$ , defined by,

$$c(r) = \int \rho(r') \rho(r' + r) dr', \quad (2)$$

where  $\rho(r)$  is the density at a position  $r$ . For a self-similar structure,  $c(r)$  also exhibits a scaling behavior,

$$c(r) \sim r^{-\alpha}, \quad (3)$$

where  $\alpha = d - d_f$  is called the co-dimension. The existence of power law behavior exhibited by both  $M(R)$  and  $c(r)$  is evidence for scale invariance. We note that an important consequence of power law behavior is that the total mass of a fractal object actually grows more slowly than the cube of its size, so that its density decreases as its size increases.

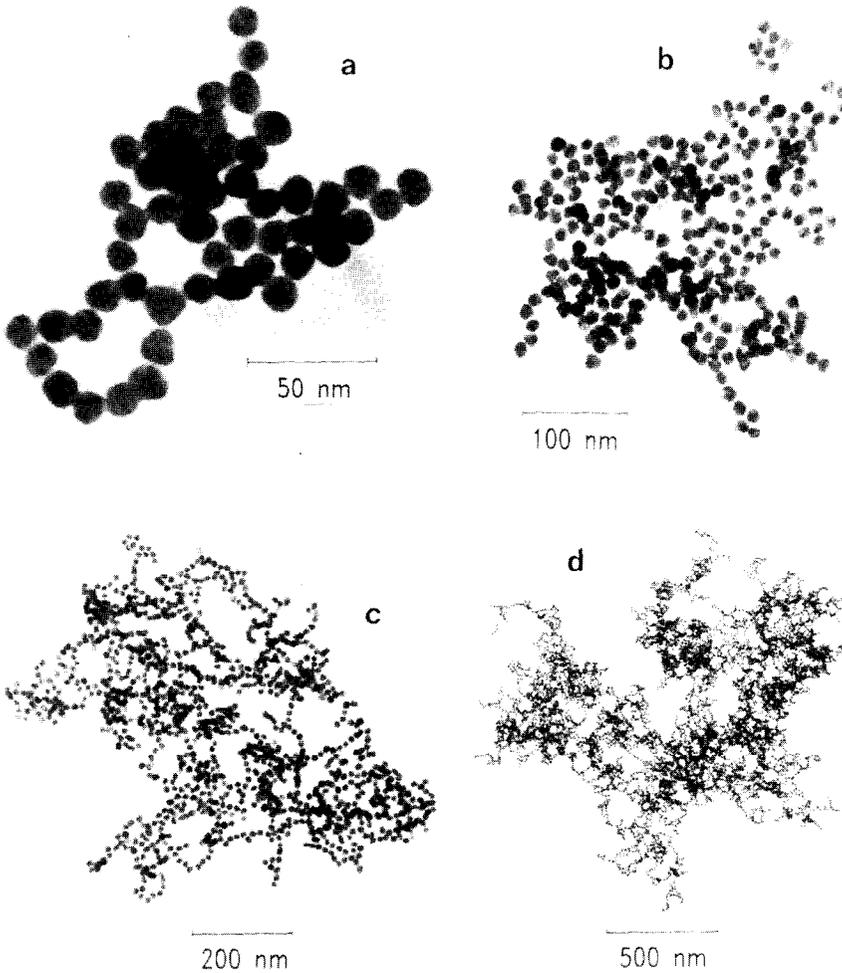


Fig. 1. TEM micrographs of a series of gold colloid clusters on a single grid.

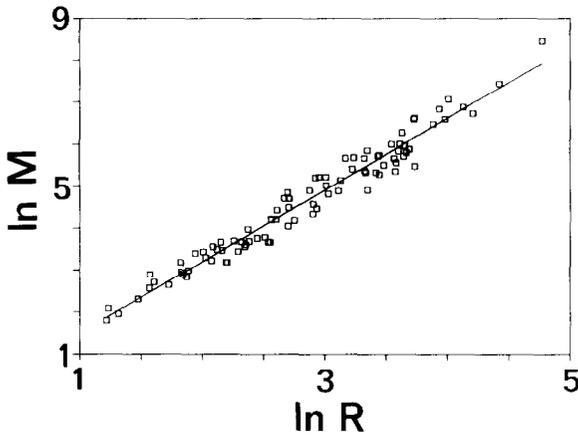


Fig. 2. Scaling of mass with size for a series of gold colloid clusters on a grid. The mass is scaled to the mass of a single particle ( $3.7 \times 10^{-17}$  g) and the radius is scaled to the diameter of a single particle (14.5 nm). The slope gives the fractal dimension, 1.75.

