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Inorganic particle gels
Theo PM Beelen

In the past year, notable progress has been made in the understanding of the fundamental principles of fractal growth of aggregates and gels. A strong interplay between experimental results involving sol-gel chemistry, precipitated gels and sophisticated computer simulations was extremely useful for finding relations between scattering data and experimental results. Finally, the development of new types of microscopy, such as atomic force microscopy, X-ray microscopy and cryo-electron microscopy, will supply experimental methods that can be used to investigate wet gels, and will be complementary to X-ray and neutron scattering techniques.

Addresses
Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands; e-mail: tgtatb@chem.tue.nl

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Abbreviations
AFM atomic force microscopy
cryo-TEM cryo-transmission electron microscopy
DLA diffusion-limited aggregation
DLCA diffusion-limited cluster-cluster aggregation
SANS small angle neutron scattering
SAXS small angle X-ray scattering
TFAFM tapping mode atomic force microscopy
USAXS ultrasmall angle X-ray scattering

Introduction
Although scientists have been familiar with inorganic gels for a long time (e.g. silica gel was manufactured 150 years ago on a large scale), many new fundamental properties and exciting applications were only discovered over the past 15 years. An important contribution to this revival was the development of sol-gel chemistry, a new approach to the preparation of oxide materials. Starting from a solution, via controlled formation of reactive M-OH groups and successive inorganic polymerization reactions, particles are formed. These primary particles combine, by diffusion or precipitation, to form a solid network: the gel. Aging, drying or densification of the wet gel results in an almost unlimited range of powders, films, fibers, monolithic glasses, and even crystals such as zeolites [1].

Also the concept of fractality, introduced by Mandelbrot [2] and applied to aggregates and gels, played a key role in the revival of inorganic gel research. In particular, the growth and form of different types of aggregates and gels could be characterized effectively using the fractal dimension, a new parameter describing the varying density within an amorphous gel. Because scattering of radiation is mass-dependent, scattering by visible light, X-rays or neutrons could be applied successfully to characterize gels at the colloidal scale. With the recent development of computing power available to scientists, computer simulations of growth processes have not only brought about fundamental understanding of the formation of gels, but are also essential for the interpretation of the scattering patterns.

Most inorganic particle gels are formed by interconnection of growing aggregates. These aggregates are formed from moving and reactive primary particles. Therefore gels can be described by two important scaling parameters: the average size of the primary particle r, and the average radius of gyration, R, of the aggregates. At scales <<R (roughly the micron range) the gel is a network of interconnected 'blobs' and can be considered to be a homogeneous system with respect to many physical or chemical properties. At the other end of the spectrum, at scales >>R, the range of approximately 1–5 nm applies, and here atomic or molecular physics and chemistry govern the reactions and properties of particles and interparticle bonds. The intermediate range, between r and R, is the range of the aggregates with their fractal morphology and fractal growth patterns. It is in this range that many important properties of materials based on inorganic particle gels are located, and the combination of new science and practical applications has caused the remarkable revival in this field during the past 15 years. The continuous supply of many papers with new ideas and results keeps the field of inorganic gels alive and with a bright future.

This review summarizes recent advances reported in the literature in the field of inorganic particle gels in a broad sense: fundamentals of aggregate growth and gelation including computer simulations, applications in sol-gel chemistry and precipitated gels, physical properties of gels and new methods to investigate this special field. The emphasis in this review is upon literature published in the period January 1995 to June 1996.

Fractal approach of aggregation and gelation
Many characteristic properties of gels are determined by the aggregates that form the building blocks of the gel. Ever since the recognition by Mandelbrot [2] that the mass of many aggregates can be described by relations such as M = R^D (where M is the mass of aggregates and the fractal dimension D, being any integer between one and three), and especially since the pioneering work of Jullien, Meakin and many other workers in this field (for a review see [3]), the basic understanding of the form and growth of aggregates has increased enormously. A good impression of the impact of the fractal approach in the field of materials-oriented physics and chemistry is...
In spite of many efforts, however, the physical basics of diffusion-limited aggregation (DLA) are still poorly understood, and, as stated by Meakin in his concise commentary [5], "It is becoming apparent that DLA is a difficult problem that poses a major theoretical challenge." This has resulted in a continuous stream of papers dealing with fundamental studies. To obtain an introduction into the kind of fundamental physical problems encountered in DLA, a contribution by Leonard M Sander [6] to the MRS symposium "Fractal Aspects of Materials" is very informative. In this paper, an overview is given of the influence of the diffusive instability in forming various growth morphologies.

