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## Static and dynamic scaling for ‘free-reptation’-limited chain–chain aggregation in two dimensions

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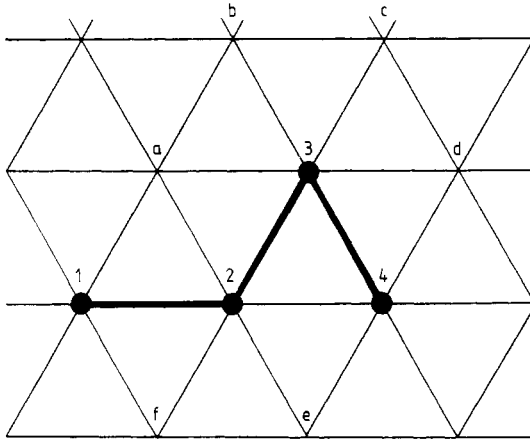
**Abstract.** Chain–chain aggregation is studied by Monte Carlo simulations on the triangular lattice.  $N$ -conserving local deformations lead to snake-like motion or ‘free reptation’ of the aggregating chains. The scaling of the chain-size distribution function is carefully examined and estimates of the static and dynamic exponents are obtained.

The dynamics of an isolated polymer chain in solution has been extensively studied using lattice models and Monte Carlo algorithms with local  $N$ -conserving deformations of the chain (Verdier and Stockmayer (1962), for a recent review see Caracciolo and Sokal (1986)). These rules lead to a snake-like motion of the chain which may be termed ‘free reptation’ since ‘reptation’ is reserved to describe the motion of a chain through a set of fixed obstacles (de Gennes 1971, Doi and Edwards 1978). These models simulate the dynamics of a chain in a good solvent in the ‘free draining’ limit where hydrodynamic interactions are ignored.

In a recent work (Debierre and Turban 1987a) a chain–chain aggregation model has been studied, in which each chain was allowed to move as a whole at random, i.e. we considered the aggregation of rigid chains in Brownian motion. The purpose of this paper is to extend this work to the case where the dynamics of the aggregation of deformable chains is controlled by the free-reptation process.

We have performed 50 Monte Carlo simulations on a  $L \times L$  two-dimensional lattice ( $L = 256$ ) with periodic boundary conditions in the low density limit ( $\rho = 0.0153$ ). We use the pure one-bead moves shown in figure 1, working on a triangular lattice (on the square lattice with the corresponding rules each bead remains indefinitely on the same sublattice and aggregation is hindered at long times). At each Monte Carlo step a bead is randomly selected and the time is incremented by  $\Delta t = 1/N_0$  where  $N_0$  is the number of monomers at  $t = 0$  ( $N_0 = 1000$ ). A move is then chosen at random among the ones allowed by the local configuration of the chain. This move is executed when the final configuration satisfies the excluded volume condition with at most one monomer per site. When an end bead is moved, the first-neighbour sites of its new location are examined and when one of them is occupied by another chain end bead, the two chains stick. We do not allow the formation of rings. In the case of rigid chains this restriction had no marked influence on the scaling properties. We intend to study this point later for reptating chains. The time evolution of a sample is illustrated in figure 2.

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**Figure 1.** A four-site chain (bold line) on the triangular lattice. Bead 2 is allowed to jump to site a and bead 3 to site e. End bead 4 may jump to sites a, b, c and d but not to site 2 which is already occupied. For end bead 1, jumps to sites a, e and f are allowed and jumps to sites 3 and 4 are not.

We first re-examine the scaling of the cluster-size distribution function (Kolb 1984, Vicsek and Family 1984, Meakin *et al* 1985). Let  $N(s, t)$  be the number of  $s$ -site chains at time  $t$ , then the chain-size distribution function is defined as

$$n(s, t) = N(s, t)/L^2. \tag{1}$$

Assuming that it is a generalised homogeneous function of  $s$  and  $t$ , one may write

$$n(b^{y_s}s, b^{y_t}t) = b^{y_n}n(s, t). \tag{2}$$

Taking successively  $b = s^{-1/y_s}$  and  $b = t^{-1/y_t}$ , one obtains

$$n(s, t) = s^{-\theta}f(s/t^z) \tag{3a}$$

$$n(s, t) = t^{-\theta z}g(s/t^z) \tag{3b}$$

where the notations  $z = y_s/y_t$  and  $\theta = -y_n/y_s$  have been used (Meakin *et al* 1985). The scaling functions behave as

