

Mott-Peierls transition in the extended Peierls-Hubbard model

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(Received 25 November 1997)

The one-dimensional extended Peierls-Hubbard model is studied at several band fillings using the density-matrix renormalization-group method. Results show that the ground state evolves from a Mott-Peierls insulator, with a correlation gap at half-filling, to a soliton lattice with a small band gap away from half-filling. It is also confirmed that the ground state of the Peierls-Hubbard model undergoes a transition to a metallic state at finite doping. These results show that electronic correlation effects should be taken into account in theoretical studies of doped polyacetylene. They also show that a Mott-Peierls theory could explain the insulator-metal transition observed in this material. [S0163-1829(98)06716-2]

Since the discovery of the metallic phase of doped polyacetylene, this material has been extensively studied,^{1,2} but the mechanism of the insulator-metal transition observed upon doping is still poorly understood. It is known that both the Peierls instability and electronic correlations play a fundamental role in the formation and properties of the insulating phase,³ and thus undoped polyacetylene is a Mott-Peierls insulator.⁴ Therefore, ten years ago, Baeriswyl, Carmelo, and Maki⁵ proposed that the insulator-metal transition was also driven by the interplay of electron-electron and electron-phonon interactions. Within the restricted Hartree-Fock approximation, they showed the possibility of such a Mott-Peierls insulator-metal transition in the Peierls-Hubbard model, which is the simplest model of polyacetylene including both interactions. Recently, several works using sophisticated numerical many-body methods, such as the Gutzwiller variational wave function⁶ and quantum Monte Carlo (QMC) simulations,⁷ have confirmed the occurrence of an insulator-metal transition in this model. On the other hand, Wen and Su, who applied the density-matrix renormalization group (DMRG) technique to this problem, disputed the existence of this transition.⁸ Hartree-Fock,⁹ and QMC (Ref. 7) simulations have also shown that the nearest-neighbor Coulomb repulsion opposes and can prevent the formation of a metallic state in the extended Peierls-Hubbard model.

As an attempt to clarify this issue, I have studied the properties of the extended Peierls-Hubbard model with parameters leading to a Mott-Peierls insulating ground state at half-filling. Accurate ground states and gaps are obtained for open chains up to 200 sites and different band fillings using the DMRG method,¹⁰ and finite-size effects are carefully analyzed. Results show that the ground state of a Mott-Peierls insulator evolves to a soliton lattice upon doping. This soliton lattice is qualitatively similar to the ground state predicted by simple electron-phonon models,^{11,12} but both the gap and amplitude of the lattice distortion decrease faster in the extended Peierls-Hubbard model than in these models when the doping increases. An insulator-metal transition occurs at a finite doping concentration in the absence of nearest-neighbor electron-electron interaction, in agreement with previous studies of the Peierls-Hubbard model.⁵⁻⁷ These results demonstrate that electronic correlations effects

are important, and should be taken into account in theoretical studies of doped polyacetylene. They also confirm that a Mott-Peierls theory⁴⁻⁶ could explain the insulator-metal transition observed in polyacetylene.

The one-dimensional extended Peierls-Hubbard model is defined by the Hamiltonian

$$\begin{aligned}
 H = & \frac{1}{4\pi t\lambda} \sum_{\ell} \Delta_{\ell}^2 - \frac{2P}{\pi} \sum_{\ell} (-1)^{\ell} \Delta_{\ell} \\
 & - \sum_{\ell\sigma} \left(t - (-1)^{\ell} \frac{\Delta_{\ell}}{2} \right) (c_{\ell+1\sigma}^{\dagger} c_{\ell\sigma} + c_{\ell\sigma}^{\dagger} c_{\ell+1\sigma}) \\
 & + U \sum_{\ell} n_{\ell\uparrow} n_{\ell\downarrow} + V \sum_{\ell} n_{\ell} n_{\ell+1}. \quad (1)
 \end{aligned}$$

