Gel, self-similarity and universality in the discrete Smoluchowski equation with finite mass

1992 J. Phys. A: Math. Gen. 25 3683

(http://iopscience.iop.org/0305-4470/25/13/018)

J. Phys. A: Math. Gen. 25 (1992) 3683–3700. Printed in the UK

Gel, self-similarity and universality in the discrete Smoluchowski equation with finite mass

Y Gabellini and J-L Meunier

Institut Non Linéaire de Nice†, Université de Nice-Sophia Antipolis, Parc Valrose, 06034 Nice Cedex, France

Received 11 September 1991, in final form 7 February 1992

Abstract. We approximately solve the Smoluchowski equation (discrete version), for gelling and non-gelling systems with finite mass and arbitrary initial conditions for various kernels (additive and multiplicative). We obtain that the approximate scaling form does not depend on the details of the kernel in contrast with already known results. Numerical simulations are presented which show that the predicted form is valid over a large range of the scaling variable n/s. The critical exponent related to the power law dependence of the distribution is shown to scale rapidly, even with low masses. This could clarify the recent difficulties of the standard theory with both experiments and numerical calculations.

1. Introduction

During recent years, much work has been done by various authors on the study of the Smoluchowski equation (SE), which may govern the irreversible aggregation of objects [1–10], whatever these objects are:

$$\dot{\mathbb{N}}(n,t) \equiv \frac{\mathrm{d}\mathbb{N}(n,t)}{\mathrm{d}t} = \sum_{i+j=n} \tfrac{1}{2}\mathbb{N}(i,t)K(i,j)\mathbb{N}(j,t) - \mathbb{N}(n,t)\sum_{i=1}^{\infty} K(n,i)\mathbb{N}(i,t) \tag{1.1}$$

where $\mathbb{N}(n,t)$ is the number of aggregates of size n at time t in the experiment. We are interested here in finite systems for which $\mathbb{N}(n,t) = 0$ for n greater than some $n_{\max}$, and $K(i,j)$ is, in general, a homogeneous function of its arguments of degree λ: $K(ai,aj) = a^{\lambda}K(i,j)$. In that case, the total mass

$$M = \sum_{n=1}^{\infty} n\mathbb{N}(n,t) \tag{1.2}$$

is conserved: $\dot{M} = 0$. This Smoluchowski equation has the peculiarity to be nonlinear and non-local and to exhibit quite different behaviour, according to the values of λ.

In general, the resolution scheme used is as follows. The continuous associated equation is constructed and then solved, somehow or other, in the high n limit [10].

† Unité Mixte de Recherche du CNRS, UMR 129.

0305-4470/92/133683+18$04.50

This resolution scheme gives some predictions for various experimental quantities such as the critical exponent τ, which describes the dependence of the distribution $\mathbb{N}$ or of its density N for high n values [9]:

$$N(n,t) \simeq n^{-\tau} \qquad N = \mathbb{N}/M \tag{1.3}$$

and suggests that the density presents a self-similar behaviour [8–10]

$$N_{ss}(n,t) \simeq \frac{1}{[s(t)]^{\theta}} \varphi\left(\frac{n}{s(t)}\right). \tag{1.4}$$

Let us notice that, within this scheme, the case of gelling systems ($\lambda \geqslant 1$) is not taken into account when the size of the system is finite.

1.1. The canonical cases

Up to now, three exact solutions of the problem are known: the Brownian case; and the Gel-0 and the Gel-1 cases, that we call standard or canonical. In these cases, the degree of homogeneity λ of the Smoluchowski kernels is respectively 0, 1 and 2, and these kernels have very different structures:

$$\begin{aligned} K(i,j) &= k \qquad \text{in the first case} \\ &= k\frac{i+j}{2} \qquad \text{in the second case (Gel-0)} \\ &= kij \qquad \text{in the third one (Gel-1)} \end{aligned} \tag{1.5}$$

with k a positive constant.

These problems can be solved by using the generating function—given later—and solving some partial differential equations [6, 11]. For the three cases, one finds an asymptotic self-similar solution, which has the same shape and can be described by three dynamical exponents which are in some way related

$$N_{ss}(n,t) = cs(t)^{-\theta}\left[\frac{s(t)}{n}\right]^{\tau} \exp\left[-\frac{n}{s(t)}\right] \tag{1.6}$$

where c is a normalization constant and $s(t)$ is the scaling parameter, somehow related to the mean size of the clusters (see further), which behaves as

$$\begin{aligned} s(t) &\propto t^{z} \qquad \text{for } \lambda < 1 \\ &\propto (t_c - t)^{z'} \qquad \text{for } \lambda > 1 \\ &\propto \mathrm{e}^{t} \qquad \text{for } \lambda = 1. \end{aligned} \tag{1.7}$$

The exponents θ, τ and z or z' have been calculated and are summarized in table 1.

Table 1. Values of the various exponents for the three standard examples.

	Brown	Gel-0	Gel-1
θ	2	2	2.5
τ	0	1.5	2.5
z	1	∞	—
z'	—	—	−2

1.2. The homogeneous kernels

Our purpose in this paper is to solve, at least approximately, two models with different structures with a continuous parameter λ, i.e. the additive model and the multiplicative one,

$$\begin{aligned} K(i,j) &= k(ij)^{\omega} \text{ with } \omega = \lambda/2 \qquad \text{(multiplicative case)} \\ &= k(i^{\lambda} + j^{\lambda})/2 \qquad \text{(additive case)} \end{aligned} \tag{1.8}$$

for a wide range of λ: $-1 \leqslant \lambda \leqslant 2$ for the multiplicative case and $-1 \leqslant \lambda \leqslant 1$ for the additive one. These models have been studied by various authors [2–10] and interpolate between the canonical examples. In particular Ernst and van Dongen [8–10], hereafter referred to as EvD, have studied the two models in the limits $n/s \to 0$ and $n/s \to \infty$, and found that in these limits the models present a different power law behaviour. As a matter of fact, the two models belong to two different universality classes in their classification. The multiplicative model belongs to class I ($0 < \lambda < 2$, $\mu > 0$) or III ($\mu < 0$), where μ is the exponent governing the small i/j limit of $K(i,j)$. For $\lambda > 0$, the exponent τ of the $n/s \to 0$ behaviour is predicted by these authors to be given by the following relation:

$$\tau = 1 + \lambda. \tag{1.9}$$

The additive model, for its part, belongs to class II ($\mu = 0$) and has been shown to exhibit different features. In particular, the τ exponent cannot be directly calculated from the continuous equation, but has been shown to obey some rigorous bounds which can be computed from [8].

