POLARONS AS
NUCLEATION DROPLETS IN NON-DEGENERATE POLYMERS

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Abstract

We present a study of the nucleation mechanism that allows the decay of the metastable phase (trans-cisoid) to the stable phase (cis-transoid) in quasi one-dimensional non-degenerate polymers within the continuum electron-phonon model. The electron-phonon configurations that lead to the decay, i.e. the critical droplets (or transition state), are identified as polarons of the metastable phase. We obtain an estimate for the decay rate via thermal activation within a range of parameters consistent with experimental values for the gap of the cis-configuration. It is pointed out that, upon doping, the activation barriers of the excited states are quite smaller and the decay rate is greatly enhanced. Typical activation energies for electron or hole polarons are \( \approx 0.1 \) eV and the typical size for a critical droplet (polaron) is about
20\AA. Decay via quantum nucleation is also studied and it is found that the
crossover temperature between quantum nucleation and thermal activation is
of order $T_c \leq 40^oK$. Metastable configurations of non-degenerate polymers
may provide examples for mesoscopic quantum tunneling.

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I. INTRODUCTION AND MOTIVATION

Quasi-one dimensional conductors provide a fascinating wealth of physical phenomena that stimulated considerable theoretical and experimental study of these systems. The proposal [1] that solitons play a central role in the electronic and transport properties of the degenerate polymer \textit{trans}-\((CH)_x\) polyacetylene was later confirmed with measurements of the optical absorption in the doped system [2,3]. Non-topological excitations corresponding to local lattice deformations that bind electron states, i.e. polarons, had also been recognized in these degenerate polymers [4,5].

Although the presence of topological solitons is associated with the ground state degeneracy of \textit{trans}-polyacetylene, polarons are not a consequence of this degeneracy and are predicted to occur upon doping also in non-degenerate isomers [5].

Non-degenerate isomers like \textit{cis}-\((CH)_x\) were studied [5] by using a continuum electron-phonon model [6]. These non-degenerate isomers feature a globally stable (lower energy) configuration (cis-transoid) and a locally stable but globally metastable (higher energy) configuration (trans-cisoid).

The properties of the polaron excitations of the stable (cis) phase were thoroughly studied within the continuum electron-phonon model and show the property of “confinement”, that is their energy grows linearly with the spatial size of the lattice distortion [5,8,10]. Because of the lack of degeneracy, there are no stable topological soliton excitations in this case.

The motivation for our study is to understand the mechanism by which the metastable configuration (trans-cisoid) decays into the stable phase (cis-transoid). In particular, we identify the electron-phonon configurations that mediate the nucleation process as polarons of the \textit{metastable phase}. These polaron configurations are the equivalent of nucleation droplets, they correspond to saddle-points of the energy functional and the critical droplets (critical radius of the polarons) are identified with the transition state. The “radius” of the polaron (droplet) is identified as the reaction coordinate and eventually quantized as a collective coordinate.
Once these configurations are identified, we estimate the activation barriers and the decay rates via thermal activation and investigate the possibility that the metastable phase decays via quantum tunneling (quantum nucleation) at very low temperatures. Upon quantization of the relevant collective coordinates that describe the droplet-polaron, we provide a WKB estimate for the rate of quantum nucleation. Understanding the relevant electron-phonon configurations that mediate the metastable decay allows us to provide an estimate for the crossover temperature between quantum nucleation and thermal activation.

Despite a very large body of theoretical and experimental work on quasi-one dimensional conductors both degenerate and non-degenerate, there has not been a consistent study of the fundamental aspects of the decay of the metastable phase.

A particularly interesting and tantalizing possibility that we explore in this article is that the decay of the metastable phase may provide an example of mesoscopic quantum tunneling.

The article is organized as follows: section II reviews the continuum model for non-degenerate polymers. In section III we study the constant dimerization configuration and establish the range of dimerization values available, scanning through values of the intrinsic dimerization consistent with experimental values of the gap in the stable (cis) phase. The energy and dimerization values obtained in this section are used to obtain the polaron excitations of the metastable phase. Section IV is devoted to the study of the electron-phonon configurations that mediate the nucleation. We construct the polaron solutions of the metastable phase; these are nucleating droplets, whose energy as a function of the “radius” of the droplet, which is identified as the “reaction coordinate”, has a barrier and is thus identified with a saddle point in function space. The dependence of the energy and activation barriers upon doping (occupation of electron bound states) is analyzed in detail. In section V we quantize the droplet configuration via collective coordinates, obtain an estimate for the decay rate via thermal activation and discuss the possibility of decay induced by doping (electrons or holes). In section VI we study the decay of the metastable phase via quantum tunneling using a WKB approximation for the collective coordinates.
of the polaron. We estimate the crossover temperature between thermal activation and quantum nucleation. Section VII summarizes our results and presents our conclusions and speculations.

II. THE MODEL HAMILTONIAN

The *cis-transoid* isomer has a slightly lower energy than the *trans-cisoid* isomer which is metastable. Because of the slightly different energy of the two configurations, there is an ‘intrinsic’ dimerization that explicitly breaks the degeneracy between the ground state configurations. As a result of this explicit symmetry breaking, kink excitations are not available.

