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Search for universality in the computer simulations of reaction-limited colloid aggregation II: Concentration effects

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Abstract. Computer simulations of reaction-limited colloid aggregation are performed to try to obtain the universal behaviour observed by experimentalists. In a previous communication the effects of reducing the sticking probability were analysed. In this report, the effects of a reduction in concentration together with a reduction in sticking probability are studied, reaching concentrations as low as 0.001 in volume fraction and sticking probabilities ten times smaller than those used by other authors. We still observe the universal behaviour only at the beginning of the aggregation process.

1. Introduction

In a previous communication by the author (González 1992) an effort was started to study the reaction-limited colloid aggregation process, via computer simulations, to try to match the results with the universal ones found in a growing number of experiments. In reaction-limited colloid aggregation (RLCA), as opposed to diffusion-limited colloid aggregation (DLCA), there have been serious discrepancies between three-dimensional simulations and experiments. Basically, the experimental outcomes yield the following three essential results: (a) The fractal dimension of the clusters ranges between 2.0 and 2.2, with a typical value being around 2.1. This fractal dimension is perhaps the only quantity for which there is a reasonably good agreement between experiments and simulations. (b) The weight-average cluster size $S(t)$ grows exponentially with time according to most workers (Weitz *et al* 1985, Lin *et al* 1989, 1990, Martin *et al* 1990); however, Broide and Cohen (1990) find that the exponential growth occurs only at the initial stages of the aggregation, crossing over to an algebraic growth at later times. (c) The cluster size distribution function $N_s(t)$ decreases monotonically with the exponent τ: $N_s(t) \sim s^{-\tau} g(s/S(t))$, where g is a cutoff function that decays rapidly to zero for values of the argument greater than one, and takes the value one for arguments smaller than one. The majority of researchers (von Schultess *et al* 1980, Bowen *et al* 1984, Weitz *et al* 1985, Lin *et al* 1989, 1990, Broide and Cohen 1990) agree on values for τ close to 1.5, but some others (Martin 1987, Rarity 1987, Rarity *et al* 1989) have obtained values near 2.

The only theory known to the author (Ball *et al* 1987) for RLCA is based on the Smolochowski equation, and results also in $\tau = 1.5$ and an exponential growth of the mean cluster size. The computer simulations in three dimensions (Family *et al* 1985, Meakin and Family 1987, 1988), in contrast, have yielded a number of exponents τ

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that do not coincide with the value 1.5, and in many of the cases their values were varying with time. Also, it was not possible to fit the curves for the weight-average cluster size either to a power law or to an exponential, over the whole range of the aggregation time. To do the simulations, however, Meakin and Family (1987, 1988) mostly use the models of Brown and Ball (1985) and Leyvraz (unpublished), that are related to RLCA but that do not correspond to the original RLCA algorithm—defined here as the DLCA algorithm plus a very small bonding probability at each collision between colloidal particles—although they sometimes use the original RLCA algorithm. In their version of the Brown and Ball model, clusters on a cubic lattice are randomly selected and moved according to the values of their diffusion constants. Each selected cluster is moved with equal probability to any set of unoccupied lattice sites in the system. If, in the new position, the cluster happens to be adjacent to another cluster(s) in the system, the clusters are combined to form a new cluster and so on. Their version of the Leyvraz model simulates RLCA in the zero density limit. Here, one works with a collection of clusters; two particles belonging to different clusters are randomly selected, with a probability proportional to the sum of the diffusion coefficients of the corresponding clusters, and brought into contact with each other. If no overlap occurs between the two clusters, they are merged and the resulting cluster is returned to the collection, taking the place of the two original clusters. These models were mainly introduced to reduce the computing time, which becomes prohibitively long for low sticking probabilities. No matter how plausible the two models appear, no-one has shown them to exactly coincide with the original RLCA algorithm defined above, which most faithfully resembles the experimental aggregation.

