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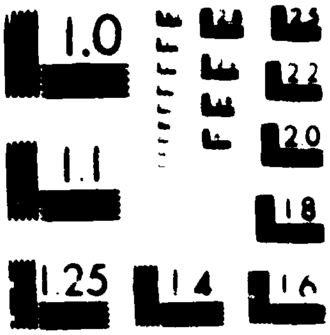
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It is found that the reaction rates of DLA aggregates are compatible with that of circular aggregates with an effective radius. The relation between the effective radius and the masses of the DLA aggregates can be described through a power law, $r_{eff} \sim N_o^{\delta}$, where r_{eff} is the radius of circular aggregate with approximately the same reaction rate as the DLA aggregate of total mass, N_o. The values for δ are 0.68 ± 0.07 and 0.79 ± 0.08 for unimolecular and bimolecular reactions, respectively. From the effective radius, the unimolecular reaction rates can be calculated by using known theories of diffusion controlled reaction.

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Dependence of the Reaction Probability of Benzene on the Size of Gaseous Niobium Clusters

by

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Comparison of the Rates of Uni- and Bi-Molecular Diffusion Controlled Reactions on Circular, Filled Aggregate and DLA Fractal Aggregate in Two Dimensions

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Abstract

The effects of irregular, open structures of two dimensional aggregates on the rates of diffusion controlled reactions are examined by computer simulation. The simulation model describes the reaction between two species, A and B, where A is randomly distributed on a two dimensional square lattice and diffuses like a random walker while B forms a fixed aggregate of different shapes and sizes. Both unimolecular (i.e., B is non-destructive but A disappears upon reaction) and bimolecular (i.e., both A and B disappear after the reaction) mechanisms are examined. Different sizes of DLA aggregates are chosen to model the irregular aggregates and to compare the reaction rates with the circular, compact aggregates of different radii. For unimolecular reaction, with the same total mass, the DLA aggregate shows a faster reaction rate than the circular one for its open structure. In the bimolecular mechanism, the sizes (or radii) of the aggregates decrease during reaction processes, and the reaction rate is slower compared to the unimolecular reaction. This shrinkage effect is more distinct

for DLA aggregates than the compact aggregates. It is found that the reaction rates of DLA aggregates are compatible with that of circular aggregates with an effective radius. The relation between the effective radius and the masses of the DLA aggregates can be described through a power law, $r_{eff} \sim N_o^{\delta}$, where r_{eff} is the radius of circular aggregate with approximately the same reaction rate as the DLA aggregate of total mass, N_o. The values for δ are 0.68 ± 0.07 and 0.79 ± 0.08 for unimolecular and bimolecular reactions, respectively. From the effective radius, the unimolecular reaction rates can be calculated by using known theories of diffusion controlled reaction.

I. Introduction

The kinetic studies of reaction rate processes occuring on solid surfaces[1,2] have been an interesting topic for different fields such as reactions on catalyst,[2-5] adsorption, desorption and growth processes[6,7] on metal or semiconductor surfaces. Unlike gas phase reactions, where the reaction rates are determined by the collision frequency, many heterogeneous reactions occuring at the surface of solids manifest that diffusion is an important step in the reactions process.[3-7]

Recent studies[8] have shown that many dendritic aggregates formed on the surface possess fractal structure and obey a scaling law, $N(R) \sim R^D$, where $N(R)$ is the number of particles within the radius R, and D is the fractal dimensionality.[14] The shape and the fitted fractal dimensionality, D, of these dendritic aggregates are similar to DLA (diffusion limited aggregate) generated by computer simulation according to the Witten-Sander model.[9] Because many molecular aggregates involved in reaction processes possess complex, irregular structures, it is difficult to model these systems by a theoretical approach. Therefore, many computer simulation studies[4,5] have been carried out to mimic possible reaction processes occuring on the two dimensional surface with irregular aggregates. Silverberg et. al.[5] have studied the effects of adsorbate interaction and aggregation on the rates of chemical reactions on surfaces. The geometric properties (size and shape) of the aggregates, and the lateral interactions are considered in their simulation. In their model, the migration rate of reactant is dependent on the associated energy changes for each step. Therefore, it is not quite clear whether the process is 'diffusion' controlled, or 'reaction' controlled.

In the present work, we study the effect of diffusion controlled process on the surface reactions involving aggregates of irregular shapes. In this case, the contact area between reactants is not a unique factor determining the reaction rate. The geometric structure would play an important role for the diffusion process and affect the reaction rate. In this study, we have chosen the DLA to model the dendritic aggregates of irregular shapes, and use computer simulation to investigate the reactions on the surface. We assume that each particle (atom or molecule) is a hard sphere, and no long range interaction is present. When two similar diffusive particles (A-A) touch each other, they repel, and reaction happens when a diffusive particle A reaches the aggregate B. Two reaction mechanisms are considered in the simulation. The first one is unimolecular process, (e.g., catalytic unimolecular decomposition, or isomerization), in which the aggregates keep the same shape and structure during the reaction. The second one is bimolecular process, where both the aggregate and diffusive particles disappear after the reaction. Because of the non-uniform shape of the aggregates, and the geometric structure of the aggregates play an important role in determing the reaction rate.

The concept of effective radius, r_{eff}, is used to compare the simulation results of the DLA clusters to circular, compact aggregates where many theoretical studies have been carried out.[10] According to the diffusion controlled reaction theories,[10] the reaction rate would increase as the aggregate radius increases. Because of the open structure of the DLA aggregates (Fig. 1), the maximum length, r_{max}, from a particle on the aggregate to the center is greater than the radius of the circular aggregate with the same total mass. However, the open structure of DLA aggregate also indicates a penetration effect which does not happen for the circular aggregates. This effect would let the probing particle to diffuse among the open spaces between the dendritic branches without reacting. Therefore, the effective radius, r_{eff}, would be smaller than r_{max} but larger than the corresponding radius of a circular aggregates with the same total mass.