These concepts can be used directly to analyze the structure of the colloidal gold clusters [14,15]. We examined colloidal aggregates formed by the addition of  $10^{-2}$  M pyridine to the colloidal suspension [4]. TEM pictures, such as those shown in fig. 1, were taken and the mass and size of each cluster was measured. Since the individual gold particles are so uniform in size, the mass of an aggregate can be determined simply by counting the number of individual particles that make up the cluster. The radius is also measured directly from the photograph, correcting for all the stages of magnification used in producing the image. The results of these measurements for a typical grid are shown in a logarithmic plot in fig. 2. The linear relationship observed is characteristic of the power law behavior expected for self-similar objects, and the slope gives the fractal dimension directly. Over several decades in  $M(R)$  and  $R$ , for this and other grids, we find that gold colloidal aggregates can be characterized as fractals with  $d_f = 1.75 \pm 0.05$ .

The internal structure of individual clusters can also be analyzed from TEM images by calculating the average mass-mass correlation functions, accounting for their finite size [14,15]. The calculated  $c(r)$  must be compared with the expected correlation function of a 2D projection of a 3D fractal object. In doing this, we rely on the result that, for  $d_f \leq 2$ , the projection of a fractal remains a fractal, with the same fractal dimension [2]. The mass-mass correlation function of the projection will also exhibit scaling, but with  $\alpha = 2 - d_f$ . This is indeed what is found for the TEM images, and values of the fractal dimensions thus obtained are  $d_f = 1.80 \pm 0.07$ . Thus, the internal structure of an individual aggregate also exhibits fractal behavior, with a fractal dimension identical to that which describes the aggregate distribution as a whole.

The results of the TEM analysis of the aggregate structure were verified using an in situ probe of the structure of the clusters still in solution. Scattering measurements [19] provide the necessary probe since, for a fractal, the scattering structure factor,  $S(q)$ , also exhibits a scaling dependence on the scattering vector,  $q$ . Thus,

$$S(q) \sim q^{-d_f}. \quad (4)$$

We have measured  $S(q)$  from a solution of aggregated colloid using small angle neutron scattering [20], and find that its behavior is consistent with eq. (4). A fit to the data yields  $d_f = 1.7$ , in excellent agreement with our TEM analysis establishing that electron micrographs provide an accurate picture of colloidal aggregates as they exist in situ in a suspending medium.

#### 4. Theoretical developments

Kinetic growth processes such as colloidal aggregation have also been the subject of renewed theoretical interest in recent years. The emphasis of much of this work has been toward developing an understanding of the nature and origin of the structures that result. Considerable progress has been made using Monte Carlo techniques to simulate kinetic growth processes. A universal feature of the models appears to be the self-similar nature of the clusters that are formed. The models investigated can be divided into two major classes. In what has become known as diffusion-limited aggregation (DLA) [21,22], the growth of aggregates takes place by the collision of an individual particle with a growing cluster. The individual particles diffuse independently and become part of the aggregate whenever a collision occurs. The second model, commonly known as cluster-cluster aggregation [23,24], takes into account the possibility that clusters themselves can diffuse and stick together. Both models have been extensively investigated, and in virtually all cases, the resultant clusters are found to be scale invariant, with the fractal dimensions depending on the growth conditions.

For comparison to our experimental results, the more relevant model seems to be that of cluster-cluster aggregation. Simulations using this model have been performed in three dimensions with the clusters undergoing Brownian motion with diffusion constants that decrease as the clusters grow [25]. The fractal dimension of the resultant clusters is found to be  $d_f = 1.8$ , in remarkable agreement with the experimentally measured value. By contrast, simulation of DLA for  $d = 3$  results in clusters with a substantially larger fractal dimension,  $d_f = 2.5$ .

While the agreement between the value of  $d_f$  that we measure and that predicted by the cluster-cluster model is quite good, many fundamental questions remain to be answered. In the models, the simple rules used to

determine the sticking of the clusters cannot be expected to adequately reflect the complex chemical and physical interactions that actually take place between the highly ramified colloidal aggregates. On a more fundamental level, the models used are all computer simulations, and while they seem to give good agreement with experiment, there is as yet no basic understanding of the very origin of the dilation symmetry of the aggregates. These are issues that still remain to be solved.