2. The model

The intention of this series of publications is to reconsider the RLCA problem via computer simulations, using different versions of the original RLCA algorithm. In the first communication (González 1992) the emphasis was put on lowering the sticking probability as much as possible. The concentration was kept, however, at a relatively high value (0.01 of volume fraction), for which the truly asymptotic behaviour of RLCA may not show up. In the present communication, the emphasis will be on lowering both the concentration and the sticking probability, as much as the computing time permits. For a short description of the model used, consider a three-dimensional cubic lattice with periodic boundary conditions, where at some intermediate time a collection of clusters made of nearest-neighbour lattice cells diffuses randomly. Pick one of the clusters at random and move it by one lattice unit in a random direction, only if a random number X uniformly distributed in the range $0<X<1$ satisfies the condition $X<D(s)/D_{\max}$, where $D(s)\sim s^{-1/D}$ is the diffusion coefficient for the selected cluster of size s, and $D_{\max}$ is the maximum diffusion coefficient for any cluster in the system. Here $D=2.1$ is the accepted value for the fractal dimension of RLCA clusters. After each cluster has been selected the time is incremented by $1/(N_c D_{\max})$, where N_c is the number of clusters in the system at that time, whether or not the cluster is actually moved. If the cluster attempts to move into the lattice cells occupied by another cluster (signifying an encounter), the move is not permitted and the moving cluster either sticks (and is merged) to the other with a small probability P_o or remains side by side with the other with probability $1-P_o$. A difference between this mode and other

aggregation models that use the original RLCA algorithm (Family *et al* 1985, Meakin and Family 1987, 1988) is that here a test for sticking is done after each collision between colloidal particles and not just after the two clusters become adjacent. Therefore, as for the sticking probability is concerned, this model is equivalent to those other models but with a value of their sticking probability of roughly P_o divided by 5 (González 1992). Three values of the volume fraction ρ were used: 0.01, 0.003 and 0.001. For each of the concentrations, seven values of the sticking probability P_o were employed: 0.5, 0.1, 0.05, 0.01, 0.005, 0.001 and 0.0005 (we recall that 0.5 corresponds to 0.1 in the other models, and may still show some features of RLCA). Finally, two simulations were done for each case, just to check for reproducibility. The number of initial particles used were 40 960, 24 000 and 13 144 for ρ equal to 0.01, 0.003 and 0.001, respectively. The simulations were stopped when a cluster reached a maximum size of 2000 ($\rho=0.01$), 1600 ($\rho=0.003$) and 1500 ($\rho=0.001$). Each of the $P_o=0.0005$ simulations with ρ equal to 0.01, 0.003 and 0.001 took roughly 27 h, 53 h and 84 h of a Cray Y-MP processor, respectively.

3. Results

In table 1 are shown the values of the fractal dimension, obtained from a least squares fitting of the log–log data for the radius of gyration versus size, for the 42 runs mentioned. All the errors (in parentheses) correspond to twice the standard deviation. From the table we see that the fractal dimension appears to approach its asymptotic value of around 2.1, with higher sticking probabilities if the concentration is low ($P_o=0.01$ for $\rho=0.001$), while it does so only with a lower sticking probability for higher concentrations ($P_o=0.005$ for $\rho=0.01$). However, it is difficult to state this conclusively due to the higher scattering of the data for lower concentrations, which is a consequence of having used less particles.

In figures 1, 2 and 3 are shown the $\ln N_s$ versus $\ln s$ curves at different times for six of the cases mentioned. In figure 1 are drawn two $\rho=0.01$ cases ($P_o=0.0005$ and $P_o=0.5$), in figure 2 we see two $\rho=0.003$ cases (again $P_o=0.0005$ and $P_o=0.5$), while in figure 3 are shown the corresponding two $\rho=0.001$ cases. We see on all of them that, after some transient time, the curves start to develop an initial slope (curves c).

Table 1.

