Exciton Kinetics in Ultrathin Molecular Wires and Pores

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When are molecular wires thin enough to show one-dimensional exciton kinetics? Cylindrical naphthalene wires (5–5000 nm radius) show a definite one- or three-dimensional transition (about 25 nm for triplet excitons at 4 K; 40 nm at 77 K). Nuclepore channel-pore membranes (polycarbonate) serve as templates and calibrators. Vycor-glass pores are effectively one dimensional. The triplet-exciton migration (multiple hopping) length is 50–100 molecules. The recombination involves free and bound excitons.

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Solid-state and stochastic problems in one dimension have been of long-standing theoretical interest.[1-5] Currently, electronics in thin wires is of much theoretical and practical interest.[6-9] The theoretical enigmas (localization, mesoscopic phenomena, boundary effects) are compounded by experimental difficulties such as minute currents, heat dissipation, shorts, nonuniformity, and suspect testing procedures. Many of these difficulties are not present for Frenkel excitons. There are no Coulomb repulsions and for triplet excitons the interactions are extremely short ranged and the surface effects are minimal.[4,10] Moreover, triplet excitons are readily localized in the bulk[11] and thus there is no localization-delocalization transition or crossover. Experimentally one can rely on optical measurements which are as simple for thin wires as for the bulk. Furthermore, sample uniformity or continuity is not a crucial factor. One can thus concentrate on the mesoscopic properties of interest, stemming from the confinement of the excitons inside a thin "wire."

Recently, porous materials and fractal networks have also been of much interest.[12-15] The difference between a fractal network and a quasi one-dimensional network is not often all that clear.[12-16] Energy transfer[13,14] and exciton kinetics[15] have been used for the characterization of such networks (e.g., pore networks of porous media). A better understanding of the characteristics of truly one-dimensional networks and the effects of sample diameter is thus of practical interest. Furthermore, molecular or polymeric chains, fibers, filaments, and networks exist in most synthetic, natural, and biological organic systems, from organic conductors to neuron transmitters. Molecular exciton kinetics in thin filaments are of relevance to all these systems.

We note that our system differs significantly from previously studied quasi one-dimensional systems.[17-20] The latter are essentially two- or three-dimensional systems with highly anisotropic exciton-exchange interactions. Thus, for a short time the exciton is confined in one dimension. However, there is always a finite probability of movement along other directions (interchain hopping), resulting in a two- or three-dimensional behavior over longer times (this usually confines the measurements to ultrashort times). Moreover, the phonons and exciton-phonon interactions in these systems are seldom one dimensional. In contrast, our systems are truly one dimensional over *long times* and there is no escape or tunneling out of the thin, one-dimensional systems. (Our ultrathin wires are obviously three dimensional on extremely *short* time scales.)

Exciton transport is usually monitored via the kinetics of trapping or annihilation.[11,15,18] The kinetic process may be unary, pseudounary, or binary (monomolecular, pseudomonomolecular, bimolecular in chemical language), e.g., trapping heterofusion, or homofusion, respectively.[4,15,21] In all these cases the "rate constant" (instantaneous reactive collision probability per unit density) is given by[21]

$$k \simeq dS/dt, \tag{1}$$

where S is the mean number of distinct lattice sites visited by a single exciton (in the absence of reactive processes). We note that Eq. (1) is valid for all topologies, in contrast to the expression $k \sim D$ (D = diffusion constant) which is valid only for three-dimensional (homogeneous) lattices. To a very good approximation one has[21]

$$S \sim t^f, \quad \tfrac{1}{2} \leq f \leq 1, \tag{2}$$

$$k \sim t^{-h}, \quad 0 \leq h = 1 - f \leq \tfrac{1}{2}. \tag{3}$$

At long times $h=0$ for three-dimensional lattices and $h=\frac{1}{2}$ for one-dimensional lattices. We note that for fractal lattices $h = 1 - \frac{1}{2} d_s$, where d_s is the spectral dimension.[21-23] The pragmatic questions we pose are as follows: How thin does a wire have to be to give one-dimensional behavior ($h=\frac{1}{2}$)? What is the nature of the crossover from three-dimensional to one-dimensional behavior? What does this crossover depend on? What can we learn from it? What is the use of thin exciton wires?

