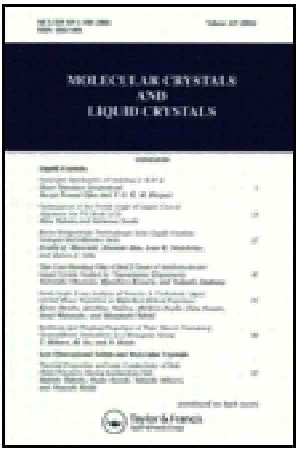

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Han-Yong Choi [a b] & Esther M. Conwell [a b]
[a] Xerox Webster Research Center, 0114-40D, Webster, NY, 14580
[b] Science and Technology Center for Photoinduced Charge Transfer, University of Rochester, Rochester, NY, 14627

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INTERCHAIN POLARON MOBILITY IN POLYACETYLENE AT FINITE TEMPERATURE

HAN-YONG CHOI AND ESTHER M. CONWELL
Xerox Webster Research Center, 0114-40D, Webster, NY 14580 and
Science and Technology Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, NY 14627

Abstract We study the interchain hopping of an anisotropic polaron in a quasi one-dimensional electron-lattice coupled system at finite temperature. By calculating overlap between wave functions before and after a polaron hop, we obtain the temperature dependence of polaron bandwidth and mobility due to interchain hopping. Formulation of this interchain dynamics is closely related to that of intrachain dynamics of small polarons obtained by Holstein in a molecular crystal model. Our results are compared with photocurrent measurements reported by Tubino *et al.*

Keywords: Band motion, hopping, Franck-Condon factor, phonons, multi-phonon scattering

It is well known that, in a semiconductor, an electron (or hole) may lower its energy by locally distorting the underlying crystal lattice. Due to the electron-phonon interaction, such a lattice deformation can provide an attractive potential well in which the electron forms a bound state. This entity, the self-trapped electron, together with its induced lattice distortion, is commonly referred to as a polaron.[1] The extension of the polaron is determined by the balance between the gain in band energy and the cost in elastic energy due to the lattice distortion. In quasi one-dimensional (Q1d) systems, polarons are quite different from those in 3d systems in that although their extension is small (~ the lattice constant) in the perpendicular direction, similar to the 3d small polaron, it can be quite large in the chain direction. This might be expected to complicate the polaron problem in Q1d. We will show, however, that the interchain dynamics can be formulated in a similar way to the intrachain dynamics for the small polaron.

Some thirty years ago, Holstein wrote a pioneering paper in which he defined a simple 1d electron phonon coupled system, called molecular crystal model (MCM), and solved for the intrachain transition probability and mobility as a function of temperature.[2] He found that, in the low temperature limit, the polaron maintains its phase coherence throughout the transition (called a diagonal transition) and thus forms a polaron band. As the temperature is increased, however, the phonon-assisted hopping (non-diagonal transition) becomes more important. In this paper, we will show that Holstein's treatment can be extended to study interchain transport in a Q1d system. The interchain problem of a Q1d system was first studied by Jeyadev and Schrieffer (JS).[3] They calculated the Frank-Condon (FC) factor (the overlap of wave functions before and after a polaron hop) at zero temperature to find interchain polaron bandwidth of a Q1d conducting polymer, polyacetylene, $(CH)_x$. In $(CH)_x$, both polarons and solitons are possible excitations of the system, and both of them are involved in intrachain dynamics. In interchain dynamics, however, only polarons can make a contribution to physical quantities such as conductivity, because individual solitons can not hop between neighboring chains. Therefore, interchain conductivity (or mobility) would be the most appropriate quantity to study if one wants to separate polarons from solitons. This provides additional motivation for our study of the interchain polaron dynamics. Intrachain dynamics of solitons and polarons in $(CH)_x$ has been studied by Conwell and Jeyadev.[4] They have calculated transport properties such as diffusivity and photocurrent of the polymer and found that the polarons show band type motion along the chain direction. In this paper, we will extend the work of JS to finite temperatures and calculate the interchain polaron mobility as a function of temperature. It will be seen that the formulation of interchain dynamics is very similar to that of intrachain dynamics of MCM developed by Holstein.

