Mobility of kinks and polarons in conjugated polymers

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The phonon-limited mobility of kinks and polarons in conducting polymers due to scattering from acoustic phonons is investigated. The effect of symmetry-breaking interactions is discussed taking into account the existence of a finite maximal speed of these excitations. A striking difference of the transport coefficients depending on the charge of the excitations is found.

I. INTRODUCTION

The original phenomenological model for conjugated polymers by Su, Schrieffer, and Heeger[1] has brought much insight into the static and dynamical properties of these substances (for a recent extensive review on experimental and theoretical aspects see Ref. 2). Besides ESR and NMR experiments, the optical properties were especially studied in detail since they are accessible experimentally with great accuracy. The transport properties of nonlinear excitations, e.g., the temperature dependence of the mobility of kinks and polarons, have been investigated to a much smaller extent; in addition, the theoretical results are discussed controversially.[3–9] The diffusion of solitons may play an important role in the motion of photoexcitations, and may be crucial in the interpretation of ESR and NMR data.

The original model with its special electron-phonon coupling is highly symmetric, and in recent years there is a growing interest in symmetry-breaking effects.[10–12] One of these symmetries, the so-called electron-hole or charge-conjugation symmetry (CCS), may be broken by different mechanisms like additional electron-phonon couplings or electron-electron interaction. In recent investigations it was found that a relevant electron-phonon coupling has a drastic effect on the optical transition matrix elements. As an effect the energy level of the excitations is shifted, and, more importantly, oscillator strengths between different transitions are redistributed.[12] Consequently, it was found that optical experiments can be explained satisfactorily.

Motivated by this success, it is natural to ask whether these symmetry-breaking contributions may also influence the transport properties of nonlinear excitations.

In the following we calculate the scattering of solitons, polarons, and bipolarons with acoustic phonons and determine the temperature dependence by a method similar to that discussed by Conwell.[13] The method of collective coordinates gives the same interaction Hamiltonian.[7,14] The calculations were done by assuming "relativistic" motion of the nonlinear excitations. Since the corresponding limiting velocities are not well known experimentally, we also discuss the dependence of the diffusion constant on these parameters. One interesting result of our investigation is the fact that the diffusion constant depends quite critically on the charge of the excitation, and this may give hints to further experimental investigations.

In Sec. II we discuss two different types of interaction in the continuum approximation.[15] These Hamiltonians are used to calculate transition matrix elements. We employ the full relativistic approach similar to that by Jeyadev and Conwell[8,9] giving rise to a mass of the nonlinear excitations which increases with their velocity. In Sec. III various results are discussed, especially the charge dependence of the mobility. An appendix is included, giving details of the analytical calculations.

II. INTERACTIONS AND MOBILITIES

We start with the simplest model of conjugated polymers, the Su-Schrieffer-Heeger (SSH) model given by[1]

$$H^{\mathrm{SSH}}=-\sum_{n,s}[t_0-\alpha(u_{n+1}-u_n)](c_{ns}^{\dagger}c_{n+1s}+\mathrm{H.c.})+\tfrac{1}{2}K\sum_n(u_{n+1}-u_n)^2 . \quad (1)$$

Here the first term describes the (displacement-dependent) hopping of the π electrons of the system, and the second term the elastic energy associated with the σ-bond compression of the underlying lattice. We consider two different CCS-breaking terms which contain a coupling between π electrons and the lattice, namely

$$H^{\beta}=\beta\alpha^2\sum_{n,s}[(u_{n+1}-u_n)-(u_n-u_{n-1})]^2c_{ns}^{\dagger}c_{ns} , \quad (2)$$

$$H^{\gamma}=-\sum_{n,s}[t_2-\gamma\alpha(u_{n+2}-u_n)](c_{n+2s}^{\dagger}c_{ns}+\mathrm{H.c.}) . \quad (3)$$

The first term, H^{β}, gives an additional contribution to the elastic energy of the lattice depending on the π-electron density on each site and has been used to explain details in the optical-absorption spectra of (bi)polarons in different conjugated polymers.[12] The second term, H^{γ}, describes a next-nearest-neighbor hopping used to explain photoluminescence experiments in cis-$(CH)_x$.[10]

