

Supersymmetric Treatment of Random Disorder in the Continuum Model of Polyacetylene

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We employ a supersymmetric functional-integral formalism based on the method of Bohr and Efetov to study the influence of both "site" and "bond" disorder on the nature of the ground state of the continuum model of polyacetylene. We find exact results for the electronic density of states and the amplitude of the Peierls dimerization as functions of the strength of the disorder. As the disorder is increased, the dimerization amplitude decreases to zero continuously for bond disorder and discontinuously for site disorder.

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The extent to which random (impurity) disorder influences the electronic properties of the soliton-bearing¹⁻³ polymer polyacetylene has been the subject of several investigations.⁴⁻¹¹ In all of these investigations, certain assumptions and/or approximations had to be made which unfortunately limit the usefulness or range of validity of the results, and as a consequence no general conclusions could be drawn. Of central importance to soliton existence and behavior in polyacetylene is the extent to which the introduction of random disorder (for example, a random distribution of impurities) influences the nature of the Peierls dimerized ground state.¹ In this Letter we report exact results for the dependence of the electronic density of states and dimerization amplitude on the strength of random disorder introduced either in (i) the hopping matrix element connecting the tight-binding electronic orbitals on neighboring (CH) groups ("bond" or "off-diagonal" disorder), such as might arise, for example, from imperfections in the spacing between neighbors, or in (ii) the on-site electronic energy ("site" or "diagonal" disorder), such as might arise from substi-

tutional impurities.¹²

Our results are obtained with an adaptation of the supersymmetry method¹³ used by Bohr and Efetov¹⁴ to treat the case of random disorder in a one-dimensional free-electron model. With this method one is able to average over the disorder at an early stage in the calculation and arrive at an effective-field theory involving the original fermion fields and a set of auxiliary boson fields which enter the effective Lagrangian in a supersymmetric fashion. This Lagrangian can be analyzed by a transfer-operator method to obtain the averaged density of states as well as correlation functions of interest. We refer the reader to Refs. 13-15 for details of the supersymmetry method and its application to one-dimensional systems. Here we only sketch the broad outlines of the method as it applies to polyacetylene and postpone the details to a more complete paper.¹⁵

Our starting point is the continuum model of the electronic properties of a polyacetylene chain introduced by Takayama, Lin-Liu, and Maki¹⁶ (TLM). The Hamiltonians for the two types of disorder are given by (when we set $v_F = 1$ in the TLM model)

$$H = \frac{1}{2}(\omega_Q/g)^2 \int dx \Delta^2(x) + \int dx \Psi^\dagger(x) [-i\sigma_3(\partial/\partial x) + (1 + \sigma_2)\delta_s U_s(x) + \{\Delta(x) + \delta_b U_b(x)\}\sigma_1] \Psi(x), \quad (1)$$

where ω_Q is the maximum phonon frequency in the discrete-lattice model of Su, Schrieffer, and Heeger¹ (SSH), g is a scaled electron-phonon coupling constant, and $\Delta(x)$ is proportional to the amplitude of the dimerization which is regarded as a static, classical field in the TLM model. The parameter pair $(\delta_s, \delta_b) = (1, 0)$ for site disorder or $(0, 1)$ for bond disorder, the $\{\sigma_i\}$ are Pauli matrices, and $\Psi(x)$ is a two-component pseudospinor field composed of right- and left-moving electron fields, $u(x)$ and $v(x)$. The uniform dimerized Peierls state is characterized by a constant value of Δ , and we shall regard Δ as a constant in what follows. The extension to the case of a spatially varying dimerization amplitude, such as occurs when a soliton is present, will be treated in a subsequent paper. The bond-disorder potential,

$U_b(x)$, is assumed to be randomly distributed with zero average and to obey a Gaussian δ -correlation law, $\langle U_b(x)U_b(x') \rangle = \gamma_b \delta(x-x')$. The site-disorder potential, $U_s(x)$, is also assumed to be δ correlated with strength γ_s , but having *nonzero* mean, $\langle U_s(x) \rangle = U_0$. In actual samples of polyacetylene, one would expect that both bond and site disorder, as well as more complicated disorder, may be present simultaneously. Thus, we must regard the disorder cases discussed here as the simplest limiting cases which nevertheless provide benchmarks for more realistic (but likely only approximate) treatments.

