Bridge Hopping on Conducting Polymers in Solution

Daniel W. Hone\textsuperscript{1} and Henri Orland\textsuperscript{1,2}

\textsuperscript{1}Institute for Theoretical Physics, University of California at Santa Barbara, Santa Barbara, CA 93106

\textsuperscript{2}Service de Physique Théorique, CEA Saclay, 91191 Gif-sur-Yvette, France

(October 31, 2018)

Abstract

Configurational fluctuations of conducting polymers in solution can bring into proximity monomers which are distant from each other along the backbone. Electrons can hop between these monomers across the “bridges” so formed. We show how this can lead to (i) a collapse transition for metallic polymers, and (ii) to the observed dramatic efficiency of acceptor molecules for quenching fluorescence in semiconducting polymers.

71.20.Hk, 61.41.+e

Typeset using REVTeX
Conducting (conjugated) polymers have been of great interest because of their unusual electrical and optical properties, combined with mechanical features very different from those of metallic conductors [1]. In solution, where the polymers are flexible, the strong conformational fluctuations can modify both the structural and electronic properties [2,3,4,5,6,7], which in suitable cases may then be sensitively controlled by environmental parameters, such as the temperature. Theoretical studies have been limited largely to numerical methods. But in an earlier paper [7] we have demonstrated the applicability of functional integral methods to these systems, allowing analytic treatment up to very late stages of the calculation, with the usual attendant advantages, including the possibility of treating realistically long chains, which are inaccessible in practice to the numerical methods.

Here we concentrate on the effects of “bridge conduction”, the hopping of electrons between monomers distant from one another as measured along the polymer backbone, but close to each other in configuration space as a consequence of the bending of the dissolved polymer. This bridge conduction is believed to be one of the important mechanisms for electron transfer reactions which play a key role in several biological processes, such as photosynthesis and cell metabolism [8,9]. A similar phenomenon is expected for many chains in solution, between monomers on different chains which approach one another, particularly when they are stretched [10]. Bridge hopping was discussed briefly in a paper by Otto and Vilgis [11], but their results suffer from a critical neglect of the fermion statistics of the electrons.

We focus here on two characteristic consequences of bridge hopping. The first, for metallic polymers (partially filled bands) is the resultant effective attraction between remote monomers, and the consequent contribution to the tendency for collapse from a swollen state. That collapse has major consequences for the electronic and optical properties of the polymer. The second, for semiconducting polymers, results from the dramatically enhanced rate for locally excited carriers to reach remote parts of the chain, by way of the bridges. We show that this reasonably explains the observed ability of a single molecule to quench the fluorescence of a full chain of hundreds of monomers or more on time scales of picoseconds,
orders of magnitude shorter than the carrier diffusion time along the chain.

Because our goal is limited to exploring these impacts of bridge hopping, we have chosen the simplest possible model. We neglect completely the dependence of the electronic hopping along the chain on the local configuration, which dependence was, in fact, the focus of our earlier paper. We also take no explicit account of chain rigidity associated with the moduli of twisting or bending. Rather, we make the usual rescaling of the monomer unit to a Kuhn, or persistence, length, with the new effective units executing a random self-avoiding walk.

Consider a polymer chain on which a gas of electrons can hop. The polymer is supposed to be on a d-dimensional lattice with lattice parameter equal to the Kuhn length \( a \). Then the partition function is the sum over self-avoiding walks for the polymer of the square of an electronic partition function, \( Z_{el}(\{r_n\}) \) (to account for the spin of the electrons), where \( r_n \) describes the position of the \( n^{th} \) lattice site visited

\[
Z = \sum_{SAW} Z^2_{el}(\{r_n\})
\]  

(1)

The electronic partition function can be written as a functional integral over Fermionic (Grassmanian) fields [12]:

\[
Z_{el}(\{r_n\}) = \int_{c_n(\beta)=-c_n(0)} D(c^+_n(t), c_n(t)) \exp \left( -\int_0^\beta dt \sum_n c^+_n(t) (\partial_t - \mu) c_n(t) \right)
\]

\[
\times \exp \left( t_0 \sum_n \int_0^\beta dt (c^+_n(t)c_{n+1}(t) + h.c.) + t_1 \sum_{m,n} \int_0^\beta dt \Delta_{rr'} c^+_m(t)c_n(t) \right)
\]  