In simulation studies of the growth process of DLA aggregate,[11] an active zone was found where most new particle join the existing cluster. The mean deposition radius, $\langle r_N \rangle$ shows a power law dependence on the total mass of the aggregate, $\langle r_N \rangle \sim N^{\nu}$. The value of ν for DLA aggregate is 0.584 ± 0.02. Our simulation of the chemical reaction is the reverse of growth process. From the simulation results, the effective radius also exhibits a scaling law behavior with respect to the total mass of the aggregate, $r_{eff} \sim N_o^{\delta}$. The values of δ for unimolecular and bimolecular mechanisms are 0.68 ± 0.07 and 0.79 ± 0.08, respectively.

II. Theoretical Background of the Diffusion Controlled Reactions:

Consider reactions between reactants A and B with the following reaction equations:

$$A + B \longrightarrow B + C \qquad (1a)$$

$$A + B \longrightarrow C \qquad (1b)$$

where both species (A and B) are randomly distributed and the reaction product C has no influence on the further reaction processes. Both of two cases, (1a) and (1b), are diffusion controlled processes.[10] The first case is like a catalytic reaction, where A particles are mobile and destructible while B is the fixed aggregate (e.g., a catalyst) and is indestrcutible. An example of this could be a catalytic unimolecular chemical process (e.g., unimolecular decomposition or isomerization). Assuming A particles are undergoing an isotropic diffusion in two dimensional lattice like a random walker, after several steps, an A particle reaches the aggregate B, and reacts (i.e., disappears) in the simulation. By counting all the survival A particles at different time t, the reaction rate can be calculated by the following equation

$$\text{Rate} = - \frac{dC_A(t)}{dt} \qquad (2)$$

$$C_B(t) = \text{constant}$$

The second case is a bimolecular surface reaction:[2,5] e.g., $O + CO \longrightarrow CO_2$. At the beginning of the reaction, one of the species, B, forms an aggregate on the surface. The other reactant A covers the surface randomly. These A particles, then, start to diffuse on the surface like random walkers. Once they reach the aggregate B, both A and B react and disappear in the simulation. Therefore, the size of aggregate B will shrink as the reaction goes on. By recording the changes of the concentration of A (or B) with time, the reaction rate law can be calculated as

$$\text{Rate} = - \frac{dC_A(t)}{dt} = - \frac{dC_B(t)}{dt} \qquad (3)$$

To simplify the problem, we take the the center of the aggregate B as the origin of the coordinates of the A particles. Assuming B particles are immobile and indestructible sinks and A particles undergo isotropic two dimensional diffusion with a diffusion constant D, then the spatial distribution of the A particles around a sink (aggregate B) can be described in terms of a space and time dependent function $\rho_A(r,t)$, normalized with respect to the mean concentration $C_A(t)$. $\rho_A(r,t)$ satisfies the diffusion equation:[10]

$$-\frac{\partial\ \rho_A(r,t)}{\partial\ t} = D\ {}^2\rho_A(r,t) \qquad (4)$$

with appropriate initial and boundary conditions.

If the system is spherically symmetric, the reactants A and B are assumed spherical with radii r_A and r_B, respectively. A reaction takes place if two particles approach one another within the contact distance r_{AB}, $r_{AB} = r_A + r_B$. By using Laplace transformation, the partial differential equation (Eq. 4) can be solved from the following boundary conditions:

$$\rho(\infty,t)=1, \qquad (5a)$$

$$\rho(r_{AB},t)=0, \quad \text{for } t > 0 \qquad (5b)$$

$$\rho(r,0)=1, \quad \text{for } r > r_{AB} \qquad (5c)$$

The reaction rate can be obtained from the diffusion flow of A particles into the boundary of the sinks B with concentration C_B,

$$\frac{dC_A(t)}{dt} = -\ k(t)\ C_B\ C_A(t) \qquad (6)$$

where the rate constant k(t) can be described as[10(d)]

$$k(t) = 2\pi D r_{AB}\ \left(\frac{\partial\ \rho(r,t)}{\partial\ r}\right)_{r=r_{AB}} \quad \text{2-dim} \qquad (7)$$

which decreases as time increases due to the concentration depletion on the boundary. The reaction rate k(t) is also dependent on the contact distance r_{AB}. The larger the radius (or the contact surface area) is, the faster the reaction rate would be.

Owen[13] has derived an analytic solution for the 2-dimensional case in cylindrical coordinates and gave a closed form of k(t) as a function of r_{AB}, and D. In a good approximation, a simple interpolation formula was found for k(t),[10(d)]

$$k(t) \sim \pi D\ (\alpha(t) + 2r_{AB}\ (\pi Dt)^{-1/2}) \qquad (8)$$

$$\alpha(t) = \mathrm{Min}\ (0.6, 4/\ln\ (4Dt/(\pi r_{AB}{}^2)))$$

However, for the aggregates of irregular shape, there is no analytic solution. Thus, the concept of effective radius, r_{eff}, which plays the role of r_{AB} in the above equation is proposed to describe the reaction rates of DLA aggregates. Once the effective radius is obtained, the unimolecular reaction rate can be calculated through the existing solutions for two dimensional disks.[10(d),13]

III. Simulation of Unimolecular and Bimolecular Reaction

The simulation is carried out on the two dimensional square lattice within a circular boundary of 300 lattice unit in diameter. The procedures of simulation are as follows: First, a aggregate B, which can be any shapes and sizes, is generated in the center of the two dimensional lattice. At time equal to zero, the A particles with a given concentration are randomly distributed on the same lattice where B already exists. Then, let A particles diffuse randomly like a random walker. Once particles A reach the aggregate B, they react. Either A alone or both A and B disappear depending on the mechanisms we are considering. During the reaction period, we keep tracing the positions of both species and record the number of all the survival (unreacted) particles (i.e., concentration) to calculate the reaction rate.