				$\rho=0.01$			
P_o	0.5	0.1	0.05	0.01	0.005	0.001	0.0005
1st run	1.89(0.04)	1.97(0.04)	2.01(0.03)	2.04(0.04)	2.14(0.04)	2.11(0.04)	2.12(0.04)
2nd run	1.85(0.04)	1.94(0.04)	2.02(0.04)	2.01(0.04)	2.16(0.04)	2.05(0.04)	2.16(0.04)
				$\rho=0.003$			
P_o	0.5	0.1	0.05	0.01	0.005	0.001	0.0005
1st run	1.87(0.05)	1.89(0.05)	2.09(0.06)	2.12(0.05)	2.06(0.04)	2.10(0.04)	2.05(0.05)
2nd run	1.83(0.04)	1.99(0.04)	2.01(0.05)	2.02(0.04)	1.99(0.04)	2.17(0.05)	1.95(0.06)
				$\rho=0.001$			
P_o	0.5	0.1	0.05	0.01	0.005	0.001	0.0005
1st run	1.94(0.06)	2.00(0.05)	2.01(0.05)	2.09(0.06)	2.23(0.06)	2.16(0.06)	2.02(0.06)
2nd run	1.80(0.06)	1.93(0.05)	1.88(0.05)	2.09(0.04)	2.10(0.06)	2.15(0.06)	2.05(0.08)

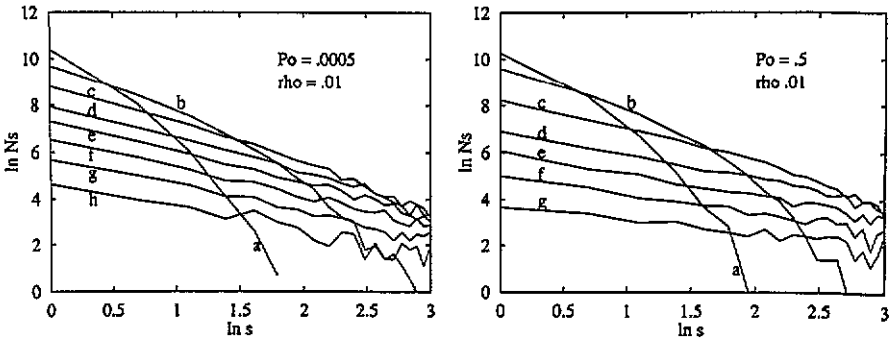

Figure 1. A log–log plot of the cluster size distribution versus size for different times, corresponding to $P_o = 0.0005$ (left) and to $P_o = 0.5$ (right), both for $\rho = 0.01$. The times of the different curves on the left are: (a) 22 026, (b) 109 098, (c) 242 802, (d) 400 312, (e) 540 365, (f) 729 416, (g) 984 609 and (h) 1 329 083, while those of the curves on the right are: (a) 45, (b) 148, (c) 446, (d) 898, (e) 1339, (f) 1998 and (g) 2981.

However, this slope (minus the exponent τ) diminishes with time for all the runs mentioned. For all cases on the left of the figures ($P_o = 0.0005$) the starting slopes are around -1.5, while the final slopes (curves g and h) are around -1 (but of course, this final slope depends on the point at which the simulation is stopped). For the cases on the right ($P_o = 0.5$) the initial slopes are around -1.2, -1.2 and -1.3 for ρ equal to 0.01, 0.003 and 0.001, respectively, while the final ones (curves g) are around -0.5, -0.8 and -0.6, also respectively. For the remaining values of P_o the situation is intermediate: in most of the cases—except for $P_o = 0.1$ and 0.5—the starting exponent τ is around 1.5 while it drops below one during the aggregation process. All the slopes after the initial ones were obtained with a least squares fitting of the data.

