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There is a strong analogy between the resonating-valance-bond (RVB) theory of high temperature superconductivity and the theory of doped conducting polymers. We have computed the properties of the one-dimensional electron–gas with repulsive electron–electron interactions and attractive interactions mediated by electron–phonon coupling. For the nearly half-filled band we find that the repulsive interactions strongly *enhance* the tendency for superconductivity. Finally, we discuss the implications of our results in terms of strategies for producing highly conducting metallic, or superconducting polymers.

I. INTRODUCTION

An old question has been endowed with renewed urgency by the discovery of high temperature superconductivity is whether superconductivity can arise from purely repulsive electron–electron interactions. This is particularly so in the light of the delicate balance that exists in these materials between magnetism, which is generally associated with strong repulsive interactions, and superconductivity. In this note we study the properties of the one-dimensional electron gas with repulsive electron–electron interactions and retarded attractive interactions mediated by the electron–phonon interaction. Among other results, we will show that while divergent superconducting fluctuations do not arise in the purely repulsive model, the addition of even very weak attractive interactions drives the system to a regime of strongly divergent superconducting fluctuations. It is important to stress that the situation here is fundamentally different than in three

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dimensions. In three dimensions, the fact that the repulsive Coulomb interactions are renormalized to a weak pseudo-potential implies that the strong repulsive interactions do not necessarily *destroy* superconductivity; in one-dimension they actually *drive* the superconducting instability. Of course, a strictly one-dimensional system can never undergo a phase transition to a state with a broken continuous symmetry. However, we make the standard argument, which we will return to in Section VI, namely, that the presence of weak interchain coupling can produce a genuine superconducting transition at a temperature which is a significant fraction of the characteristic temperature at which the superconducting fluctuations begin to diverge in the purely one-dimensional model. Thus, we will refer to a state with a divergent superconducting, charge-density-wave (CDW), or antiferromagnetic, susceptibility as being superconducting, CDW, or antiferromagnetic. Note that it is possible for more than one susceptibility to diverge in a given state.

The paper is organized as follows: in Section II, we define the discrete and continuum models of the one-dimensional electron gas with strong repulsive and weak retarded interactions. In Section III we solve the continuum model using a combination of exact results for the spectrum and renormalization group results for the correlation functions. This section is rather technical and can be skipped by the casual reader. In Section IV we analyze the electron–gas in terms of simple valence bond states and show that the results produce the same low energy physics as the "exact" solution in the appropriate region of interaction space. This analysis is almost pictorial, and can be understood without reading Section III. In Section V we discuss the relation between our results and the resonating valence bond theory of high temperature superconductivity in quasi-two dimensional systems. Finally, in Section VI we discuss the implications of our results in terms of strategies for producing more highly metallic conducting polymers, and especially for high-temperature superconducting polymers.

II. THE MODELS

The models we consider can all be considered to be various limits of the extended Hubbard-Peierls model

$$H = H_{el} + H_{el\text{-}ph} + H_{ph}. \tag{1}$$

Here H_{el} is the pure electronic extended Hubbard model

$$H_{el} = -\sum_{n,s} t_o [C^+_{ns} C_{n+ls} + \text{h.c.}]$$

$$+ h \sum_n [C^+_{n\uparrow} C_{n\downarrow} - C^+_{n\downarrow} C_{n\uparrow}] + [\mu - \tfrac{1}{4}U - V]$$

$$\times \sum_{ns} C^+_{ns} C_{ns} + U \sum_n C^+_{n\uparrow} C_{n\uparrow} C^+_{n\downarrow} C_{n\downarrow} + V \sum_n \left[\sum_s C^+_{ns} C_{ns} \right]$$

$$\times \left[\sum_{s'} C^+_{ns'} C_{ns'} \right]$$

$$+ 1/2 W_o \sum_n \left[\sum_s C^+_{ns} C_{n+ls} + \text{h.c.} \right]^2 \tag{2}$$

where C^+_{ns} creates an electron of spin s on site n, μ is the chemical potential, h is an external magnetic field, and W_o is a repulsion between bond-charge density, as distinct from the site-charge-density repulsion (U and V) present in the usual extended Hubbard model. (See discussion in Ref. 1). For widely separated sites, *i.e.* when $t \ll U$, we expect $1/2\ U > V \gg W_o$. For $\mu = h = 0$, the Hamiltonian H_{el} is charge conjugation symmetric, as can be seen by applying the charge conjugation operator defined in Ref. 2. Thus, $\mu = 0$ corresponds to a half-filled band.

The electron–lattice interaction is represented by including a dependence of the site energy and hopping matrix elements on the lattice degrees of freedom, v_n and u_n:

$$H_{el-ph} = \sum_{ns} \epsilon_n [C^+_{ns} C_{ns} - 1/2] - \sum_{ns} \delta t_{ns} [C^+_{ns} C_{n+ls} + \text{h.c.}] \tag{3a}$$

where we assume linear electron–phonon coupling,

$$\epsilon_n = \beta v_n \tag{3b}$$

$$\delta t_n = \alpha u_n \tag{3c}$$

Thus, v_n is an internal molecular coordinate at site n which couples to the site charge as in the molecular crystal model of Holstein,[3] and

u_n modulates the bond between site n and site $n + 1$, and hence couples to the bond charge as in the Su-Schrieffer-Heeger[4] (SSH) of polyacetylene. (In the SSH model, u_n is the change in the bond length, and hence is the difference in the displacements of sites n and $n + 1$, $u_n = [x_{n+1} - x_n - a]$.) Of course, u_n and v_n need not necessarily represent lattice degrees of freedom; u_n could just as well represent the effect of a localized electronic degree of freedom associated with the bond from n to $n + 1$, in which case it might be a discrete variable.

Finally, the pure lattice part consists of a sum of a kinetic energy term $T(u_n, v_n)$ and a potential energy $V(v_n, u_n)$. In the simplest cases, u_n and v_n represents fairly local modes, *i.e.* Einstein oscillators. In this case

$$H_{ph} \approx \sum_n \left\{ \frac{P_n^2}{2M} + \frac{P_n^2}{2} + \frac{K}{2} u_n^2 + \frac{K}{2} v_n^2 \right\} \tag{4}$$

where P_n and P_n are respectively the momentum conjugate to u_n and v_n. (Alternatively, if u_n represents an acoustic lattice deformation, as in the SSH model, then $u_n = x_{n+1} - X_n$ and P_n is the momentum conjugate to x_n.)

