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1988 J. Phys. A: Math. Gen. 21 1029

(http://iopscience.iop.org/0305-4470/21/4/028)

J. Phys. A: Math. Gen. 21 (1988) 1029-1042. Printed in the UK

Influence of the chain mobility on the dynamic scaling of chain–chain aggregation in two dimensions

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Received 5 June 1987, in final form 6 October 1987

Abstract. The dynamic scaling of the 2D chain-chain aggregation model with a diffusion coefficient varying with the size k of the chains as k^{γ} is investigated by Monte Carlo simulations. Assuming that the sticking probability for two chains of size k is proportional to $k^{-\varphi}$, the mean chain size grows like t^{z} with $z=(1+\varphi-\gamma)^{-1}$.

1. Introduction

The dynamics of aggregation of randomly diffusing clusters has been intensively investigated (Kolb 1984, Vicsek and Family 1984, Botet and Jullien 1984, Meakin *et al* 1985). A simple model (Meakin 1983, Kolb *et al* 1983) in which the growth results from the aggregation of clusters is believed to retain the main features of many physical phenomena such as gelation, polymerisation or coagulation (Friedlander 1977, Jullien and Botet 1987). A chain–chain aggregation model, liable to describe the linear polycondensation reactions, has been recently introduced (Debierre and Turban 1987a). In this case, unramified clusters (chains) perform a Brownian motion on a lattice and two chains irreversibly stick when their tips touch (i.e. arrive at first-neighbour positions).

The statics and dynamics of this model have been previously studied assuming a size-independent chain mobility—a simple but unphysical assumption. In this paper the diffusion coefficient is taken to be proportional to s^{γ} for an s-site chain and a systematic study of the influence of γ on the dynamics is presented.

The model and the Monte Carlo procedure are described in detail in § 2. The simulation results are analysed in § 3 using a scaling theory known to hold for most aggregation processes. The evolution of the chain radius is discussed in § 4. In § 5 a scaling law giving the dependence of the dynamic exponent z on the chain mobility exponent γ is obtained and used to determine a sticking probability exponent φ. In § 6 the form of the scaling function is discussed in the framework of the mean-field Smoluchowski theory and the conclusion is given in § 7.

2. Numerical simulations

The simulations were performed on an $L\times L$ square lattice with periodic boundary conditions, for values of the mobility exponent γ ranging from -2.0 to 0.5, in order

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0305-4470/88/041029+14$02.50

to study the variation of the dynamic exponent z with γ. The value $\gamma = -1/D$, where D is the chain fractal dimension, corresponds to the Stokes-Einstein relation for the mobility. We were limited to values of $\gamma \leqslant 0.5$ because positive γ values require more computer time. Averages were taken over 50 simulations for each γ value.

A simple scaling behaviour is expected for large time and chain size for a vanishing density on an infinite system. In practice the system size L and the density are restricted by computer memory and computer time, since decreasing ρ requires averaging over more samples in order to limit the statistical fluctuations. In a finite system saturation effects are always observed at long times (figure 1) because either one is left with a single chain or, as was the case in our simulations, the remaining chains can no longer stick due to sterical effects. The maximum time t_f (table 1) was chosen to avoid these effects.

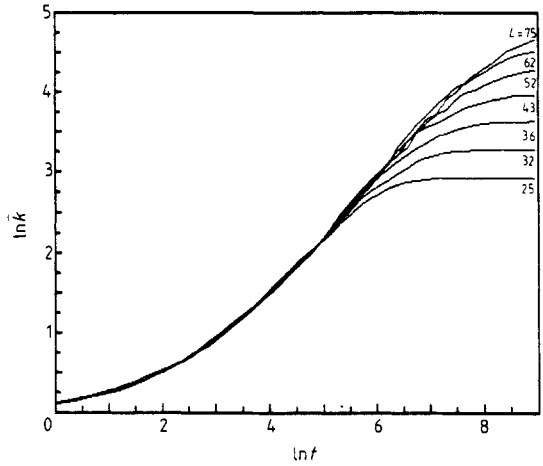

Figure 1. Log-log plot of the mean chain size $\bar{k}$ as a function of the time t. The results are from simulations performed on $L \times L$ square lattices with increasing size L, for $\gamma = 0$ and particle density $\rho \simeq 0.03$ independent of L.

We have worked with an initial monomer density $\rho \simeq 0.016$ and sample size $L = 256$. Similar values were used in a study of cluster-cluster aggregation (Vicsek and Family 1984). A preliminary study with $\gamma = 0$ (Debierre and Turban 1987a) indicated no detectable effect on the exponents and cluster-size distribution when the density or the size were changed to $\rho \approx 0.03$ and $L = 400$. Initially, $N_0 = \rho L^2 = 1024$ particles (one-site chains) are randomly distributed on the lattice sites with the restriction that nearest-neighbour occupation is forbidden. At each Monte Carlo step, a k-site chain is randomly selected among all the chains of the sample, with a probability

$$p_k = k^\gamma / p_{\max} \tag{2.1}$$

where

$$p_{\max} = \sum_k N(k, t) k^\gamma \tag{2.2}$$

is a normalisation coefficient and $N(k, t)$ is the number of chains of size k at time t. The selection with probability p_k of a k-site chain is performed as follows, in order to spare computer time. On the interval $[0, p_{\max}]$ adjacent segments are put in

correspondence with all the chains of the sample, the length of a segment being k^γ for a k-site chain. Then to each random number uniformly distributed on the interval $[0, p_{max}]$ corresponds a chain of size k with probability p_k.