$$f(x) \sim x^\delta \quad g(x) \sim x^\epsilon \quad x \ll 1 \tag{4a}$$

$$f(x) \ll 1 \quad g(x) \ll 1 \quad x \gg 1 \tag{4b}$$

so that  $n(s, t) \sim s^{-\tau}t^{-w}$  when  $x \ll 1$  with

$$\tau = \theta - \delta = -\epsilon \tag{5a}$$

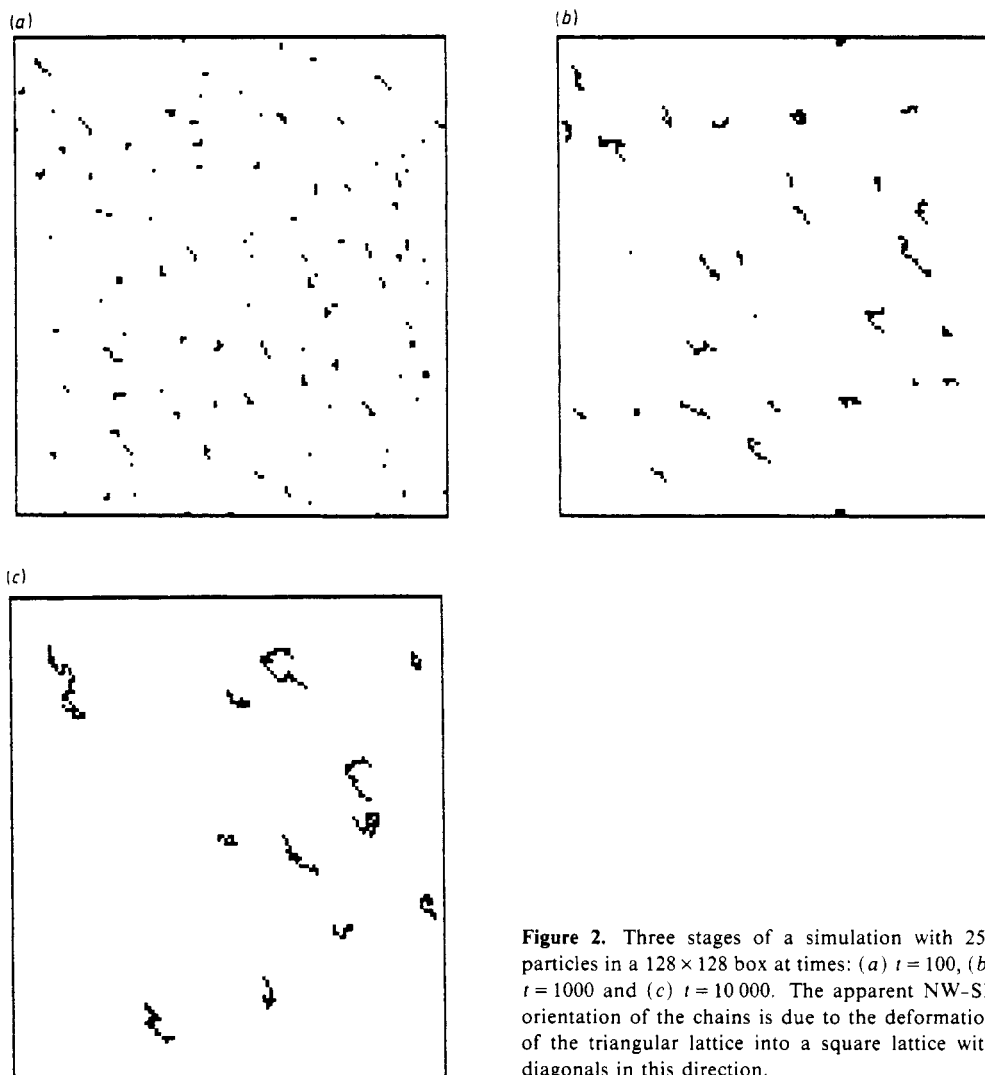
$$w = z\delta = (\theta + \epsilon)z. \tag{5b}$$