There are two interesting limits of the lattice dynamics which can be easily considered. If the lattice is fast, that is if u_n represents an optical phonon or excitonic mode which has an energy h_o large compared with the relevant electronic energy then u_n can be integrated out in the inverse adiabatic approximation. The result is an effective Hamiltonian for the electronic degrees of freedom of the same form as Eq. (2) but with renormalized values of the parameters. Since U and V are already large, the renormalization of these parameters is unimportant. However, W_o can easily become attractive

$$W_o \rightarrow W = [W_o - t_o\lambda] < 0 \tag{5}$$

where $\lambda = 8\alpha^2/\pi K t_o$ is the dimensionless bond–charge phonon coupling. We return to discuss this case in Section IV. The other limit is when the phonon is slow compared to the electronic degrees of freedom. With weak electron–phonon coupling and no electron–electron interactions, this model is just the SSH model of polyacetylene.[4] This model, and its extension to include weak,[5,6] and intermediate[7] and strong[8] electron–electron interactions has been studied extensively in the context of polyacetylene. (For a review, see Ref. 9).

Finally, for weak coupling, the model can be studied in the continuum limit. The appropriate continuum model is familiar[10–12] from "g-ology":

$$
\begin{aligned}
H_{el} = \int dx \hbar V_F \{ & \psi_s^+(x)[-i\underline{\sigma}_3 \partial_x]\psi_s(x) \\
& + g_{1\perp} \sum_s \psi_{s1}^+(x)\psi_{\bar{s}2}^+(x)\psi_{\bar{s}1}(x)\psi_{s2}(x) \\
& + g_{1\parallel} \sum_s \psi_{s1}^+(x)\psi_{s2}^+(x)\psi_{s1}(x)\psi_{s2}(x) \\
& + g_2 \sum_s \sum_{s'} \psi_{s1}^+(x)\psi_{s'}^+{}_1(x)\psi_{s'2}(x)\psi_{s1}(x) \\
& + g_3 \sum_s [\psi_{s1}^+(x)\psi_{\bar{s}1}^+(x)\psi_{\bar{s}2}(x)\psi_{s2}(x) + \text{h.c.}] \\
& + g_4 \sum_s [\psi_{s1}^+(x)\psi_{\bar{s}1}^+(x)\psi_{\bar{s}1}(x)\psi_{s1}(x) \\
& + \psi_{s2}^+(x)\psi_{\bar{s}2}^+(x)\psi_{\bar{s}2}(x)\psi_{s2}(x)] \\
& + \left(\frac{\mu}{\hbar V_F}\right) \sum_s \psi_s^+(x)\psi_s(x) + \left(\frac{h}{\hbar V_F}\right) \\
& \times [\psi_\uparrow^+(x)\psi_\uparrow(x) - \psi_\downarrow^+(x)\psi_\downarrow(x)]
\end{aligned}
\tag{6}
$$

where $\psi_x(x)$ is a two component spinor field, $\psi_{s1}^+(x)$ creates a right moving electron of spin s and crystal momentum $\pi/2a$ (corresponding to k_F for the half-filled band), $\psi_{s2}^+(x)$ creates a left-moving electron, $g_{1\parallel}$ and $g_{1\perp}$ are the backscattering matrix elements, g_2 and g_4 are the forward scattering matrix elements, and g_3 is the umklapp scattering. If these parameters are derived by taking the naive continuum limit of Eq. (2), then to first order $\hbar V_F = 2t_o a$, $g_{1\perp} = [U - 2V + 4W]a = g_{1\parallel}$, $g_2 = [U + 2V]a$, $g_3 = [U - 2V - 4W]a$, and $g_4 = (U + 2V)a$, where a is the lattice constant. (The overall phase of g_3 is a matter of convention since the Hamiltonian is invariant under the transformation $\psi_{1s}(x) \rightarrow e_1^{i\Phi}\psi_{1s}(x)$, $\psi_{2s}(x) \rightarrow e_2^{i\Phi}\psi_{2s}(x)$ and $g_3 \rightarrow e^{2i(\phi_2 - \phi_1)} g_3$.) For any model which is spin rotationally invariant, $g_{1\parallel} = g_{1\perp}$. To complete the definition of the model a regularization procedure must be specified; in this case we introduce

a band-width cutoff, $E_F \sim \hbar V_F k_F$, corresponding to the Fermi energy. Note, unlike many other workers we treat the half-filled and non-half-filled bands on an equal footing by varying μ; for large μ, g_3 becomes unimportant. g_4 is always relatively unimportant; it simply produces a shift in the spin and charge velocities, $V_c = V_F(1 + g_4)$ and $V_s = V_F(1 - g_4)$ respectively.

Similarly, the continuum version of $H_{el\text{-}ph}$ can be constructed as in Ref. 13.

$$H_{el\text{-}ph} = \sum_s \int dx \hbar V_F \psi_s^+(x)\{\Delta(x)\underline{\sigma}_2 + \phi_1(x)\underline{\sigma}_1 + \phi_2(x)\}\psi_s(x) \quad (7)$$

where $\Delta(x)$ is the $2k_F$ component of the hopping matrix modulation, $\Delta(na) \approx 1/2(-1)^n[\delta t_n - \delta t_{n-1}]$, $\phi_1(x)$ is the $2k_F$ component of the site energy modulation, $\phi_1(na) \approx 1/4(-1)^n[2\epsilon_n - \epsilon_{n+1} - \epsilon_{n-1}]$, and $\phi_2(x)$ is the $k = 0$ component of the site energy modulation, $\phi_2(na) \approx 1/4[2\epsilon_n + \epsilon_{n+1} + \epsilon_{n-1}]$. Again, there is an arbitrariness in the phase here; we have made the same choice of phase as in Eq. (6) so

$$\sum_s \langle \psi_s^+ \underline{\sigma}_2 \psi_s \rangle \neq 0 \quad (8a)$$

signifies a bond-centered charge-density wave and

$$\sum_s \langle \psi_s^+ \underline{\sigma}_1 \psi_s \rangle = 0 \quad (8b)$$

signifies a site-centered charge-density wave.

Finally, the H_{ph} is simply the Hamiltonian of an Einstein oscillator

$$H_{ph} = \int dx \left\{ \frac{\pi_\Delta^2}{2} + \frac{\pi_1^2}{2} + \frac{\pi_2^2}{2} + \frac{\omega_\Delta^2}{2}\Delta^2 + \frac{\omega_1^2}{2}\phi_1^2 + \frac{\omega_2^2}{2}\phi_2^2 \right\} \quad (9)$$

where π_Δ is the momentum conjugate to Δ, and π_a are the momenta conjugate to ϕ_a.

