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Local reactivity limited aggregation

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The diffusion limited cluster-cluster aggregation (DLCA) model in a box is modified by introducing a reactivity probability of monomers given by w^{v_i-3}, where v_i is the coordination number of a given ith monomer. For $w=1$ the DLCA model is recovered, but for $w>1$ we show by two-dimensional calculations that resulting structures exhibit three correlation domains as in base-catalyzed silica gels: compact, fractal, and homogeneous, at very small, intermediate, and large scales, respectively. Our findings are supported by numerical calculations of the scattering function $S(q)$. [S1063-651X(96)00210-3]

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In the last years numerical models have been introduced to simulate the aggregation of clusters and have proven to be ideal tools to study the aggregation of colloidal systems [1–3]. In experiments, the aggregation mechanism usually depends on the chemical conditions. For example, when the surface charges of the particles are fully screened (i.e., when the system is in neutral conditions, $p\mathrm{H}\approx 7$) it is stated that the aggregation process is only diffusion limited [4]. Numerically, this phenomenon has been accounted for by a diffusion-limited cluster-cluster aggregation (DLCA) algorithm introduced several years ago [5,6]. This model has been widely applied to explain formation of quite rigid colloidal structures like aggregates of gold particles [4], colloidal silica gels [7], etc. Recently, for the chemical conditions described above, it has been argued [8,9] that for tenuous systems (i.e., when aggregation occurs in very small or ill-defined particle systems), local restructurations need to be considered in order to explain the more compact structures obtained. With this purpose, another numerical model, the so-called fluctuating bond aggregation model [8], has been proposed as an extension of the DLCA model including clusters deformations by means of bond fluctuations.

In base-catalyzed conditions (i.e., $p\mathrm{H}>7$), particles experiment short range interactions, therefore the aggregation is limited by the reactivity of the particles. To describe this situation numerically, a sticking probability between clusters (i.e., a probability to overcome a given potential barrier) has been introduced in the DLCA algorithm: this is the so-called chemically (reaction) limited cluster-cluster aggregation CLCA (RLCA) model [10,11]. Resulting structures are more compact than in the DLCA case, in agreement with experiments on quite rigid colloidal systems where surface charges are partially screened [12]. However, Keefer [13] argues that when aggregation takes places between noncondensed particles (like tenuous systems), the reaction rate of hydrolysis should not be neglected as in the standard RLCA model. Another relevant point is that for such chemical conditions, the solubility increases drastically with increasing $p\mathrm{H}$ [14], and for $p\mathrm{H}>12$ the system becomes very close to equilibrium. Hence, the minimum surface is obtained by a nucleation phenomenon (i.e., formation of the clusters is due to particle-cluster aggregation rather than cluster-cluster). Even if the Eden model [15] describes satisfactorily the nucleation phenomenon in the limit of $p\mathrm{H}>12$, this model is not adequate to describe the gelation process of base-catalyzed silica for $8<p\mathrm{H}<12$. Experimentally, as demonstrated in a previous publication [16], base-catalyzed silica gels exhibit compact structures at very small scales and the two correlation domains observed for DLCA aggregates (fractal and homogeneous) at intermediate and large scales, respectively. Therefore, one can deduce that the very small scales are described by the Eden model and the larger scales by the DLCA model. To our knowledge, a model able to reproduce the entire distance correlation features of a base-catalyzed silica gel has not yet been proposed. In fact, the appropriate numerical description of its growth process should consider the two experimental chemical reactions: hydrolysis and condensation.

In 1992, Kallala, Jullien, and Cabane [17] introduced a numerical model (KJC model) to describe ''gelation'' (when reaction yields fractal structures) and ''precipitation'' (when reaction yields dense structures) as the two possible results of the polymerization of monomers dissolved in a solvent. The activation of bonds (hydrolysis reaction) was considered by defining a reactivity probability for each monomer given by

$$p_i=\frac{w^{v_i}}{\Sigma_j w^{v_j}}, \tag{1}$$

where w is a reactivity parameter which describes the pattern of chemical selection, and v_i the number of bonds already formed. They obtained an increasing fractal dimension of aggregates with increasing w reaching up the spatial dimension (in their case $d=3$) for $w=2$. Note that the main idea of this model is that w could be related to the $p\mathrm{H}$. However, the hierarchical procedure that they considered allows us to study only the diluted case (when the concentration c tends to 0). An additional inconvenience of their model was that it neglected kinetic aspects, thereby loosing the usual experimental competition between condensation and hydrolysis rates. In their approach, only aggregates exhibiting the same correlations at all scales can be formed.