This leads to the scaling law:

$$w = (\theta - \tau)z. \tag{6}$$

The  $m$ th moment of the distribution function

$$M_m(t) = \sum_{s=1}^{\infty} s^m n(s, t) \tag{7}$$



**Figure 2.** Three stages of a simulation with 250 particles in a  $128 \times 128$  box at times: (a)  $t = 100$ , (b)  $t = 1000$  and (c)  $t = 10\,000$ . The apparent NW-SE orientation of the chains is due to the deformation of the triangular lattice into a square lattice with diagonals in this direction.

behaves as

$$M_m(t) \sim a_m t^{z(m+1-\theta)} + b_m t^{z(\tau-\theta)} \quad (8)$$

at large times. The first moment  $M_1(t)$  gives the particle density which is time independent so that

$$\begin{aligned} \theta = 2 & & \tau < 2 \\ \theta = \tau & & \tau > 2. \end{aligned} \quad (9)$$

When  $\tau > 2$ , one gets  $\delta = 0$  and  $w = 0$ , i.e. the distribution is static. This corresponds to the case of percolation clusters (Herrmann 1986). For the aggregation process  $\theta = 2$  and  $\tau < 2$  (Vicsek and Family 1984), a result which is supported by all the available simulation results.

The number of chains at time  $t$ ,  $N(t)$ , is proportional to the moment of order zero of the chain-size distribution function so that, according to equations (6) and (8),

$$N(t) \sim t^{-z} \quad \tau < 1 \quad (10a)$$

$$N(t) \sim t^{-w} \quad \tau > 1. \quad (10b)$$

The mean chain size  $S(t) = M_2(t)/M_1(t)$  grows as

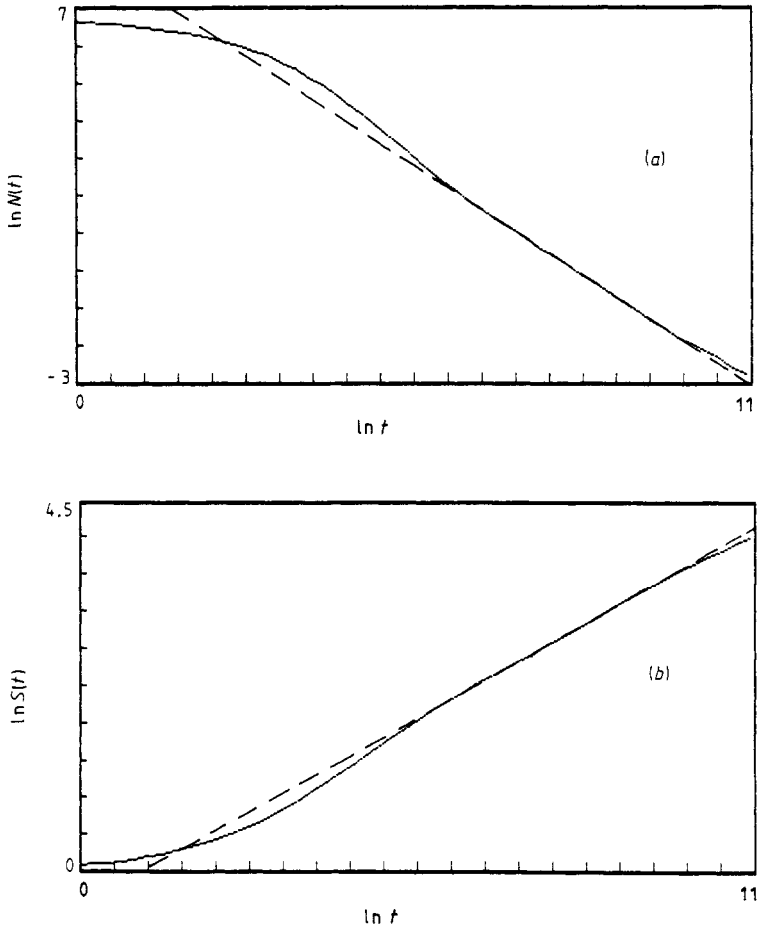
$$S(t) \sim t^z. \quad (11)$$

From the plots of  $\ln N(t)$  and  $\ln S(t)$  as functions of  $\ln t$  (figure 3), we obtain

