Thermal instability of the *trans*-polyacetylene polaron

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The *trans*-polyacetylene polaron decays to a kink-antikink pair (because of the greater entropy of the latter state) at a temperature which vanishes as the length L of the chain goes to infinity, approximately as $1/\ln L$. For a typical length of $L \sim 10^2-10^3$ Å, the corresponding temperature is 10^3-10^2 K.

I. INTRODUCTION

This work was motivated by the observation that the polaron[1-3] of polyacetylene theory[4] is not a solution of the Ginzburg-Landau (GL) equation.[5] Recall that polyacetylene theory (continuum version) is formally almost identical to BCS theory.[5] The hyperbolic-tangent order parameter of the kink solutions of the Bogoliubov equations of BCS theory[6] and polyacetylene theory[7] is also a solution of the GL equation[5] (to which BCS theory reduces in the limit $T \to T_c$).

The polyacetylene kink has a trivial temperature behavior (as shown by Takayama, Lin-Liu, and Maki[7]), for the kink is robust: at $T=0$, it is self-consistent regardless of the occupation of the midgap state; more importantly, the kink links two degenerate states, and must exist at all temperatures in the ordered state, since it can be enforced by topology. On the other hand, the polyacetylene polaron is fragile, and its existence at $T > 0$ is not so obvious. First, it is not enforced by topology, and it is therefore not required to exist at all T. Second, its self-consistency depends crucially on the occupation of the two bound states; at $T=0$, the upper must be singly occupied and the lower doubly (or the upper empty and the lower singly occupied), and so nonzero temperature may disrupt the polaron. The conclusion that the polaron disappears with increasing temperature is confirmed below.

Section II reviews results of the continuum, quasiclassical theory[7] for the single-particle energies. In Sec. III, the free energy is calculated as a function of temperature T for a chain of length $L = N_i a$; N_i is the number of ions (an even number) and a is the ionic spacing in the undimerized state. The number of electrons N_e is one greater than the number of ions ($N_e = N_i + 1$); because of the particle-hole symmetry, our results also apply when the number of electrons is one fewer than the number of ions. At $T=0$, the polaron state is self-consistent and has lower energy than both the homogeneous and kink-antikink states.[2,3] We show that the polaron solution remains self-consistent at nonzero T. Using an approximate expression for the positional and motional contribution of the solitons to the free energy, we find that, as T

increases from 0, the free energy of the polaron (P) state increases relative to that of the kink-antikink ($K\bar{K}$) state and eventually passes above the latter, essentially because the P state has only one soliton to the $K\bar{K}$ state's two. The temperature at which the P state becomes metastable with respect to the $K\bar{K}$ state vanishes in the limit of infinite chain length, approximately as $1/\ln L$. Section IV discusses approximations and related work.

II. SINGLE-PARTICLE ENERGIES

Our formalism[7] and approximations (the ions are static, and are treated classically; electron-electron interactions and interchain coupling are neglected) are standard. The electrons move in the potential energy $V(x) = 2\Delta(x)\cos(Qx)$ created by the displacements of the ions from their undimerized positions; the wave number Q is π/a, and the Fermi velocity is $v_F = \hbar Q/(2m)$. The energy eigenvalues ε and E of the Schrödinger and Bogoliubov equations[5] (the former is solved in the quasiclassical approximation) are related by $E = \varepsilon - \varepsilon_0$, where $\varepsilon_0 = \hbar^2(Q/2)^2/(2m)$ is the midgap energy. Periodic boundary conditions (rather than the Dirichlet conditions used in Ref. 8 to determine the origin of the midgap state) are applied. The number of ions N_i is even; otherwise periodic boundary conditions force a kink into the system.