Once a chain has been selected, the physical time is incremented by the quantity $\delta t = 1/p_{max}$ so that the jump frequency of a k-site chain is $\nu_k \sim p_k/\delta t \sim k^\gamma$. When $\gamma = 0$, $p_{max} = N(t)$, the total number of chains at time t, $p_k = \delta t = 1/N(t)$ and $\nu_k \sim 1$, independent of the size k. Then the chain is moved as a whole by one lattice unit in a randomly chosen direction provided no site is doubly occupied in the new position, otherwise it remains in the initial one. When the move succeeds, the first-neighbour sites of the two chain tips are examined and sticking occurs when another chain tip is found. The formation of loops is prevented as the two tips of the same chain are not allowed to stick together. Since the two tips are examined successively and a chain is renumbered as soon as it sticks, this procedure also takes into account the situation in which the two tips of a chain might become connected through another chain. The chain-size distribution function

$$n(k, t) = N(k, t)/L^2 \tag{2.3}$$

and the mean radius of gyration $\bar{R}(k, t)$, where the bar indicates an average at time t of

$$R(k, t) = \frac{1}{k}\left(\sum_{i,j} (\boldsymbol{r}_i - \boldsymbol{r}_j)^2\right)^{1/2} \tag{2.4}$$

over the chains of size k, are stored for 50 values of the physical time t_i at regular intervals on a logarithmic scale:

$$t_i = [(1.2)^{1-0.2\gamma}]^{i-1} \qquad (i = 1, 50). \tag{2.5}$$

3. Scaling for the chain-size distribution function

We assume that the chain-size distribution function is a generalised homogeneous function of the time t and chain size k:

$$n(k, t) = b^{-y_n} n(b^{y_k} k, b^{y_t} t). \tag{3.1}$$

With $b = k^{-1/y_k}$ and $b = t^{-1/y_t}$, we obtain

$$n(k, t) = k^{-\theta} f(x) \tag{3.2a}$$

$$n(k, t) = t^{-\theta z} g(x) \tag{3.2b}$$

where $z = y_k/y_t$, $\theta = -y_n/y_k$ and $x = k/t^z$. According to the Smoluchowski theory the two scaling functions $f(x)$ and $g(x)$ are assumed to behave as follows (Vicsek and Family 1984, van Dongen and Ernst 1985, Kang *et al* 1986). When $x \gg 1$, both functions decrease exponentially and when $x \ll 1$, depending on the kinetics, one expects either a power-law behaviour (class I and class II kinetics):

$$f(x) \sim x^{\theta - \tau} \qquad g(x) \sim x^{w/z - \theta} \tag{3.3}$$

or an exponential decrease (class III kinetics). Since $f(x) = x^\theta g(x)$ for class I and class II kinetics, the exponents w and τ which, according to equations (3.2) and (3.3), govern the evolution of the distribution function when $x \ll 1$

$$n(k, t) \sim k^{-\tau} t^{-w} \tag{3.4}$$

satisfy the following scaling law:

$$w = (\theta - \tau)z. \tag{3.5}$$

The mth moment of the distribuiton function

$$M_m(t) = \sum_{k=1}^{\infty} k^m n(k, t) \tag{3.6}$$

may be written as

$$M_m(t) = \int_1^{\infty} k^m n(k, t)\, \mathrm{d}k = t^{z(m+1-\theta)} \int_{t^{-z}}^{\infty} x^{m-\theta} f(x)\, \mathrm{d}x. \tag{3.7}$$

At large times, the contribution of the lower limit in the last integral is irrelevant for class III and

$$M_m(t) \sim t^{z(m+1-\theta)} \qquad \text{all } m \tag{3.8}$$

whereas for class I and class II

$$M_m(t) \sim t^{z(m+1-\theta)} \qquad m \geqslant \tau - 1 \tag{3.9a}$$

$$M_m(t) \sim t^{z(\tau-\theta)} \qquad m < \tau - 1. \tag{3.9b}$$

Since the particle density, which is given by the first moment, is a constant, one has the following two alternatives:

$$\theta = 2 \qquad \text{class III or } \tau \leqslant 2 \tag{3.10a}$$

$$\theta = \tau \qquad \tau > 2. \tag{3.10b}$$

In the second case equation (3.5) gives $w = 0$ which corresponds to a static distribution as for percolation clusters (Herrmann 1986). Thus, for a dynamic aggregation process with constant particle density, $\theta = 2$ and $\tau < 2$ for class I and class II kinetics. This result is confirmed by previous simulation results (Kolb 1984, Vicsek and Family 1984, Botet and Jullien 1984, Meakin *et al* 1985, Kang *et al* 1986, Debierre and Turban 1987a, b).

The number of chains at time t, $N(t)$, is proportional to $M_0(t)$ so that

$$N(t) \sim t^{-z} \qquad \text{class III or } \tau \leqslant 1 \tag{3.11a}$$

$$N(t) \sim t^{-w} \qquad \tau > 1. \tag{3.11b}$$

Finally, the mean size of the chains

$$\bar{k}(t) = \sum_k k^2 n(k, t) \Big(\sum_k k n(k, t) \Big)^{-1} = M_2(t)/M_1(t) \tag{3.12}$$

grows like

$$\bar{k}(t) \sim t^z. \tag{3.13}$$

The variations of $\ln \bar{k}$ and $\ln N$ with $\ln t$ shown in figure 2 indicate that either we are in class III or $\tau \leqslant 1$ for all the values of γ studied.

