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Size distribution of clusters in irreversible kinetic aggregation

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Abstract. The size distribution of clusters is derived analytically, at a given time, in a process of irreversible kinetic aggregation of diffusive clusters, which starts from a collection of a great number of individual particles. A general reduced shape is given in the scaling regime, where gelation does not occur. The time evolution is derived by use of Smoluchowski's equation. Then a scaling reasoning allows us to find the exponents in real cases and a quantitative comparison is made with numerical simulations.

1. Introduction

There have been many attempts to understand theoretically the mechanism of kinetic aggregation of diffusive particles. Several simple kinetic models have been recently introduced on which numerical simulation as well as analytical calculations have been performed. The diffusion limited aggregation (DLA) model (Witten and Sander 1981, Meakin 1983a) considers single Brownian particles sticking one by one on a single immobile growing cluster. The resulting cluster has a specific fractal structure. In the alternative clustering of clusters (Cl Cl) model (Meakin 1983b, Kolb *et al* 1983), clusters of particles as well as single particles are allowed to diffuse together and the growing mechanism results from the sticking of any kind of pair of clusters when they come in contact. It is found that the resulting clusters are much more stringy than in DLA, and this difference is even more pronounced when the space dimension increases (Jullien *et al* 1984). This model seems better adapted to describe several physical situations, such as flocculation of aerosols, coagulation of smoke particles.... Another advantage of the model is that the time enters naturally. Up to now most of the studies on Cl Cl were concerned with the geometrical aspects of the aggregates. It has been noticed that an important characteristic of the model is the existence of a given shape for the size distribution of the clusters (Botet *et al* 1984a). There is a need to study analytically the size distribution of the clusters, as well as its time evolution, in such a model. Up to now, most of the analytical calculations of size distribution and time evolution in kinetic aggregation processes were mostly concerned with the gelation phenomenon (see e.g. Hendriks *et al* 1983 and references therein). The main purpose of this paper is to extend these previous studies by focusing, instead, on the more general simple case, where gelation does not occur. In that case we will show that some specific scaling holds. Assuming some kinetic prescription, given by the knowledge, *a priori*, of a scaling of the kinetic kernels, K_{ij}'s, the size distribution of clusters is analytically derived at a given step of the aggregation process. Using Smoluchowski's kinetic equation, the general time evolution of the size distribution is derived. Then

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a scaling reasoning allows us to make precise the scaling behaviour of the K_{ij}'s in real cases and permits a quantitative comparison with numerical simulations on Cl Cl. This paper is organised as follows: in § 2, a simple derivation of the most probable size distribution is presented and applied to the case where $K_{\lambda i,\lambda j} \sim \lambda^{2\omega} K_{i,j}$ for large numbers i and j of particles in the clusters. In § 3, a more powerful mathematical treatment is presented: the averaged size distribution is calculated exactly and compared with the asymptotic results of § 2. In § 4 the time evolution is derived. Then in § 5, application to numerical simulations on Cl Cl is considered. A conclusion is given in § 6.

2. Simple derivation of the most probable distribution

Let us consider, generally, a system of N particles distributed into N_c clusters. We denote by n_k the number of clusters containing k particles. For given N and N_c, we consider the number of ways $\Omega\{n_1, n_2, \ldots, n_N\}$ of having a given configuration $\{n_1, n_2, \ldots, n_N\}$ of clusters. This number is given by a multinomial distribution (Stockmayer 1943):

$$\Omega\{n_1, n_2, \ldots, n_N\} = N! \prod_k (1/n_k!)(w_k/k!) \tag{1}$$

where w_k is the number of ways to construct a cluster of k particles from k individual particles. This implies that the initial size distribution is just N individual particles, which is the ordinary prescription. Spouge (1983a) has given a general relation relating these w_k's with the kinetic kernels $a_{i,j}$, which is valid for times far from the gelation time (McLeod 1962):

$$2(k-1)w_k = \sum_{i=1}^{k-1} \binom{k}{i} a_{i,k-i} w_i w_{k-i}, \qquad w_1 = 1. \tag{2}$$

The dimensionless numbers $a_{i,j}$ contain the i, j dependence of the Smoluchowski coefficients K_{ij} (Smoluchowski 1916) and are defined as usual such that the probability of sticking for two clusters of size i and j is proportional to $a_{i,j}\, n_i\, n_j$. Consequently they contain all the kinetic prescriptions of the aggregation process. In the following we will suupose that they verify the scaling relation

$$a_{\lambda i,\lambda j} = \lambda^{2\omega} a_{i,j}. \tag{S}$$

In this first simple approach, we interpret the relation (1) as giving the number of configurations of N_c particles obeying quantum Maxwell–Boltzmann statistics.