The $n/s \to \infty$ exponent, τ', is found to be class independent and equal to λ [10]. On the other hand, in the case of gel for multiplicative models, the EvD analysis is developed for *constant flux* and gives the following result: $\tau = (3 + \lambda)/2$. For the τ and τ' exponents, the situation is summarized in figure 1 for $0 \leqslant \lambda \leqslant 2$. The hatched area represents the EvD bounds for the additive model $n/s \to 0$ exponent.

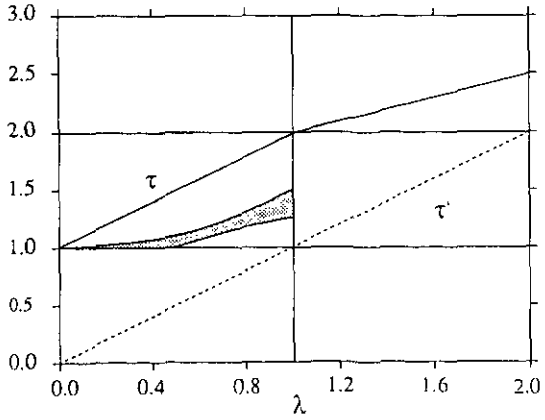

Figure 1. The τ and EvD [8–10] τ' exponents as a function of λ; the hatched area refers to the additive model.

However, the situation is still not clear from the numerical or experimental point of view [12–15]. Various authors have remarked that the scaling exponent τ, extracted from numerical calculations, presents some discrepancies with the predictions for both models. In particular, Kang *et al* [12] have shown that the τ exponent varies smoothly with time and does not agree with the predicted asymptotic behaviour in intermediate time. Moreover, Martin [13] has shown that the asymptotic predictions of Ernst and van Dongen were not completely in agreement with the experimental results on colloidal silica.

1.3. The resolution scheme

In this paper, we present a new approximate resolution scheme for the *discrete* Smoluchowski equation which is shown to lead to *universal* results for finite values of the ratio n/s for λ values less than one.

The techniques of the resolution are based first on the use of $G(x,t)$, the generating function of the distribution (discrete Laplace transform of N) defined as

$$G(x,t) = \sum_{n=1}^{\infty} N(n,t)\mathrm{e}^{nx} \qquad (x<0) \tag{1.10}$$

the pth derivative of which, with respect to x, taken at $x=0$, is denoted by $g_p(t) = G^{(p)}(0,t)$. Notice that the g_p are the moments of the distribution N:

$$g_p(t) = \sum_{n=1}^{\infty} n^p N(n,t) = \overline{n^p}. \tag{1.11}$$

The second technical point is to make use of a somewhat curious derivative that we called 'continuous' and which interpolates between the usual ones for sufficiently well behaving functions (see the appendix). These types of operators are known in mathematics, for example in distribution theory [18], but, to our knowledge, this is one of the first times that a physical application for these techniques has been found. See also [19] which develops a different but related operator.

The Laplace transform of the Smoluchowski equation leads to a partial (continuous) differential equation in G the exact solutions of which are only known in the three canonical cases.

The general equations will be approximately solved with the help of a specific form for the pth x derivative of G, $G^{(p)}(x,t)$ which interpolates between the exact solutions of the canonical models (Brown, Gel-0 and Gel-1) [11]:

$$G^{(p)}(x,t) = \frac{C}{[s(t)]^{\nu}} \frac{1}{[1-s(t)x]^{\beta}} \qquad s(t) \to +\infty \tag{1.12}$$

where C, ν and β are real parameters. The approximate resolution of the model equations, which is developed in sections 2 and 3, gives the value of the parameters.

This leads to the multiplicity distribution N, by performing an inverse discrete Laplace transform:

$$\lim_{s\gg 1} N(n,t) = \frac{1}{n^p} \frac{C}{s^{\nu+1}} \left(\frac{n}{s}\right)^{\beta-1} \mathrm{e}^{-(n/s)} \lim_{s\gg 1} \frac{1}{2i\pi} \int_{-i\pi n+n/s}^{i\pi n+n/s} \mathrm{d}u \, \frac{\mathrm{e}^u}{u^{\beta}}. \tag{1.13}$$

When $s \gg 1$ and $n/s \leqslant 1$ one obtains the self-similar solution for N:

$$N_{ss}(n,t) = \frac{C}{\Gamma(\beta)} \frac{1}{s^{\theta}} \left(\frac{n}{s}\right)^{-\tau^*} e^{-(n/s)} \tag{1.14}$$

where Γ is the gamma factorial function and

$$\theta = p + 1 + \nu \qquad \tau^* = p + 1 - \beta. \tag{1.15}$$

The initial conditions appear in the $s(t)$ function and depend on the first few moments of N. Notice that the inverse Laplace transform can only be performed if $\beta > 0$, so that the integral in formula (1.13) converges when $n \to \infty$.

1.4. The results

We obtain that the two models—additive and multiplicative—give roughly the same exponent for s/n for a given homogeneity degree λ between, say -1 and 1, an exponent which is different from the usual τ discussed earlier, and, in particular, violates the EVD bounds in the additive case.

This result is in good agreement with our numerical simulations (a Monte Carlo simulation of the irreversible aggregation process).

As it is essentially valid in the region where n is of the same order of magnitude as s, say $s/10 \leqslant n \leqslant s$, we think that our exponent must be discriminated from the EVD one which is valid in another part of the phase space ($0 \ll n \ll s$), and we will name it τ^* (see equations (1.14) and (1.15)).

