Diffusion-controlled deposition on fibers and surfaces

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Monte Carlo simulations have been carried out to investigate the deposition of particles on surfaces and fibers under conditions where the deposition is diffusion controlled. Deposits prepared under diffusion-controlled conditions have a completely different morphology from deposits prepared under conditions where diffusion is not important. For the case of deposition on thin fibers we find that the radius of gyration of the deposit is related to the number of particles in the deposit (N) by $R_g \sim N^{\delta}$ ($\delta = 0.665 \pm 0.030$) in the limit of large N and long fibers. Consequently, deposits formed on fibers under diffusion-controlled conditions have fractal characteristics similar to those associated with clusters formed under diffusion-controlled conditions. Similar, but less quantitative, results are presented for surface deposits. For two-dimensional deposits grown on a one-dimensional "surface" under diffusion-controlled conditions, the root-mean-square thickness (T) of the deposit is related to the number of particles by $T \sim N^{\epsilon}$ ($N \to \infty$). The exponent ϵ has the value 1.30 ± 0.075. Similar results were obtained in three-dimensional simulations of diffusion-controlled deposition on a surface ($T \sim N^{\epsilon}$, with $\epsilon = 1.70 \pm 0.2$). All of the results reported in this paper were obtained using two- and three-dimensional lattice models. Our results suggest that the structural characteristics of systems grown by diffusion-controlled processes are determined mainly by the dimensionality of the space in which the growth is occurring and are insensitive to geometric variables such as "surface" curvature.

INTRODUCTION

The deposition of small particles on fibers and surfaces are phenomena with important applications in the purification of air and water[1] and in the preparation of systems with specific surface properties.[2] The addition of particles or atoms to surfaces under conditions where surface reorganization can occur is a problem which has been extensively studied via computer simulations by Gilmer[3] and others. In this paper we are concerned with the deposition of particles on fibers and plane surfaces under conditions where reorganization processes do not occur and the rate of deposition is controlled by diffusional processes.

Our work in this area was stimulated by a recent paper by Witten and Sander[4] in which the results of computer simulations of diffusion-limited growth of two-dimensional clusters on a "seed" particle were described and by results from our own work on diffusion-controlled cluster formation in two-dimensional through six-dimensional space.[5] These simulations show that clusters formed on a seed particle under diffusion-controlled conditions have an associated fractal[6] or Hausdorff[7]-Besicovitch dimensionality (D) which is related to the "normal" Euclidean dimensionality (d) by the approximate relationship $D \approx 5d/6$. Clusters grown under diffusion-limited conditions have a very open structure and low average density which decreases with increasing cluster size. Despite the very open structure of the cluster, growth occurs almost entirely in

FIG. 1. Two perpendicular projections and cross sections perpendicular and parallel to the axis of a fiber on which a large number (10 067) of particles have been added by a diffusion-controlled process.

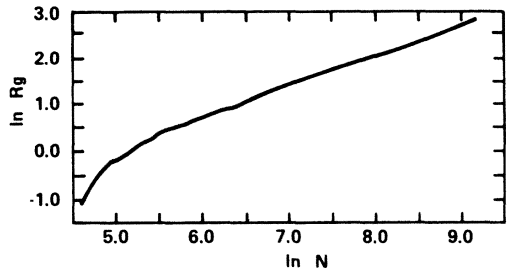

FIG. 2. Dependence of $\ln R_g$ on $\ln N$ for a typical fiber deposit. R_g is the radius of gyration about the fiber axis and N is the number of particles in the deposit.

the outer regions of the cluster and clusters grown under diffusion-controlled conditions have a completely different morphology from clusters grown under conditions where Brownian motion of the particles is not important.

In this paper we show that diffusion-limited deposition on fibers and surfaces also results in open dendritic structures with a "fractal" nature. It is hoped that the results of our computer simulations will stimulate further theoretical and experimental work on diffusion-controlled growth processes.