In the following we use the Takayama–Lin-Liu–Maki (TLM) continuum limit[15] of the Hamiltonians (1)–(3). Since the dominant scattering mechanism is the one-acoustic-phonon absorption and emission,[8,9] we are only interested in terms coupling the π-electron field $\psi_s(x)$ to

the acoustic-phonon field $\phi(x)$, which is introduced through $u_n=(4\alpha)^{-1}[(-1)^n\Delta(x)+\phi(x)]$, $x=na$. Here the first term corresponds to the $q\approx 2k_F$ component of the lattice distortion, whereas the latter represents the $q\approx 0$ contribution.) In the spirit of the original TLM model, we have neglected the quantum fluctuations of the order parameter $\Delta(x)$. The term for the TLM model has been derived by Maki,[4]

$$H_{\rm int}^{\rm TLM}=i\frac{a^2}{4}\sum_s\int dx\,\phi'(x)[\psi_s^\dagger(x)\sigma_3\overleftrightarrow{\partial}_x\psi_s(x)]\ . \tag{4}$$

The corresponding terms for the CCS-breaking models are[10,11]

$$H_{\rm int}^{\beta}=-\frac{a^2}{2}\beta\sum_s\int dx\,\Delta(x)\phi''(x)\psi_s^\dagger(x)\sigma_2\psi_s(x)\ , \tag{5}$$

$$H_{\rm int}^{\gamma}=-a\gamma\sum_s\int dx\,\phi'(x)\psi_s^\dagger(x)1\psi_s(x)\ . \tag{6}$$

Note that the contribution of the next-nearest-neighbor hopping term is of order a and not of a^2 as the TLM and β term.

Equations (4)–(6) are evaluated with the unperturbed wave functions for the kinks and polarons, respectively. The explicit form is given in the Appendix. Here we note that in contrast to the pure TLM case the CCS-breaking contributions are proportional to the charge of the excitation.

In calculating the mobility μ as function of the temperature T, we proceed in the relaxation-time approach for solving the Boltzmann equation as proposed by Conwell.[13] The transition matrix element $M_{kk'}$ for a scattering of a kink or polaron from a state with momentum k to a state with k' is given by

$$M_{kk'}=\left\langle k'N'(q)\left|\sum_{\alpha=\rm TLM,\beta,\gamma}H_{\rm int}^{\alpha}\right|kN(q)\right\rangle\ , \tag{7}$$

where $N(q)$ and $N'(q)$ are the initial and final numbers of acoustic phonons with wave vector q. The calculation of $M_{kk'}$ for the various interaction terms is sketched in the Appendix. The following steps in the calculation of $\mu(T)$ are analogous to the calculations of Jeyadev and Conwell.[8,9] The scattering probability is given by

$$S(k\rightarrow k')=\frac{2\pi}{\hbar}|M_{kk'}|^2\delta(E_{k'}-E_k\mp\hbar\omega_q)\ , \tag{8}$$

with the dispersion $\omega_q=v_s|q|$ (where v_s is the velocity of sound) and the phenomenological dispersion relation (cf. Refs. 8 and 9)

$$E_k=(\hbar^2c^2k^2+m_0^2c^4)^{1/2}+E_{p,k}-m_0c^2 \tag{9}$$

for the energy of a kink or polaron, respectively. Here $E_{p,k}$ is the creation energy of a kink or polaron with rest mass m_0. The maximum propagation velocity c of kinks and polarons is given by $c\simeq 2.6v_s$ for kinks (see Ref. 16) and for polarons by

$$c=c(r)=2r(3-2r^2)v_s \tag{10}$$

[r being the parameter characterizing the structure of a polaron (cf. Appendix)]. This last formula has been derived by Pesz[17] using the fact that the polaron amplitude $\Delta(x-ct)$ has just the same form as the one-soliton solution of a modified Korteweg–de Vries (mKdV) equation. Since this is only a crude approximation to the maximum velocity which has to be determined from the full dynamics within the lattice model, we have also used different values of c in order to show the dependence of our results on this parameter (cf. Sec. III).