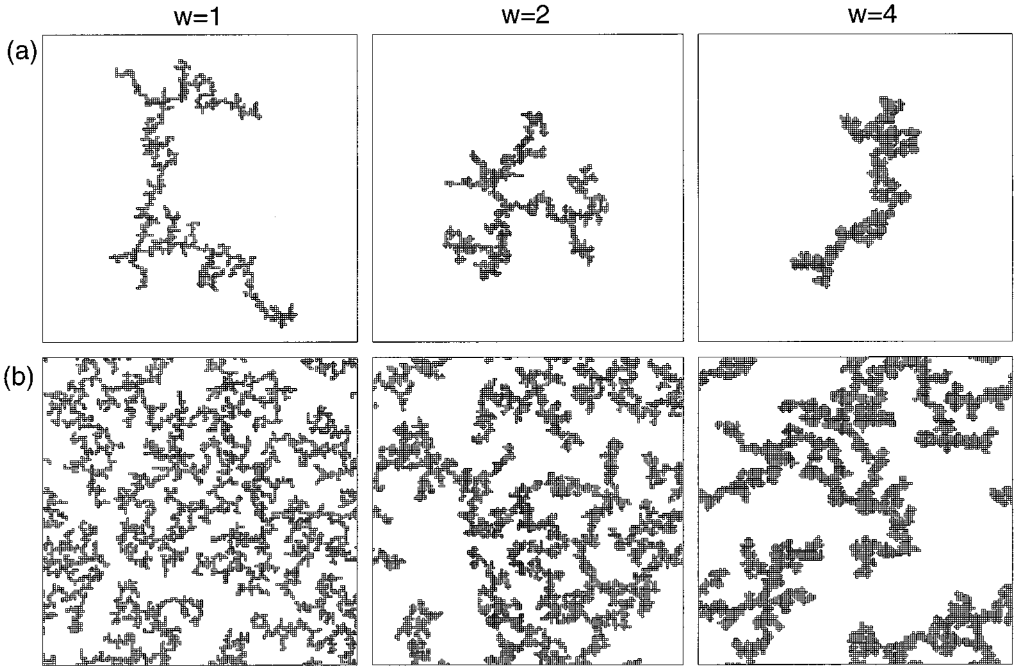

FIG. 1. Typical aggregates for $L=150$, $w=1,2,4$, and concentrations $c=0.05$ (a), and $c=0.25$ (b).

In this paper we perform the KJC model in a box for $w>1$ and a concentration larger than the gel concentration c_g (*i.e.* such that a gelling network spanning the box from edge to edge in the two space directions is obtained at the end of the aggregation process) and show that the resulting system exhibits three correlations domains as in base-catalyzed silica gels.

Our two-dimensional simulations have been performed in a square box of edge length L. For a concentration of monomers

$$c=\frac{N}{L^2}, \tag{2}$$

N monomers are initially randomly distributed on the lattice (overlaps are avoided). Taking into account that the diffusion coefficient of a system varies as the inverse of its radius, a monomer (or a cluster containing n_i monomers) is chosen randomly with a probability:

$$p_{n_i}=\frac{n_i^\alpha}{\Sigma_j n_j^\alpha} \tag{3}$$

where $\alpha(=-1/D)$ is the kinetic exponent and $D=1.45$ is the fractal dimension of DLCA aggregates in two dimensions. Then the monomer or cluster is moved by a unit step [taking into account the periodic boundary conditions (PBC)] in any of the four directions $\pm 1, \pm 1$ chosen at random. If the moving system does not try to occupy an already occupied site, the displacement is performed and the algorithm goes on by choosing another monomer or cluster. In the opposite case, the displacement is not performed but a bond between two monomers (one of each system) is established if a generated random number (uniformly distributed between 0 and 1) is smaller than a calculated sticking probability. The sticking probability p is related to the reactivity probability p_{r_i} of a monomer i, which we define here as follows:

$$p_{r_i}=\frac{w^{v_i}}{w^{2d-1}}. \tag{4}$$

Here we choose a normalization factor for p_r with an exponent $2d-1$, since this corresponds to the maximum number of bonds for a monomer able to stick to another. Therefore, the sticking probability between two monomers is given by

$$p=p_{r_i}p_{r_j}. \tag{5}$$

Typical examples of aggregates for two different concentrations and different w values are presented in Fig. 1. In Figs. 1(a) ($c=0.05<c_g$) and 1(b) ($c=0.25>c_g$) we observe that for $w=1$ the system exhibits only fractal, and fractal and homogeneous correlations, respectively, as in DLCA aggregates [16]. However, for $w=2$ and $w=4$ a compact regime appears at small scales, with a larger average size for $w=4$. Therefore, we can conclude that for $c=0.25$ and $w>1$ the aggregates exhibit three correlations domains limited by two characteristic size lengths. The first one relates to the average size r_0 of the compact "particles," and the second one is the so-called fractal persistence length ξ which corresponds to the average size of fractal aggregates. For distances larger than ξ the system is homogeneous as in the DLCA model [16].