SIMULATION RESULTS

Deposition on fibers

In our simulation of growth on fibers we start with a row of occupied lattice sites to represent the fiber. A "particle" is introduced at a lattice site chosen at random in the neighborhood of the fiber and allowed to "diffuse" by a series of jumps to nearest-neighbor lattice sites. The particle eventually either reaches a site adjacent to the fiber and is added to the fiber as part of the deposit or moves to a position a long way (≥ 2.0 times the maximum distance from the fiber to any particle in the deposit) from the fiber. If this occurs, the particle is "killed" and a new particle is started closer to the fiber and its deposit. After the first particle has been added to the fiber, a second particle is introduced and it also is eventually added to the deposit, added to the fiber, or killed. The procedure is repeated many times until a sufficiently large deposit has been grown on the fiber. In these simulations periodic boundary conditions are used in the direction of the fiber axis.

Figure 1 shows the result of such a simulation in which 10 067 particles were added to a fiber 91 lattice units long. The upper part of the figure shows two projections of the deposit. The lower part of the figure shows cross sections perpendicular to and along the fiber axis. As in the case of diffusion-controlled cluster growth,[4,5] new particles are added mainly to the outer portions of the deposit and very few particles are added to the inner regions during the later stages of growth despite the very open structure. In the case of diffusion-limited cluster formation,[4,5] the radius of gyration (R_g) is related to the number of particles (N) by $R_g \sim N^{\beta}$ (in the limit $N \to \infty$), where $\beta \approx 6/5d$ (d is the Euclidean dimensionality). For this reason we were motivated to calculate the radius of gyration about the fiber axis as a function of the number of particles added. Figure 2 shows a typical plot of $\ln R_g$ vs $\ln N$. From five deposits (average 11 275 particles per deposit) we find $R_g \sim N^{\delta}$, where $\delta = 0.665 \pm 0.031$.[8] Additional details are given in Table I.

Deposition on surfaces

Similar simulations have been carried out to investigate diffusion-controlled deposition of particles on surfaces. The methods used are very similar to those described very briefly above for deposition on fibers and in more detail for diffusion-limited cluster growth.[5] The diffusing particles are killed if

TABLE I. Radius-of-gyration exponents (δ) for diffusion-controlled deposition on fibers. Exponents are obtained from the dependence of $\ln R_g$ on $\ln N$ over the range $N_1 < N < N_2$. N_{max} is the maximum number of particles in the deposit.

Number of particles (N_{max})	$N_1 = 0.50N_{max}$ $N_2 = 1.00N_{max}$	$N_1 = 0.25N_{max}$ $N_2 = 1.00N_{max}$	$N_1 = 0.10N_{max}$ $N_2 = 1.00N_{max}$
10 158	0.693	0.684	0.655
9 629	0.669	0.651	0.648
11 969	0.683	0.683	0.683
12 587	0.632	0.627	0.623
12 035	0.649	0.647	0.658
Average 11 275	0.665±0.031	0.658±0.030	0.653±0.027

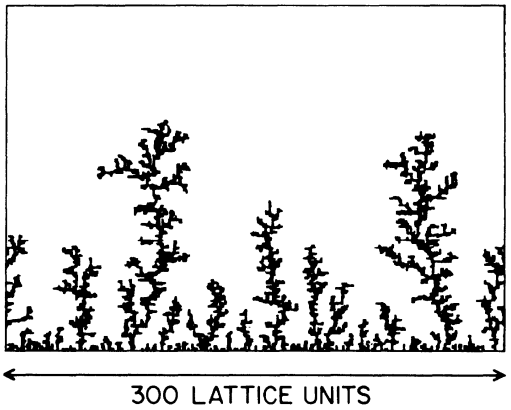

FIG. 3. Results of a two-dimensional simulation of diffusion-controlled deposition on a surface (line). For the purposes of this figure a deposit was grown from a line of 300 sites with a sticking probability of 1.0.

they reach a distance from the surface ≥ 3.0 times the maximum distance from the surface to any point in the deposit. Figure 3 shows the results of a two-dimensional simulation in which particles are deposited on a "surface" represented by a line of 300 nucleation sites. In the simulations shown in Fig. 3, a sticking probability of 1.0 was used if the particle reached a nearest-neighbor site with respect to either the surface or the growing deposit. As in simulations of diffusion-controlled cluster formation,[4,5] a very open dendritic structure develops. Despite the

FIG. 4. This figure shows the results of a two-dimensional simulation of a deposit grown in the absence of diffusion. Particles follow vertical trajectories until they contact either the original surface or part of the deposit.