Due to the time limitation of computer simulations, the largest radius of the aggregates used for this simulation is 60, which is reasonable compared to the radius of the whole system, 150. The total number of steps for the simulation is 2000, and the average distance travels by a randomly diffusing particle is $2000^{1/2} \sim 45$ lattice units. Therefore, the results of simulation would not be perturbed by the finite size effect. Each initial condition (e.g., the aggregate shape, and size) is run three times and the results are averaged to reduce the fluctuations in the reaction rate calculation. When a particle reaches the circular boundary, it would be deleted and a new particle is generated on the opposite site of the boundary. The decay of the reactant concentration, $C_A(t)$, is normalized to its initial concentration, $C_A(t = 0)$ to compare the reaction rate for different initial conditions.

The simulations are carried out with two kinds of aggregates (Fig. 2). First, circular, compact aggregates with different radii, which are equivalent to the contact distance r_{AB} in equation 7, are used. The simulation results are then used as the reference curves to determine 'r_{eff}' for the aggregates of irregular shapes. The aggregates generated by the diffusion limited aggregation process are chosen to model the irregular aggregates in real systems. The sizes of DLA aggregate are varied for comparison to the reaction rates of the circular, compact aggregate. The effective radius, r_{eff}, for each DLA aggregate (with different total mass) is determined by comparing its reaction rates to a series of compact circular aggregates to find which one will give the same reaction rate. By plotting log $N_o(r_{eff})$ vs. log (r_{eff}), a straight line is obtained and indicates a scaling law behavior. The simulations are carried out for both the unimolecular and bimolecular processes, and the scaling exponents are determined respectively.

IV. Results

The simulation consists of calculating $C_A(t)$ at different time t, for different shapes of aggregates (i.e., circular or DLA) and for different sizes of aggregates. The simulation is performed on IBM 3090 computer, and follows the procedure described in section III.

A: Effect of The Aggregate Shape:

The decay of the concentration of A at different time with differen sizes (or radii) of the aggregates are shown in part A of Fig. 3, and 4 for circular aggregates, and part B of Fig. 3 and 4 for DLA aggregates. In part A, the total mass of DLA aggregates are 2000, 1800, 1500, 1300, 1000, 800, and 500. In part B, the radii (total mass) of the circle are 60 (11310), 55 (9503), 50 (7854), 45 (6362), 40 (5027), 35 (3848), 30 (2827), and 20 (1257) lattice units. The concentration of the diffusive particle A is 0.06. For the same total mass, the DLA aggregate reacts faster than the circular one. In other words, it has larger effective radius, r_{eff}. The plot of r_{eff} vs. N_o is given in Fig. 5. The slope of straight lines, δ, is equal to 0.68 ± 0.07 and 0.79 ± 0.08 for unimolecular and bimolecular reactions, respectively.

B: Effect of the Reaction Mechanism, Unimolecular vs. Bimolecular:

In Fig. 3 and 4, the reaction mechanisms are unimolecular and bimolecular, respectively. For the bimolecular mechanism, the size (or radius) of the aggregate decreases as time increases. This would slow down the reaction in comparison to the unimolecular mechanism. The shrinkage effect is more distinct for DLA aggregates than circular ones due to its open structure.

V. Discussion

From above plots, we can see that the shape of time dependent concentration function of reactant A for DLA aggregates is similar to that of compact, circular aggregates. However, the DLA aggregates show faster reaction rate than the circular one with the same aggregate size (total mass). This difference is mostly due to the geometric structure of the aggregates which will change the boundary conditions of the differential equation, Eq. 4 and 5. Basically, the reaction kinetic for the dendritic DLA aggregate can be described by the same differential equation, Eq. 4, but with different boundary conditions. As shown in Fig. 2B, for the compact, circular aggregate, as the diffusing reactant A reaches the circular boundary of aggregate B, the reaction occurs immediately. This implies the same boundary conditions as shown in Eq. 5. However, for the irregular shape, DLA aggregate, (Fig. 2A), when reactant A reaches the region I, it can either react when reach aggregate B or still be alive and diffuses among the *dendritic* branches. Therefore, the DLA aggregate possesses complicated boundary conditions for the differential equation and does not have analytic solution.

For the DLA aggregate, because of its open structure, the maximum 'length' of branches which determines the radius of the boundary between region I and II

(Fig. 2A) is larger than the corresponding radius of circular aggregate with the same amount of total mass. Mathematically, this behavior can be found from the scaling law for fractal structures, $N(R) \sim R^D$.[14] The scaling law can be rewritten as

$$r_{max} \sim N_o^{1/D} \qquad (9)$$

For the fractal structures, it is known that $d \geq D$. Therefore, the maximum length r_{max}, is larger than the corresponding radius of compact disk. Since the value of r_{max} is related to the radius of the boundary between region I and II, which is equivalent to the contact distance r_{AB} as in equation 8, the larger the maximum length r_{max} is, the faster the reaction rate would be. However, due to the open structure of the DLA pattern, when the diffusive particle A reaches the distance which is equal to the maximum length of the branches, it may not necessarily react at that time. The particle can still diffuse but with the survivial probability decreasing with time.[12] This indicates that the real number of reacted particles A is less than that with the circular boundary for the same boundary radius. Therefore, these two conflicting factors: larger maximum lengt' and penetrating effect, would compete each other, and the simulation results show that the increase in the maximum length, r_{max}, is more importantant than the effect of the penetration among branches for the DLA aggregates. By comparing the reaction rate of DLA aggregate with given total mass with reaction rates of a series of circular aggregates with different radius, the effective radius, r_{eff}, for DLA aggregate (which is equivalent to the contact radius r_{AB} in Eq. 8) can be obtained. r_{eff} is determined as the length which is equal to the radius of circular aggregate with the approximate the same reaction rate as DLA aggregate of given total mass, N_o. Because of the dendritic, open strcture of DLA aggregate, r_{eff} is larger than $N_o^{1/2}$ (i.e., the radius of disk). However, r_{eff} is smaller than r_{max} because the diffusing reactant A may diffuse among the dendritic branches, and penetrates closer to the center of aggregate.