III. SOLUTION OF THE CONTINUUM MODEL

The continuum model with non-retarded interactions has been extensively studied, and a variety of features of the solution are known:[10–12] (i) So long as excitations involving states at the band edges can be ignored the Hamiltonian can be reexpressed as the sum of a charge

and spin part; all physical correlation functions are expressible as a product of a spin factor and a charge factor. (ii) In the perturbative expansion of different correlation functions logarithmic singularities appear in every order. Therefore one has to sum up at least the most divergent contributions *e.g.* by applying the multiplicative renormalization group (RG). We study the lowest order scaling equations because they already establish the qualitative equivalence of the model with weak bare couplings to some solvable models. The RG flows are determined by integrating out the states between E_F and E_F'. The following scaling equations are obtained so long as $E_F' >> \mu$

$$g_1' = \frac{1}{\pi V_s} g_1^2 \tag{10a}$$

$$g_c' = \frac{1}{\pi V_c} g_3^2 \tag{10b}$$

$$g_3' = \frac{1}{\pi V_c} g_c g_3 \tag{10c}$$

where g_j' signifies a derivative of g_j with respect to $\ln(E_F')$ and $g_c = g_{1\|} - 2g_2$. (When E_F' is of order μ, the scaling equations cross over to those of an incommensurate system which are the same as those in Eqs. (10) with g_3 (the umklapp scattering) set equal to zero.) (iii) The spin excitation spectrum is gapless if $g_1 > 0$, and has a gap Δ_s if $g_1 < 0$. The charge excitation spectrum is gapless if $g_c \geq |g_3|$, and has a gap Δ_c otherwise. However, the Fermi energy lies in the gap only so long as $\mu < \Delta_c$. (iv) The ground-state has a divergent antiferromagnetic susceptibility if $\Delta_s = 0$ and if the charge spectrum has a gap at the Fermi surface; it has a divergent singlet superconducting and/or CDW susceptibility if $\Delta_s > 0$ and if there is no gap to charge excitations at the Fermi surface. (v) We will show in Sect. IV that for $g_c < |g_3|$, $g_1 < 0$, and $g_3 > 0$, (*i.e.* for $U > 2V > 0$ and $W < -1/4\,(U - 2V)$) the strong-coupling limit can be completely analyzed in terms of nearest-neighbor valence bond states, in direct analogy with the RVB analysis of the 2d problem. In particular, the charge excitations are spinless solitons, which can be thought of as bosons with short ranged repulsive interactions, and the spin excitations are massive, neutral solitons.

In the half-filled repulsive Hubbard model ($U - 2V + 4W \geq 0$), antiferromagnetic fluctuations dominate over superconductivity and even on doping the system fails to become superconducting. How-

ever, the following fact is conspicuous. The scaling trajectory for the spin-degrees of freedom follows the separatrix between the $\Delta_s = 0$ and $\Delta_s > 0$ phases and eventually scales to the unstable noninteracting fixed point $g_{1\perp} = g_{1\parallel} = 0$. Thus one suspects that a small additional attraction might make the trajectories enter the $\Delta_s > 0$ phase.

We thus consider the effect of a weak retarded attraction which could arise due to a weak coupling of the electrons to almost any other degrees of freedom, since second order perturbation theory gives a negative contribution to the low energy states. We consider explicitly two extreme models of electron-lattice coupling: (i) the SSH model in which the lattice distortions modulate the electron-hopping matrix elements, ($\alpha \neq 0$, $\beta = 0$) which we will refer to as coupling to the bond charge, and (ii) the molecular-crystal (MC) model in which an optical phonon couples to the electron site energy ($\alpha = 0$, $\beta \neq 0$). The phonon propagator takes the usual Bose form, $D(k,\omega) = \omega^2(k)/(\omega^2 - \omega^2(k))$. For an SSH coupling, the coupling vanishes at zero momentum transfer, so we can approximate the dispersion by its value at the zone boundary, $\omega(k) \approx \omega(2k_F) = \omega_D$. For the MC model, we can approximate the optical-phonon dispersion by an Einstein oscillator. Thus, ω_D is roughly k independent and its frequency dependence can be approximated by

$$D(\omega) = \begin{cases} -1 & |\omega| < \omega_D \\ 0 & |\omega| > \omega_D \end{cases} \tag{11}$$

thus, we define[14,15] retarded interaction $\tilde{g}_j$ analogous to the instantaneous interactions g_j. For the SSH model $-\tilde{g}_1 = \tilde{g}_3 = 4(\alpha^2/K)a > 0$ and $\tilde{g}_2 = 0$ while for the MC model $-\tilde{g}_1 = -\tilde{g}_3 = -\tilde{g}_2 = (\beta^2/K)a > 0$.

The one loop scaling equations for this two cut-off model can be derived simply. The scaling equations for the instantaneous interaction g_j (Eqs. 10) are unaffected by the presence of retarded interactions to this order. The equations for the retarded interactions are

$$\tilde{g}_1' = \frac{1}{\pi V_F}[3/2\, g_1\tilde{g}_1 + g_3\tilde{g}_3 + 1/2\, g_c\tilde{g}_1 + \tilde{g}_1^2 + \tilde{g}_3^2] \tag{12a}$$

$$\tilde{g}_2' = 0 \tag{12b}$$

$$\tilde{g}_3' = \frac{1}{\pi V_F}[3/2\, g_1\tilde{g}_3 + g_3\tilde{g}_1 + 1/2\, g_c\tilde{g}_3 + 2\, \tilde{g}_1\tilde{g}_3] \tag{12c}$$

These results differ from earlier results[14,15] by the presence of cross-terms $g_j\tilde{g}_k$. The scaling equations for $\tilde{g}_1$ and $\tilde{g}_3$ can be combined to produce two separate scaling equations for $\tilde{g}^{\pm} = \tilde{g}_1 \pm \tilde{g}_3$

$$\tilde{g}'^{\pm} = \frac{1}{\pi V_F}[3/2\, g_1 \pm g_3 + 1/2\, g_c]\,\tilde{g}^{\pm} + \tilde{g}^{\pm 2} \tag{13}$$

which implies, among other things, that if initially $\tilde{g}_1 = \pm\tilde{g}_3$, as in both the MC and SSH models, this equality is preserved by the scaling equations. In addition to these equations, ω_D also renormalizes due to the Peierls softening;[10,11] for the SSH model

$$\omega_D' = \omega_D \frac{1}{\pi V_F}\tilde{g}^{+} \tag{14}$$

(Note that μ does not renormalize. This can be seen by bosoninzing the theory.[12] The density of electrons is then proportional to $\partial_x\Theta$, and hence the chemical potential is a topological term since it multiplies a total derivative.)