In the following, we will work with the Su–Schrieffer–Heeger (SSH) Hamiltonian of $(CH)_x$,[5]

$$H_{SSH} = \Sigma_n - [t_{\parallel} - \alpha(U_{n+1} - U_n)](C_n^{\dagger} C_{n+1} C_{n+1}^{\dagger} C_n) + (K/2)(U_{n+1} - U_n)^2, \quad (1)$$

with standard notation. Equation (1) will be taken to describe the intrachain interactions. The interchain coupling will be taken in the same form as JS.

$$H_{inter} = -t_{\perp}\Sigma_{<l,l'>}\Sigma_n(C_{l,n}^{\dagger}C_{l',n} + C_{l',n}^{\dagger}C_{l,n}), \qquad (2)$$

where $t_{\perp}$ is the hopping integral between neighboring chains, $<l,l'>$ means that the summation is over the nearest neighbor chains, the indices l and n refer to chains and sites on the chains, respectively. The Hamiltonian of Eq. (1) has been studied intensively over the last decade, and soliton and polaron solutions are found to exist in this model.[6]

We wish to calculate the thermally averaged interchain transition probability of a polaron, given as follows:

$$w = (2\pi/\hbar)\Sigma_{f,i}P(E_i)|<\Psi_f|H_{inter}|\Psi_i>|^2\,\delta(E_i - E_f), \qquad (3)$$

where $\beta = 1/k_BT$, Ψ_i and Ψ_f, wave functions for initial and final states, respectively, are the eigenfunctions of the unperturbed Hamiltonian of Eq. (1) with corresponding energies E_i and E_f. The summation over initial states is weighted by the probability $P(E_i)$ that the state E_i is occupied, which is given by the Boltzmann factor, and the delta function ensures energy conservation. Without loss of generality, we can choose two nearest neighboring chains labeled by l and l' between which a polaron makes a hop. Then the initial and final wave functions can be taken as

$$|\Psi_i> \;=\; |\Psi_{l,p,m}>\Pi_{j\neq l}|\Psi_{j,d,n}>, \qquad (4.a)$$

$$|\Psi_f> \;=\; |\Psi_{l',p,m'}>\Pi_{j\neq l'}|\Psi_{j,d,n'}>, \qquad (4.b)$$

where the subscripts p and d stand for polaron and dimerization, respectively, so that $|\Psi_{l,p,m}>$ represents a wave function of the l-th chain containing a polaron, and m,n,m',n' denote the occupation numbers of phonon states, respectively. Within the Born-Oppenheimer approximation, we take a wave function describing a particular state of a chain as a product of the electron (ϕ) and phonon (χ) parts as follows.

$$|\Psi_{l,p,m}> = |\phi_{l,p}>|\chi_{l,p,m}> = |\phi_{l,p}>\Pi_k|\chi_{l,p,mk}>, \qquad (5)$$

where k is the wavenumber labeling phonon modes, m_k the occupation number of the k-th phonon mode, and $\chi_{l,p,m}$ is the harmonic oscillator wave function of order m_k. Because $|\Psi_{l,p,m}>$ is the eigenfunction of an isolated chain it does not depend on the chain index l, so that we will drop the chain indices l and l' for brevity in the following.

Let us first calculate the Frank-Condon (FC) factor and the temperature dependence of the polaron bandwidth in the low temperature limit, where the description in terms of a polaron band is more relevant. The thermally averaged bandwidth is given by

$$W(T) = -4\Sigma_i \exp(-\beta E_i) < \Psi_f | H_{inter} | \Psi_i > / \Sigma_i \exp(-\beta E_i) \tag{6}$$

We have the factor of 4 because the bandwidth W is equal to 4 times the hopping integral in tight-binding theory. From Eqs. (2), (4) and (5), with the normalization condition $<\phi_p|\phi_p> = <\phi_d|\phi_d> = 1$, we find

$$< \Psi_f | H_{inter} | \Psi_i > = -t_\perp \Pi_{k,q} < \chi_{l,p,m_k} | \chi_{l,d,m_k} > < \chi_{l',d,n_q} | \chi_{l',p,n_q} >$$

$$= -t_\perp \Pi_{k,q} L_{m_k}((1/2)\underline{\Delta}_k{}^2) \exp(-(1/4)\underline{\Delta}_k{}^2)\, L_{n_q}((1/2)\underline{\Delta}_q{}^2) \exp(-(1/4)\underline{\Delta}_q{}^2), \tag{7}$$

where L_{m_k} is the Laguerre polynomial, and

$$\underline{\Delta}_k \equiv (M\varepsilon_k/\hbar^2)^{1/2} \underline{\delta}_k, \tag{8}$$

where M is the mass of a CH group, $\varepsilon_k = \hbar\omega_k$, with ω_k the phonon frequency, and $\underline{\delta}_k$ is the transformation of δ_i onto a normal mode coordinate, δ_i being the difference in lattice distortions between polaron and dimerized configurations. After the summation over m_k and n_q, and using the relation