Our feeling is that the universality we have found in this problem is perhaps more general and does not depend on the details of the Smoluchowski equation. We even guess that it does not depend on the equation itself, which can be considered more as an example of the phenomenon rather than as a fundamental equation.

In fact, the aggregation phenomenon provides some sort of dynamical renormalization group: the irreversible aggregation of clusters may be seen as formally equivalent to the spin block grouping in a real space renormalization process [16, 17] and it is not so surprising that some universality holds in this field, as long as the process is not close to its limits ($1 \ll s \ll M$).

Our paper is organized as follow: in section 2 we will study the multiplicative model, while section 3 is devoted to the additive one. In section 4 we discuss the validity range of the results and comment about some approximations. Numerical results will be presented in section 5 and, after some discussion, we will conclude in section 6. The continuous derivatives are presented in appendix.

2. The multiplicative model

In this section, we present our resolution of the problem for multiplicative model ($K(i,j) = k(ij)^{\omega}$, with $\omega = \lambda/2$) in the λ range between -1 and 2. In that case, the Smoluchowski equation, after rescaling of the time ($t \to Mkt$), reads:

$$\dot{N}(n,t) = \tfrac{1}{2} \sum_{i+j=n} N(i,t)N(j,t)(ij)^{\omega} - N(n,t)n^{\omega} \sum_{i=1}^{\infty} i^{\omega} N(i,t). \tag{2.1}$$

This leads to the following equation for the generating function (equation (1.10)) which, using equation (A.6) of the appendix, gives

$$\dot{G}(x,t) \equiv \frac{\mathrm{d}G(x,t)}{\mathrm{d}t} = \frac{\left[G^{(\omega)}(x,t)\right]^2}{2} - G^{(\omega)}(x,t)G^{(\omega)}(0,t) \qquad (2.2)$$

where $G^{(\omega)} = \partial_\omega G$ (continuous derivative in the x variable).

Now, we take the first x derivatives of equation (2.2):

$$\begin{aligned}
\dot{G}^{(1)}(x,t) &= G^{(\omega+1)}(x,t)\left[G^{\omega}(x,t) - G^{\omega}(0,t)\right] \\
\dot{G}^{(2)}(x,t) &= G^{(\omega+2)}(x,t)\left[G^{\omega}(x,t) - G^{\omega}(0,t)\right] + \left[G^{(\omega+1)}(x,t)\right]^2 \\
\dot{G}^{(3)}(x,t) &= G^{(\omega+3)}(x,t)\left[G^{\omega}(x,t) - G^{\omega}(0,t)\right] + 3G^{(\omega+1)}(x,t)G^{(\omega+2)}(x,t) \qquad (2.3) \\
\dot{G}^{(4)}(x,t) &= G^{(\omega+4)}(x,t)\left[G^{\omega}(x,t) - G^{\omega}(0,t)\right] \\
&\quad + 4G^{(\omega+1)}(x,t)G^{(\omega+3)}(x,t) + 3\left[G^{(\omega+2)}(x,t)\right]^2
\end{aligned}$$

which, at $x = 0$, give

$$\begin{aligned}
\dot{g}_0 &= -g_\omega^2/2 \\
\dot{g}_1 &= 0 \\
\dot{g}_2 &= g_{\omega+1}^2 \qquad (2.4) \\
\dot{g}_3 &= 3g_{\omega+1}g_{\omega+2} \\
\dot{g}_4 &= 4g_{\omega+1}g_{\omega+3} + 3g_{\omega+2}^2.
\end{aligned}$$

We now first concentrate our attention on the $\lambda \leqslant 0$ case.

2.1. $\lambda \leqslant 0$

As it has been previously announced in the introduction, we use the specific form for G:

$$G(x,t) = \frac{C}{s^\nu(1-sx)^\beta} \qquad (2.5)$$

and adjust the free parameters in order to fulfil relations (2.4). It is first easy to observe that mass conservation implies $C = 1/\beta$ and $\nu = 1$. Then, using formula (A.7) to calculate the successive derivatives of G (continuous or ordinary), we obtain that the three first relations of (2.4) are fulfilled for

$$\begin{aligned}
\beta &= \frac{1 - 2\lambda + \sqrt{1 - 4\lambda + 2\lambda^2}}{2} \\
s(t) &= (\gamma(t + t_0))^z \qquad (2.6) \\
\gamma &= \left[\frac{\Gamma(\omega+\beta)}{\Gamma(\beta)}\right]^2 \frac{1-\lambda}{2\beta} \qquad \text{and} \qquad z = \frac{1}{1-\lambda}.
\end{aligned}$$

The parameter t_0, which will also appear in all subsequent results for s in sections 2 and 3, is fixed by the initial conditions on the multiplicities $N(n,0)$.

The fourth relation is not satisfied, which means that the solution (2.5) is not exact, up to a third degree term. We will come back to this point later on. Now, using G and equations (1.14) and (1.15), one can recover the self-similar solution:

$$N_{ss}(n,t) = \frac{1}{s^2}\varphi\left(\frac{n}{s}\right)$$

with

$$\begin{aligned} \varphi(x) &= \frac{x^{-\tau^*}e^{-x}}{\Gamma(2-\tau^*)} \\ \tau^* &= 1-\beta = \frac{1+2\lambda-\sqrt{1-4\lambda+2\lambda^2}}{2}. \end{aligned} \tag{2.7}$$

Notice that in this case τ^* is negative and one recovers the bell-shaped distribution predicted by Kolb [7]. Moreover, one can remark that the dispersion $\sigma = (\overline{n^2}-\overline{n}^2)^{1/2}$ (see equation (1.11)) of the distribution is proportional to its mean value $\overline{n}$ and that the measurement of their ratio gives a direct measure for τ^*:

$$\frac{\sigma}{\overline{n}} = \sqrt{1-\tau^*} \tag{2.8}$$

2.2. $0 \leqslant \lambda \leqslant 1$

As one can observe from formula (2.6), the β coefficient is no longer real if λ is greater than $\simeq 0.3$ and the approximate solution we use loses its physical meaning; the self-similar solution when $\lambda \in [0,1]$ has thus to be calculated with the help of the first x derivative for G, in the set of equations (2.3). Taking into account the mass conservation, one obtains for $G^{(1)}$,

$$G^{(1)}(x,t) = \frac{1}{(1-sx)^{\beta}}. \tag{2.9}$$

Using the first, second and third moment of (2.4) one gets

$$\begin{aligned} \beta &= 2-\tfrac{3}{2}\lambda \\ s(t) &= (\gamma(t+t_0))^z \end{aligned} \tag{2.10}$$

with

$$\gamma = \left[\frac{\Gamma(\omega+\beta)}{\Gamma(\beta)}\right]^2 \frac{(1-\lambda)}{\beta} \qquad \text{and} \qquad z = \frac{1}{1-\lambda}. \tag{2.10}$$