In figures 4, 5 and 6 are shown, on the left, the ln $(S(t))$ versus ln (t) curves for the 21 cases mentioned, while on the right, we see the corresponding ln $(N_c(t))$ versus ln (t) curves, where $N_c(t)$ is the number of clusters at time t. In all cases $S(t)$ appears to grow exponentially initially, while it grows as a power law at later times: $S(t) \sim t^z$. The exponent z depends both on P_o and ρ, but for values of P_o that correspond to RLCA (that is, that give a fractal dimension ~ 2.1) it stays at around 2.7 for $\rho = \pm 0.01$, at around 2.5 for $\rho = 0.003$ and at around 2.4 for $\rho = 0.001$. This last value of z must

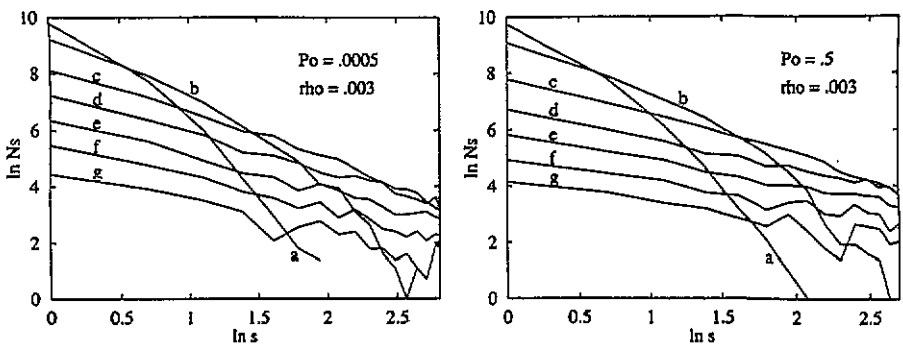

Figure 2. As in figure 1, corresponding this time to $\rho = 0.003$. The times of the different curves on the left are now: (a) 109 098, (b) 327 748, (c) 890 911, (d) 1 468 864, (e) 2 191 288, (f) 2 957 929 and (g) 3 992 787, while the times of the curves on the right are: (a) 148, (b) 493, (c) 1480, (d) 2697, (e) 4024, (f) 6003 and (g) 8103.

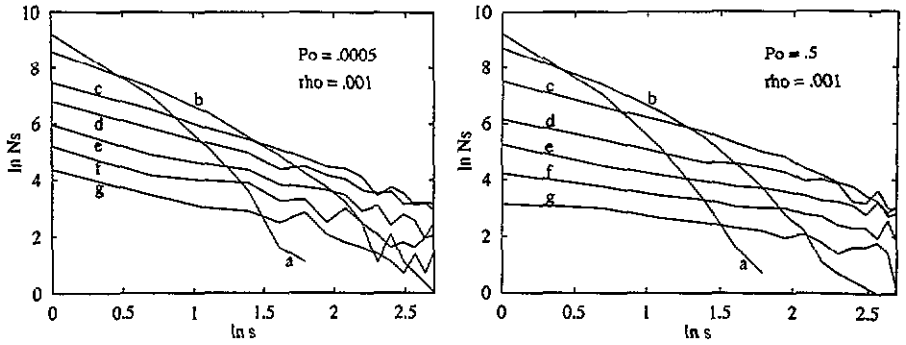

Figure 3. As in figure 1, corresponding now to $\rho = 0.001$. The times of the curves on the left are: (a) 268 337, (b) 984 609, (c) 2 676 445, (d) 3 992 787, (e) 5 956 538, (f) 8 040 485 and (g) 10 853 520, while those of the curves on the right are in this occasion: (a) 330, (b) 1097, (c) 3641, (d) 8103, (e) 12 088, (f) 18 034 and (g) 26 093.

approach the asymptotic one (that is, for low P_o and low ρ) of this version of RLCA. We notice that the limiting slopes of the ln $(N_c(t))$ curves are roughly the negatives of the ln $(S(t))$ curves. This indicates that in this version of RLCA $S(t) \sim S_n(t)$ for the later times, where $S_n(t)$ is the number average cluster size.

