QUANTUM AND THERMAL NUCLEATION IN POLYDIACETYLENE

S. Kivelson[*] and J.P. Sethna[**]

[*]*Department of Physics, S.U.N.Y. at Stony Brook, Stony Brook, N.Y. 11794, U.S.A.*
[**]*Department of Physics, Cornell University, Ithaca, N.Y. 14853, U.S.A.*

Résumé – Un modèle continu simple est développé pour le polydiacétylène (PD) et appliqué à l'étude des transitions de phases structurales apparaissant dans certains PD. On peut conclure que la transition du ETCD-PD correspond à une nucléation thermique tandis que celle du TCDU-PD correspond probablement à une nucléation "quantique".

Abstract – A simple continuum model of polydiacetylene (PD) is constructed and used to study the structural-phase-transition that occurs in certain PD's. It is concluded that the transition in ETCD-PD is thermally-nucleated while that in TCDU-PD is probably quantum-nucleated.

I. INTRODUCTION

Polydiacetylene (PD) is the name given to the family of planar linear polymers shown schematically in Fig. 1. All the members of this family have a backbone of linked diacetylene monomers (Fig. 1c). On simple chemical grounds one would conclude that this backbone could exist in one of two possible isomeric forms, the acetyne-form shown in Fig. 1a (we will refer to this as A-phase) and the butatriene-form shown in Fig. 1b (we will refer to this as B-phase). Dangling off the backbone are large organic side groups, the R's in the figure which distinguish the different members of the family. For a variety of different side groups, PD crystals can be obtained by polymerizing in the solid state. At least two polydiacelytenes, that in which R is named ETCD or R is called TCDU, undergo a reversable structural phase transition as a function of pressure or temperature which has been tentatively identified[1] as being from A-phase at low temperature or high pressure to B-phase at high temperature or low pressure.
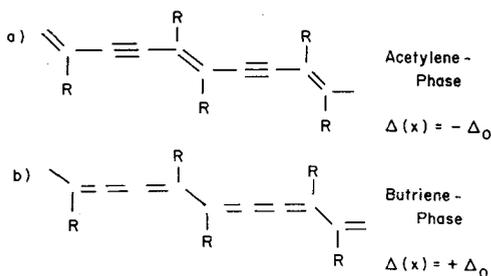

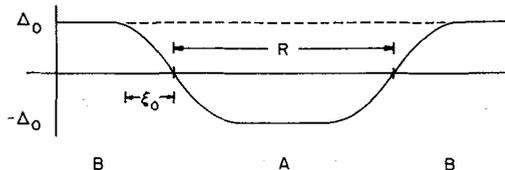Fig. 1: Schematic representation of Polydiacetylene

Fig. 2: Nucleation Droplet

In this paper we study the dynamics of this phase transition. Imagine that the system is initially at high temperature and is hence uniformly in B-phase. We then quench the system to below T_c. The transition begins to occur when a fluctuation

causes a segment of the system to convert to A-phase as in Fig. 2. This segment is
bounded by a domain wall, that is a region over which the bonding pattern changes
from B-phase to A-phase, and an anti-domain wall. We shall show that these domain
walls closely resemble the domain walls or solitons that occur in polyacetylene[2]
((CH)$_x$) and so we will refer to them as "solitons". If the segment of A-phase
produced by our fluctuation is too small, the energy to create the solitons, $2E_s$,
exceeds the free energy gained by converting B-phase to A-phase and the fluctuation
will tend to go away. On the otherhand, the larger the fluctuation, the less likely
its occurrence. Thus, the rate at which the transition is nucleated is equal the
probability per unit time of the occurrence of a fluctuation of the critical size.
At high temperatures[3], this nucleation rate is dominated by thermal fluctuation
while at low enough temperatures the quantum fluctuations are the important ones[4].

