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A Monte Carlo study of the apparent dimensions in direct electronic energy transfer of finite-size objects with fractal and regular geometries

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Abstract. We study the temporal behaviour of donors in DET fluorescence embedded in restricted-geometry objects, particulary around the crossover time t_{cr} to see the differences between the behaviour of regular restricted-geometry objects and that of actual fractal structures. All the objects show fractional apparent dimensions at around t_{cr}. The apparent dimensions of the fractal objects in addition have a periodic oscillation the peaks of which exceed the dimensions of the embedding space.

1. Introduction

Non-radiative direct electronic energy transfer (DET) between donor and acceptor molecules or groups in the condensed phase has been studied by many researchers over the last 40 years. The approach taken in these studies was to follow the quenching reaction of optically excited donors in the presence of ground-state acceptors. DET was first studied by Förster (1949) in systems where the acceptors are randomly distributed in the three dimensional (3D) rigid medium. Theoretical formulation of the excitation transfer in two dimensions (2D) was proposed by Wolber and Hudson (1979) for randomly distributed systems and by Zumofen and Blumen (1982) for regular lattices. Donor fluorescence decay functions were calculated by Hauser *et al* (1976) and Baumann and Foyer (1986) in respective dimensionalities for excitation transfer processes. These ideas have been extended to DET on fractal structures with self-similarity and dilation symmetry (Klafter and Blumen 1984, 1985). Donor fluorescence decay in these systems can produce fractional dimensions.

When the space containing the donor and acceptor molecules is very much larger than the distance over which the energy transfer takes place, the donor decay assumes a familiar form in 3D systems. However, when the donors and acceptors are confined to small spaces, curious features appear in the donor fluorescence function (Blumen *et al* 1986). These appear because the distribution of the molecules is finite. The idea of the consequence of DET in a restricted geometry was first proposed by Yang *et al* (1986, 1989) and developed theoretically by Blumen and co-workers. Some of these ideas were experimentally tested on porous silicas (Rojanoki *et al* 1986), Vycor glass (Yang *et al* 1989), cylindrical pore polymer membranes (Dozier *et al* 1986) and polymer colloids (Pekcan *et al* 1988, 1990). Fluorescent dyes and phosphorescent groups adsorbed to the surface in these spaces can undergo energy transfer within this restricted environment.

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In this work the Monte Carlo technique is used to determine the temporal behaviour of the donor intensity $I(t)$ via direct dipolar energy transfer process in various Euclidean and fractal structures. The results are fitted to the Klafter–Blumen equation which is useful in analysing simulated data to determine the dimensions from the $\mathrm{d}[\![\ln\{-\ln[I(t)]\}]\!]/\mathrm{d}(\ln t)$ versus $\ln t$ plot. The apparent dimensionality due to the finite-size effect in various geometries was studied. In fractal geometries, oscillations in the apparent dimensions arising from the dilational self-similarity of the structure were seen.

2. Theory

Our principal aim in this work was to compare the decay curves of donors embedded in fractal and regular geometrical objects of finite size (restricted geometries).

Following Förster (1949) we note that the lifetime of an isolated donor is determined by its natural decay rate. If there is an acceptor in the vicinity, the donor can also undergo induced decay via DET. For a donor–acceptor distance r the combined decay of the donor is governed by

$$f(t,r) = \exp[-t/\tau_0 - t/\tau_0(r/r_0)^{-s}]. \tag{1}$$

For dipole–dipole interaction, s is equal to 6. Angular dependences are neglected; this corresponds to averaging over all angles. r_0 is the distance where the induced decay rate due to DET is equal to the natural radiative decay rate τ_0 of the donor.