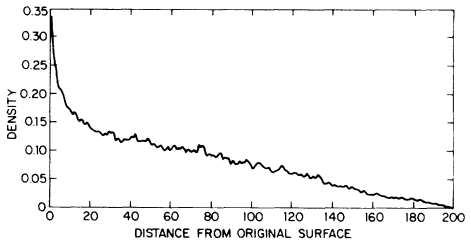

FIG. 5. Density profile for two-dimensional deposits grown to a thickness of 200 lattice units. This figure shows the average profile for six deposits each grown from a surface of 1000 lattice sites.

very open nature of the deposit, very few particles are added to the lower levels of the deposit during the latter stages of growth because most Brownian trajectories intersect the upper regions of the deposit. By contrast, Fig. 4 shows the results of a simulation in which particles are "dropped" vertically onto a surface and stick when they reach a nearest-neighbor position with respect to either the surface or the deposit. In this case the density of the deposit drops rapidly to a relatively constant "plateau" value as the distance from the surface increases and then drops rapidly to zero as the maximum thickness of the deposit is approached. Under diffusion-limited conditions the density decreases more continuously with increasing distance from the surface (Fig. 5).

Because of the results obtained from simulations of diffusion-controlled cluster formation and deposition on fibers, the relationship between the root-mean-square thickness (T) of the deposit and the number of particles in the deposit (N) was examined. Deposits were grown from 1000 sites to a maximum distance of 200 lattice units. These parameters were chosen to ensure that the finite lateral size of the simulation and the periodic boundary conditions would not significantly influence the structure of the deposit. The simulations carried out on smaller lattices were for the purpose of illustra-

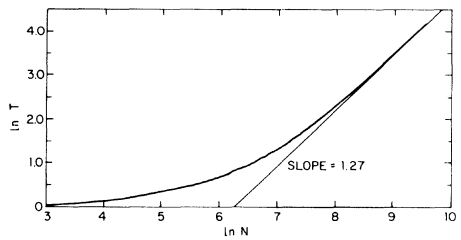

FIG. 6. Dependence of rms thickness (T) on the number of particles (N) in two-dimensional deposits on a one-dimensional surface. The straight line indicates a limiting slope of about 1.27.

TABLE II. Values of the rms thickness exponent (ϵ) obtained from deposits grown in two dimensions from 1000 lattice sites by a diffusion-controlled process. Exponents are obtained from the dependence of $\ln T$ on $\ln N$ over the ranges $N_1 < N < N_2$. N_{max} is the total number of particles in the deposit of maximum thickness 200 lattice units.

$N_1=0.50N_{max}$ $N_2=1.00N_{max}$	$N_1=0.75N_{max}$ $N_2=1.00N_{max}$	$N_1=0.90N_{max}$ $N_2=1.00N_{max}$	$N_1=0.25N_{max}$ $N_2=0.5N_{max}$
1.362	1.461	1.441	1.175
1.196	1.184	1.144	1.167
1.366	1.418	1.388	1.155
1.221	1.201	1.164	1.270
1.202	1.200	1.210	1.216
1.265	1.329	1.350	1.241
1.287	1.305	1.325	1.248
1.272	1.315	1.375	1.169
1.307	1.317	1.319	1.183
Average			
1.275±0.048	1.303±0.074	1.302±0.081	1.203±0.032

tion only (see Fig. 3, for example). Figure 6 shows how the rms thickness of the deposit (T) depends on the number of particles in the deposit (N). Figure 6 indicates a limiting power-law relationship between T and N:

$$T \sim N^{\epsilon} \ (N \to \infty) \ . \tag{1}$$

Table II shows the results obtained from nine deposits grown to a maximum depth of 200 lattice units from 1000 sites. The results given in this table indicate that the rms thickness exponent (ϵ) has an approximate value of 1.3. However, the large difference between the values for ϵ obtained over the ranges

$$0.25N_{max} < N < 0.5N_{max}$$

and

$$0.5N_{max} < N < N_{max}$$

(N_{max} is the total number of particles in the deposit) indicates that the $N \to \infty$ limit may not have been closely approached.

