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LETTER TO THE EDITOR

Aggregation by attractive particle–cluster interaction

A Block, W von Bloh and H J Schellnhuber

Fachbereich Physik and Institut für Chemie und Biologie des Meeres, Universität Oldenburg, W-2900 Oldenburg, Federal Republic of Germany

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Abstract. A quasideterministic irreversible growth model is studied, where aggregates are generated by attractive cluster-particle forces proportional to $r^{-\alpha}$. It is shown that fractal dimensions and growth site probability measures of the resulting fractal structures strongly depend on the parameter α. Comparison with experimental results indicates that this model represents a further step towards realistic simulations of growth processes.

The investigation and modelling of irreversible growth phenomena has become a mainstream topic only in the last decade. Aggregation products like colloids, gels, soot, dust and flakes (e.g. atmospheric and marine snow [1]), although ubiquitous in nature, were previously largely ignored or regarded as intractable 'messy effects' (see, however, and for instance [2]). The recent reversal of opinion has two main reasons. The first one is the key observation that the structures grown by stochastic processes are often not simply disordered, but exhibit non-trivial statistical scale-invariance over several orders of magnitude. The second reason is the introduction of the concept of fractality by Mandelbrot [3], which provides a quantitative framework for the description and classification of the types of dilational symmetry encountered here.

Meanwhile a whole field has been established, on the basis of these insights, which keeps on producing new information at a great pace (for reviews, see [4-8]). Very recently the question 'Why does nature organize itself predominantly in fractal shapes?' has attracted more and more attention; the concept of self-organized criticality may provide one possible preliminary answer [9].

Another way to shed light on this problem is the simulation of growth processes by simple, non-trivial computer models. They often produce very natural-looking aggregates whose fractal dimension D happens to agree amazingly well with experimental findings [4-7]. Examples for such successful models are diffusion-limited particle-cluster aggregation (DLA) [10], ballistic aggregation [11, 12], cluster-cluster aggregation (CCA) [13], and various modifications of these scenarios. Up to now, however, a generally accepted 'canonical' theory for the description of fractal growth has not yet emerged.

On the other hand, some basic ingredients for the formation of scale-invariant aggregates can be distilled from extensive computer simulations. An essential requirement in the context of particle-cluster aggregation concerns the fractal dimension d_w

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of the particle trajectories, which is defined by (see, for example, [14])

$$\langle r^2(t_n)\rangle \sim t_n^{2/d_w}. \tag{1}$$

Here $\langle r^2(t_n)\rangle$ is the mean square distance of the random walker from its starting point and t_n denotes the number of time steps.

Brownian motion ($d_w = 2$) generates typical tenuous DLA clusters ($D \approx 1.7$ for Euclidean dimension $d = 2$); linear trajectories ($d_w = 1$) with randomly chosen directions lead to compact structures ($D = d$) characteristic of ballistic aggregates [15]. By means of Levy-flight particle trajectories with $d_w \in [1, 2]$ one can continuously interpolate between both scenarios and the corresponding fractal dimensions of the aggregates [16]. In all cases, however, an isotropic probability distribution for the allowed particle movements is essential. Any symmetry-breaking bias, like a drift towards the centre of the cluster, gives rise to compact structures and is thus equivalent to ballistic aggregation [17].

It seems that a crucial morphologic element of diffusion-limited particle-cluster aggregation, namely the screening of the fjords by the tips of the structure, takes full effect when the particle trajectory is definitely space-filling and statistically isotropic. But this precondition is only relevant if the attaching particle has no 'information' whatsoever about the structure of the already existing cluster. By way of contrast, the necessary screening effect can also be realized as a property of the whole system by introducing a physical interaction between cluster and growth particle. This means that tenuous fractals may be grown via deterministic trajectories, which clearly have $d_w = 1$ and preferential directions!

In this paper we present a simple, novel growth model with interactions governed by the general power law $r^{-\alpha}$. This allows us to generate deliberately fractal aggregates with continuously tunable dimension that is controlled by the forced-induced screening of the inner regions of the cluster. The scaling properties of the growth-site probability-distribution, which is a powerful means of characterizing fractal growth products [18], also depend strongly on the interaction chosen. The model is not only interesting from a conceptual point of view: for certain values of the force parameter α it directly simulates realistic physical situations. In fact, the trajectories of particles in most natural growth processes are subject to deterministic, interaction-induced influences in addition to more or less severe stochastic perturbations.