The relaxation time $\tau(k)$ for a fixed k value is given by

$$\frac{1}{\tau(k)}=\frac{L}{2\pi}\int dk'\,S(k\rightarrow k')\ , \tag{11}$$

and the mobility $\mu(T)$ follows from

$$\mu(T)=\frac{e}{\hbar^2}\frac{1}{k_BT}\frac{\int dk\,\tau(k)(\nabla_kE_k)^2e^{-E_k/k_BT}}{\int dk\,e^{-E_k/k_BT}} \tag{12}$$

assuming Maxwell distribution of excitations. The corresponding diffusion coefficient $D(T)$ is calculated from the Einstein relation

$$D(T)=k_BT\mu(T)/|e|\ . \tag{13}$$

Two concluding remarks are in order.

(i) A simple consideration shows that the inclusion of CCS-breaking terms may result in a dramatic change of the diffusion coefficient (or mobility) of differently charged kink excitations. It is shown in the Appendix that the interaction Hamiltonians $H_{\rm int}^{K}$ of the TLM and γ models are of the same functional form. The ratio of the prefactors is given by

$$H_{\rm int}^{K,\gamma}/H_{\rm int}^{K,\rm TLM}=\frac{8(1-n)\gamma\alpha^2}{\Delta_0K} \tag{14}$$

and is of order 1 for charged kinks (e.g., $n=0$ or 2) and an estimated value[10] of $\gamma=0.15$ (with the SSH parameters $\alpha=4.1$ eV/Å, $K=21$ eV/Å^2, and $\Delta_0=0.8$ eV). This directly results in a ratio for the diffusion coefficients of differently charged kinks $S^{\pm}$ of

$$D(S^+)/D(S^-)\cong\left[\frac{1-8\gamma}{1+8\gamma}\right]^2 \tag{15}$$

(with $a^2/\Delta_0K\cong 1$) for the TLM model, extended with the γ term. Consequently, the diffusion (or mobility) of positively charged kinks is very much suppressed compared with the negatively charged species (cf. Sec. III).

(ii) For the (bi)polarons the CCS-breaking interactions have two effects on the mobility. First, there are new interaction terms $H_{\rm int}^{\beta}$ and $H_{\rm int}^{\gamma}$. Secondly, the CCS-breaking terms may change the polaron parameter r considerably,[12] and this clearly influences the maximum velocity $c(r)$ in (10) and the (bi)polaron mass[18]

$$m_0=m_0(r)=2m_{\rm kink}r^3\left[1-3\frac{1-r^2}{r^2}\left[\frac{\operatorname{artanh}(r)}{r}-1\right]\right]\ . \tag{16}$$

(Bi)polarons may become very massive in CCS-breaking models, a situation discussed recently in connection with polyaniline.[19]

III. RESULTS AND DISCUSSION

In Figs. 1 and 2 the intrachain diffusion constant $D(T)$ and the corresponding mobility $\mu(T)$ for both hole and electron polarons are shown using parameters appropriate for *trans*-polyacetylene. The inclusion of CCS-breaking interactions results in a reduction of both quantities compared to the TLM case studied before. In addition, a significant splitting for positively and negatively charged excitations is seen. The strong increase of the mobility $\mu(T)$ at lower temperatures (cf. Fig. 2) indicates that the one-phonon scattering process considered here becomes quite ineffective, and, consequently, different mechanisms such as trapping and/or scattering from defects determine the transport properties of the nonlinear excitations along the chain in this temperature range.

As can be seen in Fig. 1 the maximum in the diffusion coefficient $D(T)$ is shifted from $T \simeq 85$ K (TLM interaction) to higher temperatures by the β and γ interactions. This is a consequence of the effects of these CCS-breaking mechanisms on the mass of a polaron: it is shown in Ref. 12 that the inclusion of the β term strongly influences the value of the parameter r. According to the expression (16), this leads for r values greater than the TLM value $r=1/\sqrt{2}$ to an increase of the polaron (rest) mass. The temperature at which $D(T)$ exhibits a maximum is proportional to this mass resulting in the observed shift to higher temperatures.

In contrast to polarons the splitting discussed before becomes much more pronounced when bipolarons and kinks are considered (cf. Figs. 3–5). Furthermore, we now want to study the influence of the two CCS-breaking interactions on $\mu(T)$ separately. The inclusion of the next-nearest-neighbor hopping γ leads to a strong increase (decrease) of the mobility for positively (negatively) charged bipolarons. We also observe that the effects of the β and γ terms are opposite with respect to the TLM behavior, resulting in a strong competition between these two CCS-breaking interactions. This can be understood from the different sign of the corresponding coupling constant η (cf. Appendix). In spite of this difference the value of the mobility at 300 K differs by an order of magnitude for differently charged bipolarons for finite values of β and γ.