There are several interesting features that emerge from the study of this problem:
1) We derive a simple model of PD at the same level of complexity as the SSH model
of polyacetylene[2]. In the continuum limit, the two models are quite similar, except
for the presence of small terms in the model of PD which break the symmetry between
the two possible bonding configurations. This model has much broader implications
for the properties of polydiacetylene than those explored in any detail here.
(This will be contained in a future publication[5].) However, because of the
similarity with (CH)$_x$, it is easy to see that many of the same solitonic and
polaronic features of the behavior of (CH)$_x$ should also be features of the behavior
of PD. Thus, it is a possible test of the generality of the soliton model of (CH)$_x$
to see which of the expected features occur in PD as well. Indeed, since PD can be
made crystalline, it may, in some respects, be a better system than (CH)$_x$ for
testing the model. In addition, by varying the temperature (or pressure) one can
change the asymmetry between the two bonding configurations which provides another
probe of the soliton dynamics. 2) We find that the transition in ETCD-polydiacety-
lene (ETCD-PD), which has a transition temperature $T_c \approx 350°K$, is thermally nucleated
while that in TCDU-PD, where T_c is apparently $\sim 100°K$, is probably quantum nucleated.
Both these transitions are worth studying since nucleation in a highly anisotropic
medium involves hitherto unexplored issues concerning the shape of the critical
nucleation droplet. However, the possibility of studying quantum-nucleation in a
solid-state system is particularly intriguing. In addition, because of the intimate
connection between the lattice and electronic degrees of freedom in PD, it should be
possible to observe a novel phenomenon: photo-assisted quantum-nucleation. 3) From
a more general viewpoint, PD is a promising laboratory for the study of dynamics at
intermediate length scales. Because the soliton width, ξ_0, is much greater than a
lattice constant, a, the nucleation can be simply described in terms of a single
collective-coordinate which is coupled weakly to a heat bath consisting of all the
other degrees of freedom. However, ξ_0 is still a microscopic length and so the
dynamics of the collective coordinates can be deduced directly without recourse to
phenomenological assumptions.

II.   A MODEL OF POLYDIACETYLENE

In Fig. 3 we take a close up look at one unit cell of a PD chain. Each carbon atom
has four valence electrons. Three of the electrons from each of carbons 1 and 4
and two from carbons 2 and 3 go into a low lying, filled σ band. One electron from
each of carbons 2 and 3 go into a filled bonding π_x band which is formed from the P_x
orbitals on carbons 2 and 3. These bands all lie well below the Fermi surface so
that excitations out of these bands do not occur in any of the low energy processes
we will consider. These electrons can be treated as adiabatic slaves of the lattice
motion. Similarly, since the anti-bonding σ^* and π_x^* bands lie well above the Fermi
energy, excitations into these bands can safely be ignored. We are left, then, with
one electron per carbon and hence a half-filled out of plane π_z band.

There are many lattice degrees of freedom per unit cell. We wish to focus primarily
on the one lattice degree of freedom per carbon, the u_n's in Fig. 3, which produce
the bond alternation of the PD backbone shown in Fig. 1. We call all the other
lattice degrees of freedom ϕ. To lowest order in the lattice displacements, these
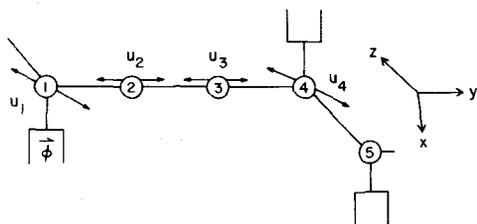
Fig. 3

Fig. 4

Fig. 3: Polydiacetylene Monomer
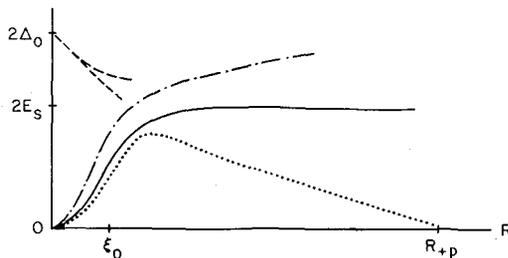
Fig. 4: Adiabatic Potential Energy Curves: (••) is $E_T(R)$ for $T<T_C$; (——) is $E_T(R)$ for $T=T_C$; (— • —) is $E_T(R)$ for $T>T_C$; (---) is $E_T^*(R)$.