Most simulations of cluster-particle growth do not take into account that the trajectories of the constituent monomers are usually affected by the already existing aggregate. A more realistic approach was pursued by Ansell and Dickinson [19] in order to model the aggregation of charged colloidal particles. Their basic simulation tool was a cluster–cluster aggregation scenario. The dynamics of the constituents was modelled by Brownian motion in the liquid under the simultaneous influence of interactive forces that are composed of a hard-core repelling term and a long-range Van der Waals attraction. Because of the N^2 calculations per time step required for N-particle CCA, however, only relatively small systems could be simulated. Therefore it is difficult to draw definite conclusions concerning scaling behaviour from the results presented there. Quite recently, Meakin and Muthukumar [20] have presented a more sophisticated approach to colloid formation based on an elaborate reaction-limited cluster–cluster-aggregation (RLCCA) scheme.

Our model is constructed on a similar physical basis, but is much easier to handle due to various conceptual simplifications. It is well known that the reasonable assumption of decreasing mobility with cluster size leads to a transition from the CCA scenario

to a model describing the diffusion-limited aggregation of monomers to more or less immobile clusters. Therefore it is both justified and useful to reduce the multiple interactions between all the constituents of the sample to the simple force law

$$F_j(r_{N+1}) \propto \frac{1}{|r_{N+1}+r_j|^{\alpha}} \frac{(r_{N+1}-r_j)}{|r_{N+1}-r_j|}. \tag{2}$$

Here F_j denotes the force exerted by the jth member in the cluster at position r_j on the not-yet-attached $(N+1)$th particle at position r_{N+1}. The parameter $\alpha > 0$ controls the decay of the interaction with distance.

As a consequence, the growth process can be simulated as follows: a seed particle is initially placed at the origin of our d-dimensional Euclidean space and the growth particles are successively launched from stochastically chosen positions on the $(d-1)$-dimensional surface of a hypersphere with radius R_s. The new position $r_{N+1}(t+\Delta t)$ of the $(N+1)$th growth particle after a time step of length Δt is calculated from the forces and the old position $r_{N+1}(t)$ according to

$$r_{N+1}(t+\Delta t) = r_{N+1}(t) + \text{constant} \times \Delta t \sum_{j=1}^{N} F_j(r_{N+1}(t)). \tag{3}$$

This is a quasi-kinetic ansatz to describe the particle trajectories with dimension $d_w = 1$: the constant in (3) is assumed to be γ^{-1}, where γ is a velocity-dependent friction coefficient. Our ansatz is physically correct whenever the relaxation time $\tau = m/\gamma$ (m = mass of the particle) and the magnitude of ∇F are small.

Let us denote by R_{cl} the current maximal distance of cluster particles from the origin. At points r satisfying $|r| \gg R_{cl}$ the resulting force vector is quite small. Therefore it is ineffective to calculate position increments for a fixed time step Δt; instead we tune Δt to enforce a fixed step length $s = F_{tot} \times \Delta t = \text{constant}$, where $F_{tot} = |\Sigma_{j=1}^{N} F_j|$. s has to be chosen small enough to rule out artificial distortions of the cluster geometry. Suitable step lengths were determined empirically as follows: for a fixed interaction exponent α an ensemble of clusters was generated by the aggregation algorithm described above for varying s. For each cluster the box-counting dimension or capacity D_B (see, for example, [21]), which is defined as

$$D_B = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)} \tag{4}$$

was calculated. Here $N(\varepsilon)$ is the number of non-empty cells when the sample is covered by a hypercubic lattice of lattice constant ε. The results for $d = 2$ and $\alpha = 3$ are summarized in table 1.

Table 1. Dependence of fractal dimension D_B on length steps s for $d = 2$ and $\alpha = 3$. The radius of the growth particles is 1.5, $N = 6000$ in all cases.

Length step s	D_B
2.0	1.57
1.5	1.58
1.0	1.55
0.5	1.49
0.2	1.49
0.1	1.48

We clearly see that D_B rapidly converges with decreasing s and remains almost unaffected by further reduction below $s < \hat{s} = 0.4 \times$ particle radius. Using the box-counting dimension as a sensitive structural probe, we can detect an optimal $\hat{s} = \hat{s}(d, \alpha)$ under general conditions in an analogous way.

The choice of the launching radius R_s may also influence the structure of the aggregate. Figure 1 shows a typical product of our growth model. The trajectories of the particles, which started from a homogeneous distribution of initial points, are explicitly indicated in this picture.

