The Anharmonic Electron-Phonon Problem

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(Received 17 May 1996)

The anharmonic electron-phonon problem is solved in the infinite-dimensional limit using quantum Monte Carlo simulation. Charge-density-wave order is seen to remain at half filling even though the anharmonicity removes the particle-hole symmetry of the model. Superconductivity is strongly favored away from half filling but the anharmonicity does not enhance transition temperatures over the maximal values found in the harmonic limit. [S0031-9007(96)01737-1]

PACS numbers: 63.20.Kr, 63.20.Ry, 74.25.Dw

Lattice anharmonicity is responsible for many different properties of solids. For example, the expansion of a crystal upon heating is due to anharmonic effects, and the phonon contribution to the thermal resistivity is due, in part, to anharmonic effects. Furthermore, lattice modes in a real crystal are never completely harmonic. Anharmonic terms always enter to higher order when expanding in the amplitude of the lattice vibrations.

But the effects of anharmonicity on the electron-phonon problem, and more specifically on superconductivity, are relatively unknown. This is surprising, because the electron-phonon problem is well studied, especially in the weak coupling limit. Here the theory of electrons interacting with harmonic phonons, initially pioneered by Migdal [1] and Eliashberg [2], has led to an accurate description of superconductivity in most low-temperature phonon-mediated superconductors. It has been found that, in the regime where the electron-phonon coupling is weak so that the Migdal-Eliashberg theory still applies to the anharmonic case, the superconducting transition temperature is not enhanced by the presence of lattice anharmonicity [3]. The situation as the coupling is increased is less clear. Recently, a new mechanism for superconductivity, driven by kinetic-energy effects, has been hypothesized in anharmonic crystals that display stronger electron-phonon coupling [4]. In this new mechanism, paired holes, in a nearly filled band, are more mobile than single holes, driving the superconductivity.

An exact treatment of lattice anharmonicity is, however, difficult from a theoretical point of view because an anharmonic "perturbation" is never small—the phonon wave functions are always dominated by the anharmonic terms in the potential as the phonon coordinate becomes large. All that is known rigorously about the anharmonic electron-phonon problem is that the ground state must contain a spin singlet [5] for even numbers of electrons on a finite lattice.

Much progress can be made in the limit of large spatial dimension [6] where the lattice many-body problem can be mapped onto a self-consistently embedded impurity problem that is solved via a quantum Monte Carlo (QMC) simulation.

Model.—The simplest electron-phonon model that includes anharmonic effects is the anharmonic Holstein model [7] in which the conduction electrons interact with local phonon modes,

$$H = -\sum_{i,j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_i (g x_i - \mu)(n_{i\uparrow} + n_{i\downarrow}) + \frac{1}{2M}\sum_i p_i^2 + \frac{1}{2} M\Omega^2 \sum_i x_i^2 + \alpha_{\rm anh} \sum_i x_i^4 , \quad (1)$$

where $c^{\dagger}_{i\sigma}$ ($c_{i\sigma}$) creates (destroys) an electron at site i with spin σ, $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$ is the electron number operator, and x_i (p_i) is the phonon coordinate (momentum) at site i. The hopping of electrons is restricted to nearest-neighbor lattice sites i and j and is governed by the hopping matrix element t_{ij} (t_{ij} is a Hermitian matrix).

The local phonon has a mass M and a frequency Ω associated with it. The anharmonic contribution to the phonon potential energy is chosen to be a quartic in the phonon coordinate with a strength $\alpha_{\rm anh}$. The deformation potential (electron-phonon interaction strength) is parametrized by an energy per unit length and is denoted g. The chemical potential is μ.

The hopping t_{ij} is isotropic with strength $t =: t^*/2\sqrt{d}$ where $t^* = 1$ to define the energy scale and d is the dimensionality. The mass is then set equal to one ($M = 1$) leaving g, $\alpha_{\rm anh}$, Ω, and the electron filling as free parameters. We set $\Omega = 0.5t^*$ which is approximately an order of magnitude smaller than the effective bandwidth ($W \approx 4t^*$), and we set $g = 1$ which is well into the strongly coupled regime in the harmonic limit.

Results.—The original Holstein Hamiltonian corresponds to the case $\alpha_{\rm anh} = 0$. Both the harmonic Holstein model and the harmonic Holstein-Hubbard model have been solved exactly in the limit of infinite dimensions via quantum Monte Carlo simulation [8,9]. These models display charge-density-wave (CDW) order near half filling and superconductivity (SC) away from half filling. As

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the phonon frequency is increased, the SC is favored relative to the CDW order. However, in the strong-coupling limit, CDW order is favored over SC because of the band-narrowing effect of the bipolaron. The quantum Monte Carlo simulations also found that the effective phonon potential (determined after integrating out the effects of the electrons) generically acquires a double-well structure signifying the high-temperature formation of a bipolaron.