One of the major contributions to the uncertainty in ϵ is the ambiguity in the position of the surface from which the particle coordinates should be measured. To overcome this uncertainty, we have fitted our simulation results to the expression

$$T = AN^{\epsilon'} + B \ , \tag{2}$$

where the parameter B expresses the uncertainty in the location of the appropriate surface from which the thickness should be measured. From the nine two-dimensional deposits grown to a maximum thickness of 200 lattice units, we obtained the results $\epsilon' = 1.305 \pm 0.064$ and $B = 1.478 \pm 0.52$. If only the first 50% of the particles added to the deposit are used we find $\epsilon' = 1.281 \pm 0.034$ and $B = 1.271 \pm 0.15$. These results indicate that the limiting ($N \to \infty$) value for the exponent ϵ is approximately 1.3. If the data from the nine simulations are averaged, the best fit between our data and Eq. (2) gives the result

$$T = 1.42 + 2.55 \times 10^{-4} N^{1.297} \ .$$

This expression gives a much better fit to our data than the simple power-law expression $T = AN^{\epsilon}$ (Fig. 7). The more general expression

$$T = AN^{\epsilon''}(1 + BN^{-\alpha}) \tag{3a}$$

or

$$T = AN^{\epsilon''} + BN^{\beta} \tag{3b}$$

has also been fitted to the results of our two-dimensional simulations. The best fit of this form for the results averaged over all nine deposits is

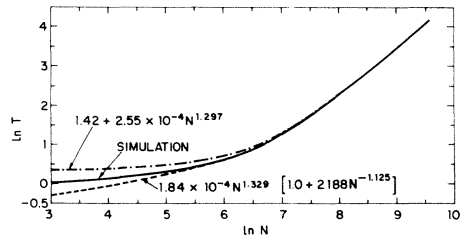

FIG. 7. Results of fitting the dependence of the rms thickness (T) on the number of particles (N) by scaling relationship of the form $T = AN^{\epsilon'} + B$ and $T = AN^{\epsilon''}(1 + BN^{-\alpha})$. Simulation results are the average results for nine deposits on 1000 original $1d$ surface sites.

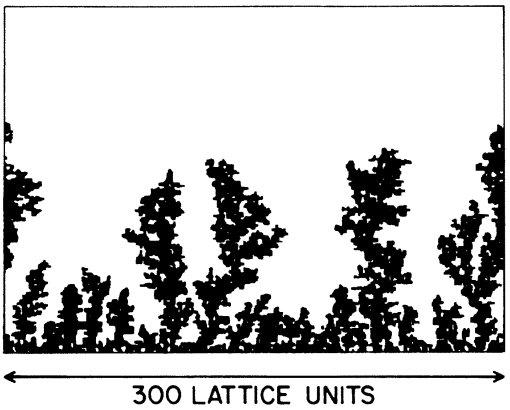

FIG. 8. A two-dimensional surface deposit grown on 300 lattice sites with a sticking probability of 0.1.

given by $T=1.84\times10^{-4}N^{1.329}$ $(1.0+2188N^{-1.125})$ (Fig. 7), where N is the number of particles deposited on 1000 original sites.

Overall, the results of this analysis can be expressed as $\epsilon\approx1.30$. Our estimate for the uncertainty of this value for ϵ is about ±0.075. Similar simulations have been carried out with sticking probabilities less than 1.0. Figure 8 shows a two-dimensional surface deposit simulated using a sticking probability of 0.1. As we have observed earlier in diffusion-controlled cluster formation,[5] a smaller sticking probability leads to a denser deposit. The *quantitative* properties of deposits grown with sticking probabilities less than 1 have not yet been investigated. However, we expect (by analogy with our results for clusters[5]) that the exponent ϵ will be insensitive to the sticking probability. Similar simulations of diffusion-controlled growth on a two-dimensional surface using a three-dimensional lattice model have been carried out.

FIG. 10. Cross section through a deposit of 32 321 particles grown on a surface of 50×50 lattice units to a maximum depth of 50 lattice units. In this simulation the particles were dropped vertically onto the surface.