In this equivalence, the number of particles in a cluster corresponds to the energy of a single quantum particle so that

$$\sum_{k=1}^{N} n_k = N_c \tag{3a}$$

(the total number of quantum particles) and

$$\sum_{k=1}^{N} k n_k = N \tag{3b}$$

(the total energy of the quantum system) are the usual constraints of the microcanonical

ensemble. Using this correspondence, it is well known that the most probable configuration, denoted $\{n_1^*, \ldots, n_N^*\}$, which corresponds to the maximum of Ω, is given by

$$n_k^* = (w_k/k!)\, e^{\alpha - \beta k} \tag{4}$$

for large values of N_c. In this last expression, $w_k/k!$ corresponds to the degeneracy of the level of energy k, i.e. here, the number of ways of constructing a cluster of size k from k indistinguishable individual particles, and α and β are two Lagrange multipliers to be determined by the constraints (3*a*, *b*). So, given the $a_{i,j}$ it is necessary to determine the w_k's, to find the most probable distribution n_k^* for given N and N_c.

Let us restrict ourselves to the case where the $a_{i,k}$'s verify the relation (S). Physically we have to restrict the values of ω to the range $\omega < 1$, since the averaged number of active sites in a cluster cannot grow faster than its size (Ziff and Stell 1980a) and this corresponds mathematically to the fact that no global solution exists if $\omega > 1$ (Leyvraz and Tschudi 1981, 1982).

Assuming (S) and trying a power law asymptotic behaviour for the w_k's in (2), it can be easily shown that

$$\frac{w_k}{k!} \underset{k\to\infty}{\sim} \left(\frac{2a_{1,1}}{\int_0^1 a(1/x, 1/(1-x))\, dx}\right) k^{-2\omega} \tag{5}$$

as long as the integral has a finite value.

For example, if $a_{i,j} = \frac{1}{2}(i^\mu j^\nu + i^\nu j^\mu)$, we find

$$w_k/k! \sim 2B^{-1}(1-\mu, 1-\nu) k^{-(\mu+\nu)}$$

which vanishes, at this order, for $\mu = 1$ or $\nu = 1$. This last result is very closely related to a derivation of Ernst *et al* (1984).

However for $a_{i,j} = ij$, the w_k's have been exactly derived (Spouge 1983a):

$$w_k/k! = k^{k-2}/k! \sim (2\pi)^{-1/2} k^{-5/2}\, e^k. \tag{6}$$

Note that the exponential term has no physical interest here since any solution of (2) is defined apart from an e^{ak} factor. At first sight, the exponent $-\frac{5}{2}$ is rather strange since it does not correspond to the analytical continuation of -2ω when $\omega \to 1$. This apparent difficulty can be easily understood if we observe that for $\omega \to 1^-$ the coefficient for $k^{-2\omega}$ vanishes: $2\Gamma(2-2\omega)/\Gamma^2(1-\omega) \sim 2(1-\omega) \to 0$ when $\omega \to 1^-$. Thus, for $a_{i,j} = ij$ the behaviour of the w_k's is given by the following term in the expansion of the $w_k/k!$ for large k. We will see, in § 3, how a more powerful mathematical treatment allows us to recover this result.

Once the asymptotic behaviour of w_k is known, the expression of n_k can be derived if the α and β Lagrange multipliers appearing in (4) are determined. The two conditions (3*a*, *b*) can be written as

$$e^\alpha = AN \frac{1}{\sum_{k=1}^N k^{1-2\omega}\, e^{-\beta k}}, \qquad \frac{N}{N_c} = \frac{\sum_{k=1}^N k^{1-2\omega}\, e^{-\beta k}}{\sum_{k=1}^N k^{-2\omega}\, e^{-\beta k}} \equiv \phi_N(\beta),$$

where

$$A = \frac{\int_0^1 a(1/x, 1/(1-x))\, dx}{2a_{1,1}}.$$

The last relation determines β if N and N_c are given. It can be easily shown that $\phi_N(\beta)$ is a monotonic decreasing function of β, going from N to 1 when β goes from

$-\infty$ to $+\infty$. Thus, in a real physical clustering process, for given N, β decreases when N_c, the number of clusters, decreases from N to 1. It is of physical interest to know if β can become negative, since, in that case, there is a finite probability for a particle to belong to a 'big' cluster. This depends drastically on the behaviour of $\phi_N(0)$, for large N, which is

$$\phi_N(0) \sim (1-2\omega)N/(2-2\omega) \qquad \text{for } \omega < \tfrac{1}{2},$$

$$\phi_N(0) \sim [(2-2\omega)\zeta(2\omega)]^{-1} N^{2-2\omega} \qquad \text{for } \omega > \tfrac{1}{2},$$

$$\phi_N(0) \sim N/\log N \qquad \text{for } \omega = \tfrac{1}{2}.$$

Thus, physically, the behaviour of the most probable size-distribution is completely different if ω is smaller or greater than $\frac{1}{2}$ (see figure 1). For $\omega > \frac{1}{2}$, β becomes negative when there is still a large number (diverging with N) of clusters; more precisely for

$$N_c = N_c^* \sim (2-2\omega)\zeta(2\omega)N^{2\omega-1}.$$

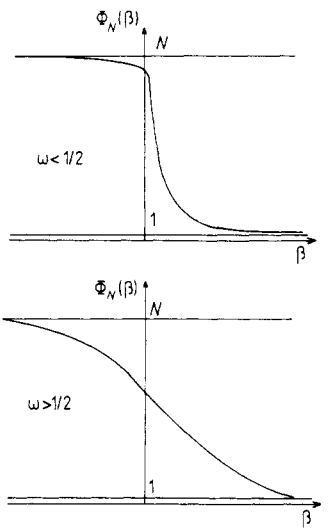

Figure 1. Sketch of the shape of the function $\Phi_N(\beta)$ in the two cases $\omega < \frac{1}{2}$, $\frac{1}{2} < \omega < 1$.