other degrees of freedom do not couple to the Fermi surface electrons. Thus, the Hamiltonian for a PD chain can be expressed in the form

$$H = H_o + H_R(\vec{\phi}) + H_{int}(\{u\},\vec{\phi}) \qquad (1)$$

where H_o is the Hamiltonian of the bare backbone, H_R is the Hamiltonian of the other lattice degrees of freedom, (called $\vec{\phi}$), and H_{int} is the interaction energy between the two types of lattice degrees of freedom. As in the SSH model[2] of $(CH)_x$, we approximate H_o by a nearest neighbor tight-binding Hamiltonian

$$H_o = -\sum_s \sum_n t_n(u_n-u_{n+1})[C^+_{n,s}C_{n+1,s}+\text{h.c.}]+\sum_n V_n(u_n-u_{n+1})+\tfrac{1}{2}M\sum_n(\dot{u}_n)^2 \qquad (2)$$

where $C^+_{n,s}$ creates an electron of spin s on site n, V is the lattice potential energy, and M is the carbon mass. The hopping matrix, t_n increases as the distance between sites n and n+1 decreases,

$$t_n(u) = \tilde{t}_n + \alpha_n u + \sigma(u^2). \qquad (3)$$

Similarly, the potential energy, V_n, can be expanded in powers of the lattice displacements:

$$V_n(u) = \beta_n u + \tfrac{1}{2}K_n u^2 + \sigma(u^2). \qquad (4)$$

This Hamiltonian is somewhat more complicated than the SSH model of $(CH)_x$ since there are multiple atoms per unit cell and hence there may be three slightly different values of each of the parameters $\tilde{t}$, α, β, and K. As in the SSH model, all these parameters should be viewed as effective parameters which incorporate the effects of the σ and π_x electrons as well as electron-electron interactions. Implicit in Eqs.(1) and (2) are the assumptions that the side groups, R, are electrically inert and that explicit electron-electron interactions can be ignored. The latter assumption appears[6] to be valid in $(CH)_x$, and so we think it is likely to be valid in chemically similar PD as well.

To allow us to focus on the interesting physics, it is convenient to simplify the model in two ways. Firstly, because the correlation length, ξ_o, is large compared to a lattice constant, a, we can consider the model in the continuum limit. This is equivalent to retaining lowest order terms in $(\xi_o/a)=(2\Delta_o/W)$ where W is the π_z band width and $2\Delta_o$ is the band-gap. The resulting Hamiltonian, as derived in Ref. 5 is:

$$H_o = \sum_s \int dx \psi_s^+(x) [-i\hbar V_F \frac{\partial}{\partial x}\sigma_z + \Delta(x)\sigma_x]\psi_s(x) + \int \frac{dx}{2ag^2}[\Delta^2(x) + \frac{\dot{\Delta}^2}{\omega_o^2}] + \frac{D}{2}\int \frac{dx}{a}\Delta(x) \qquad (5)$$

where $\psi_s^+(x)$ is, for each component of spin, s, a two component iso-spinner corres-
ponding to right and left going electrons, σ_a are the Pauli matrices, V_F is the
Fermi velocity, $\Delta(x)$ is a real scalar field which is proportional to the displace-
ment,

$$\Delta(x) \equiv -(-1)^n \alpha_n (u_n - u_{n+1}), \qquad (6)$$

where $x = (n+\frac{1}{2})a$, g^2 is the dimensionless electron-phonon coupling, and ω_o is the
bare optical phonon frequency. The term proportional to D is the only term which
breaks the symmetry between A-phase ($\Delta<0$) and B-phase ($\Delta>0$). Indeed, for D=0 we
recover the standard continuum model[7] of $(CH)_x$. In PD, we think it likely that D
is small and positive since the short "tripple" bond makes the A-phase configuration
slightly lower in energy than the B-phase. All of the parameters that enter the
continuum model can be expressed in terms of the parameters in the discrete model[5],
but since these are not known accurately, we will adopt the point of view that the
parameters are to be determined directly from experiment.