Finally, in figures 7, 8 and 9 are shown the ln $(S(t))$ versus t and the ln $(N_c(t))$ versus t curves, plotted in order to check that the initial growth is really exponential. In figure 7 two $\rho = 0.01$ cases are considered: $P_o = 0.0005$ and 0.1, while in figure 8 two $\rho = 0.003$ cases are shown: again $P_o = 0.0005$ and 0.1, ending, in figure 9, with the corresponding two $\rho = 0.001$ cases. For the figures on the left ($P_o = 0.0005$) we see that $S(t)$ starts to grow exponentially with t, but only for a small fraction of the aggregation time. However, for the figures on the right—with $P_o = 0.1$—this fraction of time becomes even smaller. For values of P_o between 0.0005 and 0.1, the situation was intermediate. It was interesting to check, in all cases, that the initial slope for the ln $S(t)$ curves was roughly twice the negative of the initial slope for ln $N_c(t)$. This indicates that, initially, $S(t) \sim S_n(t)^2$. All this is in agreement with the theoretical

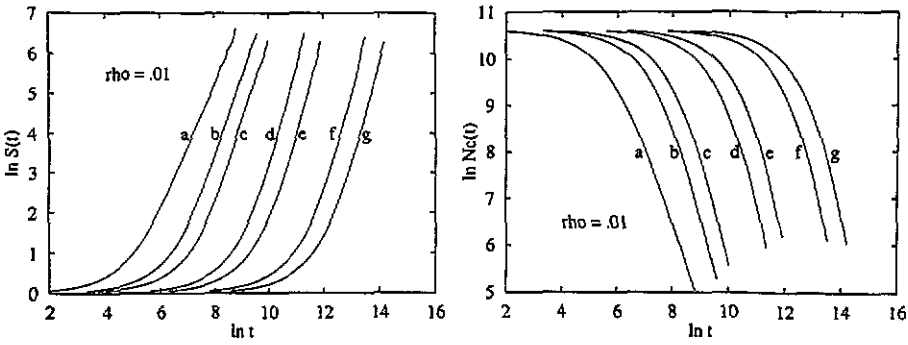

Figure 4. Left: A log–log plot of the weight-average cluster size as a function of time. Right: A log–log plot of the number of clusters versus time. The different curves correspond to the sticking probabilities (a) 0.5, (b) 0.1, (c) 0.05, (d) 0.01, (e) 0.005, (f) 0.001 and (g) 0.0005, and all of them are for $\rho = 0.01$. The limiting slopes of the weight-average cluster size curves are (a) 1.6, (b) 2.0, (c) 2.1, (d) 2.6, (e) 2.6, (f) 2.8 and (g) 2.7, while those corresponding to the curves for the number of clusters are (a) −1.8, (b) −2.1, (c) −2.4, (d) −2.4, (e) −2.6, (f) −2.7 and (g) −2.8.

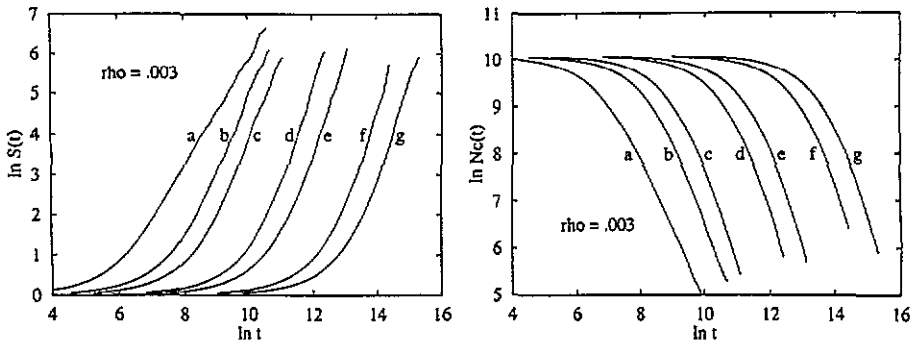

Figure 5. As in figure 4, this time for $\rho = 0.003$. The limiting slopes of the curves for the weight-average cluster size are now (a) 1.3, (b) 1.8, (c) 1.9, (d) 2.6, (e) 2.3, (f) 2.5 and (g) 2.5, while those corresponding to the curves for the number of clusters are (a) −1.5, (b) −1.9, (c) −2.1, (d) −2.2, (e) −2.2, (f) −2.4 and (g) −2.4.

results (Taylor and Sorensen 1987, Broide 1988) that if $1<\tau<2$, then $S(t)\sim(S_n(t))^{1/(2-\tau)}$, while if $\tau<1$, then $S(t)\sim S_n(t)$. If initially, $\tau=1.5$, then $S(t)\sim S_n(t)^2$, while if at the end, τ goes below one, then $S(t)\sim S_n(t)$.