The calculation of the free energy for the three states, the homogeneous (uniformly dimerized or D), polaron (P), and kink-antikink ($K\bar{K}$) states requires the single-particle energies E_n and the degeneracy factors g_n. Table I gives the scattering-state results for the D and P states; two cases must be distinguished, whether the number of ions is divisible by 4 ($N_i = 4\mathcal{N}$) or not ($N_i = 4\mathcal{N}+2$). Sums over states are cut off at low energy (because the quasiclassical energies have no lower bound) and at high energy, the latter to maintain particle-hole symmetry, and also so that the "band" (the conduction and valence bands plus any bound states in the gap) can hold exactly $2N_i$ electrons; the sum over degeneracy factors is

$$\sum_{E_n} g_n = 2N_i \; . \tag{2.1}$$

TABLE I. Scattering-state energies E_n and degeneracy factors g_n, with $E_n = \pm[\Delta_0^2 + (\hbar v_F k_n)^2]^{1/2}$.

Uniformly dimerized state; $N_i = 4\mathcal{N}$:	Uniformly dimerized state; $N_i = 4\mathcal{N} + 2$:
$k_n = 2n\pi/L$ for $n = 0, 1, 2, \ldots, \mathcal{N}$	$k_n = (2n+1)\pi/L$ for $n = 0, 1, 2, \ldots, \mathcal{N}$
$g_0 = 2$; $g_n = 4$ for $n = 1, 2, \ldots, (\mathcal{N}-1)$; $g_{\mathcal{N}} = 2$	$g_n = 4$ for $n = 0, 1, 2, \ldots, (\mathcal{N}-1)$; $g_{\mathcal{N}} = 2$
Polaron state; $N_i = 4\mathcal{N}$:	Polaron state; $N_i = 4\mathcal{N} + 2$:
$k_n L = 2n\pi - 2\arctan(\kappa/k_n)$ for $n = 1, 2, \ldots, \mathcal{N}$	$k_n L = (2n+1)\pi - 2\arctan(\kappa/k_n)$ for $n = 0, 1, 2, \ldots, \mathcal{N}$
$g_n = 4$ for $n = 1, 2, \ldots, (\mathcal{N}-1)$; $g_{\mathcal{N}} = 2$	$g_0 = 2$; $g_n = 4$ for $n = 1, 2, \ldots, (\mathcal{N}-1)$; $g_{\mathcal{N}} = 2$

(a) Homogeneous state: $\Delta(x) = \Delta_0$, independent of x [including the undimerized state with $\Delta(x) = 0$]. There are no bound states.

(b) Polaron state:[2,3]

$$\Delta(x) = \Delta_0 - \hbar v_F \kappa[t_+(x) - t_-(x)] , \quad (2.2)$$

where $t_\pm(x) = \tanh[\kappa(x \pm X)]$ and the parameters Δ_0, κ, and X are related by

$$\tanh(2\kappa X) = \hbar v_F \kappa/\Delta_0 . \quad (2.3)$$

Bound states: The energies are $\pm E_B$, where $E_B = [\Delta_0^2 - (\hbar v_F \kappa)^2]^{1/2}$; the degeneracy factor is 2 for each state. The Bogoliubov functions $u(x)$ and $v(x)$ are

$$u(x) = \alpha[1/c_+(x) + i\,\text{sgn}(E)/c_-(x)] ,$$
$$v(x) = \alpha[i/c_+(x) + \text{sgn}(E)/c_-(x)] , \quad (2.4)$$

where $c_\pm(x) = \cosh[\kappa(x \pm X)]$; these are normalized if $|\alpha| = (\kappa/8)^{1/2}$.

Scattering states: The Bogoliubov functions $u(x)$ and $v(x)$ are

$$u(x) = \mathcal{U}e^{ikx}[1 - C_- t_+(x) + C_-^* t_-(x)] ,$$
$$v(x) = \mathcal{V}e^{ikx}[1 - C_+ t_+(x) + C_+^* t_-(x)] ; \quad (2.5)$$

the constants $\mathcal{U}$, $\mathcal{V}$, and $C_\pm$ are given by

$$\mathcal{U} = (1 + \hbar v_F k/E)^{1/2}\mathcal{A} ,$$
$$\mathcal{V} = (1 - \hbar v_F k/E)^{1/2}\text{sgn}(E)\mathcal{A} , \quad (2.6)$$
$$C_\pm = \kappa(\hbar v_F k \pm E - i\Delta_0)/(2k\Delta_0) .$$