In addition to characterizing the nature of the aggregation process itself, considerable theoretical effort has been expended toward understanding the physical properties of the resultant clusters. The dilation symmetry of the aggregates leads to considerable simplification in the description of many of their properties. Thus there are predictions about the behavior of the conductivity, elasticity and thermal properties [26,27]. While these have yet to be tested experimentally, there is hope that many physical properties of these highly disordered structures will be describable in relatively simple, yet quantitative terms.

## **5. Surface chemistry of colloidal gold**

Molecular adsorbates on the colloid surface play a key role in the aggregation process. The basis of their influence can be readily understood by considering the potential between two colloidal particles, following the DLVO model [9,28]. The stability of a sol against aggregation is determined by the height of the double layer repulsive barrier, caused by the screened Coulombic potential of the charges on the surface of the gold. If this is substantially greater than  $kT$ , where  $k$  is the Boltzmann factor and  $T$  the temperature, the colloid will be stable against aggregation. This barrier will be reduced whenever the extent of the diffuse double layer surrounding the sol particles is decreased. This can be accomplished either by adding ionic salts to decrease screening length in solution or by adding molecular adsorbates which reduce the surface charge on the colloidal particles. Once the repulsive forces are diminished, particles can approach one another to distances where attractive Van der Waals interactions cause them to irreversibly bind. The potentials for these two cases are sketched schematically in fig. 3.

It is our goal to study the effect of the molecular adsorbates on the aggregation process. However, aggregation of the colloid is a required first step to obtain SERS spectra of adsorbed molecules [29]. Hence, in order to detect the species adsorbed to gold prior to the addition of molecular flocculants, we initiated the aggregation by adding sodium chlorate (0.1 M). This salt reduces the screening length in solution thus inducing aggregation, but is believed to have a low affinity for the gold surface [30]. In this fashion, we were able to duplicate the conditions on the gold surface before the addition of any

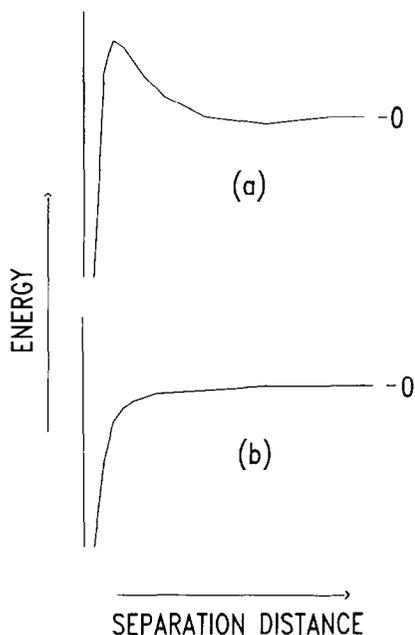


Fig. 3. Schematic representation of the interaction potential between two colloidal particles for the cases of (a) a repulsive interaction leading to a stable sol and (b) an attractive interaction leading to aggregation. After the DLVO theory [9].

molecular adsorbates. As shown in fig. 4a, the most intense SERS band in the spectrum at  $1386\text{ cm}^{-1}$  (characteristic of a carboxylate symmetric stretch), and weaker bands at  $802$ ,  $958$  and  $1416\text{ cm}^{-1}$  are all strongly suggestive of adsorbed citrate ion [31]. This confirms the hypothesis that it is the adsorbed, highly charged citrate ions, bound to the surface during the formation of the colloid, that result in the remarkable stability of the sol. Interestingly, no trace of the chlorate ion could be detected on the surface even though we were in a concentration regime where previous workers suggested that some adsorption might occur [30].

After sodium chlorate had aggregated the sol, we conducted a series of surface displacement experiments [32], using pyridine, TTF and TCNQ. The goal of these studies was twofold. Firstly, the citrate SERS bands were used to measure the kinetics and extent of charge displacement from the colloidal gold surfaces as different adsorbates were added. Secondly, we hoped to exploit the neutrality of pyridine, the electron-donating propensity of TTF and the electron-accepting propensity of TCNQ to help elucidate the chemical nature of the gold colloid surface.