The probability that an acceptor site is full is p, and the probability that it is empty $1-p$. The ensemble-averaged probability that the donor has not decayed by the time t is then

$$f(t,r) = [\exp(-t/\tau_0)]\{(1-p) + p\exp[-t/\tau_0(r/r_0)^{-s}]\}. \tag{2}$$

In real life, $p \ll 1$ as there are many sites on a given lattice but only a minute fraction are filled. In this limit the binomial distribution leading to equation (2) can be replaced by a Poisson law distribution $g(j) = \exp(-p)\, p^j/j!$, leading to

$$f(t,r) = [\exp(-t/\tau_0)]\,(\exp[\![-p\{1-\exp[-t/\tau_0(r/r_0)^{-s}]\}]\!]) \tag{3}$$

after replacing the sum over all filling numbers by the exponential whose series expansion the sum becomes. This result is correct only for very small filling probabilities p. In simulations where a calculation site corresponds to many actual sites, equation (3) is more appropriate than equation (2) and should be used, even for large values of p.

For many acceptors A_i occupying the sites $\boldsymbol{X}_i$, the lifetime of a donor located at $\boldsymbol{Y}_j$ is governed by

$$f(t,Y) = \left[\exp\left(\frac{-t}{\tau_0}\right)\right]\left[\!\!\left[\exp\left\{-p\sum_i\left[1-\exp\left(\frac{-t}{\tau_0(r_i/r_0)^{-s}}\right)\right]\right\}\right]\!\!\right] \tag{4}$$

where $r_i = |\boldsymbol{X}_i - \boldsymbol{Y}_j|$.

For acceptors distributed uniformly, the sum can be replaced by an integral. Over an infinite 3D space this integral is

$$f(t,Y_j) = [\exp(-t/\tau_0)]\{\exp[-p\rho_0(4\pi r_0^3/3)\Gamma(\tfrac{1}{2})t^{1/2}]\}. \tag{5}$$

This has been generalized by Klafter and Blumen (1984, 1985) to include all infinite and uniform media of Euclidean or fractal dimensions d as

$$f(t, Y_j) = [\exp(-t/\tau_0)]\{\exp[-p\rho_0 V_d r_0^d \Gamma(1 - d/6)t^{d/6}]\}. \qquad (6)$$

The Klafter–Blumen equation (equation (6)) is valid for infinitely extended objects of dimensions d. For restricted geometries it describes the limiting cases, i.e. the behaviour of the donors at times much shorter and much longer than the typical crossover time at which the donor sees the edge of the object that it is in ($t_{cr} = \tau_0(R_{obj}/r_0)^e$) where R_{obj} is the typical radius of the object. For times much less than this time scale the donor sees a 3D environment; at much longer times it sees the object as a point. For times comparable with this typical time scale the Klafter–Blumen equation gives no information because the concept of dimensions, whether fractal or Euclidean, requires self-similarity, but self-similarity is lost when the edge of the object is visible.

Intuitively we expect the intermediate behaviour to hold for $\frac{1}{2} < (t/t_{cr})^{1/6} < 2$. This gives about four orders of magnitude in the ratio of shortest to longest times. Most of the experiments may fall in this domain. Therefore we tried to find out when an object that seems to have fractal dimensions is really a fractal object and when one is seeing the edge effects.

3. Calculation

We simulated the decays of donors placed in the following objects: a cube, a Menger sponge of the same size, a Sierpinsky carpet, a thin long cylinder, a flat disc and a cylinder whose length is equal to its diameter (Akal 1991).

In each case the donor and the acceptor sites were placed by assigning random coordinates within the object. For the cylindrical objects the z coordinate, the azimuthal angle and the square of the radius were chosen randomly, the last for equal sampling of areas close to and far from the axis. For the Menger sponge, 20 full cubes were selected randomly, and within each cube a subcube was randomly chosen. The process was repeated until the chance that a donor and acceptor fall in the same subcube is negligibly small. Then random coordinates were chosen within that subcube. The carpet was treated in a similar way, but with four filled sectors at each step.

The interaction between the donors and acceptors was treated according to equation (4). Acceptor sites were assumed to have a Poisson distribution of average p acceptors in them. The donor had an equal probability of being in any of the randomly selected donor sites.