We consider the generalization of the SSH [1] model Hamiltonian that includes the non-degenerate case. The discrete version of the electron-phonon Hamiltonian has been introduced and discussed by Wang, Su and Martino [8], Kivelson [9] and Lu [10] and is given by (here we assume the simpler case of a unique elastic constant for the lattice distortion)

\[
H = \sum_{n,s} \left\{ \left[ t_1 - \alpha_1 (U_{2n-1} - U_{2n}) (C_{2n,s}^\dagger C_{2n-1,s} + h.c.) + \left[ t_2 - \alpha_2 (U_{2n} - U_{2n+1}) (C_{2n+1,s}^\dagger C_{2n,s} + h.c.) \right]\right] + \sum_n \frac{K}{2} (U_{2n+1} - U_{2n})^2 + \frac{M}{2} \dot{U}_n^2 \right\} (2.1)
\]

It proves convenient to introduce the parameters

\[
t_o = (t_1 + t_2)/2 \quad \alpha_o = (\alpha_1 + \alpha_2)/2 \quad (2.2)
\]

\[
\Delta_e = (t_1 - t_2) \quad \Delta \alpha = (\alpha_1 - \alpha_2) \quad (2.3)
\]

for the case \( \Delta t = 0; \Delta \alpha = 0 \) one recovers the original SSH Hamiltonian for *trans-transoid*, which is the degenerate isomer. Following the steps that led to the continuum version of the SSH model, as described by Takayama, Lin-Liu and Maki [4], one is led to the continuum version suggested by Brazovskii and Kirova [5]. As usual, since only electron states near the Fermi surface are important and the relevant phonon processes leading to the Peierls
instability involve momenta of the order $2k_F$, the Fermi spectrum is linearized near the two Fermi points, leading to a spinor description (left and right branches). The lattice displacement is written as

$$U_n = (-1)^n \left( \frac{\Delta(x)}{4\alpha_o} \right)$$

(2.4)

where the ‘gap parameter’ $\Delta(x)$ is a slowly varying function (on the scale of a lattice spacing).

The continuum Hamiltonian, as derived by Brazovskii and Kirova [5], becomes

$$H = \int dx \left\{ \frac{M}{32\alpha_o^2 a} \dot{\Delta}^2(x) + \frac{K}{8\alpha_o^2 a} \Delta^2(x) + \sum_s \left( \Psi_s^\dagger(x) \left[ (-i)v_F + \frac{a\Delta\alpha}{2\alpha_o} \Delta(x) \right] \sigma_3 \frac{\partial}{\partial x} + (\Delta(x) + \Delta_e) \sigma_1 \right) \Psi_s(x) \right\}$$

(2.5)

$$v_F = 2t_o a$$

(2.6)

where $a$ is the lattice spacing $a \approx 1.22 \text{Å}$, $\sigma_i$ are the Pauli matrices and $\Psi(x)$ is a spinor.

The label $s = 1, 2$ corresponds to the two spin projections and plays a passive role.

For slowly varying $\Delta(x)$ (on the scale of a lattice spacing) and small $\Delta\alpha$, the term proportional to $\Delta\alpha$ is a small renormalization of the Fermi velocity and of the same order as terms that have been neglected in the derivative expansion leading to the continuum limit. Thus, following the arguments presented by Lu [10], we will neglect this term. The Hamiltonian obtained is the same as that considered by Fesser, Bishop and Campbell [7] as a model for cis – (CH)$_x$.

Introducing the dimensionless electron-phonon coupling constant $\lambda$ and the bare phonon frequency $\omega_Q$ as

$$\frac{K}{8\alpha_o^2 a} = \frac{1}{\pi v_F \lambda} ; \quad \omega_Q^2 = \frac{4K}{M}$$

(2.7)

the model Hamiltonian for the non-degenerate isomer becomes

$$H = \int dx \left\{ \frac{\dot{\Delta}^2(x)}{\omega_Q^2 \pi v_F \lambda} + \frac{\Delta^2(x)}{\pi v_F \lambda} + \sum_s \Psi_s^\dagger(x) \left[ (-i)v_F \sigma_3 \frac{\partial}{\partial x} + (\Delta(x) + \Delta_e) \sigma_1 \right] \Psi_s(x) \right\}$$

(2.8)
We will concentrate, for the moment, on static configurations. Following Wang, Su and Martino [8] and Lu [10] we will assume the same value of the parameters as for the 
trans\((CH)_x\) degenerate case as proposed by Su, Schrieffer and Heeger [1]

\[ a = 1.22\text{Å} \quad ; \quad t_o = 2.5eV \]  
\[ \alpha_o = 4.1\frac{eV}{A} \quad ; \quad K = 21\frac{eV}{A^2} \]

leading to the following values of electron-phonon coupling \(\lambda\), band-width \(W\), Fermi velocity \(v_F\) and phonon frequency \(\omega_Q\)

\[ \lambda = 0.4077 \quad ; \quad W = 4t_o = 10 \text{ eV} \quad ; \quad v_F = 2t_oa = 6.10 \text{ eV} \text{Å} \quad ; \quad \omega_Q \approx 0.14 \text{ eV} \]  

in units in which \(\hbar = 1\). Since values of the intrinsic dimerization are not experimentally available (see discussions in [8,10]) we will search for a range of values for \(\Delta_e\) such as to reproduce the value for the energy gap for cis\((CH)_x\) (which is the lower energy stable ground state configuration); this value is approximately 2.05 eV [8,10].

### III. CONSTANT DIMERIZATION

The constant dimerization case corresponds to assuming \(\Delta(x) = \Delta_o\) (a space independent value). The fermions have a constant “mass” given by

\[ M_f = \Delta_o + \Delta_e \]

In the Born-Oppenheimer approximation, the electronic energy is given by the energy of the completely filled valence band when the fermions have the above “mass”

\[ E_F = -2\frac{L}{2\pi} \int_{-k_c}^{k_c} dk \sqrt{k^2v_F^2 + M_f^2} \]

with \(k_c\), the momentum cutoff, related to the band-width \(W\) as

\[ W \approx 2k_cv_F \]

Incorporating the elastic energy, we obtain the energy per site
\[
\frac{E}{N} = \frac{a}{\pi v_F} \left[ \frac{\Delta^2_o}{\lambda} - 2 \int_0^{W/2} dz \sqrt{z^2 + M_f^2} \right]
\] (3.3)