The results of adding pyridine, TTF and TCNQ to gold sols previously aggregated with sodium chlorate are summarized in fig. 4. When pyridine is

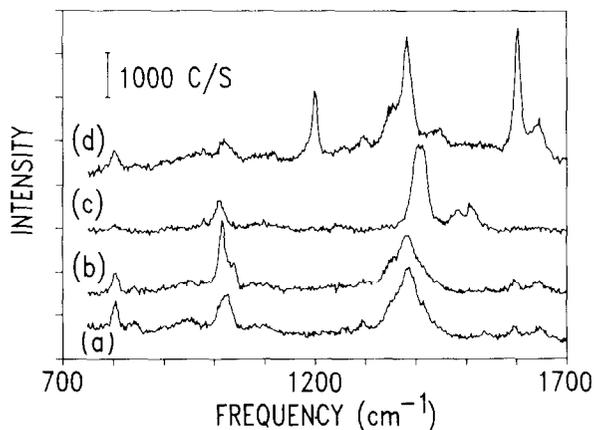


Fig. 4. SERS spectra showing the displacement results after a colloid was aggregated with sodium chlorate. The adsorbates seen are (a) citrate, (b) pyridine, (c) TTF and (d) TCNQ. Pyridine and TTF displace the previously bound citrate, while TCNQ does not.

added. Fig. 4b shows that there is a decrease in the intensity of the  $1386\text{ cm}^{-1}$  band of citrate by about 30% along with the appearance of the ring breathing modes of pyridine at  $1014$  and  $1036\text{ cm}^{-1}$ . These observations strongly suggest that citrate is displaced from the gold surface by the more strongly bound pyridine molecule. When TTF is added, fig. 4c shows that this proficient electron donor behaves much like pyridine, displacing even more of the previously adsorbed citrate. In addition, TTF is quite efficient at displacing adsorbed pyridine, suggesting the following hierarchy for attachment of electron donors to colloidal gold surfaces:

chlorate < citrate < pyridine < TTF.

However, as fig. 4d shows, TCNQ behaves very differently from both pyridine and TTF. In contrast to the electron donors in the series above, the electron acceptor TCNQ adsorbs onto the gold surface without displacing previously adsorbed citrate.

The contrasting behavior of electron donors and acceptors toward adsorbed citrate corroborates a recently proposed multi-site model for the colloidal gold surface [32]. Our SERS spectra [33] clearly show that TTF adsorbs onto gold as  $\text{TTF}^+$  and that TCNQ adsorbs as  $\text{TCNQ}^-$ , consistent with the existence of acceptor and donor sites on the gold sol. The donor, or Lewis base site, where  $\text{TCNQ}^-$  is bound has been identified with the fully reduced metal. At this site, an electron can be transferred from the metal to TCNQ, by virtue of the adsorbing molecule's high electron affinity. The acceptor, or Lewis acid site, binds not only  $\text{TTF}^+$  but, as our displacement experiments suggest, citrate ions and pyridine as well. This site has been associated with gold metal in a higher

ionization state. It is most likely Au(I), since the reducing environment of the colloidal suspension argues against the less stable Au(III). Turkevich [10] has suggested that the gold particles are formed from a polymeric complex of the reducing citrate and chloraurate ions, thus associating a strongly adsorbing citrate ion with a high oxidation state of gold at the earliest stages of the colloid formation. Our results suggest that the autocatalytic reduction of Au(III) to Au(0) in the presence of citrate does not go to completion, but that some gold remains as Au(I) to which unreacted citrate remains bound. Pyridine displaces this citrate, forming a complex of the form,  $\text{Au(I)(pyr)}_n$ , analogous to surface complexes of silver and pyridine. TTF displaces both this citrate and the pyridine, reducing the Au(I) complex by virtue of its low ionization potential to yield a surface species of the form  $\text{Au(0)TTF}^+$ .

To further test this notion of a heterogeneous colloidal surface composed of Au(0) and Au(I) in various ratios we performed experiments employing reducing agents other than citrate to form the gold colloid. Disodium acetone dicarboxylate (DSAD), an oxidative decomposition product of sodium citrate, was shown by Turkevich et al. [10] to be a much superior reducing agent than its parent. Thus we expect that colloidal gold particles prepared using the DSAD will have fewer Au(I) sites than those prepared with citrate. Indeed, when pyridine and TTF were added to a DSAD sol aggregated with sodium chlorate, we observed much weaker SERS signals than we did with the citrate sol. These results are in excellent accord with the multi-site model for gold colloidal particles.

## 6. Kinetics of aggregation

The ability to characterize the structure of the aggregates and determine the chemistry of the colloidal gold surface can be used to study the relationship between the short-range chemical and physical forces between the colloidal particles and the long-range symmetry of the structures that result. This should shed considerable new insight into the basic mechanisms of the aggregation process itself. In this paper, we discuss one important aspect of this problem. We emphasize the effect of the surface adsorbate on the aggregation dynamics, and study the effects of the change in the double layer repulsive barrier that occur with different amounts and types of adsorbates. In all cases, the solution screening length is held constant.