(2)

where \( t_0 \) is the hopping constant along the chain, \( t_1 \) is the hopping constant across a bridge, and the operator \( \Delta_{rr'} \) restricts sites \( r \) and \( r' \) to be nearest neighbors on the lattice. The antiperiodic boundary condition accounts for the Fermionic nature of the electrons. Integration over the Grassman variables yields the result:

\[
Z = \sum_{SAW} \exp \left[ 2\text{Tr} \log \left( \left( \partial_t - \mu \right) \delta_{mn} - t_0(\delta_{m,n+1} + \delta_{m,n-1}) - t_1 \Delta_{rmrn} \right) \right].
\]  

(3)

In terms of the Green’s function for the electrons along the chain,

\[
(\partial_t + H - \mu)G_0(m, t; n, t') = \delta_{mn}\delta(t - t'),
\]  

(4)
the partition function can be written as
\[ Z = z_0^2 \times \sum_{\text{SAW}} \exp \left[ 2 \text{Tr} \log \left( \delta_{mn}(t - t') - t_1 \sum_{n'} G_0(m, t; n', t') \Delta_{r_{n'r_n}} \right) \right], \] (5)
where \( z_0 \) is the partition function of the gas of electrons free to hop only along the chain (with hopping constant \( t_0 \)):
\[ z_0 = \exp \left( N \int_{-\pi}^{+\pi} \frac{dq}{2\pi} \log \left[ (1 + e^{\beta(\mu + 2t_0 \cos q)}) \right] \right). \] (6)

The chemical potential \( \mu \) is related to the filling fraction \( f \) through the identity:
\[ f = \int_{-\pi}^{+\pi} \frac{dq}{2\pi} \frac{1}{1 + e^{-\beta(\mu + 2t_0 \cos q)}}. \] (7)

Introducing the Fermionic Matsubara frequencies \( \omega_\nu = (2\nu + 1)\pi/\beta \) where \( \nu \in \mathbb{Z} \) is a relative integer, we can write the partition function as:
\[ Z = z_0^2 \times \sum_{\text{SAW}} \exp \left[ 2 \sum_{\nu \in \mathbb{Z}} \text{Tr} \log \left( \delta_{mn} - t_1 \sum_{n'} G_0(m, n', \omega_\nu) \Delta_{r_{n'r_n}} \right) \right] \] (8)

Since \( G_0 \) is the spatial Fourier transform of \( G_0(q, \omega) = 1/(i\omega - \mu - 2t_0 \cos q) \), we find by direct integration that
\[ G_0(m, n, \omega) = \frac{1}{2t_0} \frac{z_0^{m-n}}{\sqrt{\left( \frac{i\omega - \mu}{2t_0} \right)^2 - 1}}, \] (9)
\[ z_0 = \frac{i\omega - \mu}{2t_0} - \sqrt{\left( \frac{i\omega - \mu}{2t_0} \right)^2 - 1}. \] (10)

where the square root branch is chosen so that the modulus of \( z_0 \) is less than unity.

Once the Matsubara sums and the trace in the exponent of Eq. (8) are done, we are left with a purely configurational partition function with effective interactions between the monomers. In fact, one can see that there exist many-body interactions of all orders. However, if we assume the system not to be at too high a density, we can expect the two-body interactions to dominate. We can re-sum to all orders the 2-body interactions which arise in the effective configurational partition function. Expanding the exponent in Eq. (8) in powers of \( t_1 \) gives for each positive integer \( p \) a term

\[ \]
\[ \text{Tr} \left[ G_0 (m, n', \omega_\nu) \Delta_{r_{m'n'n}} \right]^p = \sum_{m_1} \sum_{m_2} G_0 (n_1, m_1, \omega_\nu) \Delta_{r_{m_1'n_1n}} G_0 (n_2, m_2, \omega_\nu) \Delta_{r_{m_2'n_2n}} \cdots G_0 (n_p, m_p, \omega_\nu) \Delta_{r_{m_{p-1}'n_pn_1}} \]  

(11)

The 2-body contribution comes from the sum of terms such that all pairs \( \{m_i, n_i\} \) involve the same two sites \( m \) and \( n \): \( \{m_i, n_i\} \) is either \( \{m, n\} \) or \( \{n, m\} \). That sum is just

\[ [G_0 (m, n, \omega_\nu) + G_0 (n, n, \omega_\nu)]^p + [G_0 (m, n, \omega_\nu) - G_0 (n, n, \omega_\nu)]^p \]