The strong enhancement of the mobility for negatively charged kinks as seen in Fig. 5 has been discussed and already explained in the previous section.

In Fig. 6, the influence of the maximum velocity c on the mobility $\mu(T)$ is shown for various values of c (in units of the sound velocity v_s). The Newtonian limit corresponds to $c \to \infty$. As discussed at length by Jeyadev and Conwell,[8,9] this limiting velocity becomes comparable to the thermal velocity at room temperature, and, thus, the effects of a varying mass cannot be ignored. Note that the resulting lowering of the mobility is not as strong with CCS-breaking interactions as compared to the TLM (deformation-potential) model (cf. Fig. 2 of Ref. 8).

In conclusion, we have demonstrated that small CCS-breaking terms drastically alter the mobility of charged nonlinear excitations in conducting polymers. These

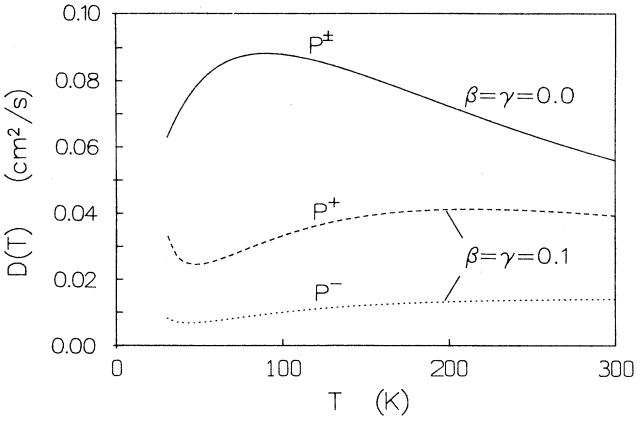

FIG. 1. Diffusion constant D as function of temperature T for differently charged polarons $P^{\pm}$. Solid line, TLM interaction with parameters appropriate for polyacetylene; dashed lines, with inclusion of symmetry-breaking interactions $\beta=\gamma=0.1$ (cf. text).

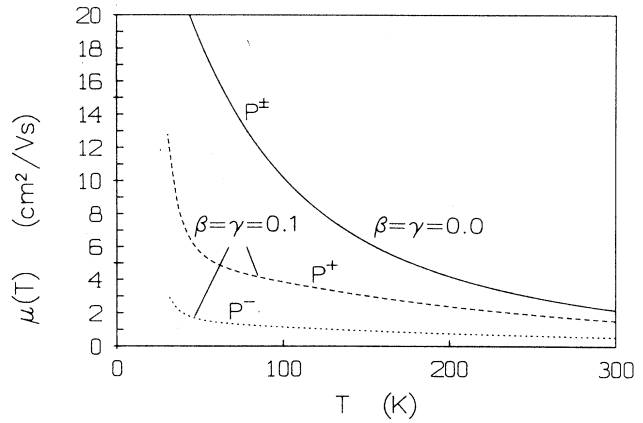

FIG. 2. Mobility μ as function of temperature T for differently charged polarons $P^{\pm}$; lines as in Fig. 1.

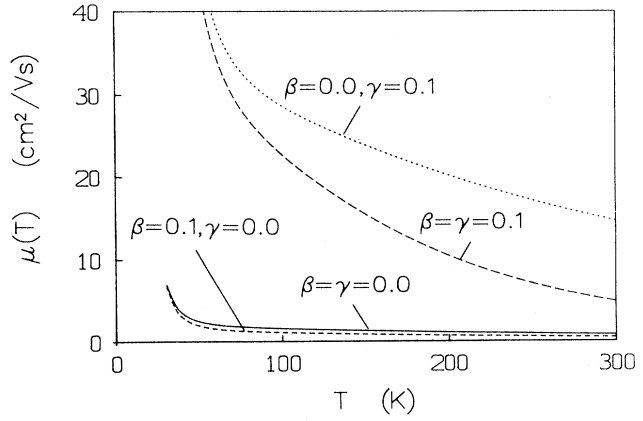

FIG. 3. Mobility μ as function of temperature T for positively charged bipolarons. The different lines correspond to different choices of interaction strengths as indicated (cf. text). TLM: absence of symmetry-breaking interactions.