The second simplification is to integrate out the other lattice degrees of freedom.
We do this formally by defining an effective Hamiltonian, H^{eff}, which involves only
the backbone degrees of freedom:

$$\exp[-H^{eff}/kT] = \int \mathcal{D}\vec{\phi}\, \exp[-H/kT]. \qquad (7)$$

There are two ways the presence of the side groups are manifest in H^{eff}. Firstly,
they can alter the effective potential slightly. Specifically, the side groups
exert a tension on the backbone which increases as the temperature increases and
the effective size of the side groups grows. The result is a slight, and unimpor-
tant renormalization of V_F as the lattice expands, and an extremely important
temperature dependent change in the symmetry breaking parameter, $D \rightarrow D(T)$. Since
B-phase is slightly longer, we expect it to be increasingly favored at high
temperature. Thus, we expect $D(T)$ to be a decreasing function of T. Near T_c,

$$D(T) = D_o [\frac{T_c - T}{T_c}] \qquad (7a)$$

where T_c is the transition temperature at which A and B-phases are energetically
equivalent, and $D_o > 0$. The second effect is to produce a time retarded kinetic
energy which is equivalent to a frequency dependent effective mass, $M(\omega)$. This is
discussed in refs. 5 and 8. The physical meaning of this effective mass is straight-
forward: If the characteristic rate of change of Δ is small, the side groups can
follow the motion adiabatically. Hence, motion of the order parameter is accom-
panied by motion of the entire side group and the appropriate mass is the zero
frequency mass, $M(0)$. We can roughly estimate $M(0)$ to be $\frac{1}{4}$ the full monomer mass
per site (4 sites per monomer). If the rate of change of Δ is fast compared to
some of the characteristic frequencies of the side groups, only a fraction of the
mass, $M(\omega)<M(0)$, accompanies the motion of the backbone. To simplify our calcula-
tions at this stage, we will replace the frequency dependent mass by a suitable
average value, $\bar{M}$. The kinetic energy term in H^{eff} is thus of the same form as
in Eq. (5), but with a renormalized phonon frequency, $\bar{\omega}_o$. If we take $\bar{M}=M(0)$, any
tunnelling rate which we calculate in this fashion is a lower bound[8] to the true
tunnelling rate, even if the characteristic time spent tunnelling is short (high
frequency).

III. SOME PROPERTIES OF THE MODEL

Since for $D(T)=0$, our model of PD is the same as the continuum model of $(CH)_x$, for
small $D(T)$ (i.e. for T near T_c) all the short distance properties of the models are
the same. We list some of them here for completeness.[7] Note, however, that topo-
logically the models are quite different. There are two possible ground state
configurations with $\Delta(x)=\pm\Delta_o$ + small corrections, where $\Delta_o = W\exp[-\hbar\pi V_F/g^2]$ is the

value of the order parameter for D=0. For D≠0, these two ground states are non-degenerate. In the presence of a constant order parameter, the electronic density of states consists of a full valence band separated by a gap $2|\Delta|$ from an empty conduction band.

Now imagine that we take a chain with $\Delta(x)=+\Delta$ (B-phase) and create a soliton anti-soliton pair a distance R apart. Let us consider the total adiabatic potential energy of the system, $E_T(R)$, as a function of R (see Fig.4). As R increases from 0 to a distance of order the electronic correlation length, $\xi_0=hv_F/\Delta_0$, the energy rises to approximately $2E_s=4\Delta_0/\pi$, that is to say twice the soliton creation energy, E_s. At this point R is still relatively small, so there is still little difference between the cases D=0 and D≠0 (compare curves in Fig.4). For R much greater than ξ_0, the total energy is minimized by a configuration of the sort shown in Fig.2 in which the solitons have width of order $2\xi_0$ and a shape (similar to the soliton shape for D=0) which is independent of R. Between the solitons lies a region of perfect A-phase. Thus, for D=0, since the two phases are energetically equivalent, the energy is independent of R (solid curve in Fig.4) with value $E_T(R)=2E_s$. For D(T)≠0, the energy changes linearly with R as B-phase is converted to A-phase.

$$E_T(R) \stackrel{\sim}{\sim} 2E_s + D(T)\Delta_0(R/a) \quad \text{for} \quad R \gg \xi_0. \tag{8}$$

$E_T(R)$ is an increasing function of R for $T>T_c$ (D(T)<0) and decreasing for $T<T_c$ (D(T)>0).