A quantitative analysis of the different correlation domains depicted in Fig. 1 can be performed by calculating the scattering function $S(q)$ which corresponds to the scattering intensity of dimensionless points located at the monomers centers M_i. With a convenient normalization, $S(q)$ is given by

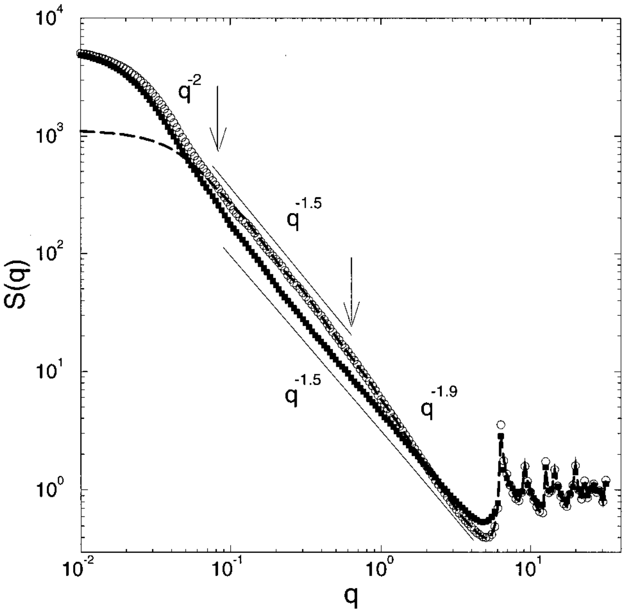

FIG. 2. Log-log plot of $S(q)$ vs q, for $L=150$, $c=0.25$, $w=1$ (black symbols), $w=4$ (open symbols), and for $c=0.05$ and $w=4$ (dashed curve). The arrow on the left indicates the crossover q_ξ between the homogeneous and the fractal regimes. The other arrow indicates the crossover q_{r_0} between the fractal and the compact regime. Each curve results from an average over three simulations.

$$S(q)=\frac{1}{N}\left|\sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{r}_i}\right|^2=\frac{1}{N}\sum_{i,j} e^{i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}, \tag{6}$$

where $\vec{r}_i=\overrightarrow{OM}_i$. This last expression can be simplified significantly by averaging over all possible three-dimensional directions of $\vec{q}$

$$S(q)=\frac{1}{N}\sum_{i,j}\frac{\sin q r_{ij}}{q r_{ij}} \tag{7a}$$

with

$$r_{ij}=M_iM_j=|\vec{r}_i-\vec{r}_j|. \tag{7b}$$

Separating the contributions $i=j$ and $i\neq j$, one gets

$$S(q)=1+\frac{1}{N}\sum_{i\neq j}\frac{\sin q r_{ij}}{q r_{ij}}, \tag{8}$$

The fact that our aggregation model has been implemented in two dimensions, does not impede us to use the last simplified expression, since it is known that in the typical power law the scattering function follows $S(q)\propto q^{-D}$, D will take the value 2 if a structure domain is found to be homogeneous in a plane of the direct space. On the other hand, the expression (8) is only valid when the aggregates are not contained in a box (i.e., when the system is a single aggregate), so we have stored the monomer connectivities in order to be able to span the aggregates out of the box by taking into account the PBC considered in our algorithm.

