

Nucleation and Aggregation of ZnS Crystallites Precipitated from a Chemical Reaction

M. S. Couto* and O. N. Mesquita

Departamento de Física, ICEx, Universidade Federal de Minas Gerais

Caixa Postal 702, Belo Horizonte 30161-960, MG, Brasil

Received March 4, 1994

The nucleation and growth of ZnS crystallites precipitated from a chemical reaction between ZnCl_2 and Na_2S in aqueous solution, are studied with the use of light scattering techniques. From the measurements it is found that the initial nuclei have sizes between 5 and 10 nm. After nucleation these nuclei start to aggregate. The average size of the aggregates increases exponentially as a function of time. Growth rates are highly dependent on the initial concentrations of Zn and S, being maximum at the stoichiometric concentration. The aggregates are fractals with measured Hausdorff fractal dimension of 2.1 ± 0.2 . Within experimental error the measured growth law together with the fractal dimension of the aggregates are in agreement with the results from computer simulations of the Reaction-Limited-Cluster-Cluster-Aggregation mechanism (RLCCA). This experiment emphasizes the utility of light scattering techniques to perform *in situ* studies of nucleation and crystal growth phenomena.

I. Introduction

With the development of sophisticated technological materials for various applications, the control of the parameters of the starting products has become increasingly necessary. Among the several starting products parameters that would be desirable to have an adequate control, the size distribution and the structure of the grains in powders are very important ones, mainly for sintering processes. In general, these starting products are the result of chemical reactions. Consequently, informations about the structure and size distribution of the grains, obtained *in situ* during the chemical reactions, are certainly very useful.

In addition, a detailed experimental study of nucleation and kinetics of growth and aggregation of particles, can provide data to check theories and computer simulations that attempt to model such complex phenomena^[1].

Light scattering techniques have been successfully used to study phenomena at the solid-liquid interface during crystal growth^[2]. The non-destructive and *in situ*

character of such techniques are of great advantage.

Our experiment consists on the study of the light of a 25 mW He-Ne laser scattered by crystallites of ZnS precipitated during the chemical reaction between Na_2S and ZnCl_2 in aqueous solution. We use the technique of Photon Correlation Spectroscopy (PCS)^[3] to obtain the sizes and growth rates, and Static Light Scattering to obtain the structure of the crystallites^[4].

II. Experimental procedure and discussion

Our apparatus is schematically shown in Fig. 1. This is the standard homodyne configuration used in PCS. What is measured is the time autocorrelation function of the scattered light intensity $\langle I_q(t)I_q(t + \tau) \rangle$, for a particular scattering wavevector $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_s$, where \mathbf{k}_0 is the wavevector of the incident light and \mathbf{k}_s is the wavevector of the scattered light. For PCS $q = 2k_0 \sin(\theta/2)$, where θ is the scattering angle. The experiments are performed with

*Present Address: RIM, Laboratory of Solid State Chemistry, Faculty of Science, Catholic University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

a Brookhaven Instruments Co. model 2030 correlator and a Spectra Physics 25mW He-Ne laser. For diffusing particles far from walls^[5], the diffusion coefficient can directly be obtained from the equation

$$\langle I_q(t)I_q(t + \tau) \rangle = A + B \exp(-2q^2 D\tau), \quad (1)$$

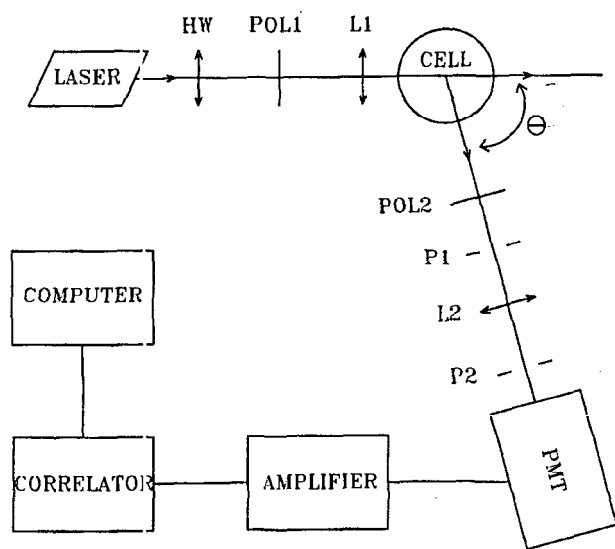


Figure 1: Light scattering set-up; HW is a half-wave plate; POL1 and POL2 are linear polarizers; L1 and L2 are lenses; P1=2mm and P2=150 μ m are pinholes; PMT is the photomultiplier.