Associated with an isolated soliton there is a state which, due to the charge conjugation symmetry of the model, must lie at exactly mid-gap. In the presence of a soliton-pair these states hyberdize to form a bonding and anti-bonding pair placed symmetrically about mid-gap as in Fig.5. The adiabatic potential curves we have discussed until now presupposed that the electrons were always in their instaneous ground state with the bonding level full and the anti-bonding level empty (see Fig.5a). However, it is possible to imagine placing the system in an excited state by promoting an electron from the bonding to the anti-bonding state (Fig.5b). The adiabatic potential energy for this state, $E_T^*(R)$, (dashed line in Fig.4) is separated from the ground state energy by exactly the energy splitting
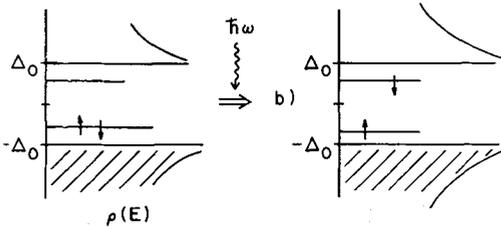

Fig. 5

Fig. 6

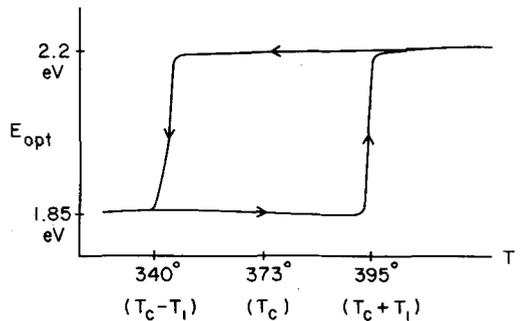Fig. 5: Density of states in presence of a soliton anti-soliton pair.

Fig. 6: Schematic representation of data from Chance et al (Ref. 1) of the optical band gap vs. temperature in ETCD-PD.

between the bonding and anti-bonding states. This splitting is just the energy gap, $2|\Delta|$, for R=0 and drops exponentially to zero for $R/\xi_0>1$.

At this point it is worthwhile to note that the traditional chemists' view of poly-diacetylene holds that electron-electron interactions are of central importance and that, in particular, the optical absorption is dominated by excitonic effects[9]. The central experimental evidence for this is that the optical absorption threshold $E_{opt} \approx 2eV$, lies at a significantly lower energy than the photo-conductive threshold, $E_{pc}-E_{opt}=0.5$ to $2eV$. $E_{pc}-E_{opt}$ is thus interpretted as the exciton binding energy. Since PD is chemically similar to $(CH)_x$, and the optical absorption spectrum looks quite similar, this observation would have significant implications for $(CH)_x$ as well.

An alternative interpretation of the same data follows directly from our model, (without including electron-electron interactions). A photo-injected electron-hole pair with energies near the band edge can "dress" themselves[10] by "rolling down" the upper (dashed) adiabatic potential in Fig.4 to form an oppositely charged soliton anti-soliton pair. However, because of the asymmetry between the two ground state phases, the solitons are confined in a neutral complex. This view explains not only the fact that the optical absorption shows none of the structure that would be expected if excitonic effects were important, but also why PD behaves exactly like cis-$(CH)_x$ (which also has asymmetric ground states). Right at $T=T_c$, the confinement energy vanishes (ignoring inter-chain coupling) and we might expect[5] to see properties more like those in trans-$(CH)_x$.

IV. NUCLEATION IN AN ANISOTROPIC MEDIUM

The theory of nucleation in an isotropic medium is well known[3,4]. Let us briefly consider how the theory applies to a single chain of PD (one-dimension) and then extend the theory to apply to a three dimensional array of chains with weak coupling between them.

