Dimensionally Frustrated Diffusion towards Fractal Adsorbers

Pradeep R. Nair and Muhammad A. Alam

Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907, USA

(Received 25 June 2007; published 20 December 2007)

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 \( \rho(t) \sim t^{1/D_F} = c \rho_0 \) \( (t \rightarrow \infty) \) is characterized by \( D_F \sim 1.71 \) in 2D surfaces and \( \sim 2.5 \) 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.

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 \( D_F \), 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 \leq D_F \leq 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.,

\[ N(t) \sim k \rho_0 t^\beta \sim k \rho_0 t^{(1/D)} , \]

where \(N(t)\) is the total number of adsorbed particles on sensor surface at time \(t\), \(k\) is a constant, and \(\rho_0\) 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

\[ I = D \int_{A_D} \nabla_n \rho ds , \]

where \(A_D\) be the dimension-dependent area of the sensor surface. Based on [9], the solution of (1) in any dimension at steady state is given by

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

where \(J\) is the incident average flux density on the adsorber, \(C_{D,SS}\) the diffusion equivalent capacitance, \(\rho_0\) 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 \(C_{D,SS} = 2\pi D/\log(W)\), 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

\[ N(t) = \rho_0 t \frac{C_{D,SS}}{A_D} . \]  

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 \(W(t) = (D t)^{0.5}\) for various integer-dimensional surfaces such that \(C_D(t) \approx K t^{-0.5}\) for planar surfaces and \(C_D(t) \approx K t^\alpha\) 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,

\[ C_D(t) \sim K t^\alpha \]  

except that the constant \(\alpha\) 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

\[ N(t) \sim k \rho_0 t^\beta \]  

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 adsorption of molecules on this Cantor surface and then will later show the equivalence of such a transform through numerical simulations.

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.
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 $\beta$ in (7) therefore reflects the fractal dimension of the Cantor surface.

To establish the explicit dependence of $\beta$ 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 (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 $\alpha$ from their respective diffusion equivalent capacitance. Since $\beta = 1 + \alpha$, equivalence of $\alpha$ dictates equivalence of $\beta.$ 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 $\alpha$, and the corresponding $\beta$ is plotted in Fig. 2. For the same $D_F$, the exponents of the nanocomposite adsorsors 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 $\rho$ (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 $\rho_0 t^\beta = \text{const}$ for...
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 $\beta = (1 + \alpha) - D_F^{-1}$, i.e.,

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

Equation (8) implies that for any finite measurement window $t$, the detection limits ($\rho_{0,\text{min}}$) 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 nanochanical 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 biosensors.

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 $t_0$ required to capture $N_0$ (constant) number of particles at different $\rho$ [i.e., slope of $\log(t_0)$ versus $\log(\rho)$ plot, for a given $N_0$ as given Eq. (8)]. Finally, we wish to make a passing observation that diffusion towards the adsorbing surface. The results specify a robust classification scheme for nanobio- and nanochanical 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.

We thank Ninad Pimparkar for showing that random stick networks are defined by specific $D_F$. This work was supported by funds from the Network for Computational Nanotechnology (NCN) and National Institute of Health (NIH).

---

*[pnair@purdue.edu]
†alam@purdue.edu

[10] Recursive geometrical fractal models have also been used to study the conductance property of infinite clusters. See R. Blumenfeld, Y. Meir, A. B. Harris, and A. Aharony, J. Phys. A 19, L791 (1986).
[14] An interesting question is if the scaling formula (2) can be generalized to fractal adsorbers with $2 < D_F < 3$, DLA growth in 3D being a well known example ($D_F \sim 2.5$). Our numerical calculations suggest that such quasi-3D adsorbers do indeed exhibit $D_F$ dependent time exponents similar to Eq. (2) (i.e., $\beta = c_1 D_F^{-1} - c_2$, for small fractal iterations $n, n < 5$), the physical origin of the time-exponent being the sequential depletion of analytes in scale-independent voids inside the 3D fractals.
[17] Extraction of time exponent using Eqs. (6) and (7) for irregular geometries is computationally intractable. Hence $C_D(t)$ has been constructed by a series of numerical estimations of the capacitance between the sensor (cantor set or nanocomposites) surface and an infinite plane, varying the separation between them as $\sqrt{t}$. The corresponding slope extracted has been corrected by a constant factor based on the theoretical estimate of the response of cylindrical sensors [8].