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Fractal-Like Exciton Kinetics in Porous Glasses, Organic Membranes, and Filter Papers

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We have measured the exciton (triplet) recombination (fusion, annihilation) characteristics of naphthalene-doped microporous materials. This technique yields the dynamic (spectral, fracton) dimension of the embedded naphthalene structure or the effective random-walk dimension of the porous network. Temperature studies separate the energetic and geometric features of the pore space. The geometric dynamic (spectral) dimensions are mostly between 1 and 2, i.e., fractal-like, and are consistent with previous results on the static (fractal or Euclidean) dimensions of the porous Vycor glass samples.

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Porous glasses, rocks, and related materials have commanded much interest lately and the fractal dimension of the pores has been the subject of much discussion.[1-4] Anomalous diffusion and the associated fracton or spectral dimension[5-7] have become a new tool in the characterization of fractal properties.[8-11] However, while the diffusion experiments require microscopic measurements, often below the optical diffraction limit,[8] the anomalous reaction kinetics, which are a direct consequence of anomalous diffusion,[12-18] can be studied via macroscopic measurements. This has been demonstrated by simulations[11-16,19] as well as by exciton-annihilation studies on isotopic alloy crystals[11,17,18] (where the exciton transport is confined to the percolation clusters of the lower–excitation-energy component). In these isotopic alloys an energetic restriction leads to clear-cut fractal spaces (incipient infinite percolation clusters) with a measured fracton (spectral) dimension[20-22] d_s' of about $\frac{4}{3}$, while the steady-state energy-transport experiments[23,24] give the fractal dimension, d_f (within three significant figures).

In this work we demonstrate that a fractal-like triplet-exciton fusion kinetics does occur in several classes of disordered media, of both intrinsic and practical interest: porous glasses, porous membranes, and filter papers. In all these matrices the exciton conductor is naphthalene (which is embedded into the porous matrices). The naphthalene domains appear to have a fractal geometry. The question of interest is whether such geometry is due only to trivial considerations (the glass wall) or whether there are also more subtle effects (e.g., naphthalene domain boundaries of fractal shape). Our experiments do unscramble simple geometric effects from energetic effects.

The sample preparation of the porous polymeric membranes (Gelman Sciences, Inc.) and filter papers (Whatman) involved soaking in solutions of naphthalene (zone refined, in spectroscopic grade hexane). The porous Vycor (7930 Corning glass) samples were prepared by naphthalene sublimation in vacuum. The original Vycor glass was treated with acids, water, and alcohol. The samples were excited at low temperatures by a 1600-W xenon arc lamp through a monochromator set at 310 nm. Spectra were collected via a 1-m JY double monochromator (with EMI 9816 QB photomultiplier tube and PAR 1109 photon counter). The delayed-fluorescence decays were obtained by shuttering of the excitation beam and using various filters with an EMI 978IR phototube and a PAR 4202 signal averager.

The principle behind the approach taken here is the relation of the instantaneous exciton-annihilation probability to the site-visitation efficiency. The instantaneous exciton annihilation is $d\rho/dt$, where $\rho(t)$ is the exciton density. The fraction of exciton population annihilated (in time dt) is $\rho^{-1}d\rho/dt$. This fraction is linear in density ρ (binary-collision theory argument). Hence the normalized instantaneous exciton annihilation probability k is given by

$$k = \rho^{-2}d\rho/dt. \tag{1}$$

Classically k is time independent ("rate constant" in chemical language). It has been shown that k is proportional to the visitation efficiency ϵ of a random walker[12,13,17] (the time derivative of the mean number of *distinct* sites visited):

$$k \sim \epsilon \sim t^{-h}, \quad 0 \leq h \leq 1, \tag{2}$$

where $h = 0$ for three-dimensional Euclidean spaces and lattices (classical result) but for $d_s' < 2$, e.g., fractal domains,[17]

$$h = 1 - d_s'/2, \quad h > 0. \tag{3}$$

The delayed fluorescence (F) is a direct consequence of the triplet-exciton fusion: $F(t) \sim d\rho/dt$. The phosphorescence (P) is due to the natural decay of the triplet-exciton population: $P(t) \sim \rho(t)$. From Eqs. (1) and (2) we get

$$F/P^2 \sim t^{-h}, \quad 0 \leq h \leq 1. \tag{4}$$

We note that under special circumstances, where one of the two fusing excitons is trapped ("hetero-