The τ^* exponent of the theory is now

$$\tau^* = 2-\beta = \tfrac{3}{2}\lambda \tag{2.11}$$

Notice that the z exponent is the same as before but that τ^* is now linear in λ. Notice also that, while we recover the standard values of the θ and z exponents, we do not recover the τ value for the small n behaviour exponent, which, in this case, is $\tau = 1+\lambda$; let us remark that our τ^* is, in a way, between the $n/s \to 0$ exponent and the $n/s \to \infty$ one, τ' ($\tau' = \lambda$).

2.3. The gelling case: $\lambda \geqslant 1$

Because in (2.10) the β exponent becomes negative for $\lambda \geqslant 1.33$, $G^{(1)}$ loses its good long-range behaviour in x and one has to work with the second derivative of G in equations (2.3). Using the second, third and fourth moments in equation (2.4) one finds the following approximate solution:

$$G^{(2)}(x,t) = \frac{C}{s^{\nu}(1-sx)^{\beta}} \tag{2.12}$$

with

$$\begin{aligned} \beta &= \frac{9 - 4\lambda + \sqrt{2\lambda^2 - 8\lambda + 9}}{4} \\ \nu &= \frac{3\lambda + 4\beta - 6}{2\beta} \\ s(t) &= (\gamma(t_0 - t))^{z'} \end{aligned} \tag{2.13}$$

with

$$\gamma = C\left[\frac{\Gamma(\omega + \beta - 1)}{\Gamma(\beta)}\right]^2 \frac{2 - \lambda - \nu^{-1}}{\beta} \qquad \text{and} \qquad z' = -\frac{1}{\lambda + \nu^{-1} - 2}$$

which leads to a non-conserving mass self-similar solution whose τ^* exponent is

$$\tau^* = 3 - \beta = \frac{3 + 4\lambda - \sqrt{2\lambda^2 - 8\lambda + 9}}{4}. \tag{2.14}$$

3. The additive model

Proceeding exactly in the same way as in the multiplicative case, but using $K(i,j) = k(i^{\lambda} + j^{\lambda})/2$, the additive kernel, one has for $G(x,t)$ the following equation:

$$2\dot{G}(x,t) = G^{(\lambda)}(x,t)G(x,t) - G^{(\lambda)}(0,t)G(x,t) - G^{(\lambda)}(x,t)G(0,t) \tag{3.1}$$

from which we can extract the first moment equations:

$$\begin{aligned} 2\dot{g}_0 &= -g_{\lambda}g_0 \\ 2\dot{g}_1 &= 0 \\ 2\dot{g}_2 &= g_{\lambda+1}g_1 \\ 2\dot{g}_3 &= 3g_{\lambda+2}g_1 + 3g_{\lambda+1}g_2 \\ 2\dot{g}_4 &= 4g_{\lambda+3}g_1 + 4g_{\lambda+1}g_3 + 6g_{\lambda+2}g_2 \end{aligned} \tag{3.2}$$

and derive the self-similar form for the model in our three regions of interest with the same approach as in section 2.

3.1. $\lambda \leqslant 0$

We take for $G(x,t)$

$$G(x,t) = \frac{1}{\beta s(1-sx)^{\beta}} \tag{3.3}$$

and use the first three moments of the distribution to constraint the parameters. This procedure gives

$$\begin{aligned} \beta &= 1 - 2\lambda \\ s(t) &= (\gamma(t+t_0))^z \end{aligned} \tag{3.4}$$

with

$$\gamma = \frac{\Gamma(\beta+\lambda)}{\Gamma(\beta+1)}\frac{1-\lambda}{2} \qquad \text{and} \qquad z = \frac{1}{1-\lambda}$$

which leads to $\tau^* = 1 - \beta = 2\lambda$ (see remark in section 2.1).

3.2. $0 \leqslant \lambda \leqslant 1$

For λ in this range the preceding form is no longer integrable, thus, as in the multiplicative case, we use the first derivative of G:

$$G^{(1)}(x,t) = \frac{1}{(1-sx)^{\beta}} \tag{3.5}$$

and find, with the help of g_1, g_2 and g_3,

$$\begin{aligned} \beta &= 2 - \tfrac{3}{2}\lambda \\ s(t) &= (\gamma(t+t_0))^z \end{aligned} \tag{3.6}$$

with

$$\gamma = \frac{\Gamma(\beta+\lambda)}{\Gamma(\beta+1)}(1-\lambda) \qquad \text{and} \qquad z = \frac{1}{1-\lambda}$$

which gives $\tau^* = 2 - \beta = \frac{3}{2}\lambda$. Notice that in this λ range, the τ^* exponent is exactly the same as in the multiplicative case which exhibits the approximate universality we propose in this λ range. See also the remark at the end of section 2.2

3.3. The gelling case: $\lambda \geqslant 1$

Now using g_2, g_3 and g_4, one finds

$$G^{(2)}(x,t) = \frac{C}{s^{\nu}(1-sx)^{\beta}} \tag{3.7}$$

with

$$\beta = \frac{3 + \sqrt{24\lambda^2 - 96\lambda + 81}}{4}$$
$$\nu = 1 \qquad C = \frac{\beta}{3} + 1 - \lambda \tag{3.8}$$
$$s(t) = (\gamma(t_0 - t))^{z'}$$

with

$$\gamma = \frac{\Gamma(\lambda + \beta - 1)}{\Gamma(\beta)}(\lambda - 1) \qquad \text{and} \qquad z' = \frac{1}{1 - \lambda} \tag{3.8}$$

which leads to a non-conserving mass self-similar solution whose τ^* exponent is

$$\tau^* = 3 - \beta = \frac{9 - \sqrt{24\lambda^2 - 96\lambda + 81}}{4}. \tag{3.9}$$

This exponent rapidly loses any meaning due to the fact that β acquires an imaginary part for $\lambda \simeq 1.2$. As a matter of fact, in this region, the additive model is not supposed to even have a self-similar solution [10]. This lack of universality is numerically studied in section 5. We show in figure 2 (and in figure 5 together with the numerical results) τ^* as a function of λ for multiplicative and additive cases.