We note here that in perfect crystalline samples the excitons move freely (at random, due to phonons), resulting in binary (bimolecular) exciton-exciton annihilation,[21,24]

$$A + A \rightarrow h\nu, \tag{4}$$

where $h\nu$ designates fluorescence (delayed). Thus the annihilation rate R and the fluorescence rate F are given by[24]

$$F \simeq R = k\rho_A^2, \tag{5}$$

where ρ_A is the free exciton density. However, in most *real* samples,[15,25] a fraction of the free excitons (A) are quickly *trapped*, giving a roughly constant density $\rho_{A'}$ of trapped excitons (A'), resulting in a pseudounary (pseudomonomolecular) annihilation reaction and rate:

$$A + A' + h\nu, \tag{6}$$

$$F \simeq R = k'\rho_A, \quad k' = k\rho_{A'}. \tag{7}$$

In addition, the triplet excitons undergo natural decay (lifetime τ):

$$A \rightarrow h\nu, \quad P = \tau^{-1}\rho_A. \tag{8}$$

The overall results are thus

$$k \sim F/P^n, \quad n = 1,2, \tag{9}$$

where $n=2$ is for perfect (trapless) samples and $n=1$ is for real samples (with traps). We note that for three-dimensional samples k (and $\log k$) is expected to be *constant in time* while for one-dimensional samples $k \sim t^{-1/2}$ and $\log k \sim \log t$ (with a slope of $-\frac{1}{2}$).

The optical setup and sample preparation have been described before.[15,25] The only significant change involves the use of channel-pore (Nuclepore[26]) polycarbonate membranes. These 6-μm-thick membranes come with well isolated, *cylindrical* pores (Fig. 1). While a given membrane has uniform pore diameters, membranes with different pore diameters are available and we used them in the range of 10 nm (100 Å) to 1 μm (10000 Å). Some typical results are shown in Fig. 2 ($T=4$ K) and Fig. 3 ($T=77$ K). We note that only the pseudounary model ($n=1$) resulted in linear slopes. The binary model ($n=2$) cannot be fitted with straight lines and, moreover, results in nonconstant k curves even for

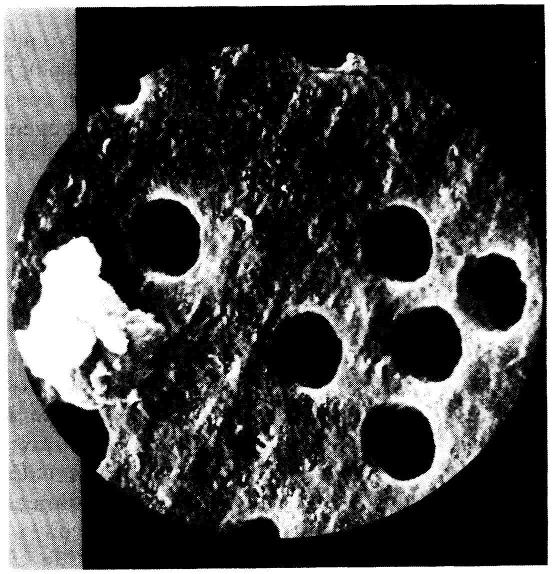

FIG. 1. Channel-pore membrane: polycarbonate (Nuclepore, Ref. 26). Enlargement about 10^4 times. Pore length 6 μm.

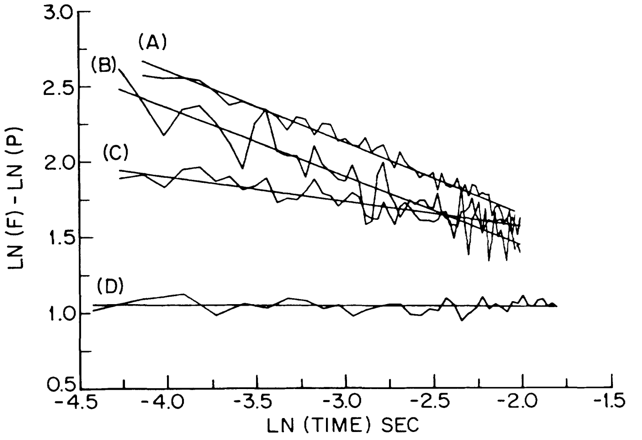

FIG. 2. Annihilation rate coefficient $R=F/P$ vs time on a log-log scale, for naphthalene-filled channel-pore polycarbonate membranes at $T=4$ K. The pore radii are (curves A) 75 Å, (curves B) 150 Å, (curves C) 250 Å, and (curves D) 400 Å. Note that the trapped (bound) exciton phosphorescence is excluded via an interference filter (centered at the free exciton peak).

