Some Consequences of an Equation of Motion for Diffuse Growth

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An equation of motion is derived for the surface harmonic measure and the surface Green's function in a class of diffusive growth processes, including diffusion-limited aggregation as a special case. These equations, in conjunction with a scaling hypothesis, imply a relation between the "multifractal" spectrum of exponents and the mass scaling of the clusters generated by these processes. Under some circumstances, this relation is inconsistent with a scaling law proposed by Turkevich and Scher.

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In many physical circumstances, the growth of structures is limited by diffusive effects. Examples include colloidal aggregation, electrodeposition, and, in some respects, solidification from a melt.[1-3] Although the essential physics underlying these phenomena was exposed by Witten and Sander in 1981, the intervening years have seen little analytical progress in a field that has been dominated by extensive and sophisticated numerical studies.[4,5] This Letter seeks to redress this balance slightly, by pointing out that certain powerful exponent relations can be generated by a quite simple analytical approach to this subject.

The Witten-Sander model may be easily described in a continuum, electrostatic language. The discussion will always be restricted to two dimensions. Consider a cluster of n particles whose surface is parametrized by s, so that the surface position is given by $\mathbf{x}(s)$. The cluster is made up of particles of size a; thus the surface is smooth on length scales smaller than a. The length of surface dw in an interval ds is given by $(dw/ds)ds$. In the space exterior to the cluster, the electric potential $\Phi(\mathbf{x})$ satisfies $\nabla^2\Phi(\mathbf{x})=0$, with $\Phi(\mathbf{x})=V_\infty=1$ on some distant outer surface, which acts as the source of particles. The local normal electric field at $\mathbf{x}(s)$ is $P(s)=\partial_{\hat{\mathbf{n}}}\Phi(\mathbf{x}(s))$; this quantity is sometimes referred to as the (unnormalized) "harmonic measure" of the surface.

In the Witten-Sander model, the probability $G(s)ds$ of the $(n+1)$st particle attaching to the cluster in the interval ds is

$$G(s)ds=\frac{P(s)(dw/ds)ds}{\int ds(dw/ds)P(s)}. \tag{1}$$

This model has been generalized by Niemeyer, Pietronero, and Wiesmann to account for the patterns formed in the dielectric breakdown of insulating media.[6] In this model, $G(s)$ is given by

$$G(s)ds=\frac{P^\eta(s)(dw/ds)ds}{\int ds(dw/ds)P^\eta(s)}, \tag{2}$$

which defines a different model for every value of η, and reduces to the Witten-Sander model if $\eta=1$.[6] One generally takes $\eta>0$.

In all of these models, the radius of r of the clusters generated in an isotropic experiment depends as a nontrivial power upon the number of particles, $n\sim r^D$.[6,7] For $\eta=1$, the mass scaling exponent D is approximately $D\approx 1.71$, and $D\to 2$ as $\eta\to 0$. It appears that D decreases with increasing η. D cannot be less than 1 for any η; it is not known if there is a critical η_c such that for $\eta>\eta_c$, $D=1$.

The phenomenology of the local electric field $P(s)$ about a cluster is now rather well understood. The most notable property of $P(s)$ is that different moments of $P(s)$ scale with independent "multifractal" exponents.[8-10] Writing the normalized electric field, or harmonic measure, $p(s)=P(s)/\int ds(dw/ds)P(s)$, one has that

$$\int ds\frac{dw}{ds}p^q(s)\sim\left(\frac{a}{r}\right)^{\tau(q)}. \tag{3}$$

The general properties of $\tau(q)$ are reviewed in several places. Here it is only relevant that $\tau(q)$ is a nontrivial monotonically increasing function of q, and that $\tau(1)=0$.[11,12]

$P(s)$ is a Green's function relating the voltage V_∞ on the distant surface to the normal electric field at $\mathbf{x}(s)$, given that the cluster surface is at zero potential. It is productive to consider also the Green's function between two different points of the surface, $H(s,s')(dw'/ds')ds'$. $H(s,s')(dw'/ds')ds'$ is defined as the normal electric field at $\mathbf{x}(s)$ if there is a unit potential in the interval ds' on the surface, and the potential on all other parts of the boundary (including V_∞, the potential on the distant boundary) is zero.

