Effect of Coulomb Interactions on the Peierls Instability

J. E. Hirsch
Department of Physics, University of California, San Diego, La Jolla, California 92093

(Received 17 May 1983)

The effect of electron-electron repulsion on the ground-state properties of one-dimensional electron-phonon systems is considered in the half-filled-band case. Two different electron-phonon models are studied, with use of a numerical simulation technique. For large phonon frequency, an on-site electron repulsion suppresses the Peierls distortion in both models, while for small phonon frequency, it enhances the dimerization in one model. The effect of a nearest-neighbor repulsion is always to enhance the ground-state dimerization.

PACS numbers: 71.38.+i, 72.15.Nj, 75.10.Lp

A detailed understanding of the properties of one-dimensional electron-phonon models is of interest to elucidate the connection between the models and various quasi-one-dimensional real materials. Although much progress has been achieved in our theoretical understanding in recent years,[1] many difficult questions remain open. Two important effects in many cases are likely to be quantum fluctuations of the phonon field and electron-electron interactions. In most theoretical treatments, one or both of these effects are neglected or treated with uncontrolled approximations. The purpose of this Letter is to report essentially exact results from numerical simulations on models where both of these effects are present.

I have studied two different models in the half-filled-band case. The first is defined by

$$H=\sum_i\left(\frac{p_i^2}{2M}+\frac{1}{2}K(q_{i+1}-q_i)^2\right)+\sum_{i,\sigma}[t-\lambda(q_{i+1}-q_i)](c_{i,\sigma}^\dagger c_{i+1,\sigma}+\text{H.c.}) \qquad (1)$$

and was proposed by Su, Schrieffer, and Heeger[2] (SSH) to describe polyacetylene [$(\text{CH})_x$]. Here, longitudinal phonon displacements couple to the electron hopping term. The second model is defined by[3]

$$H=\sum_i\left(\frac{p_i^2}{2M}+\frac{1}{2}Kq_i^2\right)-t\sum_{i,\sigma}(c_{i,\sigma}^\dagger c_{i+1,\sigma}+\text{H.c.})+\lambda\sum_{i,\sigma}q_i n_{i,\sigma} \qquad (2)$$

and describes the coupling of an intramolecular vibration mode to the local electron density. For both models, I add a Coulomb interaction of the form

$$H_1=U\sum_i n_{i\uparrow}n_{i\downarrow}+V\sum_i n_i n_{i+1}. \qquad (3)$$

U and V are presumably the dominant electron-electron interactions in quasi-one-dimensional materials.

I use a Monte Carlo technique introduced recently[4] and study finite rings of $N=24$ sites. From simulations on smaller systems ($N=16$) we concluded that finite-size effects are small for the cases studied. The only source of error in the procedure is the finite time slice $\Delta\tau$,[4] which was taken to be $1/4t$ for $U\leqslant 2$ and $1/8t$ for $U=4$ and 8. I expect the error to be at most a few percent.

Within mean-field theory, the models Eqs. (1) and (2) have a Peierls-dimerized ground state for arbitrary electron-phonon coupling λ in the absence of Coulomb interactions. We have recently reported detailed results on the effect of quantum fluctuations on the ground-state properties of these systems.[5] The effect of U on the ground-state properties of one-dimensional electron-phonon systems has been a subject of controversy. Hartree-Fock theory for the model Eq. (1)[6,7] predicts that there is a competition that results in a Peierls-dimerized charge-density-wave (CDW) ground state for small U and a spin-density-wave (SDW) ground state for large U, with a discontinuous transition[8] at a critical value U_c. On the other hand, perturbation-theory[7,9] as well as finite-chain calculations[7,10] predict that the dimerization is favored by a small on-site repulsion U. Renormalization-group (RG) results[1] predict a SDW instability and no CDW instability in the half-filled electron gas with $U>0$.

