Dimensionally Frustrated Diffusion towards Fractal Adsorbers

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Diffusion towards a fractal adsorber is a well-researched problem with many applications. While the *steady-state* flux towards such adsorbers is known to be characterized by the fractal dimension (D_F) of the surface, the more general problem of *time-dependent* adsorption kinetics of fractal surfaces remains poorly understood. In this Letter, we show that the time-dependent flux to fractal adsorbers ($1 < D_F < 2$) exhibit complex ''dimensionally frustrated'' self-similar time response and is characterized by a simple scaling law $\rho_0 t^{1/D_F} = c$ (ρ_0 is the concentration of particles, t is the time, and c is a constant). Indeed our analysis establishes the time response of technologically relevant nanonet (or nanocomposite) biochemical sensors as a test bed of time-dependent adsorption on fractal surface, providing a novel experimental measure of D_F and an obvious route to improved sensor design.

Introduction.—Irreversible capture of molecules by adsorbing surfaces is an important problem with many applications in science and technology. The examples range from growth of fractal structures due to random aggregation of particles to breakdown transient in thick dielectrics to the recent research in detection of biomolecules by nanoscale sensors [1–7]. Often the rate limiting step in these applications is the diffusion of particles to the adsorbing surface. The time evolution of these phenomena is of significant interest both for better understanding of the physical processes involved (e.g., crystal growth of fractal surface, geometry of corrosion, resistance of solar cells with fractal electrodes, etc.) as well as for design and optimization of corresponding devices and systems.

Random motion of particles in the absence of any external force is characterized by the time-dependent diffusion equation,

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho, \tag{1}$$

where $\rho(r, t)$ is the probability density or concentration of particles, and D is the diffusion coefficient. Adsorbing surface $s(D_F(t))$—characterized by its fractal dimension D_F—defines the boundary condition for Eq. (1) such that $\rho(r, t) = 0$ on $s(D_F(t))$. Since both the field density $\rho(r, t)$ as well as the fractal surface $s(t)$ evolve with time, solution of Eq. (1) represents a formidable task in modeling.

Even approximate steady-state solution of Eq. (1) (i.e., $\nabla^2 \rho = 0$), however, provides many surprises and has long been explored within the context of diffusion-limited aggregation (DLA). DLA describes the steady-state growth of adsorbing surface in response to the random aggregation of particles [1]. The assumption of quasi-steady-state field is justified on *ad-hoc* basis, i.e., the field ρ can respond faster than the evolution of the surface and hence the evolution of surface $s(t)$, rather than the kinetics of diffusion (i.e., $d\rho/dt$), dictates the incoming particle flux. Historically, two types of DLA problems have been of

broad interest: type I problems involve calculation of the geometrical characteristics of steady-state $s(t)$ [1], while type II problems involve the steady-state spatial characteristics of $\rho(r)$ with time-invariant adsorbing surface characterized by $s(D_F)$ [2]. We now know that for type I problems with isotropic flux, $s(t \to \infty)$ is characterized by $D_F \sim 1.71$ in 2D surfaces and ~ 2.5 in 3D surfaces, etc., and that for type II problems, the exponent of spatial scaling laws are related to the time-independent fractal dimension of the adsorber. In general, since the primary research focus for DLA involves evolution of adsorbing fractal surface due to particle aggregation, the transient kinetics of the aggregation process is not well explained: indeed, the use of Laplace equation ensures that regardless of the geometry, the number of captured particles $N(t)$ would scale linearly with time for all DLA problems [3].

In this Letter, we focus on a more general DLA problem that requires transient solution of (1). Specifically we obtain the kinetic exponents of adsorption that relates the net aggregated particles $N(t)$ on fractal surfaces as a function of time. We explore the time evolution of the diffusion profiles and their effect on particle aggregation until steady state is reached. In sum, while DLA requires solution of time-independent Laplace equation with (possibly) *time-dependent* $D_F(t)$, we are interested in a separate class of problems (type III) that requires time-dependent solution of Eq. (1) with *time-invariant* D_F.

