Diffusion-controlled aggregation in the continuum approximation

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A numerical solution and analytic approximation are obtained for the mean-field continuum equations corresponding to diffusion-controlled aggregation. For $d>2$ an asymptotic solution is found with the density of the cluster varying as the inverse radius, which suggests a Hausdorff dimension $D=d-1$.

In the Witten-Sander model[1,2] of diffusion-controlled aggregation, particles assemble to form an indefinitely large cluster by diffusing one by one from a large distance. The model was developed to describe aggregates of dust, soot, and other random objects, and it is potentially applicable to any growth process in which diffusion of some substance is the rate-limiting step. Some types of spinodal decomposition, flocculation, and dendritic crystal growth appear to fall into this category.[2] Diffusion-limited aggregates have a strikingly tenuous, wispy appearance, which reflects a fundamental scale-invariance property. This scaling may be seen in the density-density correlation $\langle\rho(r_1)\rho(r_2)\rangle$, where the average is taken over an ensemble of very large aggregates. Computer simulations[1-3] show that this correlation function falls as $|r_1-r_2|^{-A}$, where $A\approx d/6$ for dimension $d=2$–6. It can be shown that density profiles of this form have a "Hausdorff dimension" $D=d-A$. This means that the cluster may be considered for certain purposes as a fractal.[4] These universal power laws have yet to be explained. Recently, Muthukumar[5] has given a formula for D based on a coherent-potential approach. Tokuyama and Kawasaki have arrived at this formula by treating the aggregate in analogy with a self-repelling polymer.[6] The formula is quite consistent with the simulations, but it is based on several assumptions which we find questionable.[7]

In the paper[8] we investigate a smoothed-density or mean-field approximation[2] to the exact growth equations for the local density $\rho(r)$. We find that the mean density at a distance r varies as $1/r$, corresponding to $D=d-1$ for all spatial dimensions $d>2$. The amplitude of this power law is independent of the initial density. For $d=3$, these results have been obtained from a straightforward numerical solution of the continuum equations starting with a spherically symmetric seed (see Fig. 1). We describe below how this behavior may also be understood analytically.

The Witten-Sander model generates a disordered, connected cluster of particles on a lattice[1] of lattice spacing a. The lattice is truncated beyond a large enclosing sphere of radius R. Initially the cluster is a single particle at the center of this sphere. A second particle is introduced at random far from the origin, and it walks randomly until it reaches a site adjacent to the center. There it is adsorbed: it stops moving and becomes part of the cluster. Then another random walker is introduced; it too moves until it is adsorbed next to the cluster. This process continues until an indefinitely large cluster has been formed. Clearly

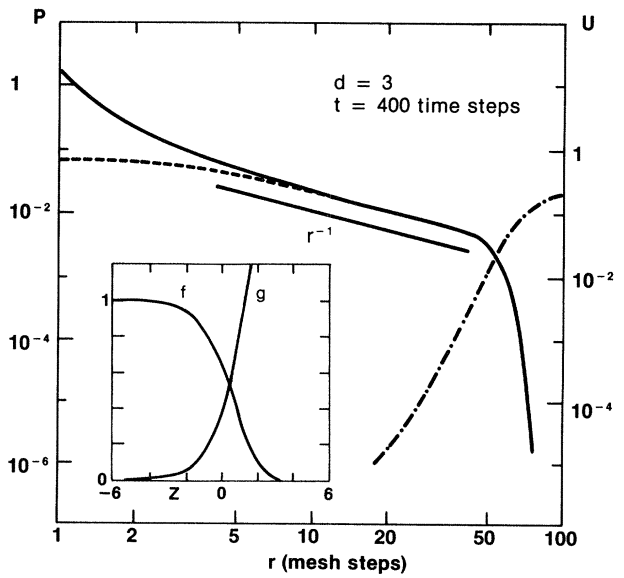

FIG. 1. Numerical solutions of the continuum equations. Curves at left are density profiles, differing only in the initial density of the "seed." Curve at right is the diffusing field u. Scales are logarithmic. Inset shows the scaling functions $f(z)$ and $g(z)$, Eqs. (15) and (16), for the case $a=0$.

this model simulates the growth of an aggregate by the adsorption of Brownian particles.

