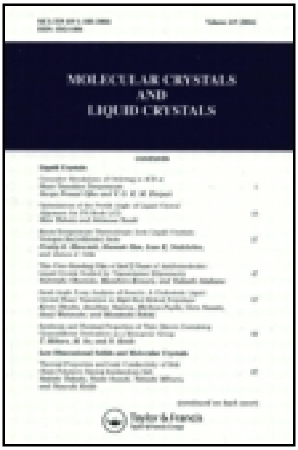

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SOLITON DIFFUSION IN POLYACETYLENE*

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Within the framework of Su, Schrieffer and Heeger model of polyacetylene, a soliton in motion couples to the optical phonon; the soliton velocity is decreased by the Bremstrahlung of the optical phonon. The characteristic relaxation time $\tau(v)$ is calculated as function of v the soliton velocity. For solitons with velocity $v > v_c$ where $v_c \sim 1.2(c_0 v_F)^{\frac{1}{2}}$ and c_0 is the acoustic phonon velocity and v_F is the Fermi velocity, this damping mechanism is efficient, while for solitons with $v < v_c$ the optical phonon cannot slow down the soliton. Making use of $\tau(v)$ thus obtained the diffusion constant D is obtained as

$$D_{/\!/} = \langle v^2 \tau(v) \rangle = D_0 \left(\frac{T}{E_F}\right) e^{-c\left(\frac{E_F}{T}\right)}$$

where $D_0 \sim 0.04\ \text{cm}^2\ \text{sec}^{-1}$, T is the temperature, E_F is the Fermi energy and c is a constant of the order of 10^{-3}. The above expression appears to describe the observed spin diffusion constant $D_{/\!/}$, both the magnitude and the temperature dependence of pristine polyacetylene quite well.

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1. INTRODUCTION

The concept of solitons introduced by Su, Schrieffer and Heeger (SSH)[1] and others[2,3] appears to be central to interprete a variety of physical properties of pristine and lightly doped trans-polyacetylene. One of remarkable observations[4,5] is that the solitons in pristine polyacetylene are quite mobile along the $(CH)_x$ chain at least at the room temperature. In this paper we shall study theoretically the soliton diffusion within the continuum version[3,6] of the SSH model. We believe that in the high temperature region where the thermal velocity of the solitons is much larger than the sound velocity, the solitons are most efficiently damped by the Bremstrahlung of the optical phonons. The predicted diffusion constant agrees with the experimental results[4,5] around the room temperature.

2. MODEL HAMILTONIAN

In the continuum limit[3,6] the SSH Hamiltonian for polyacetylene is recast as;

$$H_c = \frac{1}{2g^2}\int dx\{\,\dot{\Delta}^2(x) + \omega_Q^2\,\Delta^2(x)\,\}$$
$$+\sum_s \int dx\; \Psi_s^+(x)\,[-iv_F\sigma_3\partial_x + \sigma_1\Delta(x)]\,\Psi_s(x) \qquad (1)$$

where $\omega_Q^2 = 4K/M, \quad \Delta(x) = g(a/M)^{-\frac{1}{2}}\,\tilde{y}(x)$ (2)

and $\tilde{y}_n = (-)^n y_n$ is the staggered lattice displacement. Here a dot on $\Delta(x)$ implies the time derivative, σ_i's are the Pauli spin matrices, and $\Psi_s(x) = \begin{pmatrix} u_s(x) \\ v_s(x) \end{pmatrix}$ is the spinor field consisting with the right-going electron $u_s(x)$ and the left-going electron $v_s(x)$. It is known that in addition to the uniformly dimerized states with $\Delta(x) = \pm \Delta$, the above Hamiltonian allows a soliton state with[1,3]

$$\Delta_s(x) = \pm \Delta \tanh (x/\xi) \tag{3}$$

with the soliton energy $E_s = \frac{2}{\pi} \Delta$, where 2Δ is the Peierls energy gap and $\xi = v_F/\Delta$.

In the following we shall consider a time-dependent solution given by

$$\Delta_s(x,t) = \Delta \tanh [(x-vt)/\xi] \tag{4}$$

which describes a soliton with a uniform velocity v. This moving soliton has the energy[1,3]

$$E_s(v) = E_s + \frac{m}{2} v^2 \tag{5}$$

where $E_s = \frac{2}{\pi} \Delta$ and m is the soliton mass of the order of the electron mass.

This moving soliton now couples with the optical phonons (i.e. the fluctuations in $\Delta(x)$) through the first term in Eq(1). Substituting $\Delta(x)$ given by

$$\Delta(x) = \Delta_s(x,t) + \delta\Delta(x,t) \tag{6}$$

into Eq(1), we find the interaction Hamiltonian

$$\begin{aligned} H_I &= g^{-2} \int dx\, \dot{\Delta}_s(x,t)\, \delta\dot{\Delta}(x,t) \\ &= -g^{-2} v\, \Delta\xi^{-1} \int dx\, \mathrm{sech}^2(\tfrac{x-vt}{\xi})\delta\dot{\Delta}(x,t) \end{aligned} \tag{7}$$

Note that the coupling constant is proportional to the soliton velocity v and vanishes for v = 0.