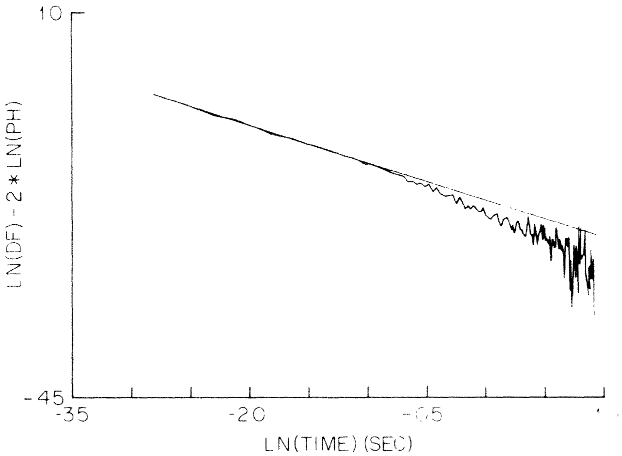

FIG. 1. Annihilation rate coefficient, $k = F/P^2 = (\mathrm{DF})/(\mathrm{Phos})$ vs time on a log-log scale, for porous Vycor glass (30 Å). $T = 6$ K and $h = 0.44$.

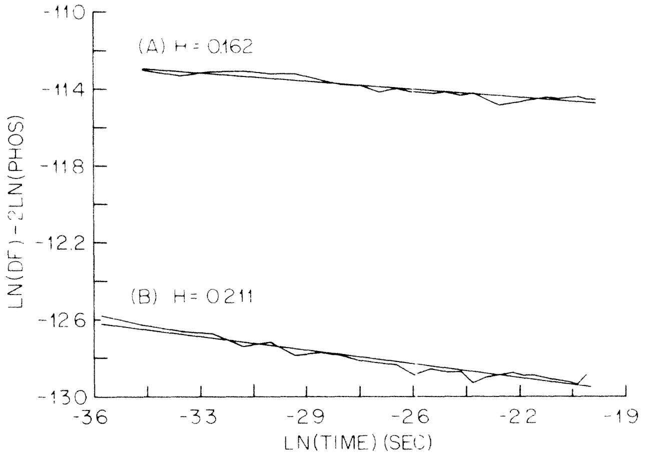

FIG. 2. Annihilation rate coefficient, $k = F/P^2 = (\mathrm{DF})/(\mathrm{Phos})$ vs time on a log-log scale, for porous polymeric membranes: (A) acetate, (B) nylon (both 0.2 μm). H is the heterogeneity exponent h.

fusion"), and is present in large abundance (relative to the freely moving excitons), one gets,[17] instead of the binary reaction (1) ("homofusion"), a pseudounary reaction:

$$k = \rho^{-1}\, d\rho/dt, \tag{5}$$

and thus

$$F/P \sim t^{-h}. \tag{6}$$

We also note that for both (4) and (6) one has at early times ($P \sim \rho \approx \mathrm{const}$)

$$F \sim t^{-h}, \quad t \to 0. \tag{7}$$

Some of our experimental results are shown in Figs. 1 and 2. The heterogeneity exponent h is extracted from the slopes of $\ln k$ vs $\ln t$. The values so obtained for h are listed in Table I, along with values for the effective spectral dimension d_s' of the fractal-like medium calculated from the relation $d_s' = 2(1-h)$. We note that for all samples at low temperatures $h > 0$. This implies that all samples exhibit a fractal-like behavior at these low temperatures. We also note that for the Vycor sample $d_s' \approx 1.1$. This value does not change much with increasing temperature. On the other hand, we observe (Table I) some drastic temperature effects on the membrane and filter-paper values. Notably, the cellulose (natural wood) filter paper approaches a classical (Euclidean) behavior at $T \approx 80$ K, i.e., $h \to 0$.

We have shown experimentally, using vapor-

TABLE I. Heterogeneity exponents and effective spectral dimensions.

Sample	Pore size (μm)	T (K)	Exponent (h) homofusion[a]	Spectral dim. (d_s')[b]
Acetate (GA8) membrane	0.2	4	0.16	1.7
		80	0	3
Acetate (GA1) membrane	0.5	4	0.47	1.1
Acetate (GA3) membrane	1.2	4	0.44	1.1
Nylon (B124) membrane	0.2	4	0.21	1.6
Glass-filter paper	0.6	6	0.42	1.2
		80	0.20	1.6
Cellulose filter paper	0.6	6	0.33	1.3
		80	0.06[c]	3[c]
Vycor porous glass	0.003	6	0.45	1.1
		58	0.5	1

[a] Error bars are ± 0.05 or less.

