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Exciton Migration on Ring Polymers

Clive A. Croxton* and Ruby M. Turner

Department of Mathematics, University of Newcastle, Newcastle, N.S.W. 2308, Australia

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ABSTRACT: We investigate the migration of excitons around flexible self-interacting hard-sphere continuum rings immersed in a molecularly coarse solvent. We find little distinction between "slow" and "fast" hops executed in times greater than or less than the configurational relaxation time of the ring. Solvent packing fraction also appears to have a minimal (though predictable) effect upon exciton migration. We do find, however, that the hopping range of the exciton is crucial in determining the migration characteristics of the system. Comparisons with recent lattice-based Monte Carlo determinations on a fcc lattice are made.[1] Finally, we investigate the modification of exciton migration on charged rings immersed in hard-sphere solvents of varying charge percentage and find that ring charge effectively doubles the number of hops required by the exciton to locate a trap on a ring of given size.

Introduction

The mechanisms for energy transfer by migrating excitons on polymers are dealt with, for example, in books by Guillet[7] and Phillips.[8] This field of study is based on early work by Förster[9] and Dexter.[10] More recent studies, e.g., by Byers et al.[11] and Janse van Rensburg et al.[1,2,6] is generally lattice-based.

An extended study of the properties of migrating excitations on linear, star, and ring polymers has recently been presented by Janse van Rensberg and Whittington[1] based essentially on self-avoiding lattice-based Monte Carlo representations of the polymer configuration around which the excitation is assumed to migrate. In their study, these authors found that the migration behavior of the exciton is largely insensitive to the topological structure of the polymer, finding essentially the same qualitative behavior for rings, stars, and chains. Two principal mechanisms of transfer of the excitation from donor to acceptor (the chromophores) along the polymer backbone are identified, and for the purposes of simplicity we assume, as did the previous authors,[1] that every segment of the sequence is potentially a chromophore capable of participating in the transfer process. Energy transfers are generally taken to occur between nearest neighbor (though not necessarily sequentially adjacent segments) chromophores, which, in the case of a good solvent having expanded ring configurations (Figure 1), implies migration around the ring rather than across it, although migrations between chromophores which are sequentially distant but spatially close will also participate in the migration process. The extent to which these cross-ring migrations contribute to the overall process will, of course, depend upon the range of the hopper, the size of the ring, and quality of the solvent, not to mention the degree of configurational change which may occur during the diffusion process. Janse van Rensberg and Whittington consider these cross-ring transfers to nonnearest[2] neighbors to be relatively unimportant, certainly for the expanded ring configurations which will tend to arise in a good solvent: we make no such assumption in this study, and, indeed, the role of cross-ring or nonnearest neighbor transitions represents one of the principal objectives of this investigation. The rate at which the jump between chromophores is executed is considered crucial in this study since for slow hoppers *we anticipate* that hopping transitions occur on a time scale considerably longer than the configurational relaxation time of the polymer ring so every transition may be assumed to take place on the conformational average configuration, while for fast hoppers the transition occurs on a configuration which still retains nonzero probability for the last previous transition. For fast hoppers, if the last previous transition was from $k \rightarrow i$, we must compute the conformational average for the ring with the additional constraint $r_{ki} \leq$ hopping range before we can find the probability that the next transition will be from $i \rightarrow j$. This substantially complicates the estimate of fast transition probabilities. Nevertheless, our primary concern here relates to the continuum description of exciton phenomena, contrary to the lattice-based analyses previously reported.

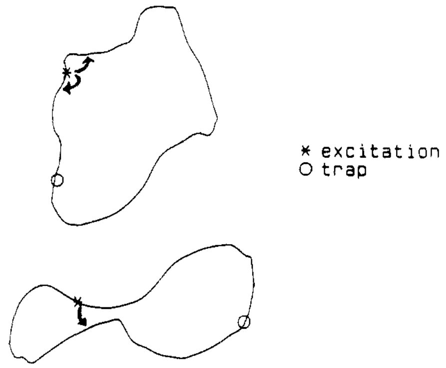

Figure 1. Exciton transitions around and across a ring in the presence of a single trap.