The extrema of this energy function are determined by the “gap equation”

\[
\frac{\Delta^2_o}{\lambda} = \int_0^{W/2} dz \frac{M_f}{\sqrt{z^2 + M_f^2}}
\] (3.4)

For the values of the parameters given by Su, Schrieffer and Heeger for the degenerate case (trans), we show in Figure (1) the energy per site (in eV) as a function of \(\Delta_o\) (in eV) for the representative value \(\Delta_e = 0.02\) eV. As the value of \(\Delta_e\) is increased, the stable minimum becomes deeper and the metastable minimum becomes shallower and closer to the origin. When \(\Delta_e \geq 0.07\) (eV) the metastable minimum disappears altogether. Numerically, the optimum range of \(\Delta_e\) that predicts a gap for the continuum theory with approximately the same error as the continuum theory prediction for the degenerate case, with the SSH values for the parameters (about 10 %) [12], is \(0.02 \leq \Delta_e \leq 0.07\). In this range we find:

| \(\Delta_e (eV)\) | \(\Delta_o^- (eV)\) | \(\Delta_o^+ (eV)\) | \(\frac{E_o^-}{N} (eV)\) | \(\frac{E_o^+}{N} (eV)\) |
|-------------------|-------------------|-------------------|-------------------|-------------------|
| 0.02              | -0.835            | -1.610            | 0.896             | -1.621            |
| 0.04              | -0.800            | -1.604            | 0.923             | -1.626            |
| 0.06              | -0.760            | -1.596            | 0.947             | -1.632            |

(3.5)

Where \(\Delta_o^\pm\) correspond to the values of \(\Delta_o\) at the metastable (-) and stable (+) minima with energy per site \(E_o^\pm/N\) respectively.

Thus, the value of the gap predicted from the global minimum \(2\Delta_o^+\) for the stable configuration is fairly close to the observed gap 2.05 eV for the lower energy cis - (CH)\(_x\) configuration (again the discrepancy is of the same order as the discrepancy between the gap predicted by the continuum model and the observed value in the degenerate case (trans), with the value of the parameters chosen by SSH [12]). For values of \(0.02\) (eV) \(\leq \Delta_e \leq 0.07\) (eV) curves very similar to figure (1) are obtained for the energy per site.
IV. POLARON SOLUTIONS

The non-degenerate case does not permit soliton (kink) type excitations (except if a very special theoretical possibility is fulfilled [13]), but allows the possibility of polaron (bag) excitations. Polars are topologically trivial electron-phonon field configurations that correspond to distortions of the lattice in which there are trapped electrons (bound states). Because of charge conjugation symmetry, bound states must appear symmetrically with respect to the middle of the gap.

For polaron solutions, the phonon field profile reaches asymptotically the values of the minima of the effective energy for the constant dimerization case, that is the minima in figure 1. The polaron solutions corresponding to the global (stable) minimum, had already been studied in references (12,14,15), these solutions reach $\Delta_o^+$ asymptotically when $|x| \to \infty$. These solutions are parametrized by two collective coordinates: the center of mass of the polaron (position), associated with translational invariance, and the radius. For the polaron solutions in the stable (lower energy) phase, the polaron energy is a linearly increasing function of the radius, for large radius. These polarons are “confined”. The reason is simple: for large radius, the polaron is exploring a region in function space that is very close to the higher (metastable) minimum, thus increasing the “volume” energy as a linear function of the radius.

In this article, we are interested in the polaron configurations in the metastable phase. We argue that these are the relevant electron-phonon configurations responsible for the decay of the metastable state.

The argument is as follows: let us assume that a polaron solution exists in the metastable phase. This configuration will reach the values of the metastable minimum for the constant dimerization case ($\Delta_o^-$) asymptotically as $|x| \to \infty$. Its profile again will be that of a “bag”, inside which the field configuration will sample the lower energy minimum in a region in space given by the radius of the polaron. However, the stable minimum has lower energy and the system gains volume energy by increasing the radius. There is a price in elastic energy
determined by the gradients of the field configuration, but in one dimension this “surface energy” is independent of the radius for large radius and bound by a value close to twice the mass of the kink-antikink pair that is the asymptotic state of the polaron for infinite radius. For small radius, the elastic term wins out and the energy is an increasing function of the radius; for large radius, the elastic energy will saturate and the volume energy will dominate; in this case the energy is a decreasing function of the radius. Thus, if a polaron solution exists with asymptotic values for the dimerization in the metastable phase, there must be a critical radius. This configuration is equivalent to the critical “droplet” configuration that Langer introduced to explain the statistical decay of a metastable state in first order phase transitions \[17\] and the “radius” of the droplet is identified with the reaction coordinate.

We will argue below that these polaron configurations will be saddle points of the energy functionals as they will be characterized by an unstable mode, a zero mode and fluctuations with positive frequencies.

To actually construct the polaron configurations, we could invoke the large body of work on the exact integrability of the continuum theory \[5,10,11,13–15\], but we prefer to go through some of the details of the calculation, as there are some subtle but important features that must be addressed.

Borrowing from the known results for the degenerate case \[11\] and for the stable minimum \[5,7,10\] (cis) we propose the static polaron solution as

\[
\Delta_p(x; x_{cm}; x_o) = \Delta_o - K_o v_f \left\{ \tanh \left[ K_o (x - x_{cm} + x_o) \right] - \tanh \left[ K_o (x - x_{cm} - x_o) \right] \right\} \quad (4.1)
\]

The fermionic potential becomes reflectionless for the integrability condition \[11,13–15\]

\[
\tanh \left[ 2 K_o x_o \right] = \frac{K_o v_f}{M_f} \quad (4.2)
\]

\[
M_f = \Delta_o + \Delta_e \quad (4.3)
\]

In the expressions above, \( \Delta_o \) can be either one of the minima of the energy functional for the constant dimerization case, i.e., \( \Delta_o \pm \).