Since when $x \ll 1$, $f(x) \sim x^{2-\tau}$ with $\tau < 2$ or $f(x) \ll 1$ in class III, $f(x)$ is always bell-shaped with a maximum value of $f_{\max} = f(x_f)$. The same is true of $g(x)$ in class III or when $\tau < 0$ ($g(x) \sim x^{-\tau}$ according to equations (3.3) and (3.5)) whereas $g(x)$ is

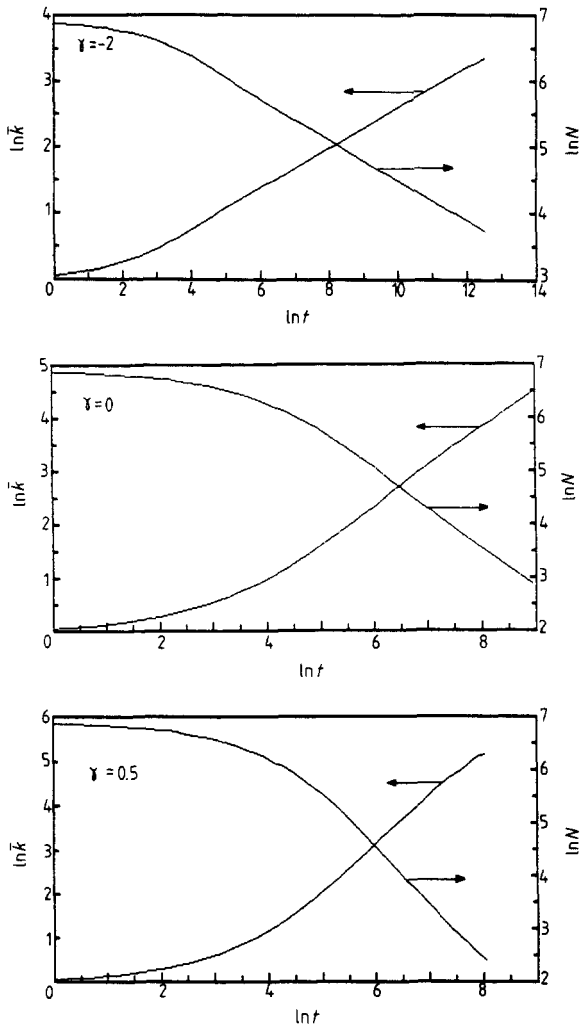

Figure 2. Log-log plot of the total number of chains N and the mean chain size $\bar{k}$ as functions of the time t, for three values of the mobility exponent $\gamma = -2.0$, 0 and 0.5. The straight parts of the ln N and ln $\bar{k}$ curves have slopes $-z$ and z respectively.

monotonic when $\tau > 0$. The limiting case $\tau = 0$ corresponds to a size-independent distribution function.

Taking the logarithm of both sides in equation (3.2a) with $\theta = 2$ gives

$$\ln n(k, t) = -2 \ln k + \ln f(x) \tag{3.14}$$

which at a given time t_α may be written

$$\ln n(k, t_\alpha) + 2 \ln k - \ln f_{\max} = \ln(f(k/t_\alpha^z)/f_{\max}). \tag{3.15}$$

For each time t_α, there is a size k_α such as $x_f = k_\alpha / t_\alpha^z$, thus the points ln k_α, ln $n(k_\alpha, t_\alpha)$ lie on a straight line, with slope -2 and intercept ln $f_{\max}$, which is the envelope of the curves ln $n(k, t_\alpha)$ against ln k. Our data are consistent with this behaviour (figure 3).