where A and B are constants and D is the diffusion coefficient of the particles. If the particles are spherical one can obtain their hydrodynamic radius R from the well-known Einstein-Stokes relation,

$$R = k_B T / 6\pi\eta D, \quad (2)$$

where k_B is Boltzmann's constant, T is the absolute temperature and η is the viscosity of the liquid where the particles are diffusing. In our case η is the viscosity of water. Because there is a strong screening of the hydrodynamic interactions inside of fractal objects, their hydrodynamic radii are close to their gyration radii. Wiltzius^[6] has measured the ratio between the hydrodynamic radius and the gyration radius for fractal silica aggregates, with a monomer size of 70 \AA , and found the number 0.72, for aggregates with average radius 500 \AA < R < 7000 \AA . He also found a slight dependence of the diffusion coefficient with scattering wavevector q , for large values of q . In order to obtain

the correct growth law, our measurements of the size of the crystallites as a function of time are performed at fixed scattering angle ($\theta = 70^\circ$).

If there is a distribution of particle sizes, there is a distribution of diffusion coefficients, consequently the autocorrelation function is not a single exponential. One of the methods to analyze such a correlation function is the method of cumulants^[3], from which one obtains an average particle radius and the standard deviation of the distribution, which is called polydispersity.

Solutions of Na_2S and ZnCl_2 are prepared with deionized water and then filtered with a 0.2 μm filter. The method of preparation of the aqueous solutions and the ways to obtain the ZnS crystallites are described by Rossetti et al.^[7]. We found that 1.5×10^{-3} M aqueous solution of Na_2S and 6.6×10^{-3} M aqueous solution of ZnCl_2 , mixed in different volume ratios, give stable crystallites^[7]. TEM images of ZnS colloids formed from solutions at 23 $^\circ\text{C}$ with excess of Zn or S, show extensive aggregation of small ZnS crystallites into loose structures^[7].

In order to carry out the experiments, the solutions are mixed in a cylindrical sample glass cell whose diameter is 4 cm and height 5 cm, with different volume ratios and consequently different initial molar concentrations of Zn and S, which we define by the ratio Zn/S. This is done in order to study the growth behaviour of the ZnS crystallites as a function of the Zn/S ratio. Before we mix the solutions, we perform PCS measurements in each one of them. Only the solutions with no observable time autocorrelation of the scattered light, for the whole range of sample times available in the correlator, are used. This procedure guarantees that the solutions are free of any spurious particles. They are then mixed without stirring, with the smaller volume solution being placed first in the cell. Typically, we work with total solution volume of the order of 40 cm^3 . With this procedure we have obtained reproducible results.

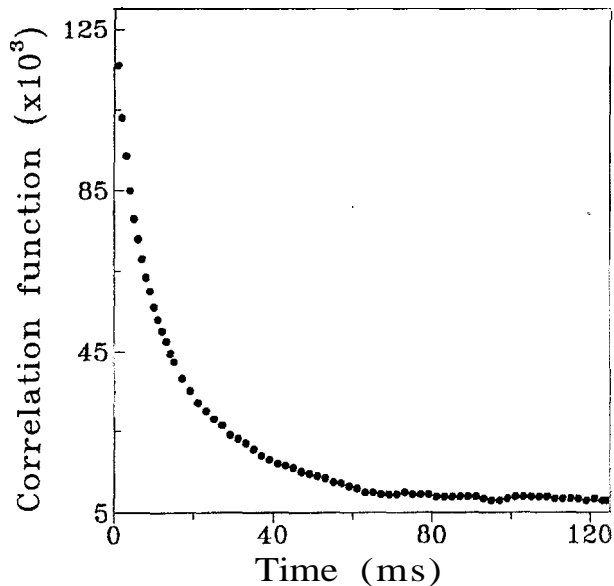


Figure 2: Measured time autocorrelation function of the light intensity scattered by ZnS crystallites.