$$(1-z)\Sigma_{n=0} z^n L_n(x) = \exp\{xz/(z-1)\} \tag{9}$$

Eq. (6) is reduced to

$$W(T) = 4t_\perp \exp(-S_T), \tag{10}$$

where

$$S_T = \Sigma_k \underline{\Delta}_k{}^2 (n_k + 1/2) = (1/2)\, \Sigma_k \underline{\Delta}_k{}^2 \coth(\beta\varepsilon_k/2), \tag{11}$$

where n_k is the average occupation number of ε_k state given by $n_k = 1/[\exp(\beta\varepsilon_k) - 1]$. The FC factor is related to the zero temperature value W(0) of the bandwidth as

$$W(0) = 4t_\perp FC, \tag{12}$$

where $FC = \exp\{-\ (1/2)\ \Sigma_k \underline{\Delta_k}^2\}$. (13)

In order to find the transformation which maps δ_i onto $\underline{\delta_k}$, we have calculated the dynamical matrices employing the method formulated by Terai and Ono.[7] Our calculations are in excellent agreement with the results reported previously. For a polaron, the dispersion relation is essentially the same as that for the dimerized case except that there appear 7 localized modes between the optical and acoustic branches. The fact that the dynamical matrices of dimerized and polaron chains are different implies that the normal coordinates are not the same for these two cases. In the following calculations, however, we will neglect the differences between them, and use the same normal coordinates for the polaron and dimerized cases. This approximation is reasonable because the phonon dispersion relations are the same apart from the localized modes. But this approximation raises an uncertainty as to which dynamical matrix to use in the normal mode transformation. As we will see, the results (for example, the FC factor) are almost the same whether we use the dynamical matrix of the chain with a polaron or that of the dimerized chain, which rationalizes above approximation. The FC factor and zero temperature value of the polaron bandwidth W(0) of Eqs. (12) and (13) were calculated by JS. They found that the FC factor and W(0) are about 0.1 and 0.03 eV, respectively. We take parameter values appropriate for polyacetylene such that $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2 and $4t_\perp = 0.3$ eV. The FC factor is found to be 0.084 and 0.088 with dynamical matrices of a chain with a polaron and of a dimerized chain, respectively. These values are a little bit smaller than the JS value. We also calculated the temperature dependence of the polaron bandwidth given by Eq. (10) and found that the band, although it decreases with temperature, does not do so rapidly, which is quite different from the small polaron theory of Holstein.

The transition rate w is calculated in a similar way to the bandwidth

$$w = (2\pi/\hbar)t_{\perp}{}^2\Sigma_{m,n,m',n'}\Pi_{k,q}\exp(-\beta\varepsilon_{mk})\exp(-\beta\varepsilon_{nq})\, 2\sinh(\beta\varepsilon_k/2)$$

$$\times 2\sinh(\beta\varepsilon_q/2)|<\chi_{p,m}\chi_{d,n}|\chi_{p,m'}\chi_{d,n'}>|^2\, \delta(E_f - E_i), \tag{14}$$

where $\varepsilon_{mk} = \varepsilon_k(m_k + 1/2)$. Writing

$$\delta(E_f - E_i) = (1/2\pi\hbar)\ell im_{t\to\infty} \int_{-t}^{+t} dt \exp\{(i/\hbar)\Sigma_{k,q}(\varepsilon_{mk} + \varepsilon_{nq} - \varepsilon_{m'q} - \varepsilon_{n'k})\, t\}, \tag{15}$$

we finally have

$$w = (t_{\perp}/\hbar)^2 \int dt\, \Gamma^2, \tag{16}$$

where

$$\Gamma \equiv \Pi_k\Sigma_{m_k,n'_k} \exp[-(\beta\text{-}it/\hbar\varepsilon_k(m_k + 1/2)]\exp[i\omega_k t(n'_k + 1/2)]$$

$$\times\ 2\sinh(\beta\varepsilon_k/2)|<\chi_{p,m_k}|\chi_{d,n'_k}>|^2 \tag{17}$$

Before calculating the transition rate w with Eqs. (16) and (17), we will first calculate w_{diag} including only those cases where phonon occupation numbers do not change during a hop. Then,

$$\Gamma \equiv \Pi_k\Sigma_{m_k}\exp[-\beta\varepsilon_k(m_k + 1/2)]\ 2\sinh(\beta\varepsilon_k/2)\ |<\chi_{p,m_k}|\chi_{d,m_k}>|^2. \tag{18}$$