4. Discussion

4.1. The validity range of the method

Let us first notice that our method is by no mean unique. In fact, one could have taken another analytical form for G and proceeded in the same way. We have chosen the form (1.12) because it is the simplest one which gives back the canonical results when $\lambda = 0$, 1 or 2.

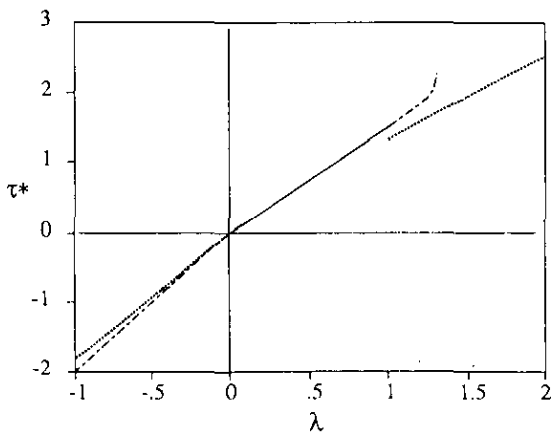

Figure 2. The τ^* exponent as a function of λ for the additive (chain curve) and multiplicative model (dotted curve).

Given that, we have now to discuss for which kinematical range in s and n the ansatz we use gives an answer close to the exact one.

In order to be specific we restrict this discussion to the intermediate λ range ($0 \leqslant \lambda \leqslant 1$) in the multiplicative case. The difference between the approximate solution, $G^{(1)}$ and the exact self-similar one can be written as follows.

$$G^{(1)}_{\text{exact}}(x,s) \simeq G^{(1)}(x,s) + \epsilon \frac{(sx)^3}{3!} + 0(sx)^4. \tag{4.1}$$

The resolution of the last equation of (2.4) gives ϵ, thanks to the nice properties of continous derivatives (A.8):

$$\epsilon = \omega(\omega - 1)\beta/3. \tag{4.2}$$

This quantity is small in the whole λ range and is equal to $\frac{1}{24}$ when $\lambda = 1$. This is a good test for the quality of the chosen ansatz. Notice that $\epsilon = 0$ for $\lambda = 0$ or 2 which exhibits the fact that our ansatz is exact in these cases. Furthermore this value of ϵ gives that the corrective term is negligible (on the imaginary axis) compared with $|G^{(1)}|$ provided $|x| < x_0 \simeq 4/s$.

Now, the range in n where the approximate formula is valid is given by the structure of the inverse Laplace transform: the same argument as in the uncertainty principle gives that the correction to the approximate density is negligible if $n \ll n_0 = 1/x_0$. The worst case is obtained for $\omega = 0.26$ which leads to $n_0 \simeq s/3.6$. This procedure gives an upper bound for this limit. Thus, from the *theoretical* point of view, our results are, at least, essentially valid for sizes greater than, say, $s/3$. However, as it will be shown in the numerical study, its validity range goes down much lower, and covers completely the size range when s is not too big. This will be numerically observed in section 5.

On the other hand, a quick examination of formula (1.13) shows that n cannot be too large compared with s, due to the importance of non-asymptotic terms in the integral. In short, the validity range of our method covers n sizes between s/k and s, and $k > 3$ can be numerically estimated.

4.2. The small n/s behaviour

Now, it is perhaps interesting to notice that if, in equations (2.2), near $x = 0$, one makes the following approximation to the first order in x:

$$G^{(\omega)}(x,t) - G^{(\omega)}(0,t) \simeq xG^{(\omega+1)}(x,t) \tag{4.3}$$

one obtains the following equation in the multiplicative case

$$\dot{G}^{(1)}(x,t) = x\left[G^{(\omega+1)}(x,t)\right]^2. \tag{4.4}$$

This equation is much simpler than the exact one, and admits the form (2.9) as an exact solution, with the same $s(t)$ as in (2.10), but with $\tau = 1+\lambda$, which is the known τ exponent of the n/s behaviour of EvD class I models. The same approximation gives

$$\dot{G}^{(1)}(x,t) = xG^{(1)}(x,t)G^{(\lambda+1)}(x,t) \tag{4.5}$$

in the additive case. We obtain the same features as previously: expression (2.9) or (3.5) is an exact solution which leads again to $\tau = 1 + \lambda$, which questions the validity of the approximation in this case [8].

4.3. Large n results

Furthermore, if in equation (2.2) or (3.1) one looks at x very close to the singularity, i.e. $G^{(\omega)}(x,t) \to \infty$, the constant terms ($G^{(\omega)}(0,t)$ or $G(0,t)$) may be neglected, and a limiting solution may be found for both models. We recover the exponent $\tau = \lambda$, which has been found to be valid for $n \gg s$. This last point is easy to understand as, near the singularity, the x value in the discrete Laplace transform (1.10) is positive and we are thus examining the high n values of the distribution.

In fact, our analysis, which consists in finding an approximate solution of the exact equation, gives good predictions in the intermediate n range (less or around s); the exact size of this range is to be determined by numerical simulations. Concerning the τ^* exponent, the results are shown in figure 5 together with the numerical results, in the following part.