One may analyze the ensemble of such aggregates by giving the probability per unit time that a given cluster gains a particle at the site x. Growth occurs only if x is a perimeter site—adjacent to a cluster site, but not itself one. Growth at a perimeter site at time step t occurs only if the random walker is present. For this treatment we suppose that the walker is adsorbed with a "sticking probability" B. Then the probability of growth at x and at time step t is $Bu(x,t)P(x)$, where $P(x)$ is defined as 1 on perimeter sites and 0 elsewhere. We may represent the cluster itself by a field ρ, which is 1 on aggregate sites and 0 elsewhere. The average increment in $\rho(x)$ during a time step is the adsorption rate at x:

$$\langle \Delta\rho \rangle_t \equiv \langle \rho(x,t+1)-\rho(x,t) \rangle_t = BU(x,t)P(x) . \tag{1}$$

The actual change of ρ is of course either 1 or 0, and is distinctly different from this average. The probability u obeys a diffusion equation:

$$\Delta u = a^2\nabla^2 u - BuP . \tag{2}$$

Here $a^2\nabla^2$ is the lattice Laplacian, i.e., the average of u over sites adjacent to x, minus $u(x)$. The probability u is normalized to unity in the enclosing sphere, and is constant over this sphere. On perimeter sites diffusing particles are removed at the same rate BuP at which they are added to the cluster. The probability field u for a particular cluster is given *exactly* by this equation. In the limit of a very large enclosing sphere the u field attains a steady state and the time derivative Δu goes to zero.[1]

It is the density correlations defined by these equations which are believed to obey the universal power laws mentioned above. Since these power laws hold even over distances indefinitely greater than the "lattice length" a, the essence of the equations should be expressible in a continuum limit, in which a is indefinitely small. To construct a continuum formalism we average the fields in the problem—ρ, u, and P—locally over space, i.e., over many lattice sites, but a small fraction of the cluster. The P field can be expressed in terms of the ρ field:

$$P(x)=\rho(x)+a^2\nabla^2\rho+O(\rho^2) . \tag{3}$$

In the continuum approximation each ρ is to be replaced by its local average. Since the ρ profile is a fractal, the local average decreases indefinitely as the size of the averaging region increases. We are thus led to neglect the terms of order ρ^2 in Eq. (3). Using this approximation for P, it is natural to postulate the following continuum approximation to Eqs. (1) and (2):

$$\frac{\partial\rho}{\partial t} = u(\rho+a^2\nabla^2\rho) , \qquad 0=\nabla^2 u - u(\rho+a^2\nabla^2\rho) . \tag{4}$$

Here we have rescaled the fields to eliminate coefficients. We have also neglected the stochastic noise in $\partial\rho/\partial t$ discussed below Eq. (1). Since the fluctuations of $\Delta\rho(x)$ from its ensemble average $\langle \Delta\rho(x) \rangle_t$ are independent at every site, these fluctuations are reduced indefinitely upon averaging over many sites. Still in neglecting these fluctuations altogether, we clearly oversimplify the problem. But the resulting deterministic system has many features of the exact equations, and it may readily be analyzed.

In these equations ρ has dimensions of inverse length squared, and u has dimensions of inverse time. Note that any overall time-dependent factor multiplying u can be compensated by changing the time scale. Thus we can confine our discussion to boundary conditions where u is at infinity constant in time. The single length parameter a can also be eliminated by rescaling $r\to ar$ and $\rho\to\rho/a^2$, but we have retained it to exhibit the singular behavior of the limit $a\to 0$. In the case of spherical symmetry, ρ and u are functions of radial position r and time t only, and

$$\nabla^2=\frac{\partial^2}{\partial r^2}+\frac{(d-1)}{r}\frac{\partial}{\partial r} . \tag{5}$$

The appropriate initial conditions specify the cluster density $\rho_0(r)$ at $t=0$, while for $d>2$ the boundary conditions for all times are

$$\left.\frac{\partial u}{\partial r}\right|_{r=0}=0 \quad \text{and} \quad u(\infty,t)=u_\infty , \tag{6}$$

where u_∞ is a constant. For convenience we shall set $u_\infty=1$.

We seek an approximate analytic solution of these equations for large t. If initially the ρ field is too small to lead to any appreciable absorption, the u field is virtually constant, and Eq. (4) is essentially a diffusion equation for ρ. After sufficient growth has occurred, the density profile assumes a Gaussian shape:

$$\rho=\frac{\rho_0\exp[t-r^2/(4a^2t)]}{(4a^2t)^{d/2}} . \tag{7}$$

At fixed r, ρ grows exponentially in t, and the absorption of the u field eventually cannot be neglected. The density profile is no longer "transparent" to the diffusing field. Then we expect u to vanish and ρ to approach a static limit $\rho(r)$. The distant u field is that of a perfect absorber of some radius R:

$$u(r)=1-[R(t)/r]^{d-2} . \tag{8}$$

We may bracket the behavior of the u field using two extreme models. In the first we imagine that the ρ field continues to grow transparently, as in Eq. (7). This greatly overestimates ρ in the strongly absorbing region. Assuming this ρ field, it is straightforward to find the corresponding u field using the Schrödinger equation which is the second half of Eq. (4). The u field grows exponentially with r for small r. The decay length $\xi(r)$, defined by $(\nabla^2 u/u)^{-1/2}$, varies as $[\rho(r)]^{-1/2}$. The boundary of the strong absorption region is the point at which the spatial variation of ρ over a distance ξ beomes appreciable. Labeling this boundary by r_1, we may express this condition by

$$\left.\frac{1}{\rho}\frac{d\rho}{dr}\right|_{r=r_1}=[\rho(r_1)]^{1/2} . \tag{9}$$