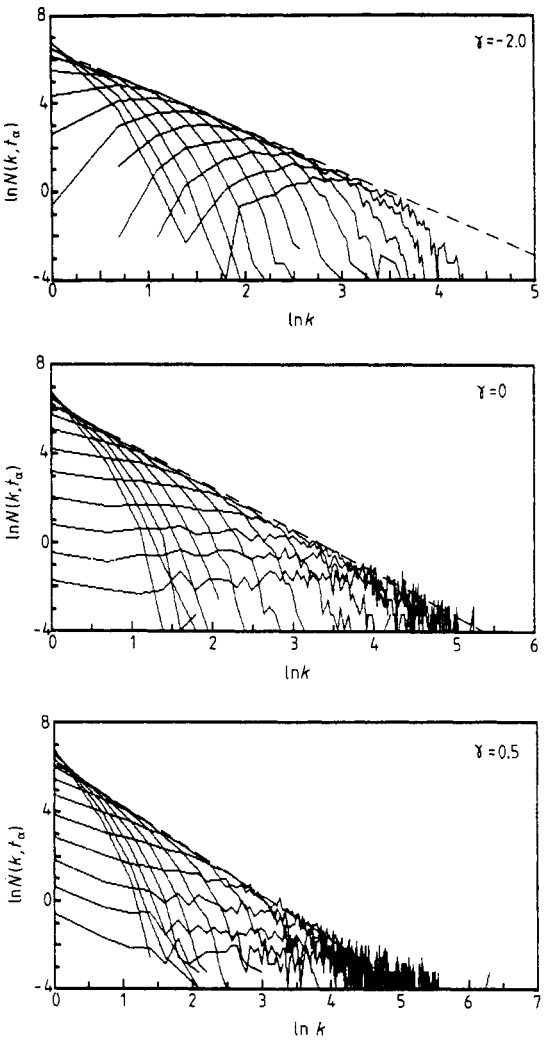

Figure 3. Plot of $\ln N(k, t_\alpha)$ against $\ln k$ at different times t_α. The slope of the envelope is close to -2 in each case for: $\gamma = -2.0$ ($t_\alpha = 21\,052$–$270\,292$, slope $= -1.89$); $\gamma = 0$ ($t_\alpha = 1255$–7584, slope $= -1.91$); $\gamma = 0.5$ ($t_\alpha = 602$–3104, slope $= -2.02$).

In the same way, in class III or when $\tau < 0$, the envelope of the curves $\ln n(k_\alpha, t)$ against $\ln t$ is a straight line with slope $-2z$. This is what is observed for $\gamma < 0$. A change of behaviour occurs near $\gamma = 0$ and there is no common tangent when $\gamma > 0$ (figure 4). To sum up, at small x one may expect a power-law behaviour with $\tau \leqslant 1$ when $\gamma \geqslant 0$ and either exponential (class III) or power-law behaviour with $\tau < 0$ when $\gamma \leqslant 0$.

4. Scaling of the radius of gyration

One may assume that the mean radius of gyration $\bar{R}$ satisfies the homogeneity relation

$$\bar{R}(k, t) = b\bar{R}(b^{y_k}k, b^{y_t}t). \tag{4.1}$$

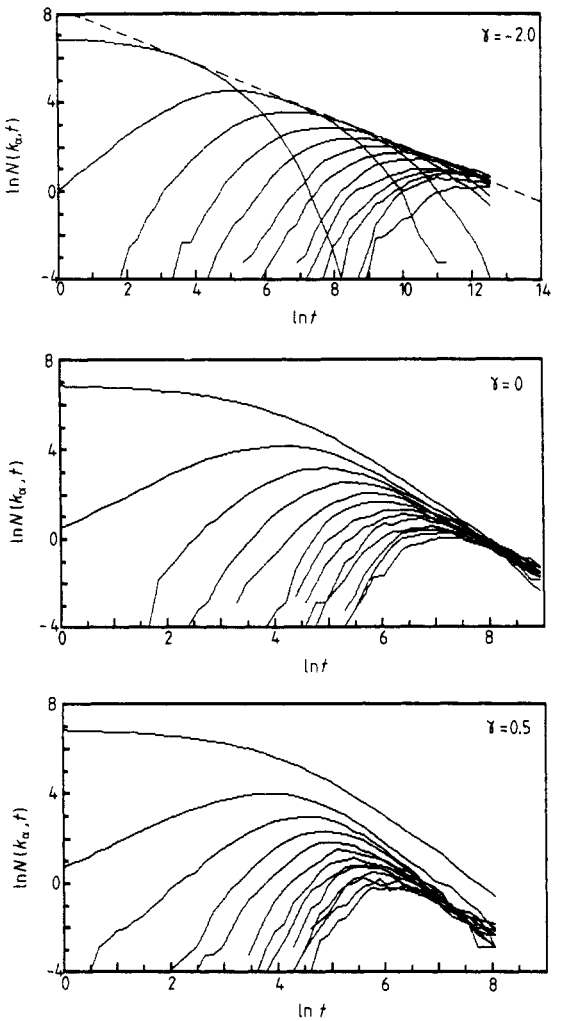

Figure 4. Plot of $\ln N(k_\alpha, t)$ against $\ln t$ for different chain sizes $k_\alpha = 1$-25. For $\gamma = -2$, the slope of the envelope is close to $-2z$. For $\gamma = 0$, the curves coalesce for large t values. For $\gamma = 0.5$, the different curves do not intersect and there is no envelope. For $\gamma = 0$ and 0.5, the common slope at large time is $-w$.

The usual procedure leads to:

$$\bar{R}(k, t) = k^{-1/y_k} q(x) = k^{1/D} q(x) \tag{4.2a}$$

$$\bar{R}(k, t) = t^{-1/y_t} r(x) = t^{z/D} r(x) \tag{4.2b}$$

where as above $x = k/t^z$, $z = y_k/y_t$ and $D = -y_k$ is the fractal dimension of the chains ($k \sim \bar{R}^D$).

Figure 5 gives the variations of $\ln k$ with $\ln \bar{R}(k, t)$ for different values of γ. It turns out that $q(x)$ is almost constant ($r(x) \sim x^{1/D}$) and the slope gives D.