5. Numerical results

5.1. The simulation method

We use a Monte-Carlo type simulation for the agglomeration phenomenon, starting from M monomers. At each step of the simulation, two clusters are randomly chosen, proportionally to the total mass of their mass sector: $P(i) \propto iN(i)$. Then, the two clusters aggregate with a probability proportional to $K(i,j)/ij$. The time is then implemented by a constant quantity Δt.

This technique is similar, but different and faster, to Meakin's one [20], who chose the clusters to be proportional to their multiplicity in their mass sector and aggregated them proportionally to $K(i,j)/K_{\max}$. Particularly, in the case of gel, it avoids any critical slow-down and goes beyond the theoretical gelling point [11].

5.2. Universality

We start the evolution with 10^5 monomers and characterize the degree of evolution by the mean size of the agglomerates in the sample, $s^* = \overline{n^2}/M = g_2$.

5.2.1. The first result of the simulation is that, for $s^* \leqslant 20$ (the heaviest cluster has a mass $n_{\max} \simeq 100$), it is quite impossible to see any difference between the multiplicative and additive models for $-1 < \lambda < 1$. We present in figure 3 the multiplicity distribution for the two models, when $s \simeq 10$. The λ exponents for the two models are -1 for figure 3(*a*) and 0.5 for figure 3(*b*).

5.2.2. In contrast, figure 4 shows that for $\lambda > 1$, there is no universality at all, the gel occurs much more rapidly in the additive case, and the system is much more sensitive to initial conditions than in the multiplicative one. In order to exhibit these two points, we start from initial conditions consisting of 10^4 monomers plus one polymer of size 100, with $\lambda = 1.5$. After approximately 10^4 iterations, the statistical sample shows somewhat different behaviour for the two models.

Now, we can define an aspect ratio as

$$A = m'/m \tag{5.1}$$

where m is the mass of the heaviest cluster in the sample and m' the mass of the previous one, and one can compare this quantity for the two models at the end of

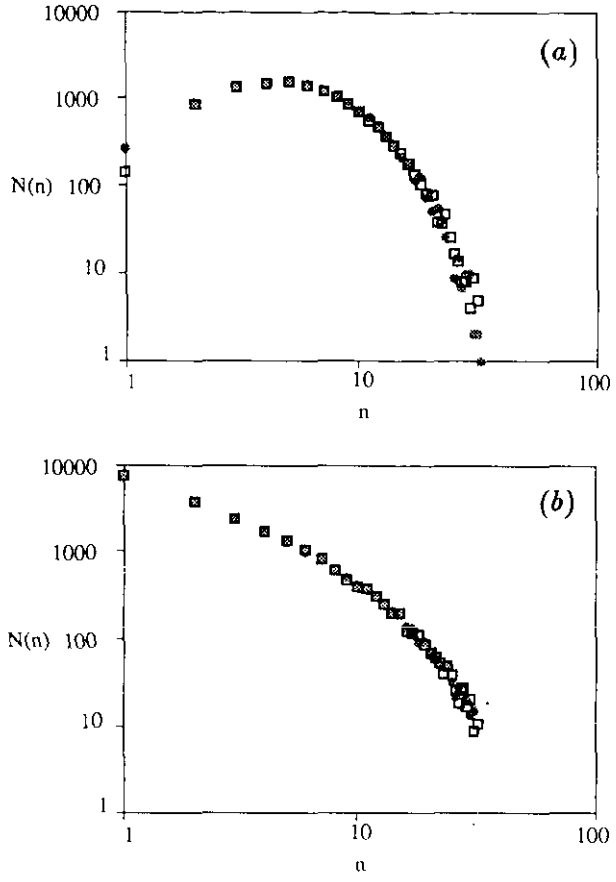

Figure 3. (*a*) Number of aggregates of size n as a function of n for $n_{max} = 100$ ($\lambda = -1$): open squares, multiplicative model; full circles, additive model. (*b*) Number of aggregates of size n as a function of n for $n_{max} = 100$ ($\lambda = 0.5$): open squares, multiplicative model; full circles, additive model.

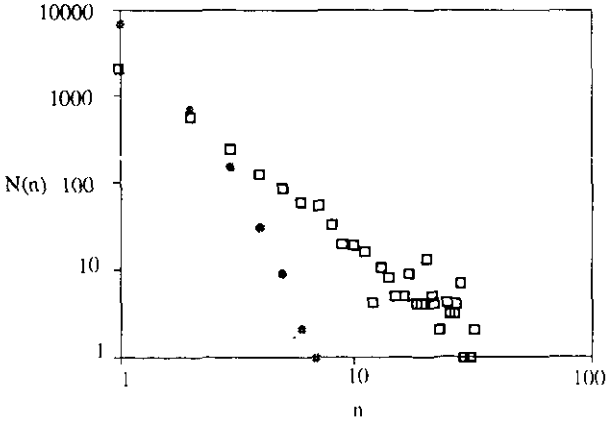

Figure 4. Number of aggregates of size n as a function of n after 10^4 iterations ($\lambda = 1.5$): open squares, multiplicative model; full circles, additive model.

the simulation. In the multiplicative case we find $A = 0.16$ which means that the statistical sample is around its gelling point [11], in the additive case this quantity is $A = 6 \times 10^{-3}$ showing that the system is already in a gel phase and that there is a very heavy isolated cluster in the sample ($m = 1175$).

5.3. The τ^* exponent

In order to determine the τ^* exponent numerically, we fit the multiplicity distribution $N(n)$ with the self-similar shape $N(n,t) \propto n^{-\tau^*} e^{-n/s}$. This fit is constructed as a χ^2 linear minimization of the logarithm of the data, weighted with their multiplicity. In other words, we use a χ^2 defined as

$$\chi^2 = \sum_{i=i_{\min}}^{i_{\max}} N(i)_{\text{num.}} [\log(N_{\text{num.}}) - \log(N_{\text{th.}})]^2 \qquad (5.2)$$

$$N_{\text{th.}}(i) = c i^{-\tau^*} e^{-is^{-1}}.$$

We fit the theoretical parameters using either the whole sample of 10^4 particles, or $i_{\min} \simeq s^*/10$ and $i_{\max} \simeq s^*$ depending on the value of λ. In fact, when s^* is less or equal than 10, the whole data range can be described properly by the self-similar solution, which is not the case when s^* is greater than, say, 20.