At a given step of the aggregation process, when the number of clusters becomes smaller than N_c^*, the size distribution's tail changes from decreasing into increasing exponential behaviour. This is the signature of the gelation process in the case of finite number of particles (see figure 2) and gives an alternative way to study this phenomenon in real cases. Nevertheless, in that case, the location of the intersection of $\phi_N(\beta)$ with N/N_c is of non-trivial analytical nature, even if its qualitative general behaviour can be easily found as shown in figure 1.

On the contrary, this phenomenon does not occur if $\omega < \frac{1}{2}$, which precisely the case that we will mostly consider in this paper. In that case, we have, asymptotically,

$$\phi_N(\beta) \sim (1-2\omega)/\beta \qquad \text{when } N \to \infty, \beta \to 0.$$

This leads immediately to the fact that there exists a general scaling relation for large

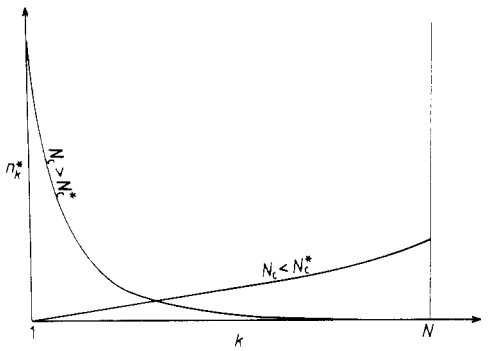

Figure 2. Sketch of the shape of the size distribution in the case $\frac{1}{2} > \omega > 1$.

N, between the reduced distribution Nn_k^*/N_c^2 and a reduced number of particles $k/\bar{k} = N_c k/N$,

$$Nn_k^*/N_c^2 \sim f_\omega(N_c k/N)$$

where

$$f_\omega(x) = \frac{(1-2\omega)^{1-2\omega}}{\Gamma(1-2\omega)} x^{-2\omega} \, e^{-(1-2\omega)x} \tag{7}$$

is a reduced function, normalised at $\int_0^\infty f_\omega(x)\,dx = 1$, independent of N and of N_c and, consequently, independent of the time. Finally, let us note that this function (valid for x not too small) is entirely determined by the scaling relation (S) and that the knowledge of the whole analytical form of $a_{i,j}$ is not necessary.

Let us note that for ω tending to $-\infty$, i.e. for $K_{ij} = 0$ everywhere, except for the smallest possible i and j, one recovers the exact trivial solution:

$$\lim_{\omega \to -\infty} f_\omega(x) = \delta(x-1)$$

where $\delta(x)$ is the Dirac delta function. In that case only clusters of the same size are allowed to stick together, as in the hierarchical model recently introduced by Botet *et al* (1984a) which appears here as the limit of ClCl when only the smallest clusters can move.

Let us summarise now the results of this section.

For $\omega < 0$: the size distribution function exhibits a maximum at $k = [2\omega/(2\omega-1)]N/N_c$.

For $0 < \omega < \frac{1}{2}$: the size distribution is always decreasing.

In both the above cases, i.e. for $\omega < \frac{1}{2}$, there exists a general scaling relation so that at different N_c, i.e. at different steps of the aggregation process, the system remains identical to itself after a given renormalisation of the variables n_k and k. An example of such a behaviour is precisely given by the clustering of clusters process in its scaling regime as described in Kolb *et al* (1983) and Botet *et al* (1984a).

For $\omega > \frac{1}{2}$: the shape of the size distribution function inverts at a finite time, which is the signature of the gelation phenomenon. There are, in general, no such trivial global scaling laws as those considered here and the physics before and after gelation must be treated differently.

