Superconductivity in Models of Conducting Polymers

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The possibility of superconductivity in polymers is studied in one-dimensional models of interacting electrons coupled to acoustic phonons or intramonomer vibrations. For acoustic phonons, the dimerized state is stable and superconductivity does not occur, in disagreement with recent work by Zimanyi, Kivelson, and Luther. For intramonomer vibrations in an incommensurate (highly doped) system, superconductivity strongly competes with charge-density waves and is favored by high phonon frequencies, well screened electronic interactions, and n-type doping.

The possibility of superconductivity in polymers has been an open problem for a long time.[1] It is of renewed urgency due to the recognition of important similarities between conducting polymers and high-T_c and organic superconductors: (i) moderate or strong electron-electron interactions, and (ii) short coherence lengths. Even ceramic or powder samples of the latter materials are good superconductors while observation of superconductivity in the inorganic polymer $(SN)_x$ (whose electronic structure is *not* representative of conjugated polymers) demonstrates that the typical fibrillar morphology of polymers is not detrimental to superconductivity.[2] Starting from standard one-dimensional (1D) models of conducting polymers, we discuss under what conditions the competition or cooperation of electron-electron and electron-phonon interactions can bring about singlet superconductivity (SS). Our program is also rewarding theoretically: While the crossover between superconductivity and density waves in the 1D electron gas is well understood,[3] little is known about the influence of electron-phonon coupling and finite retardation on this crossover.[4,5]

Our main results are as follows: (1) The dimerized

charge-density-wave (CDW) ground state of the Su-Schrieffer-Heeger (SSH) model[6] is stable against electron-electron interactions and phonon quantum fluctuations for any band filling. Superconductivity does *not* occur, due to negligible electron-phonon *forward* scattering. This contrasts with predictions of a recent theory by Zimanyi, Kivelson, and Luther[5] but rationalizes the absence of superconductivity in polyacetylene [$(CH)_x$] despite impressive preparative progress. (2) Dominant SS fluctuations are found for a Holstein on-site electron-phonon coupling[7] describing the coupling to the vibrational degrees of freedom of a monomer. This model exhibits a very delicate interplay between CDW and SS if doped into the incommensurate (IC) limit (> 5%). Here (i) SS is weakened by increasing electron-electron interactions but (ii) the screening range of the potential is decisive. Badly screened interactions are detrimental but SS is only slightly disfavored for good screening; (iii) then, hole superconductors are more likely than electron superconductors. (iv) High phonon frequencies are most crucial for SS. We finally suggest directions how to meet these requirements in real materials.

Our first model is given by the Hamiltonian[8]

$$H_0 = -t_0 \sum_{n,s} c_{n+1,s}^{\dagger} c_{n,s} + \text{H.c.} , \tag{1}$$

$$H_{\text{SSH}} = \alpha \sum_{n,s} [u_{n+1} - u_n][c_{n+1,s}^{\dagger} c_{n,s} + \text{H.c.}] + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \sum_n \frac{p_n^2}{2M} , \tag{2}$$

$$H_{\text{int}} = \sum_{n,m,l,p,s,s'} V(n,m,l,p) c_{n,s}^{\dagger} c_{m,s'}^{\dagger} c_{l,s'} c_{p,s} + \delta\mu \sum_{n,s} c_{n,s}^{\dagger} c_{n,s} . \tag{3}$$

In the SSH model $H_0 + H_{\text{SSH}}$, the hopping integral t_0 is modulated via the coupling constant α by acoustic phonons $u_{n+1} - u_n$. K is the spring constant and M is the ion mass. The electron-electron interaction (3) which, restricted to neighboring sites, includes $U = 2V(0,0,0,0)$ and $V = 2V(0,1,1,0)$ of the extended Hubbard model, and $W = 2V(0,0,1,1)$ and $X = 2V(0,0,1,0)$ involving bond charges. W and X are corrections to the zero-differential-overlap approximation required by translational invariance.[8] Definite inequalities exist among these parameters reflecting the screening range of $V(n,m,l,p)$,[9,10]