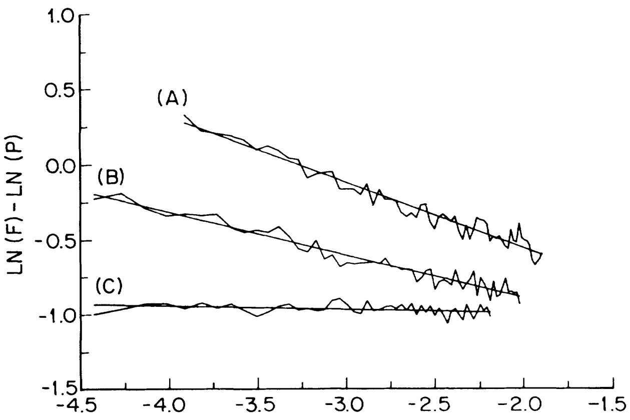

FIG. 3. Annihilation rate coefficient $R=F/P$ vs time on a log-log scale, for naphthalene-filled channel-pore polycarbonate membranes at $T=77$ K. The pore radii are (curves A) 250 Å, (curves B) 400 Å, and (curves C) 1000 Å.

the thickest wires (1.2 μm). The totality of the h values (negative slopes), for all wires (each at 4 and 77 K), is given in Fig. 4.

We observe that the thinnest wires yield a value $h \cong 0.5$, while the thickest wires give $h \cong 0$, for both temperatures. Actually, *extrapolation to zero diameter* yields $h \rightarrow 0.49 \pm 0.02$. On the other hand, micrometer-sized wires have $h \rightarrow 0.02 \pm 0.02$. These two limiting values are in excellent agreement with the theoretically expected values of $h = \frac{1}{2}$ and $h = 0$, respectively.[27] The crossover (between $h \cong 0$ and $h \cong \frac{1}{2}$) occurs at diameters of about 500 to 800 Å at 4 and 77 K, respectively. The crossovers are relatively sharp and their temperature dependence is relatively mild. The higher value at higher temperatures is consistent with a somewhat faster hopping rate. In our interpretation the crossover radius is roughly consistent with the average *cruising range* λ (end-point to end-point distance) of the exciton, *within its lifetime.*

An indirect, rough estimate for the naphthalene cruising range in similarly prepared samples was given[15] as $\lambda = 1000$ Å. This is in excellent agreement with our present result ($\lambda \cong 500$ Å). Obviously, for wires with radius $r \gg \lambda$ the excitons do not "feel" the pore boundaries while for $r \ll \lambda$ the excitons are severely confined along two of the three directions. We note that the polycarbonate excitation energy values are so much higher than those of naphthalene that there is a vanishing probability for barrier crossing or tunneling ($\Delta E > 100kT$ even at 77 K).

Regarding previously studied *random-pore* membranes (Gelman Sciences, Inc.),[15] we notice that these are prepared by an entirely different process, resulting in an apparent self-similar distribution of pore sizes (see picture in Ref. 21). As pointed out before,[15] the exciton annihilation method is heavily biased towards small pores. Thus the previously derived h values can now be calibrated in terms of *weighted pore sizes* (for the nylon, acetate, etc., pores of Ref. 15). Specifically, a range of h values between 0.1 and 0.3 can be interpreted in terms of a weighted–pore-size distribution of a few hundred angstroms. This is in contrast to the much larger nominal pore sizes, based on filtration experiments. On the other hand, it is possible to retain a fractal-like interpretation,[15] where $h = 1 - \frac{1}{2} d_s$ and d_s is an effective spectral dimension. This also explains how different h values may be obtained by different experimental methods. For instance, the photodimerization method[25] which is based on the diffusion of excited molecules in solution, does result in a somewhat higher range of h values for the same random-pore membranes probably because of a different weighting. An interesting exception to the random-pore membranes appears to be the natural (cellulose) filter papers. These are not likely to contain a self-similar distribution of minipores. The $h = 0$ result[15] points towards nearly cylindrical pores, with a diameter distribution that has a cutoff higher than 1000 Å.