There are several important consequences of Eqs. (12) that are immediately apparent. A positive derivative implies that $\tilde{g}_j$ scales toward large negative values as high energy degrees of freedom are integrated out. For dominantly repulsive interactions, the cross terms are the most important, since $g_j >> \tilde{g}_j$. For the SSH model of $H_{el\text{-}ph}$ the first term in Eq. (12a) is negative, while all the other terms are positive, including the $\tilde{g}^2$ terms while in Eq. (12c) the first term is positive, and all other terms are negative. Thus, as g_1 scales to zero, and g_c and g_3 scale to larger magnitudes according to Eqs. (10), $\tilde{g}_1$ in particular, and $\tilde{g}_3$ also scale to larger magnitudes at an ever-increasing rate, and this rate is proportional to the strength of the electron–electron repulsion. If we make the crude approximation

$$-(3/2\, g_1 + g_3 + 1/2\, g_c) \approx -(3/2)\,\mathrm{AUa} >> \tilde{g} \text{ for } E_F >> E_F' > \omega_D,$$

then

$$\tilde{g}_1(E_F') \approx \tilde{g}_1[E_F/E_F']^{\theta} \tag{15}$$

where $\tilde{g}_1$ is the bare value of $\tilde{g}_1$, $\tilde{g}_1(E_F')$ is its renormalized value after integrating out the states between E_F and E_F', $\theta = (3/2)\mathrm{A}\ \mathrm{Ua}/\pi V_F$, and A is a number of order one which depends weakly on E_F'. For $|\tilde{g}| > g$, the scaling is even faster.

The perturbative scaling equations break down when $g_j/\pi V_F$ gets to be of order one, and even the notion of scaling equations becomes dubious; it is only in the vicinity of the (unstable) fixed point at $g_j = 0$ that we can safely ignore the irrelevant interactions that are generated as we integrate out the high energy degrees of freedom. Faced with this, one traditionally notes that the value of E_F' at which g_j gets to be of order one is a characteristic energy of the problem which can roughly be identified as the gap Δ. In the present problem, a crossover in the scaling equations can also occur when $E_F' \sim \omega_o$ where ω_o is defined by the expression $\omega_o = \omega_D(\omega_o)$ and $\omega_D(E_F')$ is the renormalized value of ω_D after that states with energy between E_F and E_F' have been integrated out. Hence ω_o is the physical phonon frequency. Because it is the simplest case, we will discuss here the situation in which $\omega_o > \Delta_c, \Delta_s$. (The case $\Delta_c, \Delta_s >> \omega_o$ has been treated[5-9] in the context of polyacetylene near half-filling and is qualitatively similar to the present results. The case $\Delta_c > \omega_o > \Delta_s$ is complicated and will be treated in a future communication.) When $E_F' \sim \omega_o$, g_j and $\tilde{g}_j$ represent practically the same scattering process, and we can approximately represent their combined action in terms of a single, non-retarded interaction

$$g_j^T = g_j(\omega_o) + \tilde{g}_j(\omega_o) \tag{16}$$

where $g_j(\omega_o)$ and $\tilde{g}_j(\omega_o)$ are obtained by integrating the scaling equations from E_F to ω_o. (There is also a small renormalization of the Fermi-velocity[14] which arises from integrating out the states with $E_F' \sim \omega_o$.) The result is that the properties of the system at energies small compared to ω_o can be derived from a standard g-ology model with interactions g_j^T, and band-width ω_o.

Several important physical consequences of the scaling equations can be derived simply:

(i) Even if the bare interactions are dominantly repulsive (*i.e.* $g_1 >> |\tilde{g}_1|$), if ω_o/E_F is sufficiently small, the low energy properties of the system will correspond to a negative g_1^T. Thus, the system will have a non-zero spin-gap and the possibility of divergent superconducting and CDW susceptibilities. Moreover, as shown in Eq. (15), this gap will be larger, the stronger the repulsive interactions.

(ii) Because of the decoupling between the spin and charge degrees of freedom the gap in the spin excitation spectrum is approximately independent of doping concentration for low concentration.

(iii) Despite the fact that the low energy properties are character-

istic of attractive interactions, at high energies or temperature, $E >> \omega_o$, the fact that the bare interactions are repulsive implies that the dynamic anti-ferromagnetic susceptibility should be large.

To obtain explicit expressions for the correlation functions, we must find a model along the scaling trajectory which we can solve in a controlled approximation. At present, we can only do this in a rather crude level of approximation. Here we sketch the results. The appropriate excitation spectrum, and the spin and charge factors for each correlation function of the g-ology model in Eq. (6) can be related[10–12] exactly (via bosonization) to the solution of a massive Thirring model

$$H_{MT} = \int dx \psi^+(x)[-iV_o\sigma_z\partial_x + \Delta_o\sigma_x + \mu_o]\psi(x) - g_o \int dx \psi_1^+(x)\psi_2^+(x)\psi_2(x)\psi_1(x) \tag{17}$$

where for the spin degrees of freedom

$$V_o = V_s = V_F\, 5/4\, [1 + 3/10\, \gamma_{1\|}] \tag{18a}$$

$$\mu_o = 0 \tag{18b}$$

$$\Delta_o = \Delta_s = E_F\gamma_{1\perp} \tag{18c}$$

and

$$g_o/\pi V_F = 3/2(1 + 5/6\gamma_{1\|}) \tag{18d}$$

while for the charge degrees of freedom

$$V_o = V_c = V_F \cdot 5/4\, (1 + \gamma_4 + 3/10\, \gamma_c) \tag{19a}$$

$$\mu_o = \mu \tag{19b}$$

$$\Delta_o = \Delta_c = E_F\gamma_3 \tag{19c}$$

and

$$g_o/\pi V_F = 3/2(1 + \gamma_4 + 5/6\, \gamma_c) \tag{19d}$$

where $\gamma_j = g_j/\pi V_F$ are dimensionless coupling constants. The spectrum of this model for $\mu = 0$ has been computed by Bethe ansatz, however the correlation functions are not known. The model is, of course, soluble on the Luther-Emery (LE) line where $g_o = 0$. However, we cannot simply assume that the correlation functions of the original model can be related to the solutions of the model on the LE line by using of the scaling equations, since the scaling equations are only exact near the unstable fixed point at $g_j = 0$. Away from this point, the irrelevant interactions which are generated upon integrating out the high energy states cannot be ignored, and since the LE lines occur when γ_1 and/or $\gamma_c = -6/5$, the irrelevant interactions can, in principle, be substantial.