The significance of the distinction between the fast and slow transitions relates directly to the configurational relaxation time of the ring. The "fast" hopper effectively diffuses on the instantaneous configurations assumed by the ring, while the "slow" hopper diffuses on a configurationally averaged structure. Both kinds of hopper are investigated in the present study. As Janse van Rensburg and Whittington observe,[1] there are considerable advantages in restricting the study to ring polymers for which we may reasonably assume all segments are effectively equivalent. Such an assumption is not justified in the case of most other chain topologies for which terminal effects at the ends of the sequence, for example, may substantially modify the diffusive behavior. Finally, we introduce the concept of "exciton traps" whereby a randomly diffusing exciton is captured by a "trap" where it is either radiated away or used to perform a chemical reaction. The number of traps on the ring is, of course, of crucial significance, and our continuum studies necessarily restrict our investigations to no more than two traps per ring. Moreover, our continuum studies based upon the iterative convolution (IC) approximation un-

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fortunately restrict our investigations to relatively small rings, particularly in the case of the fast diffusion when repeated configurational averaging is an essential feature of the study. Accordingly we restrict our "fast" investigations to rings of size $N < 40$, while conceding that the cubic lattice-based treatments of earlier authors dealt with substantially greater N than this. In the present study we aim no more than to demonstrate that our continuum results are consistent with the lattice-based results of Janse van Rensburg and Whittington.[1] For example, on the basis of their lattice-based Monte Carlo studies, these authors find little or no distinction in the migratory properties of both fast and slow excitons around self-avoiding single trap rings in a good solvent, and we seek to determine the ability of the IC approximation to describe such systems.

To apply the IC method to a polymer of N segments, first initialize $Z(r_{ij}) = e^{-\Phi(r_{ij})/kT}$ for every (i,j) pair, $1 \leq i, j \leq N$, where Φ is the total pair potential. Calculate the IC approximation

$$Z(r_{ij}) = e^{-\Phi(r_{ij})/kT} \prod_{\substack{1 \leq k \leq N \\ k \neq i,j}}{}' \int Z(r_{ik})\, Z(r_{kj})\, d\mathbf{r}_{ik}$$

for every pair (i,j) where Π' is a weighted geometric mean. Repeat the calculation until all $Z(r_{ij})$ are converged.

The Model

In the present study the rings are modeled as a perfectly flexible, closed sequence of hard-sphere, self-avoiding spherical segments of unit diameter. The configurational properties of the sequence are determined on the basis of the iterative convolution (IC) approximation which has been extensively described elsewhere.[3] The solvent, in those cases where one is present, is modeled as a hard-sphere Percus fluid also of unit diameter, present at a packing fraction $\eta = {}^1/_6\pi\rho\sigma^3$, where $\sigma = 1$ is the particle diameter and ρ is the number density of the solvent particles. As in previous analyses involving polymer chains immersed in a solvent,[3] we first determine the radial distribution $g_{(2)}(r)$ of pairs of particles in the system based upon the Percus–Yevick approximation, from which we may establish the potential of mean force $\psi(r) = -kT \ln g_{(2)}(r)$ which is taken to operate between ring segments in the presence of a solvent. This has been found to provide a working description of chains immersed in a solvent and has been described extensively elsewhere. This "effective interaction" between segments is then used in the IC approximation to establish the configurational properties of the ring— in particular, the normalized spatial probability distributions $Z(r_{ij})$ developed between a specified pair of ring segments, i,j, on the basis of which we are able to determine the probability of the transition $i \rightarrow j$. In Figure 2 we show a representative selection of the $Z(r_{i,i+15})$ distributions for rings of size $N = 30$ under various conditions of solvent packing. Since the probability of an exciton jump between chromophores is essentially range-dependent, it is immediately apparent that increasing solvent density collapses the ring, raising the probability of cross-ring transitions. It is important to appreciate that the Z-functions shown in Figure 2 do not represent instantaneous spatial distributions within the ring, but rather the configurationally averaged probability distributions with which a slow hopper is confronted. We draw attention to the progressively "structured" form of the Z-function as the solvent density is increased: this derives quite simply from the role of the surrounding solvent in determining the spatial distribution of ring segments and is a characteristic feature of previous IC calculations in which a substantial solvent contribution is introduced.