Typical $S(q)$ curves are reported in Fig. 2 for $L=150$ and different concentrations and w values. We focus on the intermediate linear regime, which is bonded by the Guinier regime at $q_R\approx 2\pi/R$ [the gyration radius R is the typical upper cutoff of the spanned aggregate, with $S(q_R)=N$] and the damped oscillations regime at $q_a\approx 2\pi/a$ (a is the monomer size). In Fig. 2, the curves in black and open symbols corresponds to $c=0.25$, for $w=1$ and $w=4$, respectively. The first curve exhibits the following two typical correlations for $c>c_g$ of DLCA aggregates

$$\begin{aligned} S(q)&\propto q^{-2} \quad \text{for } \frac{2\pi}{R}<q<\frac{2\pi}{\xi},\\ S(q)&\propto q^{-D} \quad \text{for } \frac{2\pi}{\xi}<q<\frac{2\pi}{a}, \end{aligned} \tag{9}$$

where $D\approx 1.5$ (a value close to the fractal dimension of DLCA aggregates in a two-dimensional space). The second curve exhibits an additional crossover in the interval $2\pi/\xi<q<2\pi/a$. Actually, for $w=4$ and $c=0.25$ one has

$$\begin{aligned} S(q)&\propto q^{-2} \quad \text{for } \frac{2\pi}{R}<q<\frac{2\pi}{\xi},\\ S(q)&\propto q^{-D} \quad \text{for } \frac{2\pi}{\xi}<q<\frac{2\pi}{r_0},\\ S(q)&\propto q^{-1.9} \quad \text{for } \frac{2\pi}{r_0}<q<\frac{2\pi}{a}. \end{aligned} \tag{10}$$

On the other hand, we note in Fig. 2 that for $w=4$ and $c=0.05$ the $S(q)$ curve (dashed line) does not exhibit the homogeneous regime $[S(q)\propto q^{-2}]$ at small q since in this case $c<c_g$. We observe that in the other two regimes (at larger q values), the curve is superimposed to the $S(q)$ curve with $c=0.25$ and same $w=4$. In fact, as also observed in Fig. 1, it seems that the average size r_0 does not depend significantly on c.

In Fig. 3 we show a log-log plot of $S(q)q^2$ vs q for $c=0.25$ and $w=1$ (solid curve), $w=2$ (dotted-dashed curve) and $w=4$ (dashed curve). We use the convenient $S(q)q^2$ representation in order to emphasize the w dependence of the $S(q)$ curves in the $2\pi/r_0<q<2\pi/a$ compact regime. In this figure, the arrows indicate the position of the crossover wave vectors ($q_r\approx 2\pi/r_0$). Note that q_r is shifted towards small q values when w increases (for $w=1$, as the compact regime does not exist, one can assume that $q_r=q_a$). This result is consistent with those observed in Fig. 1, since it corresponds to an increasing average size r_0 with increasing w. Furthermore, we observe that for increasing w the slope in this regime vanishes, because the dimension of the compact objects at small length scales approaches the spatial dimension 2. In fact, for $q_r<q<q_a$ and from the power law $S(q)\propto q^{-D}$ we found $D=1.7$ for $w=2$ and $D=1.9$ for $w=4$. However from Fig. 1 it is clear that at small scales and for $w>1$, the system is compact. If the value $D=2$ is not obtained, it may be due to the small number n of monomers which form our ‘‘particles’’ ($n\approx 10$ and $n\approx 20$, for $w=2$ and $w=4$, respectively). The situation should be different when considering both L and w larger but the computation time would be prohibitive for our algorithm with the selected

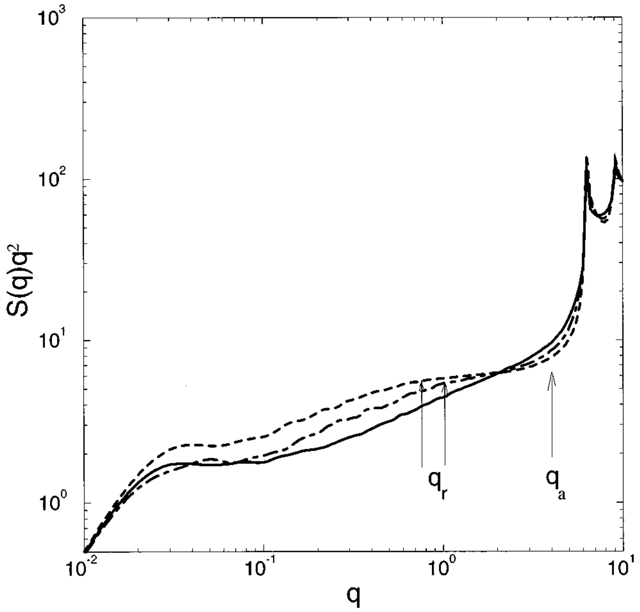

FIG. 3. Log-log plot of $S(q)q^2$ vs q, for $L=150$, $c=0.25$, and $w=1$ (solid curve), $w=2$ (dotted-dashed curve) and $w=4$ (dashed curve). The arrows indicate the crossovers positions q_r and q_a. Each curve results from an average over three simulations.

set of parameters. In fact, using a RS/6000 IBM computer, for $L=150$, $w=4$ and $c=0.25$, about 48 hours of CPU is needed for each configuration.