Substituting Eq. (18) into Eq. (16), and using the relation

$$(1 - z)\Sigma_{n=0}\, z^n\{L_n(x)\}^2 = \exp\{2xz/(z-1)\}I_0\{2x\sqrt{z/(1-z)}\}, \tag{19}$$

for the summation over m_k, we obtain

$$w_{diag} = (t_{\perp}/\hbar)^2 \int dt \exp(-2S_T)\exp\{2\Sigma_k \ln[I_0\{(\underline{\Delta_k}^2[n_k(n_k + 1)]^{1/2}\}]\} \tag{20}$$

where I_0 is the modified Bessel function. Because $\ln I_0(x) \approx x^2/4$, the exponent of Eq. (20) vanishes as 1/N in the thermodynamic limit. Therefore, we have

$$w_{\mathrm{diag}} = (t_{\perp}/\hbar)^2 \int dt \exp(-2S_T), \tag{21}$$

which has the same form as the small polaron theory of Holstein.

Now we include non-diagonal contributions to the transition rate as well as diagonal ones. Equation (17) was evaluated by O'Rourke[8] previously in a problem of thermal ionization in polar crystals to give

$$\Gamma^2 = \exp\{-\Sigma_k \underline{\Delta_k}^2[\coth(\beta\varepsilon_k/2) - \mathrm{csch}(\beta\varepsilon_k/2)\cos(\omega_k t - \phi)]\}, \tag{22}$$

where $\cos\phi = \cosh(\beta\varepsilon_k/2)$. (23)

The total transition rate can be rewritten as follows by substituting Eqs. (22) and (23) into Eq. (16).

$$w_{\mathrm{tot}} = (t_{\perp}/\hbar)^2 \int dt \exp\{-\Sigma_k \underline{\Delta_k}^2[\coth(\beta\varepsilon_k/2)(1-\cos\omega_k t) - i\sin\omega_k t]\}. \tag{24}$$

The transition rate due to the multi-phonon scattering of the polaron, w_S, is obtained by subtracting diagonal rate w_{diag} given by Eq. (21) from w_{tot} of Eq. (24).

$$w_S = (t_{\perp}/\hbar)^2 \exp(-2S_T) \int dt[\exp\{\Sigma_k \Delta_k^2 \mathrm{csch}(\beta\varepsilon_k/2)\cos(\omega_k t)\} - 1], \tag{25}$$

in the same form as Holstein's small polaron problem. Detailed derivation of Eq. (25) from (24) is given by Holstein. In the low temperature limit, in which the exponent of $\cos\omega_k t$ is small, we obtain

$$w_S = (t_{\perp}/\hbar)^2 \exp(-2S_T)\{F(0) + (1/4)\Sigma_k F(k)^2\}. \tag{26.a}$$

where $F(k) \equiv \underline{\Delta_k}^2 \mathrm{csch}(\beta\varepsilon_k/2)$. (26.b)

This expression will be used later when we consider the transport properties of the system in the low temperature regime. In the opposite limit, in which the exponent of $\cos\omega_k t$ is large, the scattering due to the multi-phonon process becomes dominant, and Eq. (25) can easily be evaluated with the method of steepest descents.

$$w_S = (t_\perp/\hbar)^2 \exp(-2S_T)\exp\{\Sigma_k \Delta_k{}^2 \operatorname{csch}(\beta\varepsilon_k/2)\}$$

$$\times \{\Sigma_k \Delta_k{}^2 \omega_k{}^2 \operatorname{csch}(\beta\varepsilon_k/2)/2\pi\}^{-1/2}. \tag{27}$$

Present theory can be applied to study the transport properties. We will focus on the mobility, μ, which is related to the diffusivity, D, through the Einstein relation

$$\mu = eD/k_B T. \tag{28}$$

We can define the "transition" temperature T_t at which the mean lifetime of the localized state,

$$\tau_p = 1/(2w_S) \tag{29}$$

is equal to the mean polaron bandwidth. T_t is to be considered as defining the boundary between the two regions of high and low temperature, in which the random site jump and band descriptions of polaron motion are respectively valid. We find T_t is about 0.05 eV or 600°K in polyacetylene. For $T > T_t$, the diffusivity is given by

$$D = a^2 w_S, \tag{30}$$

where a is the interchain spacing and w_S is given by Eq. (27). And for $T < T_t$, we have

$$D = \langle v^2 \tau_p \rangle = 2(t_\perp/\hbar)^2 a^2 \tau_p \exp(-2S_T), \tag{31}$$

where τ_p is given by Eqs. (26) and (29). From Eqs. (26), (29) and (30), we can see that the lifetime of localized state τ_p becomes infinite as the temperature is reduced because w_S vanishes in the zero temperature limit. Therefore, the diffusivity D diverges in the zero temperature limit as expected. This divergence will be removed, however, if we include defect scattering. It is interesting to compare the transverse diffusivity $D_\parallel$ with the longitudinal value, $D_\perp$. At T = 300°K, we obtain $D_\perp \approx 0.005$ cm²/sec. $D_\parallel$ for solitons is determined to be about 0.04 cm²/sec from the experimental data.[9] The mobility, μ, calculated with Eqs. (28), (30) and (31) is plotted in Fig. 1.

