Exciton annihilation on dendrimeric trees

Subhadip Raychaudhuri[a], Yonathan Shapir[b], Shaul Mukamel[c],*

[a]Department of Biomedical Engineering, University of California Davis, Davis CA 95616, USA
[b]Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, USA
[c]Department of Chemistry, University of California Irvine, Irvine, CA 92697-2025, USA

Abstract

Exciton–exciton annihilation on Cayley tree like dendrimer molecules are investigated via Monte Carlo simulations. Annihilation reaction of the type $A + A \rightarrow 0$ is considered to calculate the exciton density decay for multiexciton diffusion on dendrimers. Exciton density decays as a power law with a continuously varying exponent in a linear potential. For the case of realistic nonlinear potential of phenylacetylene dendrimers (Phys. Rev. Lett. 77 (1998) 4656) the excitons accumulate around the free energy minimum and annihilate each other quickly.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Extended dendrimers (Fig. 1) are large nanoscale Cayley-tree-like macromolecules shown to exhibit light harvesting capabilities. Recent experimental and theoretical studies have shown that the electronic excitations of these dendrimers are spatially localized within each linear segment [1–5]. For these dendrimers, lengthening of the linear phenyl acetylene branches toward the core leads to a hierarchy of localization lengths. Hence the exciton energy decreases gradually from the

periphery to the center of the molecule [6]. This *energy funnel* and the fact that large number of absorbing elements exist at the periphery of tree-like molecules, make extended dendrimers suitable as single molecule artificial antenna systems.

In our previous papers [7,8] we calculated the mean first passage time (MFPT) for exciton diffusion on dendrimers in a nonlinear potential obtained from time-dependent Hatree–Fock (TDHF) method [9,10]. The MFPT for a center-bound exciton in the TDHF potential suggested, in contrast to the case of linear potential, an optimal dendrimer size for their use as light harvesting antennas. When quenched randomness in the energy was taken into account it made our

---

*Corresponding author. Tel.: +949 824 7600.
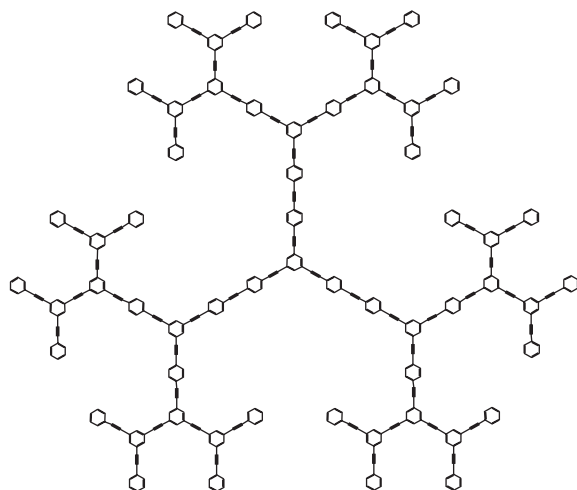E-mail address: smukamel@uci.edu (S. Mukamel).

Fig. 1. Extended phenylacetylene dendrimers with $g = 4$ generations.

argument stronger in favor of an optimal dendrimer size. All of these studies, however, were incomplete in one respect. We always considered single exciton diffusion whereas multiexciton dynamics seems to be more appropriate for light harvesting dendrimers. For multiexciton diffusion, exciton–exciton annihilation processes need to be considered.

Exciton annihilation has attracted much experimental and theoretical attention in recent years [11–13,5,16]. The decay in the number density of particles has been calculated in typical diffusion-controlled reactions like A + A → 0 (annihilation) or A + A → A (coagulation). Below some critical dimensions fluctuations become important leading to a power-law decay of the number density of particles with nontrivial exponents. However, above the critical dimension, mean-field equation yields the correct exponent for the density decay.

In this paper, we address the issue of exciton annihilation (A + A → 0) for both linear and TDHF potential on a tree. Monte Carlo (MC) simulation is used to calculate the density decay due to A + A → 0 annihilation. For the case of a linear potential the density of excitons decays as a power law. Interestingly, the exponent varies continuously as the hopping probability is changed. Exciton annihilation rate in TDHF potential is found to be faster than that in the case of linear

potential and does not show a power-law density decay.

The paper is organized as follows. In Section 2 we briefly describe the known results for A + A → 0 reaction. Section 3 is devoted to the methods of MC simulation. The results of simulations are presented in Section 3. We discuss our findings and make some concluding remarks in Section 4.