3. SOLITON RELAXATION

A moving soliton can emit optical phonons and slow down it's velocity. The characteristic relaxation time $\tau(v)$ is evaluated as;

$$
\begin{aligned}
(2\tau(v))^{-1} &= \tfrac{1}{2}(g^{-2}v\Delta\xi^{-1})^2 g^2 \int_{-\infty}^{\infty} dk\, M_k^2\, \omega_0(k) \\
&\quad \times \delta(E_s(v) - E_s(v') - \omega_0(k)) \\
&\quad \times (1 - e^{-\beta\omega_0(k)})^{-1}
\end{aligned}
\tag{8}
$$

where

$$v' = v - m^{-1}k$$

$$M_k = \int_{-\infty}^{\infty} dx\, e^{ikx}\, \mathrm{sech}^2\left(\frac{x}{\xi}\right) = 2\pi\xi\eta\, \mathrm{cosech}(\pi\eta) \tag{9}$$

and $\eta = \tfrac{1}{2}\xi k$

and $\omega_0(k)$ is the optical phonon frequency given by[7]

$$\omega_0(k) = \omega_0\left[\frac{\sqrt{1+\eta^2}}{\eta}\sinh^{-1}\eta\right]^{\frac{1}{2}} \tag{10}$$

and

$$\omega_0 = (2\lambda)^{\frac{1}{2}}\omega_Q \quad \text{and} \quad \lambda = g^2(\pi v_F \omega_Q^2)^{-1} \tag{11}$$

In deriving Eq(8) use is made of the propagator for the optical phonon

$$\langle T(\delta\Delta\ \delta\Delta)\rangle(\omega_\nu, k) = g^2(\omega_\nu^2 + \omega_0^2(k))^{-1} \tag{12}$$

where $\omega_\nu = 2\pi T\nu$ the Matsubara frequency.

The k integral in Eq(8) is easily done and we find;

$$
\begin{aligned}
\tau(v)^{-1} &= g^{-2}(2\pi\Delta v\eta\, \mathrm{cosech}(\pi\eta))^2\omega_0(k)(1 - e^{-\beta\omega_0(k)})^{-1} \\
&\quad \times \left|v - m^{-1}k - \frac{\partial\omega_0(k)}{\partial k}\right|^{-1}\Bigg|_{k=k(v)}
\end{aligned}
\tag{13}
$$

and $k(v)$ is determined by

$$k(v-(2m)^{-1}k) = \omega_0(k) \tag{14}$$

which has two solutions;

$$k_\pm(v) \cong mv\{\ 1 \pm [1 - (\frac{v_c}{v})^2]^{\frac{1}{2}}\} \quad \text{for } v > v_c$$

and

$$v_c = \left(\frac{2\omega_0}{m}\right)^{\frac{1}{2}} \simeq \left(\frac{8}{\pi}\sqrt{2\lambda}\, c_0 v_F\right)^{\frac{1}{2}} \sim 1.2(c_0 v_F)^{\frac{1}{2}} \tag{15}$$

and c_0 is the acoustic phonon velocity.

For $v < v_c$ we don't have k which satisfies Eq(14), implying that for $v < v_c$ the soliton cannot emit optical phonon.

Substituting $k_\pm$ thus found into Eq(13), we obtain

$$\tau^{-1}(v) \simeq g^{-2}(2\pi\Delta)^2\omega_0 v\left[1 - \left(\frac{v_c}{v}\right)^2\right]^{-\frac{1}{2}}(1-e^{-\beta\omega_0})^{-1} \times \left[(\eta_-\operatorname{cosech}(\pi\eta_-))^2 + (\eta_+\operatorname{cosech}(\pi\eta_+))^2\right] \tag{16}$$

where $\eta_\pm = \frac{1}{2} m\xi v \left\{1 \pm \left(1 - \frac{v_c^2}{v^2}\right)^{\frac{1}{2}}\right\}$ (17)

Here we have neglected the k dependence of $\omega_0(k)$ for simplicity. Furthermore the second term in the last bracket of Eq(16) is always negligible in comparison with the first term and we will drop the second term hereafter.

Within the present approximation $\tau(v)$ is roughly proportional to $v^{-1}(1 - v_c^2/v^2)^{\frac{1}{2}}$ for $v > v_c$ which takes the maximum value at $v = \sqrt{2}\, v_c$. For solitons with $v < v_c$, the present model gives $\tau(v) = \infty$, implying that the optical phonon cannot decelerate these slow solitons. Therefore the relaxation of these slow solitons should be due to defects or other extrinsic mechanism in polyacetylene.