Figure 1 shows results for the dimerization order parameter for the SSH model and parameters used in the literature to describe polyacetylene,[2] which are, in the present units, $t=1$, $K=0.25$, $\lambda=0.29$, $\omega=2(K/M)^{1/2}=0.066$. These simulations were done at a temperature $T=0.013$ which should ensure that fluctuations are quantum rather than thermal. Also shown are Hartree-Fock results.[6,7] As reported earlier, quantum fluctuations reduce the dimerization from the mean-field result, the

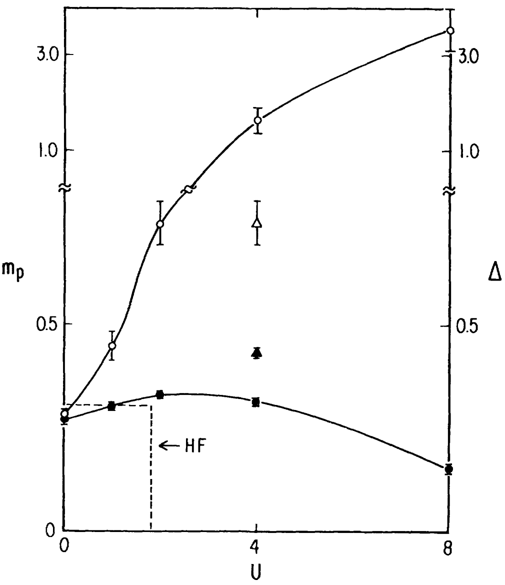

FIG. 1. Phonon order parameter (full circles) m_p and electronic gap (open circles) Δ vs U for the SSH model, with $\omega = 0.066$, $\lambda = 0.29$, $K = 0.25$, $t = 1$. The lines are drawn to guide the eye. The dashed line is Hartree-Fock results (Refs. 6 and 7). The full and open triangles are $4\lambda m_p$ and Δ for the case $U = 4$, $V = 2$.

effect being small for this phonon frequency. A finite U first *increases* the dimerization beyond its mean-field value. This has been recently emphasized by Mazumdar and Dixit.[10] As U increases further, the dimerization starts to decrease. For large U, the model becomes equivalent to an antiferromagnetic Heisenberg model with exchange coupling,

$$J_{i,i+1} = 2t_{i,i+1}^2/U, \tag{4}$$

and the lattice distortion is due to a spin-Peierls mechanism.[11] For the case $\omega = 0$, we would therefore expect the dimerization to decrease but remain finite for any $U < \infty$. As a check on the present results for the case $U = 8$ I have done simulations for that case.[12] The results for the dimerization agree with those obtained by direct simulation of the SSH model within statistical error.

The inclusion of a nearest-neighbor repulsion V enhances the dimerization further, as seen in Fig. 1. In the large-U limit, one can argue that the effective exchange is $J = 2t^2/(U - V)$ so that the effect of V can be represented by an effective on-site repulsion $U_{\text{eff}} = U - V$. However, for the case studied (Fig. 1) the effect on the dimerization is larger than this argument would predict. In weak coupling, RG analysis[1] predicts that the system goes into the CDW region as the "backward scattering" $g_1 = U - 2V$ changes sign, which indicates that a nonzero V favors dimerization. One could expect that the effect of V is represented by $U_{\text{eff}} = U - 2V$, but the results show that this is not the case either. One has to describe the model by two independent parameters U and V.

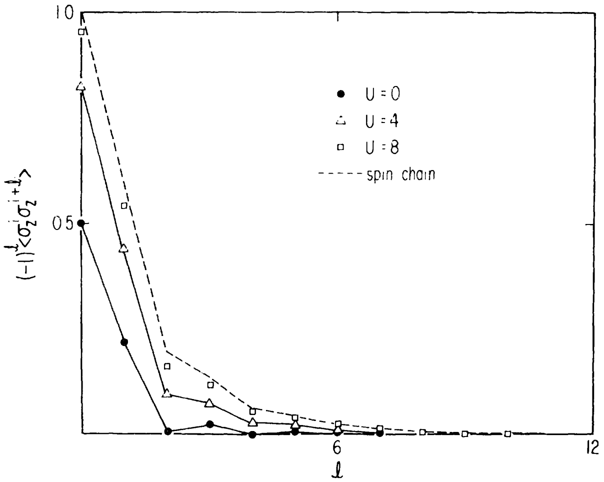

FIG. 2. Staggered spin-spin (z-component) correlation function for the case of Fig. 1. The dashed line is results for a dimerized Heisenberg chain, with exchange couplings given by Eq. (4) for $U = 8$.