In our model, the aggregation of monomers is very slow, since, as deduced from Eq. (4), the reactivity probability of a monomer decreases when w increases. In fact, the growth process speeds up only when there are no remaining single monomers, i.e., when all of them are stick-in-particles (a compact set of n monomers) or fractal clusters. When a monomer belongs to a particle or a cluster, it is multiconnected so the sticking probability p_r becomes close to 1. At this stage, the growth process is governed by a diffusion limited cluster-cluster aggregation mechanism of these condensed particles.

We would like to point out that the resulting three correlation domains for $w>1$, are consistent with those reported by Skjeltorp [18] in a two-dimensional aggregation experiment of polystyrene spheres with surface charges partially screened by added salt. The resemblance between our aggregate for $w=4$ and the polystyrene aggregate of the Skjeltorp's experiment is remarkable (compare Fig. 1(b), $w=4$, with Fig. 3 of Ref. [18]). Skjeltorp argues that the compact structures at small length scales obtained in his experiments are due to some rearrangement of the spheres migrating from the first nearest-neighbor site reached to an energetically more favorable neighbor site. In our model, this situation corresponds to a monomer with a high v_i connectivity value. Furthermore, we have shown that our model is able to simulate the formation of particles and fractal clusters as formed in base-catalyzed silica gels [16]. Unfortunately, quantitative comparison between our model and this experimental system requires three-dimensional calculations, which by now are hard to consider for the reasons mentioned above. On the other hand, the model as presented here leads also to DLCA aggregates for $w<1$, since in this case $p_r \geqslant 1$. However, if we eliminate the normalization factor of (4), for $w<1$ the sticking probability between single monomers becomes equal to one, and is smaller for monomers sticking to already connected monomers. In other words, at the early stages the aggregation process favors very tenuous structures. Preliminary calculations show that at small length scales the structures are less compact than for typical DLCA aggregates, but with similar fractal correlations, as reported by Meakin and Muthukumar [19] in a study using a reaction-limited aggregation hierarchical model with repulsive interactions.

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[1] F. Family and D. P. Landau, *Kinetics of Aggregation and Gelation* (North-Holland, Amsterdam, 1984).
[2] R. Jullien and R. Botet, *Aggregation and Fractal Aggregates* (World Scientific, Singapore, 1987), p. 1.
[3] P. Meakin, *Phase Transitions and Critical Phenomena* (Academic, New York, 1988), Vol. 12, p. 235.
[4] D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, Phys. Rev. Lett. **53**, 1657 (1984).
[5] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983).
[6] M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983).
[7] M. Foret, J. Pelous, and R. Vacher, J. Phys. (France) I **2**, 791 (1992).
[8] R. Jullien and A. Hasmy, Phys. Rev. Lett. **74**, 4003 (1995); **75**, 2454(E) (1995).
[9] E. Anglaret, A. Hasmy, and R. Jullien, Phys. Rev. Lett. **75**, 4059 (1995).
[10] R. Jullien and M. Kolb, J. Phys. A **17**. L639 (1984).
[11] M. Kolb and R. Jullien, J. Phys. Lett. **45**, L977 (1984).
[12] D. A. Weitz, J. S. Huang, and J. Sung, Phys. Rev. Lett. **54**, 1416 (1985).
[13] K. D. Keefer, in *Better Ceramics Through Chemistry*, edited by C. J. Brinker, D. E. Clark, and D. R. Ultrich, MRS Symposia Proceedings No. 32 (Materials Research Society, Pittsburgh, 1984).
[14] D. W. Schaefer, Rev. Phys. Appl. **24**, C4-121 (1989).
[15] M. Eden, Proceedings of the Fourth Berkeley Symp. Math. Stat. Prob. (University of California Press, Berkeley, 1961), Vol. 4, p. 223.
[16] A. Hasmy, E. Anglaret, M. Foret, J. Pelous, and R. Jullien, Phys. Rev. B **50**, 6006 (1994).
[17] M. Kallala, R. Jullien, and B. Cabane, J. Phys. (France) II **2** 7 (1992).
[18] A. T. Skjeltorp, Phys. Rev. Lett. **58**, 1444 (1987).
[19] P. Meakin and M. Muthukumar, J. Chem. Phys. **91**, 3212 (1989).