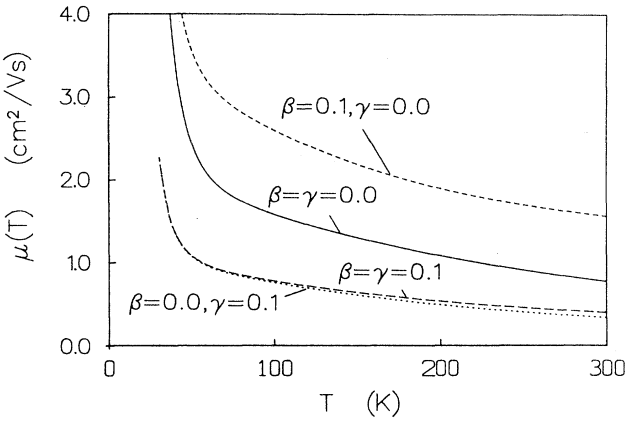

FIG. 4. Mobility μ as function of temperature T for negatively charged bipolarons; lines as in Fig. 3.

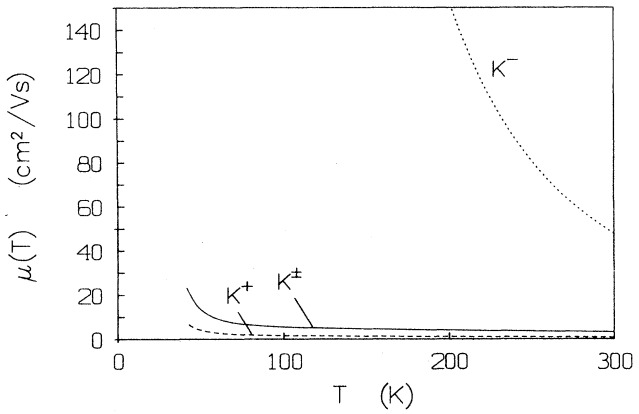

FIG. 5. Mobility μ as function of temperature T for differently charged kinks $K^{\pm}$; lines as in Fig. 1.

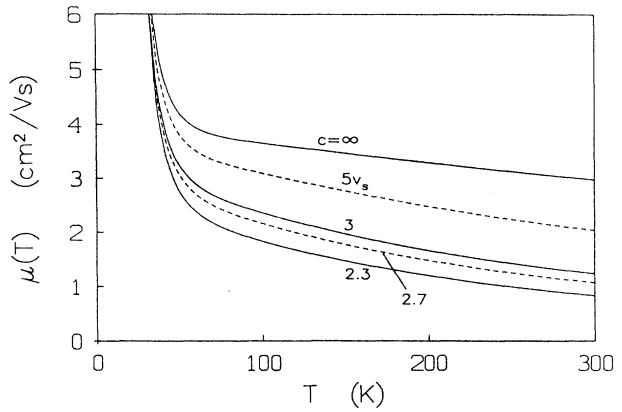

FIG. 6. Mobility μ as function of temperature T for negatively charged polarons for various values of the maximal velocity c as indicated (cf. text).

effects discussed here, e.g., the splitting of the mobility for differently charged species, may possibly be experimentally observable. Unfortunately, the only method so far for determining the mobility along a single chain is the ESR which couples only to neutral kinks; therefore, charge-dependent effects cannot be detected. An investigation of (bi)polaron mobilities in substances like polythiophene and the polyanilines, where the inclusion of CCS-breaking interactions for the interpretation of optical-absorption data has been proven quite useful, promises the possibility of testing our theoretical predictions.