I also show in Fig. 1 the optical gap in the electronic spectrum, obtained from the imaginary-time dependence of the current-current correlation function.[12] In the absence of Coulomb interactions, this agrees with the value for the phonon order parameter (appropriately scaled), as predicted by mean-field theory. For nonzero interactions, the difference between it and the phonon order parameter can be defined as the "Coulomb gap." Note how it rises rapidly with U, and decreases when V is turned on. The effect of V on the electronic gap seems to be well described by a $U_{\text{eff}} = U - V$.

Figure 2 shows the spatial decay of the staggered spin-spin correlation function for the case discussed above. Note the slower decay when the Coulomb interaction is turned on. However, the system is clearly not in a SDW state as predicted by Hartree-Fock theory, but correlations appear to decay exponentially. For comparison, I also show the spin-spin correlations obtained from Monte Carlo simulations on a dimerized Heisenberg chain,[12] with couplings J_1 and J_2 given by Eq. (4) for the case $U = 8$. The results for the SSH model are close to these. The effect of a nearest-neighbor V is to suppress the spin-spin

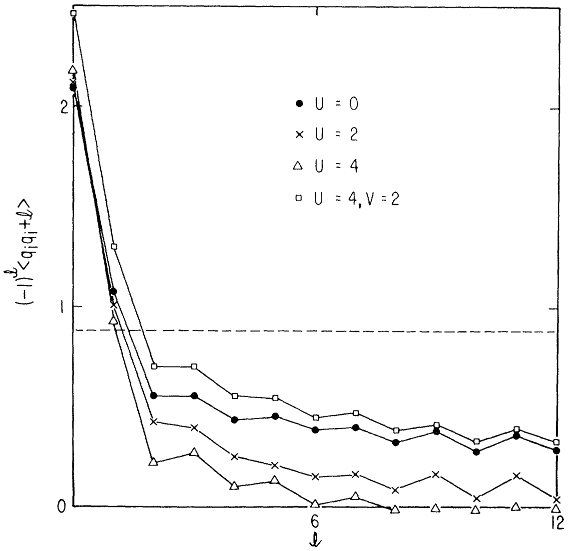

FIG. 3. Staggered phonon spatial correlation function for the SSH model; $\omega = 1$, $\lambda = 0.35$, $K = 0.25$, $t = 1$. The dashed line is the mean-field results for $U, V = 0$.

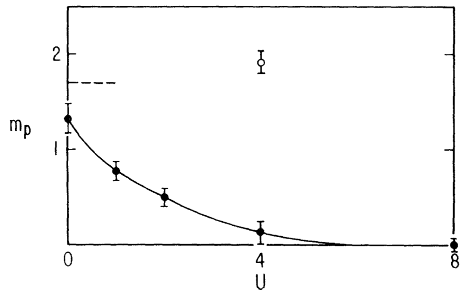

FIG. 4. Phonon order parameter m_p vs U for the molecular-crystal model; $\omega = 0.1$, $\lambda = 0.636$, $K = 0.25$, $t = 1$. The open circle is m_p for the case $U = 4$, $V = 2$. The dashed line indicates the mean-field results for $U, V = 0$.

correlations, as one would expect.

In Fig. 3 I show results for the phonon staggered spatial correlation function in the SSH model for a phonon frequency $\omega = 1$. Note the large on-site fluctuations due to the high phonon frequency. Here, a nonzero U *decreases* the dimerization. This can be understood in the light of our recent study[5] where we showed that models with *spinless electrons* are very sensitive to quantum fluctuations. The effect of a large U is identical to the Pauli exclusion principle for spinless particles, and quantum fluctuations tend to destroy the dimerization. From RG results in the $\omega = \infty$ limit,[12] I expect a transition to an undimerized state at $U_c = 4\lambda^2/K$. The results for $\omega = 1$ appear to be not too far from this prediction. In the presence of a nonzero V, the dimerization is again strongly enhanced.