One can clearly realize that the density of trajectories—or equivalently, field lines—varies considerably in the vicinity of the cluster. Thus, if the particles are released from positions that are too close to the cluster, then they get attached to certain surface sites of the cluster with unphysically high probability. If they start, on the other hand, far away from the aggregate, then they are able to scan the overall force field and to adjust their moves accordingly. As a consequence, the structure and its fractal dimension will settle to a definite quality and quantity with increasing R_s.

The aggregate depicted in figure 1 exhibits non-trivial scaling behaviour similar to DLA structures, despite the fact that the morphogenetic mechanism is rather of ballistic-

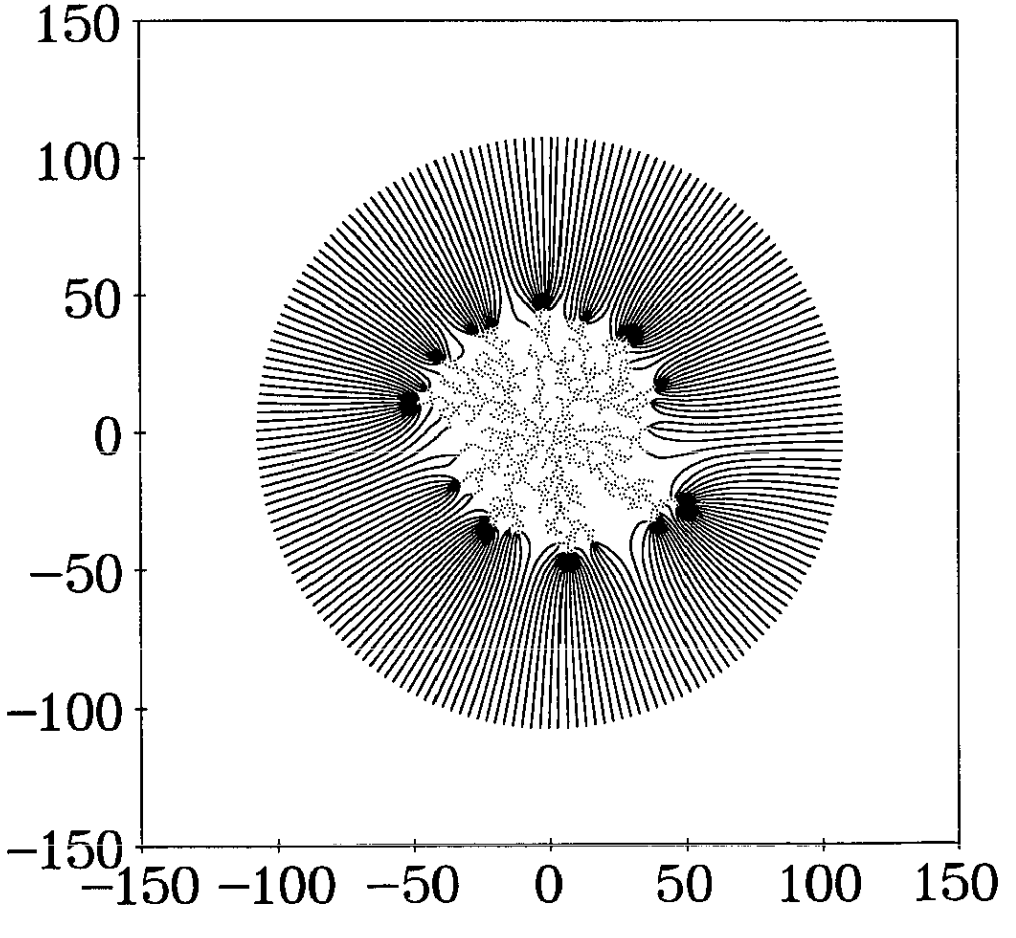

Figure 1. A small aggregate, $d = 2$, $N = 1000$, grown according to the rules given in the text. The trajectories associated with equidistant starting-points are also depicted to give an estimate of the growth-site distribution measure.