$$z = 0.43 \pm 0.02. \quad (12)$$

Let  $\bar{R}(t)$  be the mean radius of gyration of the chains at time  $t$ , then the fractal dimension of the chains is such that

$$S(t) \sim \bar{R}(t)^D. \quad (13)$$



**Figure 3.** (a)  $\ln N(t)$  and (b)  $\ln S(t)$  as a function of  $\ln t$ . The slope of the straight part is, respectively,  $-z = -0.43 \pm 0.02$  and  $z = 0.42 \pm 0.02$ .

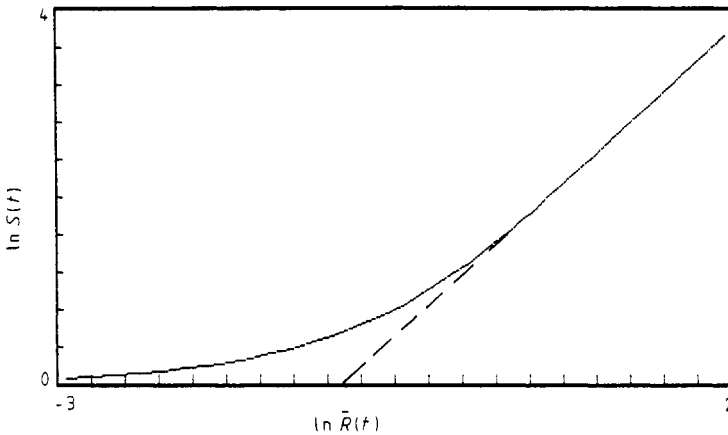


Figure 4.  $\ln S(t)$  as a function of  $\ln \bar{R}(t)$ . The straight line has a slope  $D = 1.30 \pm 0.04$ .

From the log-log plot of  $S(t)$  against  $\bar{R}(t)$  (figure 4) we deduce

$$D = 1.30 \pm 0.04 \tag{14}$$

a value which may be compared to  $D = 1.32 \pm 0.04$  obtained for Brownian chain-chain aggregation (Debierre and Turban 1987a) and to  $D = 1.29 \pm 0.01$  for particle-chain aggregation (Bradley and Kung 1986, Debierre and Turban 1986). The fractal dimension of the self-avoiding walk  $D_{SAW} = \frac{4}{3}$  is close to these values although it falls outside the confidence interval in the case of particle-chain aggregation.

Let us now consider the chain-size distribution function itself. At different times  $t_i$  or different sizes  $s_i$ , equations (3a) and (3b) with  $\theta = 2$  lead to

$$\ln n(s, t_i) = -2 \ln s + \ln f(s/t_i^2) \tag{15a}$$

$$\ln n(s_i, t) = -2z \ln t + \ln g(s_i/t^z). \tag{15b}$$

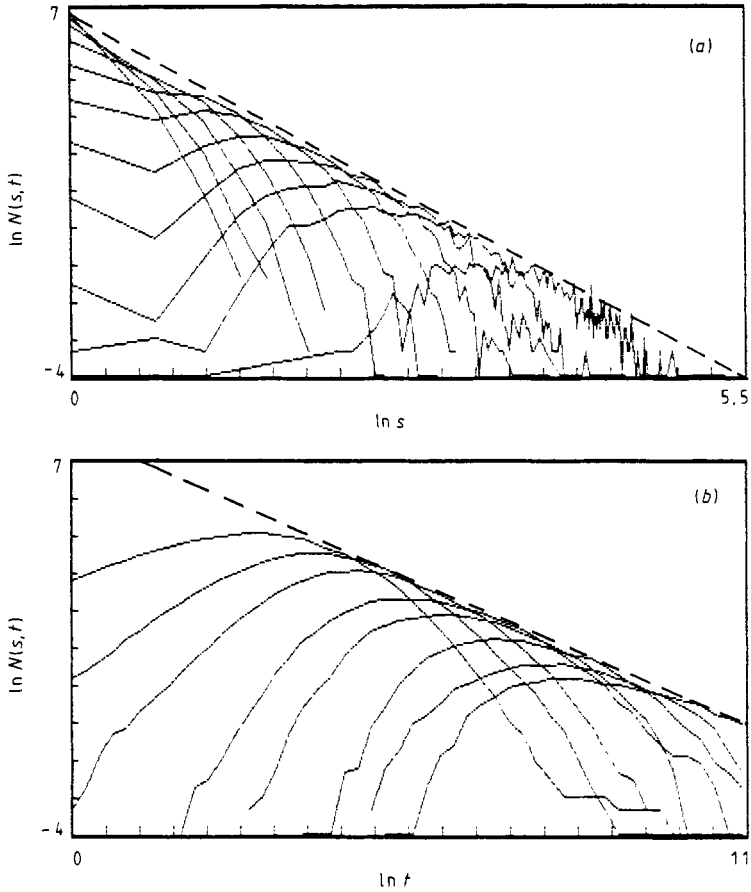
According to equations (4) and (5),  $f(x)$  always has a maximum  $f_{\max}$  for some intermediate value  $x = x_f$  since  $\tau < 2$ , whereas  $g(x)$  has a maximum  $g_{\max}$  for  $x = x_g$  only when  $\tau < 0$ . Then one may write

