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Crossover in diffusion-limited aggregation

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We consider a generalization of the Witten-Sander model for aggregation to allow for a finite density of diffusing particles. In a continuum treatment we show that for small aggregates we recover the previous behavior that the density of the aggregate decreases inversely with the radius, but larger aggregates cross over to having constant density. Our results are in qualitative agreement with numerical simulations of the discrete model.

Witten and Sander[1] recently introduced a simple model for kinetic processes leading to the aggregation of large random structures such as soot particles, dust, or smoke. In this Rapid Communication we consider a simple generalization of the continuum model for these processes which exhibits an interesting new crossover behavior.

The Witten-Sander model was based on the assumption that particle diffusion to the aggregate is the limiting step in growth. Briefly, the process was the repeated attachment of randomly walking particles to the growing object. The result of computer simulations[1,2] is that the objects grown were very diffuse and dilation symmetric; their Hausdorff dimension is less than the dimension d of space and independent of short-range details (such as lattice type). These remarkable facts gave impetus to studies[3,4] of a continuum version[1] of the model in the limit of vanishing density of diffusing particles. Here we generalize this continuum model to allow for the case of a finite density of these particles. The density of diffusing particles is represented by $u(\vec{r},t)$ and that of the aggregate by $\rho(\vec{r},t)$. Then the generalized equations for diffusion and attachment are given by

$$\frac{\partial u}{\partial t}+\frac{\partial \rho}{\partial t}-D\nabla^2 u=0 \quad , \tag{1a}$$

$$\frac{\partial \rho}{\partial t}=Ku(\rho+a^2\nabla^2\rho) \quad . \tag{1b}$$

Here D is the diffusion coefficient, a the radius of the particles, and K the average "absorption" of particles by the aggregate. Equation (1a) expresses the conservation of diffusing particles. The form of Eq. (1b) is discussed in Refs. 1 and 3: It expresses the fact that particles can attach to the aggregate when they are less than a distance a from it. A simple rescaling of $\vec{r}$, t, ρ, u, and a allows us to put the equations in the form

$$\xi\frac{\partial u}{\partial t}=\nabla^2 u-u(\rho+a^2\nabla^2\rho) \quad , \tag{2a}$$

$$\frac{\partial \rho}{\partial t}=u(\rho+a^2\nabla^2\rho) \quad . \tag{2b}$$

Here ξ is proportional to the parameter by which u is scaled, and if we take $u\rightarrow 1$ far from the aggregate $\xi\sim u_\infty$, where u_∞ is the asymptotic density of diffusing particles before rescaling. The Witten-Sander process corresponds to the limit $\xi\rightarrow 0$ (very few particles diffusing at one time). In this limit, Eqs. (2) were studied by Ball, Nauenberg, and Witten,[3] and by Nauenberg[4] for the case that u and ρ are taken to be functions of radius alone (and time) for dimension $d>2$. The result for an arbitrary initial seed is that there is a growing front for the aggregate that propagates with constant velocity v and width $\lambda=v\sqrt{t}$; behind the front ρ varies as $(d-2)/vr$ and outside the aggregate $u\sim 1-(vt/r)^{d-2}$. This behavior can be interpreted as representing the average of a diffuse, "fractal" object with Hausdorff dimension $d-1$. This value does not agree very well with the Hausdorff dimensions found in the simulations of Refs. 1 and 2 except for large d. We believe that the spherically averaged theory becomes a progressively better representation of the model as d increases just as mean-field theories of phase transitions are better for large d.

In this paper we present analogous results for the case of ξ finite for any dimension of space, d. We were motivated by theoretical considerations and by recent computer simulations of Voss and Meakin,[5] who found that for a finite number of particles diffusing at the same time the aggregates are no longer fractal, but approach a fixed, constant density. We will demonstrate that this behavior follows from the continuum equations: While initially ρ drops as $1/r$ as in the $\xi=0$ limit, there is a crossover for times $t>t_c$, where $t_c=(d-2)/v^2\xi$, to a constant value ρ equal to ξ.

To construct an analytic solution of Eq. (2) for the case of spherical symmetry, we follow the lines of previous work.[3,4] We will consider long-time behavior only, and assume a solution of the form

$$\rho=\frac{1}{\lambda^2}f(z) \quad , \tag{3a}$$

$$u=\frac{v}{\lambda}g(z) \quad , \tag{3b}$$

$$z=\frac{r-vt}{\lambda} \quad , \tag{3c}$$

where v is the velocity and λ is the width of the growing front. It is easy to see that we can approximate

$$\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{d-1}{r}\frac{\partial}{\partial r} \approx \frac{\partial^2}{\partial r^2} \ , \quad (4)$$

because the neglected term for $d > 1$ is of higher order in a systematic power series solution in $1/t$. For $d > 2$ we expect this solution to be applicable for times $t > t_c$, while for $t < t_c$ there is an analogous power series in $1/\sqrt{t}$ discussed in Ref. 4 for the limit $\xi = 0$.