The normalization constant $\mathcal{A}$ is found from

$$|\mathcal{A}|^2 = k^2 W/[2L(k^2 + \kappa^2)] , \quad (2.7)$$

where W is a correction factor for the finite length:

$$W = \{1 - 2\kappa/[L(k^2 + \kappa^2)]\}^{-1} ; \quad (2.8)$$

the normalization condition for both bound and scattering states is

$$\int [|u_n(x)|^2 + |v_n(x)|^2]dx = 1 . \quad (2.9)$$

(c) Kink-antikink state: The energies and degeneracy factors for the state are found from the polaron results given above and in Table I by setting $\hbar v_F \kappa = \Delta_0$.

III. FREE ENERGY

The free energy is split into electronic and ionic contributions:

$$F = F_{el} + F_{ion} . \quad (3.1)$$

The electronic contribution F_{el} is found from $F_{el} = U_{el} - TS_{el}$, where

$$U_{el} = \sum_{E_n} g_n f_n E_n , \quad (3.2a)$$

$$S_{el} = -k_B \sum_{E_n} g_n[f_n \ln f_n + (1 - f_n)\ln(1 - f_n)] ; \quad (3.2b)$$

here $f_n = \{\exp[\beta(E_n - \mu)] + 1\}^{-1}$ is the Fermi function and μ is the chemical potential relative to the midgap energy. The dependence on the order parameter $\Delta(x)$ is through the energy eigenvalues E_n (and the degeneracy factors g_n). Omitting a term which vanishes due to the particle-hole symmetry of the model, one finds

$$F_{el} = \sum_{E_n} g_n((f_n - 1/2)\mu - k_B T \ln\{2\cosh[\beta(E_n - \mu)/2]\}) . \quad (3.3)$$

The calculation of the ionic contribution to the free energy is more difficult. The sine-Gordon model was investigated in Refs. 9 and 10, but we know of no similar treatment of the trans-polyacetylene model, which is less simple. We approximate F_{ion} as

$$F_{ion} = \Lambda^{-1} \int \Delta^2(x)dx - k_B TN_s \ln(L/\lambda_s) . \quad (3.4)$$

The first term is the ion-ion interaction, and the second comes from the thermal motion and positional entropy of the N_s solitons. We ignore both the thermal motion of the ions and soliton-soliton interactions. In the second term, λ_s is the thermal de Broglie wavelength of the soliton: $\lambda_s = h/(2\pi m_s k_B T)^{1/2}$ with m_s the mass of the soliton; the expression is valid at thermal energies large compared to the spacing of the single-soliton energy levels $[k_B T \gg (\hbar\pi/L)^2/m_s]$. Because of the approximations, the above expression is a poor approximation for the ionic contribution to the free energy, but the errors largely cancel on calculating differences in free energies. The ion-ion interaction energy for the homogeneous, polaron, and kink-antikink states is, respectively,

$$\Lambda^{-1} \int \Delta^2(x)dx$$

$$= \frac{\pi \hbar v_F}{\Lambda} \times \left\{ \frac{\Delta_0^2 N_i}{4\varepsilon_0}, \frac{\Delta_0^2 N_i}{4\varepsilon_0} - \frac{16\kappa a \varepsilon_0}{\pi^2}, \frac{\Delta_0^2 N_i}{4\varepsilon_0} - \frac{4\Delta_0}{\pi} \right\} . \quad (3.5)$$

The free energy is to be minimized with respect to any variational parameters (Δ_0, for example) in the order pa-

rameter $\Delta(x)$, subject to the constraint on the number of electrons (which determines the chemical potential):

$$\sum_{E_n} g_n f_n = N_e \ . \tag{3.6}$$

Self-consistency of the polaron at $T > 0$: The parameters Δ_0 and κ of the polaron solution are found variationally; the equations $\partial F / \partial \Delta_0 = 0$ and $\partial F / \partial \kappa = 0$ are