(12)

Re-summing over all \( p \), we find the exact 2-body interaction:

\[ \frac{Z}{z_0^2} \approx \sum_{\text{all walks}} \exp \left\{ -\frac{g}{2} \sum_{m \neq n} \delta(r_m - r_n) + \sum_{\nu = -\infty}^{+\infty} \sum_{m,n} \{\log [1 - t_1 (G_0 (m, n, \omega_\nu) + \gamma (\omega_\nu))] + \log [1 - t_1 (G_0 (m, n, \omega_\nu) - \gamma (\omega_\nu))]) \Delta_{r_{m'n'n}} \right\} \]

(13)

where \( \gamma (\omega) = G_0 (n, n, \omega) = \left[ 2t_0 \sqrt{(i\omega - \mu)^2 - 4} \right]^{-1} \) is the equal site Green’s function.

Introducing an effective interaction \( w \):

\[ w(m - n) = -2T \sum_{\nu = -\infty}^{+\infty} \log \left\{ \left[ 1 - t_1 (G_0 (m, n, \omega_\nu)) \right]^2 - t_1^2 \gamma^2 (\omega_\nu) \right\} \]

(14)

we can write the partition function as

\[ Z \approx z_0^2 \times \sum_{\text{all walks}} \exp \left( -\frac{g}{2} \sum_{m \neq n} \delta(r_m - r_n) - \frac{\beta}{2} \sum_{m,n} w(m - n) \Delta_{r_{m'n'n}} + \text{3-body terms} \right) \]

(15)

From Eq. (8) we see that \( G_0 (m, n, \omega) \) decays exponentially at large separation \( |m - n| \), so that the effective interaction \( w(n) \) tends to a finite constant:

\[ \lim_{n \to \infty} w(n) = -2T \sum_{\nu = -\infty}^{+\infty} \log \left( 1 - \frac{t_1^2}{(i\omega_\nu - \mu)^2 - 4t_0^2} \right) \]

(16)

This quantity turns out to be negative, and thus there is an overall attraction between distant monomers, due to lateral hopping of the electrons. To lowest non-vanishing order in \( t_1 \) we have

\[ \lim_{n \to \infty} w(n) = -\frac{t_1^2}{t_0} \frac{e^{-\beta \mu} \sinh 2 \beta t_0}{(1 + e^{-\beta (\mu + 2t_0)}) (1 + e^{-\beta (\mu - 2t_0)})} \]

(17)
As a consequence we may expect that, at low enough temperature, the chain will collapse to a globular state. Indeed, we know from numerical studies [14] that a self-avoiding polymer with attraction of strength $u$ between monomers which are nearest neighbors on the lattice undergoes a $\theta$-collapse transition at a temperature equal to $T_\theta \simeq 3.64u$. If the long distance part of the attraction $w(n)$, which is approximately constant, dominantly controls the collapse transition, as we might expect, then this second order transition should occur at a temperature given by $T_c = 3.64 |w(\infty)|$. In Fig. 1 we plot $T_c$ as a function of the bridge-hopping parameter $t_1$ for various filling fractions, within this approximation of constant $w(n)$.

At shorter distances along the chain, the behavior of $w(n)$ can be captured by expanding the expression (14) for the effective interaction to lowest order in $t_1$. We find

$$w(n) \approx -4t_1 \int_{-\pi}^{+\pi} \frac{dq}{2\pi} \frac{e^{iqn}}{1+e^{-\beta(\mu+2t_0 \cos q)}},$$

(18)

This can be calculated numerically, but it is instructive to look at its low temperature limit, $\beta t_0 \gg 1$, for which we have a simple analytic expression:

$$w(n) = -4t_1 \frac{\sin \pi fn}{\pi n}$$

(19)

where $f = 1 - \frac{1}{\pi} \text{Arccos} \left( \frac{\mu}{2t_0} \right)$ is the filling fraction of the electronic band. Therefore, the monomer interaction oscillates with separation, with wavevector proportional to the filling, and decays as the inverse separation along the chain. In Fig. 2 we plot $w(n)$ as a function of distance $n$ for several values of the bridge-hopping strength $t_1$ and two temperatures.