Then f and g satisfy the equations

$$f' = -g(f + a^2 f''/\lambda^2) \ , \quad (5a)$$

$$g' = 1 - f - hg \ , \quad (5b)$$

where $h = \xi\lambda v$, and we have normalized f to 1 as z approaches $-\infty$. Since f goes to zero as z approaches $+\infty$, we have, in this limit,

$$g \to 1/h \quad (6a)$$

and

$$\lambda^2 = 1/\xi \ , \quad (6b)$$

where Eq. (6b) follows from the condition $u(\infty) = 1$. From (6b) and (3a) we see that ρ approaches the constant ξ inside the aggregate.

It is now straightforward to write down the asymptotic behavior of the solutions of Eqs. (5a) and (5b) both inside and outside the aggregate. For $z \to -\infty$,

$$f = 1 - be^{pz} \ , \quad (7a)$$

$$g = bpe^{pz} \ , \quad (7b)$$

where $p = (h^2/4 + 1)^{1/2} - h/2$, and b is a constant. Similarly, as $z \to +\infty$ we can write, in general,

$$f = c_+ e^{-z/k_+} + c_- e^{-z/k_-} \ , \quad (8a)$$

$$g = \frac{1}{h} - e^{-hz} + d_+ e^{-z/k_+} + d_- e^{-z/k_-} \ , \quad (8b)$$

where

$$\frac{1}{k_\pm} = \left(\frac{2}{h}\right)\left(\frac{v}{2a}\right)^2 \left\{1 \pm \left[1 - \left(\frac{2a}{v}\right)^2\right]^{1/2}\right\} \ , \quad (8c)$$

and $c_\pm$ are contants determined by integrating Eqs. (5a) and (5b).

The examination of this limit is the key to the *velocity selection* mechanism for this problem. We first note that $v = 2a$ plays a special role in Eq. (8c); thus for $v < 2a$, f and g become oscillatory, decreasing with a single decay rate, while for $v > 2a$ they have two different decay rates. For $v = 2a$, $k_+ = k_- = h/2$, and Eqs. (8a) and (8b) are replaced by

$$f = (c + c'z)e^{-2z/h} \ , \quad (9a)$$

$$g = \frac{1}{h} - e^{-hz} + (d + d'z)e^{-2z/h} \ , \quad (9b)$$

where c, c', d, and d' are constants. Problems of this sort, where there exists a family of propagating solutions with arbitrary v, are familiar in situations involving nonlinear parabolic partial differential equations,[6] including the dendritic growth problem.[7] In our case, we can find the selected velocity v by applying a comparison theorem of Aronson and Weinberger,[6] which implies that any two solutions to our equations that do not cross at a given time t will never cross at any later time. Thus for all initial seeds which are bounded by the maximum decay rate $ze^{-z/h}$ in Eqs. (7)–(9) the velocity $v = 2a$ is selected. This value agrees with direct numerical evaluations of Eqs. (2a) and (2b). An example is shown in Fig. 1 which exhibits the expected crossover from $\rho \sim 1/r$ to $\rho \sim \xi$ at $t \sim t_c$. Numerical solutions to the asymptotic kink equations are illustrated in Fig. 2.

We now discuss the solutions [Eqs. (9a) and (9b)] in the context of the original aggregation problem. From Eqs. (3) and (9) we see that, outside the aggregate,

$$\rho \sim (r - vt)\exp[-(r - vt)/a] \ , \quad (10a)$$

$$u \sim 1 - \exp[-(r - vt)/l] \ , \quad (10b)$$

where $l = D/v$ and $v = 2aKu_\infty$. Here we have introduced a new length l; clearly, l diverges as $u_\infty \to 0$. Indeed, we see from (10b) that l has the interpretation of a boundary layer width and is analogous to the diffusion length in the dendri-