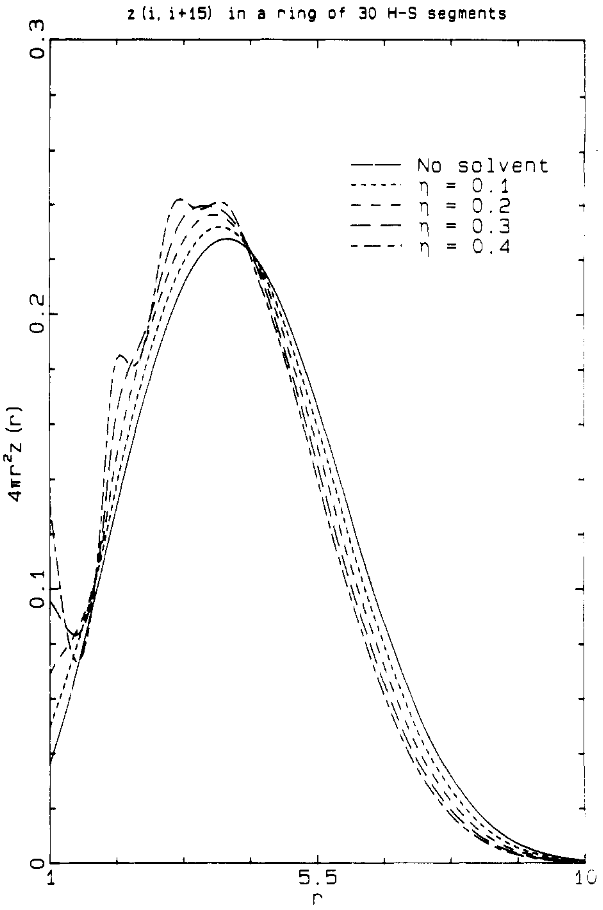

Figure 2. Spatial probability distribution $Z(r_{i,i+15})$ across ring of size $N = 30$ at various solvent packing fractions. Note how the short-range form of the Z-function depends sensitively upon the solvent density and that this effectively determines the probability of the hopping transition (eq 1).

Fast hoppers, of course, use ring configurations which also depend on the last previous transaction. In both cases the next transition is determined by a Monte Carlo process in which the probability of making the jump from i to j is

$$\int_{r_{ij}=1}^{r_{\text{jump}}} Z(r_{ij})\, d\mathbf{r}_{ij} \Big/ \sum_{k=1}^{N} \int_{r_{ik}=1}^{r_{\text{jump}}} Z(r_{ik})\, d\mathbf{r}_{ik} \qquad (1)$$

where $r_{\text{jump}} = 1.125$. In other words, the jump $i \rightarrow j$ is technically permissible between chromophores within the range $r_{\text{jump}} < (1.125)$—with a probability as established in eq 1. For fast hoppers, the configuration of the ring should remain unchanged between jumps. Because we are working with an average configuration, all we know is that if the last jump was from segment k to segment i we must have $r_{ki} \leq r_{\text{jump}}$. We model this by truncating $Z(r_{ki})$ (adding ∞ to $\Phi(r_{ki})$ for $r_{ki} > r_{\text{jump}}$ for this pair only) and repeating the IC calculation to obtain an average configuration for a ring subject to this extra constraint. We draw attention to the subtle dependence of the hopping probability, certainly for cross-ring transfers, upon solvent density and range of the hopper. It is apparent from the short-range form of the integrand in eq 1 that the relative magnitude of the probabilities may actually show a reversal with increasing solvent density if the range of the integral is such that the form of the integrands actually cross, as shown in Figure 2. This structure of the Z-functions derives essentially from the solvent structure and is not generally a feature of previous ring-hopping studies despite its obvious relevance.

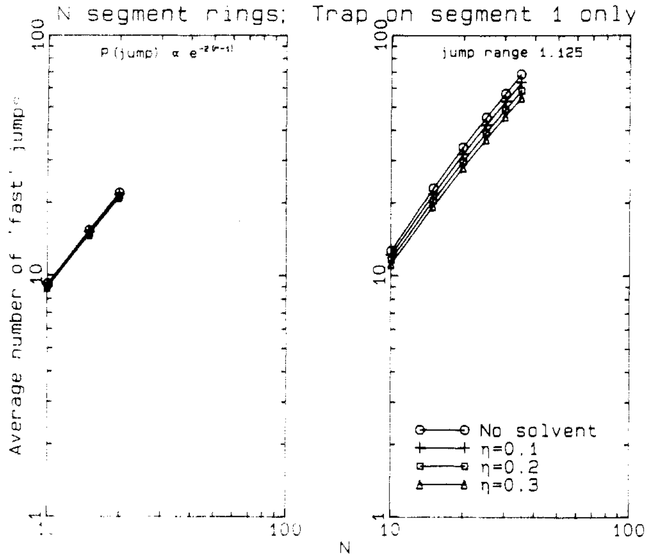

Figure 3. log-log plots of the average number of hops required to locate a single trap on rings of various sizes. A variety of solvent densities is investigated for two possible range criteria. The plots reveal the essentially exponential relationship between average number of jumps and ring size N, at least for the ring sizes investigated here.

