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MONTE CARLO SIMULATION OF EXCITON TUNNELING ON A HIERACHY OF CLUSTERS IN DOPED MOLECULAR CRYSTALS

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Abstract A stochastic model with hopping and self trapping on cluster states at low temperature is introduced. It is assumed that hopping and trapping are described for excited triplet states by variable range processes such as tunneling. Cluster states are statistically formed aggregates with a hierachy of decreasing energies according to the cluster size. This energy stair case results in self trapping on the cluster states and introduces a dependency of hopping transport on the topology of the concentration dependent cluster distribution.

INTRODUCTION

Hopping transport in disordered media has received much attention in recent years.[1] Stretched exponential or algebraic decay laws are expected whenever there are parallel or sequential relaxation processes. Conceptionally, it can be discriminated between spatial, energetic and temporal disorder. In case of molecular crystals spatial disorder can be realized via a binary mixture on regular lattice sites.[2] Energetic disorder is observed for orientationally disordered crystals formed by molecules lacking inversion symmetry.[3] Temporal disorder is due to the fact that interactions responsible for the transport are of variable range and fall off exponentially in case of triplet energy transport.[4] In this case no closed solutions are possible and Monte Carlo simulations are useful to elucidate transport properties. Examples of simulations for variable range hopping are known[1,4-6], but are not applicable in the present situation because they do not include energy[4] or spatial[6] disorder or deal with correlations of both.[1,5] In the case of chemically mixed crystals, as is the subject of the present investigation, spatial disorder is realized via a binary system, but due to strong intermolecular interactions between p-dichlorobenzene guest and p-dibromobenzene host molecules statitistically formed clusters (dimers, trimers, etc.) are distinguishable with respect to their triplet

excitation energies[7] resulting in dispersive triplet energy transport[8,9]. In this publication we present for the first time results of simulations where transport of excitation energy is modelled by an energy stair case formed by guest clusters of increasing size.

THE MODEL AND SIMULATION METHOD

The model describes hopping transport on guest monomers and clusters on a squared lattice. Clusters with n nearest guest neighbors on a square host lattice are called clusters of size n. We assume hopping rates which depend exponentially on the distance r_{ij}. The rates are $W_{ij}=W_o e^{-r_{ij}/r_o}$ for $n_i \leq n_j$ and $W_{ij}=0$ for $n_i > n_j$ for hopping from the lattice site i to j, i and j belonging to clusters of size n_i and n_j, respectively. Thus hopping is allowed only to clusters of the same or larger size.

Besides the mean displacement $\langle r \rangle$, the number I_n of excitons on clusters of size n is calculated. Moreover, we introduce a quantitiy $d(t,c) = \frac{1}{N_{ex}} \sum_{n=1}^{N_{ex}} \bar{d}_n(c)\ I_n(t,c)$, which characterizes the mean hopping distance. $\bar{d}_n$ is the mean distance between clusters of size n which can be determined at the beginning of the calculation by a cluster analysis.

For simulation we did not use the minimal process algorithm but a more intuitive approach which allows an online visualization of the process on the screen of our workstation. We choose a random distance and a random angle for the hopping distribution and determine the nearest lattice site of this continuous lattice point. Then we check whether a hop to this site is allowed. In the meantime we did preliminary calculations with the minimal process algorithm which show the same behaviour as with our intuitive approach.

Numerical Results

To get some visual insight in the qualitative behavior of the process we first performed simulations with on-line visualisation for hopping on the energy stair case and symmetric hopping with the same starting and boundary conditions. For these qualitative calculations we choose a 50*50 lattice, 50 excitons and 5000 time steps.

In the table below we compare for both cases the results for <r> at three doping concentrations.

	1.3%	3.4%	11%
symmetric hopping	6.1	19.5	46
staircase hopping	6.2	12.5	11.6

It is obvious already from these results that <r> is almost the same for low concentrations but differs considerably for higher concentrations, where trapping increases due to the rapidly increasing formation of larger clusters with lower and lower energies. Fig. 1 shows the striking difference of site visiting for large doping concentrations.