$$U > V(> X > W) \text{ and } U > X(> V \geq W) , \tag{4}$$

for a badly (well) screened potential, respectively (terms

in parentheses are eventually negligible[10]). We treat this model by a renormalization-group (RG) analysis based on a continuum field theory.[4,5,11] It correctly describes low-energy properties of the lattice model, restricting us to weak coupling but has the advantage of treating the interaction of electrons among themselves and with phonons of arbitrary frequency on equal footing. This is essential since the phonon frequency ω_{ph} dramatically influences the competition between different interaction terms and thus the physics of the model.[4,11] To assess the tendency towards CDW or SS order, we compute renormalized exponents α of correlation functions

$$R_{\text{CDW}}(2k_F + q) \sim |v_F q|^{-\alpha_{\text{CDW}}} , \quad R_{\text{SS}}(q) \sim |v_F q|^{-\alpha_{\text{SS}}} . \tag{5}$$

For *physically realistic potentials* (4), a half-filled system dimerizes for arbitrary ω_{ph}.[11] For strong interactions, a crossover to a (dimerized) spin-Peierls phase occurs. From our computing $\alpha_{CDW(SS)}$ in the IC limit [$Y_\rho = Y_X = 0$ in Eqs. (5)–(9) of Ref. 12], we see that long-range dimerization is lost at any $\omega_{ph} > 0$; however, very strong short-range bond order survives and SS fluctuations are severely depressed. Moreover, repulsive interactions then decrease SS.[4] *A CDW-SS crossover does not occur in the interacting SSH model.* This conclusion disagrees with Ref. 5; ours is based on a search for the *most divergent instability* in the 1D model. Reference 5 considers an SS divergence much weaker than CDW sufficient for asserting a SS ground state in 3D. Work on 3D arrays of coupled chains[12] shows, however, that the 3D ordered ground state with the highest critical temperature is the one whose 1D fluctuations has *the strongest divergence*, even when interchain tunneling is the only transverse coupling mechanism, as assumed by Zimanyi, Kivelson, and Luther. Inclusion of interchain Coulomb interaction would further enhance the CDW transition. Our theory suggests that a polymer as simple as $(CH)_x$ *cannot* become a superconductor.

The absence of a CDW-SS crossover in models based on electron-acoustic phonon coupling is due to the inefficient coupling at small wave vectors q,[13] while coupling at $q \approx 2k_F$ favoring CDW's is good. The situation changes dramatically for a dispersionless phonon mode; physically, such modes are relevant if *intramonomer* (intramolecular) *vibrations are well coupled to electrons* (as is the case in organic conductors). They couple with comparable efficiency at small and large q,[13] and there is a nontrivial competition between CDW and SS. The Hamiltonian is $H_0 + H_{int} + H_{intra}$ with

$$H_{intra} = g \sum_{n,s} q_n c_{n,s}^\dagger c_{n,s} + \sum_n [\Pi_n^2/2m_r + (f/2)q_n^2],\qquad (6)$$

where g is the coupling constant to a normal mode, q_n is characterized by a restoring force f and a mass m_r.[7] For

a half-filled band, strong umklapp processes practically always yield a CDW ground state. However, in the IC regime, umklapp scattering is absent, resulting in a strong competition between CDW and SS which sensitively depends on the model parameters. Then, we derive the following RG equations:

$$d\beta_\rho^{-1}/dl = (Y_{ph}^{(1)} - Y_{ph}^{(2)})\mathcal{D}(l)/2,\qquad (7)$$

$$d\beta_\sigma^{-1}/dl = [Y_\sigma^2 + Y_{ph}^{(1)}\mathcal{D}(l)]/2,\qquad (8)$$

$$dY_\sigma/dl = Y_\sigma(2 - 2\beta_\sigma) - Y_{ph}^{(1)}\mathcal{D}(l),\qquad (9)$$

$$dY_{ph}^{(1)}/dl = -Y_{ph}^{(1)}(3 - \beta_\rho - \beta_\sigma - Y_\sigma),\qquad (10)$$