4. DIFFUSION CONSTANT

The diffusion constant of the soliton in the parallel direction to the $(CH)_x$ chain is obtained from

$$D_{/\!/} = \langle v^2 \tau(v) \rangle \tag{18}$$

where the bracket means the thermal average.

More explicitly it is given by

$$\begin{aligned} D_{/\!/} &= 2 \left(\frac{m\beta}{2\pi}\right)^{\frac{1}{2}} \int_{v_c}^{\infty} v^2 dv \; \tau(v) \; e^{-\frac{m}{2}\beta v^2} \\ &= 2g^2 \omega_o^{-1} \; (2\pi \; m v_F)^{-2} (1-e^{-\beta\omega_o}) \left(\frac{m\beta}{2\pi}\right)^{\frac{1}{2}} I(\alpha) \end{aligned} \tag{19}$$

where

$$I(\alpha) = \int_0^{\eta_c} d\eta \eta^{-1} [(\frac{\eta_c}{\eta})^2 - 1]^2 \sinh^2(\pi\eta) e^{-\alpha(\frac{\eta}{\eta_c} + \frac{\eta_c}{\eta})^2} \tag{20}$$

and

$$\begin{aligned} \eta_c &= \frac{1}{2} m\xi v_c \sim 5.5(c_o/v_F)^{\frac{1}{2}} \\ \alpha &= \frac{1}{8} m\beta v_c^2 = 0.18 \; c_o v_F \; v_T^{-2} \end{aligned} \tag{21}$$

and $v_T = (\beta m)^{-\frac{1}{2}}$ is the thermal velocity of the soliton. When $\alpha \lesssim 1$, where our expression for D is aplicable, $I(\alpha)$ is simplified as

$$I(\alpha) \simeq (\frac{\pi^{5/2}}{8\alpha^{3/2}} \eta_c^2 + (2\pi)^{-3} \eta_c^2 \; e^{2\pi\eta_c}) \; e^{-4\alpha} \tag{22}$$

The temperature dependence of D is controlled mainly by two factors $(1-e^{-\beta\omega_o})$ and $(m\beta)^{-1}e^{-4\alpha}$; the first factor increases rapidly as temperature decreases around $T \sim \omega_o k_B^{-1}$ then saturates to a constant value, while the second factor gives an over all T $e^{-A/T}$ dependence.

Just taking the first term in Eq(22), Eq(19) is simplified as

$$D_{/\!/} = D_o (1-e^{-\beta\omega_o}) (\frac{v_T}{v_F})^2 \; e^{-0.7 \; c_o v_F (v_T)^{-2}} \tag{23}$$

and

$$D_o = \frac{1}{32} g^2 (\omega_o v_c)^{-1} \xi^2 = \frac{\pi}{64} \omega_o (v_F/v_c) \xi^2 \tag{24}$$

For polyacetylene with $\lambda = 0.2$, Eq(24) yields $D_o \simeq 0.04 \; \mathrm{cm}^2 \mathrm{sec}^{-1} = 0.27 \times 10^{15} \; a^2 \mathrm{sec}^{-1}$, with $a = 1.2 \; A^o$

the lattice constant. Furthermore in the case of polyacetylene ω_o = 1700 K and at the room temperature Eq(23) is approximated by

$$D_{/\!/} \simeq D_o\left(\frac{T}{E_F}\right) e^{-2.8 \times 10^{-3}\left(\frac{E_F}{T}\right)} \tag{25}$$

where we have made use of an estimated values of $c_o \simeq 4 \times 10^5$ cm/sec and $v_F \simeq 10^8$ cm/sec.

It appears that Eq(25) with the estimated D_o is consistent with the spin diffusion constant measured by Nechtschein et al[4] and Holczer et al[5] for pristine polyacetylene at the room temperature. Furthermore Eq(25) predicts that D decreases with the temperature, which appears also to be consistent with the observation[5]. Certainly it is desirable to have a more detailed measurement of D, so that the predicted temperature dependence of D can be tested. On the other hand we don't think that our expression (25) will apply to the low temperature region, say T = 4K, where the other mechanism like trapping by defects will dominate the soliton relaxation in these temperature regions.

In the intermediate regime where the dopant concentration c is 1 ~ 6%, the polyacetylene is not metallic as the polyacetylene does not exhibit the Pauli susceptibility. Therefore it is possible that large electric conductivity observed in this regime is due to the motion of charged solitons. Then the parallel conductivity along the $(CH)_x$ chain is related to D by the Einstein relation as

$$\sigma = e^2T^{-1}D\ n_c \simeq e^2n_c\ D_oE_F^{-1}(1-e^{-\beta\omega_o})e^{-C\left(\frac{E_F}{T}\right)} \tag{26}$$

where n_c(~ c) is the charged soliton density. However, it should be borne in mind that the motion of charged solitons may be quite different from that of neutral solitons due to the fact the former solitons are scattered by the potentials introduced by the dopants. If it is the case, the simple relation will no longer be valid.

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