Since the spin-spectrum has a gap, this does not produce major difficulties in handling the spin degrees of freedom. The only effect of the irrelevant interactions is to renormalize the spin-gap; the gap cuts off the antiferromagnetic and triplet-superconducting fluctuations, and the spin contribution to the singlet-superconducting and CDW susceptibilities is a constant factor proportional to the square of the gap.[11]

For the doped system, the irrelevant interactions change the charge excitations from non-interacting quasi-particles to an interacting system. Thus, it is not reasonable to scale as far as the LE line. If we scale the system to the vicinity of the LE line, so that

$$X = \left|\frac{g_c}{2\pi V_F}\right| \ln\left(\frac{E_F'}{\Delta}\right) << 1$$

the model is still soluble in the sense that scattering between the negative and positive energy states can be trated in perturbation theory[17] in X. In studying the low energy properties of the system, we can linearize the spectrum about μ, which results in a new effective Hamiltonian, of the same form as H_{MT}, but with $\Delta_o = 0$ (massless Thirring model) and the remaining terms determined up to perturbative corrections in powers of X from the parameters of the original model according to $V_o = V_c(\mu - \Delta_c)/\Delta_c$, the band-width cutoff $E_F = |\mu - \Delta_c|$, and the interaction g_o unchanged. The massless Thirring model is exactly soluble by bosonization. To minimize the importance of the irrelevant interactions, we would like to stop the scaling where γ_j is as small as possible. However, the smaller the value of g_o where we stop scaling (hence the closer γ_c is to $-6/5$), the more accurate

is our perturbative solution of the MT model. The optimal accuracy is thus obtained if we scale to the point E_F' where both

$$X = \left|\frac{g_c}{2\pi V_c}\right| \ln\left(\frac{E_F'}{\Delta_c}\right) \text{ and } Y = |\gamma_c| \ln\left(\frac{E_F}{E_F'}\right)$$

are smaller than 1. This can be done with only moderate accuracy. What this means is that while the low energy, long wavelength properties of the charge excitations are well approximated by a Massless Thirring model, we can only approximately determine the dependence of the parameters of that model on the bare parameters. Fortunately, none of our conclusions are extraordinarily sensitive to the precise values of any of these parameters.

Combining all these results we obtain an approximate expression for the two divergent susceptibilities at low temperatures, $kT < \min\{\Delta_s, E^*\}$: the superconducting susceptibility is obtained as:

$$\chi_{SS} \sim \left(\frac{\Delta_s}{hV_s}\right)^2 (E^*/kT)_c^{2-\theta^{-1}} \tag{20}$$

and for the incommensurate CDW susceptibility we obtain

$$\chi_{CDW} \sim (\Delta_s)^2 (E^*/kT)^{2-\theta_c} \tag{21}$$

where the exponents

$$\theta_c = \left(\frac{1 + \gamma_4 + 1/2\gamma_c}{1 + \gamma_4 - 1/2\gamma_c}\right)^{1/2} \tag{22}$$

and the characteristic energy below which the fluctuations begin to diverge is the minimum of Δ_s and

$$E^* = |\mu| - \Delta_c. \tag{23}$$

As mentioned above we can only roughly calculate the value of θ_c in terms of the parameters of the original model, but since both X and Y must be small, $0 > \gamma_c > -6/5$, and hence $1/2 < \theta_c < 1$—the CDW susceptibility is thus the most divergent, but the superconducting susceptibility is likely comparably divergent. It is easy to see as well that the stronger the bare repulsive interactions the larger the Δ_s, and hence the stronger the fluctuations. The only important role of the retarded interactions is to produce a gap in the spin spectrum.

IV. VARIATIONAL ANALYSIS IN TERMS OF VALENCE BOND STATES

In this section we consider the purely electronic Hamiltonian given in Eq. (2) in the strong coupling limit $U - 2V >> t$, and $W < 0$. We consider the case of attractive bond charge interaction $W_o \to W < 0$ in Eq. (2). We treat this problem in terms of a variational ansatz for the ground state and the low lying excited states.

Our ansatz wave function for the ground state for the half-filled band is constructed out of a product of nearest-neighbor valence bond pairs. Because of the one-dimensional geometry, there are only two such states we can construct, as shown in Fig. 1a. Thus, for instance, $|\psi_A\rangle$ is the state

$$|\psi_A\rangle = \prod_n{}' b^\dagger_{2n} + |0\rangle \tag{24a}$$

where

$$b^+_n = \frac{1}{\sqrt{2}} [C^+_{n\uparrow} C^+_{n+1\downarrow} + C^+_{n+1\uparrow} C^+_n \downarrow] 0\rangle \tag{24b}$$

where the prime signifies that the product is over half the number of sites and the phase convention for the valence bond states is defined in Eq. (24b). Since $|\psi_A\rangle$ and $|\psi_B\rangle$ are macroscopically distinct, we must choose one or the other to be the ground state (broken symmetry). Thus, as with the Laughlin[18] state in the quantum Hall effect, we have constructed a variational trial state with no variational parameters. The variational ground state energy is easily evaluated to second order in t:

$$\langle\psi_A|H|\psi_A\rangle = -N\,(5/4\,J) = E_o \tag{25}$$

where N is the number of sites and

$$J = -W + 2t^2/(U - V) \tag{26}$$

is the effective coupling. This is a fairly good variational energy, but we do not consider it worthwhile to compare it to variational energies of states with different symmetry.

As long as our variational ansatz is a good approximation to the true ground state, it has broken symmetry; perturbative corrections cannot change this conclusion. It can be characterized by a charge density wave order parameter

$$\hat{\phi} = (-1)^n \frac{8}{3}\left\{\left[\sum_s C^+_{ns}C_{n+1s} + \text{h.c.}\right]^2 + \frac{5}{8}\right\} = (-1)^n \frac{4}{3}\underline{S}_n\cdot\underline{S}_{n+1} \tag{27a}$$

where

$$\underline{S}_n = \frac{1}{2}\sum_{ss'} C^+_{ns}\,\underline{\sigma}_{ss'}C_{ns'}. \tag{27b}$$

In A-phase

$$\langle\psi_A|\,\hat{\phi}_n|\psi_A\rangle = 1 \tag{28}$$

while in B-phase

$$\langle\psi_B|\hat{\phi}_n|\psi_b\rangle = -1. \tag{29}$$

All other correlations are short-ranged for the half-filled band since, as we shall see, there is a gap to spin and charge excitations.