$$dY_{ph}^{(2)}/dl = Y_{ph}^{(2)},\qquad (11)$$

with the following abbreviations:

$$\beta_\rho \simeq 1 - \{\bar{U}_{eff}/2 + \bar{V}(2 - \cos[2k_F a])$$
$$+ 2\bar{W}(2\cos^2[k_F a] - 1) + \bar{X}\cos[k_F a]\},$$

$$\beta_\sigma \simeq 1 + Y_\sigma,$$

$$Y_\sigma = \bar{U}_{eff}/2 + \bar{V}\cos[2k_F a] + 2\bar{W} + \bar{X}\cos[k_F a],$$

$$Y_{ph}^{(1)} = Y_{ph}^{(2)} = 2g^2/\pi(t_0 + X/8)f,$$

where $\bar{U} = U/2\pi(t_0 + X/8)\sin[k_F a]$, etc., and $l = \ln[E(0)/E(l)]$. Note that

$$\mathcal{D}(l) = [\omega_{ph}/E(0)]\exp[-\omega_{ph}/E(l)]$$

is the *exact* bare phonon propagator at the renormalized electronic energy scale $E(l)$ and sensitively depends on the ratio of the phonon frequency $\omega_{ph} = (f/m_r)^{1/2}$ and this scale. This is an important difference from previous work[5] where the approximate form $\Theta[\omega_{ph} - E(l)]$ was used. The exact expression yields an important renormalization of electron-electron by electron-phonon interactions at $E(l) > \omega_{ph}$ in (7)–(11). Moreover, the effective on-site interaction $\bar{U}_{eff} = \bar{U} - Y_{ph}\{1 - \exp[-\omega_{ph}/E(0)]\}$ is renormalized already at
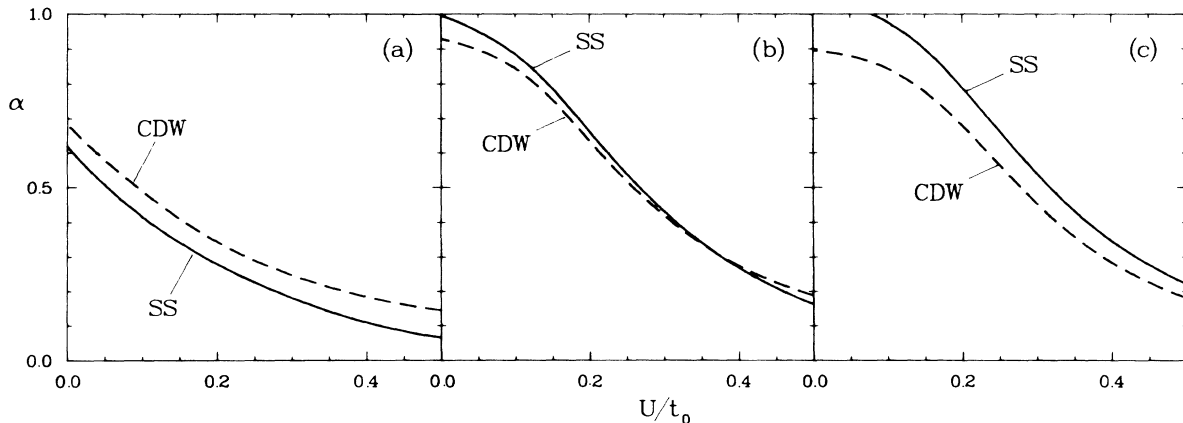

FIG. 1. Exponents α of SS and CDW correlation functions for electron-phonon coupling (6) as a function of U. $g^2/\pi t_0 f = 0.125$, (a) $\omega_{ph}/E_F = 0.1$, (b) 0.5, and (c) 1.0.

$E(0) \approx E_F$.