We have chosen the coupling of the phonon coordinate to the total electronic charge (rather than the charge fluctuation) and have chosen a purely quartic anharmonic potential because these choices yield a Hamiltonian that does not have particle-hole symmetry, and hence is generic for anharmonic effects. A more standard choice would be to couple the coordinate to the charge fluctuations, and to include both cubic and quartic contributions to the phonon potential. The particle-hole asymmetry is then tuned by the strength of the cubic terms, but this introduces another parameter into the model, which we wanted to avoid here.

An initial analysis of the anharmonic model can be made by employing the Born-Oppenheimer approximation in the strong-coupling limit ($t_{ij} = 0$) [4]: the phonon frequency is assumed to be smaller than any of the other energy scales so the phonons can be approximated by static lattice distortions corresponding to the minimum of the local phonon potential energy. Since the phonons couple linearly to the electronic charge, the equilibrium phonon coordinate varies when there are zero, one, or two electrons on a site. The origin $x_0 = 0$ is chosen to correspond to the case with no electrons on a site. Then x_1 and x_2 denote the equilibrium coordinates with one or two electrons on a lattice site. In the harmonic case the relative distances $x_1 - x_0$ and $x_2 - x_1$ are identical, which is a requirement for particle-hole symmetry. When our choice for a lattice anharmonicity is turned on, the equilibrium phonon coordinates with one and two electrons on a lattice site all move toward the origin, but the relative distances are no longer symmetric, rather the distance $x_2 - x_1$ becomes significantly smaller than $x_1 - x_0$, as can be seen in Fig. 1(a).

The lattice anharmonicity and subsequent asymmetric shift of the equilibrium phonon coordinate have two main effects: (1) the model may allow a new type of kinetic-energy driven superconductivity to emerge [4] and (2) the effective electron-electron attraction is dramatically reduced as can be seen by a plot of the bipolaron binding energy in Fig. 1(b). Thus the lattice anharmonicity generates an effective *retarded* repulsive interaction between the electrons which may be strong enough to destroy the kinetic-energy driven superconductivity. The lattice anharmonicity also removes the nesting instability of the CDW at half filling and weak coupling.

The anharmonic Holstein model is solved exactly in the infinite-dimensional limit via QMC simulation. The algorithm is straightforward, and has been described numerous times before [8–10], so it will not be repeated here.

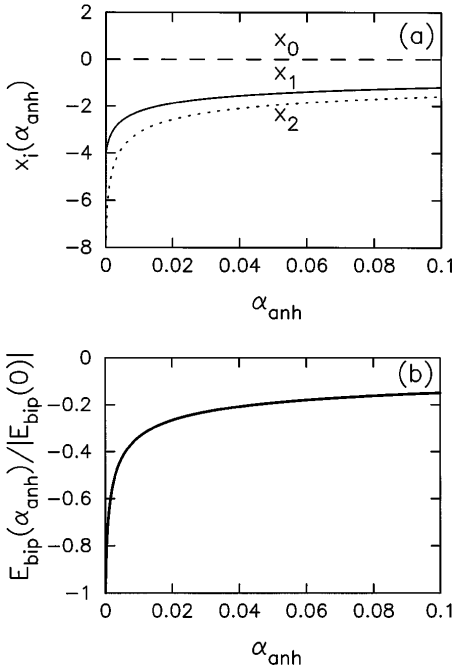

FIG. 1. (a) Phonon coordinates at the minima of the anharmonic phonon potential with zero (x_0), one (x_1), and two (x_2) electrons on a site as a function of α_{anh} in the atomic limit ($t_{ij} = 0$). (b) Reduction of the bipolaron binding energy as a function of α_{anh} in the atomic limit ($t_{ij} = 0$).

We find that at half filling the system orders in a commensurate CDW phase. The results of the QMC simulation are presented in Fig. 2. The solid dots represent the QMC transition temperatures, and the dashed line is a guide to the eye. The solid line is the result of a strong-coupling perturbation theory expansion [11] that predicts that the system evolves from CDW order (solid line) to SC order (dotted line). We find no evidence for such an evolution in the QMC solution. Rather, the system remains in the CDW-ordered state even though there is no particle-hole symmetry remaining in the model. It is

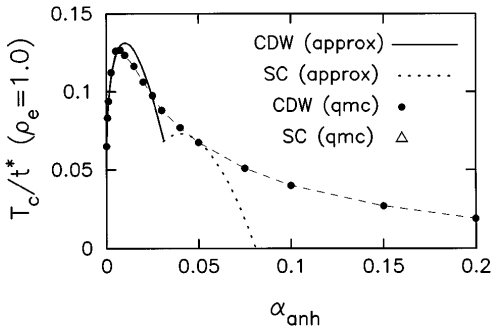

FIG. 2. Charge-density-wave transition temperature at half filling as a function of α_{anh}. The QMC results (dots—no SC transitions were found at half filling with the QMC) are compared to the strong-coupling perturbation theory for CDW order (solid line) and SC order (dotted line). The dashed line through the QMC points is a guide to the eye.

possible that as the strength of the anharmonicity is increased further that the SC order may overtake the CDW order, but it is difficult to see that behavior with the QMC simulations because the transition temperatures become too small to be reliably determined.