Many practical and theoretical problems belong to the type III DLA problems: a specific problem of significant current interest is the irreversible adsorption of biomolecules on nanonet (also called nanocomposite) sensors [4,5]. Towards the eventual goal of exploring kinetics of diffusion towards nanocomposite sensors ($1 < D_F < 2$), we have recently demonstrated that the net aggregation of biomolecules on integer-dimensional sensors (e.g., planar, cylindrical, and spherical surfaces) is characterized by simple scaling laws [8]. In this Letter, we generalize the transient solution to show that fractal adsorbers

($1 < D_F < 2$) exhibit "dimensionally frustrated" time response which is dictated by the subtle interaction between one- and two-dimensional diffusion profiles at various time scales. Despite this complex time response, remarkably, the particle aggregation on a fractal adsorber follows the same simple scaling law as their integer-D_F counterparts, except that the time exponent is now determined by the dimensionality of the fractal surface, i.e.,

$$N(t) \sim k\rho_0 t^\beta \sim k\rho_0 t^{(1/D_F)}, \qquad (2)$$

where $N(t)$ is the total number of adsorbed particles on sensor surface at time t, k is a constant, and ρ_0 is the density of analyte particles far from the interface. In the following sections, we first intuitively interpret and then numerically validate the aforementioned scaling relationship.

Solution to Eq. (1) with fractal surface.—Consider an isolated adsorbing surface introduced to a static field at time $t = 0$. The particle flux at the sensor surface is given by

$$I = D \int_{A_D} \nabla_n \rho \, ds, \qquad (3)$$

where A_D be the dimension-dependent area of the sensor surface. Based on [9], the solution of (1) in any dimension
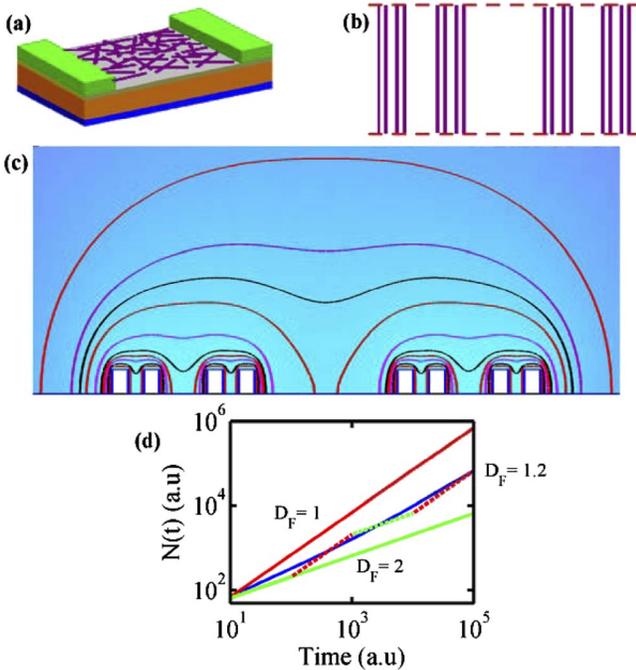

FIG. 1 (color online). (a) Schematic of nanocomposite sensor. (b) 2D equivalent Cantor surface with same D_F as in (a). (c) Contour plot illustrating temporal self-similarity of the diffusion profiles. White rectangles indicate the side view of cantor set sensor shown in (b). As time progresses, the diffusion fronts move away from sensor surface alternating between 1D and 2D behavior. (d) Schematic representation of time response as a sequence of contributions from 1D and 2D responses, corresponding to Fig. 1(c). Solid lines indicate simulation results while the dotted lines are for illustration.