If a mean radius $\bar{R}(t)$ is defined by taking an average on the size k at time t:

$$\bar{R}(t) = \sum_k kn(k, t)\bar{R}(k, t)\left(\sum_k kn(k, t)\right)^{-1} \tag{4.3}$$

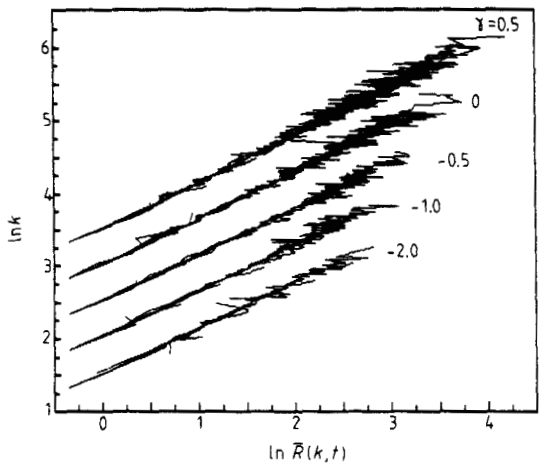

Figure 5. Plot of $\ln k$ against $\ln \bar{R}(k, t)$ for different values of γ. The curves are systematically shifted by one ordinate unit (ordinates given for the lowest curve $\gamma = -2$). The slopes give D values slightly increasing from 1.26 for $\gamma = -2$ to 1.33 for $\gamma = 0.5$. The fluctuations at large k are due to the small number of chains involved in the average.

then equations (3.2*b*) and (4.2*b*) lead to

$$\bar{R}(t) \sim t^{z/D} \tag{4.4}$$

so that the mean chain size

$$\bar{k} \sim t^{z} \sim \bar{R}^{D} \tag{4.5}$$

and $\bar{R}(t)$ may also be used to get D (figure 6). Similar values of the fractal dimension are obtained in both ways, slightly increasing with γ (table 1) and close to the self-avoiding walk value $D_{\text{saw}} = \frac{4}{3}$.

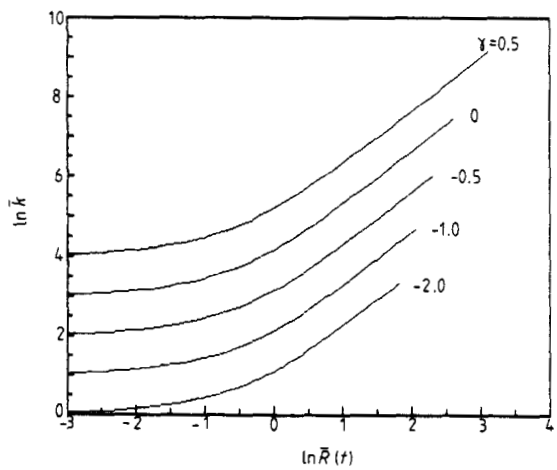

Figure 6. Plot of $\ln \bar{k}$ against $\ln \bar{R}(t)$ for different values of γ. (The curves are shifted as in figure 5.) $\bar{R}(t)$ is the mean radius of gyration of all the chains in the sample at time t. The straight parts of the curves have a slope D slightly increasing from 1.28 for $\gamma = -2$ to 1.34 for $\gamma = 0.5$.

Table 1. Maximum time t_f, static and dynamic exponents D, z, τ and w obtained for different values of γ. τ and w are only estimated for the positive values of γ for which the scaling function $g(x)$ is monotonic. Also given are the parameters A and a obtained from a least-square fit of $g(x)$ by $Ax^{-\lambda}\exp(-ax)$ with $\lambda = \gamma - 0.36$. The value of z for the 'free reptation' limited chain-chain aggregation model (third line) is nearly equal to that for $\gamma = -1$, but A and a are not the same in both cases; since the 'free reptation' model has been studied on the triangular lattice, geometrical correction factors are expected.

γ	t_f	D	z	τ	w	A	a
−2.0	2.7×10^5	1.27	0.31	—	—	15	8
−1.0	4.5×10^4	1.29	0.44	—	—	10	9
rept	—	1.30	0.43	—	—	3	6
$-1/D$	3.0×10^4	1.30	0.49	—	—	12	11
−0.5	1.8×10^4	1.30	0.55	—	—	13	12
−0.25	1.2×10^4	1.30	0.63	—	—	15	15
0	7.6×10^3	1.32	0.74	0.1	1.4	14	19
0.25	4.9×10^3	1.33	0.87	0.3	1.5	15	27
0.5	3.1×10^3	1.34	1.10	0.4	1.8	30	58

5. Sticking probability and scaling law for z

A simple scaling argument has been proposed (Kolb 1984, Botet and Jullien 1984) giving a relation between static and dynamic exponents of the cluster-cluster aggregation model. It may be extended to the case of diffusion-limited chain-chain aggregation in the following way. Let us assume that the chain size remains close to its average value $\bar{k}$. This is expected to occur for large negative values of γ where monomers react first, then dimers and so on, leading to a narrow size distribution. Consider a supperlattice with lattice parameter $\bar{R}$ and N_0 monomers. There are $N_0/\bar{k}$ chains on the $(L/\bar{R})^d$ cells of the superlattice. The cell occupation probability is

$$p = (N_0/L^d)(\bar{R}^d/\bar{k}) \sim \bar{R}^{d-D}. \tag{5.1}$$

A given chain stays on the same cell during a time

$$\Delta t \sim \bar{k}^{-\gamma}\bar{R}^2 \sim \bar{R}^{2-\gamma D}. \tag{5.2}$$

During the random walk of a chain on the superlattice, another chain is encountered with probability p at each step of length $\bar{R}$. Let us assume that the two chains stick together with a probability $p(\bar{k}) \sim \bar{k}^{-\varphi}$ during the time interval Δt they spend on nearest-neighbour cells. Then the number of steps n necessary for the chain to stick is such that

$$npp(\bar{k}) \sim 1 \tag{5.3}$$

and the characteristic sticking time is

$$\bar{t} - n\Delta t \sim \Delta t/(pp(\bar{k})) \sim \bar{R}^{2-d+D(1+\varphi-\gamma)}. \tag{5.4}$$