We measure the dynamics in two ways: a qualitative measure of the aggregation kinetics is obtained simply by observing the change in color of the sol. By measuring the time taken for the sol to turn blue, an approximate measure of the aggregation rate is obtained. More precise measurements of the kinetics are obtained using dynamic light scattering to measure the mean size of the clusters as a function of time [13,15].

Adding concentrations of  $10^{-3}$  M or greater of pyridine causes the gold sol to aggregate very rapidly, turning it blue in less than a minute. The addition of TTF causes substantially more rapid aggregation than the addition of an equal amount of pyridine. In contrast, in addition of TCNQ causes no aggregation whatsoever at all concentrations. These results can be easily understood by considering the conclusions of the SERS study. Both the pyridine and the TTF displace the negatively charged citrate ions from the surface, thereby reducing the height of the double layer repulsive barrier which had stabilized the colloid. However, the pyridine is a neutral adsorbate, while TTF is actually adsorbed as a positive ion. Since the surface is initially negatively charged, the effective change in the total surface charge of the colloid is greater upon addition of TTF than of pyridine. This causes a greater reduction in the double layer repulsive barrier, accounting for the faster aggregation rate observed for TTF. In contrast, TCNQ does not displace the citrate ions, and, furthermore, is adsorbed as a negative ion, increasing the total charge on the surface. This will have the effect of increasing the height of the double layer repulsive barrier, and actually making the colloid even more stable against aggregation, consistent with our observations.

In addition to its dependence on the nature of the adsorbed molecule, the aggregation rate is also quite sensitive to the amount of adsorbate added to the solution. We show an example of this behavior in fig. 5, where we have plotted the aggregation rate, defined as the inverse of the time taken for the colloid to turn blue, as a function of concentration of pyridine in the aggregating solution added. For pyridine concentrations below  $10^{-3}$  M, the aggregation proceeds quite slowly. As the concentration is increased above  $10^{-3}$  M, there is

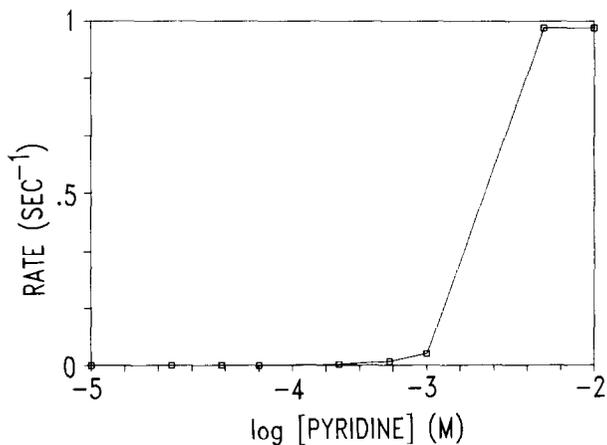


Fig. 5. Variation of the aggregation rate of gold colloids with the concentration of pyridine in a solution added in a one to ten mixture.

a sudden and dramatic increase in the aggregation rate by at least two orders of magnitude. However, it reaches a plateau at a concentration of about  $10^{-2}$  M, and we observe no further increase in the aggregation rate at higher concentrations. This behavior, which is also seen with the use of ionic flocculants [30], is probably due to a combination of effects. The amount of pyridine adsorbed on the surface, and hence the degree of reduction of the double layer repulsive barrier is presumably governed by some type of Langmuir adsorption kinetics, which will produce a relatively sharp onset of pyridine adsorption as the concentration of pyridine in solution is increased. Furthermore, the aggregation kinetics are quite sensitive to the exact height of the double layer potential barrier, and the probability that two particles will overcome the barrier and stick together upon collision will have an exponential dependence on the barrier height and hence the amount of charge displaced from the surface by pyridine adsorption. The combination of these two effects will result in the very sharp increase in the aggregation rate that we observe.

While measuring the aggregation rate by monitoring the color changes in the sol gives quick and qualitative results, a more precise description of the dynamics of the aggregation must be obtained with quasielastic light scattering. Using this technique, we measure the mean cluster radius as a function of time after the addition of the pyridine, and see a distinct difference in the behavior above and below the sharp change shown in fig. 5. When a high concentration of pyridine is added to the solution, the cluster size grows very rapidly initially, but much more slowly at later times, as shown in fig. 6. In contrast, if a lower concentration of pyridine is added, the aggregation rate is initially very low, but increases at later times, as shown in fig. 7. If an intermediate concentration of pyridine is added, the aggregation behavior is