The energy of spin excitations can also be estimated variationally by constructing a plane wave of spin soliton states of the sort shown in Fig. 1b.:

$$|\psi_{2ns}\rangle = \left[\prod_{m<n} b^+_{2m}\right] C^+_{2ns}\left[\prod_{m>n} b^+_{2m-1}\right]|0\rangle \tag{28a}$$

in terms of which

$$|\chi_{ks}\rangle = \sqrt{\frac{2}{N}}\sum_n{}' e^{2ikn}\,|\psi_{2ns}\rangle. \tag{28b}$$

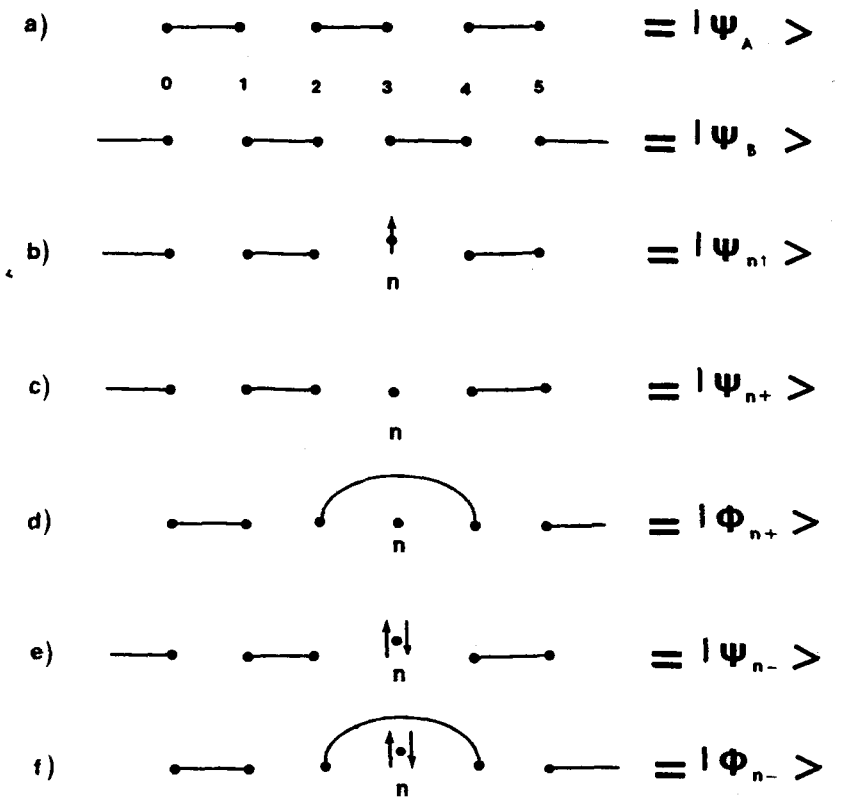

FIGURE 1 Diagrammatic representation of valence bond states. Here a line between two sites represents a singlet pair on those two sites.
a) The two possible valence bond ground states. The numbers label the lattice sites.
b) A spin-soliton on site n. Here the isolated site n is occupied by a single electron of the indicated spin.
c) A positively charged soliton. Here the isolated site n is unoccupied.
d) A positively charged soliton with extended valence bond pair. Note that from a topological point of view, the soliton is on site $n + 1$ (or $n - 1$), not on site n.
e) A negatively charged soliton. (see c).
f) A negatively charged soliton with an extended valence bond pair.

The dispersion relation of the spin quasi-particle is then computed according to

$$E(k) = \frac{\langle \psi_{ks} | H | \psi_{ks} \rangle}{\langle \psi_{ks} | \psi_{ks} \rangle} - E_o \tag{29a}$$

$$= J\left\{\frac{5}{4} - \frac{2}{3}\left[\frac{5\cos(2k) - 4}{5 - 4\cos(2k)}\right]\right\} \tag{29b}$$

In computing $E(k)$ we have used the relations

$$\langle \psi_{ns} | H | \psi_{n+2ms} \rangle = \left(\frac{1}{2}\right)^m \left\{ E_o + \frac{5}{4} J + |m| \frac{J}{2} \right\} \tag{30}$$

and

$$\langle \psi_{ns} | \psi_{n+2ms} \rangle = \left(\frac{1}{2}\right)^{|m|} \tag{31}$$

$E(k)$ is minimal for small k, $E(k) \approx \Delta_s[1 + Ak^2]$ where $\Delta_s = 7/12$ J and $A = 144/7$.

Note that the spin excitation is indeed a topological soliton in that it is a domain wall between A-phase and B-phase. Thus, spin quasiparticles must be created in soliton-anti soliton pairs (the gap to spin excitations is $2\Delta_s$), and they can never pass each other. To construct multi-soliton wave-functions, they can be treated as hard-core bosons or spinless fermions. (In one dimension, there is not distinction between the two.) Their quantum numbers are easily determined by inspection: they are locally charge neutral and they have spin 1/2. An important consequence of their topological nature is that even a very dilute gas of them destroys the long range charge density wave order. In particular, if we consider the charge-density wave correlation function in the presence of a finite concentration of these neutral solitons

$$\langle \hat{\phi}_n \hat{\phi}_{n+m} \rangle = \left\langle exp\left[i\pi \sum_{l=n+1}^{n+m} \hat{N}_n \right] \right\rangle \sim |m|^{-\alpha} \tag{32}$$

where $\hat{N}_n$ is the soliton number operator such that $\hat{N}_n = 1$ if site n is occupied by a soliton (regardless of its spin) and $N_n = 0$ if site n is unoccupied, and α is an exponent which can be computed in terms of the density–density correlation function of the soliton gas, and depends somewhat on the soliton–soliton interactions (see discussion of the Massive-Thirring model above).