The operators $c_{\ell\sigma}^{\dagger}$ ($c_{\ell\sigma}$) create (destroy) an electron of spin σ at site ℓ , $n_{\ell\sigma} = c_{\ell\sigma}^{\dagger} c_{\ell\sigma}$ and $n_{\ell} = n_{\ell\uparrow} + n_{\ell\downarrow}$. t is the resonance integral for an undistorted lattice, and fixes the energy scale; λ is the electron-phonon coupling constant; and U and V are the on-site and nearest-neighbor Coulomb repulsion. As this model has an electron-hole symmetry, only hole doping is examined. The doping rate y is defined as the fraction of electrons removed from a neutral chain (which corresponds to a half-filled band). The usual dimerization order parameter Δ_{ℓ} describes the lattice degrees of freedom. A linear term with constant P is explicitly included in the lattice elastic energy instead of the constraint on the dimerization order parameter used in previous works,^{6,8} in order to reduce the average bond-length variation. The value of $P > 0$ is determined by the condition that the linear term in the elastic energy equals zero in the ground-state configuration at half-filling. The lattice dynamics is completely neglected in this approach, and the electron-phonon interaction is taken into account only through the coupling between electrons and a classical lattice relaxation.

To determine the ground state of Hamiltonian (1), one has to find both the lattice configuration $\{\Delta_{\ell}\}$ and the electronic wave function which minimize the total energy. Using a finite system DMRG algorithm,¹⁰ one can compute the electronic ground state, its energy, and the gradient of this energy (thanks to the Hellmann-Feynman theorem) for any given lattice configuration, and thus perform the minimiza-

tion of the total energy with respect to lattice degrees of freedom $\{\Delta_{\ell}\}$.^{6,8} In principle, direct electronic excitations can also be obtained by calculating excited states of the electronic part of Hamiltonian (1) for a fixed lattice configuration. Unfortunately, while the DMRG method gives excellent results for ground states, it is more difficult to obtain results for specific excited states. Therefore, I have only calculated charge gaps, which can easily be obtained from ground-state energies for different band fillings.⁶ The charge gap is believed to be equal to the lowest optical-absorption energy in the thermodynamic limit of the Peierls-Hubbard model ($V=0$). In the extended Peierls-Hubbard model ($V\neq 0$), the relation between the charge gap and optical gap is complicated by the presence of excitons.¹³ In this work, I have assumed that the charge gap is roughly equivalent to the gap between the ground state and the lowest charge excitation band, which will be called the optical gap, in the thermodynamic limit.

All calculations have been carried out for several chain lengths up to 200 sites, and results have always been extrapolated to an infinite chain. Only open chains are considered, because the DMRG method performs much better in this case than for periodic boundary conditions. Computations have been performed, so that numerical errors on the ground-state dimerization parameter Δ_{ℓ} are smaller than $10^{-3}t$. Numerical errors on gap values are estimated to be less than $10^{-2}t$ at half-filling, and around $10^{-3}t$ away from half-filling. All these estimations of the accuracy are based on an analysis of the behavior of DMRG results as a function of the number m of quantum states kept per block. The largest value of m used in this work ranges from 80 for short chains (50 sites) at half-filling, to 400 for long chains (200 sites) away from half-filling. Truncation errors are typically between 10^{-6} and 10^{-7} . I have also checked the accuracy of DMRG calculations against exact numerical results for long (up to 100 sites) noninteracting ($U=V=0$) chains, and against exact results for the one-dimensional Hubbard model ($\Delta_{\ell}=0$ and $V=0$).¹⁴ Excellent agreement has been found in both cases.

My results at half-filling are in good agreement with results obtained previously with DMRG (Ref. 15) and other many-body techniques like exact diagonalizations, quantum Monte Carlo simulations, and variational methods.³ They confirm that undoped polyacetylene is a Mott-Peierls insulator, which can be described with a reasonable accuracy by the extended Peierls-Hubbard models. I have determined appropriate parameters for polyacetylene by comparing model predictions to experimental values for the optical gap at half-filling, the optical transition energies induced by photogenerated neutral, and charged solitons and the neutral soliton spin density obtained from magnetic resonance experiments.^{1,2} This comparison shows that $\lambda=0.1$, $U=4V=2.5t$, and $t=2.7$ eV seem to be appropriate for polyacetylene, in agreement with previous studies.^{3,6}

It is important to realize that in the Mott-Peierls regime the optical gap at half-filling is essentially a correlation gap as in the one-dimensional Hubbard model,¹⁴ although the electron-phonon coupling and the Peierls instability are responsible for features like the dimerization and the existence of solitons. For instance, DMRG calculations predict an optical gap $E_g=0.74t$ for the parameters mentioned above. As