Thus, the polaron profile is parametrized in terms of \( x_o \) and \( x_{cm} \), the “center of mass”; later we will treat these as “collective coordinates”. The “radius” of the polaron is \( 2|x_o| \). The
center of mass coordinate \( x_{\text{cm}} \) reflects the underlying translational invariance, the energy is independent of this coordinate.

Before proceeding further to the computation of the polaron energy, it proves illuminating to understand some features of the polaron solution and the integrability condition: i) the polaron solution (and consequently the electronic spectrum) is an even function of \( K_o \). We choose \( K_o > 0 \); ii) for a given \( x_o \), the integrability condition (4.2) determines \( K_o \); this condition also determines that the sign of \( x_o \) is given by the sign of \( M_f \). This is an important point. The stable minimum (\( \Delta_o^+ \)) always corresponds to \( M_f > 0 \), and consequently \( x_o > 0 \). The polaron of the stable phase decreases the value of the local dimerization in the region of the lattice distortion, thus sampling a region of higher energy density (trans). When \( x_o \) becomes large the energy will grow linearly with \( x_o \). This is the “confining” mechanism in the stable phase.

Now consider the case in which \( \Delta_o \) is the value at the metastable minimum (\( \Delta_o^- \)). In this case \( M_f < 0 \) and consequently \( x_o < 0 \). The polaron in this phase increases the value of the local dimerization in the distortion region, thus sampling regions with lower energy density. Thus for large \( |x_o| \) the energy will decrease linearly with \( |x_o| \) and it becomes favorable for the system to produce large polarons. But, clearly, there will be an energy barrier to do so because, for small radius, the elastic energy will gain as will be shown below.

iii) The integrability condition (4.2) yields non-trivial solutions for \( K_o \) only when \( 2|x_o| > v_f/|M_f| \).

For \( 2|x_o| < v_f/|M_f| \) there is no polaron solution and the only available solution is that for constant dimerization. The physical reason for this is that \( v_f/|M_f| \) is the Compton wavelength of the fermions, and there cannot be bound states localized within a region in space smaller than the Compton wavelength.

In the other limit when \( |x_o| \to \infty, K_o \to |M_f|/v_f \), the electronic bound states (see below) merge at the middle of the gap (zero energy). In this case, the polaron looks like a widely separated kink-antikink pair, each with a localized fermionic zero mode; the two bound states correspond to the symmetric and antisymmetric combinations of the fermionic “zero mode”
wave functions, split-off in energy because of the (small) overlap of their wave-functions.

It remains to compute the energy of the polaron. There are two contributions: the elastic contribution from the term $\Delta^2(x)$ in the Hamiltonian, and the electronic energy. Due to the reflectionless nature of the potential, the electronic spectrum is known exactly \cite{5,11}: there are two electron bound states at energies $\pm \omega_o = \pm \sqrt{M_f^2 - K_o^2 v_f^2}$ (the wave functions of these bound states are localized at $x_{cm} \pm x_o$) and the conduction and valence continuum states with dispersion $E_c = \pm \sqrt{k^2 v_f^2 + M_f^2}$. The valence and conduction bands are both depleted by one state per spin degree of freedom, the scattering phase shifts of the valence band states are \cite{11}

$$\delta(k) = 2 \tan^{-1} \left[ \frac{K_o}{k} \right]$$ (4.4)

The form of the bound states and continuum electronic wave functions has been given exactly by Campbell and Bishop \cite{11} for the polarons in the *degenerate case*. Their results can be applied vis a vis to our case because they are properties of the electronic “Dirac” equation in the presence of a spatially varying background configuration whose profile is the same as in the degenerate case. The reader is referred to those articles for more details.

The difference in energies between the polaron and the constant dimerization case is written as

$$\delta E = \delta E_l + \delta E_{el}$$ (4.5)

$$\delta E_l = \frac{1}{\pi v_f \lambda} \int dx \{ \Delta^2_p(x; x_{cm} ; x_o) - \Delta^2_o \}$$ (4.6)

$$\delta E_{el} = (n^+ - n^-) \omega_o - 2 \sum_k [\omega^p(k) - \omega^o(k)]$$ (4.7)

where we have assumed that the positive and negative energy bound states are occupied with $n^+$, $n^-$ electrons, respectively ($n^\pm = 0, 1, 2$), the factor 2 accounts for the two spin projections and $\omega^{p,o}$ are the energies of the states in the valence band, with and without the polaron, respectively. We find

$$\delta E_l = \frac{8 \Delta_1 K_o x_o - 4 K_o v_f}{\pi \lambda}$$ (4.8)
\[
\delta E_{el} = (n^+ - n^-)\omega_o + \frac{4}{\pi} K_o v_f + \frac{4}{\pi} K_o v_f \left( \frac{\Delta_o}{\lambda M_f} \right)
+ \frac{4}{\pi} \omega_o \left( \frac{\pi}{2} - \tan^{-1} \left[ \frac{K_o v_f}{\omega_o} \right] \right) \tag{4.9}
\]

The first term in (4.8) has the important physics that we were looking for. Whereas the rest of the terms in (4.8,4.9) reach a constant value when \(|x_o| \to \infty\), it is this first term that dominates the contribution to the energy in this limit.

As argued above, for the polaron in the metastable state \(x_o < 0\), whereas for the polaron in the stable state \(x_o > 0\). Thus, in the metastable state, as the size of the polaron becomes large, the energy becomes large and negative, linearly with the size. In the stable state it becomes large and positive linearly (this is the confining mechanism found in [5,7,10]).