An important step towards a theoretical framework for DLA was given by Erzan, Pietronero and Vespignani [7••]. Applying their 'fixed scale transformation' these authors can explain the self-organized critical nature and the origin of fractal structures in DLA, including the analytical calculation of critical exponents such as the fractal dimension. Also, a paper by Halsey [8] discussing branching phenomena in DLA might be an important step in understanding the origin of mass gradients during the growth of fractal aggregates.

Another significant contribution at the most recent MRS symposium on fractals was made by Arneodo and his group [9•]. To create a two-dimensional DLA pattern, they developed a well considered experimental system by forming an aggregate consisting of silver particles. Applying an electroless deposition technique, migration and convection were avoided as well as electrochemical side reactions, with only diffusion as the rate limiting step [10]. Both the morphology and the fractal dimension of the resulting experimental two-dimensional DLA pattern showed a very strong resemblance to simulated DLA patterns. To achieve a comparative structural characterization of both types of aggregates, an analysis based on wavelets was applied. Wavelet transforms can be regarded as a mathematical microscope whose position in the aggregate and magnification can be varied [11,12]. When examining DLA with wavelet transforms, one reveals progressively, and quite naturally, the successive generations of branching and (multi)fractal properties, showing the wavelet transform microscope as a very promising tool. In a recent letter [13], wavelets were used to analyze the inner structure of diffusion-limited aggregates and the oscillations of the fractal dimension D around the average value D = 1.65; the oscillations were described using a set of complex fractal dimensions.

The distinction of two different regions, a frozen internal zone which free particles never enter and an external active zone to which new particles bond, was applied by Boularot and Albinet [14]. They showed that the angular distribution in DLA obeys a multifractal statistic, and also that the law governing the tip effect, in relation to the penetration of free moving particles in the active zone, was independent of the cluster size.

An interesting contribution to the discussion on multifractality in DLA is presented in a paper by Jestczemski and Sernetz [15]. Based on a formalism published by Vicsek et al. [16,17], 'thin' and 'fat' fractals were defined and constructed with Vicsek's deterministic fractal. DLA and arterial blood vessels were given as typical examples for thin and fat multifractals, respectively. In my opinion, however, it would be very interesting to investigate whether aging, and maybe even pore formation, in DLA aggregates could be described by the crossover from thin to fat fractals: the picture of arterial blood vessels strongly resembles pore formation in aged silicas, as proposed by Dokter et al. [18].

Branching in DLA was also studied by Eugene Stanley and his group [19•]. After removing dangling side branches, the ramification of DLA in two, three and four spatial dimensions were studied. Although in every dimension the number of branches increased with increasing radius, in two dimensions the number of branches levels off at larger distances, indicating a fixed number of main branches in DLA. Contrary to this, at higher dimensions the skeleton continues to ramify with increasing number of main branches. This suggests not only a fundamental difference between two- and three-dimensional DLA (including the need for care when using two-dimensional models to study experimental three-dimensional systems!), but also may explain the deviations from self-similar behaviour (multifractality) in two-dimensional DLA.