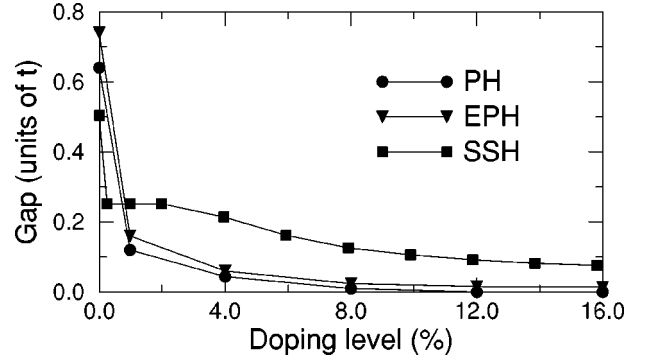


FIG. 1. Optical gap (in units of t) of the Peierls-Hubbard (PH) model, extended Peierls-Hubbard (EPH) model, and SSH model as a function of doping.

the gap is only $\sim 0.04t$ for $U=V=0$ and $\lambda=0.1$, electronic correlations account for at least 94% of the gap. Consequently, one expects this gap to be strongly reduced as soon as the system is doped, because electronic correlations do not contribute to the formation of a gap away from half-filling in the Hubbard model. A strong experimental evidence for this reduction is the difference between the gap at half-filling (1.8 eV) and the energy of the optical transition induced by photogenerated charged solitons (0.45 eV), which corresponds to the gap of a lightly doped chain in our simplified model.

I have investigated the extended Peierls-Hubbard model at several dopant concentrations up to $y=16\%$ in the Mott-Peierls regime. In this regime, the system evolves upon doping from the Mott-Peierls insulating state to a soliton lattice with a small gap. The evolution of the optical gap upon doping is shown in Fig. 1 for the polyacetylene parameters mentioned previously. As expected, the gap is strongly reduced to $\sim 0.17t$ as soon as the system is doped. The amplitude of the lattice distortion and the gap decrease with increasing doping, but no transition to a metallic state is found up to the highest doping studied in this work ($y=16\%$). It is possible that a transition occurs at a higher doping, but this would not be relevant for the transition observed in polyacetylene around $y=6\%$. Quantum Monte Carlo simulations⁷ have also shown that the lattice distortion survives at high doping for $V=U/2$. For $y>4\%$, the amplitude of the lattice distortion Δ_{ℓ} corresponds exactly to the value of the gap if both quantities are extrapolated to an infinite chain. Therefore, away from half-filling the gap is a band gap generated by the lattice modulation, though electronic correlations contribute indirectly to its formation because they increase the amplitude of the lattice distortion.⁶

The soliton lattice found in the doped extended Peierls-Hubbard model is qualitatively similar to the soliton lattice predicted by simple electron-phonon models.¹² However, it is important to realize that the evolution of the gap and lattice distortion amplitude upon doping is different from the predictions of the Su-Schrieffer-Heeger¹¹ (SSH) model (shown in Fig. 1 for $\lambda=0.2$). To reproduce the results obtained in the extended Peierls-Hubbard model with the SSH model, one would need to use an effective electron-phonon coupling which decreases with increasing doping. Moreover, such a doping-dependent parameter $\lambda(y)$ should change abruptly at half-filling to reproduce the sudden disappearance of the correlation gap. Finally, one notes that the energy

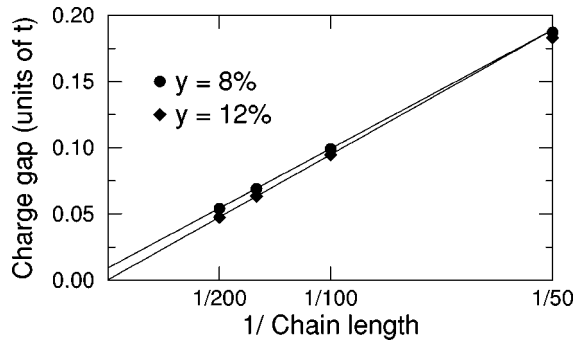


FIG. 2. Charge gap (in units of t) of the Peierls-Hubbard model as a function of the inverse system size for two different doping levels. Lines are linear extrapolations.

scales involved in both approaches differ by an order of magnitude. For instance, my calculations indicate a gap of about 0.07 eV at $y=8\%$, while the SSH model predicts 0.4 eV.⁶ These results demonstrate that electronic correlation effects in such one-dimensional systems are not reproduced by simple single-electron models with an effective electron-phonon coupling, contrary to a basic assumption of the SSH theory of conducting polymers.^{1,11} Thus the electron-electron interaction and electronic correlation effects should be taken into account in theoretical studies of doped polyacetylene.