When the length scale is changed by a factor b ($\bar{R}' = b^{-1}\bar{R}$, $\bar{k}' = b^{-D}\bar{k}$), $\bar{t}$ is rescaled by a factor b^{y_t} ($\bar{t}' = b^{y_t}\bar{t}$) with

$$y_t = d - 2 - D(1+\varphi-\gamma) \tag{5.5}$$

and the dynamic exponent z is given by

$$z = y_k/y_t = [(2-d)/D + (1+\varphi-\gamma)]^{-1}. \tag{5.6}$$

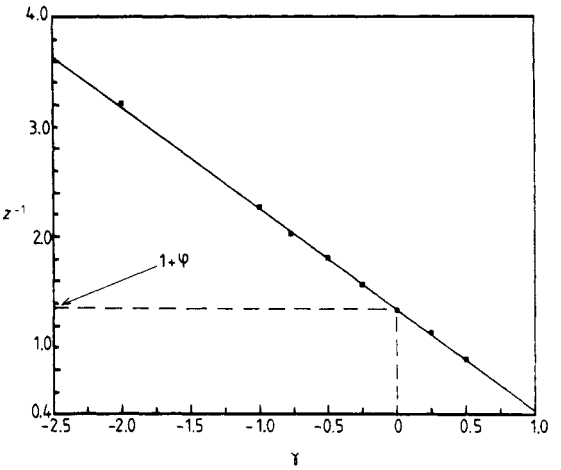

Figure 7. The inverse of the dynamic exponent z plotted against the chain mobility exponent γ. The slope of the line obtained by a least-squares fit is -0.92 and $z^{-1}(0) = 1.36$.

A linear relation between z^{-1} and γ is supported by our numerical results in the range of γ values investigated (table 1 and figure 7), the slope is near to -1 and we obtain the following estimate for the sticking probability exponent:

$$\varphi = 0.36 \pm 0.02 \tag{5.7}$$

a value which is independent of γ. During the time interval Δt (equation (5.2)) where the two chains are close together, the number of steps is $\Delta n \sim \bar{k}^{\gamma} \Delta t \sim \bar{R}^2$. Assuming that the number of times the two chains come into contact is proportional to Δn and that contacts occur between all the monomers of the two chains with the same probability, a contact will involve two end monomers with a probability proportional to $\bar{k}^{-2}$ so that we have

$$p(\bar{k}) \sim \bar{k}^{-2(1-1/D)} \tag{5.8}$$

for the sticking probability and $\varphi = 0.46 \pm 0.05$, not too far from the observed value. Surprisingly no qualitative change in the dynamics is observed for the positive values of γ studied. When $\gamma > 0$, the large chains move faster than the small ones and the aggregation process is of the particle-chain rather than of the chain-chain type. This change probably occurs at higher γ values for which unfortunately the simulations are much longer.

6. Scaling functions in the Smoluchowski theory

A mean-field description of colloidal aggregation, in which the variation of the cluster structures and the spatial fluctuations of the concentrations $n(k, t)$ are neglected, is provided by the Smoluchowski equation (Smoluchowski 1916):

$$\partial n(k, t)/\partial t = \tfrac{1}{2} \sum_{i+j=k} K(i, j) n(i, t) n(j, t) - n(k, t) \sum_{j} K(k, j) n(j, t) \tag{6.1}$$

which might be valid at and above a critical dimension $d_c = 2$ (Kang and Redner 1984, Kang *et al* 1986, Ziff *et al* 1985). The change in the k-mer concentration is equal to

the gain by combination of i- and j-mers such as $i+j=k$, minus the loss by combination of k-mers with any other j-mers. The kernel $K(i,j)$ contains all the kinetics and structural features of the model.

For symmetric homogeneous kernels

$$K(ai, aj) = a^{\lambda} K(i,j) = a^{\lambda} K(j,i) \tag{6.2a}$$

$$K(i,j) \sim i^{\mu} j^{\nu} \qquad j \gg i;\ \lambda = \mu + \nu \tag{6.2b}$$

the exponent z is given by (Botet and Jullien 1984, Kang *et al* 1986):

$$z = (1-\lambda)^{-1} \tag{6.3}$$

and the asymptotic behaviour of the scaling function $g(x)$ is known in the scaling limit (van Dongen and Ernst 1985).

For large x values, the gain term in equation (6.1) dominates and

$$g(x) = Ax^{-\lambda} \exp(-ax) \qquad x \gg 1;\ \nu < 1 \tag{6.4}$$

whereas when $x \ll 1$, depending on μ, three different classes are obtained:

$$\text{class I} \qquad \mu > 0 \qquad g(x) = Bx^{-\tau} \qquad \tau = 1+\lambda \tag{6.5a}$$

$$\text{class II} \qquad \mu = 0 \qquad g(x) = Bx^{-\tau} \qquad \tau < 1+\lambda \tag{6.5b}$$

$$\text{class III} \qquad \mu < 0 \qquad g(x) \sim \exp(-|b| x^{-|\mu|}). \tag{6.5c}$$