The averaged density of states can be expressed¹³ as $\langle \rho(E) \rangle = \pi^{-1} \langle \text{Im} G^R(x, x; E) \rangle$, where the retarded Green's function can be formally written in terms of the

(unknown) eigenfunctions $\{\phi_k\}$ and eigenvalues $\{E_k\}$ of the full Hamiltonian as

$$G^R(x, x'; E) = \sum_k \frac{\phi_k^*(x)\phi_k(x')}{E - E_k + i\delta} = \sum_k \phi_k^*(x)\phi_k(x')G^R(k; E), \tag{2}$$

where $G^R(k; E)$ is represented¹³ as a function integral over supervectors $\Phi_k \equiv (\begin{smallmatrix} \chi \\ \xi \end{smallmatrix})$:

$$G^R(k; E) = -i \int d\Phi_k^* d\Phi_k \Phi_{\alpha k} \Phi_{\alpha k}^\dagger \exp[i\Phi_k^\dagger \{E - E_k + i\delta\} \Phi_k]. \tag{3}$$

In Eq. (3) the subscript α takes either of two values which indicate the fermionic (χ) or bosonic (S) components of Φ_k (each of the components χ and S is itself a two-component vector containing "right- and left-moving" fields so that the superfield Φ_k is a four-component object).

The averaging over the disorder can now be done¹³ with the result that the average of the retarded Green's function can be written in terms of an effective Lagrangian¹⁵ involving superfields alone, and the remaining functional integrations may be performed with the aid of a transfer-integral operator technique,¹⁷ which leads to an effective Schrödinger problem involving the following supersymmetric Hamiltonian for the two cases ($i = s, b$):

$$H_i = -\frac{1}{\mu} \left\{ \frac{\partial^2}{\partial S^* \partial S} + \frac{\partial^2}{\partial \chi^* \partial \chi} \right\} + \mu(\Delta^2 - E^2 + 2\delta_s U_0 E) \Phi^* \Phi + \beta_i (\Phi^* \Phi)^2, \tag{4}$$

where $\beta_b \equiv 2\Delta^2 \gamma_b + \gamma_b^2/2$, $\beta_s \equiv 2E^2 \gamma_s$. We note here that $\Phi^* \Phi = (|S|^2 + |\chi|^2)$. The averaged density of electronic states is obtained from the imaginary part of the Green's function as noted above. This in turn can be expressed in terms of the analytically continued ($\mu \rightarrow i$) ground-state eigenfunction¹³⁻¹⁵ of H_i to yield exact results for the two cases ($i = s, b$):

$$\langle \rho_i(E) \rangle = 4\pi^{-2} \beta_i^{1/3} |E - \delta_s U_0| \frac{\text{Ai}'(z_i)\text{Ai}(z_i) + \text{Bi}'(z_i)\text{Bi}(z_i)}{[\text{Ai}^2(z_i) + \text{Bi}^2(z_i)]^2}, \tag{5}$$

where $z_i \equiv \beta_i^{-2/3} [\Delta^2 - E^2 + 2\delta_s U_0 E]$ and $\text{Ai}(z_i)$ and $\text{Bi}(z_i)$ are Airy functions¹⁸ of the first and second kinds, respectively. These results are very similar to that obtained some time ago by Halperin¹⁹ for the one-dimensional free-electron gas in the presence of disorder.

The density of states given by Eq. (5) depends on the dimerization amplitude (order parameter), Δ , which remains to be determined. This is accomplished by minimization of the total averaged energy with respect to Δ with due regard given¹⁵ to the fact that the cutoff¹⁶ required for the electronic energy spectrum in the TLM model now depends on Δ and the disorder strength γ_i because of the altered density of states and the requirement that the total number of electrons to be accommodated is the same¹² as in the valence band of the unperturbed TLM model. In Ref. 15 we give the details of this straightforward procedure which involves a numerical search for the value of Δ which satisfies both requirements.