Factoring out the natural decay by defining $\Phi(t) = \exp(t/\tau_0)\sum_j f(t, Y_j)$, one obtains from equation (6)

$$\ln\{-\ln[\Phi(t)]\} = \ln[p\rho_0 V_d r_0^d \Gamma(1 - d/6)] + (d/6)\ln t. \qquad (7)$$

For each object we plotted $\partial[\![\ln\{-\ln[\Phi(t)]\}]\!]/\partial(\ln t)$ versus $\ln t$. Equation (7) indicates that these are the dimensions that the donor sees at that time. Of course the dimensions are a well defined quantity for only self-similar media but Klafter–Blumen dimensional analysis is often used for restricted geometries.

4. Results and discussion

The decay curves indicate that all objects appear as zero dimensional, i.e. point like at times long compared with the critical time at which the donor sees the edge of the object. For times much shorter than the crossover time the dimensions tend towards the actual geometrical dimensions of the object. The smaller-dimensional objects reach their geometrical dimensions.

The geometrical dimensions seen by the donors in the thin rod are 3 for $t \ll t_{cr1} = \tau_0(R_{rod}/r_0)^e$. For times between t_{cr1} and $t_{cr2} = t_{cr1}(l_{rod}/2R_{rod})^6$ the rod would be expected to be seen as a one-dimensional object, and for times greater than t_{cr2} it would be seen as a point. Figure 1(*a*) shows that, between t_{cr1} and t_{cr2}, $d = 1$ is reached. At shorter times, $d = 3$ is not reached within the resolution of this simulation. The geometrical dimensions of the flat disc are 2 for $t \ll t_{cr} = \tau_0(R_{disc}/r_0)^6$. These dimensions are almost reached (figure 1(*b*)).

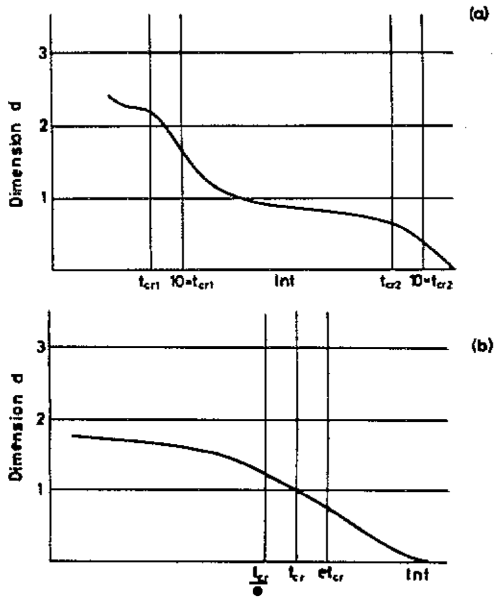

Figure 1. Plots of d versus $\ln t$ in regular geometrical objects of low dimensions: (*a*) thin rod; (*b*) flat disc. In the figure, t_{cr} is the crossover time as defined in the text and, in (*a*), t_{cr1} and t_{cr2} refer to the times at which the donors see the radius and the ends of the rod, respectively.

Rotund objects such as the cube and thick cylinder have a harder time reaching $d = 3$ (figures 2(*a*) and 2(*b*)). Moreover, at very small times, sampling errors render this calculation useless.