ACKNOWLEDGMENTS

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APPENDIX

In this Appendix we give details of the calculations which have been sketched in Sec. II. In order to obtain the different interaction terms the electronic parts of $H_{\rm int}$ [Eqs. (5) and (6)] are evaluated with the unperturbed TLM functions in the spirit of a perturbation expansion. For the kink this can be done easily, and one obtains

$$H_{\rm int}^{K,\rm TLM}=\eta_K^{\rm TLM}\int dx\, F^{\rm TLM}(\phi)G_K^{\rm TLM}(\Delta_K) \tag{A1}$$

and

$$H_{\rm int}^{K,\beta(\gamma)}=\eta_K^{\beta(\gamma)}q_K\int dx\, F^{\beta(\gamma)}(\phi)G_K^{\beta(\gamma)}(\Delta_K) \tag{A2}$$

for the β or γ interactions, respectively. Here n is a coupling constant, q_K the charge of a kink, ϕ the phonon field as introduced in Sec. II, and Δ_K the kink profile. The various functions are

$$\eta_K^{\rm TLM}=\frac{a^2}{4\pi\lambda\Delta_0\xi_0},\quad \eta_K^{\beta}=\frac{a^2}{4\Delta_0}\beta,\quad \eta_K^{\gamma}=-\frac{a}{2\Delta_0}\gamma\ ,$$
$$F^{\rm TLM}=F^{\gamma}=\phi'(x),\quad G_K^{\rm TLM}=G_K^{\gamma}=\Delta_K'(x)\ , \tag{A3}$$
$$F^{\beta}=\phi''(x),\quad G_K^{\beta}=\Delta_K(x)\Delta_K'(x)\ .$$

For polarons, the corresponding evaluation of $\langle\psi_s^{\dagger}(x)\sigma_3\overleftrightarrow{\partial}_x\psi_s(x)\rangle$ in the TLM case is quite lengthy; it turns out to be much simpler to calculate this expression with the help of the (Bogoliubov–de Gennes–Andreev) equations of motion. One obtains

$$\langle\psi_s^{\dagger}(x)\sigma_3\overleftrightarrow{\partial}_x\psi_s(x)\rangle=\frac{i}{v_F}\mathrm{Re}\{\langle\epsilon_{ks}f_{ks}^{\dagger}(x)1f_{ks}(x)\rangle + [2\Delta^2(x)/\pi v_F\lambda]\}\ , \tag{A4}$$

with $f_{\pm}=u\pm iv$, and $\psi=\sum\binom{v_k}{v_k}a_k$, where a_k is the annihilation operator for electrons in state k. The resulting TLM-interaction term is much more complicated than the corresponding expression obtained from a deformation-potential approach as proposed by Jeyadev and Conwell,[8,9] and we obtain

$$H_{\rm int}^{P,\rm TLM}=\eta_p^{\rm TLM}\int dx\, F^{\rm TLM}G_p^{\rm TLM}(\Delta_p)$$

with $\eta_p^{\rm TLM}=-a^2/4v_F$, and

$$G_p^{\mathrm{TLM}}=b_1(r)\left[\frac{1}{\hbar_+^2}+\frac{1}{\hbar_-^2}\right]-\frac{c_1(r)}{\hbar_+\hbar_-}+\frac{c_2(r)}{\hbar_+^2\hbar_-^2},\quad r=\kappa_0\xi_0,\quad \hbar_\pm=\cosh[\kappa_0(x\pm x_0)]\ , \tag{A5}$$

$$b_1(r)=\frac{r\Delta_0^2}{2v_F}(n_+-n_-)(1-r^2)^{1/2}+\frac{2r^2\Delta_0^2}{\pi v_F}\left[\frac{1}{2\lambda}-\frac{1}{2}\frac{(1-r^2)^{1/2}}{r}\arcsin\left[2r(1-r^2)^{1/2}\pi t_0\frac{[(\pi t_0)^2+\Delta_0^2]^{1/2}}{(\pi t_0)^2+r^2\Delta_0^2}\right]\right],$$

$$c_1(r)=\frac{2\Delta_0^2}{\pi v_F\lambda}\frac{2r^2}{(1-r^2)^{1/2}},\quad c_2(r)=\frac{2\Delta_0^2}{\pi v_F\lambda}\frac{r^4}{1-r^2}\ .$$

For the other (β,γ) interactions this procedure yields, in a similar form as for the kink case,

$$\eta_p^\gamma=\eta_k^\gamma\frac{r}{2},\quad \eta_p^\beta=\eta_k^\beta\frac{1}{2r}\ ,$$
$$G_p^\gamma=\Delta_0\left[\frac{1}{\hbar_+^2}+\frac{1}{\hbar_-^2}\right],\quad G_p^\beta=\Delta_p'(x)\Delta_p(x) \tag{A6}$$

(which is in fact different from the corresponding expression for kink, since kink and polaron profiles are different). It is clear that the CCS-breaking interactions are proportional to the charge of the excitations under consideration.