As can be seen in figure 5, where we have plotted the τ^* exponent for both models as a function of λ, together with their respective theoretical curves, our numerical simulation corroborates the theoretical approach of the problem quite well.

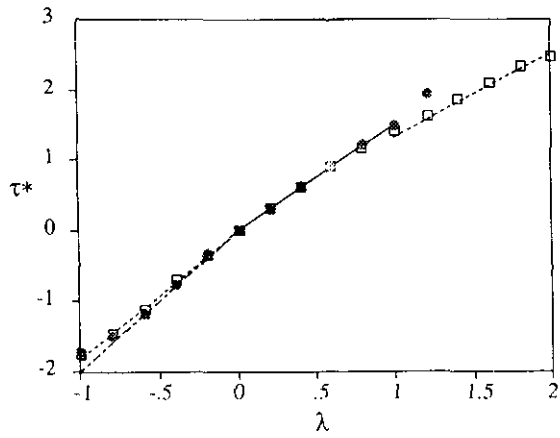

Figure 5. The τ^* universal exponent as a function of λ for the additive and multiplicative model. Numerical results: open squares, multiplicative model; full circles, additive model.

The error bars, which are not shown in figure 5 for the sake of legibility, are of the size of the difference between the numerical points and the theoretical curve. Now, in order to test the stability in time of τ^*, we follow a 10^5 particle sample for both models up to $s^* \simeq 100$ for $\lambda = 0.5$. The τ^* value remains stable in this range as can be seen in figure 6, where it is given as a function of $n_{\max}$ for our two models. For higher values of s^* our fit has strong statistical errors due to the natural fluctuations in the numerical calculation, and cannot be trusted. The fact that the EVD exponent can only be reached for very high values of s^* is well known [12–14],

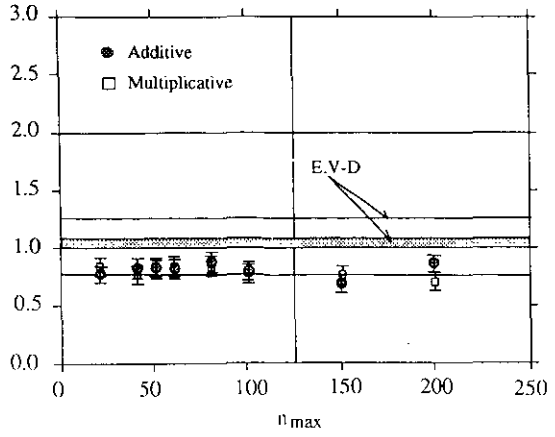

Figure 6. τ^* exponent as a function of the maximal mass in the sample, compared with the EVD predictions. The results are calculated for $\lambda = 0.5$: open squares, multiplicative model; full circles, additive model.

and has been observed in the experimental results of Broide and Cohen [15] which worked with 10^7 polystyrene spheres.

One can also note that the results we obtain are consistent with those of Kang *et al* [12]; the τ exponent they find for $\lambda = 0.8$ in the multiplicative case is the same as for $\lambda = 0.75$ in the additive one: a value of 1.3 (intermediate times) for both models. This result can now be well understood within our scheme, as we can guess that, in their intermediate range, the universality we found is supposed to hold. As a matter of fact, we are in good agreement with the rest of their results.

6. Conclusion

In this paper, we have shown the existence of a new universal exponent, τ^*, for the aggregation phenomenon at intermediate times, which can be observed early in the development of the process and can be measured without ambiguity. This would permit early analyses of the experimental events and thus the prediction of its time evolution. In particular, the possibility of the gelling process coud be determined rapidly by a measurement of the τ^* exponent.

This analysis is valid over a large range of the homogeneity degree of the model: $-1 \leqslant \lambda \leqslant 1$. In particular, we recover the bell-shaped type of distribution introduced by Kolb [7] for λ negative. The numerical calculations follow the theoretical predictions remarkably well.

With respect to the positive values of λ, our result lies between the τ and τ' values found by EVD for $n/s \to 0$ and $n/s \to \infty$ and is valid in a wide range of the phase space, say $s/10 \leqslant n \leqslant s$. In the gelling region, the additive model loses its universality, exhibits a rapid gel and is very sensitive to the initial conditions.

One can also approximate the τ^* value for the multiplicative model in the gelling case ($\tau^* \simeq (1 + 2\lambda)/2$) and summarize the whole λ range in table 2.

Note also that our analysis follows the same direction as the Taylor and Sorensen [21] one, but the fact that we use the discrete Smoluchowski equation instead of the continous one means that we avoid any divergence problems near $n/s \to 0$. On the other hand, we have shown that the moments of the distribution which are needed

Table 2. Values of the various universal exponents as a function of λ.

	$\lambda < 0$	$0 < \lambda < 1$	$1 < \lambda < 2$
τ^*	$\simeq 2\lambda$	$\simeq \frac{3}{2}\lambda$	$\simeq (1+2\lambda)/2$
z	$1/(1-\lambda)$	$1/(1-\lambda)$	—
z'	—	—	$\simeq 2/(1-\lambda)$
θ	2	2	$\simeq (3+\lambda)/2$

in order to construct the asymptotic solution are related to the λ parameter: for negative values of λ the first three moments, g_0, g_1 and g_2 can be used in the calculation of the self-similar solution; for λ between 0 and 1, in order to prevent any divergence of the inverse Laplace transfore, we used g_1, g_2 and g_3, and in the gelling case, for the same reason, g_2, g_3 and g_4 are the building tools of the theory. This is why we do not completely understand the arguments of the above authors who used essentially the zeroth-order moment to solve the problem for any $\lambda \geqslant 1$.

In this paper we have not focused our attention on the attractor character of the solution, which, in any case, has been numerically verified. We postpone this discussion to a forthcoming paper together with the discussion of the aggregation phenomenon in the presence of an incoming constant flux of monomers.

Acknowledgments

It is a pleasure to thank here L Gil, who has participated to the early stage of this work, and Y Demay for many discussions on the mathematical aspects of the problem.

