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Soliton diffusion in polyacetylene. II. Acoustic phonons

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The soliton diffusion due to the coupling to acoustic phonons in polyacetylene is analyzed theoretically within the Su, Schrieffer, and Heeger model. It is shown that in the temperature region $T \ll \frac{1}{2}\omega_0$, where ω_0 (~ 2000 K) is the optical-phonon frequency, the acoustic phonon dominates the soliton damping. Furthermore, for $T \gg T_0$, the single-phonon process dominates the soliton diffusion where $T_0 = 2mc^2$, and m and c are the soliton mass and the acoustic-phonon velocity, respectively. The one-dimensional model predicts the temperature-dependent diffusion constant $D \propto T^{1/2}$, while the three-dimensional model predicts $D \propto T^{-1/2}$. The latter temperature dependence appears to be consistent with some of the recent nuclear-magnetic-resonance experiments.

I. INTRODUCTION

In paper I of this series,[1] (which will be referred to as I), we have studied the soliton diffusion due to the optical-phonon scattering in polyacetylene. We find that the soliton diffusion constant thus calculated is consistent with that inferred from the magnetic resonance experiments at room temperature.[2,3] However, the diffusion constant due to the optical phonon increases exponentially at low temperatures, which is in contradiction to the magnetic resonance experiments.[3]

The object of this paper is to study the diffusion constant due to the acoustic-phonon scattering. The transport lifetime of the soliton is due to either the single-phonon process or the multiphonon process. We shall see in the following, contrary to the case of the optical phonon, the single-phonon process dominates the soliton diffusion for $T \gg T_0 \equiv 2mc^2$, where m is the soliton mass and c is the acoustic-phonon velocity. Putting appropriate values for m and c, we find $T_0 \sim 10$ K. Therefore, in the temperature region of experimental interest, the single-soliton process dominates the soliton diffusion. In this temperature region, the one-dimensional model predicts the soliton diffusion constant. $D \cong A(T/E_F)^{1/2}$, with $A \simeq 10$ cm^2/sec is a constant independent of T. The diffusion constant decreases as the temperature decreases, where E_F (5 eV) is the Fermi energy of the electron in polyacetylene. This temperature dependence may be consistent with that inferred from some of the magnetic resonance experiments[3] but it disagrees with the one from the other group.[4] Furthermore, the magnitude of D is by a factor of $10-10^2$ larger than that deduced experimentally. One possible way to improve the present calculation is to include the effect of three-dimensional acoustic phonons. In reality, polyacetylene usually forms a tangled fibrous matrix. Therefore, it seems to be more likely that the soliton couples with acoustic phonons which propagate in the three-dimensional space. Within this generalized model and with reasonable assumptions as to new parameters which characterize the three-dimensional phonon coupling, we find that the transport lifetime of soliton can be reduced roughly by a factor of 10. This implies also that the actual soliton diffusion is likely to be dominated by the three-dimensional phonons. The resulting diffusion constant D behaves like $(E_F/T)^{1/2}$ as the temperature decreases. This temperature dependence is also consistent with some of the recent proton spin resonance experiments.[4]

II. SINGLE-PHONON PROCESS

Since the interaction Hamiltonian between a soliton and acoustic phonon has been already derived in I, we shall consider here the transport lifetime of soliton due to the single-phonon process [see Fig. 1(a)]. The transport lifetime within the present approximation is given by

$$\tau_1^{-1}(p) = 2\pi \sum_k |V_k|^2 (1+N_k)\delta(E_p - E_{p-k} - \omega_k) \times \left[1 - \frac{p-k}{p}\right], \quad (1)$$

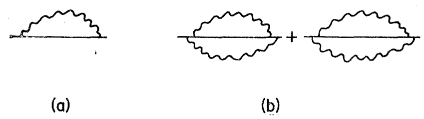

FIG. 1. Single-phonon process (a) and the multiphonon process (b) are shown. Here wavy lines are the phonon propagator and the solid line is the soliton propagator.

where

$$V_k = ig^{-1}c\Delta(2L)^{-1/2}\omega_k^{1/2}f(k) ,$$
$$\omega_k = c\mid k\mid ,\ f(k)=\pi\xi k\ \mathrm{csch}(\tfrac{1}{2}\pi\xi k) , \quad (2)$$
$$E_p = E_s + \frac{1}{2m}p^2,\ N_k=(e^{\beta\omega_k}-1)^{-1} ,$$

and m is the soliton mass and c ($\equiv \frac{1}{2}\omega_Q a$) is the acoustic sound velocity.