The nature of the charge excitations can be studied by a similar variational ansatz. To study the charge $+e$ soliton states, we consider diagonalizing the Hamiltonian in the subspace of states of the sort

shown in Figs. 1c and 1d. $|\psi_{n+}\rangle$ is a state with a positively charged soliton at position n

$$|\psi_{n+}\rangle = \left[\prod_{m<n} b^+_{2m}\right]\left[\prod_{m>n} b^+_{2m-1}\right]|0\rangle \tag{33}$$

and $|\tilde{\psi}_{n+}\rangle$ is a state with a positively charged soliton at position n and a long bond connecting sites $n-1$ and $n+1$

$$|\tilde{\psi}_{n+}\rangle = \left[\prod_{m<n-1} b^+_{2m}\right]\frac{1}{\sqrt{2}}\left[C^+_{2n-1\uparrow}C^+_{2n+1\downarrow} + C^+_{2n+1\uparrow}C^+_{2n-1\downarrow}\right]\prod_{m>n+1} b^+_{2m-1}|0\rangle. \tag{34}$$

The approximate eigenstates are thus of the form

$$|\chi_{k+}\rangle = \frac{1}{\sqrt{N}}\sum_m e^{2ikm}\{u_k|\psi_{2m+}\rangle + v_k|\tilde{\psi}_{2m+1+}\rangle\} \tag{35}$$

and u_k/v_k is computed from the solution of the characteristic equation. The resulting excitation spectrum is

$$\begin{aligned} E^{(+)}_k &= \frac{U}{2} + \frac{5J}{2} + 4W \pm \sqrt{\left(\frac{3J}{4}\right)^2 + 4t^2\sin^2(k)} \\ &\approx \frac{U}{2} \pm 2t|\sin(k)| \end{aligned} \tag{36}$$

where the second line is valid for $t \gg J$. By charge conjugation symmetry, the analogous states with negative charge can be obtained by placing two electrons on the positively charged solitons.

As with the neutral quasi-particles, these charged quasi-particles are topological solitons. For the half-filled band, the gap to charge excitations is thus Δ_c where

$$\begin{aligned} \Delta_c &= \frac{U}{2} + \frac{5J}{2} + 4W - \sqrt{\left(\frac{3J}{4}\right)^2 + 4t^2} \\ &\approx \frac{U}{2} - 2t. \end{aligned} \tag{37}$$

The quasi-particles have charge $\pm e$ and spin 0. At finite concentration (that is, at non-zero chemical potential) the charge density wave correlation function behaves as in Eq. (18) where N_n now measures the occupation number of charged solitons. Similarly, we expect power-law correlations for the super-conducting fluctuations

$$\langle C^+_{n\uparrow} C^+_{n+1\downarrow} C_{m\downarrow} C_{m+1\uparrow} \rangle \sim \left(\frac{1}{|n-m|}\right)^{\alpha} \tag{38}$$

where at this level of approximation, α is the *same* exponent as in Eq. (32) for the CDW correlation. Again, the charged quasi-particles could equally well be characterized as hard-core bosons or spinless fermions.

V. THE RELATION TO RVB THEORY

The RVB theory is based on a variational ansatz similar to the one in Section IV for the ground state of the half-filled band in a two-dimensional Hubbard model, and on an analysis of the quasi-particle excitations. Like that theory, we have found superconductivity from dominantly repulsive, short-ranged interactions in a nearly half-filled Hubbard model. At high temperatures or energies, both the 1d and 2d systems behave like a fluctuating Heisenberg anti-ferromagnet.[10,20] We find that in one-dimension the charge excitations are spinless solitons, and the spin-excitations are chargeless solitons, as they are in the RVB state.[21] We find, moreover, that there is a gap in the spin excitation spectrum, which is consistent with the two-dimensional analysis of Kivelson, Rokhsar, and Sethna,[21] and the earlier analysis of Fazekas and Anderson,[22] and in contrast to the recent work of Baskaran, Zou, and Anderson,[19,20] but this could be special to one-dimension where there is no valence bond resonance. While the difference between bosons and spinless fermions is not clear in one-dimension, the fact that the characteristic energy scale for superconducting fluctuations is determined by the degeneracy temperature of the holes, E^*, rather than some lower, pairing energy, suggests that they are best thought of as bosons with repulsive interactions. This is again reminiscent of the RVB theory where the holes are bosons.[21]

VI. STRATEGIES FOR PRODUCING HIGHLY CONDUCTING AND SUPERCONDUCTING POLYMERS

There can be no finite temperature phase transition in a one-dimensional system, and, other than for the half-filled band, there is not even a broken symmetry state at zero temperature. Nonetheless, the fact that the superconducting susceptibility begins to diverge below the hole degeneracy temperature $E^* = h^2/2m^* (\pi/a)^2 x^2$, where m^* is the hole effective mass and x is the hole concentration per site, implies that if stabilized by interchain interactions, systems which condense into the valence bond state described above are good candidates for high temperature-superconductors. There are several features which determine the optimal materials for finding high temperature-superconductivity:

A. The formation of a valence bond state:

For this it is necessary for the system to have a nearly half-filled band. Far from a half-filled band, the system can lower its energy by breaking valence bonds, and forming a more normal metallic state. In terms of the continuum model, this is reflected in the fact that far from half-filling, g_3 has negligible effect so that the scaling of g_1 to larger negative values in Eq. (13) is much slower at best, and may even change directions. Of course, for the half-filled band, the system is insulating and for x too small, the value of E^* is also small, and any disorder will localize the holes. The optimal value of x is thus the largest value of x which does not destroy the valence-bond state. Two signatures of systems with a tendency to form this state are that they form a bond-charge density wave when the band is half-filled, and that the charge carriers formed on doping are spinless. These are, of course, also features of the SSH model of polyacetylene, and apparently are properties of most conducting polymers.[9]

B. Small value of the hole effective mass, m*:

A second quantity which sets the scale of E^* is the hole effective mass, m^*. In the limit we have considered here, where the electron–phonon interactions are weak, the hole effective mass is a number greater than, but of order one times the band effective mass (see Eq. (36)). When the electron–phonon coupling is much stronger than the electron–electron interactions, and especially for $\hbar\omega_o \ll \Delta_s$, we expect a large polaronic increase in the effective mass. In this limit, the

effective mass is proportional to the ion mass $M = K/\omega_0^2$ according to[4]

$$m^* = A\,M\left(\frac{\bar{U}^2}{a}\right)\left(\frac{a}{\xi}\right) \tag{39}$$

where A is a number of order 1, $\bar{U}$ is the magnitude of the Peierls distortion, and ξ is the width of the charged soliton. (That Coulomb interactions tend to reduce the hole effective mass can be seen[5] even in this limit, where, to first order in U, ξ is an increasing function of U, and hence m^* is a decreasing function.) Ideally, one wants to find a system with the smallest electron-phonon coupling needed to stabilize the valence bond state. In polyacetylene, there is a moderate increase in the soliton effective mass due to electron-phonon coupling; it is found experimentally[24] to be $m^* \approx 3m_e$.