In Fig. 1, one can also see that the gap of the Peierls-Hubbard model with $\lambda=0.1$ and $U=2.5t$ vanishes at a critical doping between 8% and 12%. These results confirm the existence of a transition to a metallic state at a finite doping.⁵⁻⁷ They also show that the electron-electron interaction can either support or oppose the Peierls instability away from half-filling, depending on the parameters used, as predicted by the restricted Hartree-Fock approximation.^{5,9} It should be noted that my numerical results agree quantitatively with those presented in Ref. 8, but additional calculations and an analysis of finite-size and chain-edge effects lead to a different conclusion. Figure 2 shows the charge gap as a function of the system size for $y=8\%$ and 12%. The value of the gap extrapolated to an infinite chain is clearly finite for $y=8\%$, but vanishes for $y=12\%$ within numerical errors ($\sim 10^{-3}t$). The lattice dimerization parameter Δ_m is shown in Fig. 3 for a 200-site chain at $y=12\%$. The shape of Δ_m looks similar for $y=8\%$, except that the amplitude is smaller at higher doping. However, in the insulating phase ($y \leq 8\%$), the amplitude of the distortion in the middle of the chain tends to a finite value as the chain length increases. This confirms that this lattice modulation is a genuine Peierls distortion. On the other hand, in the metallic regime ($y \geq 12\%$), the amplitude decreases as a power law with an exponent -0.66 as the system size increases. This behavior

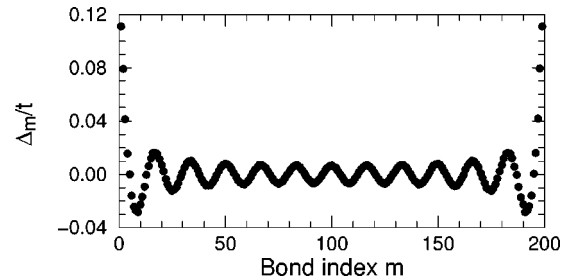


FIG. 3. Lattice dimerization parameter Δ_m of the Peierls-Hubbard model at $y=12\%$.

demonstrates that the lattice distortion is a chain-edge effect with a very slow asymptotic decay. The amplitude of these Friedel oscillations is known to decrease asymptotically as a power law with an exponent -1 in a one-dimensional Fermi liquid, but density fluctuations are strongly affected by electron-electron interaction and the exponent can be as small as $-\frac{1}{2}$ in a Luttinger liquid.¹⁶

In conclusion, I have investigated the ground state of the extended Peierls-Hubbard model in the Mott-Peierls regime, which is appropriate for polyacetylene. Results show that the ground state evolves from a Mott-Peierls insulator with a correlation gap at half-filling to a soliton lattice with a small band gap away from half-filling. It is also confirmed that an insulator-metal transition occurs in the Peierls-Hubbard model at a doping concentration between 8% and 12%. These results clearly show that electronic correlations effects are important, and should be taken into account in theoretical studies of doped polyacetylene. They also suggest that the primary mechanism of the insulator-metal transition in polyacetylene is the interplay between electron-phonon and electron-electron interactions, which induces a transition upon doping from an insulating state with a gap of ~ 1.8 eV to a state with a gap which is two orders of magnitude smaller. Obviously, this theoretical investigation of the properties of an ideal, infinite, and isolated chain cannot describe the properties of actual physical systems. Understanding the insulator-metal transition of polyacetylene will require a study of a more realistic model, including lattice dynamics, interchain couplings, interaction with dopant ions, and disorder.¹⁷ In the future I plan to study such models with DMRG, particularly the effects of quantum lattice dynamics.

I thank S. White and D. Baeriswyl for helpful comments and discussion. I wish to acknowledge support from the Swiss National Science Foundation. This work was also supported in part by the Campus Laboratory Collaborations Program of the University of California and by the NSF under Grant No. DMR-9509945. Some of the calculations were performed at the San Diego Supercomputer Center.

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