**Computer simulations of aggregation, gelation and aging**

After an initial paper by Witten and Sander [20], several algorithms have been developed to simulate the diffusion of particles resulting in aggregates and the percolation of these aggregates to form a gel [3]. During the past decade many improvements to the basic diffusion- or reaction-limited cluster-cluster algorithms have been introduced and tested by comparison with experimental results, including mainly small angle scattering spectra from X-rays (SAXS) or neutrons (SANS). Also, static wide angle light scattering has been used for transparent systems. Because X-rays and neutrons are scattered by inner-core electrons and atomic nuclei, respectively, the scattering intensity is determined by the mass density and therefore fractal mass distributions in aggregates can be recognized immediately. An efficient system has been developed by Van Garderen, Pantos and coworkers [21,22]. By using the computer
program GRASP, the formation of aggregates and gels can be simulated. With another computer program, DALAI, the corresponding scattering spectra are calculated, using the coordinates of the primary particles provided by GRASP. In this way simulations are extremely useful, because hypotheses concerning aggregate formation, aging reactions or other transformations within gels can be tested immediately by comparing experimental SAXS or SANS data with scattering spectra calculated from these simulations.

A nice example of this strategy is given in a letter by Jullien and Hasmy [23•]. Because cluster deformations probably play an important role during the sol-gel transformation, the diffusion-limited cluster-cluster aggregation (DLCA) model was modified using the bond fluctuation algorithm. It was shown that in this modified model, contrary to DLCA, gelation only occurred at concentrations, c, above a threshold value $c_g$, and that the calculated SANS curves were very similar to experimental SANS curves of base-catalyzed aerogels.

The relation between cluster-cluster aggregation and scattering was highlighted by Sciortino, Belloni and Tartaglia [24•], especially to search for characteristic length scales in cluster-cluster arrangements with regard to the description of the depletion region which develops around the growing clusters. In accordance with experiments, simulations showed that scaling in the time development of scattered intensity was observed only for compact (nonfractal) clusters, and if fractal clusters were present (for example, in DLCA) scaling was observed only close to the gelation point.

An interesting theoretical point concerns the equivalency between percolation and DLCA as proposed, for example, by Gimel et al. [25] for high concentrations. Hasmy and Jullien [26] show that, at concentrations above the gelation concentration $c_g$, a crossover length $L_c$ exists between percolation and aggregation. At increasing c this $L_c$ vanishes and the percolation regime shows up at all length scales in the gel.

In most applications, a real description of the system cannot be given by the basic and simple DLCA model. Therefore many papers deal with extensions of this model which are tailor-made and adapted for specific applications as much as possible.

Aging phenomena play an important role during the conversion of an inorganic particle gel into a more solid system, for example, if a porous material is formed. Without aging, the ramified and weak structures will collapse during drying. Van Garderen et al. [22] tested several types of aging by DLCA simulations. They showed that dissolution and reprecipitation of silica particles (Ostwald ripening) could not explain the simultaneous increase and decrease of the fractal dimension at small and large length scales, respectively, as observed in experimental scattering data of aged silica gels. When small movements of singly connected branches were allowed, however, resulting in multiconnected particles, the calculated SAXS spectra showed both the small and large length scale properties of experimental SAXS plots [27].

Bos and van Opheusden [28] showed that with the introduction of Brownian dynamics and an interaction Lennard–Jones potential, the formation of fractal aggregates and gels with continuous reorganization could be simulated. During this reorganization, the number of particles in the largest cluster decreased. Although significant scaling regions are still found in both two- and three-dimensional simulations, probably due to reorganization effects, no universal results for the fractal dimension could be found and the fractal dimension, instead of decreasing, was increasing anomalously with increasing scattering vector $q$ [29].

The influence of external flows was investigated by Warren, Ball and Boelle [30•]. In the absence of a barrier (excluding reaction-limited aggregation), the nature of aggregation is determined by the Peclet number, $Pe = UR/D$ (where $U$ is the magnitude of the flow, $R$ is the aggregate size and $D$ denotes the mutual diffusion constant). For $Pe << 1$ diffusion is dominating, whereas for $Pe >> 1$, convection-limited growth will always take over. To discern growth by convection from ballistic growth, screening of the fluid streamlines of small particles in the interior of big aggregates becomes important and results in the formation of convection-limited aggregates with fractal dimensions $D_f = 2.5$, slightly higher than for DLCA as is expected. An approach from the other limit was proposed by Dirkse and Cawley [31], by investigating the use of the range between ballistic and convectional DLA using two-dimensional simulations. In agreement with Warren et al. [30•], they found $D_f$ values between 1.7 and 2.0, depending on the accessibility of the fjords in the aggregate by the flowing particles.