In classes II and III more explicit results require the knowledge of the kernel. In the Brownian aggregation of clusters the appropriate kernel is the product of a capture cross section by a diffusion coefficient for the relative motion of the clusters (Ziff *et al* 1985):

$$K_{\mathrm{cl}}(i,j) \sim (i^{1/D} + j^{1/D})^{d-2} (i^{\gamma} + j^{\gamma}). \tag{6.6}$$

This expression may be understood as follows. Consider a pair of clusters with size i and j performing a fractal random walk with dimension d_{w} on a lattice. In the reference frame where the j-mer is at rest, the jump frequency ν_{ij} (relative diffusion coefficient, Chandrasekhar (1943)) of the i-mer is $i^{\gamma} + j^{\gamma}$. The i-mer is surrounded by a sphere of influence of radius $R_{ij} = i^{1/D} + j^{1/D}$ and during a time $\mathrm{d}t$, $\nu_{ij}\,\mathrm{d}t$ steps are executed and a volume of influence $\mathrm{d}\Omega_{ij}$ is swept. This volume may be measured by covering it with non-intersecting spheres of volume R_{ij}^{d} centred on the trajectory. Each sphere contains $R_{ij}^{d_{\mathrm{w}}}$ steps so that $\nu_{ij} R_{ij}^{-d_{\mathrm{w}}}\,\mathrm{d}t$ spheres are needed and

$$\mathrm{d}\Omega_{ij}/\mathrm{d}t = \nu_{ij} R_{ij}^{d-d_{\mathrm{w}}}. \tag{6.7}$$

Equation (6.6) follows with $d_{\mathrm{w}} = 2$ for a Brownian trajectory.

For the chain-chain aggregation one must take care of the sticking probability. This may be done by introducing a homogeneous correction factor in equation (6.6):

$$K(i,j) = K_{\mathrm{cl}}(i,j) h(i,j) \tag{6.8a}$$

$$h(ai, aj) = a^{-\varphi} h(i,j) \tag{6.8b}$$

$$h(i,i) = p(i) \sim i^{-\varphi}. \tag{6.8c}$$

Then

$$\lambda = (d-2)/D + \gamma - \varphi \tag{6.9}$$

a value which is consistent with equations (6.3) and (5.6).

According to equation (6.6), when $d \geq 2$ and $j \gg i$, one obtains

$$K_{cl}(i,j) \sim j^{\gamma+(d-2)/D} \qquad \gamma \geq 0 \tag{6.10a}$$

$$K_{cl}(i,j) \sim i^{\gamma} j^{(d-2)/D} \qquad \gamma < 0 \tag{6.10b}$$

so that $\mu = 0$ when $\gamma \geq 0$, $\mu < 0$ when $\gamma < 0$ and there is a critical value of the diffusion exponent $\gamma_c = 0$ for cluster-cluster aggregation where the scaling function changes from a power law to an exponential at small x. The simulation results for $d = 3$ (Meakin *et al* 1985, Ziff *et al* 1985) are in reasonable agreement with the mean-field predictions. The situation is less clear in two dimensions where logarithmic corrections are expected.

The scaling functions for chain-chain aggregation, $f(x)$ and $g(x)$, with γ between -2.0 and 0.5 are displayed in figure 8. We have only included plots of the scaled distribution function at large times. The data collapse is reasonable for both $f(x)$ and $g(x)$ thus confirming the homogeneity assumption in equation (3.1). This automatically

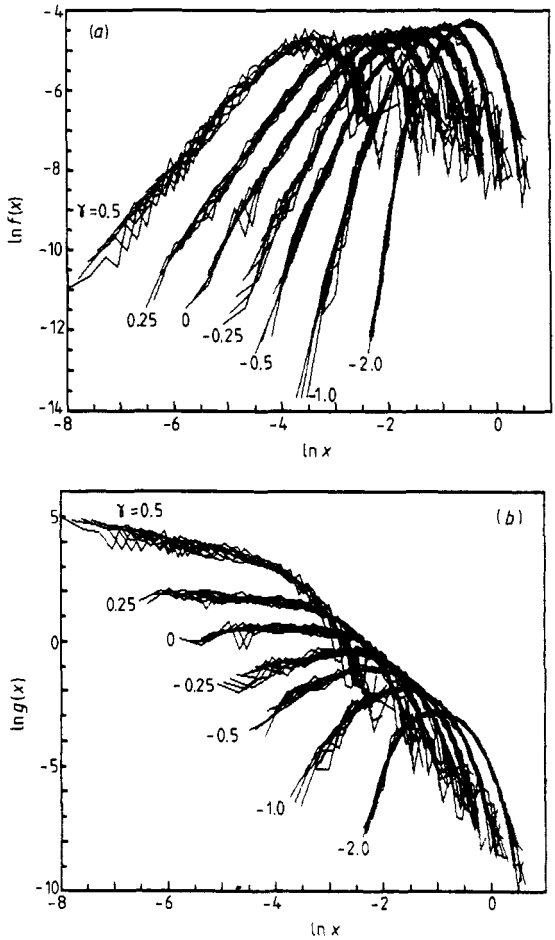

Figure 8. Plots of (*a*) $\ln f(x)$ and (*b*) $\ln g(x)$ against $\ln x$ for ten of the last times t_i ($i = 40$–49), for different values of γ. Note that $\ln f(x)$ is always bell-shaped while $\ln g(x)$ is bell-shaped only when $\gamma < 0$. In both cases the data for $k = 1$ have been discarded. For chain size $k \gg 1$, $n(k, t)$ has been averaged on a small interval centred on k.