I now discuss results for the molecular-crystal model, Eq. (2). Here, the behavior was qualitatively similar for small and large phonon frequency. Figure 4 shows results for the phonon order parameter for $\omega = (K/M)^{1/2} = 0.1$. Here, a nonzero U strongly suppresses the Peierls distortion. This is to be expected, since there is no spin-Peierls mechanism in this model because the phonons are on-site, and the on-site repulsion is in direct competition with the electron-phonon coupling. This is most clearly seen in the large-ω limit, where the electron-phonon coupling is equivalent to an on-site *attraction* $U_\lambda = -2\lambda^2/K$.[5] The presence of a nonzero V favors double occupancy of sites and this will clearly enhance the dimerization in this model. In the $\omega = \infty$ limit, I expect from theoretical arguments that any nonzero V will give dimerization for $U < 2\lambda^2/K$.[12]

In conclusion, for the case of intermolecular vibrations (SSH model) and small ω I have demonstrated the existence of a "generalized Peierls transition" encompassing both the ordinary Peierls ($U = 0$) and the spin-Peierls (antiferromagnetic Heisenberg model) limits. However, these concepts derive from perturbation theory, and in considering the fully coupled system there is no real basis for a sharp distinction between both regimes. For the case of intramolecular vibrations, there is no spin-Peierls mechanism and the Peierls distortion is suppressed by on-site Coulomb repulsion. I believe that the ordered phase will disappear in this case for large U even for $\omega = 0$. More detailed studies of this and other questions are in progress.

As we have seen, systems that exhibit a Peierls transition are not necessarily characterized by weak Coulomb interactions. In the case of longitudinal phonons and low phonon frequency, quite the opposite can be true. I have demonstrated the inadequacy of the Hartree-Fock approximation, which predicts for the case of polyacetylene that only $U/t < 1.8$ is consistent with a dimerized ground state.[6,7] Thus, the present results open up the possibility that $(CH)_x$ could be characterized by appreciable Coulomb interactions, particularly if the nearest-neighbor repulsion is large. The influence of these on the properties of solitons should be reexamined.

The present results also suggest that in real materials, Peierls transitions are predominantly going to occur by coupling to intermolecular rather than intramolecular modes. Intramolecular

Peierls transitions are suppressed both by the effect of the on-site repulsion U and by the finite phonon frequency[5] which is likely to be much higher in these modes.

Part of the numerical results reported here were obtained on a CDC 7600 computer of Los Alamos National Laboratory, paid by funds from the Institute for Theoretical Physics, University of California, Santa Barbara. I am grateful to D. Campbell for his support. Helpful discussions with M. Grabowski are gratefully acknowledged. This work was supported by the National Science Foundation through Grant No. DMR-82-17881.

---

[1] See, for example, V. J. Emery, in *Highly Conducting One-Dimensional Solids*, edited by J. Devreese, R. Evrard, and V. Van Doren (Plenum, New York, 1979), p. 247, and references therein.

[2] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B 22, 2099 (1980).

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

[4] J. E. Hirsch, D. J. Scalapino, R. L. Sugar, and R. Blankenbecler, Phys. Rev. Lett. 47, 1628 (1981), and Phys. Rev. B 26, 5033 (1982).

[5] J. E. Hirsch and E. Fradkin, Phys. Rev. Lett. 49, 402 (1982), and Phys. Rev. B 27, 4302 (1983); E. Fradkin and J. E. Hirsch, Phys. Rev. B 27, 1680 (1983).

[6] K. R. Subbaswamy and M. Grabowski, Phys. Rev. B 24, 2168 (1981).

[7] S. Kivelson and D. Heim, Phys. Rev. B 26, 4278 (1982).

[8] To be precise, for large U there is a small region of coexistence between CDW and SDW states with Hartree-Fock theory (Ref. 7).

[9] P. Horsch, Phys. Rev. B 24, 7351 (1981).

[10] S. Mazumdar and S. N. Dixit, preceding Letter [Phys. Rev. Lett. 51, 292 (1983)].

[11] J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1983), Vol. 3, p. 355.

[12] J. E. Hirsch, to be published.