The subsequent calculations are analogous to the ones given in Ref. 8; the acoustic-phonon field is written as

$$\phi(x)=\frac{4\alpha}{\sqrt{N}}\sum_q\phi(q)e^{iqx}\ ,$$
$$\phi(q)=\left[\frac{\hbar}{2M_{\mathrm{CH}}\omega_q}\right]^{1/2}(a_q+a_{-q}^\dagger) \tag{A7}$$

with $\omega_q=v_s|q|$. The necessary integrals over x are complicated (especially in the case of polarons), but can be computed by analytical continuation onto the strip as is usual for hyperbolic functions; some of these integrals are

$$\frac{1}{\xi}\int dx\ e^{iqx}\frac{\tanh(x/\xi)}{\cosh^2(x/\xi)}=\frac{i\pi q^2\xi^2}{2\sinh(\pi q\xi/2)}\ , \tag{A8a}$$

$$\frac{1}{\xi}\int dx\frac{e^{iqx}}{\hbar_+^2\hbar_-^2}=\frac{\pi i}{r}\frac{e^{iqx_0}}{\sinh^2(2\kappa_0x_0)\sinh(\pi q/2\kappa_0)}\left[e^{-2iqx_0}\left[i\frac{q}{\kappa_0}-2\coth(2\kappa_0x_0)\right]+i\frac{q}{\kappa_0}-2\coth(2\kappa_0x_0)\right], \tag{A8b}$$

$$\frac{1}{\xi}\int dx\ e^{iqx}\left[\frac{1}{\hbar_+^3\hbar_-}-\frac{1}{\hbar_-^3\hbar_+}\right]=\frac{\pi i}{r\sinh(\pi q/2\kappa_0)\sinh(2\kappa_0x_0)}\left[\frac{2q}{\kappa_0^2}-4\frac{qx_0}{\kappa_0}\coth(2\kappa_0x_0)\right]. \tag{A8c}$$

In Refs. 8 and 9, it is shown that, due to conservation of energy and momentum, only long-wavelength acoustic phonons [$\lambda\geq 40a$ ($50a$) for kinks (polarons)] have to be considered in one-phonon-emission and -absorption processes. Therefore, these integrals can be approximated by their values for small q (cf. Ref. 9). The resulting interaction operators are, for the kink,

$$H_{\mathrm{int}}^K=\sum_q H^{ac}(q)(1+8\tilde\gamma_k+\tilde\beta q^2)\ ,$$
$$H^{ac}(q)=(2iv_s\Delta_0/g)\left[\frac{\hbar}{2L}\right]^{1/2}\omega_q^{1/2}(a_q-a_q^\dagger),$$
$$g=4\alpha(a/M_{\mathrm{CH}})^{1/2}\ , \tag{A9}$$
$$\tilde\beta=\frac{4\alpha^2a^2t_0}{\Delta_0K}(1-n)\beta,\quad \tilde\gamma=(1-n)\gamma\ ,$$

and, for the polaron,

$$H_{\mathrm{int}}^P=\frac{4\alpha\xi}{\sqrt{N}}(\hbar/2M_{\mathrm{CH}})^{1/2}\times\sum_q\frac{\omega_q^{1/2}}{v_s}\left[-f_1+\frac{f_2}{v_s^2}\omega_q^2\right](a_q-a_q^\dagger)\ ,$$
$$f_1=\frac{ia}{2t_0}\left[\frac{1}{r}b_1(r)-\frac{c_1(r)\kappa_0x_0}{r\sinh(2\kappa_0x_0)}+\frac{c_2(r)}{r\sinh^2(2\kappa_0x_0)}[2\kappa_0x_0\coth(2\kappa_0x_0)-1]\right]-\frac{i\Delta_0}{2t_0}\gamma(n_++n_--2) \tag{A10}$$
$$f_2=\frac{\beta a\Delta_0^2}{4t_0\kappa_0}(n_++n_--2)(-i)\times\left[2\kappa_0x_0+\frac{r^2}{(1-r^2)^{1/2}}\frac{1}{\sinh(2\kappa_0x_0)}\times[1-2\kappa_0x_0\coth(2\kappa_0x_0)]\right].$$