3. Exact derivation of the averaged distribution

The main approximation of the previous treatment lies in the derivation of (4) by maximising the weight Ω of the configuration. This implies that the number of particles as well as the number of clusters are large, but it is rather difficult to estimate the corrective terms. The aim of this section is to present a more rigorous derivation of such a quantity as the averaged distribution defined by

$$\bar{n}_k = \sum_{\pi(N,N_c)} n_k \Omega\{n_1, n_2, \ldots, n_N\} \Big/ \sum_{\pi(N,N_c)} \Omega\{n_1, n_2, \ldots, n_N\} \tag{8}$$

where $\Omega\{n_1, n_2, \ldots, n_N\}$ is given by (1) and where $\pi(N, N_c)$ designates the ensemble of configurations $\{n_1, n_2, \ldots, n_N\}$ verifying (3*a*, *b*). The starting point is a straightforward extension of a theorem of Fine (1959), which can be written as:

Theorem. If $A_l(x) = \Sigma_{n>0}\, a_l(n) x^n$ are formal polynomials, then

$$\prod_{l\geqslant 1} A_l(x^l y) = \sum_{N\geqslant 0} \sum_{N_c=0}^{N} x^N y^{N_c} \sum_{\pi(N,N_c)} \prod_{l\geqslant 1} a_l(n_l). \tag{9}$$

Note that here we avoid the problem of convergence of infinite series or products since we only deal with formal polynomials. Let us now introduce the partition function

$$Z(N, N_c; \boldsymbol{\beta}) = \sum_{\pi(N,N_c)} \Omega\{n_1, n_2, \ldots, n_N\} \exp\left(-\sum_l \beta_l n_l\right)$$

where $\boldsymbol{\beta} = \{\beta_1, \beta_2, \ldots, \beta_N\}$ is a sequence of real numbers, written here as a formal vector.

Starting from the expression of Ω, and using the extended theorem of Fine, the generating function for Z can be calculated as

$$\sum_{N\geqslant 0} \sum_{N_c=0}^{N} x^N y^{N_c} Z(N, N_c; \boldsymbol{\beta}) = \exp\left(y \sum_{l\geqslant 1} x^l \frac{w_l}{l!} e^{-\beta_l}\right)$$

and, in a similar way, one has

$$\sum_{N\geqslant 0} \sum_{N_c=0}^{N} x^N y^{N_c} \frac{\partial Z}{\partial \beta_k}(N, N_c; \mathbf{0}) = -y x^k \frac{w_k}{k!} \exp\left(y \sum_{l\geqslant 1} x^l \frac{w_l}{l!}\right).$$

It appears that, due to the multinomial character of the distribution Ω, the generating function of $\partial Z/\partial \beta_k$, at $\boldsymbol{\beta} = \mathbf{0}$, is proportional, up to a monomial $x^k y$, to the generating function of Z, and consequently $(\partial Z/\partial \beta_k)(N, N_c; \mathbf{0})$ is proportional to $Z(n-k, N_c - 1, \mathbf{0})$. This interesting peculiar feature allows us to write

$$n_k = (w_k/k!) Z(N-k, N_c - 1)/Z(N, N_c),$$

$$\sum_{n\geqslant 0} x^n Z(N_c + n, N_c) = \frac{1}{N_c!}\left(\sum_{l\geqslant 0} x^l \frac{w_{l+1}}{(l+1)!}\right)^{N_c}, \tag{10}$$

since

$$n_k = -(\partial \log Z(N, N_c; \boldsymbol{\beta})/\partial \beta_k)_{\boldsymbol{\beta}=\mathbf{0}}.$$

The set of relations (10) appears as a very useful tool for both analytical and numerical studies. For numerical studies, it is more convenient to rewrite the second relation of

(10) in the recurrence form

$$Z(N, N_c) = \frac{1}{N_c} \sum_{k=1}^{N-N_c+1} \frac{w_k}{k!} Z(N-k, N_c-1) \tag{11}$$

the meaning of which is just a renormalisation of the total number of clusters. An example of application is given in figure 3, where n_k has been calculated exactly by use of the recursion relations, (2) for the w_k's, and (11) for the $Z(N, N_c)$, for $N = 40$ and $\omega = -1$, and plotted in the reduced form (7). One can compare, on this plot, the shape of the most probable distribution as derived approximately in § 2 and the shapes of the averaged distribution for a finite total number of particles.

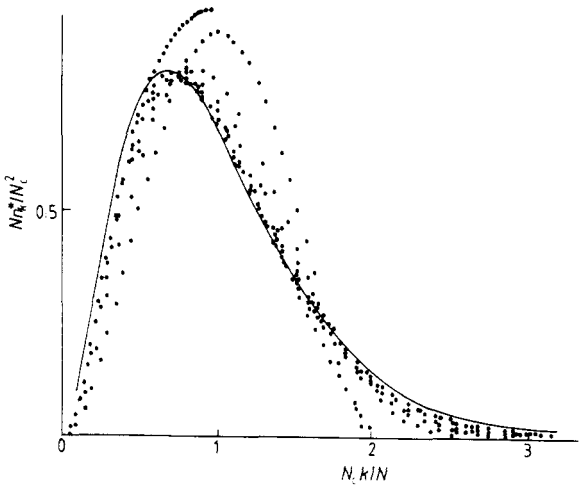

Figure 3. Comparison between the analytical approximation form of the most probable distribution (formula (7)) given by the full curve and the exact averaged distribution obtained numerically for $N = 40$ and $a_{i,j} = (ij)^{-1}$ given by the points.

