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LETTER TO THE EDITOR

The relation between diffusion along fractal surfaces and observable diffusion

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Abstract. Fractal solid surfaces are presented as being built up from repeating fractal units of size ξ equal to the surface upper self-similarity cutoff. Taking into account the difference between real diffusion pathways of particles of size λ and their observable projections we distinguish three types of observable diffusion: (i) the classical law for $\lambda > \xi$; (ii) anomalous time dependence for $\lambda \ll \xi$ and short times; (iii) normal time dependence but anomalous behaviour of the observable diffusion coefficient for $\lambda \ll \xi$ and long times. Crossovers occur from (iii) to (i) with increasing λ and from (ii) to (iii) with increasing time.

It was found recently that the roughness of solid surfaces is adequately and conveniently described by the notion of fractal dimension. Analysis of surface area measurements on the basis of adsorption data shows that a large variety of solid surfaces are characterised by a constant slope of the log-log relation between surface area and size of adsorbed molecules (Pfeifer and Avnir 1983, Avnir *et al* 1984, Pfeifer 1984). A different experimental approach revealed the fractal properties of fracture surfaces of metals (Mandelbrot *et al* 1984). These observations demonstrate that many solid surfaces are fractal objects within a range of at least two to four orders of magnitude of the 'unit' sizes. While their lower self-similarity cutoff is appropriate to interatomic distances, no precise estimates of the upper cutoffs are available at present, to our knowledge. The surface fractal dimension is very often considerably greater than two and reaches values close to three in some cases (Avnir *et al* 1984). Various experimental techniques confirm these conclusions (see Avnir (1986) for a summary).

The fractal character of the solid surfaces should have a significant effect on surface transport processes as processes on smaller length scales would have longer pathways than processes on larger length scales. It is important to realise, however, that in the length scale of experimental observation of surface transport phenomena the fractal surface appears as a smooth two-dimensional surface and the observer measures the actual projection of the real process onto his idealised plane of observation.

Our purpose here is to account for the difference between real pathways and their projections on a smooth observation plane. This allows us to distinguish three types of observable diffusion and two crossovers between them.

A specific feature of the fractal surfaces relevant to this letter and also typical for other natural fractals is that their self-similarity range is limited from above. This allows us to consider a fractal surface as consisting of repeating fractal units of size ξ which is the upper self-similarity cutoff. In other words, self-similarity is replaced by translational invariance for distances greater than ξ. We also assume that the solid

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support of the fractal surface is non-porous so that the diffusants cannot be 'lost' into its volume. This presentation of the fractal surface makes possible the following types of observable diffusion depending on time t and λ which refers to diffusant size (or to the length of the elementary diffusion process if longer).

(i) $\lambda > \xi$. In this case the fractal character of the surface is not 'felt' by the diffusing particle. Real diffusion pathways coincide with observable pathways and a classical, $\langle x^2 \rangle = 4Dt$, dependence will be observed for any time.

(ii) $\lambda < \xi$.

(*a*) Anomalous diffusion for short times when $\langle x^2 \rangle < \xi^2$ (diffusion within one fractal surface unit).

(*b*) Normal, $\langle x^2 \rangle \sim Dt$, diffusion for long enough times when $\langle x^2 \rangle \gg \xi^2$ (diffusion over many fractal units).

There are two crossovers between these three types of observable diffusion: crossover from (ii*b*) to (i) with increasing λ, manifested as a transition from anomalous to normal behaviour of the observable diffusion coefficient, and crossover from (ii*a*) to (ii*b*) with increasing t. The latter crossover is similar to the crossover from anomalous to normal diffusion on infinite random clusters *above* the percolation threshold (Gefen *et al* 1983, Pandey *et al* 1984 and references therein). In the framework of this analogy, the surface self-similarity cutoff ξ corresponds to the correlation length in percolating clusters as these two parameters determine the crossover ranges.

For a quantitative treatment of the anomalous case (ii*a*) we describe diffusion and Brownian motion along a fractal surface by using the familiar equation

$$\partial c/\partial t = D\nabla^2 c \tag{1}$$

which follows from the matter balance in linear thermodynamic approach. Equation (1) describes diffusion processes in spaces where concentration c, ∇c and $\nabla^2 c$ respectively, can be suitably defined. This condition poses a certain problem when considering fractal surfaces as a surface of fractal dimension between two and three which has an infinitely large area and the distance between two points on it can be infinitely great. However, real particles diffusing along solid surfaces are of finite size and do not 'feel' details in surface structure smaller than their own size. Thus, their diffusion trajectories form, in fact, a set of smoothed simply connected surfaces of finite metrics enveloping the fractal surface. In these surfaces (parametrised by λ) (1) is certainly applicable. Correspondingly, c can be defined as the particle density on the enveloping surface and the distance between two points of the fractal surface is the geodesic length along the enveloping surface. The analogous length in percolating clusters embedded in regular lattices is often termed the 'chemical' distance (Havlin *et al* 1985).