To compare the energy in the metastable state with the results quoted in the literature for the stable case, it proves convenient to introduce the variables \(\theta\) and \(\gamma\) as

\[
K_o v_f = |M_f| \sin(\theta) ; \quad \omega_o = |M_f| \cos(\theta) ; \quad 0 \leq \theta \leq \frac{\pi}{2} \tag{4.10}
\]

\[
\gamma = \frac{\Delta_o}{\lambda M_f} \tag{4.11}
\]

Finally, the energy difference in terms of these variables is given by

\[
\delta E = \frac{4}{\pi} |M_f| \left\{ \gamma \tanh^{-1} \left[ \sin(\theta) \right] + \sin(\theta) - \gamma \sin(\theta) + \frac{\pi}{4} (n^+ - n^-) \cos(\theta) + \cos(\theta) \left( \frac{\pi}{2} - \theta \right) \right\} \tag{4.12}
\]

It is important to recognize that, for the minimum at the metastable state, \(\gamma < 0\).

This expression is similar in form to the one found in references ([5,7,10,15]) with the only difference being the subtleties associated with the signs for the metastable case.

To contrast the polaron solutions in the metastable state to those in the stable state, let us look at the extremum condition obtained from the energy function(4.12). The integrability condition (4.2) relates \(K_o\) (and \(\omega_o\)) and phase shifts to \(x_o\). The value of \(x_o\) is obtained from the extremization condition of the energy. Because \(x_o\) is a monotonically increasing function of \(\theta\) in the interval \(0 \leq \theta \leq \pi/2\), it proves more convenient to extremize with respect to \(\theta\). We obtain the equation
\[ \theta - |\gamma| \tan(\theta) = \frac{\pi}{4}(n_+ - n_- + 2). \quad (4.13) \]

For \(|\gamma| > 1\) the only solution is the trivial one, \(\theta = 0\), however this value of \(|\gamma|\) is not within the allowed range of parameters that describe a metastable situation. For \(|\gamma| < 1\) there are several interesting possibilities:

i) for \((n_+ - n_-) = -2\) there are always two solutions, one corresponding to the trivial case \(\theta = 0\) and another non-trivial solution. This is in marked contrast with the stable situation for which, at these values of the occupation for the bound states, there is only the trivial solution. Thus, in the metastable case there is always a polaron solution for the ground state configuration \(n_+ = 0, n_- = -2\). Because the energy difference between the constant dimerization and the spatially varying case vanishes at \(\theta = 0\) and grows linearly with negative slope for large \(|x_o| (\theta \to \pi/2)\), this polaron solution corresponds to a maximum of (4.12) as will be shown explicitly below.

ii) When \(n_+ - n_- + 2 > 0\) non-trivial solutions are available for a particular range of parameters and will be studied numerically below. However, we find that whenever non-trivial solutions are available, they always appear in pairs. A similar analysis as presented above reveals that the solution with the smallest value of \(\theta\) corresponds to a minimum and the largest to a maximum of (4.12). These solutions correspond to polaron-like configurations in which a lattice distortion traps electrons in positive and negative energy bound states and are the analog of the polaron solutions found in references ([5,7,10]) for the stable configuration.

Figures (2.a,b,c) show the energy as a function of \(r_o = M_f x_o/v_f\) for \(n_+ - n_- = -2; -1; 0\) for \(\lambda = 0.4077, \Delta_e = 0.02\ eV\). For \(n_+ - n_- = 0\), there is no minimum or maximum, i.e. there are no solutions to the extremum equation (4.13); we will refer to this case as the “dissociation curve”, for reasons that will become clear later. Similar curves are obtained for \(\Delta_e = 0.04\ eV\), where again there are polaronic solutions only for \(n_+ - n_- = -2; -1\) and dissociation curves for \(n_+ - n_- \geq 0\). For \(\Delta_e = 0.06\ eV\) only for the ground state configuration \(n_+ - n_- = -2\) there is an extremum “polaron” solution corresponding to a
maximum of the energy, for all other values of \( n_+ - n_- \) we find dissociation curves without extrema. From the figures, one finds that in all cases the typical size of the polaron solutions is \( 2|x_o| \approx 20 - 40 \text{Å} \).

V. DECAY OF THE METASTABLE STATE: THERMAL ACTIVATION

We are now in condition to study the mechanism that leads to the decay of the metastable state. The polaron configurations corresponding to the maximum of the energy (4.12) are identified as Langer’s critical droplets [17,18] or the “transition state” [19]. These configurations correspond to a saddle point of the energy functional in the multidimensional configuration space. The “critical droplet” is determined by the value \( x_o = x_o^* \) at which the energy (4.12) is a maximum (the maxima in figures 2.a-c). If we consider small fluctuations around the critical droplet (transition state) configuration, we find that there is one “zero mode” corresponding to translations, one unstable mode corresponding to dilation of the radius of the droplet and, presumably, infinitely many perpendicular directions with positive real frequencies, for small oscillations around the droplet configuration. The presence of the translational and unstable mode is easy to understand. Because of translational invariance the energy does not depend on the position of the polaron, that is, the coordinate \( x_{cm} \) is cyclic. Then, a fluctuation around the polaron solution of the form

\[
\delta_o(x) = a_o \frac{\partial \Delta_p(x)}{\partial x}
\]

with \( a_o \) constant and small, corresponds to a shift of the polaron position

\[
\Delta_p(x; x_{cm}; x_o) + \delta_o(x) \approx \Delta_p(x; x_{cm} - a_o; x_o)
\]

but, by translational invariance, the energy functional is invariant under such a shift. Thus, the function

\[
f_o(x; x_{cm}; x_o) = \frac{\partial \Delta_p(x)}{\partial x}
\]
and the collective coordinate $a_o$ determine a “flat” direction in functional space associated with the “zero mode”. Notice that the function $f_o(x)$ is antisymmetric and has one node.