We consider now the peculiar case $a_{i,j} = (ij)^{\omega}$. In the same spirit, let us develop now two remarks on the mathematical structure of the sequence $w_k/k!$, which with the help of generating functions allows us to recover the results of § 2. The auxiliary generating function of $w_{l+1}/(l+1)!$ denoted hereafter as $\phi(x)$, which appears on the right-hand side of the last relation of (10), is a solution of the following set of relations, which can be straightforwardly derived from (2):

$$\begin{aligned} &2\mathrm{d}\phi/\mathrm{d}x = (a_\phi)^2, \\ &a_\phi(x) = \sum_{l \geqslant 0} (l+1)^{\omega} \frac{w_{l+1}}{(l+1)!} x^l, \\ &\phi(0) = 1. \end{aligned} \tag{12}$$

As an example, it is very easy to derive the averaged distribution of clusters in the case $a_{i,j} \equiv 1$. In that case, one has $a_\phi \equiv \phi$ and the solution of (12) is just

$$\phi(x) = (1 - \tfrac{1}{2}x)^{-1}$$

which, inserted in (10), gives

$$n_k^* = \frac{(N-N_c)!(N-k-1)!}{(N-1)!(N-N_c-k+1)!} N_c(N_c-1).$$

This exact expression can be compared, for $1 \ll N_c \ll N$, with

$$n_k \sim (N_c^2/N)\exp(-N_c k/N)$$

given by (7).

The second remark is that the recurrence relation (2) can be rewritten as

$$\tfrac{1}{2}\left(\sum_{k\geqslant 1} k^{\omega}\frac{w_k}{k!}e^{kx}\right)^2 = \sum_{k\geqslant 1} k\frac{w_k}{k!}e^{kx} - \sum_{k\geqslant 1}\frac{w_k}{k!}e^{kx}$$

by introducing now the generating functions ϕ, $d\phi/dx$ and a_ϕ in the variable e^x to take the same notations as Hendriks *et al* (1983). These authors, in their appendix A, make the connection between the non-analytic singularities of generating functions of the form $\Sigma_{k\geqslant 1} c_k e^{kx}$ near $x=0^-$ and the asymptotic behaviour of the c_k's when k becomes large. Let us introduce the following notations: (i) $(-\alpha)$ means a term of the form $c_\alpha x^{-\alpha}$, where c_α is a real coefficient, and x the variable considered; (ii) $(-\alpha)^*$ has the same meaning, but with $c_\alpha \neq 0$.

If we consider $w_k/k! = \Sigma_m (-\alpha_m)^*$, where α_m is an increasing sequence of real numbers (all different), we get, using appendix A of Hendriks *et al* (1983),

$$\left\{\sum_m (\alpha_m-\omega-1)^* + (0) + (1) + \ldots\right\}^2 = \sum_m (\alpha_m - 2)^* + \sum_m (\alpha_m - 1)^* + (0) + (1) + \ldots,$$

$$\alpha_m - \omega - 1 \notin N, \qquad \alpha_m - 1 \notin N. \tag{13}$$

The last two conditions are needed since the explicit form taken for $w_k/k!$ forbids logarithmic terms (if that was not the case, the log term on the left-hand side of (13) would induce a $\log^2$ term which cannot be cancelled; a log term on the right-hand side of (13) is forbidden because all the α_m's are different). Two cases must be considered according to the sign of $\alpha_0 - 2$; however, we will consider only the case $\alpha_0 - 2 < 0$ since it yields to the condition $\omega < 1$ as will be seen. If $\alpha_0 - 2 < 0$, when x approaches 0 by negative values, $(\alpha_0 - 2)^*$ is the dominant diverging term of the right-hand side of (13), and it must be cancelled by the dominant diverging term of the left-hand side. That is

$$(\tfrac{1}{2}\alpha_0 - 1)^* = (\alpha_0 - \omega - 1)^*.$$

This relation reads

$$\alpha_0 = 2\omega.$$

Then the equality of the coefficients of these dominant terms gives

$$(-\alpha_0)^* = 2[\Gamma(2-2\omega)/\Gamma^2(1-\omega)]k^{-2\omega}$$

which is another derivation of the formula (5), in this particular case. Meanwhile, this method is much more powerful than the elementary one described in § 2 and we can derive the following general expansion for the $w_k/k!$ (but it is rather tedious work):

$$\frac{w_k}{k!} = 2\frac{\Gamma(2-2\omega)}{\Gamma^2(1-\omega)}k^{-2\omega} + \sum_{l\geqslant 1}(-2\omega - l) + \sum_{l\geqslant 1}(-\omega - l - \tfrac{1}{2}) \qquad \text{for } \omega < 1.$$

Let us note that, for $\omega = 1$, this expression gives, at first order, $w_k/k! \sim (-\frac{5}{2})$ which is the correct result (formula (6)), so that this last derivation of the w_k's is valid for all $\omega \leqslant 1$ and the apparent paradox noted in § 2 is explained. It is interesting to note that, since now we know the singularities of the generating function of $w_k/k!$, we can derive from (10) the asymptotic behaviour of $Z(N_c+n, N_c)$ for large n. This leads to the more precise formula (for $\omega < \frac{1}{2}$)

$$n_k \sim \frac{(1-2\omega)^{1-2\omega}}{\Gamma(1-2\omega)} \frac{N_c}{N-N_c}\left(\frac{N-N_c}{N_c k}\right)^{2\omega}\left(1-\frac{k}{N-N_c}\right)^{(1-2\omega)N_c}$$

which can be compared with the asymptotic formula (7).

