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LETTER TO THE EDITOR

Irreversible aggregation of clusters at high density

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Abstract. We consider two-dimensional clustering for a high density of clusters. We find that three regimes can be distinguished and give the criteria for crossover between them. The numerical value of the gelation threshold strongly depends on the system size.

In recent years irreversible aggregation of matter has become a widely studied phenomenon. Numerous applications like the formation of colloids, soot and even clouds have been described by it. The subject has been reviewed on several occasions [1-4].

One of the prominent models used to study the formation of clusters through aggregation is 'clustering of clusters' [5]: all clusters in the system simultaneously undergo a Brownian motion on a regular lattice. Whenever two clusters get as close as one lattice spacing from one another they merge irreversibly and form one larger cluster. In this way ever larger clusters are formed with time. It is by now well established that in the 'flocculation regime', i.e. when the distance between the clusters is much larger than their linear size, the clusters are fractals, which implies that their density decreases with their size like a power law [5-8]. What happens, however, when the distance betwen the clusters is less than their radius [9]? This is the question we want to deal with in this letter.

We consider the following model. At time $t=0$ a fraction ρ_0 of the sites of a square lattice of size $L\times L$ with periodic boundary conditions are occupied. If two occupied sites are nearest neighbours they belong to the same cluster. The initial density ρ_0 must be less than the percolation threshold $p_0=0.592\,75$; otherwise there exists a spanning cluster before the clusters start to move. The number of occupied sites s that belong to a cluster is called its mass. The process of aggregation now is a repeated application of the following growth step. A cluster is chosen at random and moved with a probability proportional to s^α by one lattice spacing in any of the four directions. α is a parameter of the model. For the case $\alpha=-\infty$ the smallest cluster is always chosen and is always moved. If after a move any site of the cluster becomes the nearest neighbour to a site of another cluster the two clusters become one single cluster. This process is continued until only one cluster is left in the system†. During the process several quantities are monitored: the total number of clusters N, the average cluster

† A film, based on numerical simulations, illustrating 'clustering of clusters' as studied here, has been written by M Kolb.

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mass $\bar{s} = \Sigma s^2 / \Sigma s$(the sums are over all the clusters), the mass of the largest cluster s_{max}, the average number n of clusters that merge together per move and the average shortest distance λ between two neighbouring clusters (asymptotically λ and n are related through $\lambda \propto n^{-1/2}$). The 'time' t is increased by N^{-1} always when a cluster is picked—independent of whether it is moved or not (for $\alpha = -\infty$ this definition of time is not physically meaningful as in reality one has to wait infinitely long between any two moves).

Relevant to colloidal aggregation are negative values of α, i.e. when smaller clusters move faster than larger ones. In this letter we will consider two representative values, $\alpha = -2$ and $\alpha = -\infty$. In figure 1 we show how n^{-1}, the number of moves needed for one cluster merging, changes with time for different values of α and ρ_0. Clearly in all cases three regimes can be distinguished: for small times (regime I) the average shortest distance λ between clusters increases and so does n^{-1}; this is the flocculation regime where each cluster is fractal with a fractal dimension $D \simeq 1.43$ (in $d = 2$). Then n^{-1} reaches a maximum at t_1 and from there on clusters get closer to each other and n^{-1} decreases. In this regime II (the 'compactification regime') the individual clusters will lose their fractal character since their density cannot decrease beyond ρ_0 when they become larger; every cluster feels the presence of the neighbours. This goes on until n^{-1} reaches a minimum at a time t_2. At this point the finite size of the lattice is felt: one cluster spans the system from side to side (gelation). From there on (regime III) all the other clusters will move until they finally merge into the spanning cluster. The clusters close to the spanning cluster (which for $\alpha < 0$ is practically immobile) aggregate quickly; the ones further away will need more time. So in this regime n^{-1} again will increase with time. After having described the different regimes of aggregation qualitatively in this way we will devote the rest of this letter to analysing in more detail what happens at t_1 and t_2.