We first reduce H_{int} (3) to the Hubbard model. Figure 1 shows the evolution with U of the correlation-function exponents α_{CDW} and α_{SS} at fixed electron-phonon coupling for different ω_{ph}. It is found that in general that SS is weakened by increasing U as is, to a lesser extent, CDW. Increasing U destroys SS and establishes a CDW (yielding, for larger U, a spin-density wave). Let us turn to more realistic electron-electron potentials. More important than their strength then is the screening length, determining important additional terms (4). For bad screening, V must be included. V, however, strongly acts in favor of CDW's implying that badly screened electronic interactions are unfavorable for SS. For well screened interactions, $X(<U)$ is essential; it scales with t_0 and must therefore be included in a consistent tight-binding approach.[10] X is not charge conjugation symmetric. In a more than half-filled band, fixing, e.g., $X = U/2$, the curves shown in Fig. 1 would start out practically flat from their $U = 0$ values and exhibit only weak negative slopes for $U/t_0 < 1$. Also, the CDW-SS crossover is pushed to much higher values of U and to lower ω_{ph}. For less than half-filled bands, the trend is opposite. We conclude that well screened interactions of moderate strength present a favorable situation for SS; then, charge-conjugation symmetry breaking is relevant and hole superconductors are more likely than electron superconductors (a situation given in both organic and oxide superconductors).

The phonon frequency strongly controls the CDW-SS competition. In Fig. 1, with increasing ω_{ph}, there is an increasing range of U values where SS fluctuations clearly dominate CDW ones. The frequency dependence of α_{CDW} and α_{SS} (the 1D equivalent of the isotope effect) is shown in Fig. 2. Notice that the coupling constants have been scaled down by a factor of 100 with respect to Fig. 1. Then, the model without electronic interaction seems to display SS at all ω_{ph}; possibly, for $\omega_{ph} = 0$ CDW and

SS are degenerate. This points towards an interesting yet unexplored CDW-SS crossover in the IC Holstein model at finite ω_{ph} as a function of Y_{ph}. Adding a $U > 0$ increases the tendency towards CDW, in particular, at low phonon frequencies. The physical origin of this isotope effect is different from that of BCS theory where it reflects the energy scale of the attractive pairing interaction. Here, CDW and SS both are due to the interaction of electrons with the same phonons, and the isotope effect is due to the different scale dependence of the $q \approx 2k_F$ and $q \approx 0$ parts of this interaction $(Y_{ph}^{(1,2)})$ and their competition in influencing the electronic properties [cf. (7)-(11)]. The variation of T_c with ω_{ph} in a 3D array of chains is related to, though not identical to, that of α_{SS}.

Using two models of interacting electrons coupled to acoustic phonons or intramonomer vibrations, we have shown that the former only yields CDW ground states, while in the latter there is a delicate interplay between CDW and SS allowing for an SS ground state in a wide range of parameters. Solving a model including both phonon modes, in addition to electron-electron interactions, is a relevant problem for complete knowledge on the conditions under which SS occurs but is currently beyond the reach of our method. It can be studied by numerical simulation as can be the extension of our results to stronger coupling, probably relevant for some materials. From our study of the two models, we predict a destructive interference between the CDW's due to the acoustic and intramonomer phonons which modulate the charge density on the bonds and sites, respectively;[14] thus in the IC regime (typically > 5% doping) SS will survive in the complete model.