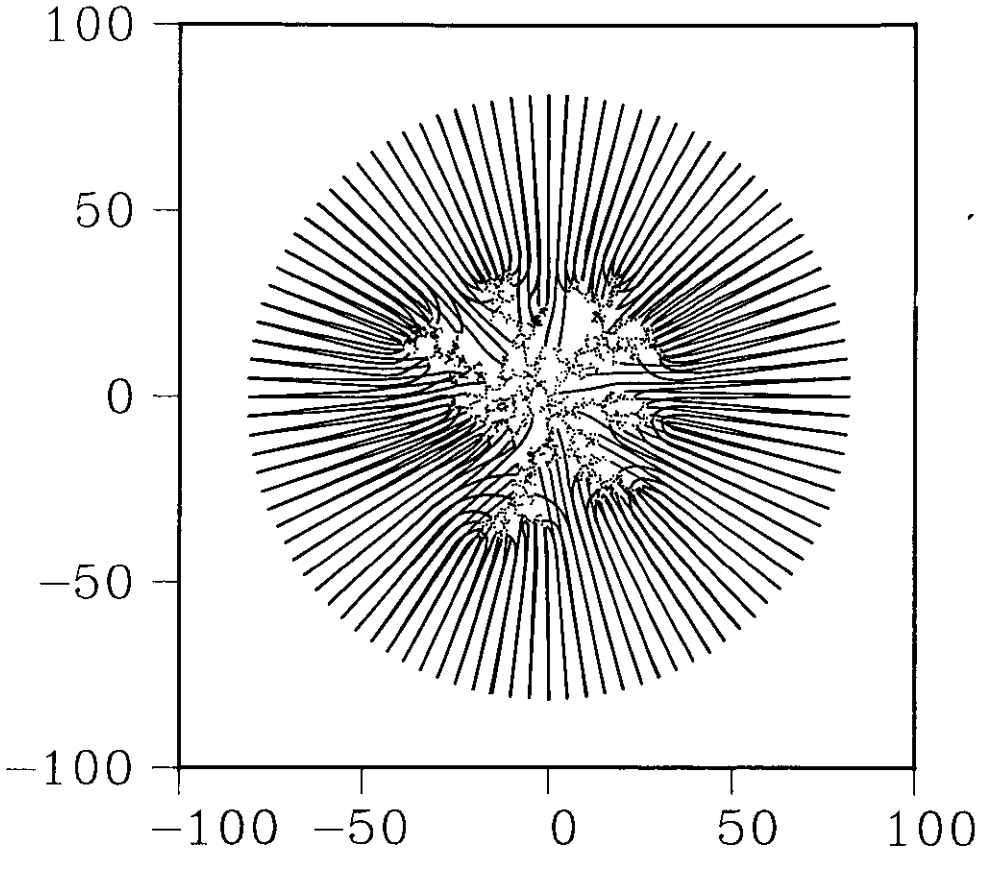

Figure 2. Comparison of the lines of the diffusion field (in black) with the lines of the $\alpha = 1$ interaction field (in red) as defined by a typical fractal DLA cluster ($N = 1000$).

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aggregation type. But in contrast to the ballistic-aggregation scenario, the particles head for the centre of *force*—not of the aggregate! On the other hand, if we add a sufficiently large random displacement vector to the right-hand side of (3), then the process would generate true DLA clusters.

Even without such an additional stochastic element it may seem that our model is equivalent to DLA in the special case $\alpha = 1$ ($d = 2$), as particle aggregation is governed by a potential U satisfying the Laplace equation. This is not true, however: the DLA potential has to satisfy $U(p) = 0$ at all perimeter sites p of the cluster, which behaves like a conductor. Our aggregates rather resemble dielectrics for any choice of α and the potential is directly obtained from the spatial distribution of the constituents! The $\alpha = 1$ structures may also be interpreted as conglomerates of gravitational masses in 2D Euclidean space. It is quite instructive to elaborate the differences between this case and DLA a little bit further. To that end we have calculated the Laplacian fields resulting from the two corresponding boundary conditions for the *same* fractal cluster (produced by DLA). Figure 2 demonstrates that the interactive scenario induces field lines, which may be tangent to the perimeter and penetrate much deeper into the aggregate.

The model presented here is closely related to physical reality, in particular in the case of $\alpha = 6$ (Van der Waals interaction) or $\alpha = 3$ (direct dipole–dipole interaction).

Figure 3 contrasts aggregates that were generated by our algorithm for different values of the interaction exponent. The distance of the launching positions from the seed particle was chosen sufficiently large to guarantee that the field lines meet the starting surface in an isotropic and radial way ($R_s \approx 2 \times R_{cl}$).

The qualitative dependence of the structure on α is obvious. For $d = 2$ the variation of the fractal dimension D_B with the interaction exponent α was systematically investigated. The results are summarized in table 2 and especially demonstrate the strong reduction of D_B with increasing α.