Now consider a small fluctuation of the polaron solution around the value of $x_o = x_o^*$ with $2x_o^*$ the value of the radius of the polaron corresponding to the maximum of the energy function $\Delta_p$. This fluctuation is determined by the function

$$\delta_1(x) = a_1 \frac{\partial \Delta_p(x)}{\partial x_o} \bigg|_{x_o = x_o^*}$$

(5.4)

For small $a_1$

$$\Delta_p(x; x_{cm}; x_o^*) + \delta_1(x) \approx \Delta_p(x; x_{cm}; x_o^* + a_1)$$

(5.5)

Since $x_o^*$ corresponds to a maximum of the energy functional, the coordinate $a_1$ determines (locally) an unstable direction in function space around the extremum solution. It is important to notice that the function $f_1(x)$ is symmetric (nodeless) and is thus orthogonal to $f_o(x)$.

Generalizing Holstein’s 

20–22 treatment of the large polaron to incorporate $x_o$ as a collective coordinate, we write the quantum expansion around the polaron solution as

$$\hat{\Delta}(x) = \Delta_p(x - \hat{x}_{cm}; \hat{x}_o) + \sum_{l>1} a_l f_l(x - \hat{x}_{cm}; \hat{x}_o)$$

(5.6)

where the functions $f_l(x)$ are constrained to be orthogonal to $f_o(x)$ and $f_1(x)$ and correspond to the stable modes of oscillations around the polaron solutions.

From the Hamiltonian (2.8) we find

$$H = \frac{M_o^2}{2} \dot{x}_{cm}^2 + \frac{M_1^2}{2} \dot{x}_o^2 + E(x_o) + \cdots$$

(5.7)

with

$$M_o^2 = \int dx \frac{\left[ \partial \Delta_p / \partial x \right]^2}{\lambda \pi v_f \omega_Q^2}$$

(5.8)

$$M_1^2 = \int dx \frac{\left[ \partial \Delta_p / \partial x_o \right]^2}{\lambda \pi v_f \omega_Q^2}$$

(5.9)
and where the dots represent the coordinates associated with other functional directions and interactions, and \( E(x_o) \) is the Born-Oppenheimer energy (4.12) in terms of \( \theta(x_o) \). The masses \( M_o \) and \( M_1 \) are numerically found to have a very weak dependence on \( x_o \) for values of \( x_o \) in the region of interest (near the maxima and minima). We find

\[
M_o \approx M_1 \approx 4.2 \text{ (eV } \text{Å}^2)^{-1}
\]  

(5.10)

Following Langer [17] and Affleck [18] (see also [19]) the decay rate of the metastable state is obtained as

\[
\Gamma = \frac{\Omega}{2\pi} \text{Im} F
\]

(5.11)

where \( \text{Im} F \) is the imaginary part of the analytically continued free energy computed in the saddle point approximation around the polaron solution corresponding to the maximum of the energy function (i.e. the transition state) and \( \Omega \) is the (unstable) frequency at the top of the barrier along the functional direction determined by dilation of the radius of the polaron. Near the maximum of the energy function, along the unstable direction, the Hamiltonian becomes

\[
H = E(x^*_o) + \frac{M^2_o}{2} \dot{x}_o^2 + \frac{M^2_1}{2} \dot{x}^2 - \frac{M_1}{2} \Omega^2 (x_o - x^*_o)^2 + \cdots
\]

(5.12)

where \( E(x^*_o) \) is the energy at the top of the barrier (the maximum) and the dots again stand for the stable modes and possible interactions. We find numerically the following values for the energies at the maxima (\( E(x^*_o) \)), minima (\( E_{min} \)), bound state energies \( \omega_{o \pm} \) at the maxima (+) and minima (−) respectively, and unstable frequency \( \Omega \) at the top of the barrier (\( \Delta n = n_+ - n_- \)).

| \( \Delta \epsilon(eV) \) | \( \Delta n \) | \( E(x^*_o)(eV) \) | \( E_{min}(eV) \) | \( \omega_{o+}(eV) \) | \( \omega_{o-}(eV) \) | \( \Omega(eV) \) |
|---------------------|---------|-----------------|-----------------|----------------|----------------|----------------|
| 0.02                | -2      | 0.792           | -               | 0.032          | -               | 0.031          |
| 0.02                | -1      | 0.838           | 0.722           | 0.070          | 0.535          | 0.103          |
| 0.04                | -2      | 0.573           | -               | 0.066          | -               | 0.077          |
| 0.04                | -1      | 0.672           | 0.655           | 0.171          | 0.425          | 0.070          |
| 0.06                | -2      | 0.393           | -               | 0.102          | -               | 0.149          |
Thus, we see that the unstable frequencies at the top of the barriers are typically of the same order of magnitude as the bare phonon frequencies.

The decay rate is thus obtained by calculating the partition function at the saddle point, the unstable mode is treated via an analytic continuation, normalized to the partition function in the metastable well. The zero mode leads to a volume dependence \( \Gamma \) \([17]\) and we find

\[
\frac{\Gamma}{L} = \frac{\Omega}{2\pi \sin(\Omega/k_BT)} [M_0k_BT]^{1/2} \exp \left[ -\frac{E(x_o^*)}{k_BT} \right] [K].
\] (5.14)

\([K]\) is the ratio of the square root of the determinants for the stable modes around the extremum polaron solution and the constant dimerization solution for the metastable well at finite temperature. The computation of this ratio of determinants is beyond our capabilities, it is a dimensionless number, presumably of order one, as the frequency scales in both cases are of the same order of magnitude. The singularities in (5.14) at \( T = \Omega/2\pi k_B n \) have been discussed by Wolynes \([23]\) and the reader is referred to that article for details. In our case for \( n \neq 0 \) these values of the temperature are below the crossover value for thermal activation to quantum nucleation (see discussion below) and the rate given by (5.14) is no longer applicable. As shown in the table above, \( 0.4eV \leq E(x_o^*) \leq 0.8eV \) thus for temperatures \( T \approx 100 - 200K \) the Kramers-Arrenhius factor in (5.14) is fairly large and the lowest energy state in the metastable phase (trans), the constant dimerization, is fairly long-lived.