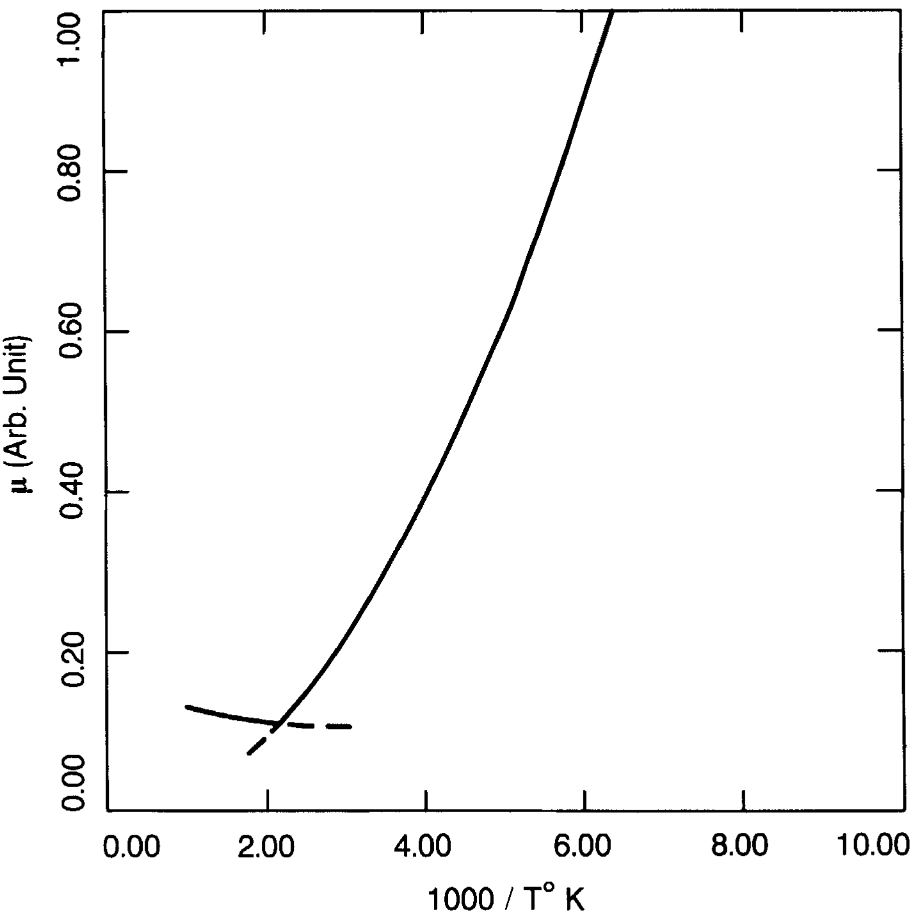

FIGURE 1 Mobility as a function of inverse temperature. Curve a (b) is obtained from Einstein relation of Eq. (28) with the high (low) temperature expression of diffusivity given by Eq. (30) (Eq.(31)).

An appropriate experiment to compare with is the photocurrent measurement with an electric field applied perpendicular to the chain direction reported by Tubino *et al.*[10] It shows temperature independent (flat) behavior below 150°K. This indicates that other scattering mechanisms are certainly more important than phonons below 150°K. As the temperature is increased, the photocurrent is observed to increase in agreement with our calculation. Even though the slope of increase is steeper than our calculation, we believe that the increase in μ can be attributed to the shift from band motion to hopping.

In conclusion, we have calculated the transition rate and mobility of a polaron as a function of temperature. We have extended Holstein's treatment of MCM to Q1d polarons and also the calculation by JS to finite temperature. Despite quite different underlying physics between interchain dynamics and the Holstein's small polaron problem, it is shown that the interchain dynamics can be formulated in a similar way as Holstein's small polaron. This is because in both problems we are essentially calculating the overlap of harmonic oscillator wave functions. Present calculation can further be improved by including the transverse phonons, localized vibrational modes and defect scattering. Research in this direction will be very important and interesting.

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