A. Single Chain Theory: Again consider a system which is initially in its high temperature equilibrium state (B-phase) which is then quenched to a tempera-ture $T<T_c$. The total adiabatic potential energy required to create a segment of A-phase of length R is given by the dotted line in Fig.4. Thermal fluctuations which are large enough to nucleate the phase transition ($R \gtrsim R_{+p}$ in the figure) occur at a rate which is determined by the Boltzman factor for activation over the barrier. It is thus easy to see that[3]

$$\nu_T = \nu_o \exp[-V_o/kT] \tag{9}$$

where ν_T is the thermal nucleation rate per monomer, ν_o is an "attempt" frequency which is typically of the order of a phonon frequency, $\nu_o \sim 10^{13}$Hz, and V_o is the height of the barrier to nucleation. (V_o is the energy of the classical critical configuration droplet[3].) As can be seen in Fig.4, $V_o \lesssim 2E_S$, and $V_o \approx 2E_S$ for small asymmetry (T near T_c). Similarly, the low temperature quantum-nucleation rate is easily calculated using the instanton bounce method,

$$\nu_Q = \tilde{\nu}_o \exp[-2S(T)/\hbar] \tag{10}$$

where ν_Q is the nucleation rate per monomer, $\tilde{\nu}_o$ is an attempt frequency which is probably of the same order as ν_o, $S(T)$ is the WKB tunnelling factor through the barrier,

$$S(T) = \int_o^{R_{+p}} \sqrt{2M^*(R)V(R)} \; dR, \tag{11}$$

and $M^*(R)$ is the soliton effective mass. (Formally, $2S(T)$ is the action along the instanton path, $\Delta_I(X|R)$, which is parameterized by R,

$$M^*(R) = \int \frac{dx}{g^2\omega_Q^2 a} \left(\frac{d\Delta_I}{dR}\right)^2, \tag{12}$$

and R_{tp} is the classical turning point.) For $R>>\xi_0$, $M^*(R)$ can readily be seen to approach a limit of one half the soliton effective mass, M_S^*. As discussed in Ref.2, the soliton mass is given by an expression of the form

$$M_S^* = (\ ) \ \bar{M} \ \overline{(u/a)^2} (a/\xi_0) \qquad (12a)$$

where $\bar{u}$ is the average value of the lattice displacement, u_n, and ( ) is a number of order one. Thus, even though $\bar{M}$ is many times a carbon mass, because the $(u/a)<<1$ and the soliton width, ξ_0, is much greater than a, M^* is of order a few electron masses[1]. From our earlier estimate of the adiabatic mass, $M(0)$ and measured values of the lattice displacements[1], we find an approximate upper bound value of $M_S^* \lesssim 5 \ m_e$. Thus, for small asymmetry, when over most of the range of the integral in Eq.(11), $E_T(R)$ and $M^*(R)$ are given by their asymtotic forms, Eqs.(8) and (12) respectively, the integral can be evaluated analytically:

$$S(T) = S_0 (R_{tp}/\xi_0) \qquad (13)$$

where $S_0=(8/3)\sqrt{M_S^* E_S} \ \xi_0 \lesssim 10$, $(R_{tp}/a)=(2E_S/D(T)\Delta_0)\gtrsim(R_0/a)[T_c/(T_c-T)]$, and $(R_0/a)=(2E_S/D_0\Delta_0)$, determines the scale of sizes of the critical droplet.

Finally, we consider the possibility of photo-induced nucleation. Here, we must distinguish between two possible processes: 1) Classical photo-induced soliton pair production and, 2) Quantum mechanical photo-assisted soliton pair production. The first process resembles the photo-conductive process we discussed previously. If light with energy $\hbar\omega \gtrsim 2|\Delta|$ is absorbed by the system, the resulting electron-hole pairs become soliton anti-soliton pairs, which in turn nucleate the phase transition. The second process occurs when $\hbar\omega<2|\Delta|$ and is described in detail in Ref.11. However, heuristically it can be viewed as follows. For $\hbar\omega<2|\Delta|$, no transition can occur until a (quantum) fluctuation of the lattice produces states in the gap which differ by an energy $\hbar\omega$ as in Fig.5. Now, the photon can be absorbed leaving the system in an excited electronic state. As a result, at (imaginary) times before the transition occurs, the lattice sees the ground state adiabatic potential energy $V_\omega(R)=E_T(R)$ while after the transition it sees an adiabatic potential $V_\omega(R)=E_T^*(R)-\hbar\omega$. As a result, the WKB tunnelling factor, $S(T)$, is replaced by a frequency dependent action, $S(T,\omega)$,