$$\ln n(s, t_i) + 2 \ln s - \ln f_{\max} = \ln (f(s/t_i^2)/f_{\max}) \tag{16a}$$

$$\ln n(s_i, t) + 2z \ln t - \ln g_{\max} = \ln (g(s_i/t^z)/g_{\max}). \tag{16b}$$

It follows that the curves  $\ln n(s, t_i)$  against  $\ln s$  have a common tangent with slope  $-2$ , each curve being in contact with the envelope when  $\ln s = \ln(x_f t_i^2)$ . The same is true for  $\ln n(s_i, t)$  against  $\ln t$  when  $\tau < 0$ . The slope of the envelope is then  $-2z$  and the contacts occur when  $\ln t = \ln[(s_i/x_g)^{1/z}]$ . This is just the behaviour displayed in figure 5 where the slopes of the envelopes are very near to the expected values. It follows that  $\tau < 0$ .

An anomalous behaviour is observed for  $s = 1$  (figure 5(a)). This may be traced to the fact that with our Monte Carlo algorithm the diffusivity and the sticking probability are lower for monomers than for dimers.



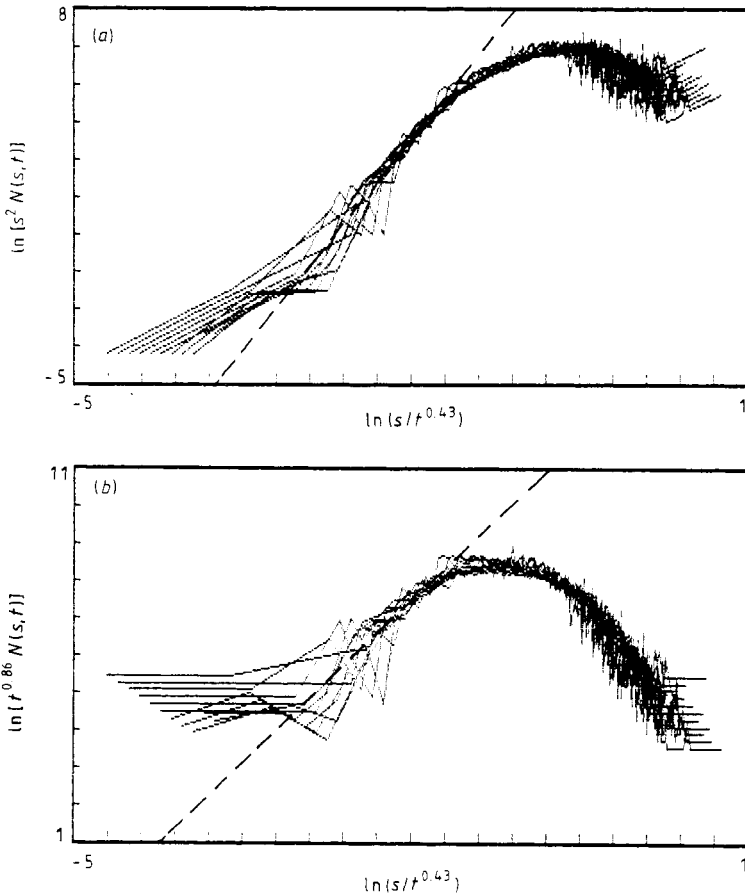
**Figure 5.** (a)  $\ln N(s, t)$  plotted against  $\ln s$  at times  $t = 2, 5, 12, 28, 69, 169, 414, 1010, 2465, 6018, 56\,052$ . The slope of the envelope is  $-1.92$  (to be compared to  $-2$ ) and it intersects the vertical axis at a value close to  $\ln f_{\max}$  as expected. (b)  $\ln N(s, t)$  plotted against  $\ln t$  for  $s = 2, 3, 4, 6, 8, 12, 16, 20$ . The envelope has a slope equal to  $-0.83$  ( $-2z \approx -0.86$ ).