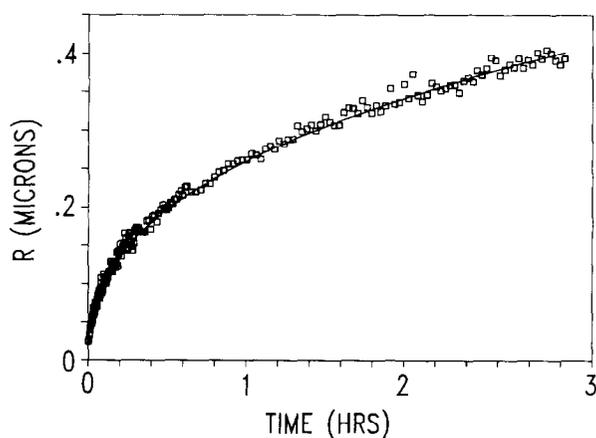


Fig. 6. Dependence of the mean cluster size on time for diffusion-limited, rapid aggregation of gold colloids.

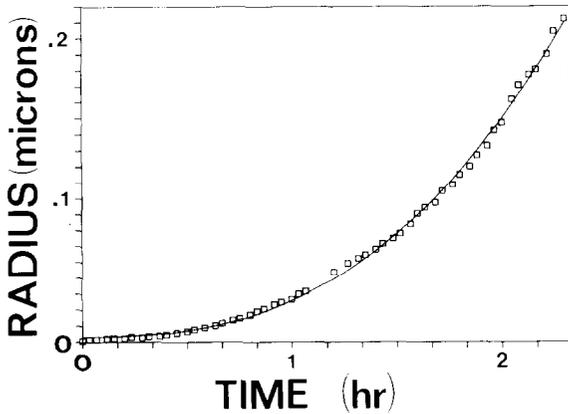


Fig. 7. Dependence of the mean cluster size on time for the slow aggregation of gold colloids, dominated by the sticking probability.

initially similar to that of the slow aggregation, but at later times becomes more similar to the fast aggregation.

These results can be understood in a qualitative sense by considering the knowledge of the surface chemistry gleaned from SERS and of the fractal nature of the aggregates derived from the TEM studies. In the case of the rapid aggregation, sufficient pyridine is added to displace nearly all the citrate, reducing the double layer repulsive barrier to a height less than  $kT$ . Thus the gold colloids will stick on every collision. In this case, the aggregation rate is solely limited by the time taken for the clusters to diffuse and collide. As the clusters grow larger, the mean spacing between them increases, while their diffusion constant decreases, thus increasing the average time taken for each collision. This accounts for the decrease in the rate as the aggregation proceeds. In contrast, if only a small amount of pyridine is added, the repulsive barrier is only reduced slightly, and relatively few collisions will actually result in the colloid particles sticking. Thus the rate-limiting step in the aggregation process is no longer the diffusion time, but rather the time taken for enough collisions to occur for the particles to stick together. Because of the tenuous nature of the fractal structures of the aggregates, the larger clusters will have more appendages and branches, resulting in a higher number of points touching on each collision. This will increase the sticking probability for larger clusters causing an increase in the aggregation rate, as is observed. In the intermediate regime, the aggregation will initially be limited by the time taken for sufficient collisions to occur to cause the particles to stick. However, as the particles grow, their diffusion constants decrease while the mean distance between them increases. Thus the time taken for them to diffuse and collide will ultimately dominate and become the rate-limiting step in the aggregation process. There-

fore, the aggregation will initially behave like that of the slow aggregation, but will ultimately change over to the diffusion-limited behavior of the fast aggregation.

Knowledge of the fractal structure of the clusters can be used to produce a more detailed description of the aggregation dynamics in the diffusion-limited case. We begin by considering the average cluster at a time,  $t$ , with a mass,  $M(t)$ , and calculate the growth of this average cluster,  $dM/dt$ . We assume that most of the growth comes from the collisions of clusters of roughly equal size, as suggested by our measurements of the  $q$  dependence of the first cumulat of the autocorrelation function of the scattering light. Thus we take  $dM \sim M$ . Our suspensions are extremely dilute (volume fraction of particles about  $10^{-6}$ ), so that the collision rate for clusters,  $1/dt$ , can be determined using Fick's law; thus  $1/dt$  scales as  $CDR$ , where  $C$  is the concentration of aggregates of mass  $M$ ,  $D$  is their diffusion constant and  $R$  their radius. Since the number of initial gold particles is conserved,  $C = C_0/M$ , where  $C_0$  is the initial concentration of the colloidal particles. Finally, since  $D \sim R^{-1}$ , we find that  $1/dt \sim 1/M$  so that the rate of mass increase,  $dM/dt$ , is a constant that scales as  $C_0$ . To find the rate law governing cluster growth, we take advantage of the fractal relationship between the mass and the radius and integrate to obtain

$$R \sim t^{1/d_f} C_0^{1/d_f}. \quad (5)$$

In fig. 8, we have replotted the data from fig. 6 and show the time dependence of the mean radius in a logarithmic plot. As predicted, a linear behavior is obtained and the slope is 0.57, which, using eq. (7), results in a value of  $d_f = 1.75$ , in excellent agreement with the earlier studies of the structure of the