With the fractal objects we also noted the tendency to reach their nominal fractal dimensions; however, in these objects there is also an oscillation in the Klafter–Blumen dimensions (9). This effect can be seen in the Menger sponge (figure 3(*a*)), but it is much more pronounced in the Sierpinsky carpet (figure 3(*b*)), a dust-like object. These oscillations are found because the volume over which the charge density is integrated increases rapidly when the filled parts of the fractal object become visible to the donor and it increases slowly when the empty parts become visible. Note that the Klafter–Blumen dimensions are defined from the infinitesimal increase in the volume when the radius is increased infinitesimally. Thus they are not the same as the fractal dimensions. However, the Klafter–Blumen dimensions when averaged

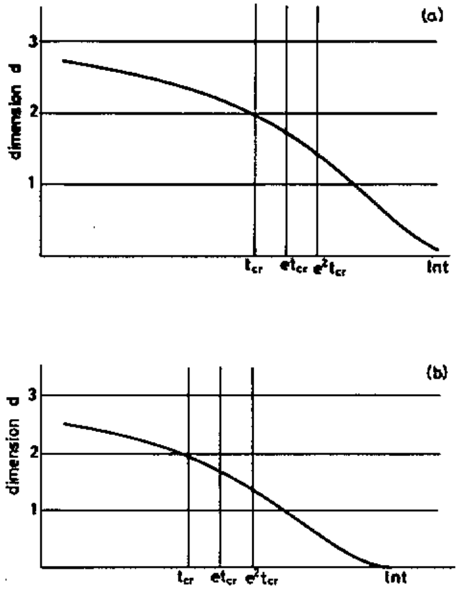

Figure 2. Plots of d versus $\ln t$ in regular geometrical objects of high dimensions: (a) cube; (b) thick cylinder. (t_{cr} is the crossover time.)

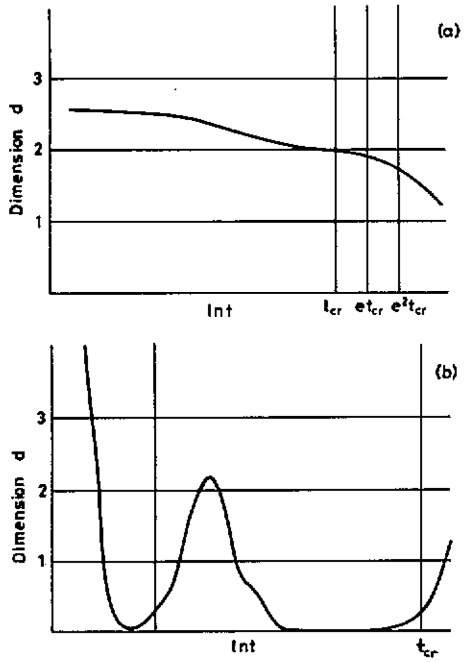

Figure 3. Plots of d versus $\ln t$ in fractal objects of high and low dimensions: (a) Menger sponge; (b) Sierpinsky carpet. (t_{cr} is the crossover time.)

over a self-similarity scale of the fractal object give its fractal dimensions. For this reason the peaks observed in the Klafter–Blumen dimensions may and do exceed the dimensions of the space in which the object is embedded. This is most clearly seen in dust-like objects such as the Sierpinsky carpet ($d = \log 4/\log 3 = 1.26$). The more dust is like the carpet, i.e. with lower fractal dimensions, the higher are the peaks of the Klafter–Blumen dimensions. In the Menger sponge, a continuous object, these oscillations are seen only in the slope of the dimensions as they decrease near t_{cr}.

The transition region where for shorter times the object is seen at high dimensions and for longer times it is seen at lower dimensions is as large as expected. Even though it is possible to tell a Menger sponge ($d = \log 20/\log 3 = 2.73$) from a regular cube ($d = 3$), this takes many measurements to tell where the edge of the object is. Without finding the size of the object, one can easily be misled into believing that a fractal object has been found when one is merely seeing the edge of a regular geometrical object. The situation in real life is even more difficult because finite-size-restricted geometrical objects occur in all sizes. The edge effects will begin at times ten times shorter than the critical time for the smallest bodies and last until about ten times the critical time for the largest bodies. Thus, only for times much shorter than the crossover time for the smallest objects can one see the dimensions correctly; for almost all time intervals, DET decay curves will give a lower estimate of the dimensions and can lead the experimenter into believing that a fractal object has been found when it has not.

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