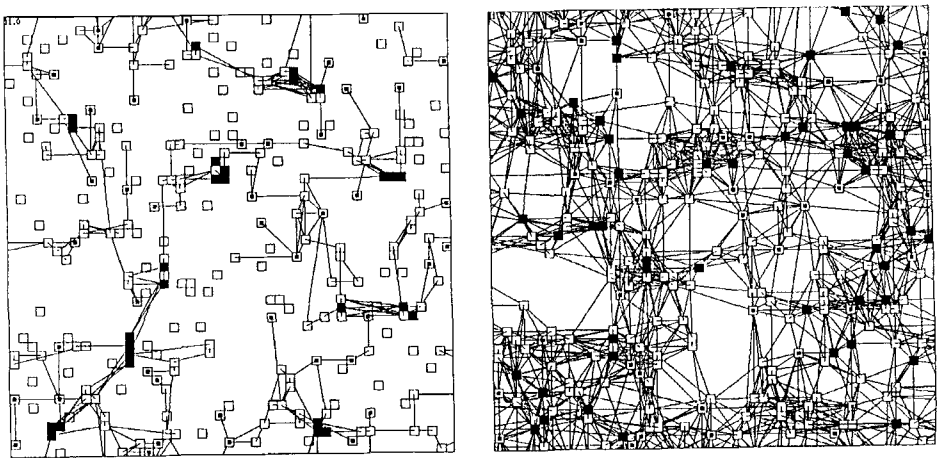

Fig. 1 Histogram of 50 exciton paths for c=11%. □ guest molecule, ▣ starting point, ■ end point. Left: staircase hopping, right: symmetric hopping.

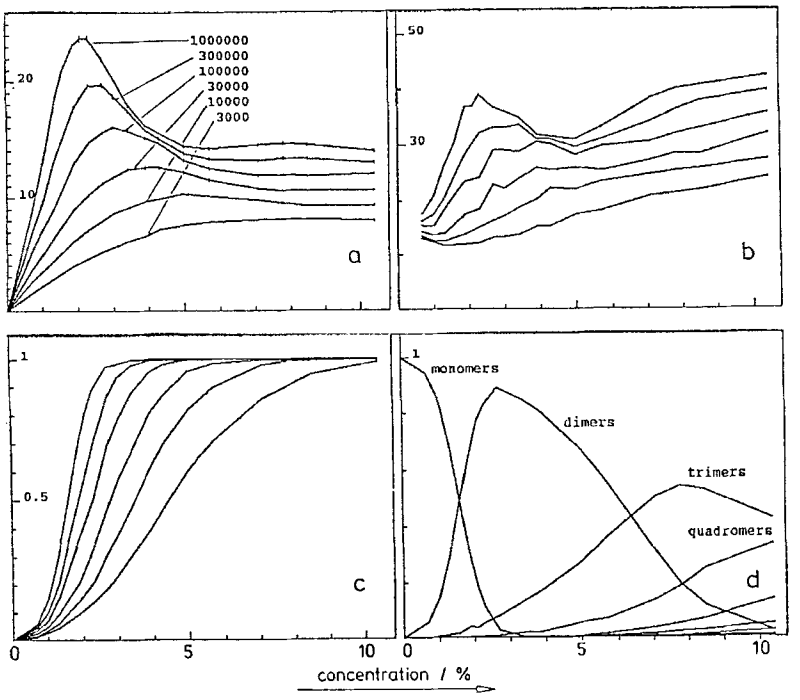

Fig. 2 <r> (a), d (b), $1-I_1$(c), and I_n after 10^6 time steps (d). The parameter are time steps from $3 \cdot 10^3$ to 10^5. $r_0=1$ in all cases.

For a reliable simulation of <r>, I_n and d as a function of time and doping concentration we have performed calculations on a 5000 * 5000 lattice for 5000 excitons. Fig. 2 shows for $r_0=1.0$ the average displacement <r> (2a), the mean hopping distance d (2b), the relative population I_n for clusters with n>1 (2c) and the exciton populations I_n on the individual clusters of seize n after 10^6 time steps (2d). Obviously, <r> is strongly correlated with d because it has minima and maxima at the same concentrations. Comparison of Figs. 2a, 2b and 2d clearly shows that the (time dependent) first maximum of <r> and d at about 2.5% is correlated with the maximum of the dimer population where for <r> the second one at 7.8% is correlated with the maximum of the trimer population. Fig. 3 shows as a function of time the concentration c_m where the first maximum for <r> is observed and the corresponding value $\langle r \rangle_m$ for $r_0=1.5$ and $r_0=1.0$. Whereas $\langle r \rangle_m$ increases with time (approximately $\langle r \rangle_m \sim t^{0.2}$), c_m varies only slightly with time at the