Figure 9 shows a cross section through a deposit of about 15 000 particles grown on a surface of 100×100 lattice units to a maximum depth of 60 lattice units under diffusion-controlled conditions. For comparison, a similar cross section through a deposit of 32 321 particles obtained by using a lattice model in which particles are dropped vertically onto

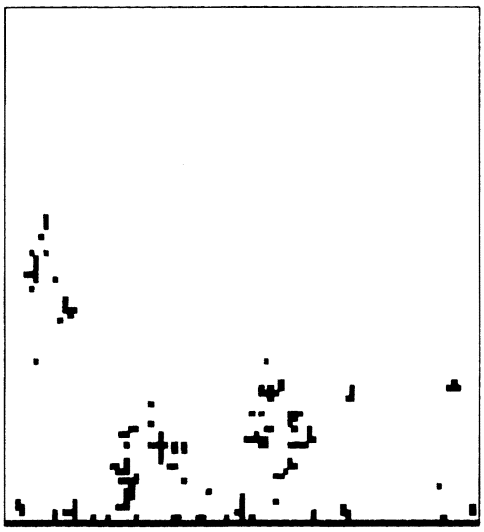

FIG. 9. Cross section through a deposit of about 15 000 particles grown on a surface 100×100 lattice units to a maximum depth of 60 lattice units under diffusion-controlled conditions.

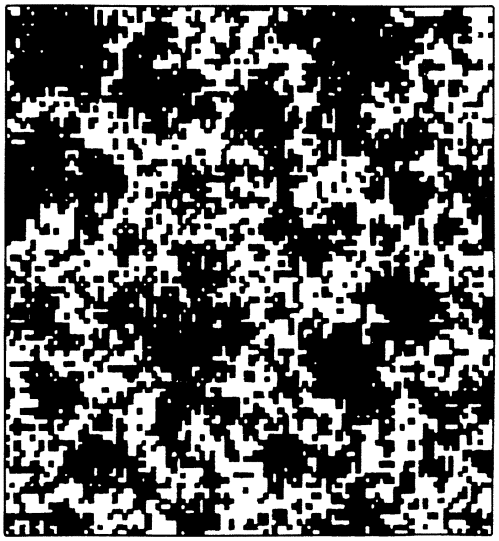

FIG. 11. A view from the top of the deposit where the cross section is shown in Fig. 9. White areas are the original surface not covered by the deposit at any depth.

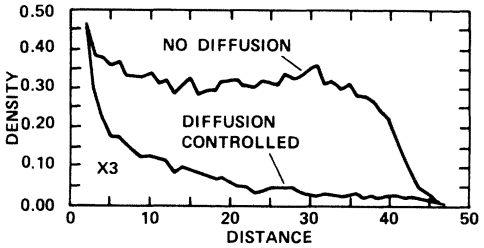

FIG. 12. Comparison of the density profiles of two deposits in the limits of no diffusion and diffusion-controlled deposition.

a surface is shown in Fig. 10. In this simulation the original surface area was 50×50 lattice units and the particle was incorporated into the deposit when it reached a lattice site which was the nearest neighbor to an occupied lattice site. In the three-dimensional simulations periodic boundary conditions are used in both directions parallel to the original surface. A comparison of Figs. 9 and 10 demonstrates that diffusion-limited deposition leads to a completely different morphology than deposition under conditions where diffusional motion is absent. Figure 11 shows a view from the top of the deposit whose cross section is shown in Fig. 9. Taken together, Figs. 9 and 11 (and many similar figures) indicate that the three-dimensional deposits resemble a "forest" of "trees" growing out of the surface. The tallest trees have the largest growth rates. Smaller trees quickly become inaccessible to the diffusing particles and stop growing. Figure 12 compares the density profiles obtained in the two simulations. Other simulations gave qualitatively similar results. When diffusion is absent, the density falls rapidly to a constant value with increasing distance from the original surface and then falls steeply again when the maximum thickness of the deposit is approached. Under diffusion-controlled conditions, the density decreases more or less continuously with increasing distance from the original surface. In addition, the average density of the deposit formed under diffusion-controlled conditions is considerably smaller than that for the deposit formed under conditions where diffusion is not a significant process.