2. Known results: A + A → 0

Systems of mutually annihilating or coagulating particles occur in various branches of physical sciences: nuclear reactions, chemical combinations, biological reactions and other interactions. Diffusion-controlled reactions of the form A + A → 0 or A + A → A have been widely studied [5,16] using exact theoretical calculations as well as extensive numerical simulations. Often local fluctuations in particle density of these systems render the mean-field description invalid below some critical dimensions.

Exact solutions have been reported on single-particle annihilation A + A → 0 on Euclidean lattices. The density of particles decay as a power law

$$n(t) \sim t^{-d/2} \quad \text{for } d < d_c$$
$$\sim t^{-1} \quad \text{for } d \geqslant d_c, \qquad (1)$$

where $d_c = 2$ is the upper critical dimension for this process. Above the upper critical dimension fluctuation effects can be neglected and the mean field rate equation $\partial n / \partial t \sim -n^2$ yields the correct behavior for the density $n(t) \sim 1/t$. A drift-field does not change the decay rate of number of particles. However, the hopping probability was assumed to be uniform for all sites on the lattice. For finite systems, $n(t)$ crosses over from power law to exponential decay due to finite size effects.

3. Simulation methods

We applied MC simulations to investigate the annihilation of excitons on Cayley-tree-like dendrimers. First we simulated the process on an

one-dimensional (1D) lattice. For the case of uniform hopping in 1D (linear potential) our simulations just confirmed the known results. For the TDHF potential, however, hopping rates vary from site to site, and no general result exist for this case even in one dimension. Next, we simulated the annihilation process on a Cayley tree structure for both linear and TDHF potential.

For simulations in 1D, we used lattices up to 10^5 sites. We could go up to $g = 16$ generations (= 65535 sites) for the Cayley-tree simulation. Absorbing and reflecting boundary conditions were used at the center and at the periphery, respectively. One MC step corresponded to the number of hopping attempts equal to the number of remaining particles. Particles were allowed to hop to one of its nearest neighbor sites. When two particles occupied the same site they annihilated each other $A + A \rightarrow 0$ and are taken out of the lattice. Initial densities were 10% of the full occupancy and those particles were placed randomly on the lattice sites. The density of particles was calculated after each MC step. The long time asymptotic behavior of the density decay did not depend on the initial number of excitons. Simulation data was averaged over different realizations of the random walk (diffusion). To obtain good statistics more averaging was necessary for smaller system sizes.

4. Results

4.1. Linear potential

The potential is of the form $V(n) = n\varepsilon$, where n is nth generation of the tree.

1D: The density decay was found to behave as $n(t) \sim t^{-1/2}$ as expected.

Cayley-tree: Let us denote the probability of going outward (inward) along a single branch at the nth node to be p_n (q_n). From detailed balance we obtain $p_n/q_n = \exp\{-\beta(V(n) - V(n-1))\} = \exp\{-\beta\varepsilon\} = p/q$ (independent of n). Note this definition of p (q) does not include the factor c (branching ratio). In the absence of any external potential, $p = q = \frac{1}{2}$. However, due to the tree structure the probability of going outward for a

particle is c (= branching ratio) times higher than the probability of going inward. For dendrimers $c = 2$, hence it is twice as likely for a particle to diffuse outward than toward the center. The density of excitons decay as power law $n(t) \sim t^x$, with $x \simeq 0.79$ (Fig. 2). This result is consistent with earlier simulations carried out by Argyrakis and Kopelman [16].
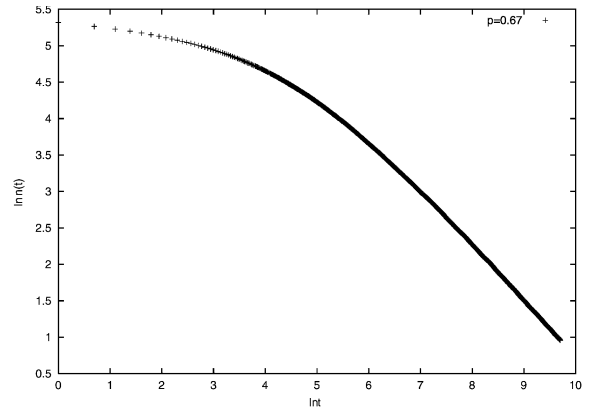