The sum over the phonon momentum k is replaced by integral and we obtain

$$\tau_1^{-1}(p)=\theta(v^2-c^2)\frac{2m(v-c)^2}{v^2} \times \left[\frac{c\Delta}{g}\right]^2 \mid f_0\mid^2(1+N_{2m(v-c)}) , \quad (3)$$

where $v = \mid p\mid /m$ is the velocity of the soliton and

$$f_0 \simeq f(0)=2 . \quad (4)$$

As is easily seen for $v<c$, τ_1 diverges, which implies that for solitons with velocity v less than c, the single-phonon process is not available. We shall see in Sec. III that for solitons with $v<c$, the multiphonon process provides the lifetime, which is of the same order of magnitude as Eq. (3) for $v>c$. However, the scattering rate due to the multiphonon process decreases exponentially with the soliton velocity and we can neglect the multiphonon process except in the region $v\sim c$, in the temperature region $T \gg T_0$ ($\equiv 2mc^2$). On the other hand, at lower temperatures, $T \lesssim T_0$, the multiphonon process becomes of prime importance.

We shall now consider here a possible generalization of Eq. (1) in the presence of three-dimensional phonon. At this point one may wonder if the three-dimensional phonon is consistent with the Su, Schrieffer, and Heeger (SSH) model, which is after all a one-dimensional model. Indeed in the case of the optical phonon, the one dimensionality is the essential feature of the SSH model; the three-dimensional optical phonon implies the three-dimensional dimerization order which excludes the possibility that the soliton is a low-energy excitation. On the other hand, the three-dimensional acoustic phonon can be incorporated into the SSH model, since the acoustic phonon does not disturb the one-dimensional dimerization order in the SSH model. The simplest generalization of Eq. (1) will be

$$\tau_3^{-1}(p)=2\pi d^2\sum_k \mid V_k'\mid^2(1+N_k)\,\delta(E_p-E_{p-k_1}-\omega_k) \times \left|1-\frac{p-k_1}{p}\right| \quad (5)$$

and

$$V_k' = ig^{-1}c\Delta(2V\omega_k)^{-1/2}c\mid k_1\mid f(k_1) , \quad (6)$$

where d is the average interchain distance, k_1 is the momentum component parallel to the $(CH)_x$ chain. We assume further that the phonon dispersion is given by

$$\omega_k=[c^2k_1^2+c_\perp^2(k_2^2+k_3^2)]^{1/2} , \quad (7)$$

where c is the sound velocity parallel to the chain direction and $c_\perp$ is the sound velocity perpendicular to the chain direction.

The k_2 and k_3 integrals are easily done and we find

$$\tau_3^{-1}(p)=\frac{d^2}{4\pi\mid p\mid}\left[\frac{c\Delta}{g}\right]^2\frac{c\mid f_0\mid^2}{c_\perp}\theta(v-c)I(v) , \quad (8)$$

where

$$I(v)=\int_0^{2m(v-c)}dk\,k^3(1+N_k)$$

and

$$N_k=(e^{\beta(k/2m)(2p-k)}-1)^{-1} . \quad (9)$$

The asymptotic behaviors of $I(v)$ are calculated as

$$I(v)=\begin{cases}\beta^{-1}(2m)^3\left[v^2\ln\left[\frac{v}{c}\right]-\frac{1}{2}(v-c)(3v-c)+\frac{1}{4}\beta m(v-c)^4 + \frac{1}{90}(\beta m)^2(v-c)^5(v+5c)\right], & \text{for } \beta m v^2 \ll 1 \\ 4m^4(v-c)^4+\frac{\pi^4}{15}(\beta v)^{-4}, & \text{for } \beta m v^2 \gg 1\end{cases} \quad (10)$$

which may be interpolated as

$$I(v)=\beta^{-1}(2m)^3(v-c)^3\left[\frac{1}{3v}+\tfrac{1}{2}\beta m(v-c)\right]. \tag{11}$$

Again, as in the case of the one-dimensional model, τ_3 diverges for $v<c$. Therefore, for solitons with $v<c$, the multiphonon process is indispensable to obtain a finite transport lifetime even in the three-dimensional model. We note also that we cannot take d and $c_\perp$ arbitrarily within the present model, as the available transverse phonon momentum $k_\perp=(k_2^2+k_3^2)^{1/2}$ is limited by $dk_\perp<\pi/2$. This implies other conditions like $mv^2\lesssim 4\pi c_\perp d^{-1}$ and $k^2/(2m)<4\pi c_\perp d^{-1}$. This can give the transport relaxation rate somewhat larger than the one-dimensional model.