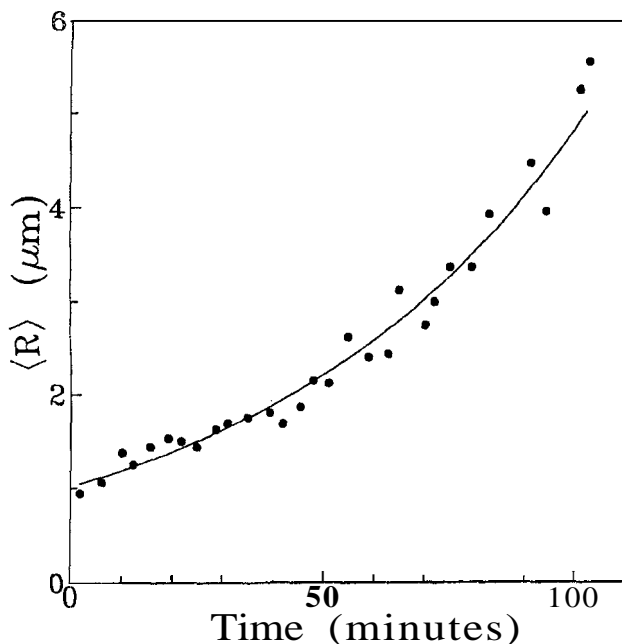


Figure 3: Time evolution of the average radius of the aggregates for $Zn/S=4.4$. The dots are the experimental points and the continuous curve is the fit using $\langle R \rangle = R_0 \exp(Ct)$.

A typical correlation function of the light scattered by the ZnS crystallites is shown in Fig. 2. In Fig. 3 we show the time evolution of the average radius of the ZnS crystallites for $Zn/S=4.4$. The measured average radius (dots) as a function of time is well fit by an exponential function like $\langle R \rangle = R_0 \exp(Ct)$ (continuous curve), where R_0 and C are constants. The polydispersity increases as a function of time, indicating that the width

of the size distribution increases as the growth proceeds. The constant C , and consequently the growth rate of the crystallites, is highly dependent on the ratio Zn/S . In Table 1 we show the data for different Zn/S ratios. The maximum time of observation for the longer runs is 1700 minutes, hence this imposes a lower limit in the measurement of C . If an observable growth is not detected during 1700 minutes, we write in Table 1 that C is smaller than 0.0006 min^{-1} . In particular, for the stoichiometric concentration $Zn/S = 1$, the growth rate is so fast that it cannot be measured within our time resolution of about 1 minute, which is the time for accumulation of a correlation function. The observed trend in the data is that for $Zn/S = 1$ the growth rate is maximum. The growth rate decreases as one moves far from $Zn/S = 1$, both decreasing or increasing this ratio, but drops faster for decreasing Zn/S ratio. What is probably happening is that the excess of Zn or S ions attaches to the surface of ZnS crystallites causing a Coulomb repulsion between them. Due to the electrolyte, there is a Debye screening of this Coulomb repulsion and the particles can then come closer. As the particles get closer, the short range Van der Waals attraction may become larger than the Coulomb repulsion and aggregation may occur. This is the classical picture for colloidal aggregation proposed by Derjaguin-Landau-Verwey-Overbeck, the so-called DLVO model of aggregation^[8,9]. The rate of aggregation is then determined by the amount of surface charges in the crystallites and the ionic strength of the electrolyte. The strong dependence on the growth rates obtained as a function of the Zn/S ratio, the exponential growth law and the increase in polydispersity, suggest that aggregation of the ZnS crystallites, rather than growth of single crystals, is occurring. If this scenario of aggregation is a reasonable one, there should be a connection between the growth law and the structure of the aggregates.

Computer simulations of various aggregation models indicate a connection between the growth law and the fractal dimension of the aggregates. For the purpose of comparison with our data we will consider the Reaction-Limited-Cluster-Cluster- Aggregation model

(RLCCA) in three dimensions^[1]. In this model, particles of initial radius r_0 (monomer radius) are executing Brownian motion. When two monomers collide they have a certain probability to stick together and form a 2-particle unit. It can collide with another monomer and form a 3-particle unit or collide to another 2-particle unit and form a 4-particle unit, and so on. By this mechanism it is clear that the average size of the aggregates increases in time as well as the polydispersity. Depending on the value of the sticking probability, different growth laws and fractal dimensions can be obtained. For a sticking probability equal to one (Diffusion-Limited-Cluster-Cluster-Aggregation model, DLCCA), computer simulations show that the rate of the growth as a function of time is a power law and the Hausdorff fractal dimension of the aggregates is 1.75. For a sticking probability smaller than one (RLCCA model) computer simulations show an exponential growth law, with the rate of growth highly dependent on the sticking probability, and a Hausdorff fractal dimension of 2.1^[1]. This fractal dimension obtained by simulation is insensitive to the mechanism of transport of the particles considered, diffusion or convection for example. The dimension is also insensitive to the actual dependence of the diffusion coefficient with mass of the aggregates. In some simulations it was used D inversely proportional to the mass of the aggregates, in others it was taken constant. Both simulations give the same fractal dimension as a result. The choice of D or the mechanism of transport affects only the rate of aggregation.