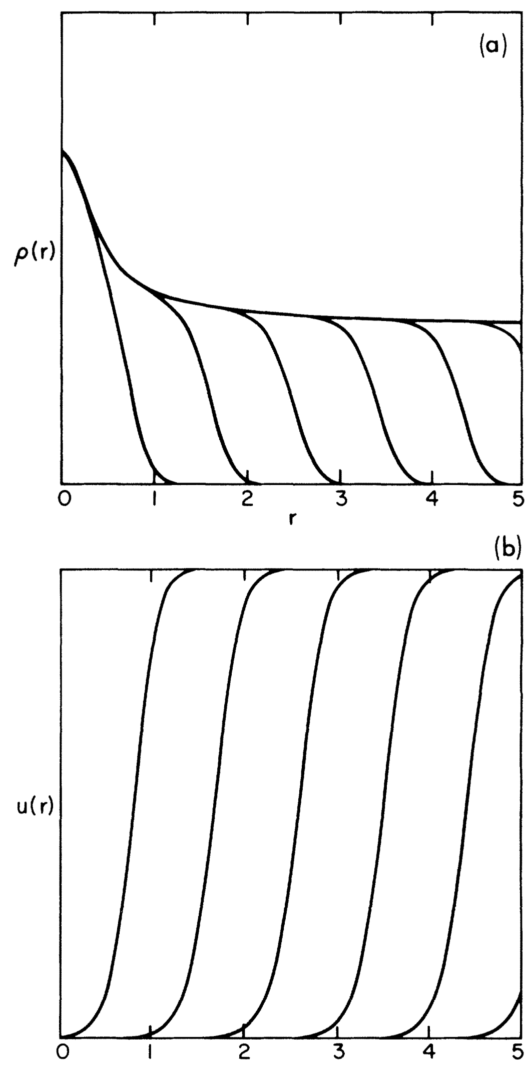

FIG. 1. (a) Numerical solution of Eq. (2) for $\rho(r)$ for $\xi = 100$, $a = 0.05$. The curves are at different times from $t = 10$ to $t = 60$. (b) Numerical solution for $u(r)$.

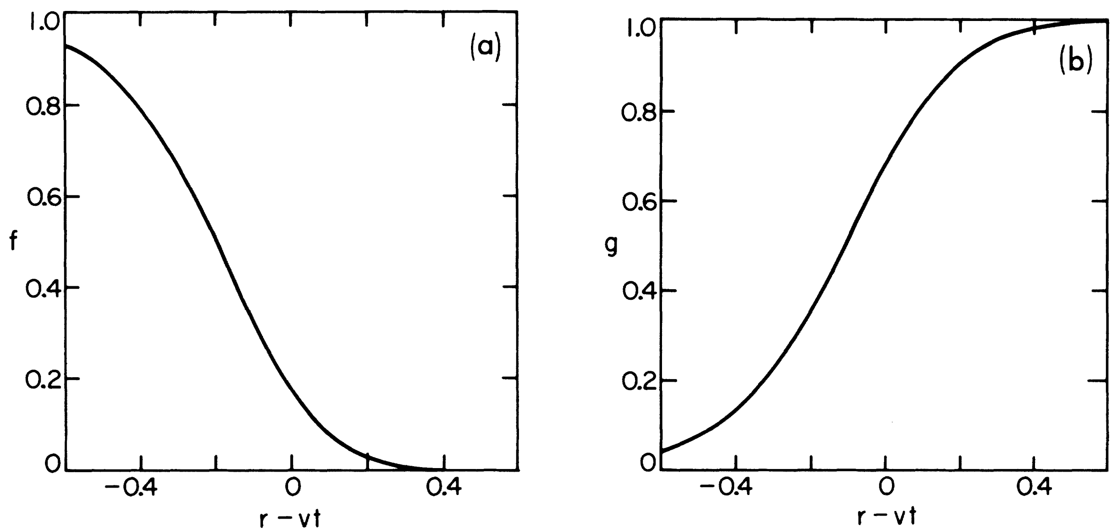

FIG. 2. (a) Numerical solution to Eq. (5) for the kink $f(z)$, for $\xi = 100$, $a = 0.05$. (b) Solution for $g(z)$.

tic growth problem.[7] In the limit $u_\infty = 0$, h goes to zero in Eqs. (5) to (9) and there will be a change from exponential decay of u and ρ to the previously derived behavior,[3,4] $f \sim \exp(-z^2/2)$, $u \sim z$, where $z = (r - vt)/\lambda$ and $\lambda = v\sqrt{t}$, but v is a different velocity. The length l gives the scale at which the crossover occurs for the size of the aggregate less than l, $\rho \sim (d-2)u_\infty l/r$, but when the size is greater than l, $\rho \sim u_\infty$. This behavior is evident in Fig. 1.

We can only speculate about further relationships between this spherically symmetric solution and a solution to the equations including angular variations. However, it is encouraging that we see behavior closely related to numerical simulations.[5] It is tempting to guess that the diverging length l will also be present in the full problem, conceivably in the form

$$l \sim \xi^{-\Theta} , \tag{11}$$

where Θ is a new "critical exponent" for this problem, not obviously related to the Hausdorff dimension. In the present treatment of the spherical case, $\Theta = 1$. The significance of l is that the object would look fractal until its size approaches l, and then it becomes a solid.

We have attempted to show here that the generalized aggregation model defined by Eqs. (2a) and (2b) has interesting properties which make it well worth further study. Two particular features are noteworthy. The generalized model behaves similarly to the Eden growth process,[8] in which all boundary sites are equally likely to grow. This is understandable as ξ becomes large: u becomes constant everywhere except for a thin boundary layer and feeds all boundary sites equally. Finally, if u is reinterpreted as a temperature field, it can be seen that the model with ξ finite might serve as an alternative approach to the usual Stefan treatment of the solidification problem.[7] Work on this aspect is in progress.

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