A model describing the influence of fractal aggregate structure on coagulation and settling in aquatic systems has been studied by Grant, Poor and Relle [32]. They applied Smoluchowski's coagulation kernels in combination with fractal aspects. Assuming a vertical water column with a supplement of particles at the top and gravitational settling of the aggregates, the results agreed very well with experimental data obtained in Lake Zurich [33].

Although not applied to systems of inorganic particle gels, simulations of mixed particles, as described by Dickinson [34], could be very useful for sol-gel systems because many important results are obtained using two or more metals. In a two-dimensional system, Dickinson's model takes account of differing attractive or repulsive interactions between like and unlike particles, as well as differing
rates of irreversible bond formation, and this results in the formation of many different types of aggregates and gels.

A remarkable study concerning gelation time was performed by Anglaret, Hasm and Jullien [35]. It is well known that gelation time may be influenced by the size or dimensions of the container, a nuisance for scientists performing gelation in narrow cells (for example, for in situ SAXS). Contrary to loose arguments concerning the influence of the walls, Anglaret et al. [35] showed with simulations that the presence or absence of observed container size effects in base-catalyzed and noncatalyzed silica gels respectively, might be expected due to flexibility effects of clusters.

Although the availability of computer systems with annually growing computing power is a condition sine qua non to perform simulations, in many cases this is not enough for ‘real’ simulation processes, because to investigate several orders of magnitude in aggregation and gelation, the involvement of millions of particles is necessary. Because movements of particles or aggregates are similar in a sense, the benefit of using parallel programming speaks for itself. Kaufman et al. [36] showed that DLA clusters of up to 130 million particles can be calculated at hourly timescales by using parallel processing, but also one has to be careful to avoid effects introduced by the use of parallel computers. Machta and Greenlaw [37•] investigated the efficiency of parallel computing in simulations using different models and showed that, for example, DLA is very inefficient compared to percolation.

### Sol-gel methods

Compared to the 150 years preceding the introduction of sol-gel methods, the past decade witnessed an explosive increase of papers dealing with inorganic gels. As premature precipitation of metal hydroxides could be avoided with control hydrolysis, many new systems could be studied. Moreover, after the formation of primary particles resulting in a sol, the conversion to a gel or some other phases provided possibilities for new materials.

In spite of many successful applications, however, sol-gel techniques are clearly not a panacea for all problems. As stated in an excellent paper on the present and future status of sol-gel science and technology [38••], John Mackenzie is right in arguing that despite many elegant solutions to scientific or technical problems up to now only a few processes have found industrial applications, emphasizing the academic nature of the subject. Therefore, after mentioning a few general reviews on special topics, we want to discuss in this review only some of the papers dealing with new methods or developments, as many publications in the cascade of articles published describe research that has no real experimental or theoretical information of general interest.

A review of industrially successful multicomponent ceramic precursor powders is given by Woolfrey and Bartlett [39]. Aspects of sol-gel processing for electronic applications are discussed by Spiccia and West [40], including multicomponent systems as superconductors. A review of this latter topic is also given by Lina Ben–Dor [41], and the complicated sol-gel chemistry in multicomponent systems is also discussed by Bartlett and Woolfrey [42] with Ti/Zr/Al complexes as typical examples.

It will not be surprising that catalysis, with its demand for tailor-made materials necessary in selective catalysis, is a fruitful area for sol-gel applications. Four years after his first review on this subject, Pajonk published an updated review [43•], with a selection of frequently used sol-gel precursors and four examples of catalysts prepared by the sol-gel method. Also a valuable review, with much emphasis on scientific principles instead of giving just an exhaustive list of publications in this field, is given by Ward and Ko [44••]. In this paper, attention is also paid to catalytic membranes, a promising development combining separation and catalysis. An interesting contribution in this latter field was given by the group of Verwey and Keizer [45,46], tailoring pore size and porosity of silica membranes by variation of pH in the sol-gel synthesis. A more general discussion concerning sol-gel controlled porosity was presented by Brinker et al. [47•].