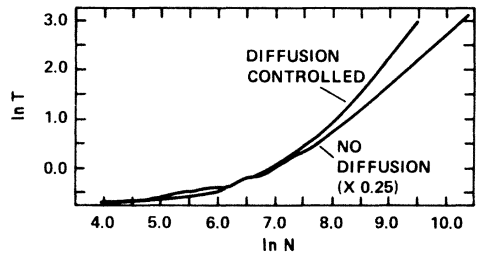

FIG. 13. Relationship between root-mean-square thickness and number of particles for diffusion-controlled deposition and deposition via vertical trajectories without diffusion.

As in our other simulations, the relationship between rms thickness and the mass (number of particles) of the deposit was examined. Some of our results are shown in Fig. 13. As $N\rightarrow\infty$ (N is the number of particles in the deposit) the relationship between the root-mean-square thickness $T_{\rm rms}$ and the number of particles seems to be approaching a power-law form

$$T_{\rm rms}\sim N^{\epsilon}\ .$$

For deposition in the absence of diffusion, ϵ has a value of approximately 1.0 (a slightly large value is obtained as a result of finite-size effects). Under diffusion-controlled conditions the value of the exponent ϵ is substantially larger than 1.0. Table III shows the values obtained for ϵ from eight deposits grown to a depth of 60 lattice units on 100×100 surfaces. The results shown in Table III indicate that ϵ is approximately 1.55. However, as in the case of two-dimensional deposits, the large difference between the results obtained for $0.25N_{\rm max}<N<0.5N_{\rm max}$ indicates that the true limiting value for ϵ may be substantially larger. As in the case of two-dimensional deposits, a major contribution to the uncertainty in ϵ arises from the uncertainty in the effective position of the surface from which the deposit coordinates should be measured. Consequently, a function of the form of Eq. (2) was fitted to our results. From the eight three-dimensional deposits we find $\epsilon'=1.622\pm 0.061$ and $B=0.827\pm 0.084$. The best fit of this form to the averaged data for all eight deposits is given by

$$T=4.27\times 10^{-6}N^{1.602}+0.806\ .$$

The dependence of the rms thickness (T) on the number of particles in the deposit has also been fitted to the more general form of Eq. (3a). From six deposits grown to a depth of 60 lattice units from a surface of 100×100 lattice sites, the results $\epsilon'=1.80\pm 0.16$ and $\alpha=1.45\pm 0.10$ were obtained. The best fit to the averaged results of eight deposits is given by

$$T=5.17\times 10^{-7}N^{1.816}(1.0+1.27\times 10^{5}N^{-1.43})$$

(Fig. 14). Taken together, these results indicate that $T\sim N^{\epsilon}$ ($N\rightarrow\infty$) with the exponent (ϵ) having a value of 1.70 ± 0.20. Simulations have also been carried out to investigate the effects of sticking probabilities less than 1.0 on three-dimensional surface deposits. As in the case of clusters grown under diffusion-controlled conditions[5] and two-

TABLE III. Values for the rms thickness exponent (ϵ) obtained from three-dimensional deposits grown to a maximum depth of 60 lattice units from a surface of 100×100 lattice sites by a diffusion-controlled process. Exponents are obtained from the dependence of $\ln T$ (rms thickness) on $\ln N$ (number of particles in deposit) over the range $N_1<N<N_2$. $N_{\max}$ is the total number of particles in the deposit.

$N_1=0.50N_{\max}$ $N_2=1.00N_{\max}$	$N_1=0.75N_{\max}$ $N_2=1.00N_{\max}$	$N_1=0.90N_{\max}$ $N_2=1.00N_{\max}$	$N_1=0.25N_{\max}$ $N_2=0.50N_{\max}$
1.529	1.612	1.547	1.208
1.495	1.417	1.364	1.258
1.621	1.551	1.452	1.232
1.513	1.509	1.489	1.341
1.523	1.636	1.615	1.179
1.421	1.561	1.545	1.182
1.565	1.727	1.905	1.157
1.494	1.505	1.437	1.312
Average			
1.520±0.048	1.565±0.079	1.544±0.138	1.234±0.055

dimensional surface deposits (see above), a low sticking probability leads to denser deposits.