III. MULTIPHONON PROCESS

As in the case of the optical-phonon process discussed in I, the transport relaxation time for soliton due to the multiphonon process is approximately given by[1,5]

$$\tau_M(p)^{-1}=2\pi\sum_{p'kk'}|T_{p'k',pk}|^2N_k\delta(E_p-E_{p'})\left[1-\frac{pp'}{p^2}\right], \tag{12}$$

where

$$T_{pk,p'k'}=\delta_{p+k,p'+k'}V_kV_{k'}\left[\frac{1}{E_p+\omega_k-E_{p+k}-\sigma}+\frac{1}{E_p-E_{p-k'}-\omega_{k'}-\sigma'}\right] \tag{13}$$

and

$$\sigma=-i\pi\sum_q|V_q|^2\delta(E_p-E_{p+k-q}-\omega_q+\omega_k)$$

$$\sigma'=-i\pi\sum_q|V_q|^2\delta(E_p-E_{p-k'+q}+\omega_q-\omega_{k'}), \tag{14}$$

where V_k, ω_k, and E_p have been already defined after Eq. (1). Two terms in Eq. (13) arise from the processes shown in Fig. 1(b).

Making use of the explicit form of σ and σ', we can rewrite

$$\sum_{k_1k'}|T_{pkp'k'}|^2N_k=2\pi\sum_k|V_k|^2|V_{p-p'+k}|^2N_k[\gamma_1^{-1}\delta(E_p+\omega_k-E_{p+k})+\gamma_2^{-1}\delta(E_p-E_{p'-k}-\omega_{p+k-p'})] \tag{15}$$

with

$$\gamma_1=\int dq\,|V_q|^2\delta(E_{p+k}-E_{p+k-q}-\omega_q)$$

$$=\frac{m}{|\bar p|}|V_{2(|\bar p|-mc)}|^2\theta(\bar p^2-(mc)^2)$$

and

$$\gamma_2=\frac{m}{|p_1|}[|V_{2(p_1-mc)}|^2\theta(mc-p_1)+|V_{2(p_1+mc)}|^2\theta(mc+p_1)]$$

and

$$\bar p=p+k \text{ and } p_1=p-k'. \tag{16}$$

Substituting these in Eq. (15), we find

$$\tau_M^{-1}(p)\cong 2m\left[\frac{c^2\Delta}{gv}\right]^2|f(2mc)|^2[\theta(c-v)(2c-v)N_{2m(v-c)}+\theta(c+v)(2c+v)N_{2m(v+c)}+N_{2mc}F(v)] \tag{17}$$

and

$$F(v)=\theta(v-3c)(v-2c)+\theta[-(v+3c)](-2c-v)+\theta(3c-v)\theta(v-c)(2c)^{-1}(v-c)\,|v-2c|$$
$$+\theta(3c+v)\theta(-v-c)(2c)^{-1}(-v-c)\,|v+2c|\ . \qquad (18)$$

Here we have neglected v dependences of the structure factor $f(k)$, as they introduce only small corrections of order of a few percent.

The total relaxation time, which includes the single-phonon process as well as the multiphonon process is given by (for the one-dimensional model)

$$\tau^{-1}(p)=\tau_1^{-1}(p)+\tau_M^{-1}(p)\ , \qquad (19)$$

where $\tau_1^{-1}(p)$ has been given in Eq. (3). From Eq. (18), we see that, for solitons with $v<c$, the multiphonon process provides the relaxation time, which is of the same order of magnitude as for $v>c$. On the other hand, in the temperature region $T \gtrsim T_0$, the single-phonon process dominates the soliton diffusion, since most of solitons have velocity $v>c$. A similar calculation applies also for the three-dimensional model.

IV. DIFFUSION CONSTANT

The diffusion constant of soliton is now evaluated by[1]

$$D=\langle \tau(v)v^2\rangle = \left[\frac{\beta m}{2\pi}\right]^{1/2}\int_{-\infty}^{\infty}dv\,v^2\tau e^{-1/2\beta m v^2}\ . \qquad (20)$$

Here we shall consider the one-dimensional model and the three-dimensional model separately. Furthermore, we limit ourselves in the temperature region $T \geq T_0$ for simplicity.