Though this method is a more powerful tool to find general corrective terms of the $1/k$ expansion of such a quantity as $w_k/k!$, it is difficult to use it for complicated kernels $a_{i,j}$. This is related to the fact that corrective terms (and so, the transient physical terms) depend explicitly on the whole analytical structure of the $a_{i,j}$'s, contrary to the general dominant term (the steady-state physical one).

4. Evolution with time

The physical diffusion time can be introduced through Smoluchowski's equation (Smoluchowski 1916). This equation is usually written in terms of the concentrations $c_i = n_i/VN$ where V is the total volume of the system, so that c_i is the proportion of i-clusters by unit of volume. Using the n_i's it reads

$$NV\frac{dn_k}{dt} = \tfrac{1}{2}\sum_{\substack{i+j=k \\ i \neq k/2}} K_{i,j} n_i n_j - n_k \sum_{\substack{i=1 \\ i \neq k}}^{N-k} K_{i,k} n_i + K_{k/2,k/2} n_{k/2}(n_{k/2}-1)/2 - 2K_{k,k} n_k (n_k - 1)/2 \tag{14}$$

where we have considered two extra terms of importance for finite N: the third term exists only if k is even and the fourth only if $k < N/2$. This can be written in the more standard form

$$\frac{dn_k}{dt} = \frac{K}{NV}\left(\tfrac{1}{2}\sum_{i+j=k} a_{i,j} n_i n_j - n_k \sum_{i=1}^{N} a_{i,k} n_i - \tfrac{1}{2} a_{k/2,k/2} n_{k/2} + a_{k,k} n_k\right) \tag{15}$$

where $K_{i,j} = K a_{i,j}$. Fortunately we have not to solve exactly the diffusion–time-dependent equation (15) as a whole, because we know already the most probable size distribution of the n_k's in terms of N_c. We just need an equation for dN_c/dt, which can be exactly found by summing equation (15) for all k:

$$\frac{dN_c}{dt} = \frac{K}{NV}\left(-\tfrac{1}{2}\sum_{\substack{i=1 \\ j=1}}^{N} a_{i,j} n_i n_j + \sum_{i=1}^{N/2} a_{i,i} n_i\right). \tag{16}$$

Replacing n_i with the help of expression (7), we have

$$\sum_{i,j=1}^{N} a_{i,j} n_i n_j = 2a(N - N_c)$$

where $a = e^{\alpha}$ and

$$\sum_{i=1}^{N/2} a_{i,i} n_i = N \sum_{i=1}^{N/2} e^{-\beta i} \Big/ \sum_{i=1}^{N} i^{1-2\omega} e^{-\beta i}.$$

All these sums are well convergent (because $\beta > 0$) and we find

$$dN_c/dt \sim -\alpha_\omega (N - N_c)(N/N_c)^{2\omega - 2} + \beta_\omega (N/N_c)^{2\omega - 1}$$

giving a remarkably simple relation governing the decay of the number of clusters with respect to the diffusion time. The expressions for α_ω and β_ω are

$$\alpha_\omega = \frac{(1-2\omega)^{1-2\omega}}{\Gamma(1-2\omega)} A \frac{K}{V}, \qquad \beta_\omega = \frac{(1-2\omega)^{-2\omega}}{\Gamma(1-2\omega)} \frac{K}{V},$$

and A is the constant introduced after equation (5). The straightforward integration yields

$$N_c/N \sim [1 + \alpha_\omega (1-2\omega) t]^{-1/(1-2\omega)}.$$

The most important conclusion is that for $1 \ll N_c \ll N$ an interesting scaling occurs, namely

$$N_c/N \sim a_\omega t^{-1/(1-2\omega)} \qquad \text{for } \omega < \tfrac{1}{2}$$

where

$$a_\omega = [(1-2\omega)\alpha_\omega]^{-1/(1-2\omega)}.$$

The same treatment can be performed at the gelation point $\omega = \frac{1}{2}$. One finds

$$N_c/N = \exp[-(2Kt/v)^{1/2}].$$

If this is reported into (7), one finds the scaling relation

$$n_k \sim k^{-2} \Phi(kt^{-1/(1-2\omega)})$$

which is similar, in spirit, to conjecture 2 of Leyvraz and Tschudi (1982); equation (28) of Lushinikov (1973), equation (3) of Ernst *et al* (1982), with $\tau = 2$ and $\sigma = 2\omega - 1$ (Ernst *et al*'s notations) which satisfies the scaling relation $\sigma + \tau = 2\omega + 1$ (equation (13*b*) of Ernst *et al* (1982)).