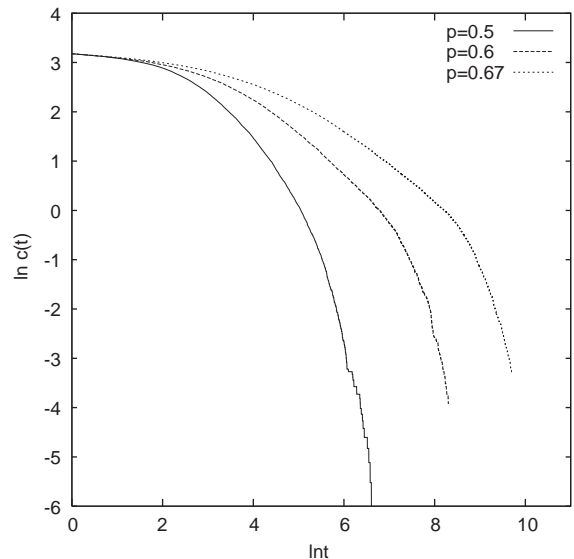Fig. 2. The log–log plot of exciton density versus time for unbiased hopping on a tree.

Fig. 3. The log–log plot of exciton density versus time for with changing p.

Unlike the 1D case, the density decay exponent on a tree changes continuously (Fig. 3) as we vary the hopping probability p. As we decrease p, the excitons tend to hop more toward the center of the molecule. As a result, the exciton annihilation is speeded up due to two separate effects: (a) chances of encounter between two excitons go up, (b) absorption at the center increases as more excitons are funneled toward the center. Hence, the decay exponent x increases as p goes down. $p = \frac{2}{3}$ ($\approx$ 0.67) is a transition point where the inward bias of $p/q = 2$ is exactly cancelled by the outward bias arising from the branching ratio $c = 2$. For $p < \frac{2}{3}$, there is funneling toward the center of the dendrimer.

4.2. TDHF potential

Electronic structure calculations by Tretiak et al. for polyacetylene dendrimers showed [9,10] a strong nonlinear dependence of the exciton energy on n. Excitation energies were calculated using TDHF technique and fitted to the form

$$\varepsilon(n) = A \left(1 + \frac{L}{g - (n-1)} \right)^{0.5}, \qquad (2)$$

where $A = 2.80 \pm 0.02$(e.v.) and $L = 0.669 \pm 0.034$.

1D: This was done to compare with the results of the linear potential case, though it does not have any relevance for real dendrimers which are tree-like. Due to the nonlinear nature of the potential, the hopping rate, unlike the linear potential case, varies from site to site. The density decay was again found to be a power law $n(t) \sim t^x$ with $x \sim 0.53 \pm 05$.

Cayley-tree: This is the most interesting case concerning exciton annihilation on phenylacetylene dendrimers. The hopping probability p_n was found to be different for different generations due to the nonlinear nature of the potential. The density of excitons seemed to decay faster than a power law (Fig. 4).

This can be explained by the free energy bottleneck located somewhere at the center of the molecule. The excitons eventually accumulate around that free energy minimum and annihilate
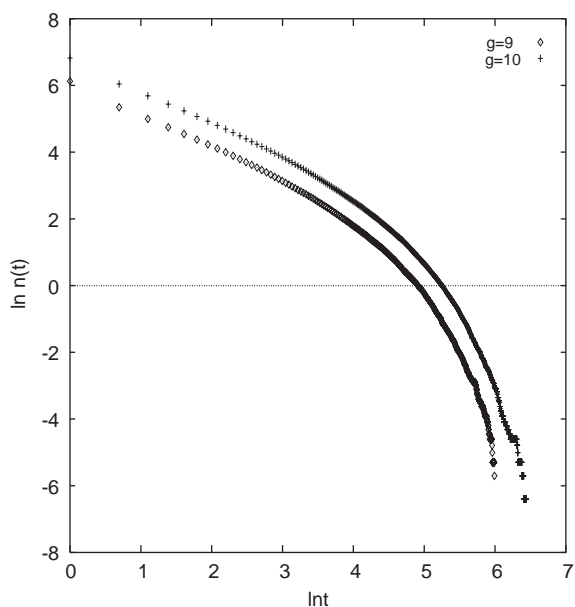