The influence of α is even more felt in the spectrum of scaling indices for the growth site probability density, which defines a measure on the fractal in the limit $N \to \infty$. This measure may be evaluated by test particles indicating potential growth sites without actually contributing to the cluster [22]. For finite samples consisting of N elements it is approximated by

$$p_\nu(\varepsilon) = \frac{N_\nu(\varepsilon)}{N} \tag{5}$$

where $N_\nu(\varepsilon)$ is the number of test particles ending in the νth box of edge ε. The resulting multifractal measure [23] can be characterized through the spectrum of *generalized fractal dimensions* $D_B(q)$, $q \in \mathbf{R}$ [24], defined as

$$D_B(q) = \lim_{\varepsilon \to 0} \frac{1}{q-1} \frac{\ln \sum_{\nu=1}^{N(\varepsilon)} [p_\nu(\varepsilon)]^q}{\ln \varepsilon}. \tag{6}$$

Figure 4 depicts the result of the multifractal analysis of the growth zones of aggregates for $d = 2$, $\alpha = 2$ and 5; this analysis was carried out using a novel, effective box-counting algorithm [25].

Our general finding is that the spectrum of dimensions $D_B(q)$ strongly depends on α and that, in particular, the limit dimension $D_B(\infty)$—which quantifies the scaling behaviour of the densest regions of the growth measure—monotonically decreases with increasing α to reach the value 0 for $\alpha \to \infty$.

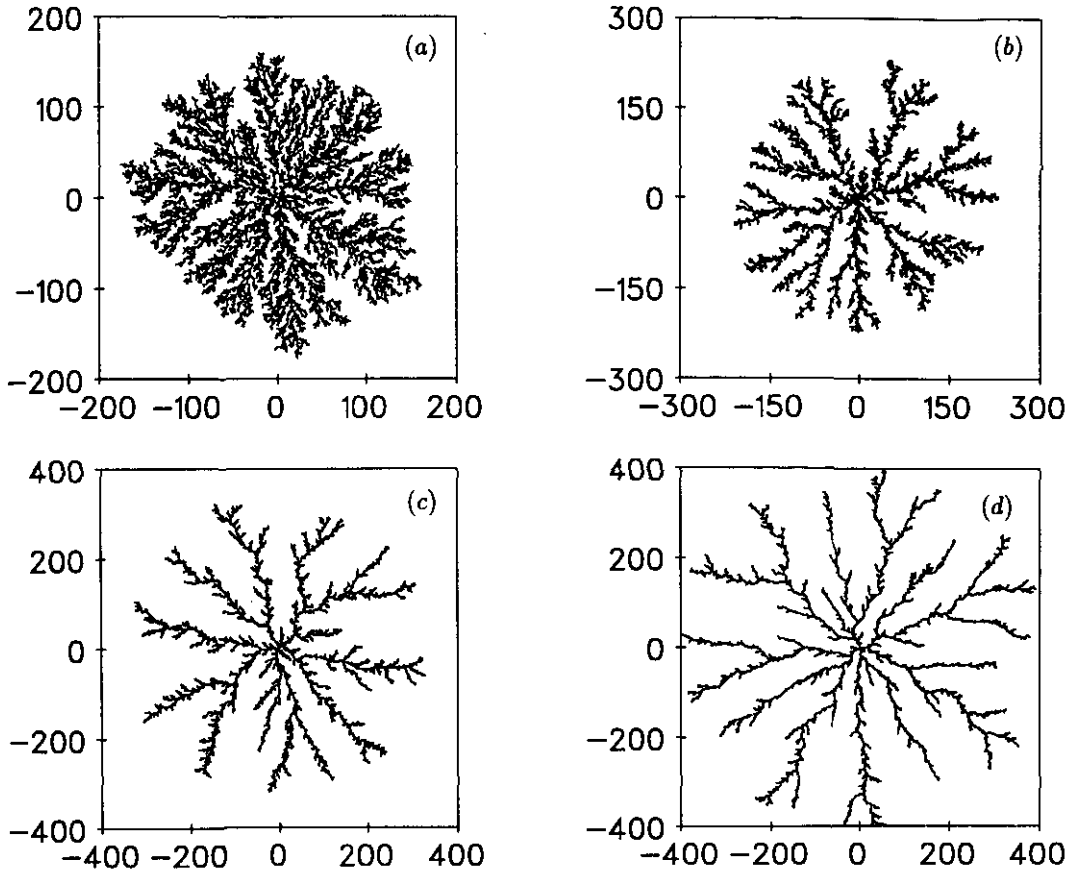

Figure 3. Aggregates grown for different exponents α of the attractive particle-cluster interaction. (*a*) $\alpha = 2$, (*b*) $\alpha = 3$, (*c*) $\alpha = 4$, (*d*) $\alpha = 5$. In all cases $d = 2$ and $N = 12\,000$.