This general result is physically important since it tells us that only one exponent is needed, here the exponent ω of the Smoluchowski coefficients $K_{\lambda i, \lambda j} \sim \lambda^{2\omega} K_{i,j}$, to find all the other exponents governing the time evolution of the system. This exponent depends now on the type of diffusion considered, and does not depend on the whole analytical form of the $K_{i,j}$'s provided that the scaling relation (S) holds.

5. Comparison with numerical simulations

To compare the preceding results with some specific numerical simulations it is necessary to relate the ij dependence of the K_{ij}, i.e. the exponent ω, to the precise kinetic prescriptions of the simulation. Consider, as in Kolb *et al* (1983), a system of kinetically growing clusters, in which each cluster of size k, before sticking another cluster, diffuses randomly in space of dimension d, along a trajectory of dimension d_w ($d_w = 2$ for the random walk) with a velocity v_k depending on its size k: $v_k \sim k^\alpha$ ($\alpha = -\frac{1}{2}$ for a perfect gas). In their motion the clusters stay rigid. Let us show how, under the essential assumption that some general scaling holds, in both space and time, the exponent ω can be expressed in terms of the other exponents, which are the kinetic exponents d_w and α and the geometrical exponents d and D, where D is the fractal dimension of the clusters, as measured in the simulations.

Using the definition of d_w and α, the time t necessary for a cluster of size k having a walk of length l is given by

$$t \sim l^{d_w} k^{-\alpha}.$$

In terms of a characteristic radius $r_k \sim k^{1/D}$ of the cluster, this becomes

$$t \sim l^{d_w} r_k^{-D\alpha}.$$

Let us now perform a change of length scale in the whole system, such that each length is rescaled by a factor b:

$$l = bl'.$$

The corresponding time rescaling, to let the system be invariant, must be

$$t \sim b^{d_w - D\alpha} t'.$$

We assume now that the time evolution can be described by a Smoluchowski equation with kinetic coefficient $K_{i,j}$. This equation (written correctly in terms of concentrations) being scale invariant, the $K_{i,j}$, which have the dimension of a volume divided by a time, must be rescaled as

$$K_{i,j} \sim b^{d - d_w + D\alpha} K'_{i',j'}.$$

We conclude that the general scaling relation

$$K_{\lambda i, \lambda j} \sim \lambda^{\alpha + (d - d_w)/D} K_{i,j}$$

is verified in this prescription. This is exactly the scaling (S) with

$$2\omega = \alpha + (d - d_w)/D.$$

Let us recall that this relation holds only in the scaling regime; in particular, the condition $\omega < \frac{1}{2}$ implies

$$\alpha < \alpha_c = +1 - (d - d_w)/D.$$

Let us insist that this derivation of ω is only valid under the assumption that a global Smoluchowski equation holds to describe the kinetics of the system, which corresponds to some kind of mean-field-like hypothesis.

An exact analytical expression for the $K_{i,j}$'s can be performed in our case by a direct argument. We define a hitching radius R_h of a cluster by the following property: the probability is zero that the distance between the centres of two sticking clusters is less than $R_h(i) + R_h(j)$. This defines a sort of hard nucleus for a cluster.

Because of the self-similarity of the cluster, we have either

$$R_h(i) \sim i^{1/D} \qquad \text{or } R_h(i) \equiv 0.$$

In the last case, the cluster is called transparent. This is a notion closely related to an argument of Herrmann (1984) used to determine the upper critical dimensionality of the mole trap model.

If the motion of the clusters is a walk of fractal dimension d_w, the quantity $K_{i,j} n_i n_j$ which is proportional to the probability that a cluster of size i sticks a cluster of size j is such that

$$K_{i,j} n_i n_j \propto \sigma_{ij} \tilde{V}_{i,j} n_i n_j$$

where

$$\sigma_{ij} \propto (R_{h,i} + R_{h,j})^{d-d_w}$$

is a relative cross-section which, after the definition of R_h, is a compact volume of radius $R_{h,i} + R_{h,j}$ in a space of dimension $d - d_w$, and $\bar{V}_{i,j}$ is the mean relative velocity, which, due to the isotropy of the velocities, is given by

$$\bar{V}_{i,j} = (V_i^2 + V_j^2)^{1/2}.$$

We conclude that

$$K_{i,j} \propto (i^{1/D} + j^{1/D})^{d-d_w} (i^{2\alpha} + j^{2\alpha})^{1/2}$$

if $V_i \sim i^\alpha$.

We recover here the scaling relation

$$K_{\lambda i, \lambda j} = \lambda^{(d-d_w)/D+\alpha} K_{i,j}.$$

This kind of expression is well known in the Brownian ($d_w = 2$) case and for compact ($D = d$) clusters (see e.g. Lai *et al* (1971), Hidy *et al* (1970)).