at steady state is given by

$$I = JA_D = C_{D,SS}[\rho_0 - \rho(s)], \qquad (4)$$

where J is the incident average flux density on the adsorber, $C_{D,SS}$ the diffusion equivalent capacitance, ρ_0 is the "equilibrium" particle concentration at a distance W from the adsorber surface, and $\rho(s)$ is the particle concentration at the adsorber surface. $C_{D,SS}$, in general, is a simple analytical function of W [e.g., for planar surfaces $C_{D,SS} = D/W$, for cylindrical surface $C_{D,SS} \approx 2\pi D/\log(W)$, etc.]. The incident flux must balance the particle flux, so that $J = dN/dt$. The time evolution of particle aggregation, with $\rho(s)$ set to zero in Eq. (4), is then given by

$$N(t) = \rho_0 t \frac{C_{D,SS}}{A_D}. \qquad (5)$$

For integer-D_F surfaces, the transient response of particle aggregation can now be derived based on a perturbation approach reported in [8]: as time progresses, the particle concentration near the adsorbing surface decreases as they diffuse to the adsorber and are captured on the surface. Assuming quasiequilibrium conditions, this phenomenon can be accounted by defining a new diffusion equivalent capacitance $C_D(t)$ by replacing W in $C_{D,SS}$ by $W(t) \approx (Dt)^{0.5}$ for various integer-dimensional surfaces such that $C_D(t) \approx Kt^{-0.5}$ for planar surfaces and $C_D(t) \approx Kt^0$ for cylindrical surfaces, etc. With this $C_D(t)$, Eq. (5) solves Eq. (1) (almost) exactly for integer-D_F surfaces.

For fractal adsorbing surfaces, the form of $C_D(t)$ is not known; however, we posit that the diffusion equivalent capacitance can be expressed by same general form as in integer-D_F surfaces,

$$C_D(t) \sim Kt^\alpha \qquad (6)$$

except that the constant α is now not limited to 0 or -0.5, but is a characteristic of the fractal dimension of the adsorbing surface. Therefore, the transient response of fractal sensor would be given by inserting (6) in (5) such that

$$N(t) \sim k\rho_0 t^\beta \qquad (7)$$

with time exponent $\beta = 1 + \alpha$, by definition.

Interpretation of Eq. (7).—To explore the origin of (6) or (7) for fractal adsorbers and for computational feasibility, we propose a "Cantor transform", i.e., we construct a quasi-2D Cantor surface [illustrated in Fig. 1(b)] which has the same D_F as the fractal adsorber shown in Fig. 1(a). This (novel) Cantor transform retains many characteristic features of scaling of the original surface while being a more efficient tool, conceptually and computationally, for reaction-diffusion systems due to its self-similar scale-invariant structure [10]. We now study the time-dependent adsorbtion of molecules on this Cantor surface and then will later show the equivalence of such a transform through numerical simulations.

Figure 1(c) shows that the diffusion contours during initial times resemble the individual elements on the Cantor surface and hence appear as a series of isolated cylindrical ($D_F = 1$) adsorbers characterized by time exponent $\beta \sim 1$ [Fig. 1(d)]. As time progresses, adjacent diffusion fronts merge, and at this length scale, the surface appears planar ($D_F = 2$) with $\beta \sim 0.5$. This 2D diffusion is again followed by 1D diffusion, thereby completing the first cycle [see Fig. 1(c) and 1(d)]. Subsequently, the scale invariance of the Cantor surface dictates that a local cluster of Cantor elements appear as one composite cylinder with $D_F = 1$ diffusion until the next adjacent clusters merge and diffusion reverts back to planar diffusion ($D_F = 2$) in cycle 2 and so on. This dimensional frustration of diffusion profiles at various time scales reflects the spatial scale invariance of the underlying fractal adsorber. Since the clustering of elements of Cantor set is according to a power law (specific value defined by D_F), the time transition from 1D to 2D diffusion is also characteristic of D_F and hence the response is scale invariant in $\log(t)$ plot [shown schematically in Fig. 1(d), see inset of Fig. 2 for numerical verification]. The time exponent β in (7) therefore reflects the fractal dimension of the Cantor surface.