We now briefly summarize the main results of the simulations: (1) The fractal dimension indeed reaches the value of around 2.1 for low enough values of the sticking probability, independently of the volume fraction ρ used ($0.001<\rho<0.01$). (2) After some transient time, the log–log plots of the cluster size distribution function versus size start to develop a straight line. However, the slope (minus the exponent τ) diminishes with time for all cases considered ($0.001<\rho<0.01$), initially being around −1.5 for low bonding probabilities. (3) For low sticking probabilities, the weight- and number-average cluster sizes start increasing exponentially with time in all cases considered ($0.001<\rho<0.01$), but only for a small fraction of the whole aggregation time. However, for higher bonding probabilities, this fraction of time becomes even smaller. In all cases considered, there was a crossover to a power law growth for later times, with the asymptotic value of the exponent z—that is, for sticking probabilities within the RLCA limit—depending on concentration. It was found, in all cases, that at the beginning $S(t)\sim S_n(t)^2$, while at the end $S(t)\sim S_n(t)$.

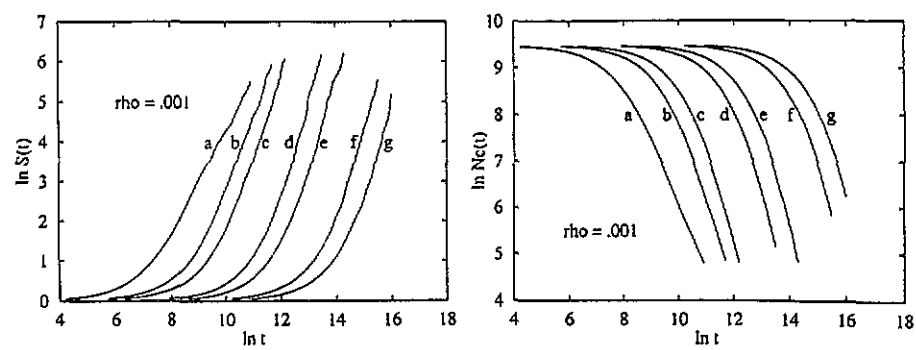

Figure 6. As in figure 4, now for $\rho = 0.001$. The limiting slopes of the curves for the weight-average cluster size are in this case (a) 1.3, (b) 1.8, (c) 2.0, (d) 2.5, (e) 2.4, (f) 2.4 and (g) 2.5, while those corresponding to the curvews for the number of clusters are (a) −1.4, (b) −1.8, (c) −2.2, (d) −2.4, (e) −2.4, (f) −2.1 and (g) −2.2.

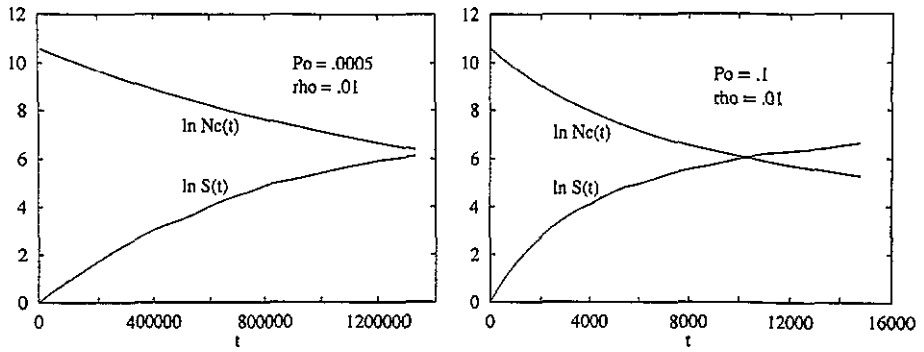

Figure 7. A semi-log plot of the weight-average cluster size and of the number of clusters both as a function of time, for $\rho = 0.01$ and two values of the sticking probability: $P_o = 0.0005$ (left) and $P_o = 0.1$ (right).