When combining this result with the result of § 3 one obtains in the scaling regime

$$N_c / N \sim t^{-\gamma}$$

with

$$\gamma = (1-2\omega)^{-1} = D/[D(1-\alpha) - (d-d_w)] > 0.$$

This result has been directly found through a direct mean-field scaling reasoning (without using Smoluchowski's equation) and gives a correct understanding of the time evolution of simulations of ClCl (Kolb 1984). Here, we are more concerned with the shape of the size distribution. Let us report some quantitative comparison with ClCl in two dimensions, with various exponents. In the simulations, a random walk has been considered, so that $d_w = d = 2$ and thus $\omega = \frac{1}{2}\alpha$. In figure 4 we give the fit of the reduced size-distribution, as directly determined, at different times, in the simulation with the theoretical curve

$$f_\omega(x) = \frac{(1-2\omega)^{1-2\omega}}{\Gamma(1-2\omega)} x^{-2\omega} \, e^{-(1-2\omega)x}.$$

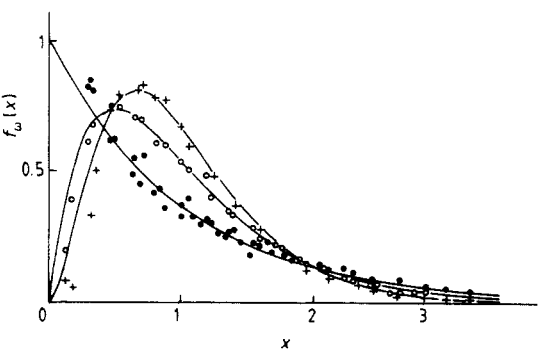

Figure 4. Comparison between the analytical reduced size-distribution (formula (7)) and the results of numerical simulation for $d = d_w = 2$ and $\alpha = 0, -1, -2$ with 1024 particles in a square box 128×128 (averaged over 20 trials). Full circles, open circles and crosses correspond to the simulation for $\alpha = 0, -1, -2$ respectively. The full curves correspond to the analytical formula (7) with $\omega = 0, -\frac{1}{2}, -1$.

In these fits there is only one adjustable parameter which is the normalisation constant for the numerical curves. We have conveniently rescaled the numerical curves so that they coincide with the theoretical curves for $x = 1$. One can see that the agreement is very good. In particular the location of the maximum, which is given here by

$$x_m = -2\omega/(1-2\omega) = -\alpha/(1-\alpha),$$

is correctly recovered: for $\alpha = -\frac{1}{2}$, $x_m = 0.5$, for $\alpha = -1$, $x_m = 0.66$. Furthermore, the curve for $\alpha = \omega = 0$ exhibits no maximum as is expected. However, one observes some discrepancies at low x in that case. This is due to the fact that the formula given for f_ω is not valid for low x. In that case, it must be replaced by a non-trivial function which depends on the analytical structure of the $K_{i,j}$'s (for example, for $K_{i,j} \sim (ij)^\omega$, it is easy to show that, for small x, $f_\omega(x) \sim e^{-\alpha x^\omega}$ which, for $\omega < 0$, decreases faster than any power of x as x tends to 0).

6. Conclusion

We have been able to derive the analytical form of the size distribution of clusters, and to make precise its time dependence, in a process of kinetic aggregation of diffusive clusters. All these calculations are valid in a scaling regime where all the quantities depend on length and time with power laws. In particular, all these results become wrong when gelation occurs. In that regime, we have been able to reproduce quantitatively the shape of the size distribution of clusters found in numerical simulations of clustering of Brownian clusters. Moreover, we have been able to relate the exponent defining the scaling of the kinetic kernels with the exponent involved in the numerical simulations. This implies that scaling occurs only if large clusters do not move too quickly. Quantitatively, the exponent α of the speed of the clusters ($v_i \sim i^\alpha$) must be smaller than a critical value α_c. For $\alpha < \alpha_c$, a general scaling holds: the whole distribution of clusters is self similar for different lengths and for different times and the fractal dimension of the cluster has a given value, while for $\alpha > \alpha_c$ the self similarity is broken: a big cluster starts to grow much more quickly than the others, with a different fractal exponent which is that of Witten and Sander (1981) as observed in the recent simulations of Meakin (1984), and studied in detail in Botet *et al* (1984b). This will be the subject of further works, both analytical and numerical, to study more carefully the gelation transition which occurs for $\alpha > \alpha_c$.

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Note added. In the whole paper, we have always emphasised that the existence, for $\omega < \frac{1}{2}$, of a reduced shape for the size distribution function, as well as a power law behaviour with time, occurs only under the condition $1 \ll N_c \ll N$, i.e. consequently, only for intermediate times $0 \ll t \ll \infty$. For $\omega < 0$, such behaviour perhaps persists up to $t \to \infty$. However, for $0 < \omega < \frac{1}{2}$, the asymptotic behaviour for $t \to \infty$ is certainly different, as shown recently by Leyvraz (1984). This is due, in that case, to the occurrence of gelation with an infinite gelation time. We acknowledge many discussions and advice from M Ernst, E Hendriks, F Leyvraz, J P Spouge and R M Ziff who helped us to clarify this point.

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