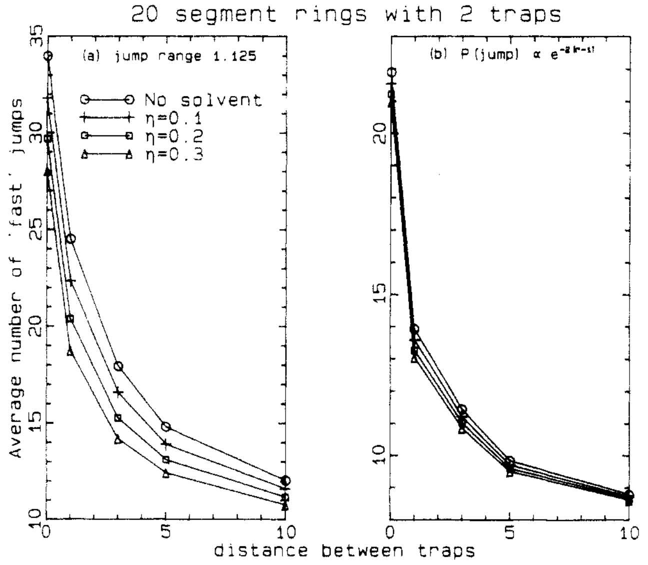

Figure 4. Average number of hops for a fast hopper for various trap separations, solvent densities, and hopping range.

An alternative proposal for the determination of the $i \rightarrow j$ jump probability is

$$\int_{r_{ij}=1}^{\infty} Z(r_{ij}) \exp(-c(r_{ij}-1))\,\mathrm{d}\mathbf{r}_{ij} \Big/ \sum_{k=1}^{N} \int_{r_{ik}=1}^{\infty} Z(r_{ik}) \times \exp(-c(r_{ik}-1))\,\mathrm{d}\mathbf{r}_{ik} \quad (2)$$

where c is an arbitrarily chosen constant. Time constraints associated with repeated configurational averaging restricted investigations of this jump criterion for the "fast" hopper to $N \leq 20$. For fast hoppers the equivalent of the restriction $r_{ki} \leq$ hopping range is to add $kTc(r_{ki} - 1)$ to the effective potential for the pair involved in the last transition. It is clear from the Z-functions shown in Figure 2 that the transition probability of excitons determined on the basis of eq 1 and 2, in which the short-range form of the Z-function is the determining factor, depends sensitively upon the nature of the surrounding solvent.

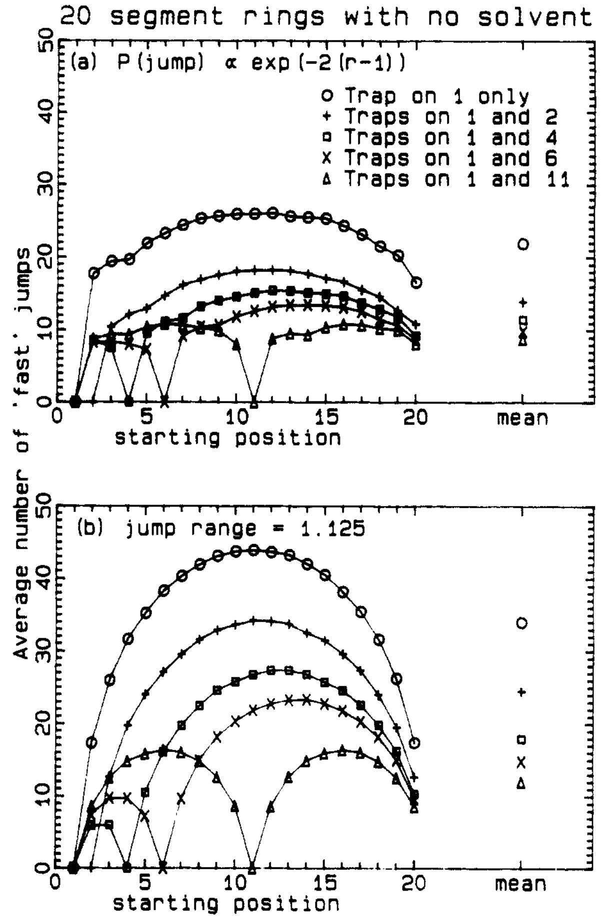

Figure 5. Average number of hops required for various two-trap locations on a ring $N = 20$ with no solvent.