4. Conclusions

As a conclusion, it appears that we start with an RLCA algorigthm that very soon crosses over into something different (not DLCA, which has a bell-shaped distribution). The mere fact that the exponent τ diminishes over the course of time prevents dynamic scaling in this version of RLCA. This is not meant to imply, of course, that the RLCA problem cannot be described by a scaling distribution. The many experimental evidences already mentioned show this dynamic scaling and should be taken seriously. The theoretical work by Ball *et al* (1987) is also in support of dynamic scaling. This only means that the model, though perhaps closer to reality than other RLCA models, is still perfectible. In this respect it is worth remembering two important factors mentioned earlier (González 1992) that haven't been taken into account yet: the rotational diffusion of the clusters and the true step length of a Brownian particle or cluster. As already noticed in González (1992), in RLCA there are many encounters between two colloidal particles, before they go away, if the step length is much shorter than the diameter. This may change the situation and lead to a constant exponent $\tau = 1.5$ plus a mean cluster size growing exponentially with time, for a bigger fraction of the whole aggregation time. Those two factors will be considered in future publications. One more possibility, the finite size of our system, looks doubtful to contribute to this non-universal behaviour, now that we have been able to consider

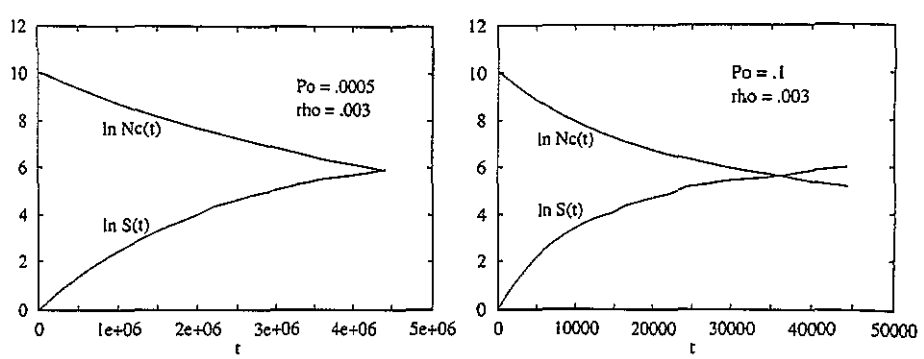

Figure 8. As in figure 7, now for $\rho = 0.003$ and two values of the sticking probability: $P_o = 0.0005$ (left) and $P_o = 0.1$ (right).

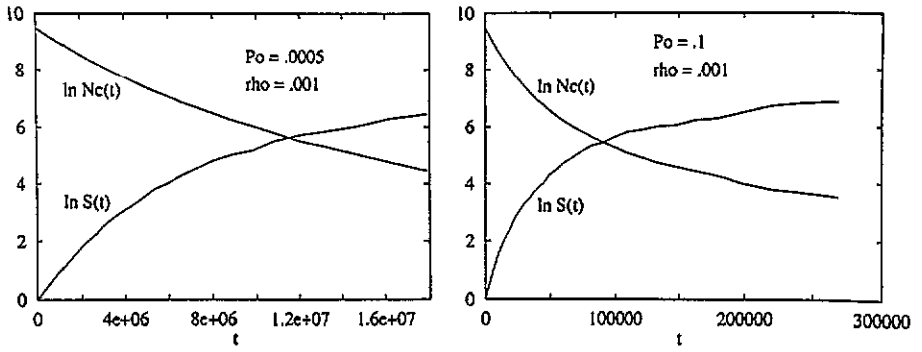

Figure 9. As in figure 7, this time for $\rho = 0.001$ and two values of the sticking probability: $P_o = 0.0005$ (left) and $P_o = 0.1$ (right).

simulations with as many as 40 960 particles (for $\rho = 0.01$). As we can see from the corresponding results (table and figures), those simulations are the least noisy of all, as long as we stop the simulations when there are still sufficiently many clusters.

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