The present theory can give some (admittedly very general) guidelines for selection of suitable monomer candidates. They must be more complicated than (CH) to allow for internal vibrational modes; good coupling to electrons can probably be reached best in symmetrical
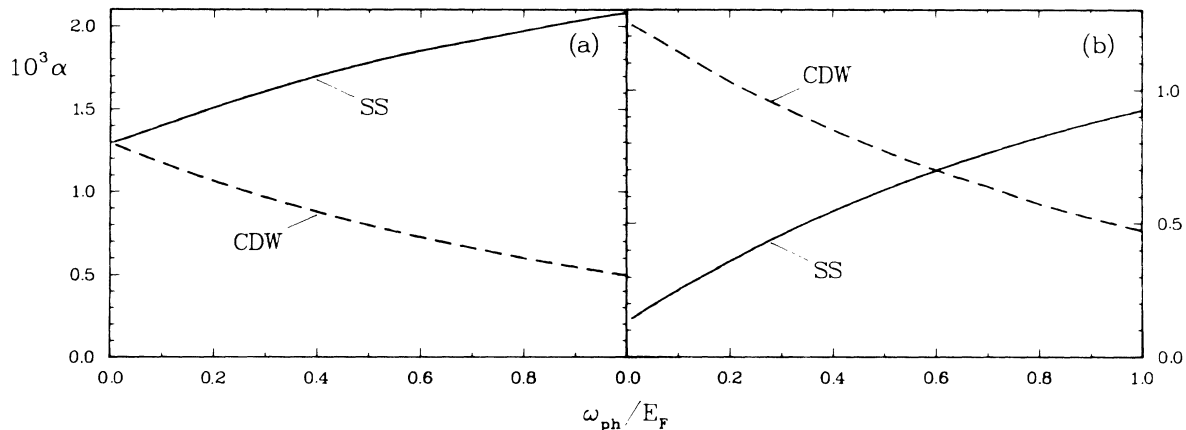

FIG. 2. Exponents α of SS and CDW correlation functions for interaction (6) as a function of ω_{ph}/E_F. $g^2/\pi t_0 f = 0.00125$, (a) $U/t_0 = 0$ and (b) 0.005.

structures. Side chains are to be avoided since they reduce the electron density and thus the screening. Notice that electron-electron interactions in polymers like $(CH)_x$ are believed to be weak (though not negligible) and well screened.[15] Since there is an upper limit to ω_{ph}, one should attempt to reduce the electronic bandwidth to increase the all-important ratio ω_{ph}/E_F. Experience with organic conductors suggests as a possibility the substitution of some carbon by sulfur or selenium, simultaneously increasing the transverse hopping required for a finite T_c. Experimentally, the proximity of a given material to superconductivity will show up, among others in an anomalous conductivity enhancement at low temperature,[16] and the absence of a specific-heat enhancement by electron-phonon interaction.

[1]W. A. Little, Phys. Rev. 134, A1416 (1964).

[2]R. L. Greene, G. B. Street, and L. J. Suter, Phys. Rev. Lett. 34, 577 (1975).

[3]J. Sólyom, Adv. Phys. 28, 201 (1979).

[4]J. Voit and H. J. Schulz, Phys. Rev. B 37, 10068 (1988).

[5]G. T. Zimanyi, S. A. Kivelson, and A. Luther, Phys. Rev. Lett. 60, 2089 (1988).

[6]W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979).

[7]T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959).

[8]S. Kivelson, W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 58, 1899 (1987); 60, 72 (1988).

[9]C. Wu, X. Sun, and K. Nasu, Phys. Rev. Lett. 59, 831 (1987); D. Baeriswyl, P. Horsch, and K. Maki, Phys. Rev. Lett. 60, 70 (1988); D. K. Campbell, J. T. Gammel, and E. Y. Loh, Jr., Phys. Rev. B 38, 12043 (1988).

[10]A. Painelli and A. Girlando, Synth. Met. 27, A15 (1988).

[11]J. Voit, Phys. Rev. Lett. 62, 1053 (1989).

[12]R. A. Klemm and H. Gutfreund, Phys. Rev. B 14, 1086 (1976); Yu. A. Firsov, V. N. Prigodin, and Chr. Seidel, Phys. Rep. 126, 245 (1985).

[13]J. Voit and H. J. Schulz, Mol. Cryst. Liq. Cryst. 119, 449 (1985).

[14]A. Madhukar, Chem. Phys. Lett. 27, 606 (1974), and S. Kivelson and D. Hone, Phys. Rev. B 28, 4833 (1983), have reached this conclusion in studies of related models for adiabatic phonons and $V(n,m,l,p) \equiv 0$.

[15]A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. 60, 781 (1988).

[16]A. Luther and I. Peschel, Phys. Rev. Lett. 32, 992 (1974).