The Green's function $H(s,s')$ also plays an important role in the theory of the double-layer impedance between an electrolyte and a metallic surface.[13] It can be shown that $H(s,s')$ is a symmetric function of s,s'. In two dimensions, $H(s,s')$ has a particularly simple representation involving the conformal map between the surface $\mathbf{x}(s)$ and a straight line.[13]

If all surfaces are at the same potential, then the electric field will be everywhere zero. Thus, since the fields

superpose linearly,

$$P(s)+\int ds'\frac{dw}{ds'}H(s,s')=0. \tag{4}$$

Given a surface $\mathbf{x}(s)$ and its corresponding $P(s)$, $H(s,s')$, it is not difficult to calculate the changes in $P(s)$, $H(s,s')$ if the surface is changed infinitesimally. The new surface will be given by $\mathbf{x}(s)+\delta\mathbf{x}(s)$, and the parametrization of the new surface will be fixed by the requirement that $\delta\mathbf{x}(s)$ be everywhere normal to the old surface, so that $\delta\mathbf{x}(s)=f(s)\hat{\mathbf{n}}(s)$, where $\hat{\mathbf{n}}(s)$ is the unit normal to the surface at s.

It is convenient to calculate first the changes in the purely geometrical quantities dw/ds and $\theta(s)=\cos^{-1}[\hat{\mathbf{n}}(s)\cdot\hat{\mathbf{z}}]$, the angle between the surface normal and a fixed direction $\hat{\mathbf{z}}$. It is simple to show that[14]

$$\delta(dw/ds)=[d\theta(s)/ds]f(s), \tag{5a}$$

$$\delta(\theta(s))=(dw/ds)^{-1}[df(s)/ds]. \tag{5b}$$

To find the change in $P(s)$, let us return to $\Phi(\mathbf{x})$, the potential exterior to the cluster given that the potential on the old surface $\Phi(\mathbf{x}(s))=0$ and the potential on the distant surface is $\Phi_\infty=V_\infty=1$. Write $\Phi'(\mathbf{x})=\Phi(\mathbf{x})+\delta\Phi(\mathbf{x})$ as the potential given that the potential on the new surface is zero, $\Phi'(\mathbf{x}(s)+\delta\mathbf{x}(s))=0$. To first order in $f(s)$, this implies that $\delta\Phi(\mathbf{x}(s))=-P(s)f(s)$. Thus the electric field normal to the old surface arising from $\delta\Phi(\mathbf{x})$ is [recalling the definition of $H(s,s')$]

$$\partial_{\hat{\mathbf{n}}}\delta\Phi(\mathbf{x}(s))=-\int ds'\frac{dw}{ds'}H(s,s')P(s')f(s'). \tag{6}$$

Corrections due to the fact that the normal derivative should be evaluated on the new and not the old surface are higher order in $f(s)$.

In the foregoing, the $O(f)$ change in $P(s)$ due to the $O(f)$ change in Φ has been calculated. There is also an $O(f)$ change in $P(s)$ due to a change in the position at which the gradient of Φ is evaluated. The parametrization of the new surface is related to the old by the requirement that lines of constant c be everywhere normal to the surface; also, electric field lines are normal to the surface. Thus the variation in $\partial_{\hat{\mathbf{n}}}\Phi$ due to the change in the position of the surface can be related to the local stretching of the surface, as the flux piercing a line between $\mathbf{x}(s)$ and $\mathbf{x}(s+ds)$ will not change with the movement of the surface. It follows, after a brief calculation, that

$$\delta(\partial_{\hat{\mathbf{n}}}\Phi(\mathbf{x}))=-P(s)(dw/ds)^{-1}\delta(dw/ds), \tag{7}$$

where $\delta(dw/ds)$ is given by Eq. (5a).