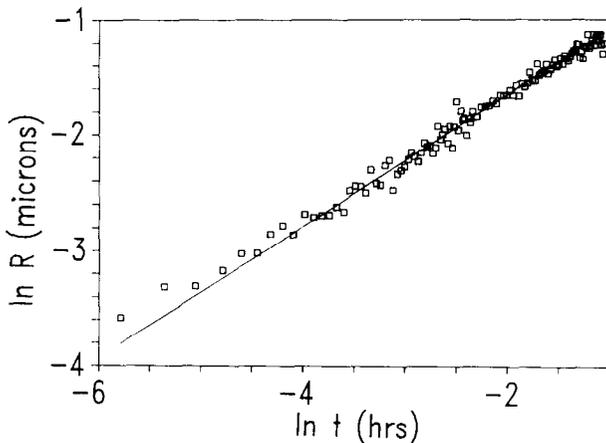


Fig. 8. Data of fig. 6 plotted logarithmically to show the scaling behavior of the growth of the cluster size in time. The slope is the inverse of the fractal dimension, 0.57.

aggregates. We have also measured the scaling of the aggregation behavior with  $C_0$ , and again find good agreement with our prediction [13].

We note that the physics used to obtain the behavior of  $dM/dt$  is the same as that used by Smoluchowski [8] to calculate the depletion of the clusters of each mass in the aggregation process. The results we obtain for  $dM/dt$  can also be obtained using the Smoluchowski equations. However, the traditional Smoluchowski approach to the kinetics does not account in any way for the structure of the aggregates, and, in order to obtain the correct behavior of  $R$ , which is what is measured, we must also include the fractal nature of the structure of the aggregates.

The success of the traditional Smoluchowski approach to the kinetics is even poorer when applied to the case of slow aggregation. In this case the rate-limiting step is the probability of overcoming the double layer potential barrier, and this depends much more sensitively on the details of the structure of the clusters, a feature not included at all within the Smoluchowski approach. Again it is possible to use our knowledge of the structure of the clusters to make an improved, yet still crude, model of the aggregation kinetics [15]. While the details of this model will be presented elsewhere, we note here one intriguing implication that arises. If the fractal dimension is treated as a variable, the data are best fit by a larger value,  $d_f = 2.3$ . There is in fact some preliminary evidence in support of this from the TEM micrographs of the clusters formed this way. Interestingly, Schaefer et al. [34] have measured a value of  $d_f = 2.12$  for silica colloids aggregated very slowly by the addition of salt.

Although these results are somewhat speculative, and must be further verified experimentally, they have profound implications. The range of the interaction forces between individual gold particles extends roughly one particle diameter from their surface. This is orders of magnitude less than the total size of the clusters ultimately formed, which have radii roughly  $10^2$  to  $10^3$  times the single-particle diameter. Nevertheless, it appears that small changes in these very short range forces can have large effects on the long-range structure and symmetry of the clusters. Developing a detailed understanding of this effect and its origins is certainly one of the major challenges to be addressed in the reviving interest in the kinetic aggregation process.

## 7. Concluding remarks

In this review we re-examined one of the classic problems in colloid science – the aggregation of colloidal particles – with the aid of recent conceptual and experimental advances. The analysis of the long-ranged structure of colloidal aggregates in terms of their fractal dimension combined with a detailed chemical understanding of the colloidal surface gained by SERS has led to a

considerably better understanding of the flocculation process. Our major goal has been to use these macroscopic and microscopic level descriptions to learn about the kinetics of aggregation, but we believe that many other properties of disordered systems can be explored with a similar experimental approach.

The ability to change the fractal dimension of a colloidal aggregate by subtle variations in surface potential seems a particularly inviting prospect. Indeed, for the case of slow aggregation discussed briefly in this paper, we already see evidence for such structural changes. We expect that other ways of producing random structures will follow from an increased understanding of colloid surface chemistry. Being able to produce a variety of random systems whose structures have been quantitatively analyzed, should lead to major and significant advances in our understanding of the properties of disordered materials.