DISCUSSION

The Monte Carlo simulations in this paper illustrate that deposits grown under diffusion-limited conditions have a completely different morphology from deposits grown under conditions where diffusion (before deposition) is not important. In the case of deposition on a long fiber, this aspect of diffusion-controlled deposition can be expressed in terms of a power-law relationship between the radius of gyration (R_g) of the deposit and the number of particles (N) with a nonclassical exponent, i.e., $R_g\sim N^{\delta}$ ($\delta=0.665\pm0.030$) in the limit $N\to\infty$. In this respect diffusion-controlled deposition on fibers is similar to diffusion-controlled cluster formation.[4,5]

Our results for diffusion-controlled deposition on surfaces in two and three dimensions lead to similar conclusions. However, in this case the uncertainties in the value of the exponent are larger, particularly in the case of three-dimensional deposits. We are planning to carry out additional simulations to obtain more accurate values for the rms thickness exponent in $3d$ deposits and to explore other properties of deposits grown under diffusion-controlled conditions. In the case of two-dimensional surface deposits, the dependence of T on N was fitted by $T=AN^{\epsilon}$, $T=AN^{\epsilon}+B$, and $T=AN^{\epsilon}(1+BN^{-\alpha})$. All three ways of analyzing these results gave similar results for the exponent ϵ. For the three-dimensional surface deposits, the more general expression $T=AN^{\epsilon}(1+BN^{-\alpha})$ gave a substantially larger estimate for the exponent ϵ than the two simpler expressions.

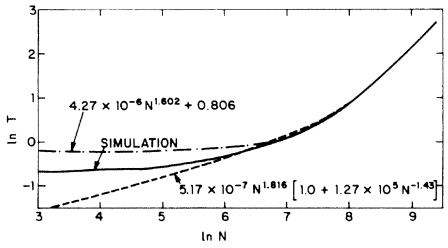

FIG. 14. Results of fitting the dependence of the rms thickness (T) on the number of particles (N) by relationship of the form $T\sim AN^{\epsilon'}+B$ and $T=AN^{\epsilon''}(1+BN^{-\alpha})$. These simulation results are the average of eight deposits on a 100×100 surface grown to a depth of 60 lattice units.

For clusters grown in two-dimensional space using the Witten-Sander[4] model analysis of the density-density correlation function and the dependence of the radius of gyration on the number of particles indicates that the average density at a distance r from the center of the cluster [$\rho(r)$] should depend on r according to $\rho(r)\sim r^{-\alpha}$ for distances (r) both larger than several lattice units and smaller than the overall dimensions of the cluster. Numerical simulations similar to those described in this paper[4,5] show that α has the value of 0.30 ± 0.06. Similarly, for the surface deposits grown using the two-dimensional lattice model discussed in this paper, the relationship $T\sim N^{\epsilon}(N\to\infty)$ implies a density profile of the form $\rho(r)\sim r^{-\alpha_s}$, where r is the distance from the surface. This relationship is expected to be valid for intermediate values of r with deviations near the upper and lower interfaces. The nu-

merical estimate for the exponent ϵ obtained in this paper implies that α_s has the value 0.23 ± 0.05.

For three-dimensional clusters we have found that $\rho(r) \sim r^{-\alpha}$ ($\alpha = 0.50 \pm 0.06$) from the dependence of the radius of gyration on the number of particles in the cluster.[5] The dependence of the rms thickness on the number of particles in the three-dimensional surface deposits ($T \sim N^{\epsilon}$; $\epsilon = 1.70 \pm 0.2$) implies a density profile of the form $\rho(r) \sim r^{-\alpha_s}$ with the exponent (α_s) having the value of 0.41 ± 0.07. Similarly, for the (three-dimensional) fiber deposits the dependence of the radius of gyration on the number of particles ($R_g \sim N^{\delta}$; $\delta = 0.665 \pm 0.030$) implies a density profile of the form $\rho(r) \sim r^{-\alpha_f}$, where r is the distance from the fiber. Our corresponding numerical estimate for α_f is 0.50 ± 0.07. While the density profile exponents are somewhat smaller for surface deposits than for deposits on single particles or fibers, our results suggest that the structural characteristics of systems formed by diffusion-controlled processes are determined mainly by the dimensionality of the space in which the growth process is occurring and are insensitive to features such as surface curvature. Within the accuracy of our simulations the density profile exponents are equal for clusters, fiber deposits, and surface deposits.

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