Thus, we obtain finally that[15]

$$\delta P(s)=-\int ds'\frac{dw}{ds'}H(s,s')P(s')f(s')-P(s)\left[\frac{dw}{ds}\right]^{-1}\delta\left[\frac{dw}{ds}\right]. \tag{8}$$

A similar calculation may be performed for $\delta H(s,s')$, with use of $\Phi_D(\mathbf{x};s')ds'$, the potential in all space given a unit potential in ds' and a zero potential on all other surfaces. The result is

$$\delta H(s,s')=-\int ds''\frac{dw}{ds''}H(s,s'')H(s'',s')f(s'')-H(s,s')\left[\frac{dw}{ds}\right]^{-1}\delta\left[\frac{dw}{ds}\right]. \tag{9}$$

Note that with use of Eq. (4), Eq. (8) can be obtained from Eq. (9).

Equation (8) can be used to study the behavior of the moments of the electric field in the growth models discussed above. Suppose that one has a particular cluster, and that $f_{s''}(s')$ is the change in the shape of the cluster caused by the addition of a particle at s''. Clearly $f_{s''}(s')$ will be localized to within a distance a about s''. The change in the average of the qth moment of the electric field will be

$$\delta\left[\int ds\frac{dw}{ds}P^q(s)\right]=\int ds\frac{dw}{ds}P^{q-1}(s)\left\{-q\int ds'\frac{dw}{ds'}H(s,s')P(s')f_{s''}(s')\right\}-(q-1)\int ds\,\delta\left[\frac{dw}{ds}\right]P^q(s). \tag{10}$$

In the η models discussed above, the probability of a particle landing at a position s is given by Eq. (1). Let us represent averaging over the different probabilities of clusters appearing by brackets $\langle\rangle_n$, where the subscript represents the number of particles in the cluster. Then it follows directly from Eqs. (1), (5a), and (10) and the short-range nature of $f_{s''}(s')$ that

$$\frac{d}{dn}\left\langle\int ds\frac{dw}{ds}P^q(s)\right\rangle_n=-q\left\langle\frac{\int ds(dw/ds)\int ds'(dw/ds')P^{q-1}(s)H(s,s')P^{\eta+1}(s')}{\int ds(dw/ds)P^\eta(s)}\right\rangle_n$$
$$-(q-1)\left\langle\frac{\int ds(d\theta/ds)P^{q+\eta}}{\int ds(dw/ds)P^\eta(s)}\right\rangle_n. \tag{11}$$

This reduces to a particularly simple form if $q=1$. Recalling Eq. (4) and the symmetry of $H(s,s')$, we obtain

$$\frac{d}{dn}\left\langle \int ds \frac{dw}{ds} P(s) \right\rangle_n = \left\langle \frac{\int ds (dw/ds) P^{\eta+2}(s)}{\int ds (dw/ds) P^{\eta}(s)} \right\rangle_n. \quad (12)$$

This equation is the central result of this study. The reader will note that the only significant approximation that has been made thus far, aside from a certain laxness about the precise definition of $f_{s''}(s')$, is the assumption that the continuum growth equations (5a) and (5b) may be applied to an aggregate.[16] Even this assumption does not contribute directly to Eq. (12).

To proceed further, it is necessary to make more problematical assumptions. The first assumption is that $\langle \int ds (dw/ds) P^q(s) \rangle$ can be written in a scaling form involving the three characteristic length scales a, r, the size of the cluster, and R, the distance to the outer surface,

$$\left\langle \int ds \frac{dw}{ds} P^q(s) \right\rangle = a^{1-q} f_q\left(\frac{a}{r}\right) g_q\left(\frac{r}{R}\right), \quad (13)$$

with the further requirement that $f_q(a/r)$ have the multifractal form $f_q(a/r) \sim (q/r)^{\tau(q)}$. In two dimensions, one expects $g_q(r/R)$ to have a logarithmic form, as the total flux absorbed by a cluster depends logarithmically upon r/R.