Results

(a) Single Traps. As emphasized from the outset, our objective in this study is to establish the qualitative form of exciton diffusion around and across continuum single-trap ring polymers as a function of ring size and solvent density: we do not, for example, propose the determination of exponent relations appropriate to asymptotically large rings as $N \rightarrow \infty$. However, it is immediately apparent from Figure 3 that log-log plots of the average number of jumps versus ring size N suggests an exponential relationship between these two quantities, as found in previous Monte Carlo treatments.[4-6] Moreover, these conclusions appear to stand regardless of the range of the hopping criterion, whether a "fast" or "slow" hopper is studied, and the solvent conditions. As we would expect, there is a minor predisposition to smaller average numbers of jumps for collapsed rings occurring at high solvent densities. The similarity in the log-log plots for both fast and slow hoppers leads us to conclude that configurational adjustment of the ring in the course of exciton migration is not important, at least for the range of ring sizes investigated here. The effect of increasing solvent density, while minimal, nevertheless is, as expected, associated with collapse of the ring—that is, the number of cross-ring transitions increases with the average number of jumps required to locate the trap somewhat reduced.

These qualitative conclusions appear fully consistent with the cubic lattice-based ring studies of Janse van Rensberg and Whittington.

(b) Multiple Traps. The complexity arising from the introduction of multiple traps restricts our continuum investigations to a maximum of two traps only on each ring. With the traps in fixed positions, the calculations

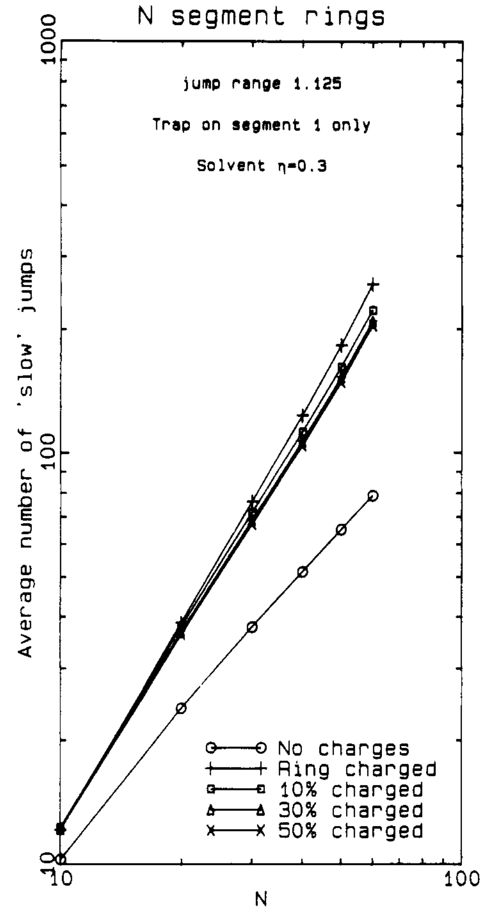

Figure 6. Effect of charge on ring and solvent at a solvent density of $\eta = 0.3$. We observe the charging of the ring has the primary effect, after which the percentage of solvent charge plays a relatively minor role.

have to be averaged over all possible starting positions of the exciton on the ring. The average number of jumps required for a fast hopper to locate one of the two traps is shown for various trap separations in Figure 4a,b on a ring of 20 segments. Again, the system seems relatively indifferent to the nature of the solvent but appears highly sensitive to the hopping range of the exciton. Similar conclusions apply in Figure 5a,b, where we show the average number of hops required by an exciton to locate one of the two traps, but in the absence of any solvent. The number of jumps required appears highly sensitive to the range of the exciton, and we conclude that this is the determining feature in exciton migration.

(c) Charged Rings. Finally, given the sensitivity of the migration of the exciton to ring size and shape, we investigate the effects of charge both on the ring and in the surrounding solvent. In the case of charged rings immersed in an uncharged hard-sphere solvent we would expect the ring to be expanded due to the electrostatic interaction within the ring. On the basis of a hopping probability which is highly range-dependent (eq 1), electrostatic charge on a ring substantially reduces the prospect of cross-ring transfers and restricts migration of the exciton to nearest neighbor transitions around the circumference of the ring. This is clearly shown in Figure 6, where the introduction of ring charge virtually doubles the number of jumps required for the exciton to dissipate in the single trap. This illustrates the importance of cross-ring transitions despite their minimal contribution assumed by other authors.[1] Of course, as the percentage of surrounding solvent is charged, so the ring charge is partially countered and the initial uncharged results are partially recovered, but the percentage of the solvent charged has a subordinate effect on the average number of jumps to the charging of the ring itself (Figure 6). The results presented here are for the relatively high solvent density of $\eta = 0.3$: lower solvent densities yield qualitatively similar results.

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