The effect of reaction mechanisms, unimolecular vs. bimolecular, is also examined in the simulation. For the bimoulecular case, the aggregate sites will disappear when reached by the diffusive A particles, and the effective radius r_{eff} of the aggregate will shrink as reaction goes on. Since the time dependent reaction rate constant, k(t), depends on r_{AB} which is decreasing with time for bimolecular mechanism and is a constant for unimolecular case, the bimolecular reaction rate is slower than the unimolecular mechanism. Because of the open structure of dendritic, DLA aggregate, for the same amount of particle B (aggregate) consumed, the change in the maximum length, r_{max} is larger for the DLA than the circular aggregate. Therefore, the shrinkage effect is a more dominant for the DLA than the circular aggregates, and for the aggregate with smaller sizes than the one with larger sizes. Due to the complexity of the shrinkage effect on the geometric boundary of the aggregates for bimolecular mechanism, and the random positions of the aggregate sites being reacted, there is no analytic solution available even for the compact, circular aggregates. The results of r_{eff} for bimolecular mechanism can only describe qualitative behavior, and can not give actual reaction rate.

In the simulation of growth kinetic of DLA aggregate,[9] the growth can be described in terms of an active zone defined as the region where new particle join the existing cluster. This zone is characterized that the Nth particle is deposited to the aggregate with (N - 1) particles at a distance r_N from the center of mass. The mean deposition radius $\langle r_N \rangle$ shows a power law scaling behavior to the total mass of the aggregate,

$$\langle r_N \rangle \sim N^{\nu} \qquad (10)$$

The value of ν for DLA aggregate is 0.584 ± 0.02.[9] In this paper, we study the diffusion controlled reaction which is the reverse of the growth process. If we plot the r_{eff} versus N_0 in the log log scale, a straight line can be obtained as shown in Fig. 5 for both unimolecular and bimolecular mechanism. The slope, δ, is equal to 0.68 ± 0.07 and 0.79 ± 0.08 for uni- and bi-molecular mechanism, respectively. The difference in the values of ν and δ (for unimolecular mechanism) between the growth and the reaction process could be due to the initial distribution of the diffusive particles A. For the growth process, all the probing particles are staying at far away from the aggregate. However, in our simulation, the probing particles A are randomly distributed on the whole lattice initially. This would allow some particles staying among the branches of the aggregates in the beginning of the reaction. These particles could react with the sites close to the center of aggregate without feeling the screening effect from the outer branches. The meaning of δ for bimolecular mechanism is not very clear, and it is difficult to compare the values of ν and δ.

For the bimolecular mechanism, the reaction consumes the same amount of reactants A and B. If the number of reactant A reacted is compatible with the total number of aggregate B, the relative change of r_{eff} would be larger during the reaction period, and the shrinkage effect is more dominant in the smaller aggregate. These factors would lead to a smaller value of δ compared to the unimolecular case. However, the total amount of reactant A (initial concentration) would also affect the exponent δ. Because of the complexicity of the shrinkage effect, there is no theoretical equation to predict the reaction rate even for the circular boundary. The comparison between two kinds of aggregates gives only the qualitative results, and there is no direct correlation between the values of the δ exponent for uni- and bi-molecular mechanism.

In the earlier simulation of Silverberg et. al.,[5] they have studied the effect of the geometric properties of aggregates to the reaction kinetics. The reaction rate is dependent on the number of surface sites which are available for the diffusive particles to react. However, for the dendritic DLA aggregates, because of the strong screening effect, even though the surface area is linear to the total mass of the aggregate,[12] only those sites which are located at outer branches of the aggregate are useful for the reaction to occur. Therefore, the diffusing reactant A might feel different screen effect of the irregular surface (boundary) for the 'diffusion' controlled process and the 'reaction' controll process. In the present study, the 'diffusion' controlled process is investigated, and we have concentrated on how the radii of these 'active zone' are varied during the reaction with the size of aggregates. With the help of known results of diffusion controlled reaction on compact, circular disk (Eq. 8), the information of reaction rate can be obtained from a single parameter, r_{eff}, for the irregular shape aggregates.

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Figure Captions:

Figure 1:

The aggregate gernerated by the diffusion limited aggregation process as described in reference 9. The total mass of the aggregate is 12,000 lattice points.

Figure 2:

The slape of aggregate used for the simulation. (A) DLA aggregate with 2000 lattice point. (B) Circular aggregate with radii equal to 50.

Figure 3:

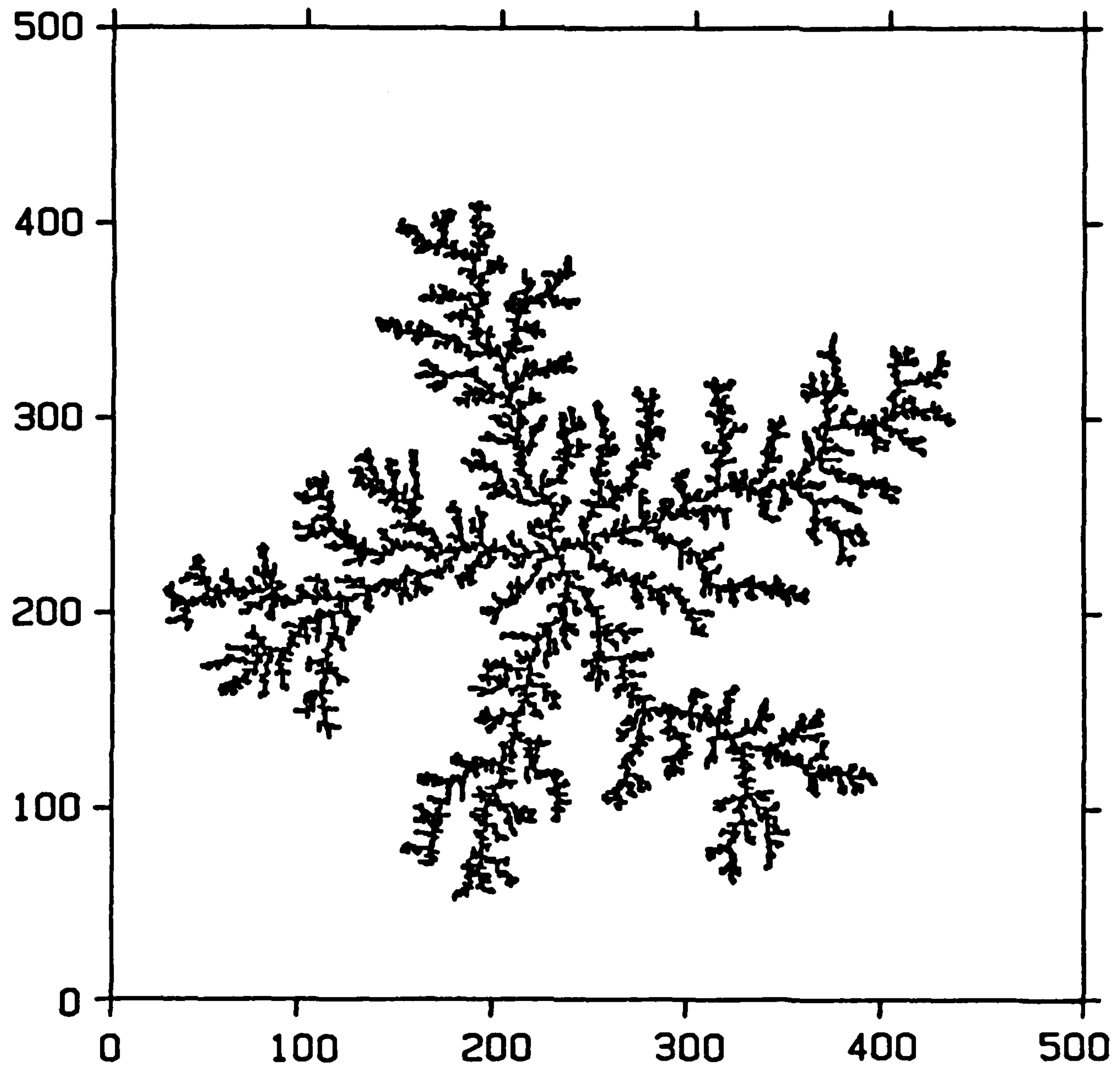
Plot of the reactant A concentration $C_A(t)$ at different time t. $C_A(t)$ is normalized to the initial concentration $C_A(t=0)$. The simulation is carried out for unimolecular mechanism for the DLA aggregate (part A) and circular aggregate (part B). In part A, the total mass of DLA aggregates are ——— 2000, ---- 1800, — — — 1500, —·—·—· 1300, —— — — 1000, —··—··—800, amd ——— 500, respectively. In part B, the radii (total mass) of circular aggregates are ——— 60 (11310), - - - - 55 (9503), — — — 50 (7854), —·—·—45 (6362), ---- 40 (5027), —··—·· 35 (3848), ——— 30 (2827), and ——— 20 (1257), respectively. For the same total mass, the DLA aggregates react much faster than the circular one i.e., DLA aggregate has larger effective radius.

Figure 4:

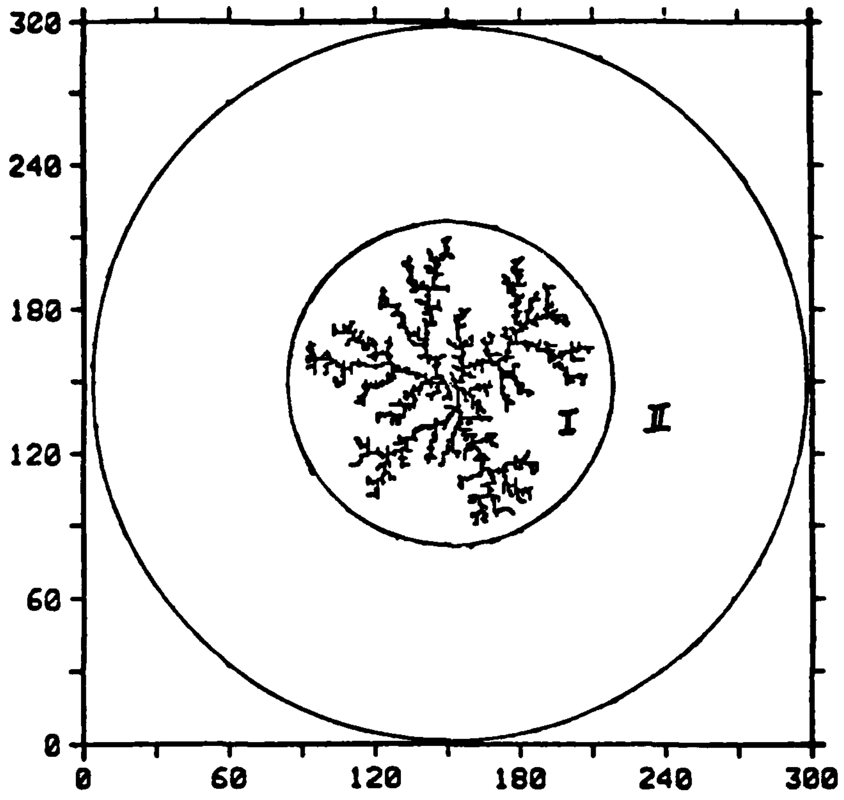
Plot of the reactant A concentration $C_A(t)$ at different time. $C_A(t)$ is normalized to the initial concentration $C_A(t=0)$. The simulation is carried out for bimolecular mechanism for the DLA aggregate (part A) and circular aggregate (part B). In part A, the total mass of DLA aggregates are ——— 2000, – – – – 1800, — — — 1500, —·—·—1300, — — — — 1000, ——··——·· 800, and ——— 500, respectively. In part B, the radii (total mass) of circular aggregates are ——— 60 (11310), — — — — 55 (9503), — — — 50 (7854), —·—·—45 (6362), – – – – –40 (5027), —··——··-35 (3848), ——— 30 (2827), and ——— 20 (1257), respectively. For the bimolecular mechanism, the size (or radius) of the aggregate decreases as time increases which would slow down the reaction in comparison to the unimolecular mechanism. The shrinkage effect is more dominant for DLA aggregate than the circular one due to its open structure.