$$\frac{2}{\Lambda} = -\sum_{E_n}^b \frac{g_n f_n}{E_n L} - \sum_{E_n}^s \frac{g_n f_n}{E_n L} \ , \tag{3.7a}$$

$$\frac{2}{\Lambda} = -\sum_{E_n}^b \frac{g_n f_n \kappa}{2 E_n} - \sum_{E_n}^s \frac{g_n f_n}{E_n L} \frac{k_n^2 W_n}{k_n^2 + \kappa^2} \ , \tag{3.7b}$$

where the sums are over the bound (b) and scattering (s) states. On the other hand, the self-consistency equation

$$2\Delta(x)/\Lambda = -\sum_{E_n} g_n f_n [u_n(x) v_n^*(x) + \text{c.c.}] \tag{3.8}$$

yields (from results listed in Sec. II) the two relations

$$\frac{2}{\Lambda} = -\sum_{E_n}^s \frac{g_n f_n W_n}{E_n L} \ , \tag{3.9a}$$

$$\frac{2}{\Lambda} = \sum_{E_n}^b \frac{g_n f_n E_n}{2(\hbar v_F)^2 \kappa} - \sum_{E_n}^s \frac{g_n f_n E_n W_n}{(\hbar v_F)^2 L (k_n^2 + \kappa^2)} \ . \tag{3.9b}$$

But Eq. (3.9a) is a linear combination of Eqs. (3.7a) and (3.7b), and Eq. (3.9b) is a second. Hence the polaron is self-consistent (as at $T = 0$), regardless of the length of the chain, when the three quantities Δ_0, κ, and μ are determined as described above; of course, the three equations must have solutions.

We assume that the chains are long enough that finite-size corrections (of order $1/N_i$) to the amplitudes Δ_0 are negligible. The temperature region of interest is $T < 0.1 \Delta_{00}/k_B$; the dependence of the amplitudes on T is therefore also negligible, and the amplitudes Δ_0 of the three states are equal to the BCS amplitude at zero temperature, Δ_{00}. We assume also that T is low enough that the thermal depletion of the valence band is negligible; the requirement (well satisfied at the temperatures considered below) is

$$e^{\beta(\mu + \Delta_{00})} \gg \frac{L}{\xi} \left[\frac{2 k_B T}{\pi \Delta_{00}} \right]^{1/2} \ . \tag{3.10}$$

(a) Homogeneous (D) state. At $T = 0$, the chemical potential μ lies at the bottom of the conduction band. With increasing T, the large density of states in the conduction band forces μ to decrease rapidly toward midgap (since the model has particle-hole symmetry) so that the number of electrons remains fixed. If the Fermi function for all the conduction-band states is $\ll 1$ (the chemical potential must be well below the lowest state; the assumption surely fails when $k_B T \leq$ the spacing of the levels at the bottom of the band), Eq. (3.6) gives the following expression which determines the chemical potential:

$$1 = e^{\beta \mu} \frac{2L}{\pi \xi} K_1(\beta \Delta_{00}) \ , \tag{3.11}$$

where $K_1(z)$ is a modified Bessel function[11] and $\xi = \hbar v_F / \Delta_{00}$. Using the asymptotic expansion of the Bessel function, we find the free energy of the D state as

$$F_D(T) = F_D(T = 0) - k_B T$$
$$- k_B T \ln\{(L/\xi)[2 k_B T/(\pi \Delta_{00})]^{1/2}\} \ . \tag{3.12}$$

One sees that the free energy decreases rapidly with increasing T. The large term comes from the entropy of the conduction-band states (but large terms cancel in the two contributions to the free energy).