The average shortest distance λ between two clusters is given by the difference of the distance r between the centres of the clusters and their linear size R. r is given by $r = LN^{-1/d}$, where the average number of clusters N can be expressed as $N = \rho_0 L^d / \bar{s}$. On the other hand one has asymptotically for fractal clusters $R = c\bar{s}^{1/D}$ where c is a proportionality constant. This gives

$$\lambda = r - R = \rho_0^{-1/d} \bar{s}^{1/d} - c\bar{s}^{1/D}. \tag{1}$$

As long as $\lambda > R$, i.e. $\rho_0 < \bar{s}^{(D-d)/D}$ one is in regime I. Since $\bar{s}$ grows monotonically with time and $D < d$ the distance λ of equation (1) continually decreases. The time t_1 is given in figure 1 by the maximum of n^{-1}, i.e. when the two terms in equation (1) are of the same order. So at t_1

$$y = \rho_0 \bar{s}^{(d-D)/D} \propto (R/r)^d \tag{2}$$

is of order unity. y will be used as a scaling variable that distinguishes flocculation (regime I) where $y \ll 1$ from the compactification (regime II) where $y \gg 1$. For times larger than t_1, in regime II, a new phenomenon occurs: since the distance between the clusters cannot become negative the two terms of equation (1) must increase in the same way. This is only possible if $D = d$. This argument tells us that after time t_1 the clusters will no longer be fractal, but dense.

Let us now try to numerically verify the above statements. If we assume that the location of t_1 is defined through $\rho_0 \propto \bar{s}^{-z}$, we find $z \simeq 0.43$ which is in fair agreement with our prediction $z = (d - D)/D$. One consequence of y in equation (2) being a scaling variable is that the maximum of n^{-1} occurs for the same values of R/r

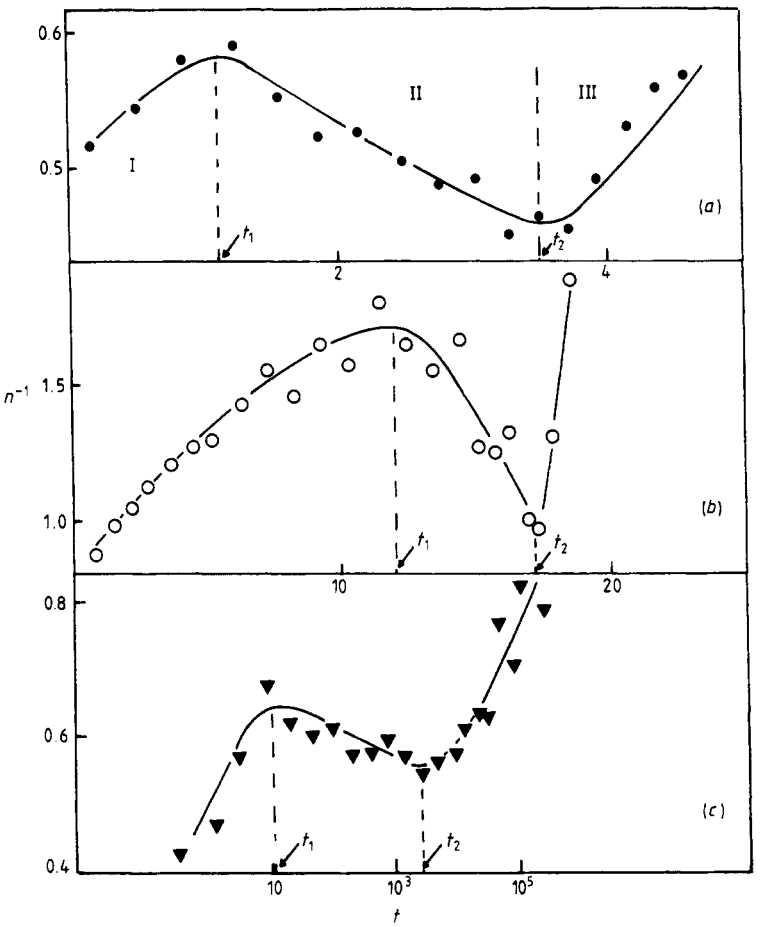

Figure 1. n^{-1} as a function of time t for (*a*) $\rho_0 = 0.5102$, $\alpha = -\infty$, (*b*) $\rho_0 = 0.3333$, $\alpha = -\infty$ and (*c*) $\rho_0 = 0.5102$, $\alpha = -2$. The scale of t in (*c*) is logarithmic. The linear size of the system is $L = 200$ and the data were obtained from averaging over 20 independent samples.