The exponents  $\tau$  and  $w$  may be estimated from the behaviour of a single curve for small  $s/t^z$  values. One expects from equations (3)–(5) that for long times the curve  $\ln n(s, t)$  against  $\ln s$  has a slope  $-\tau$  on the small  $s$  side. In the same way, the curve  $\ln n(s, t)$  against  $\ln t$  on the large  $t$  side has a slope  $-w$ . The anomalous behaviour for small  $s$  values makes this direct determination of  $\tau$  and  $w$  difficult (figure 5), but it is possible to estimate these exponents from the scaling functions  $f(x)$  and  $g(x)$  shown in figure 6 where we have plotted  $\ln(s^2 N(s, t))$  against  $\ln x$  and  $\ln(t^{2z} N(s, t))$  against  $\ln x$  for different sizes and times. Following equation (3),  $\tau$  has been estimated from the size dependence of  $f(x) \sim x^{2-\tau}$  and  $w$  from the time dependence of  $g(x) \sim x^{w/z-2}$  at small  $x$ , and we obtain

$$\tau = -2.9 \pm 0.7 \tag{17}$$

$$w = 2.1 \pm 0.3 \tag{18}$$

in agreement with the scaling law (equation (6)).



**Figure 6.** Log-log plots at times between  $t = 6018$  and  $t = 56\,052$ . (a) The scaling function  $f(x)$  against  $x$ . For  $x \ll 1$ , the slope of the straight line is roughly equal to 4.9 so that  $\tau = -2.9 \pm 0.7$ . This function exhibits a maximum  $f_{\max}$  as predicted by the scaling analysis. (b)  $g(x)$  against  $x$  (since  $\tau < 0$ ,  $g$  has a maximum). For small  $x$  values, one obtains  $w = 2.1 \pm 0.3$ .

A dynamic scaling theory has been developed for cluster-cluster aggregation when the clusters are in Brownian motion with a size-dependent diffusion coefficient proportional to  $s^\gamma$  (Kolb 1984, Botet and Jullien 1984). The exponent  $z$  is given by

$$z = [1 - \gamma - (d - 2)/D]^{-1}. \tag{19}$$

We have recently studied a two-dimensional chain-chain aggregation model in which rigid chains perform a random walk on the lattice, with a size-dependent diffusion coefficient (Debierre and Turban 1987b). Assuming that during the time interval  $\Delta t \sim \bar{R}^2 s^{-\gamma}$  where two chains remain close to each other, they stick with a probability  $p_s \sim s^{-\varphi}$ , equation (19) becomes

$$z = [1 - \gamma + \varphi - (d - 2)/D]^{-1}. \tag{20}$$

Our results with  $\gamma$  in the range  $-2 < \gamma < 0.5$  are in good agreement with equation (20) and we obtain  $\varphi = 0.36$ . Since the centre of mass of a free-reptating chain is in Brownian



motion for long times (Caracciolo and Sokal 1986) with a diffusion coefficient varying as a power of the chain size  $s$ , if the sticking exponent  $\varphi$  is assumed to be the same as for rigid chains, then the value  $z=0.43$  obtained for the free-reptation model corresponds to a  $s^{-1}$  variation of the chain diffusion coefficient. This is the behaviour conjectured in the free-draining limit (de Gennes 1972, Caracciolo and Sokal 1986) and observed in recent simulations (Naghizadeh and Kovac 1986).

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