Very interesting developments involve the use of surfactants or other structure-directing devices. An extended review is given by Livage [48]. Although much attention is given to the underlying basic chemistry, the critical point, where the sol-gel system has to be converted into the regular structure of molecular sieves, is hardly discussed. A valuable paper on this point was presented at the Faraday Discussions on Gels (Paris, September 1995) by John Ramsay [49••]. In inverted micelles and lamellar phase systems, silica and zirconia gels were produced from the alkoxides and investigated by SANS. Under shear, oriented silica gels with anisotropic structure were formed, and with cylindrical micelles silicas containing pores of controlled size could be obtained, in close resemblance with MCM41-type molecular sieves. Also, with nonionic surface active agents, the gelation process could be modified drastically by limiting condensation reactions and particle growth in TEOS [50], resulting in microporous materials. In TiO$_2$ [51], the modification of the gel structure is brought to the fore by fractal dimensions, probably by polydispersity of the initial hydrolysis.

Although the role of the synthesis gel is not clear during the preparation of zeolites, changing fractal dimensions during preparation suggest an active role for molecules used as templates. An excellent overview of widely different organic molecules used for structure-direction in
molecular sieves and zeolites is given Mark Davis, Stacey Zones and coworkers [52].

To improve sol-gel preparations efficiently, a thorough knowledge of basic reactions is necessary. A general up-to-date review on the chemistry of alkoxides is published by Mehrotra and Singh [53•] and the rather new field of nonaqueous sol-gels, including advantages and possibilities, is reviewed by Vioux and Leclerq [54]. Studying the sometimes very complicated clusters in these papers it is not amazing that a trial and error policy in improving existing sol-gel recipes or finding new routes will not be very fruitful. A few arbitrary examples that apply clever modifications of the basic chemistry to improve sol-gel preparations are given in papers by Miller and Ko [55] on controlling prehydrolysis, by Pozarnsky and McCormick [56] on transesterification reactions, and by Chen and Vilminot [57] and Dutoit, Schneider and Baiker [58] on the use of new and modified alkoxide ligands.

**Precipitated gels**

As stated before, experimental papers dealing with inorganic particle gels rely heavily on sol-gel techniques. In important industrial processes (for example, the preparation of many types of silica), however, alkoxides are too expensive, and gels are formed by controlled settling or precipitation of aggregates and built directly by condensation reactions of metal hydroxides. Although at short reaction times aggregates and gels are too small to be sensitive to gravity, and often mechanisms such as DLCA can be observed, growing particles transform the movements from diffusion to settling especially if stirring prevents the formation of extended gels (precipitated silica). The crossover from the diffusion into the settling regime was studied by Allain et al. [59] with CaCO$_3$ suspensions. Growth and aging (Ostwald ripening) of primary particles during aggregation and precipitation of silica was investigated by Bolt et al. [60] using SANS.

Precipitated gels are often fractal, even if the primary particles are strongly anisotropic, as Brunner et al. [61•] showed during experiments with Fe(III) hydroxide particles. Using ultrasmall angle scattering of X-rays (USAXS) large aggregates, up to nanometer-size and consisting of rod-like particles, could be studied.

While investigating the role of acetate anions in the formation of copper precursors used to prepare superconductors, Livage and coworkers [62] synthesized and characterized copper(II) hydroxide gels. The choice of salt and the OH:Cu ratio appeared to be very crucial.

**Physical properties**

An excellent review on the chemical and physical factors that control the response of silica gel to heating, mechanical deformation and drying was given by Scherer [63••] in his Ralph Iker Award Lecture. Shrinkage [64•] and cavity formation [65•] during drying of silica gels are discussed more elaborately in preceding papers in cooperation with Smith and Anderson. Different (visco)elastic behavior in water and inert solvents is explained by aging of the network [66].

Sol-gel transitions in fractal systems have been studied using rheometry for barium titanate gels, by Pirard's group [67], resulting in different growth models for three t/gel regimes as found from rheological results (t denotes time and tgel denotes gelation time (time to form a gel, starting with a sol or suspension).