$$S(T,\omega) = \int_0^{R_{tp}(\omega)} \sqrt{2M^*(R)V_\omega(R)} \ dR, \qquad (14)$$

and hence the photo-assisted nucleation rate is of the form

$$Q(\omega) = \gamma_0 I(\omega)\exp[-S(T,\omega)/\hbar] \qquad (15)$$

where $I(\omega)$ is the intensity of the incident radiation and γ_0 is a complicated pre-factor (see Ref.11). For example for T near T_c and $\hbar\omega<<2E_S$, the effect of the light is to lower the barrier, uniformly, by an amount $\hbar\omega$, so $S(T,\omega)=S(T)[1-\hbar\omega/2E_S]^{3/2}$.

    B. Multi-Chain Theory: Now, let us extend our horizons to include the effects of interchain interactions. Since A-phase is slightly ($\sim 1\%$) shorter than B-phase, there is a certain strain involved in having nearest-neighbor-chains in different phases. Thus, there is an effective interaction between chains, $W_\perp$ per monomer. To create a segment of A-phase in a crystal of otherwise perfect B-phase chains costs an interaction energy $ZW_\perp(R/a)$ where Z is the number of nearest neighbors and R is the length of the segment. Since the chains are far separated, we expect that $W_\perp$ is small. The effect of $W_\perp$ is to alter the adiabatic potential energy, $E_T(R)$, from its value in Eq.(8) to

$$E_T(R) = 2E_S-[\Delta_0 D(T)-ZW_\perp](R/a) \quad \text{for} \quad R>>\xi_0. \qquad (16)$$

It is immediately apparent that $E_T(R)$ is still an increasing function of R for $T=T_c$ (D=0). Only if the system is quenched to a temperature below T_c-T_1 will nucleation on a single chain be possible, where T_1 is defined by the relation $D(T_c-T_1)=ZW_\perp/\Delta_0$. For small $W_\perp$, it follows from Eq.(7) that $T_1=T_c(ZW_\perp/D_0\Delta_0)$. Note that if we had started our thought experiment at low temperature with a crystal of perfect A-phase material, and heated it above T_c we would have discovered that nucleation on a single chain is impossible unless we heat the system to a temperature greater than T_c+T_1. (See also the discussion of chain ends below.)

This is still not the full story since when we introduce interchain coupling, we introduce the possibility of three-dimensional nucleation. Multichain nucleation is possible when the quench depth is insufficient to permit single-chain nucleation ($T_c > T > T_c - T_1$). The cross-over from truly one dimensional nucleation to fully three dimensional nucleation is discussed in ref.5. However, if we assume that interchain coupling is weak in PD, we conclude that multi-chain nucleation simply does not occur on human time scales. For instance, consider the relatively simple case of thermal nucleation. To create a region of A-phase on two chains requires that we create 4 solitons. Thus, the two chain nucleation rate is smaller than the one chain nucleation rate by a factor of $f = \exp[-2E_s/kT]$. As a function of the quench depth, the nucleation rate changes discontinuously by a factor of f as the quench depth is increased from just above $T_c - T_1$ to just below. Since $2E_s \sim 1eV$ in PD, at $T = 350°$, which is approximately the transition temperature of ETCD-PD, the one-chain-nucleation rate per monomer (when single chain nucleation is possible) is $\nu_T \sim 0.1$ Hz, while $f \sim 10^{-14}$ so the two-chain nucleation rate is extremely small. As a result, we expect the transition to show the same hysteretic behavior (as in Fig.6) regardless of the time scale of the experiment. The case of multi-chain quantum nucleation is not only more complicated, but also irrelevant to PD, and so will not be treated here.