ensures that the scaling law $w=(2-\tau)z$ is satisfied in class I or II. It appears that the scaling functions for different values of γ have a common tangent but we found no explanation for this behaviour. We verified through least-squares fits of $g(x)$ with A and a as free parameters that the behaviour at large x is consistent with equation (6.4). The values of the parameters are given in table 1. When $\gamma \geqslant 0$, $g(x)$ is always monotonic so that a power law is expected when $x \ll 1$. The fits led to the values of the exponent τ given in table 1. We always have $\tau < 1+\lambda$ corresponding to class II behaviour and also $\tau < 1$, as required when $N(t) \sim t^{-z}$. When $\gamma \leqslant 0$, on the grounds of Smoluchowski theory, a power law with $\tau < 0$ (class II) or an exponential (class III) are equally plausible. Unfortunately it was not possible to discriminate between both cases on the basis of the fits alone. However, effective τ values obtained when a power law is assumed are found to be rapidly decreasing with λ when $\gamma < 0$, whereas the variation is linear when $\gamma > 0$. This might indicate a change from class II to class III at a critical value $\gamma_c \approx 0$. The behaviour of $h(i,j)$ when $j \gg i$ governs, through the exponent μ, the dynamics of the system (class I, II or III). A simple guess would be

$$h(i,j) \sim (ij)^{-\varphi/2} \tag{6.11a}$$

for which:

$$\mu = -\varphi/2 \qquad \gamma \geqslant 0 \tag{6.11b}$$

$$\mu = \gamma - \varphi/2 \qquad \gamma < 0 \tag{6.11c}$$

i.e. $\mu < 0$ and class III behaviour for all the values of γ, in contradiction with the simulation results. Taking

$$h(i,j) \sim (i^{\varphi} + j^{\varphi})^{-1} \tag{6.12a}$$

gives

$$\mu = 0 \qquad \gamma \geqslant 0 \qquad \text{class II} \tag{6.12b}$$

$$\mu = \gamma \qquad \gamma < 0 \qquad \text{class III} \tag{6.12c}$$

in agreement with the simulations. But this choice is only an *ad hoc* assumption and a numerical study of the kernel is needed to clarify this point.

7. Conclusion

The dynamics of chain-chain aggregation is qualitatively similar to that of cluster-cluster aggregation. The evolution of the size distribution function with the mobility exponent γ is comparable, changing from monodisperse to polydisperse when γ increases. The case of chains moving through reptation (Debierre and Turban 1987b) corresponds to $\gamma = -1$, i.e. to a monodisperse distribution. The main difference with cluster-cluster aggregation is that the process is both diffusion and reaction limited since two chains do not stick at each contact but have to look for their tips before they stick. This may be taken into account by the introduction of a sticking probability $h(i,j)$ which is homogeneous of degree $-\varphi$, where the sticking exponent φ is found to be independent of γ.

The evolution of the scaling functions $f(x)$ and $g(x)$ with the mobility exponent γ has been analysed in the framework of the Smoluchowski theory. The kernel appropriate for cluster-cluster aggregation must be changed by the factor $h(i,j)$ for

the sticking probability which is not explicitly known. Since logarithmic corrections to the Smoluchowski theory might affect the dynamics in two dimensions, we intend to study the kernel in three dimensions.

The dynamics of chain–chain aggregation in three dimensions has been studied and will be published soon. The influence of d_w, the fractal dimension of the chain motion, will be examined in a study of ballistic aggregation which is beginning. Finally let us mention that in real polycondensation reactions the chain may not stick indifferently at both ends; only specific reactions between functional end groups are allowed and the dynamics is affected (Leyvraz and Redner 1986). Results in this direction have also been obtained.

References

Botet R and Jullien R 1984 *J. Phys. A: Math. Gen.* **17** 2517
Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
Debierre J-M and Turban L 1987a *J. Phys. A: Math. Gen.* **20** L259
—— 1987b *J. Phys. A: Math. Gen.* **20** 4457
Friedlander S K 1977 *Smoke, Dust and Haze: Fundamentals of Aerosol Behaviour* (New York: Wiley)
Herrmann H J 1986 *Phys. Rep.* **136** 153
Jullien R and Botet R 1987 *Aggregation and Fractal Aggregates* (Singapore: World Scientific)
Kang K and Redner S 1984 *Phys. Rev.* A **30** 2833
Kang K, Redner S, Meakin P and Leyvraz F 1986 *Phys. Rev.* A **33** 1171
Kolb M 1984 *Phys. Rev. Lett.* **53** 1653
Kolb M, Botet R and Jullien R 1983 *Phys. Rev. Lett.* **51** 1123
Leyvraz F and Redner S 1986 *Phys. Rev. Lett.* **57** 163
Meakin P 1983 *Phys. Rev. Lett.* **51** 1119
Meakin P, Vicsek T and Family F 1985 *Phys. Rev.* B **31** 564
Smoluchowski M 1916 *Z. Phys.* **17** 585
van Dongen P G J and Ernst M H 1985 *Phys. Rev. Lett.* **54** 1396
Vicsek T and Family F 1984 *Phys. Rev. Lett.* **52** 1669
Ziff R M, McGrady E D and Meakin P 1985 *J. Chem. Phys.* **82** 5269