Table 1 - Data of some experimental runs with exponential growth law $\langle R \rangle = R_0 \exp(Ct)$ for various initial concentration ratio of Zn/S .

Zn/S	$R_0(\mu m)$	$C(\text{min.}^{-1})$
0.09	0.19	<0.0006
0.09	0.20	<0.0006
0.22	0.11	<0.0006
0.22	0.18	<0.0006
0.44	0.25	0.003
1.00	23	>1
4.00	1.13	0.015
4.40	1.38	0.013
4.40	1.06	0.012
10.00	1.30	0.010
10.27	1.34	0.012

Our PCS measurements are in agreement with the RLCCA mechanism of aggregation. For this picture to be consistent we have to measure the Hausdorff fractal dimension, D_H , of the aggregates.

The fractal dimension of the aggregates can be obtained by static light scattering measurements. The average intensity of the scattered light by the aggregates, as a function of the scattering angle, is proportional to the structure factor $S(q)$, and $\langle I(q) \rangle = I_0 S(q) \cdot S(q)$ is the Fourier Transform of the pair correlation function $g(r)$ [3]. For fractals $S(q) \propto q^{-D_H}$; this holds for $r_0 \ll 1/q \ll \xi$, where r_0 is the monomer size and ξ is the mean size of the fractal. A more general expression for $S(q)$, and then for $\langle I(q) \rangle$ can be obtained if one assumes that $g(r)$ decays exponentially like $\exp(-r/\xi)$ and the monomers are spheres of radius r_0 [4,10],

$$\langle I(q) \rangle = I_0 \left\{ 1 + \frac{D_H \Gamma(D_H - 1)}{(qr_0)^{D_H} \left(1 + \frac{1}{q^2 \xi^2}\right)^{\frac{(D_H-1)}{2}}} \sin[(D_H - 1) \tan^{-1}(q\xi)] \right\} \times \left[\frac{\sin(qr_0) - qr_0 \cos(qr_0)}{(qr_0)^3} \right]^2 \quad (3)$$

where $\Gamma(D_H - 1)$ is the gamma function of $D_H - 1$. From this expression we see that for $1/q \ll r_0$, $\langle I(q) \rangle \propto q^{-4}$ which corresponds to the form factor of a

spherical monomer; for $r_0 \ll 1/q \ll \xi$ (scaling region), $\langle I(q) \rangle \propto q^{-D_H}$ which corresponds to the structure factor of a fractal aggregate; for $1/q \gg \xi$, the typical

wavelengths are much larger than the average size of the aggregates, then $\langle I(q) \rangle$ levels off and becomes constant. In Fig. 4 it is shown a typical data of the scattered intensity as a function of the scattering wavevector (dots) in a log-log plot, and the fit using Eq. 3 (continuous curve), with the use of a non-linear least square fitting program and with I_0 , r_0 , D_H and ξ as free parameters. Since the use of visible light limits the value of $1/q$ to about 30 nm, we do not have much accuracy in the determination of r_0 . Consequently only an estimated value for r_0 is obtained. From the best fit we obtain for all experimental runs that r_0 is within the range from 5 to 10 nm. For different samples we obtain slightly different fractal dimensions. Since no correlation was found between this variation and the parameters of the experiment for the concentrations used, we take as a measured fractal dimension the average over the data of 20 different runs. The measured fractal dimension for the aggregates is then,

$$D_H = 2.1 \pm 0.2 .$$

The exponential growth of the average aggregate size and the fractal dimension above are consistent with a RLCCA mechanism of aggregation.