  C. Effect of Chain Ends: So far we have considered only bulk nucleation. However, in any real experiment the chain lengths are finite. It is therefore important to determine the effect of chain ends and in particular to determine whether chain end nucleation dominates bulk nucleation. The answer to this question depends, to some extent, on the chemistry of chain ends. The nature of the chain ends has not been studied but is probably something that can be controlled experimentally to some extent. It seems likely that if the chains always consist of an integral number of monomer units, chain ends will always prefer one of the phases over the other. Let us assume that it is energetically favorable for chain ends to have a bonding configuration corresponding to A-phase. (There is circumstantial evidence from crystals containing low polymer concentrations that this is the case[1].) Moreover, we assume that, as is the case in $(CH)_x$ (see Su[12]), the energy required to force a chain to end in the "wrong" (that is B) phase is greater than the soliton creation energy. In that case chain ends are always in A-phase, even for temperatures above T_c when most of the chain is in B-phase. Thus, there is a soliton pinned to each chain end. Two consequences follow at once. Firstly, if we start with a sample in equilibrium at high temperature and cool it to below T_c, the phase transition is not nucleated. The solitons merely come in from the chain ends and annihilate. On the other hand, when we heat from low temperature, nucleation occurs preferentially in the bulk, at least a few soliton widths away from the edge. On short chains, that is chains that are less than several soliton widths long, the nucleation rate will be substantially smaller than on long chains and the transition temperature will be increased. In the absence of short chains, similar histeretic behavior to that shown in Fig.6 will still occur, however the lower transition temperature must now be interpreted as $T = T_c$.

Note that, if it were energetically favorable for chain ends to be B-phase like, the same considerations apply with the roles of A and B phases interchanged. Only if there is a variety of chemically different chain ends do we run into trouble. If some ends favor A- and some B-phase, then the phase transition can be seeded in either direction at chain ends. It is thus necessary to look only at chemically homogeneous samples.

V.   NUCLEATION IN POLYDIACETYLENE

The experimental information on the phase transition in PD is far from complete. There is, as yet, no definitive x-ray crystalography confirming that the transition is indeed the one studied here[13], nor have there been any direct studies of the dynamics of the phase transition. Moreover, there is evidence that the typical

chain lengths, at least in the TCDU-PD crystals, are of order $L \sim 5$ to 10 monomers or 2-4 soliton widths[1]. It will thus not be possible to make extensive comparisons between theory and experiment until better crystals are made and more extensive experiments performed. We therefore conclude with a demonstration that when and if such crystals become available, it is plausible that these effects will be observed.

A. Thermal Nucleation: The curve in Fig. 6 is actually a schematic representation of measurements of the optical band gap, E_{opt}, vs. temperature of ETCD-PD. The observation of such a sharp histeresis loop is in accord with the predictions of the theory. As discussed previously the predicted nucleation rate, $\nu_T \sim 0.1$ Hz, is such as to make this interpretation plausible. In TCDU-PD the transition is centered at about $T_c = 100°$. Thus the thermal nucleation rate is $\nu_T \sim 10^{-35}$ Hz. We conclude that thermal nucleation does not occur in TCDU-PD near T_c.

B. Quantum Nucleation: Let us imagine that S_O in Eq. (13) is equal to 10, which as we have discussed is likely to be an overestimate, and let us take 10^{13} Hz to be a characteristic value of the prefactor in Eq.(10), ν_O. Then, the rate of quantum nucleation is of order 1 Hz per monomer when $(R_{+p}(T)/\xi_O) \sim 3$. That is certainly an experimentally accessible rate. How deep a quench is required to produce this value of R_{+p}, or indeed whether it is possible for any quench depth, depends on the unknown value of D_O, the asymmetry parameter (see Eq.(7)). So long as $\Delta_O D(0)$, the asymmetry energy at T=0, is greater than $2E_s(a/3\xi_O) \sim 0.07$ eV, then a quench to T=0 will produce a value of $R_{+p} < 3\xi_O$, and hence a humanly observable nucleation rate. If we make the plausible assumption that D(0) is of order 1, this inequality is amply satisfied.

The actual experimental situation in TCDU-PD is depressing. The transition is described[1] as "sluggish", meaning that it is spread out at least from $10°$ to $300°$. Since thermal nucleation is so strongly suppressed, we would like to attribute this spread to quantum nucleation on short chains of variable length. However, until experiments on crystals with fewer defects, i.e. longer chains, are performed, such an attribution is, at best, highly speculative.

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