(b) Polaron (P) state. The chemical potential is at the upper bound state at $T = 0$, and remains there at low T: the Fermi function at the upper bound-state energy must remain equal to $\frac{1}{2}$ since there are no states near in energy. Like the chemical potential of the D state, the chemical potential of the P state must eventually drop to midgap, but the drop for the P state is preempted by the instability of the polaron. If $\hbar v_F \kappa / \Delta_{00}$ remains equal to $1/\sqrt{2}$ at low T (this assumption has been checked numerically), then the single-particle energies do not change with T, and the free energy is

$$F_P(T) = F_D(T = 0) + (2\sqrt{2}/\pi - 1)\Delta_{00}$$
$$- 2 k_B T \ln 2 - k_B T \ln(L/\lambda_P) \tag{3.13}$$

at low T. We have used the known difference[2,3] in the energies between the D and P states at $T = 0$. The electronic entropy of the P state does not vanish as $T \to 0$, but the term is of order k_B (rather than $N_i k_B$). The last term in Eq. (3.13) is the contribution from the motion of the polaron; if the polaron is pinned, this term is replaced by $- W_P$, where $W_P (> 0)$ is the pinning potential. Further, we have

$$W_P > k_B T \ln(L/\lambda_P) \tag{3.14}$$

as long as the pinned polaron is stable compared to the free polaron, and hence both pinned and free polarons are stable against the D state.

(c) Kink-antikink ($K\bar{K}$) state. At $T = 0$, the chemical potential μ is at midgap; it must remain there for an infinitely long chain at $T > 0$. For finite chains, $\mu = k_B T \ln 3$ at low T; the temperature above which this approximation fails decreases to zero (probably as $1/\ln L$) as the length L of the chain increases. The free energy is then

$$F_{K\bar{K}}(T) = F_D(T = 0) + (4/\pi - 1)\Delta_{00}$$
$$- k_B T \ln(\tfrac{256}{27}) - 2 k_B T \ln(L/\lambda_{K\bar{K}}) \ . \tag{3.15}$$

This expression omits the interaction between the solitons (which is justified for long chains); more seriously, it neglects also interchain interactions, as discussed in Sec. IV.

One sees easily that the free energies of the P and $K\bar{K}$ states cross at a temperature determined by

$$(4 - 2\sqrt{2})\beta \Delta_{00}/\pi = \ln(L \lambda_P / \lambda_{K\bar{K}}^2) \ ; \tag{3.16}$$

above this temperature, the polaron is at most metastable with respect to a $K\bar{K}$ pair. An order-of-magnitude esti-

mate of the instability temperature is obtained by putting $m_{K\bar{K}}=m_P=m_e$ (the electron mass), although $m_{K\bar{K}}$ and m_P are certainly larger than m_e. Inserting a typical length (undisrupted conjugation length) $L \sim 10^2-10^3$ Å, we find $T \sim 10^3-10^2$ K.

IV. DISCUSSION

The result of Sec. III, namely that the *trans*-polyacetylene polaron is unstable above a temperature which vanishes in the thermodynamic limit, was obtained under several approximations. The most serious is our neglect of interchain interactions (including structural coupling, Coulomb correlations, and interchain hopping). On the one hand, the structural coupling tends to bind the kink and antikink, reducing the free energy of the kink-antikink state below our estimate (which assumes that the entropy is that of two free solitons); on the other hand, it is known that the polaron becomes unstable in the presence of interchain coupling.[12] As for the other approximations, the thermal motion of the ions should not change the differences in the free energies of the macroscopic states in the harmonic approximation; also, we see no reason to expect anharmonic effects or electron-electron interactions to favor the polaron state over the others. More realistic calculations are desirable.

As discussed in Ref. 4, clear experimental evidence exists for kinks (charged and neutral), but not for polarons, in *trans*-polyacetylene. In view of (i) our result, (ii) little experimental evidence for the polaron, and (iii) that the stability of the polaron even at $T=0$ has recently been questioned,[13] the existence of the *trans*-polyacetylene polaron appears doubtful, unless it is pinned at impurities or crystalline defects.

Our result has no applicability to the *cis*-polyacetylene class of polymers (which includes polypyrrole and polyphenylene), for here the ground state is nondegenerate.

Our work questions the thermal stability of one self-trapped soliton, the polaron. The thermal stability of another, the Davydov soliton,[14] has also been questioned;[15] for the latter the instability arises from random-noise forces, and the soliton is stable at low T. In contrast, the decay of the polaron is due to the lower free energy of a state with more solitons, and the decay takes place at arbitrarily low T in the thermodynamic limit.

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