Appendix

A1. Continuous derivative: definition

In order to introduce the continuous derivatives, let us recall the Cauchy formula for the calculation of the nth derivative of an analytical function:

$$f^{(n)}(z) = \frac{n!}{2i\pi} \oint \frac{f(z')}{(z'-z)^{n+1}} \, dz'. \tag{A.1}$$

In this formula, the integration has to be done along a contour surrounding z. The continuous derivative of an analytical function can be defined by the same formula with a non-integer n:

$$f^{(\alpha)}(z) = \frac{\Gamma(\alpha+1)}{2i\pi} \oint \frac{f(z')}{(z'-z)^{\alpha+1}} \, dz'. \tag{A.2}$$

However, in this case the function to be integrated has a cut in the z-plane and the Cauchy formula is no longer valid unless the integration path crosses the cut sufficiently far away so the integrand is zero. In other words, this formula is valid for

such functions which have the following behaviour in at least the left or right complex half-plane:

$$z^{\alpha} f(z) \to 0 \qquad \text{when } |z| \to \infty. \tag{A.3}$$

This is crucial in this work. As the Laplace transform of the multiplicity is analytical in the left half-plane, we will define the cut of $(z' - z)^{\alpha+1}$ on the right-hand side of the complex plane, i.e. the argument θ of z will be defined from 0 to 2π. Now, using equation (A.2) and taking the discontinuity of the function, one obtains the following formula:

$$f^{(\alpha)}(x) = \frac{1}{\Gamma(-\alpha)} \int_0^{+\infty} \frac{f(x-r)}{r^{\alpha+1}} \, \mathrm{d}r \qquad (x \in \mathbb{R},\ x < 0). \tag{A.4}$$

This defines the continuous derivative for functions, the behaviour of which is given by (A.3).

A2. Some useful derivatives

We list here some useful examples of continuous derivatives:

$$\partial_{\alpha} f(cx) = c^{\alpha} f^{(\alpha)}(cx) \tag{A.5}$$

$$\partial_{\alpha} \mathrm{e}^{cx} = c^{\alpha} \mathrm{e}^{cx} \tag{A.6}$$

and

$$\partial_{\alpha} \frac{1}{(1-cx)^{\beta}} = \frac{\Gamma(\alpha+\beta)}{\Gamma(\beta)} \frac{c^{\alpha}}{(1-cx)^{\beta+\alpha}}. \tag{A.7}$$

In this last formula, one can let c go to ∞, which gives the derivative of a power of x:

$$\partial_{\alpha}(-x+\epsilon)^{\theta} = \frac{\Gamma(\alpha-\theta)}{\Gamma(-\theta)}(-x+\epsilon)^{\theta-\alpha}. \tag{A.8}$$

Notice that $\partial_{\alpha}(-x+\epsilon)^{n}$ does not exist if α is less than n, as x or $x^{n-\alpha}$ does not tend to zero as x goes to $-\infty$. If α is greater than n, its derivative can be calculated and gives zero. Notice also that if there is a convergence problem near $x = 0$ in formula (A.4), it should be taken as a principal value distribution. Finally, the continuous derivative definition gives back the usual derivative, when α is an integer, when applied to a well behaving function (decreasing when $x \to -\infty$).

References

[1] Von Smoluchowski M 1917 *Z. Phys. Chem.* **92** 129

[2] Drake R L 1972 *Topics in Current Aerosol Research* vol 3, ed G M Hidy and J R Brock (New York: Pergamon)

[3] Golovin A M 1963 *Izv. Akad. Nauk SSSR Ser. Geofiz.* 5 783; 1963 *Bull. Acad. Sci. USSR, Geophys. Ser.* **5** 482

[4] Ziff R M, Ernst M H and Hendriks E M 1983 *J. Phys. A: Math. Gen.* **16** 2293

[5] Ziff R M, Ernst M H and Hendriks E M 1984 *J. Colloid. Interface Sci.* **97** 266

[6] Hendriks E M 1984 *J. Phys. A: Math. Gen.* 17 2299
Spouge J L 1985 *J. Phys. A: Math. Gen.* **18** 3063
[7] Kolb M 1984 *Phys. Rev. Lett.* **53** 1653
[8] van Dongen P G J and Ernst M H 1985 *Phys. Rev. Lett.* **54** 1396
[9] Ernst M H 1986 *Fractals in Physics* ed L Pietronero and E Tosatti (Amsterdam: North-Holland) p 289
[10] van Dongen P G J and Ernst M H 1988 *J. Stat. Phys.* **50** 295 and references quoted therein
[11] Gabellini Y and Meunier J-L *Preprint* Nice NTH90/19
[12] Kang K, Redner S, Meakin P and Leyras F 1986 *Phys. Rev.* A **33** 1171
[13] Martin J E 1987 *Phys. Rev.* A **36** 3415
[14] Helgesen G, Skjeltorp A T, Mors P M, Botet R and Julien R 1988 *Phys. Rev. Lett.* **61** 1736
[15] Broide M L and Cohen R J 1990 *Phys. Rev. Lett.* **64** 2026
[16] Kogut J and Wilson K 1973 *Phys. Rep.* C **12**
[17] Niemeijer T and Van Leuven J 1975 *Phase Transitions and Critical Phenomena* vol VI 64 (New York: Academic) p 2026
[18] Guelfand I M and Chilov G E 1965 *Les Distributions* (Paris: Dunod)
[19] Dattoli G, Richetta M and Torre A 1990 *Nuovo Saggiatore* **5/6** 19
[20] Meakin P *On Growth and Form* ed H E Stanley and N Ostrowsky (Dordrecht: Martinus Nijhoff) p 111
Family F and Landau D P 1984 *Kinetics of Aggregation and Gelation* (Amsterdam: North-Holland)
Pietronero L and Tosatti E 1986 *Fractals in Physics* (Amsterdam: North-Holland)
Vicsek T 1989 *Fractal Growth Phenomena* (Singapore: World Scientific)
[21] Taylor T W and Sorensen C M 1987 *Phys. Rev.* A **36** 5415