The initial rise in T_c occurs because of the reduction in the bipolaron binding energy E_{bip} as the strength of the anharmonicity increases. In the strong-coupling regime, the transition temperature is inversely proportional to E_{bip} ($T_c \propto t^{*2}/E_{\mathrm{bip}}$) with a proportionality constant determined by retardation effects. As the bipolaron unbinds, the system evolves from preformed-pair physics to BCS-type physics where pair formation and condensation both occur at T_c. This then causes the transition temperature to drop as α_{anh} is increased further. Of course, the quantitative value of the transition temperature is determined by properly accounting for the retardation effects of the complicated electron-phonon interaction, but the qualitative effects are well described by this simple picture based on the bipolaron binding energy and strong-coupling physics.

The unbinding of the bipolaron can be dramatically illustrated by extracting the effective phonon potential from the QMC simulation [8]. The probability distribution for the local phonon coordinate x is measured for each of the imaginary time slices and is then equated to an activated form for the effective potential $P(x) = \exp[-V_{\mathrm{eff}}(x)/T]$. This effective phonon potential includes the effects of the interaction of the electrons with the phonons. In the harmonic limit, it was seen to evolve from a harmonic form $(x - x_1)^2$ to a symmetric double-well form as the coupling strength increased [8]. The double well signified bipolaron formation, since the number of electrons on a lattice site was either zero or two for each of the minima (centered around x_0 and x_2). The results for the effective phonon potential in the anharmonic model at half filling and $T = 0.125t^*$ are presented in Fig. 3. The effective potential is plotted versus a rescaled phonon coordinate for different values of α_{anh}. Note that the addition of anharmonicity squeezes the phonon coordinate toward the origin, and makes the effective phonon potential asymmetric (corresponding to the loss of particle-hole symmetry). The barrier height decreases as α_{anh} increases, as required by the reduction of the bipolaron binding energy. Note that the maximum CDW T_c occurs when the barrier height is on the order of T_c ($\alpha_{\mathrm{anh}} \approx 0.0075$).

In order to find SC solutions, we must dope the system off half filling. The phase diagram for three different values of α_{anh} is shown in Fig. 4. In Fig. 4(a), a small value of $\alpha_{\mathrm{anh}} = 0.005$ is chosen. This result is close to the harmonic result. Nevertheless, even at this small value of α_{anh}, the phase diagram is not symmetric with respect to reflection about half filling, signifying the particle-hole asymmetry. We compare to the particle-hole symmetric strong-coupling perturbation theory, which predicts CDW order to survive until doped well off of half filling. Note that the case of less than half filling is approximated much better by the perturbative calculation than the greater than half-filling case.

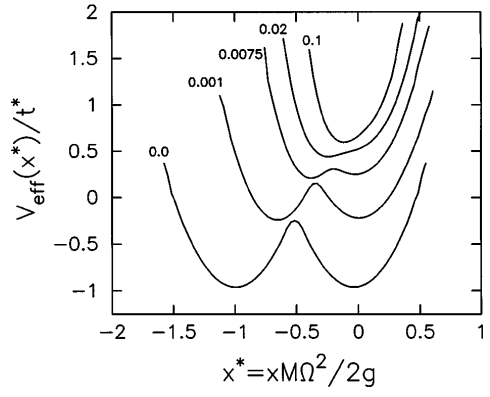

FIG. 3. Effective phonon potential for the anharmonic Holstein model at half filling and $T = 0.125t^*$. The labels on the curves are the values of α_{anh}. The potentials are shifted by adding a constant to them to separate the curves.