In Fig. 1 we present the results for Δ as a function of increasing disorder for representative values of the dimensionless electron-phonon coupling constant¹⁶ λ . Note that for the bond-disorder case Δ decreases in a continuous manner along an almost BCS-like curve until a critical value $\gamma_{b,c}$ is reached above which the dimerization amplitude is identically zero implying the destruction of the Peierls state. As γ_b approaches $\gamma_{b,c}$ from below we find that the dimerization decreases as $\Delta = [(\gamma_{b,c} - \gamma_b)/2]^{1/2}$. For the site disorder case the formalism above was carried out with γ_s and U_0 treated as general independent parameters, but for the purpose of plotting

representative results we consider the specific simple case of attractive δ -function impurities with average strength κ_0 and concentration²⁰ c . Then $U_0 = -c\kappa_0$ and $\gamma_s = c\kappa_0^2$. Fixing κ_0 (we choose $\kappa_0 = 1$) then leaves the concentration as the variable parameter determining the "strength" of the site disorder. Note that there is a *discontinuous* drop of Δ to zero at a critical value of concentration c_c . This discontinuity results from the existence of two branches of solutions for the energy minimization problem, one of which is a "metastable" minimum corresponding to $\Delta = 0$ which becomes lower in energy than the finite- Δ solution when the concentration

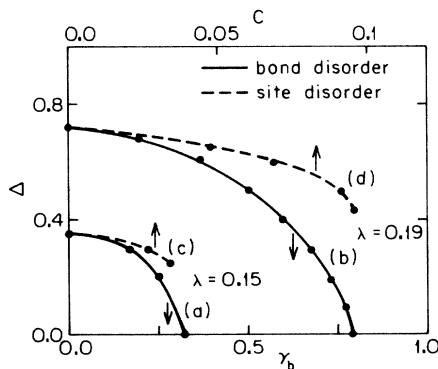


FIG. 1. Dimensionless dimerization amplitude Δ as a function of disorder strength γ_b for bond disorder [curves a and b] and of concentration c for site disorder [curves c and d] for two values of the electron-phonon coupling λ .

exceeds the critical value. This behavior is similar to that obtained by Gomez-Santos and Ynduráin¹¹ using a single-impurity approximation for the discrete-lattice SSH model¹ in the presence of substitutional impurities.

In the top panel of Fig. 2 we plot the dimensionless density of states per unit length for several bond-disorder strengths. Note that for small values of γ_b there exists a "pseudogap" in the density of states, while for larger values there is a significant density of states in the energy region where a gap would exist [curve (a)] in the pristine Peierls state; curve (d) represents the situation where $\gamma_b > \gamma_{b,c}$ and the dimerization order parameter Δ has vanished. There is an exact zero in the density of states at $E=0$ for all values of γ_b . This is a consequence²¹ of the facts that the disorder function, $U_b(x)$, is symmetrically distributed about zero and that its "off-diagonal" presence does not destroy the electron-hole symmetry³ possessed by the TLM Hamiltonian. We also note that the local maxima appearing as remnants of the square-root divergences in the pure system are gradually suppressed as γ_b is increased and they disappear altogether for $\gamma_b > \gamma_{b,c}$.

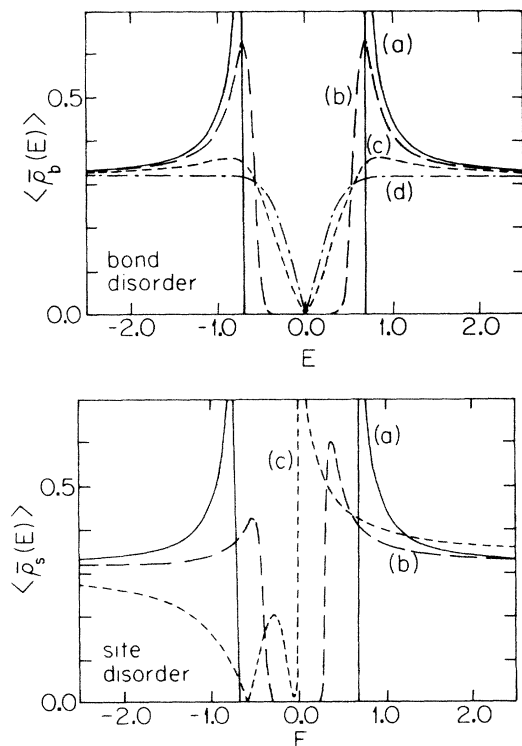


FIG. 2. Dimensionless density of electronic states per unit length (with $\lambda=0.19$). Top panel: $\langle \bar{\rho}_b(E) \rangle \equiv \langle \rho_b(E) \rangle / L$ for several bond-disorder strengths: curve a, $\gamma_b=0.0$ [$\Delta=0.7$]; curve b, $\gamma_b=0.1224$ [$\Delta=0.65$]; curve c, $\gamma_b=0.4604$ [$\Delta=0.5$]; and curve d, $\gamma_b=1.204$ [$\Delta=0.0$]. Bottom panel: $\langle \bar{\rho}_s(E) \rangle \equiv \langle \rho_s(E) \rangle / L$ for three site-disorder (impurity) concentrations c . Curve a, $c=0.0$ [$\Delta=0.7$]; curve b, $c=0.096$ [$\Delta=0.43$]; and curve c, $c=0.55$ [$\Delta=0.0$].