Figure 5:

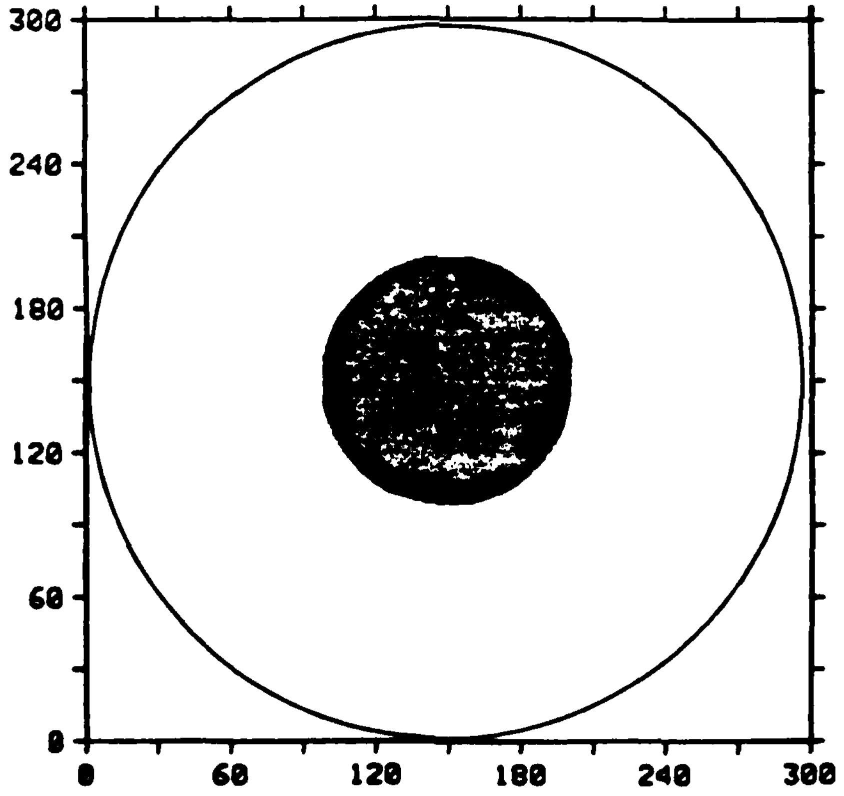
The log-log plot of r_{eff} with N_o, where r_{eff} is the radius of circular aggregate with the same reaction rate as the DLA aggregate of N_o total mass. Plots A and B are the results of unimolecular and bimolecular mechanism respectively.