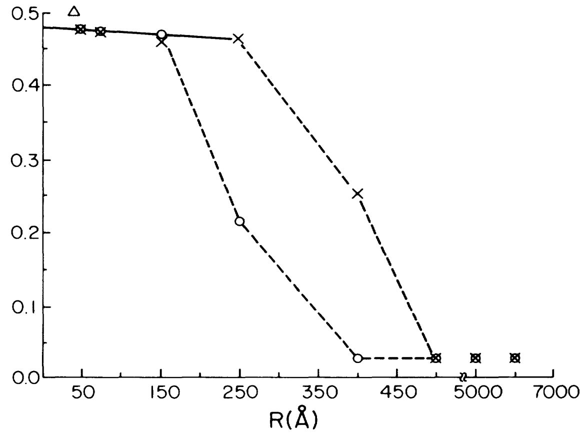

FIG. 4. Exponent h vs wire radius r (in angstroms), at 4 K (circles) and 77 K (crosses). The 20-Å point (triangle) is for porous Vycor (Ref. 15). Note break in scale.

Of particular interest is the resolution of the porous-glass (Vycor) dilemma.[15] The nature of the pore network has been highly controversial.[12-16] It has been argued on one hand that it is a random (percolationlike) network with a fractal dimension on the order of 2.[13] On the other hand it has been argued to be nonfractal but essentially one dimensional.[12,15,16] With use of the exciton kinetics technique it was argued[15] that the effective spectral dimension is 1.05, i.e., effectively one dimensional. Our present study uses the same approach for "calibrated" cylindrical pores which are obviously nonfractal and one dimensional. We have included the older[15] Vycor-glass measurements as a data point in Fig. 4. It essentially falls on the same curve as the new, polycarbonate data. The Vycor data are thus totally consistent with a one-dimensional pore topology.[28,29]

In summary (1) we have produced cylindrical molecular crystal wires down to a radius of 5 nm. (2) The recombination process involves free and bound excitons (heterofusion). (3) The triplet-exciton kinetics fits a multiple-hopping model. (4) The overall migration range is about 25 nm at 4 K and 40 nm at 77 K. (5) The *long-time* exciton transport is strictly *one dimensional* in the ultrathin wires. (6) The *fractal-like* kinetics model works well in a low-dimensional *nonfractal* system. (7) The porous-glass (Vycor) channels are described well by a nonfractal, quasi one-dimensional topology. (8) The exciton annihilation method appears to be a reliable tool for the probing of spectral dimensions and low-dimensional topologies.

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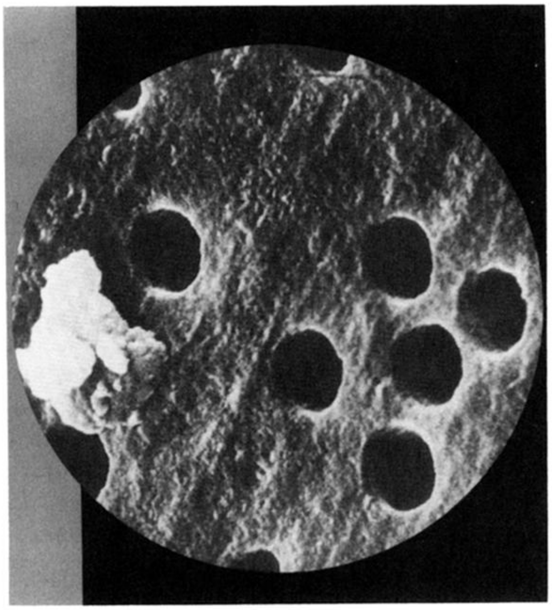

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