In the bottom panel of Fig. 2 we plot the dimensionless density of states per unit length for the site-disorder case. Its "diagonal" presence in the Hamiltonian (1) shifts the energy spectrum to the left because of the negative mean value of the disorder function $U_s(x)$ [see above]. Note that for $c > c_c$ a power-law divergence ($\rho_s \sim E^{-2/3}$) occurs as $E=0$ is approached from above, followed by a very rapid exponential drop just below $E=0$ to a very small value. A peak occurs between this minimum and an exact zero [due to the assumed symmetric distribution of $U_s(x)$ about its mean] at lower energy.

In Fig. 3 we plot the dependence of the critical disorder parameters, $\gamma_{b,c}$ and c_c , on the dimensionless electron-phonon coupling constant, λ . The numerical results for $\gamma_{b,c}$ are very well fitted by the expression $\gamma_{b,c} = (0.154 - 0.435\lambda) \exp[-3/4\lambda]$ for small λ . In fact, the exponential dependence agrees precisely with the behavior obtained from a small- λ (small- γ_b) analysis based on the asymptotic properties¹⁸ of the Airy functions appearing in Eq. (5). For λ values larger than about 0.2 there are significant corrections as can be seen in the inset of Fig. 3 where we plot $-\ln \gamma_{b,c}$ vs $1/\lambda$. We have not succeeded in obtaining an approximate analytic expression for the site-disorder case, because of the discontinuous behavior which precludes a small- Δ analysis.

Much remains to be done before detailed comparisons with experiment will be possible. A promising approach would involve the controlled introduction of disorder via substitutional impurities and subsequent measurement of quantities³ which are sensitive to the density of states, such as optical absorption, photoconductivity, etc. If reliable estimates of the average impurity-potential strength can be made, then at least a crude comparison with the theoretical results reported here may be attempted. On the theoretical front, more realistic types¹²

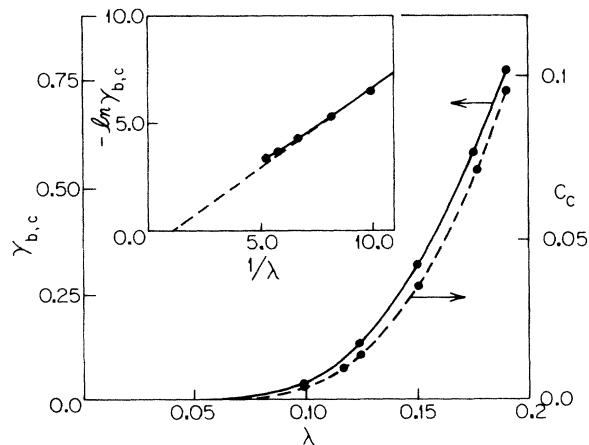


FIG. 3. Dimensionless critical strength $\gamma_{b,c}$ for bond disorder and critical impurity concentration c_c for site disorder as a function of the dimensionless electron-phonon coupling constant λ . Inset: $-\ln \gamma_{b,c}$ vs $(1/\lambda)$.

of disorder need to be considered as discussed above and three-dimensional effects³ will need to be incorporated. Our results should provide useful starting points for these efforts.

Clearly the destruction of the Peierls dimerized state for disorder strengths above the critical values would appear to preclude the existence of solitons which serve as "domain walls" between the two equivalent dimerized ground states in the pristine model. Below criticality, however, the dimerized state still exists and so, therefore, should solitons. Several interesting questions then arise, including (i) the nature of the localized mid-gap electronic state¹ associated with the soliton [presumably this state gives a smeared peak (for low disorder) rather than a delta function in the density of states], (ii) whether the soliton helps or hinders the stability of the Peierls state when the disorder is nearly critical, and (iii) the manner in which the disorder influences the signature of soliton states in response properties such as optical absorption. These and other questions are currently under investigation using a supersymmetric effective Lagrangian which incorporates the spatial variation of the dimerization amplitude.

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