500
400
300
200
100
0
0
100
200
300
400
500

A


300
240
180
120
60
0
0
60
120
180
240
300
I
II

B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240
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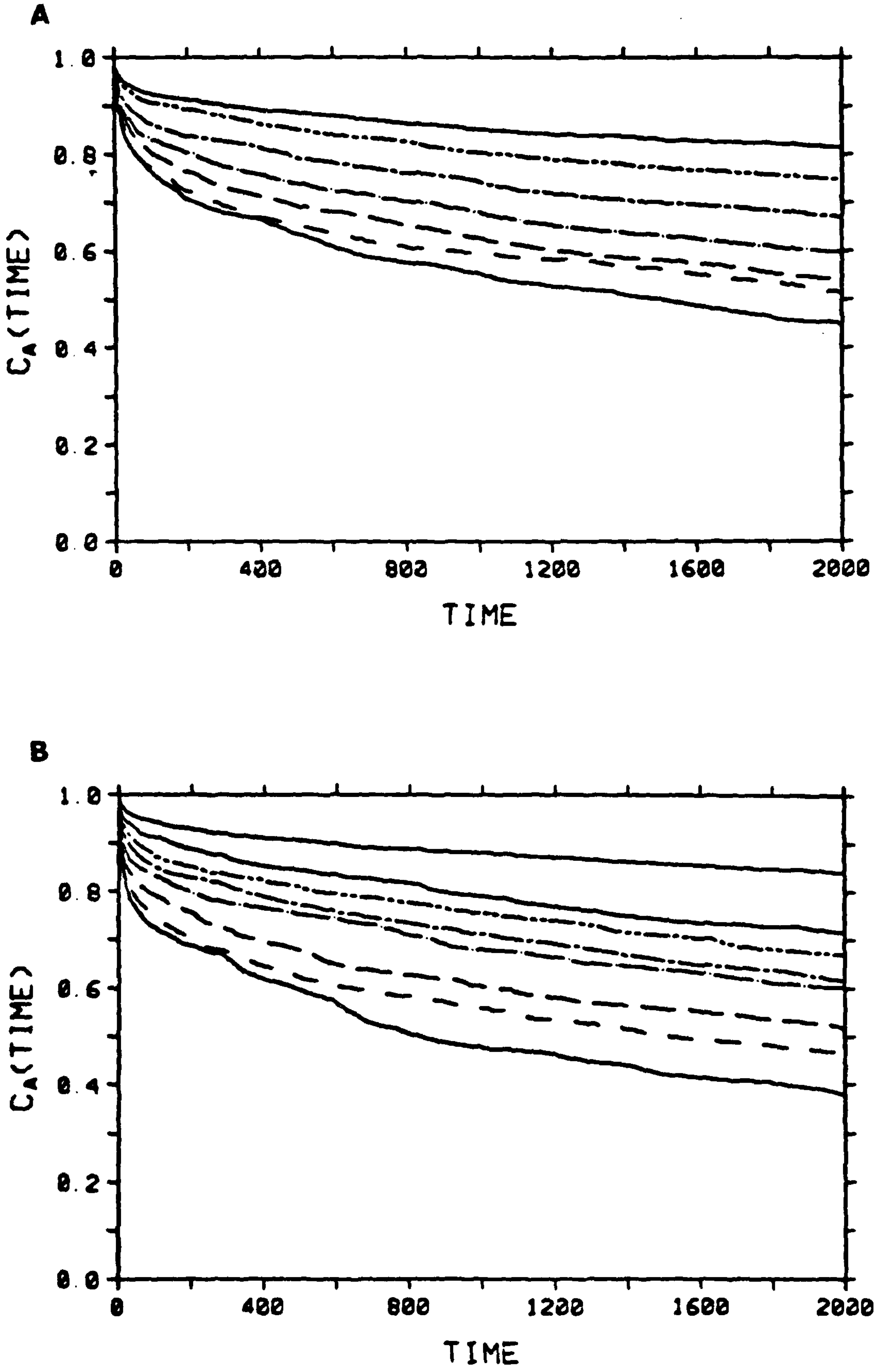
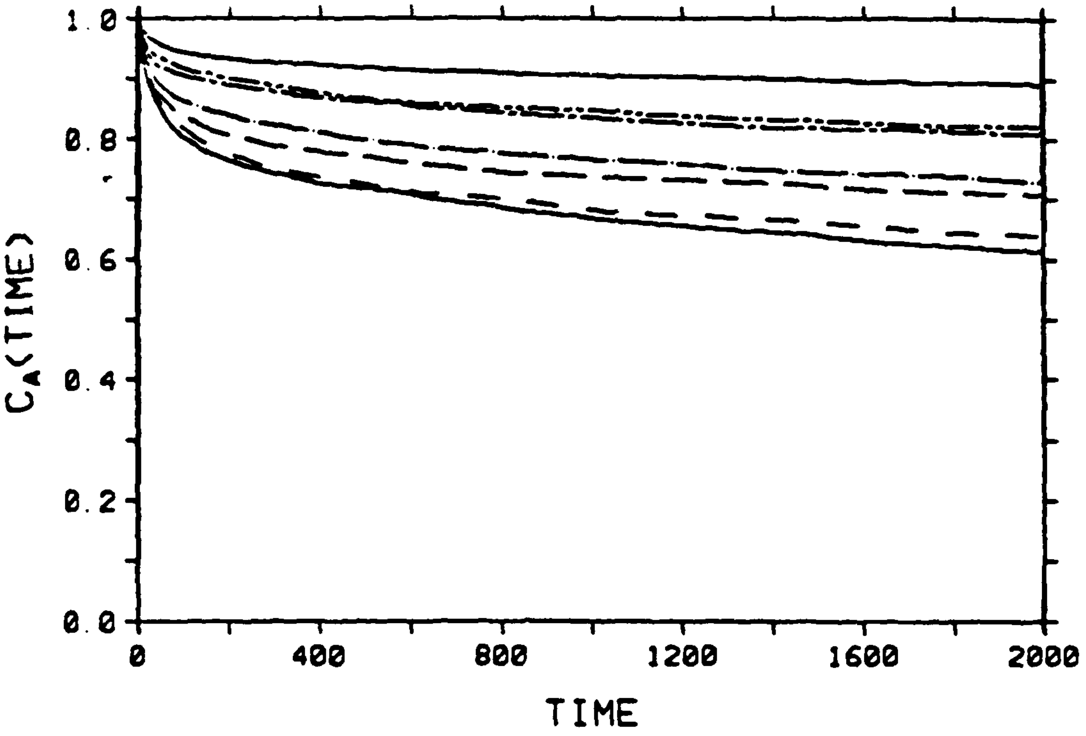
60
0
0
60
120
180
240
300

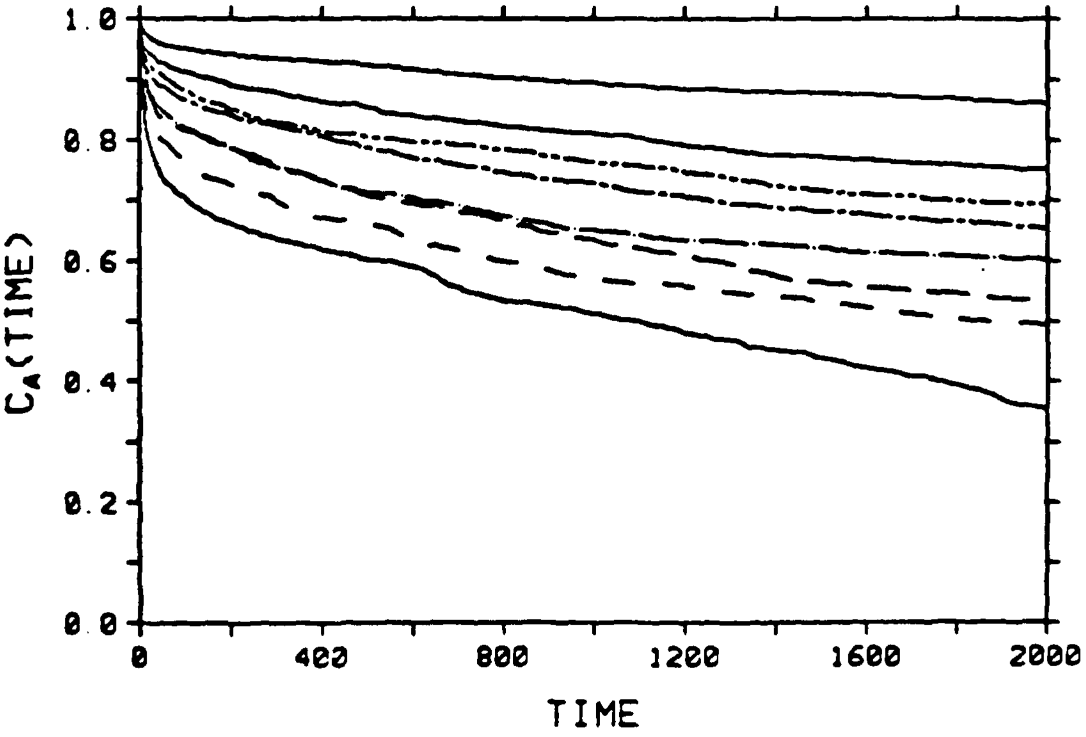

A
1.0
0.8
0.6
0.4
0.2
0.0
C_A(TIME)
0
400
800
1200
1600
2000
TIME
B
1.0
0.8
0.6
0.4
0.2
0.0
C_A(TIME)
0
400
800
1200
1600
2000
TIME