To establish the explicit dependence of β to D_F, we construct a series of Cantor surfaces with various D_F and use finite element method to numerically solve Eq. (1) with the boundary condition $\rho(s(D_F)) = 0$ on the surface. The inset of Fig. 2 shows the integrated flux $N(t)$ for a wide variety of Cantor surfaces with various D_F. The time exponents $\beta = 1 + \alpha$ as a function of D_F are extracted by fitting $N(D_F, t)$ versus t profiles and plotted in Fig. 2
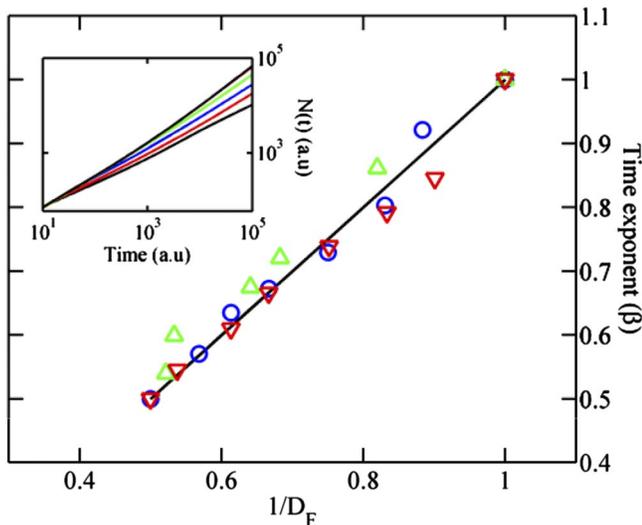

FIG. 2 (color online). Variation of time exponent with fractal dimension of sensors. Circles represent the slope extracted by solving the time-dependent diffusion equation numerically for cantor set sensors [Eq. (1), inset shows the time response]. Down triangles represent the time exponents of cantor set sensors while up triangles represent nanocomposites sensors [Fig. 1(a)], based on numerical estimation of the diffusion equivalent capacitance [Eq. (6)].

(shown as circles). Numerically, for finite systems, $\beta \sim (1/D_F)^\gamma$ with $\gamma \sim 1$ (renormalization group estimates may eventually improve the bound).

Uniqueness of time exponents.—While the kinetics of fractal absorption was established above with reference to Cantor surface [Fig. 1(b)], we now provide strong numerical evidence that Eq. (2) is more general and that all quasi-2D fractal surfaces [e.g., Fig. 1(a)] defined by the same fractal dimension are characterized by same kinetic exponent $\beta(D_F)$. Since complete time-dependent solution is computationally prohibitive, we prove the equivalence of fractional diffusion with fractal surfaces defined by Fig. 1(a) and 1(b) by indirectly comparing α from their respective diffusion equivalent capacitance. Since $\beta = 1 + \alpha$, equivalence of α dictates equivalence of β. Figure 3 shows the variation of capacitance $C_D(t)$ with time for Cantor set sensor and composite adsorbers of different D_F. Figure 3 also allows determination of α, and the corresponding β is plotted in Fig. 2. For the same D_F, the exponents of the nanocomposite adsorbers match those from Cantor surface within the margin of error, thereby establishing the uniqueness of Eq. (2) for general fractal surfaces. As a further test, different manifestations of composite adsorbers for a given D_F gave similar time exponents (results not shown).