Table 2. Effect of α on D_B. For fixed α the fractal dimension is calculated by averaging over eight clusters consisting of 10^4 particles each. The value 0.2 is chosen for the step length s.

Exponent α	Fractal dimension D_B
2	1.70 ± 0.04
3	1.49 ± 0.02
4	1.34 ± 0.01
5	1.27 ± 0.01
6	1.22 ± 0.01

The latter limit means that cluster-particle aggregation is dominated by the minimal distance in (2), so our model crosses over to growth by shortest-path travel [26]. Note, however, that such a scenario rather sensitively depends on the initial conditions in an off-lattice realization, while it is prone to artefacts when studied on lattices. For instance, a hexagonal lattice induces smaller fractal dimensions than a quadratic one.

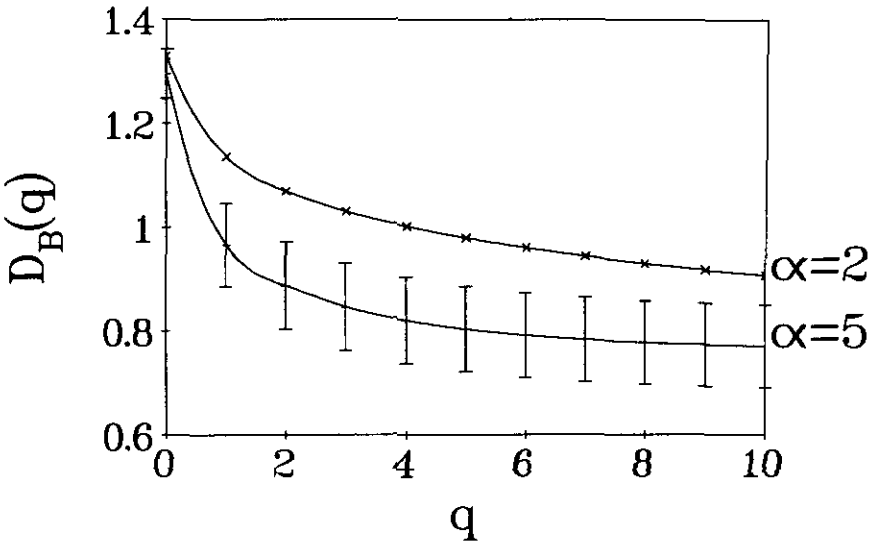

Figure 4. Comparison of the spectra of generalized fractal dimensions $D_B(q)$, $q \in \mathbf{R}$, for aggregates generated with $\alpha = 2$ and $\alpha = 5$.

The main result of our investigation is that the introduction of interactions between particles and clusters makes it possible to grow fractal aggregates in a deterministic way; the dimensions of structure and growth measure depend strongly on the force law and differ drastically from DLA in the limit of large α. Our findings are consistent with experiments on aggregation of charged silica colloids on a surface [27], where the measured fractal dimension is significantly below the predictions of the Witten–Sander model. By way of contrast, our results for the Van der Waals exponent $\alpha = 6$ (see table 2) are only slightly smaller than the data produced in the experiment. The residual deviation can be explained by two facts. (i) Real particles are distributed more or less homogeneously on the liquid's surface and may be incidentally close to growth nuclei. Therefore they tend to penetrate into the fjords of the aggregates with higher probability than the particles in our conceptually simpler computer simulation. (ii) Deterministic trajectories will be perturbed in real experiments by stochastic influences of Brownian type. This effect will also increase the fractal dimension of the aggregates.

We emphasize that our simulations offer only one possible explanation for the findings of Hurd *et al* [27]. Final answers certainly require further scrutiny of the experimental set-up.

Our scenario also provides, on the other hand, efficient ways to determine the scaling behaviour of the negative exponents ($q < 0$) of the growth site probability measure of aggregates. The basic idea is to track down the field line bundles emanating from the massively screened regions; this procedure works particularly well in the Laplacian cases [28]. Details will be presented elsewhere. The behaviour of negative moments is a topic of intense and controversial discussion, especially in the context of possible phase transitions in the DLA model (see, for example, [29]).

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