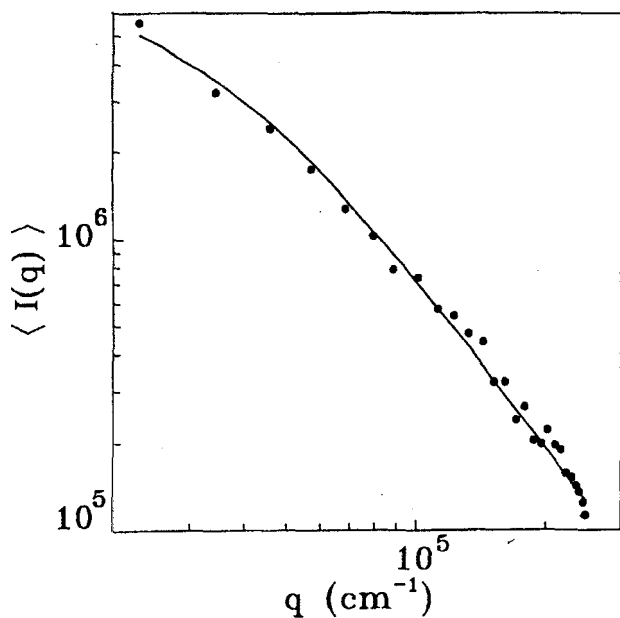


Figure 4: Log-log plot of the scattered intensity as a function of the scattering wavevector. The dots are the experimental points and the Eq. 3 described in the continuous curve is the best fit. From this fit one obtains r_0 between 5 and 10 nm, $D_H = 2.0$ and $\xi = 320$ nm.

III. Conclusions

A chemical reaction between ZnCl_2 and Na_2S in aqueous solution, both completely soluble in water for the concentrations used at room temperature, gives as a result ZnS which is highly insoluble in water. Immediately after the mixing of the solutions, nucleation of ZnS crystallites occur due to the high supersaturation of ZnS . The available ZnS is consumed in the nucleation process resulting in small nuclei of sizes estimated to be between 5 and 10 nm. These nuclei perform Brownian motion in the liquid, collide with each other and aggregate. The aggregates collide again and stick together to form even larger units, and so on. When we use non-stoichiometric concentrations, the excess ions of Zn or S attach to the surface of the ZnS crystallites and via double-layer repulsion and Debye screening, the sticking probability can be varied. The process of aggregation when the sticking probability is smaller than one, is named Reaction-Limited-Cluster-Cluster-Aggregation (RLCCA) and was modeled previously by computer simulations. From these simulations it was obtained an average aggregate radius which grows exponentially as a function of the time and a Hausdorff fractal dimension of 2.1.

From our light scattering experiments, performed *in situ* during the chemical reactions, we obtain an exponential growth law and a Hausdorff fractal dimension of 2.1 ± 0.2 for the aggregates. The growth rates are dependent on the ratio Zn/S and it is maximum for the stoichiometric concentration, Zn/S=1. These results are consistent with the RLCCA mechanism of aggregation. The mechanism of aggregation proposed above is consistent with the TEM images of ZnS colloids reported in Ref.[7]. Our experiments demonstrate the utility of light scattering techniques to study nucleation, growth and aggregation phenomena, during chemical reactions.

Acknowledgements

We thank the Brazilian Agencies: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos

(FINEP) for supporting this research. M.S.Couto thanks CNPq for a Master's degree fellowship and O.N.M. thanks CNPq for a RHAE fellowship. We greatly appreciate the hospitality at the Laboratory of Solid State Chemistry of the Catholic University of Nijmegen, where this paper was written.

References

1. On *Growth* and Form, NATO Advanced Study Institute, Series B: Physics, edited by H. E. Stanley and N. Ostrowsky (Nijhoff, Dordrecht, 1986).
2. L. M. Williams, H. Z. Cummins, L. O. Ladeira and O. N. Mesquita, Phys. Rev. **A45**, 3880 (1992) and references therein.
3. Photon Correlation and *Light Beating Spectroscopy*, edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1974).
4. J. Teixeira in reference 1.
5. M. I. M. Feitosa and O. N. Mesquita, Phys. Rev. **A44**, 6677 (1991).
6. P. Wiltzius, Phys. Rev. Lett. **58**, 710 (1987).
7. R. Rossetti, R. Hull, J. M. Gibson and L. E. Brus, J. Chem. Phys. **82**, 552 (1985).
8. B. V. Derjaguin and L. Landau, Acta Phys. Chim. **14**, 633 (1941).
9. E. J. Verwey and J. Th. Overbeck in *Theory of Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
10. A. K. Sood, Hyperfine Interactions **37**, 365 (1987).