A. One-dimensional model

Substituting $\tau(p)$ given in Eq. (19), we obtain

$$D_1=(4m)^{-1}\left[\frac{g}{c\Delta}\right]^2\left[\frac{\beta m}{2\pi}\right]^{1/2}\times\int_c^{\infty}dv\,v^4e^{-(1/2)\beta m v^2}A(v)\ , \qquad (21)$$

where

$$A(v)\simeq[(v-c)^2(1+N_{2m\,|v-c|})+c(2c+v)N_{2m(v+c)}+\tfrac{1}{2}(2c-v)(v-c)N_{2mc}]^{-1}\ . \qquad (22)$$

Here we have neglected the contribution from solitons with $v<c$, since it is negligible when $T \geq T_0$. Further, when $T \geq T_0$, the integrand can be expanded in powers of η [$\equiv 2\beta mc^2$] and we obtain

$$D_1=\frac{\pi}{2m}\left[\frac{v_F}{c}\right]\left[\frac{\omega_0}{\Delta}\right]^2(\pi\eta)^{-1/2}e^{-1/4\eta}(1+2\eta)\ , \qquad (23)$$

where use is made of the relations[6]

$$g^2=\lambda\omega_Q^2\pi v_F$$

and

$$\omega_0^2=2\lambda\omega_Q^2 \qquad (24)$$

and ω_0 is the optical-phonon frequency of polyacetylene.[7]

Substituting typical values for polyacetylene $\omega_0/\Delta=0.25$, $c\simeq 3\times 10^5$ cm/sec, and $m=3m_e$, we find $D\simeq 0.3$ cm^2/sec for $T=300$ K, for example.

The resulting diffusion constant appears to be by a factor of $10-10^2$ larger than that inferred for soliton in polyacetylene from the magnetic resonance experiments.[2–4] Furthermore, the predicted temperature dependence $D\sim T^{1/2}$ has not been seen in any of these experiments. As we have already noted, a reasonable extension of the present model to the three-dimensional model appears to provide a somewhat larger soliton relaxation rate and smaller diffusion constant.

B. Three-dimensional model

Now inserting $\tau_3(v)$ given in Eq. (8) into Eq. (20), and ignoring the contribution from the region $v<c$, we obtain

$$D_3=\frac{3\pi c_\perp\beta}{(mcd)^2}\left[\frac{g}{c\Delta}\right]^2\int_c^{\infty}dv\frac{v^4}{(v-c)^3}e^{-(1/2)\beta m v^2}[1+\tfrac{3}{2}\beta m v(v-c)]^{-1}$$
$$\cong\frac{3\pi c_\perp\beta}{(mcd)^2}\left[\frac{g}{\Delta}\right]^2\left[\frac{\beta m}{2\pi}\right]^{1/2}I_3 \qquad (25)$$

where

$$I_3=(\beta m)^{-1}e^{-(1/4)\eta}\left[\int_0^\infty \frac{dx\, e^{-x}}{1+3x}+O(\eta^{1/2})\right]$$

$$\cong 0.3856(\beta m)^{-1}e^{(-1/4)\eta}\ . \qquad (26)$$

Here we have ignored the divergence in the integral (25), as it should be eliminated by the multiphonon relaxation, and expanded the integral in power of η. To the lowest order in η, we obtain

$$D_3=0.289\pi^{1/2}\frac{1}{m}(mcd)^{-2}\left[\frac{\omega_0}{\Delta}\right]^2 \times\frac{c_\perp v_F}{c^2}\eta^{1/2}e^{-(1/4)\eta}\ . \qquad (27)$$

The above diffusion constant is somewhat smaller than that for the one-dimensional model. Furthermore, the three-dimensional model predicts $D\propto T^{-1/2}$, which appears to have been observed on some of the recent magnetic resonance experiments.[4]

V. CONCLUDING REMARKS

We have studied theoretically the soliton diffusion in polyacetylene within SSH model. The diffusion constant of soliton may be decomposed into two contributions

$$D^{-1}=D_a^{-1}+D_0^{-1} \qquad (28)$$

and

$$D_a=D_1\ (\text{or } D_3)$$

$$D_0=D_0'(e^{\beta\omega_0}-1)\ , \qquad (29)$$

$$D_0'\sim 10^{-2}\ \text{cm}^2/\text{sec}\ ,$$

where D_a is the diffusion constant calculated in the present paper, while D_0 is due to the optical phonon as calculated in I. At higher temperatures, $T>\frac{1}{4}\omega_0$, the soliton diffusion is dominated by D_0. As temperature is decreased, the acoustic-phonon process becomes more and more important. Then in the intermediate-temperature region $T_0\lesssim T<\frac{1}{4}\omega_0$, the one-dimensional model predicts $D\propto T^{1/2}$ while the three-dimensional model predicts $D\propto T^{-1/2}$.

The latter behavior appears to be seen in some of the recent proton spin resonance experiments.[4] The absolute magnitude of the predicted diffusion constant, however, appears to be still somewhat larger (say by a factor of 10) than that inferred from experiments. In much lower temperature $T\lesssim T_0$, the present model predicts that the diffusion constant diverges like $D\propto e^{\eta}$, implying that the other mechanism which is not considered here may become of importance. In any event, it is of great interest to study the soliton diffusion constant below $T=1$ K.

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