**A. Induced decay**

The lowest energy configuration in the metastable state is that for constant dimerization with the valence band completely filled. Upon doping with electrons (or holes) the metastable phase, the energetically most favorable configuration corresponds to the formation of a polaron in the Born-Oppenheimer surface corresponding to \( n_+ - n_+ = -1 \) with either one electron in the bound state at \(+\omega_o\) and two electrons in the bound state at \(-\omega_o\) (electron polaron) or one electron in the bound state at \(-\omega_o\) (hole polaron). On this energy
surface, the lowest energy polaron configuration corresponds to the minimum (available for $\Delta_e \leq 0.06 \text{ eV}$).

From the table above, we see that the difference in energy between the minimum and maximum polaron configuration on these surfaces ($E(x^*_o) - E_{\text{min}}$) is typically an order of magnitude smaller. In this situation, the activation energy barriers are of order $\Delta E \approx 0.02 - 0.1 \text{ eV}$, and the decay rate is dramatically enhanced.

Upon further doping, the Born-Oppenheimer surface may change to $n_+ - n_- \geq 0$ and the dissociation curve is reached for almost all phenomenologically available values of $\Delta_e$. In particular, this is always the case for bipolarons $n_+ = n_-$ for the range of parameters consistent with the phenomenology of cis-polyacetylene; this is another major difference with the polarons in the stable phase. In this case, there are no barriers and the system decays instantaneously. The decay process, in this situation, cannot be studied under the assumptions of quasi-equilibrium implied in the treatment of metastable decay and a time dependent non-equilibrium treatment would have to be used.

The first excited and dissociation curves may also be reached by absorption of photons of energy $\hbar \nu = |M_f| + \omega_o$ and electronic transitions to the bound state with energy $+\omega_o$. An absorption peak in this energy range will be the telltale of electron bound states, just as absorption peaks in the degenerate case reveal the existence of electrons bound to solitons \[24\]. Since $\omega_o$ is typically very small, these states may appear as mid-gap states at $\hbar \nu \approx 1\text{ eV}$. However, there is no room for confusion with bound states on solitons, because solitons are not available in the non-degenerate case.

**VI. DECAY VIA QUANTUM TUNNELING**

At very low temperatures (to be quantified later), we expect that the metastable state will decay via quantum tunneling. In order to understand quantum tunneling in multidimensional space, one must search for the configurations that extremize the classical action in imaginary (euclidean) time. These configurations constitute the "most probable escape
path” [23,24], and are solutions to the classical equations of motion in euclidean time [27],
dubbed “bounces” [28–32].

In terms of the collective coordinate $x_o$ representing the radius of the polaron, this “most
probable escape path” or “bounce” corresponds to the classical trajectory in the inverted
potential $-E(x_o)$ between the two classical turning points corresponding to the energy of
the metastable state. For the ground state Born-Oppenheimer curves ($n_+ - n_- = -2$) this
energy is zero, whereas for the higher energy surfaces ($n_+ - n_- = -1$) the energy is that of
the minimum and marked with a dashed line in figure (2.b). This approach was previously
used by Kivelson and Sethna [33] to study photoinduced soliton-pair production.

To exponential accuracy in the semiclassical WKB approximation, the decay rate per
unit length is given by

$$\frac{\Gamma}{L} \approx \exp \left[ -\frac{2S_o}{\hbar} \right] \quad (6.1)$$

with $S_o$ the action of the classical trajectory in euclidean time at energy $E$ between the two
classical turning points $x_-; x_+$:

$$S_o = \int_{x_-}^{x_+} dx_o \sqrt{2M_o[E(x_o) - E]} \quad (6.2)$$

Again, the total decay rate will have prefactors in front of the WKB exponential in (6.1);
this prefactor involves the ratio of the determinants of the quadratic fluctuations. We are
unable at the moment to calculate the prefactor and content ourselves with an estimate of
the exponential, which is the leading term in the semiclassical approximation.

We can provide a rough estimate of the crossover temperature between thermal activation
and quantum nucleation by comparing the WKB factor to the Arrhenius-Kramers activation
factor, thus obtaining the approximate estimate for the crossover temperature

$$k_B T_c \approx \frac{\hbar \Delta E}{2S_o} \quad (6.3)$$

where $\Delta E$ is the activation barrier ($E(x_o)$ for the ground state or $E(x_o) - E_{min}$ for the
higher energy surface). The action $S_o$ is calculated numerically and we find:
Thus, we see that, typically, the crossover temperature is of the order of $T_c \approx 40 - 100K$ depending on the value of the intrinsic dimerization, and may be amenable to experimental realization.