A



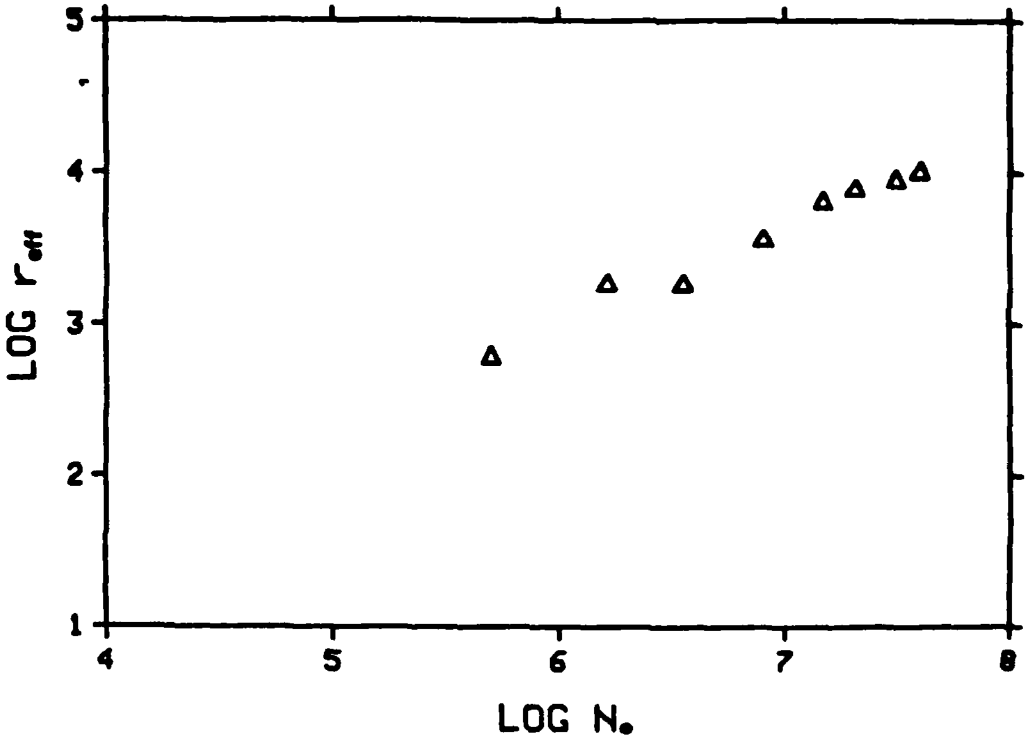
1.0
0.8
0.6
0.4
0.2
0.0
C_A(TIME)
0
400
800
1200
1600
2000
TIME

B

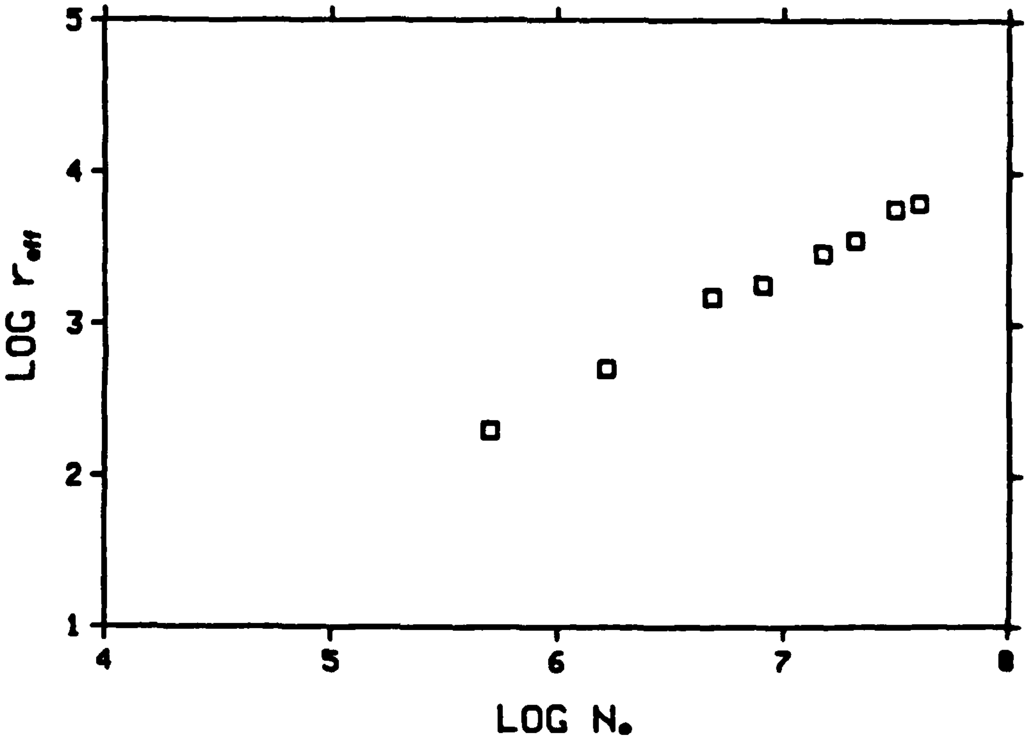


1.0
0.8
0.6
0.4
0.2
0.0
C_A(TIME)
0
400
800
1200
1600
2000
TIME

A



B



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