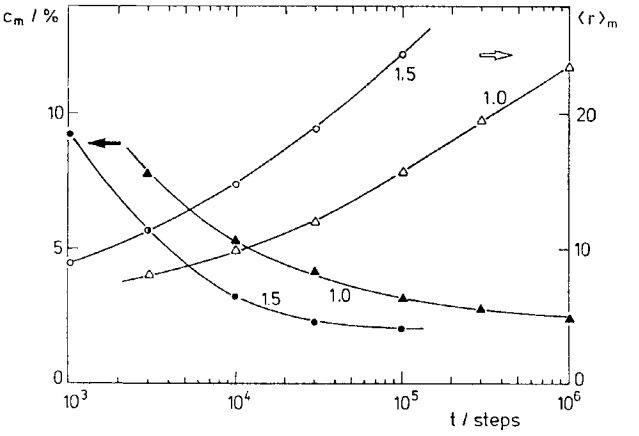

Fig. 3 $\langle r \rangle_m$ and c_m as a function of time. For definitions see text.

longest times calculated. For a given triplet state life time which provides a cut-off at long times c_m can be identified as an optimum concentration for long range hopping transport. The time dependence of $\langle r \rangle$ and of the monomer population I_1 is shown in Fig. 4a and b, respectively. For small values of the doping concentration ($1,3 < c < 2$)

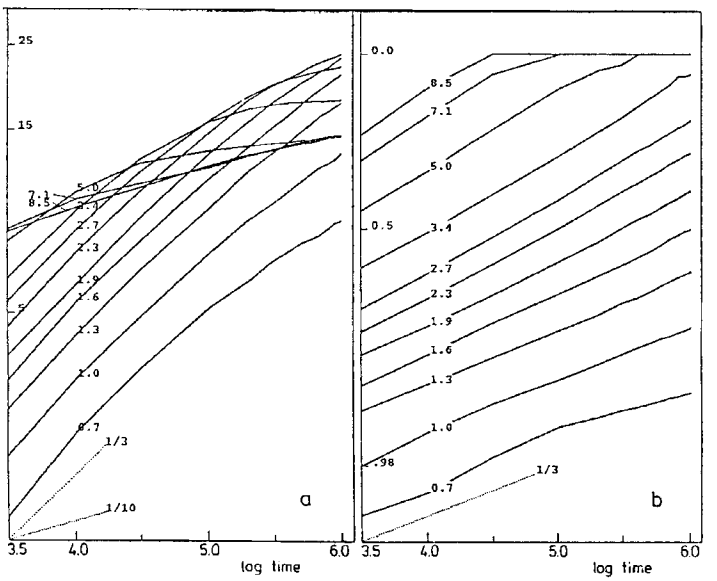

Fig. 4 Log $\langle r \rangle$ versus log t (a) and log(-ln I_1) versus log t (b). Concentrations are between 0.7 and 8.5%. Slopes with increments of 1/3 or 1/10 are indicated.

as well as large values (c>6), <r> shows approximately a power law behaviour according to $\langle r\rangle \sim t^{\gamma}$ with γ between 1/3 and 1/8, respectively. In the very low concentration range the transport is on monomers whereas at the highest concentrations larger clusters dominate. In the range in between the time dependence is rather complex.

The time dependence of the monomer population I_1 (Fig. 4b) and thus the experimentally accessible phosphorescence intensity is well described by a stretched exponential decay law $I_1 \sim \exp(-t^{\beta})$. The value of β increases monotonically with c from about 0.3 to 0.6.

To conclude, the results from these simulations show the striking difference of hopping transport on an energy stair case as compared to symmetric hopping. At a given time an optimum doping concentration for long range transport can be deduced and related to the cluster topology. At higher concentrations transport is self trapped on large clusters. Qualitatively, the phosphorescence intensity is predicted to be a stretched exponential decay as has been observed experimentally.[8,9]

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