**Investigating gels: new methods and techniques**

Two serious problems have to be solved by experimental scientists studying gels: what techniques are available to investigators at the required length scales (1 nm–100 µm), and how to avoid damaging the vulnerable gel structures during the experiments.

As already stated in the introduction, SAXS and SANS are two of the most applied methods in this field. In most experiments, however, only length scales between 1 and 100 nm can be investigated due to the available wavelength of X-rays and neutrons. For larger length scales, scattering of light might be used, but this is only possible for transparent gels. Therefore, it is often a better solution to use X-rays, as in the case of SAXS, but at ultrasmall angles (USAXS). This can be done with a Bonse-Hart camera, and provides good results, for example, for silica as shown recently by Ise's group [68]. Monitoring spectra with the scanning Bonse-Hart camera and a laboratory X-ray source is very time-consuming, however, and therefore gelation processes cannot be studied. With synchrotron radiation, USAXS can be carried out much more efficiently [61•,69], especially if, at the ESRF (Grenoble), the source with the highest brilliance can be used [70]. Preliminary results of studies on gel transformations during the in situ preparation of silicate are very promising (PPEA De Moor, TPM Beelen, RA Van Santen, unpublished data).

After its introduction 10 years ago, atomic force microscopy (AFM) is now becoming an increasingly versatile and reliable technique. An excellent review of the state of the art, especially in relation to colloid and interface chemistry, is given by Patricia Maurice [71•]. Although use of the AFM in mineral water interface chemistry has only just begun, developments such as tapping mode AFM (TPAFM) create possibilities to scan the surface of soft and wet materials. Borne et al. [72] have applied TPAFM successfully to (soft, dry) silica aerogels and the results correspond to SAXS data.

The use of electron microscopy is restricted to stable and dry systems for inorganic particle gels, and, due to the high vacuum, wet gels cannot be investigated. Recently, however, two developments have created new
and exciting possibilities. The first is X-ray microscopy. With the high brilliance synchrotron radiation, the old idea of Röntgen to use X-rays for transmission microscopy is now realized. Morrison [73] and Kunz [74] have described the X-ray microscopes at the Daresbury Laboratory (Warrington, UK) and HASYLAB/DESY (Hamburg, Germany), respectively, and first results on wet clays [75] and wet fractal silica aggregates [76] have been published. This new technique is now in a phase of development that will allow it to start producing relevant results in material research. The second alternative is cryo-transmission electron microscopy (cryo-TEM). To enable one to apply the desired high vacuum, the wet sample is frozen to liquid nitrogen temperature. The freezing has to be done extremely fast to create glassy ice, avoiding the formation of ice crystals which would destroy the vulnerable gel structures. The state of the art of cryo-TEM is described by Talmon [77], with much emphasis on experimental possibilities and pitfalls. Cryo-TEM has already found many applications, especially in biology, but also in inorganic colloidal systems; the direct visualization of fluid colloidal structures has been applied successfully, for example by Almgren, Edwards and Gustafsson [78].

Concluding remarks

Research on inorganic particle gels has seen an explosive growth in both applied and fundamental studies during the past decade. In the past year, there has again been considerable progress in modeling and, in constructing a firm theoretical background for fractal growth of aggregates and gels, much progress has been made. Fed by the interplay of both these theoretical developments and with applications in sol-gel chemistry or precipitated gels, computer simulations provided much insight into the influence of specific chemical or physical interactions on fractal growth. With the still increasing possibilities of parallel programming, without doubt simulations will be extremely useful in the coming years.

The traditional bottleneck in studying gels, caused by the lack of experimental methods to study wet gels or in situ growth of fractal aggregates, might be less narrow in the coming years because promising developments in X-ray microscopy, cryo-TEM and AFM will complement data obtained with ‘traditional’ scattering methods.

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

• of special interest
•• of outstanding interest


Relations between fundamental properties of diffusion, and several possibilities for (fractal) morphology, are discussed.


A new framework to explain the origin of fractal structures and the analytical calculation of the fractal dimension in DLA.


The development and application of skeleton algorithm to study the ramification of branches in DLA.


47. MRS Symposium Series no 368.