Another (but related) criterion for the crossover temperature is obtained from the quasiequilibrium approach \[32\]. It is based on the properties of the “bounce” solution in Euclidean time corresponding to a classical trajectory with period $\beta \hbar$ in the inverted potential well. These trajectories give the leading semiclassical contribution to the equilibrium partition function. The smallest period for trajectories in the inverted potential corresponds to the harmonic oscillations with frequency $\Omega$ at the bottom of the (inverted) well (see equation 5.12). Thus the maximum temperature for which there are “bounce” solutions in Euclidean time is given by

$$ \beta \hbar = \frac{2\pi}{\Omega} $$

leading to an estimate for the crossover temperature \[19\]

$$ T_c = \frac{\hbar \Omega}{2\pi k_B}. $$

With the values of $\Omega$ from (5.13), we find the estimate for crossover temperature based on this criterion to be $50K \leq T_c \leq 100K$ which is consistent with the previous estimate based on the comparison of the Arrenhius-Kramers and WKB factors. For $T < T_c$ the decay process will be dominated by quantum nucleation and will be fairly insensitive to temperature, whereas for $T > T_c$ the decay will be dominated by thermal activation and the rate will depend strongly on temperature via the Arrenhius-Kramers factor in the decay
rate. Again, quantum decay will be accompanied by the presence of electron bound states at energies $\pm \omega_0$ and may be detected via absorption peaks, just as in the degenerate case, where the absorption peak at the middle of the gap signals the presence of solitons.

Quantum nucleation can also be induced by doping, thus moving from one Born-Oppenheimer surface, for example the ground state, to the next for which $n_+ - n_- = -1$. We see that the height and width of the barrier for this surface are much smaller, resulting in a ten-fold reduction of the WKB action. Thus, the transmission probability, i.e. the nucleation rate, is greatly enhanced. Upon further doping, the dissociation curve is reached and there is no quasi-stationary state; one must resort to a full real time non-equilibrium calculation of the decay probability in this case.

The decay through quantum nucleation occurs via the spontaneous production of a fairly large droplet; this is a tunneling process. The size of the droplet will be roughly determined by the value of the coordinate $|x_o|$ at the classically forbidden turning point below the barrier, i.e. the “escape point”. For the lowest energy surface, this value is typically $\approx 40\text{Å}$ whereas for the first excited surface it is about $\approx 20\text{Å}$. Because of these large values of the radius of the quantum droplet, the bound states will be very close to the middle of the gap and this quantum droplet looks like a kink-antikink pair widely separated.

The telltale signal for the decay of the metastable (trans-cisoid) state, either via thermal activation or quantum nucleation, will be electron bound states with energies very near the middle of the gap (because for the typical sizes of the polarons, the energy $\omega_0$ is very small) and detected through absorption peaks at about $\hbar\nu \approx 1eV$. These peaks could not be confused with solitons as these topological excitations are not available in the non-degenerate isomers. Furthermore, the different regimes for thermal activation and quantum nucleation may be separated by plotting the logarithm of the nucleation rate versus $1/T$: activated processes lead to an approximate straight line with negative slope, whereas for quantum nucleation there should be a flat plateau. Our analysis for the crossover temperature leads to the prediction that such a plot should have a plateau for temperatures smaller than about $40K$. 

22
We must say that at the moment we are not aware of experiments that have either looked at or reported on these possibilities.

VII. CONCLUSIONS AND SPECULATIONS

The motivation of this work was to study the mechanism responsible for the decay of the metastable (trans-cisoid) configuration to the stable (cis-transoid) isomer in non-degenerate polymers. We have identified the electron-phonon configurations that play the role of the nucleation droplets as polarons in the metastable phase, and have studied their properties within the range of parameters for the intrinsic dimerization compatible with a gap of about 2 eV in the electronic spectrum for the cis-isomer. In the undoped, lowest energy metastable configuration, typical barrier energies are of the order of about 0.4–0.8 eV depending on the intrinsic dimerization parameters. Upon doping with electrons or holes, higher energy Born-Oppenheimer surfaces become available and activation barriers become smaller by almost an order of magnitude; thus, upon doping, the metastable decay is induced and the rate is enhanced dramatically. For large doping, dissociation curves become available without activation barriers; in this case a full time dependent non-equilibrium study will be needed to understand the decay.

We obtained an estimate for the decay rate via thermal activation by treating the relevant coordinates of the polaron (center of mass and radius) as collective coordinates and evaluated numerically the necessary activation barriers and unstable frequencies to obtain the rate approximately. We also performed a semiclassical WKB calculation to estimate the decay rate via quantum nucleation and to establish the crossover temperature that separates the regimes between thermal activation and quantum nucleation. We found these temperatures to be approximately $T_c \leq 40K$.

We speculate that metastable isomers in non-degenerate polymers may be candidates to study mesoscopic quantum tunneling. Typical values for the sizes of critical droplets (polarons) are 20 – 40Å. The telltale signal that the metastable decay is mediated by polarons
will be electron bound states with energies very near the middle of the gap. These states may be detected via absorption peaks at about 1 eV, just as the electron states bound to solitons in the degenerate case. There is no possibility to confuse the metastable polarons with solitons as the latter are not available excitations in the non-degenerate case. Furthermore, our rough estimate for the crossover temperature should be amenable to experimental confirmation by plotting the logarithm of the nucleation rate versus $1/T$. In the thermally activated regime this should be almost a straight line with negative slope, the curve should flatten and reach a plateau at temperatures $T \leq 40K$, regime in which the nucleation rate is insensitive to temperature signaling quantum nucleation.

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**Figure Captions:**

**Figure 1:** $\frac{E(\Delta_0)}{N}$ (eV) vs. $\Delta_0$ (eV) for $\lambda = 0.4077$; $\Delta_e = 0.02$ eV.

**Figure 2.a:** $\delta E(r_o)$(eV) (equation (4.12)) vs. $r_o = M_f x_o/v_f$, for $n_+ - n_- = -2$. The "bounce" trajectory has zero energy.

**Figure 2.b:** $\delta E(r_o)$(eV) (equation (4.12)) vs. $r_o = M_f x_o/v_f$, for $n_+ - n_- = -1$. The dashed line represents the energy for the "bounce" trajectory.

**Figure 2.c:** $\delta E(r_o)$(eV) (equation (4.12)) vs. $r_o = M_f x_o/v_f$, for $n_+ - n_- = -2; -1; 0$.