C. Large value of the interchain Josephson coupling

A single soliton cannot hop between chains. At high temperatures the interchain hopping must be dominated by some form of incoherent inter-soliton hopping[25] as shown in Figure 2a in which an electron hops from a neutral solition on one chain to a charged solition

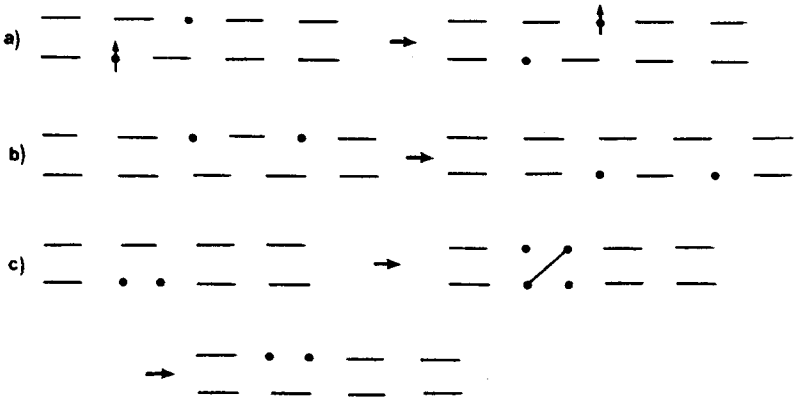

FIGURE 2 Interchain coupling-schematic representations of:
a) Intersoliton hopping
b) Incoherent soliton pair hopping
c) Josephson coupling or coherent soliton pair hopping. In the virtual intermediate state there is a neutral soliton on each chain. It is clear that this process can also be viewed as the coherent tunneling of a valence bond (*i.e.*, a real space Cooper pair) between chains.

on another, or effectively charged and neutral soliton on neighboring chains swap places. This process is proportional to the concentration of neutral solitons hence at $T < \Delta_s$, this process should produce a conductivity $\sigma_\perp \sim \rho_s kT$, where $\rho_s = 1/\pi V_s$ is the density of states for neutral solitons in the absence of interactions. An analogous process has been proposed[26] to explain the conductivity in the C direction in $YBa_2Cu_3O_{7-x}$. At $T < \Delta_c$, this process makes an exponentially small contribution to the conductivity, $\sigma_\perp \sim e^{-\Delta s/kT}$. Here incoherent soliton pair hopping[27] shown schematically in Figure 2b could make a significant contribution to the conductivity. However, we consider it more likely that coherent pair tunneling, *i.e.* Josephson tunelling, should be the most significant process for $T < \Delta_s$. As is clear from Figure 2c, in the absence of polaronic effects, this should produce a Josephson coupling T per unit cell between neighboring chains of order

$$T = A_o\, t_\perp^2/\Delta_s \tag{40}$$

where A_o is a number of order 1 and $t_\perp$ is the interchain hopping matrix element. In the presence of strong coupling to slow ($\hbar\omega_o \ll \Delta_s$) phonons, this coupling will be reduced by a Frank-Condon factor. However, calculations[28] done in the pure SSH model suggest that even here, the Frank-Condon factor reduces t by a small amount only.

In the presence of a Josephson coupling between chains, a true phase transition to a superconducting state can occur. Following Efetov and Larkins's[30] self-consistent harmonic approximation, we estimate the superconducting transition temperature according to

$$T\chi_{ss}(T_c) = kT_c \tag{41}$$

where χ_{ss} is the one-dimensional singlet superconducting susceptibility, which we estimated in Eq. (20). Thus

$$kT_c \sim A\,(E^*)\left[\left(\frac{t_\perp}{t_o}\right)^2 \frac{\Delta_s}{E^*}\right]^x \tag{42}$$

where $x = \theta_c/(3\theta_c - 1)$ is between 0.5 and 1, and again A is a number of order 1.

We see that to attain a high T_c, the ideal system should have a

large T, hence moderately well coupled chains ($t_\perp$ not too small) and weak electron–phonon coupling.

D. SUPPRESSION OF THE 3-D CDW INSTABILITY BY FRUSTRATION

The other instability which generally competes with superconductivity in quasi-one-dimensional systems is the CDW or Peierls instability; in the present model we have seen that the CDW susceptibility is at least as divergent as the SS susceptibility. Thus, if the system is to be metallic or superconducting, the 3-D CDW instability must be suppressed. Fortunately, this can be done rather straightforwardly by introducing a small amount of disorder into the system to frustrate the CDW order. A small degree of disorder in the arrangement of the dopant atoms will tend to pin the CDW with random relative phases on different polymer chains, thus making phase-locking between neighboring chains difficult. By contrast, such disorder will have small effect on the metallic state,[29] nor on the superconducting transition. Alternatively, if the polymer chains interweave with each other, as shown in Figure 3, this will frustrate the CDW transition, since the CDW coupling is an intrinsically "anti-ferromagnetic" in that it favors the opposite sign of the order parameter on neighboring chains,[31] while it will have little effect on the superconducting transition since the Josephson coupling is "ferromagnetic." The conclusion is that while good polymer alignment and perfection are desirable to enhance coherence effects, perfect crystallinity may not be a desirable goal, since a polymer crystal, like the charge transfer salts before them, will likely condense into a semiconducting Peierls state at low temperature rather than remaining metallic, or becoming a superconductor.

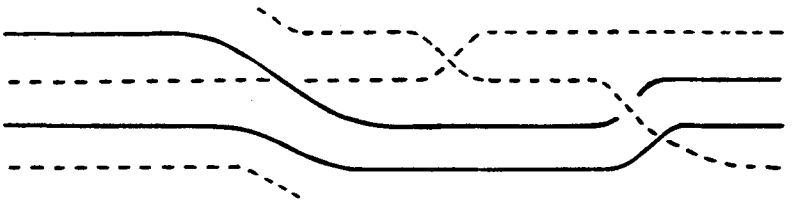

FIGURE 3 Schematic view of the sort of interweaving of polymer chains that frustrates the CDW instability. To the left, the phases of the order parameter on the various chains are chosen to minimize the interchain coupling (—— represents positive order parameter) and (---- represents a negative order parameter). Note the frustration produced by the interweaving.

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