independent of the initial density ρ_0. We have determined $\lambda/r = 1 + cR/r$ ($c' =$ constant) to be $\lambda/r = 0.026$, 0.029 and 0.113 for $\rho_0 = 0.25$, 0.33 and 0.51 all for $\alpha = -2$. The agreement between $\rho_0 = 0.25$ and $\rho_0 = 0.33$ is good. However for 0.51 the scaling regime seems to be too small. In the regimes I and II we suggest that the y given in equation (2) is also a scaling variable for the cluster mass distribution $n_s(t, \rho_0)$ which is defined as the average number of clusters of mass s found per site:

$$n_s = \bar{s}^{-2} f(x, y) \qquad x = s/\bar{s}. \tag{3}$$

Finally we want to discuss the gelation transition at t_2 (where one cluster spans the system). Because of the monodispersity in the cluster mass distribution [8] we expect t_2 to be given by the time when the typical linear cluster size becomes of the order of the system size, i.e.

$$L \propto \bar{s}^{1/d} \tag{4}$$

where the exponent $1/d$ stems from the fact that the clusters are supposed to have become compact in regime II. In figure 2 we show that t_2, which is defined by the

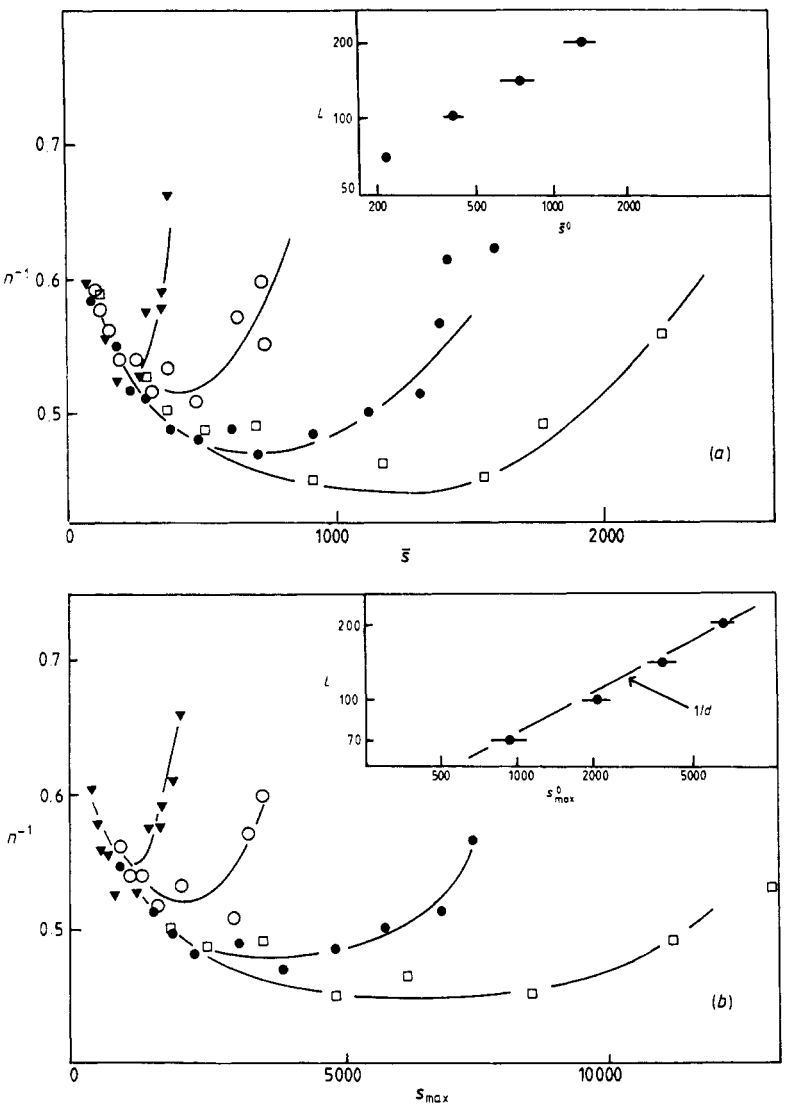

Figure 2. n^{-1} as a function of (*a*) the average cluster mass $\bar{s}$ excluding the largest cluster and (*b*) the mass s_{max} of the largest cluster alone for $\alpha = -\infty$, $\rho_0 = 0.5102$ and for different system sizes L. The lines are drawn to guide the eye. The minima $\bar{s}^0$ and s^0_{max} of each curve are plotted in the inset, double logarithmically against L. The slope lies between 1.6 and 2.0 for (*a*) and between 1.7 and 2.1 for (*b*). Values of L are 70 (▼), 100 (○), 140 (●) and 200 (□).