Using Eq. (7) for ρ, this gives

$$[r_1/(2a^2t)]^2=\rho_0[4a^2t]^{-d/2}\exp[t-r_1^2/(4a^2t)] . \quad (10)$$

The exponential controls the time dependence of r_1. Up to logarithmic corrections,

$$r_1=2at . \quad (11)$$

The effective radius R_1 appearing in the distant u field is equal to r_1 up to a factor of order unity. In the actual growth the ρ field is everywhere smaller than in this example. Thus the u field is larger than this estimate, and R should be smaller than R_1. This example shows that R can grow no faster then linearly with time.

An opposite limiting case can be constructed by considering the radius r_2 at which absorption first becomes appreciable at large distances. For very large distances the absorption length $\xi(r)$ is exponentially large; for smaller distances it diminishes. The absorption must be negligible as long as $\xi(r)$ is much greater than any other length. The absorption must thus become negligible beyond r_2 such that $\xi(r_2)=r_2$. Thus $\rho(r_2)^{-1/2}=r_2$. We now choose a density profile given by Eq. (7) for $r\geq r_2$ and *constant* for $r<r_2$. Again, in this case $r_2\sim at$. This profile is "marginally opaque;" that is its effective radius R_2 is a fraction of r_2. But this profile is everywhere smaller than the actual one, except for $r>r_2$, where the absorption is negligible anyway. The u field should thus be *larger* in this example than in the actual case. Thus we expect the actual R to be greater than R_2. This example shows that the actual R grows no slower than linearly with time. Together the two examples indicate that the effective radius R is some fixed fraction of $2at$.

Given that $R(t)$ is proportional to t, we may show that $\rho(r)$ attains a power-law form for $r\ll R$. For this, we use the mass conservation implicit in Eq. (4): Since $\partial\rho/\partial t=\nabla^2 u$, the growth rate of the cluster mass dN/dt is equal to the flux of the u field from infinity, $\int \nabla u\, ds$. Using Eq. (8) for the distant u field, we obtain a relation between N and R

$$\frac{dN}{dR}\frac{dR}{dt}=S(d)(d-2)R^{d-2} , \quad (12)$$

where $S(d)$ is the area of the unit sphere in d dimensions. Since dR/dt is a constant v the solution for $N(R)$ is a simple power law:

$$N=\frac{S(d)}{v}\frac{d-2}{d-1}R^{d-1} , \quad (13)$$

i.e., the mass scales with absorption radius as in a fractal object with $D=d-1$. We note that if the mass N arises from a time-independent density $\rho(r)$ for $r<R(t)$, then $\rho(r)=(d-2)/(vr)$. This argument is valid only for $d>2$ because we have assumed that u approaches a constant as $r\to\infty$.

We now discuss how the ρ and u fields interpolate between the outer, transparent solution and the inner, static one, giving further arguments that the growth velocity v is a constant. In the intermediate region $r\sim at$, our strategy is to seek an approximate solution of Eq. (4) which can be asymptotically matched to the solutions in the opaque and in the transparent regime. In this transition region we set $\nabla^2\cong\partial^2/\partial r^2$ in Eq. (4) and require that ρ and u depend on r and t only through the single variable

$$z=\frac{r-R(t)}{\lambda(t)} , \quad (14)$$

where $R(t)$ and $\lambda(t)$ are undetermined functions of t. On dimensional grounds such a "kink" solution must have the form

$$\rho=\frac{1}{\lambda^2}f(z) \quad (15)$$

and

$$u=\frac{v}{\lambda}g(z) . \quad (16)$$

Substituting these expressions in Eq. (4) and neglecting terms proportional to $\dot{\lambda}/\lambda$, which we assume to become small for large t, we obtain two ordinary differential equations for $f(z)$ and $g(z)$,

$$\frac{dg}{dz}=1-f , \quad (17)$$

$$\frac{df}{dz}=-g\left[f+\frac{a^2}{\lambda^2}\frac{d^2f}{dz^2}\right] . \quad (18)$$