The surfaces introduced above of diffusion trajectories enveloping the fractal surface will be different for different values of λ. With decreasing λ they become more indented and the distance l measured along them between two fixed points on the fractal surface increases. It is important to note in this connection that the 'chemical' distance between two points in a lattice cluster is constant since it is measured in units of the lattice period which actually represents the lower self-similarity cutoff, while in the case considered here this cutoff is determined by the diffusant size λ.

For a point source, the solution of (1) along an enveloping surface is the axially symmetric Gauss distribution:

$$c(l, t) = \frac{l}{2\pi\sigma^2} \exp\left(-\frac{l^2}{2\sigma^2}\right) \tag{2}$$

where l is the axial geodesic coordinate and $\sigma^2 = \langle l^2 \rangle \sim Dt$. Equation (2) describes a normal diffusion process along a simply connected two-dimensional envelope.

The observable particle distribution $c(r, t)$ follows from $c(l, t)$ through

$$c(r, t) = \int p(r|l)c(l, t)\,\mathrm{d}l \tag{3}$$

and the observable mean square displacement is

$$\langle r^2 \rangle = \int r^2 c(r, t)\,\mathrm{d}r. \tag{4}$$

Here $p(r|l)$ shows the distribution of r at fixed l. Its shape for percolating clusters in two dimensions at criticality was found by Havlin *et al* (1985) by numerical simulation and curve-fitting. For fractal surfaces $p(r|l)$ is not known but, nevertheless, a simple argument based on a plausible assumption allows us to determine the effect of the surface fractal dimension on $\langle r^2 \rangle$.

For this purpose we use the conclusion of Havlin *et al* (1985) that $p(r|l)$ of percolating clusters can be expressed in terms of a single scaled variable $u = r/l^{\nu}$ where ν is a geometrical exponent and assume that $p(r|l)$ of the fractal surface units has the same property, $p(r|l) = (\lambda^{\nu-1}/l^{\nu})p(\lambda^{\nu-1}r/l^{\nu})$. Then

$$\frac{\langle r \rangle}{\lambda} \sim \left(\frac{\langle r^2 \rangle}{\lambda^2}\right)^{1/2} \sim \left(\frac{l}{\lambda}\right)^{\nu} = \left(\frac{l}{\lambda}\right)^{2/d_f} \qquad (\text{for } \lambda \ll r < \xi). \tag{5}$$

In (5) we also use the relation between ν and the fractal dimension, $d_f\nu = \varphi$ (Martin 1985), where φ is a topological exponent equal to 2 for the surfaces considered here. Combining (2)–(5) gives the observable diffusion law:

$$\langle r^2 \rangle \sim \lambda^{2(1-\nu)}(Dt)^{\nu} \tag{6}$$

where $1 \geqslant \nu \geqslant \frac{2}{3}$ for $2 \leqslant d_f \leqslant 3$. As expected, $\langle r^2 \rangle \to 0$ when $\lambda \to 0$, and $\langle r^2 \rangle \sim Dt$ in the smoothness limit $d_f = 2$. Equation (6) is valid for short times (diffusion within one surface unit).

The observable mean square displacement depends on two parameters—D and λ. However, the real diffusion coefficient also depends on the diffusant size. If the migrating particle obeys the Einstein–Stokes relation, $D\lambda = \text{constant}$, it follows from (6) that

$$\langle r^2 \rangle \sim \lambda^{2-3\nu}. \tag{7}$$

Consequently, particles of different size diffusing along a fractal surface would separate less than on a smooth surface. Qualitatively, this effect is quite clear: smaller particles are quicker, but their pathways on a fractal surface are longer.

For long times (diffusion over many fractal units), (5) is replaced by $r \sim 1$ and (6) is transformed to a linear time dependence of $\langle r^2 \rangle$. The observable diffusion coefficient is related to the real coefficient by

$$D_{\text{obs}} = D_{\text{real}}(\xi/l_{\xi})^2 \tag{8}$$

where $l_{\xi}(\lambda)$ is the fractal unit size measured along the enveloping surface. From (5) and (8) it follows that

$$D_{\text{obs}}(\lambda) \sim D_{\text{real}}(\lambda)(\lambda/\xi)^{(d_f-2)} \qquad (\text{for } \lambda \leqslant \xi). \tag{9}$$

Equation (9) shows that a crossover from anomalous to normal dependence of D_{obs} on λ occurs with increasing λ to values equal to or greater than the surface upper self-similarity cutoff.

Equation (9) probably provides a better possibility for experimental exploration than (6) because the anomalous time dependence in (6) exists only for short times which may turn out to be out of experimental reach. Besides processes of surface diffusion (for example, diffusion of proteins and low molecular weight compounds along biological membrane surfaces), (6) and (9) may also have application to the interpretation of experimental results on nucleation of adsorbates, surface chemical reactions, etc.

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