minimum of n^{-1}, strongly depends on L. In the inset of figure 2 we try to determine the exponent governing this relation and find a value consistent with equation (4). A precise determination of the exponent, however, is not easy because the minima of figure 2 are quite shallow and the statistical fluctuations are quite strong. The relation (4) confirms our previous finding [9] that for the infinite system the gel time is infinite. Evidence that the aggregation process in regime III behaves differently from regimes I and II can be seen when plotting the cluster mass distribution. In figure 3 $f(x, y)$

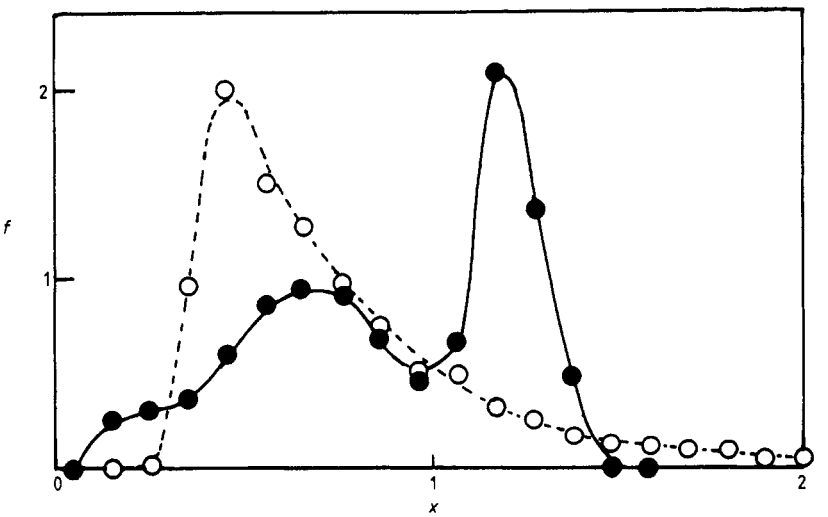

Figure 3. The scaling function $f(x, y)$ defined in equation (3) is plotted as a function of $x = s/\bar{s}$ for $\rho_0 = 0.3333$, $\alpha = -\infty$ and $L = 200$ at a time $t < t_1$ (flocculation) where $y \ll 1$ (○) ($\bar{s} = 74$) and at a time $t > t_2$ (past the gel point) (●) ($\bar{s} = 5555$). In the flocculation regime $f(x, y)$ is monodisperse (bell shaped) and past the gel point of the finite system $f(x, y)$ develops a second peak.

defined in equation (3) is plotted as a function of x for $t < t_1$ and for $t > t_2$. In the latter case a second peak develops for large values of $x = s/\bar{s}$.

Concluding, we found that at finite initial densities ρ_0 and finite system sizes L clustering of clusters goes through three regimes separated by two crossover times t_1 and t_2 with t_1 given by $\rho_0 \propto \bar{s}^{(D-d)/D}$ and t_2 by $L \propto \bar{s}^{-1/d}$. In particular this means that after t_1 clusters become compact and that the gel time t_2 goes to infinity with L.

The computations have been performed at the CIRCE in Orsay, France.

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