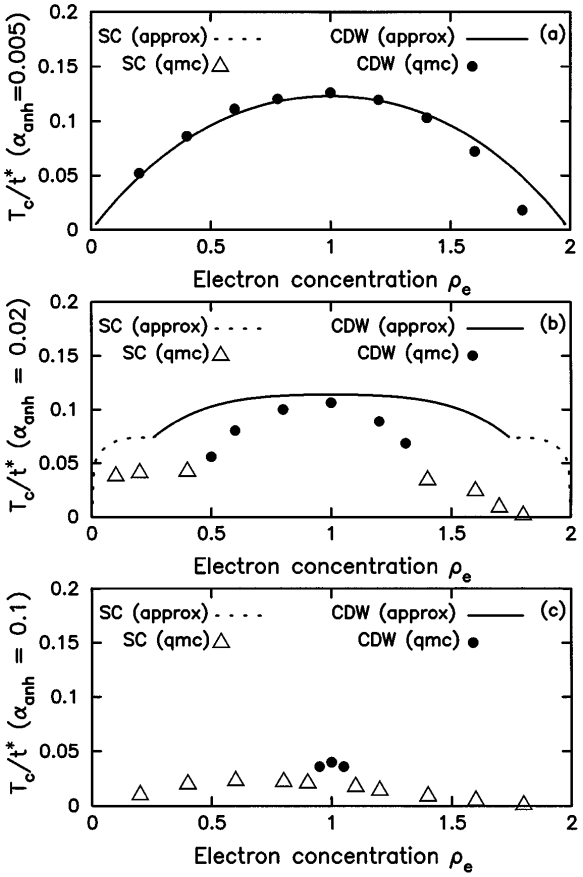

FIG. 4. Phase diagrams for the anharmonic Holstein model at three different values of α_{anh}: (a) 0.005, (b) 0.02, and (c) 0.1. The solid dots are CDW phases, the open triangles are SC phases. The solid lines are a strong-coupling approximation to the CDW T_c, and the dotted lines are a strong-coupling approximation to the SC T_c.

Figure 4(b), has $\alpha_{\text{anh}} = 0.02$ which lies at a point beyond where the CDW T_c is maximal. The perturbative approximation is less accurate here, but displays the correct order-of-magnitude estimate for the phase diagram. We see how the anharmonicity favors the superconducting solutions, pushing the CDW-SC phase boundary toward half filling. SC is favored because the squeezing of the phonon coordinate toward the origin enhances the Frank-Condon overlap factors associated with electronic hopping and increases the effective electronic bandwidth.

Figure 4(c), takes the large value $\alpha_{\text{anh}} = 0.1$. The strong-coupling theory fails in this regime, and so it has not been included in the plot. We see once again how the increase in α_{anh} now suppresses the transition temperatures, and how it moves the CDW-SC boundary closer to half filling. There is no evidence for the new SC mechanism. We also found no evidence for incommensurate CDW order, either at half filling or away from half filling.

The effect of anharmonicity on the electron-phonon problem has some aspects that are similar to and some aspects that are different from the effect of an instantaneous Coulomb repulsion [9]. In both cases the superconducting order is favored by the additional interaction relative to the charge-density-wave order, in the sense that the SC-CDW phase boundary moves toward half filling. But the SC-CDW phase boundary moves much more rapidly toward half filling with the anharmonic interaction because the squeezing of the phonon coordinate toward the origin strongly favors superconductivity. In addition, the anharmonicity generically breaks the particle-hole symmetry, while the Coulomb repulsion does not. This leads to an asymmetric shape of the phase diagram. Furthermore, the CDW transition temperature is moderately suppressed even for large values of the anharmonicity. Whereas, if the Coulomb repulsion is increased to large enough values, the CDW T_c will plummet to zero and SDW order will take over.

We have analyzed the effect of anharmonicity on the electron-phonon problem in the regime where the harmonic model has formed bipolarons. We find that the anharmonicity generically breaks particle-hole symmetry and produces phase diagrams that are not symmetric about half filling. The anharmonicity acts in some respects as a retarded "Coulomb repulsion," since it greatly favors SC solutions relative to CDW ones. However, in the infinite-dimensional limit, we did not find any enhancement to T_c's for the anharmonic model relative to the maximal values found in the harmonic case. Furthermore, we found no evidence for any kind of novel superconducting mechanism driven by kinetic-energy effects. We also studied the effective phonon potential and discovered that the anharmonicity squeezes the phonon coordinates closer to the origin, rapidly suppressing the bipolaron formation. We also verified that the strong-coupling perturbation theory accurately describes the anharmonic Holstein model in the regime where the system still has preformed pairs.

We would like to acknowledge useful conversations with W. Chung, J. Hirsch, and J. Serene. J. K. F. acknowledges the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (ACS-PRF No. 29623-GB6) and an Oak Ridge Associated University Junior Faculty Enhancement Award for partial support of this research. M. J. acknowledges support of NSF Grants No. DMR-9406678 and No. DMR-9357199. G. D. M. acknowledges support by the University of Tennessee and by Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under Contract No. DE-AC05-96OR22464. This research was also supported in part by Grant No. DMR950010P from the Pittsburgh Supercomputing Center, sponsored by the National Science Foundation.

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