The final assumption is that the expectation value of the ratio on the right-hand side of Eq. (12) can be approximated by the ratio of the expectation values of the two moments. Physically, this corresponds to the assumption that the $\tau(q)$ do not vary widely between different realizations of the aggregates. Of course, such an assumption can only be justified *a posteriori*, or by a direct numerical study of the issue.

With these assumptions we have from Eq. (12) that $n \sim r^{\tau(\eta+2)-\tau(\eta)}$, or

$$D = \tau(\eta+2) - \tau(\eta). \quad (14)$$

Because this relation was derived from the growth equations, perturbations (such as weak lattice effects) that only slightly change the growth equations should not affect the validity of this exponent relation, as long as the scaling and factorization assumptions still hold. Note that a deterministic growth process in which $f(s) \propto [P(s)]^{\eta}$ will also lead to Eq. (14). This equation does not make an exact prediction for any model; it is rather a consistency relation that might, *a priori*, apply to any "fixed point" of a diffusive growth process. For instance, a smoothly growing flat surface, an unstable solution of the growth equations for any η, satisfies Eq. (14). In this case, $\tau(q)=q-1$, and $\tau(\eta+2)-\tau(\eta)=D=2$, the value for a compact cluster. For off-lattice diffusion-limited aggregation ($\eta=1$), $\tau(3)-\tau(1)=\tau(3)$ was reported by Halsey, Meakin, and Procaccia to have the value $\tau(3)=1.712\pm0.01$, in good agreement with the generally accepted $D\approx1.71$.[8] On a square lattice with $\eta=1$, it seems that as $n\to\infty$, $D\to1.5$, and $\tau(q)=\min(\frac{1}{2}q, q-1)$ for $q>1$.[17] Thus $\tau(3)=\frac{3}{2}=D$ also in this case.[18]

Equation (14) has interesting implications in the limit $\eta\to\infty$. In general, as $q\to\infty$, $\tau(q)\to\tilde{\alpha}q$, where $\tilde{\alpha}$ is the scaling exponent of the strongest local singularity in the flux $P(s)$ reaching the structure.[8,11] Thus, as $\eta\to\infty$, $D\to2\tilde{\alpha}$, which is consistent with the expectation that as $\eta\to\infty$, $D\to1$, and $\tilde{\alpha}\to\frac{1}{2}$. For any η we have $D\geq2\tilde{\alpha}$.

Turkevich and Scher have proposed a scaling relation linking D to this local singularity exponent $\tilde{\alpha}$.[19] For general η, this relation is $D=2+\eta(\tilde{\alpha}-1)$. Comparing this to the bound $D\geq2\tilde{\alpha}$, I conclude that for $\eta\geq2$ these two relations, taken together, are inconsistent with the existence of self-similar clusters with nontrivial $\tau(q)$. As such structures are apparently observed in numerical simulations, at least for $\eta=2$ and $\eta=3$, one of the two exponent relations quoted above must be wrong for $\eta\geq2$.[6,10] This suggests some promising directions for incisive numerical study.

The extension of these ideas to higher dimensionalities is straightforward, and will be addressed in a separate communication.

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[16]Strictly speaking, Eqs. (5a) and (5b) are only valid for deviations $f(s)$ much less than the scale δw on which the derivative is taken. In aggregation problems, these are both of order a; it is thus rather ambitious to apply Eqs. (5a) and (5b) to these problems. Note also that Eq. (11) was derived by assuming $f_{s''}(s') = (dw/ds')^{-1}\delta(s'-s'')$. A factor of the volume of an individual particle (dimensionally $\sim a^2$) has thus been excluded from Eqs. (11) and (12).

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