[b] Error bars are ± 0.1 or less (but −1 for the entry 3 for cellulose filter paper, if pure heterofusion, which is unlikely).

[c] Heterofusion (pure).

deposited naphthalene,[9,25] as well as by simulations,[26] that random energetic disorder can also result in fractal-like kinetics (and thus in an effective h and d_s'). Moreover, geometric and energetic effects do superimpose[27] in a way that is analogous to the "subordination principle" of Klafter, Blumen, and Zumofen.[2] In the latter, the spectral dimension d is effectively reduced by a constant factor accounting for a "continuous-time random walk" with an anomalous hopping-time distribution (infinite second moment). We note here that this continuous-time random-walk model has been shown to be equivalent to models of energetic disorder.[2] We can thus separate the roles of geometric and energetic disorder via temperature studies. In the limit where the thermal energy is large compared to the inhomogeneous line broadening (which we observe spectroscopically), the effects of the energetic disorder are minor and the geometric effect dominates. Table I shows that both in glass (synthetic) and cellulose (natural) *filter papers* the triplet excitons of the naphthalene embedded in the pores move anomalously (at low temperatures) because of energetic disorder. However, it appears that while the glass filter paper has a pore network with a real fractal-like structure (geometric spectral dimension of 1.6), the natural filter paper has $h \approx 0$, which is consistent with $d_s \geqslant 2$, i.e., a nonfractal (Euclidean) pore network (which would be more efficient for biological diffusion processes).

The low spectral-dimension value ($d_s' = 1.1 \pm 0.2$) for our samples of porous Vycor (which supposedly is the same as that used by Dozier, Drake, and Klafter[8]) is consistent with a number of literature claims. Even *et al.*[1] argued that $d_f = 1.7$ for their porous Vycor sample (not necessarily the same as ours) and interpreted it in terms of a percolation backbone. This would result in $1 < d_s \leqslant \frac{4}{3}$. Dozier, Drake, and Klafter[8] have chosen to model their porous-glass sample with a three-dimensional percolation cluster ($d_f \approx 2.5$). This gives $d_s' \approx 1.3$. Yang, Evesque, and El-Sayed[3] quote a totally different model (for an unspecified sample) consisting of a simple cubic lattice made of interconnecting spheres and cylinders. If the cylinders are narrow enough, they (literally) become the 'bottleneck" for the exciton recombination reaction and thus result in a one-dimensional effective topology ($d_s' = 1$). [We note that we have also modeled[28] a similar quasi one-dimensional network (parallel connected lines) and got $d_s' \approx 1$ over the appropriate time scale.] Our experimental values are thus quite believable but not yet very discriminating (a 10% error in h translates into a 20% error in d_s'). We note that for any connected fractal structure, $1 \leqslant d_s' \leqslant 2$. [A fractal "dust" will result in $d_s' < 1$ ($h > 0.5$); however, the annihilation efficiency on a "dust" structure is quite low, resulting in extremely low delayed fluorescence signals.]

The dynamic range of our present measurements are limited by a 5-ms shutter resolution (which can be improved) and the 2–3-s triplet lifetime (limiting signal/noise). We estimate that the corresponding length scale for exciton migration is on the order of 1000 Å (0.1 μm). We note that the nominal pore sizes (Table I) give upper limits, rather than mean values, for the membranes and filter papers. Because of the much faster excitation migration in Euclidean (ordered) spaces (the bulk migration is at least 2 orders of magnitude more efficient than migration in fractal-like domains) we believe that our data on these samples characterize the more numerous but narrower microporous networks, rather than the nominal pore sizes. The only exception is the porous Vycor glass sample whose pore size is a mean value based on molecular-adsorption measurements.[8]

In conclusion, the studies of naphthalene embedded in polymeric membranes, filter papers, and Vycor glass samples have demonstrated a fractal-like exciton annihilation kinetics. Temperature studies establish both the subordination of geometric and energetic disorder and a technique for assessing the relative roles of geometric and energetic constrains. The network spectral dimension is usually in the range $1 < d_s' < 2$, but some samples are consistent with $d_s' = 1$ and others with $d_s' = 3$.

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