We seek a solution of Eqs. (17) and (18) subject to the boundary conditions

$$\lim_{z\to-\infty}[1-f(z)]=\frac{dg(z)}{dz}=0 . \quad (19)$$

For $a=0$ we can integrate these equations, to obtain

$$g=[2(f-1-\ln f)]^{1/2} \quad (20)$$

and

$$\int_{f_0}^{f}\frac{d\psi}{\psi(\psi-1-\ln\psi)^{(1/2)}}=-(2z)^{1/2} . \quad (21)$$

The integration constant f_0 determines the location of the origin $z=0$. We choose this for convenience so that $g(z)-z\to 0$ for large positive z. In this case we have

$$\lim_{z\to\infty} f(z)\cong Ae^{-z^2/2} , \quad (22)$$

where $A=0.366$, and for large negative z

$$\lim_{z\to-\infty} f(z)=1-Be^{z} ,$$
$$g(z)=Be^{z} , \quad (23)$$

where $B=0.661$.

For general z we obtain $f(z)$ and $g(z)$ by numerical integration; see the inset of Fig. 1. For the case $a\neq 0$, this solution is applicable for $z\lesssim\lambda/a$, but for $z>\lambda/a$ the function f becomes oscillatory and is given asymptotically by

$$f=\frac{B}{z^p}\sin\left[\frac{\lambda}{a}z+\phi\right] , \quad (24)$$

where $p=1/2a^2$. We presume that Eqs. (17) and (18) cease to be applicable before these large-z oscillations appear.

We must now match this kink solution for $z<\lambda/a$ to the d-dimensional asymptotic solution for the ρ in the transparent region, Eq. (7). In this domain the diffusion field u satisfies the free Laplace equation and has the form of Eq. (8). Expanding Eq. (8) in powers of $x=r-R$, we have to order (x/R)

$$u=(d-2)\frac{x}{R} . \tag{25}$$

Comparing Eq. (25) with the asymptotic form of the kink solution for u, Eqs. (16) and (22), we find

$$\frac{\lambda^2}{v}=\frac{R}{(d-2)} . \tag{26}$$

To obtain a matching condition for ρ, we now approximate u by setting

$$u\cong\frac{v}{\lambda^2}x \quad \text{for } x\leq\frac{\lambda^2}{v} , \tag{27}$$

$$u\cong 1 \quad \text{for } \frac{\lambda^2}{v}\leq x . \tag{28}$$

Hence the solution for ρ in the transparent region, Eq. (7), remains valid down to $r\cong R+\lambda^2/v$, where it must be joined to the asymptotic kink solution, Eq. (22). Equating the arguments of the exponential terms, we obtain the condition

$$t-\frac{(R+\lambda^2/v)^2}{4a^2t}=-\frac{\lambda^2}{2v^2} . \tag{29}$$

This relation together with Eq. (26) determines R and λ as a function of time. We find

$$R=vt \quad \text{and} \quad \lambda=v(\beta t)^{1/2} , \tag{30}$$

where

$$v=\frac{2a(1+\beta/2)^{1/2}}{(1+\beta)} \tag{31}$$

and $\beta=1/(d-2)$. Since $\dot{\lambda}/\lambda=1/2t$, this justifies *a posteriori* neglecting terms of this form in deriving Eqs. (17) and (18). Note that the location of the matching point $x\cong\lambda^2/2a$ corresponds also to the limit of the range beyond which the kink solution becomes oscillatory, Eq. (24).

These features have been confirmed by a direct numerical integration of Eq. (4) for three dimensions. Figure 1 shows the ρ and u profiles after they have reached their ultimate form. Two initial ρ fields of step-function form were used—one of small amplitude and one of large. It is clear that the initial amplitude does not affect the ultimate power law or its amplitude. The u integration was done starting from the origin, taking $u(0)$ and its r derivative equal to unity. The first and second derivatives were represented numerically as first or second differences. Three distinct spatial regions are evident in the ρ profile. In the opaque region of small r the growth has ceased and ρ is well approximated by the power-law dependence $\rho\sim r^{-1}$. This region is bounded by a narrow transition region, where ρ falls off and u increases rapidly. Beyond this region, ρ vanishes and u is practically constant.

The mean-field equations appear to be a promising starting point for understanding diffusion-limited aggregation, with its spatial fluctuations and nontrivial power laws. Even this simplest continuum treatment of diffusion-limited aggregation shows why the average density of the aggregate declines indefinitely as its size grows. To these equations the effects of fluctuations can be systematically added to improve the description. These fluctuations must be treated in order to investigate the local correlations of the density and demonstrate scale invariance of the structure.

Other refinements of the present treatment have appeared since this work was completed. A systematic treatment of the kink region[9] confirms the qualitative picture given here. The effect of nonspherical initial conditions[10] has been shown to be important, as suggested above.

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