Due to these oscillations in $w(n)$ the interaction between monomers can be attractive or repulsive, depending on their distance along the chain, and on the filling fraction. This is an effect of the Pauli principle, and may induce the appearance of modulated and incommensurate phases. We note that this might preempt the collapse transition discussed above. The search for such exotic phases is underway and will be presented in a forthcoming publication.

The simplest method to study the system (at least qualitatively) with the full variation of
$w(n)$ along the chain is to make a virial expansion, which will converge rapidly at sufficiently low polymer density. A straightforward calculation to first order in the Mayer function yields:

$$
\frac{Z}{z_0^2 Z_0} = 1 + \sum_{m<n} \alpha_d \frac{(-1 + 2d(\exp(-\beta w(m-n)) - 1))}{(n-m)^{d/2}} + ..., \quad (20)
$$

where $\alpha_d$ is a constant of order unity. As can be seen from this equation, the interaction term is a balance between the hard-core term $-1$ and the effective interaction due to electron hopping. As was shown by Flory, a collapse transition occurs when the second virial term vanishes, that is

$$
\sum_{n=1}^{\infty} \frac{1}{n^{d/2}} \left\{ \prod_{\nu=-\infty}^{+\infty} \left[ 1 - t_1 (g(n, \omega_\nu) + \gamma (\omega_\nu)) \right]^2 \left[ 1 - t_1 (g(n, \omega_\nu) - \gamma (\omega_\nu)) \right]^2 - \frac{2d+1}{2d} \right\} = 0 \quad (21)
$$

where $g(n, \omega_\nu) = G_0(n, 0, \omega_\nu)$. The collapse temperature obtained in this way looks very similar to the results shown in Fig. 1, but the values are systematically higher by about 50%. This is expected in the sense that the low order virial expansion leaves out fluctuation effects and always overestimates critical temperatures.

The observed quenching [8], by localized acceptors, of the fluorescence from recombination of distantly created electron-hole pairs requires ultrafast electron transfer over those long distances (transit times small compared to the recombination times, of order picoseconds). The relevant long distance motion is described by the electron self-energy at small wavevectors (approximately good quantum numbers, since the disorder can be averaged on the long length scales of interest). In order to calculate this self-energy operator, we must proceed in the reverse order of the preceding section, namely first trace out the polymer degrees of freedom so as to obtain an effective electronic Hamiltonian. To lowest order in $t_1$ the system is in the swollen phase, and the relevant configurational ensemble is the set of self-avoiding walks. Then the effective action for the electrons in first order perturbation theory gives for the partition function,

$$
Z \approx Z_{SAW} \int_{c_n,\sigma} \mathcal{D}(c_{n,\sigma}^+(t), c_{n,\sigma}(t)) \exp \left(- \int_0^\beta dt \sum_{n,\sigma} c_{n,\sigma}^+(t) (\partial_t - \mu) c_{n,\sigma}(t) \right)
$$
\[
\times \exp \left( t_0 \sum_{n,\sigma} \int_0^\beta dt (c_{n,\sigma}^+(t) c_{n+1,\sigma}(t) + h.c.) + t_1 \sum_{m,n} \int_0^\beta dt \langle \Delta_{m,n} \rangle_{SAW} c_{m,\sigma}^+(t) c_{n,\sigma}(t) + O(t_1^2) \right) \tag{22}
\]

where \( \langle \Delta_{m,n} \rangle_{SAW} \) denotes the expectation value of the nearest-neighbor operator over self-avoiding walks. This is a standard quantity in polymer theory [15]. It is related to the probability distribution for the end of the chain through

\[
\langle \Delta_{m,n} \rangle_{SAW} = P(r = a, m - n) \sim \frac{A_d}{|m - n|^{\nu d + \gamma - 1}}, \tag{23}
\]

where \( \nu \approx 3/5 \) (in \( d = 3 \)) is the wandering exponent of a self-avoiding walk, \( \gamma \approx 7/6 \) is the susceptibility exponent and \( A_d \) is a non-universal constant of order unity. Note that this expression is valid for \( |m - n| \to \infty \). Since this calculation is done to first order in \( t_1 \), it does not describe the collapsed phase, so that if we were interested in the diffusion properties in the globular phase discussed in the previous section, we would have to take averages in that phase. The self-energy of the chain is given by

\[
\Sigma(q) \approx -2t_0 \cos q - 2t_1 A_d \sum_{n=3}^\infty \frac{\cos(qn)}{n^{\nu d + \gamma - 1}} \\
\sim B_d + 2t_1 A_d C_d q^{\nu d + \gamma - 2} + t_0 q^2 \tag{24}
\]

where \( B_d \) is a constant which produces a shift in the chemical potential of the electrons, and \( C_d \) is given by

\[
C_d = \int_0^\infty du \frac{1 - \cos u}{u^{\nu d + \gamma - 1}} \approx 1.58 \text{ in } 3d
\]