Calculating the matrix elements M_{kk}, with these interaction operators as given in Eq. (7), the final result for the diffusion constant as given by Eq. (13) up to an integration which has to be done numerically reads, for the kink with maximal velocity c,

$$D_k(T)=\frac{\hbar g^2 c^3}{2\Delta_0^2 k_0 v_s^3}\left\langle f^K(y)\frac{y^2}{1+y^2}\right\rangle_T \tag{A11}$$

with $k_0=m_0c/\hbar$, m_0 the kink rest mass, and $Y=k/k_0$,

$$[f^K(y)]^{-1}=|1+8\tilde{\gamma}+\tilde{\beta}k_0^2(y_{ab}^b)^2|^2 y_{ab}^b(e^{v_s/c\eta y_{ab}^b}-1)^{-1}\left[\frac{v_s}{c}+\frac{|y|-y_{ab}^b}{[(|y|-y_{ab}^b)^2+1]^{1/2}}\right]^{-1}$$
$$+\Theta(y_s-|y|)|1+8\tilde{\gamma}+\tilde{\beta}k_0^2(y_{ab}^f)^2|^2 y_{ab}^f(e^{y_s/c\eta y_{ab}^f}-1)^{-1}\left[-\frac{v_s}{c}+\frac{|y|+y_{ab}^f}{[(|y|+y_{ab}^f)^2+1]^{1/2}}\right]^{-1}$$
$$+\Theta(|y|-y_s)|1+8\tilde{\gamma}+\tilde{\beta}k_0^2(y_{em})^2|^2(1-e^{-v_s/c\eta y_{em}})^{-1}y_{em}\left[\frac{v_s}{c}-\frac{|y|-y_{em}}{[(|y|-y_{em})^2+1]^{1/2}}\right]^{-1},$$

$$y_s=\frac{k_s}{k_0}=\frac{v_s}{c}\frac{1}{[1-(v_s/c)^2]^{1/2}},\quad k_s=\frac{m_0 v_s}{\hbar[1-(v_s/c)^2]^{1/2}}.$$

The expressions

$$y_{ab}^b=2\frac{v_s/c(1+y^2)^{1/2}+|y|}{1-(v_s/c)^2},$$

$$y_{ab}^f=2\frac{v_s/c(1+y^2)^{1/2}-|y|}{1-(v_s/c)^2},$$

and

$$y_{em}=2\frac{|y|-v_s/c(1+y^2)^{1/2}}{1-(v_s/c)^2}$$

are the same as in Refs. 8 and 9 (ab and em denote absorption and emission, respectively). Here the bracket $\langle x(y)\rangle_T$ means the thermal average

$$\langle x(y)\rangle_T=\frac{\int_0^\infty dy\, x(y)\exp[-\eta(1+y^2)^{1/2}]}{\int_0^\infty dy\exp[-\eta(1+y^2)^{1/2}]}$$

with $\eta=m_0c^2/k_BT$. The corresponding result for the polaron is

$$D_p(T)=\frac{M_{CH}v_s\hbar c^3}{8a\alpha^2\xi^2 k_0}\left\langle f^P(y)\frac{y^2}{1+y^2}\right\rangle_T \tag{A12}$$

with

$$[f^P(y)]^{-1}=|-f_1+f_2k_0^2(y_{ab}^b)^2|^2(e^{v_s/c\eta y_{ab}^b}-1)^{-1}y_{ab}^b\left[\frac{v_s}{c}+\frac{|y|-y_{ab}^b}{[(|y|-y_{ab}^b)^2+1]^{1/2}}\right]^{-1}$$
$$+\Theta(y_s-|y|)|-f_1+f_2k_0^2(y_{ab}^f)^2|^2(e^{v_s/c\eta y_{ab}^f}-1)^{-1}y_{ab}^f\left[-\frac{v_s}{c}+\frac{|y|+y_{ab}^f}{[(|y|+y_{ab}^f)^2+1]^{1/2}}\right]^{-1}$$
$$+\Theta(|y|-y_s)|-f_1+f_2k_0^2(y_{em})^2|^2(1-e^{-v_s/c\eta y_{em}})^{-1}y_{em}\left[\frac{v_s}{c}-\frac{|y|-y_{em}}{[(|y|-y_{em})^2+1]^{1/2}}\right]^{-1}$$

and all other parameters as before.

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