### Acknowledgements

We gratefully acknowledge the many contributions to this work of our colleagues including John Huang, Manny Oliveria, James Sung and John Dunsmuir. We have also benefited from stimulating and enlightening discussions with Tom Witten, Alan Creighton, Robin Ball and Bruce Ackerson.

### References

- [1] M. Faraday, *Phil. Trans. Roy. Soc. London* A147 (1857) 145.
- [2] B.B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).
- [3] R.K. Chang and T.E. Furtak, Eds., *Surface-Enhanced Raman Scattering* (Plenum, New York, 1982).
- [4] J.A. Creighton, C.G. Blatchford and M.G. Albrecht, *J. Chem. Soc. Faraday Trans. II*, 75 (1979) 790.
- [5] J.A. Creighton, in: *Surface-Enhanced Raman Scattering*, Eds. R.K. Chang and T.E. Furtak (Plenum, New York, 1982) p. 315.
- [6] G. Mie, *Ann. Physik* 25 (1908) 377.
- [7] F. Kirchner and R. Szigmondy, *Ann. Physik* 15 (1904) 573.
- [8] M. von Smoluchowski, *Physik. Z.* 17 (1916) 593.
- [9] E.J.W. Verwey and J.T.G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
- [10] J. Hillier, J. Turkevich and P.C. Stevenson, *Trans. Faraday Soc. Disc. II* (1951) 55.
- [11] M. Horisberger, *Gold Bull.* 14 (1981) 90.
- [12] J. Turkevich, G. Garton and P.C. Stevenson, *J. Colloid Sci.* 9 (1954) 26.
- [13] D.A. Weitz, J.S. Huang, M.Y. Lin and J. Sung, *Phys. Rev. Letters* 53 (1984) 1657.
- [14] D.A. Weitz and M. Oliveria, *Phys. Rev. Letters* 52 (1984) 1433.
- [15] D.A. Weitz and J.S. Huang, in: *Proc. Intern. Topical Conf. on the Kinetics of Aggregation and Gelation*, Eds. F. Family and D.P. Landau (North-Holland, Amsterdam, 1984) p. 19.
- [16] B.J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
- [17] J.E. Martin and B.J. Ackerson, *Phys. Rev.* A31 (1985) 1180.

- [18] P.G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- [19] S.K. Sinha, T. Freltoft and J. Kjems, in: *Proc. Intern. Topical Conf. on the Kinetics of Aggregation and Gelation*, Eds. F. Family and D.P. Landau (North-Holland, Amsterdam, 1984) p. 87.
- [20] S.K. Sinha, D.A. Weitz, R. Pynn and J.S. Gethner, to be published.
- [21] T.A. Witten, Jr. and L.M. Sander, *Phys. Rev. Letters* 47 (1981) 1400.
- [22] T.A. Witten, Jr. and L.M. Sander, *Phys. Rev. B* 27 (1983) 5686.
- [23] P. Meakin, *Phys. Rev. Letters* 51 (1983) 1119.
- [24] M. Kolb, R. Botet and R. Jullien, *Phys. Rev. Letters* 51 (1983) 1123.
- [25] P. Meakin, *Phys. Rev. A* 29 (1984) 997.
- [26] S. Alexander and R. Orbach, *J. Physique Lettres* 43 (1982) L625.
- [27] R. Rammal and G. Toulouse, *J. Physique Lettres* 44 (1983) L13.
- [28] H.R. Kruyt, *Colloid Science*, Vol. 1 (Elsevier, Amsterdam, 1952).
- [29] C.G. Blatchford, J.R. Campbell and J.A. Creighton, *Surface Sci.* 120 (1982) 435.
- [30] B.V. Enustun and J. Turkevitch, *J. Am. Chem. Soc.* 85 (1963) 3317.
- [31] O. Siiman, L.A. Bumm, R. Callaghan, C.G. Blatchford and M. Kerker, *J. Phys. Chem.* 87 (1983) 1014.
- [32] C.J. Sandroff and D.R. Herschbach, *Langmuir* 1 (1985) 131.
- [33] C.J. Sandroff, D.A. Weitz, J.C. Chung and D.R. Herschbach, *J. Phys. Chem.* 87 (1983) 2127.
- [34] D.W. Schaefer, J.E. Martin, P. Wiltzius and D.S. Cannell, *Phys. Rev. Letters* 52 (1984) 2371.