We see that in 3d, the motion of the electrons is super-diffusive, with a self-energy which behaves as \( \Sigma(q) \sim q^{29/30} \) for small \( q \). As a result, the Einstein law is modified and is replaced by

\[
R \sim (t_1 t)^{30/29} \tag{26}
\]

where \( R \) is the radius of the region in which the electrons diffuse during the time \( t \). For the times of interest in the fluorescence quenching problem, of order a picosecond, and for bridge hopping energies of order 0.1 eV this suggests distances of order a few hundred Kuhn lengths, enough to explain the observed quenching amplification. The only other proposed
mechanism of which we are aware is intrachain Forster transfer, dipolar communication from
the created exciton to the chain region near the quenching center, but we do not know of
a quantitative estimate of the effectiveness of that mechanism. Our estimates of the bridge
hopping contribution suggest that, if this is dominant, the quenching efficiency should drop
off rapidly for chains an order of magnitude longer, say, than those of about 1000 monomers
which have been observed to date; we hope such experiments will be undertaken.

We are grateful to Thomas Garel, Alan Heeger and André-Marie Tremblay for helpful
conversations. This work was supported in part by the National Science Foundation Grant
PHY99-07949.
REFERENCES

[1] Conjugated polymers: the novel science and technology of highly conducting and non-linear optically active materials, eds. J.L. Brédas and R. Silbey, (Kluwer Academic Publishers, Dordrecht, 1991).

[2] K. C. Lim and A. J. Heeger, J. Chem. Phys. 82, 522 (1985).

[3] O. Inganas, W. R. Salaneck, J. E. Osterholm and J. Laakso, Synth. Met. 22, 395 (1988).

[4] G. Rossi and A. Viallat, Phys. Rev. B 40, 10036 (1989); J. Chem. Phys., 92, 4548, 1990; J. Chem. Phys. 92, 4557 (1990).

[5] R. Tubino, R. Dorsinville, W. Lam, R. R. Alfano, J. L. Birman, A. Bolognesi, S. Destari, M. Catellani and W. Porzio Phys. Rev. B 30, 6601 (1984).

[6] D.W. Hone, P.A. Pincus, C. Singh and G. Rossi, Synth. Met. 41-43, 3419 (1991).

[7] D.W. Hone and H. Orland, J. Chem. Phys. 108, 8725 (1998).

[8] L. Chen, D.W. McBranch, H-L Wang, R. Helgeson, F. Wudl and D.G. Whitten, Proc. Nat. Acad. Sci. 96, 12287 (1999).

[9] I. Bertini, H.B. Gray, S. Lippard and J. Valentine, Bioinorganic Chemistry (University Science Books, Mill Valley, CA, 1994).

[10] D.N. Beraran, J.N. Betts and J.N. Onuchic, Science 252, 1285 (1991).

V.S. Pande and J.N. Onuchic, Phys. Rev. Lett. 78, 146 (1997)

[11] D.S. Pearson, P.A. Pincus, G.W. Heffner, S.J. Dahman, Macromolecules 26, 1570 (1993).

[12] J.W. Negele and H. Orland Quantum Many-Particle Systems (Addison-Wesley, Redwood City, 1988).

[13] M. Otto and T.A. Vilgis, Phys. Rev. B 50, 13228 (1994).
[14] H. Meirovitch and H.A. Lim, J. Chem. Phys., 92, 5144 (1990)

[15] P-G de Gennes, Scaling Concepts in Polymer Physics (Cornell, Ithaca, 1979).
FIGURES

FIG. 1. The collapse temperature $T_c$ as a function of the bridge hopping rate $t_1$ for half filling, $f = 0.5$ (solid line) and for $f = 0.2$ (dashed line).

FIG. 2. The effective interaction $w(n)$ for half filling, $f = 0.5$ (solid line) and for $f = 0.2$ (dashed line). The temperature is taken to be $T = 0.1$, and $t_1 = 0.1$. 