Discussion.—In addition to relevance to any generic type III DLA problems involving fractal surfaces, Eq. (2) has particularly important implications for detection limit of biomolecule by nanoscale sensors composed of mats of carbon nanotube (CNT) and Si nanowire (NW). These nanocomposite biosensors have recently been proposed as an alternative to planar sensors for ultra sensitive detection of biomolecules. The D_F of these random-stick networks (stick length, L_S) is a unique function of the stick density ρ (relative to their percolation threshold, $\rho_{perc} \sim L_s^{-1.8}$ [11]) and is bracketed by $1 < D_F < 2$. Previously, Ref. [8] established that $\rho_0 t^\beta = $ const for
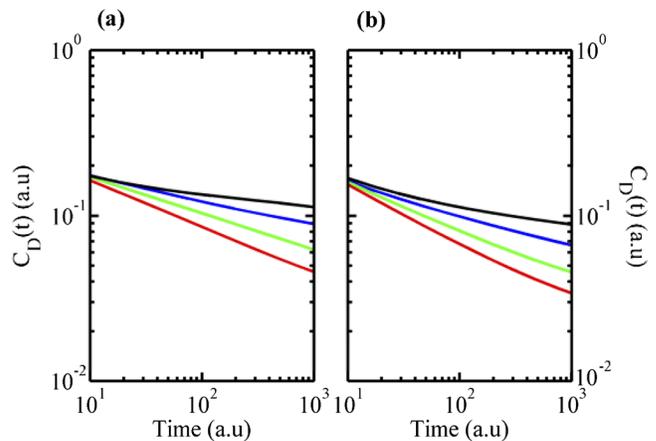

FIG. 3 (color online). Diffusion equivalent capacitance as a function of time [Eq. (6)] evaluated for cantor set sensors [(a), see Fig. 1(b)] and random nanocomposite sensors [(b), see Fig. 1(a)] for different fractal dimensions [17].

integer-D_F sensors, where $\beta = 1$ for cylindrical sensors ($D_F = 1$), while $\beta = 0.5$ for planar sensors ($D_F = 2$). Equation (2) implies that for fractal adsorbers, the corresponding scaling law is given by $\beta = (1 + \alpha) \sim D_F^{-1}$, i.e.,

$$\rho_0 t^{(1/D_F)} = \text{const.} \qquad (8)$$

Equation (8) implies that for any finite measurement window t_s, the detection limits ($\rho_{0,\min}$) of such fractal sensors will always be higher than planar sensors (approached by high-density network), but lower than single-CNT or single-NW sensors (approached by reduced density sensor). This observation is indeed consistent with the reported detection limits of nanocomposite sensors [7] and nanosensor arrays [12]. To our knowledge, this is the first interpretation of the puzzle of composite sensors that the collective sensitivity of N sticks is actually poorer than a single stick sensor. Equation (8) provides a natural framework to classify wide variety of nanobio- and nanochemical sensors reported in the literature. In addition, it is well known that electrical response of the percolative network in Fig. 1(a) increases with network density [11], while the detection limit decreases with density [Eq. (8)]—providing a previously unanticipated route to optimization of high-performance nanocomposite biosesnors.

Our results also provide a simple experimental technique to determine the fractal dimension of adsorbers. Currently, optical diffraction on isotropic fractals allows experimental extraction of D_F [13]. Since the time exponent in biosensors uniquely related to D_F, we speculate that D_F of any adsorber ($1 < D_F < 2$) can be easily determined from the transient capture dynamics (reflected in evolution of electrical signals) of adsorbers [14]. Specifically, D_F can either be directly determined from the transient behavior [inverse slope of $\log(N)$ versus $\log(t)$ plot, Eq. (2)] at a particular analyte density or from the scaling of time t_s required to capture N_0 (constant) number of particles at different ρ [i.e., slope of $\log(t_s)$ versus $\log(\rho)$ plot, for a given N_0 as given Eq. (8)]. Finally, we wish to make a passing observation that diffusion towards fractal adsorbers may be classified among and can be an additional example of the general class of problems (e.g., zero-point entropy of common ice [15], magnets on triangular lattice [16], etc.) with characteristics dictated by geometrical frustration of the underlying phenomenon.

To summarize, we showed that fractal adsorbers exhibit self-similar time response and their behavior alternates from a planar system to that of a cylindrical system. Despite this complexity, the transient kinetics is encapsulated by a simple scaling law [Eq. (2)] with time exponent inversely proportional to the fractal dimension of the adsorbing surface. The results specify a robust classification scheme for nanobio- and nanochemical sensors and interprets the puzzle why nanocomposite sensors are many orders of magnitude more sensitive than FET based sensors, yet despite years of efforts, continue to be less sensitive than isolated nanowire/nanotube sensors.

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