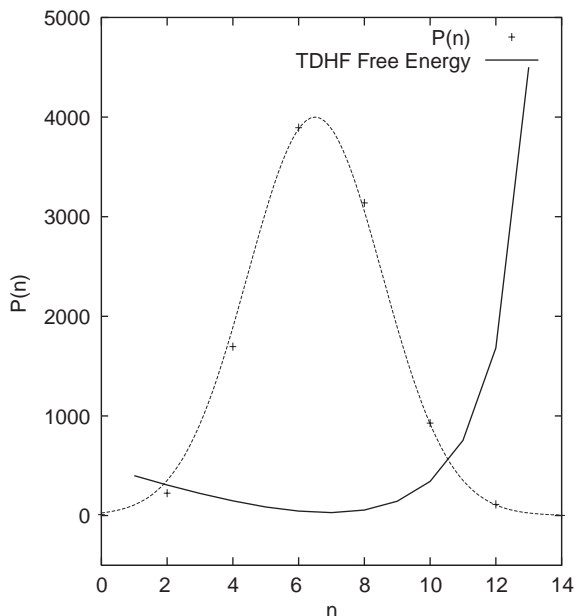Fig. 4. The log–log plot of exciton density versus time for TDHF potential on dendrimers.

Fig. 5. Total number of excitons annihilated at different generations (summed over time).

each other quickly. In Fig. 5 we show that most of the excitons are annihilated on that generation in the middle of the molecule.

5. Conclusion

Exciton annihilation of the type $A + A \rightarrow 0$ on the Cayley-tree geometry are studied via MC simulations. For a linear potential (uniform hopping rates) the exciton density decay is a power law, with a continuously varying exponent depending on the bias. In the case of the TDHF potential, relevant for phenylacetylene dendrimers, the hopping rates change from one generation of the tree to another. In this case, the exciton decay is not algebraic. This fact is attributed to the free energy minimum somewhere in the center of the molecule. Most of the excitons crowd at this free energy bottleneck and get killed quickly. This provides another reason for an optimal size for the dendrimer antennas. Beyond the optimal size, the excitons tend to gather in the middle of the molecule at the free energy minimum, they diffuse slowly to the center and annihilate each other quickly.

6. Acknowledgments

References

[1] R. Kopelman, M. Shortreed, Z. Shi, W. Tan, Z. Xu, J. Moore, A. Bar-haim, J. Klafter, Phys. Rev. Lett. 78 (1997) 1239.

[2] D.A. Tomalia, A.M. Naylor, W.A. Goddand, Chem. Int. Ed. Engl. 29 (1990) 138.

[3] V. Blazani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26.

[4] J. Frechet, Science 263 (1994) 1710.

[5] C. Devadoss, P. Bharathi, J.S. Moore, J. Am. Chem. Soc. 118 (1996) 9635;
M. Shortreed, Z-Y. Shi, R. Kopelman, Mol. Cryst. Liq. Cryst. 28 (1996) 95;
M.R. Shortreed, S.F. Swallen, Z-Y. Shi, W. Tan, Z. Xec, C. Devadoss, J.S. Moore, R. Kopelman, J. Phys. Chem. B 101 (1997) 6318.

[6] A. Bar-Haim, J. Klafter, R. Kopelman, J. Am. Chem. Soc. 119 (1997) 6197;
A. Bar-Haim, J. Klafter, J. Phys. Chem. B 102 (1998) 1662;
A. Bar-Haim, J. Klafter, J. Lumin. 76–77 (1998) 197;
A. Bar-Haim, J. Klafter, J. Chem. Phys. 109 (1998) 5187.

[7] S. Raychaudhuri, Y. Shapir, V. Chernyak, S. Mukamel, Phys. Rev. Lett. 85 (2000) 282.

[8] S. Raychaudhuri, Y. Shapir, V. Chernyak, S. Mukamel, Phys. Rev. E 65 (2002) 021803.

[9] S. Tretiak, V. Chernyak, S. Mukamel, J. Phys. Chem. B 102 (1998) 3310.

[10] S. Tretiak, V. Chernyak, S. Mukamel, Phys. Rev. Lett. 77 (1996) 4656.

[11] L. Valkunas, G. Trinkunas, V. Liuolia, R. van Grondelle, Biophys. J. 69 (1995) 1117.

[12] K. Kang, S. Redner, Phys. Rev. A 32 (1985) 435.

[13] V. Kuzovkov, E. Kotomin, Rep. Prog. Phys. 51 (1988) 1479.

[14] V. Privman, Nonequilibrium Statistical Mechanics in One Dimension, Cambridge University Press, Cambridge, 1997.

[15] D. ben-Avraham, S. Havlin, Diffusion and Reactions in Fractals and Disordered Systems, Cambridge University Press, Cambridge, 2000.

[16] P. Argyrakis, R. Kopelman, Chem. Phys. 261 (2000) 391.