

Gap ratio in anharmonic charge-density-wave systems

J. K. Freericks¹ and Veljko Zlatić²

¹*Department of Physics, Georgetown University, Washington, DC 20057-0995*

²*Institute of Physics, Zagreb, Croatia*

(Received 22 February 2001; published 31 July 2001)

Many experimental systems exist that possess charge-density-wave order in their ground state. While this order should be able to be described with models similar to those used for superconductivity, nearly all systems have a ratio of the charge-density-wave order parameter to the transition temperature that is too high for conventional theories. Recent work explained how this can happen in harmonic systems, but when the lattice distortion gets large, anharmonic effects should play an increasingly important role. Here we show that the explanation for the large gap ratios survives for anharmonic systems as well.

DOI: 10.1103/PhysRevB.64.073109

PACS number(s): 73.20.Mf, 63.20.Ry, 74.25.Dw

The appearance of stripe ordering in materials related to the high-temperature superconducting oxides¹ and of charge and orbital ordering in the colossal magnetoresistance materials,² has provided a renewed interest in the physics that drives charge-density-wave order. This phenomenon has been seen in a wide variety of materials ranging from quasi-one-dimensional systems (where Peierls distortion physics is important) such as the organic conductors,³ to the di- and trichalcogenides⁴ such as 2H-TaSe₂ or NbSe₃, so-called A15 materials⁵ such as V₃Si, blue bronzes⁶ such as KMoO₃, cubic oxides⁷ such as Ba_{1-x}K_xBiO₃, and Verwey transition materials⁸ such as Fe₃O₄.

There has been much theoretical work on this problem as well. The dynamical mean field theory was employed to solve for the charge-density-wave phase in the ordered state⁹ and the puzzle of the large gap ratio was resolved for harmonic systems.¹⁰ The resolution involves properly accounting for phonon renormalizations, for nonvanishing effects from vertex corrections, and from effects due to nonconstant electronic density of states (since conventional Migdal-Eliashberg approaches cannot produce gap ratios $2\Delta/T_c$ larger than about eight). The anharmonic problem was also examined with dynamical mean-field theory¹¹ and it was found that the transition temperature satisfied a scaling law with the wave-function renormalization parameter for a wide range of parameter space.

Here we concentrate on the issue of whether or not the gap ratio can remain large when anharmonic effects are present. The scaling law for the transition temperature shows that anharmonicity does not have a dramatic effect on T_c , but as the system is cooled down to $T=0$, the lattice distortion becomes larger and larger, generating the full charge-density-wave gap. Naively, we would expect anharmonicity to reduce the lattice distortion (relative to a harmonic system) because the higher powers in the phonon potential do not allow the phonon coordinate to move as far away from the origin. Hence, one expects that anharmonicity will generically reduce the gap ratio, since T_c will be unaffected, but Δ will be reduced relative to the results of a harmonic system with the same value of the wave-function renormalization parameter. We need to verify whether this effect occurs and determine how large it can be to see whether one

can still explain the large gap ratios of charge-density-wave systems in the presence of anharmonic potentials.

We will be investigating the static anharmonic Holstein model, whose Hamiltonian is^{12,11}

$$H = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i (g\bar{x}_i - \bar{\mu})(n_{i\uparrow} + n_{i\downarrow}) + \frac{1}{2}\bar{\kappa} \sum_i \bar{x}_i^2 + \alpha_{an} \sum_i \bar{x}_i^4. \quad (1)$$

Standard notations are used here: $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (destroys) an electron at lattice site i with spin σ , $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the electron number operator, $\bar{\mu}$ is the chemical potential, and \bar{x}_i is the phonon coordinate at lattice site i . We examine the static (or classical) phonon case here, so there is no kinetic energy of the phonon. The hopping of the electrons is restricted to nearest neighbors on a hypercubic lattice in d dimensions. We take the limit $d \rightarrow \infty$ and scale $t_{ij} = t^*/(2\sqrt{d})$ in order to have nontrivial results.¹³ The rescaled hopping integral t^* determines our energy scale ($t^* = 1$). The bare density of states becomes a Gaussian $\exp(-\epsilon^2)/\sqrt{\pi}$, with ϵ the band energy. The local phonon is taken as a classical variable, so it only has a spring constant κ associated with it. The anharmonic potential is chosen to be of the simplest form, a quartic term with a strength α_{an} . The deformation potential (or electron-phonon interaction strength) is denoted by g and measures an energy per unit length.

It is useful to shift the phonon coordinate, in order to see explicitly the particle-hole symmetry present in the harmonic model. We shift $\bar{x}_i \rightarrow x_i + x'$ with $g\langle n \rangle + \bar{\kappa}x' + 3\alpha_{an}x'^3 = 0$ (with $\langle n \rangle$ the average total electron filling), to transform the Hamiltonian into

$$H = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i (gx_i - \mu)(n_{i\uparrow} + n_{i\downarrow} - \langle n \rangle) + \frac{1}{2}\kappa \sum_i x_i^2 + \beta_{an} \sum_i x_i^3 + \alpha_{an} \sum_i x_i^4, \quad (2)$$

with $\kappa = \bar{\kappa} + 12\alpha_{an}x'^2$, $\beta_{an} = 4\alpha_{an}x'$, and $\mu = \bar{\mu} - gx'$. It is the presence of the cubic term, when $\alpha_{an} \neq 0$ that removes

the particle-hole symmetry¹⁴ from the problem when $\mu=0$ and $\langle n \rangle = 1$, since the Hamiltonian is no longer unchanged under the transformation $n_{i\sigma} \rightarrow 1 - n_{i\sigma}$ and $x_i \rightarrow -x_i$. Note that the system still will possess charge-density-wave order at half filling and weak coupling (for all small $g > 0$) because the band structure is still nested at half filling, even though the Hamiltonian is not particle-hole symmetric.

Our calculations are performed using standard techniques of dynamical mean-field theory:^{9,10} we iterate a series of equations to self consistency that involve (i) determining the local Green's function from the self energy (by integrating over the noninteracting density of states), (ii) extracting the effective medium (by removing the self energy from the local Green's function), (iii) calculating the probability distribution of the phonon coordinate (by solving the atomic path integral in a time-dependent field), (iv) extracting the electronic self energy (after determining the local Green's function from an integral over the phonon coordinate distribution). This procedure is standard (even for the case of the ordered phase), and we do not describe any further details here. Our calculations are performed at half filling $\langle n \rangle = 1$. In the harmonic case, we have $\mu=0$, but the anharmonic problem must have the chemical potential adjusted as a function of temperature to yield the right filling.

When the system is in an ordered charge-density-wave state, there are two probability distributions for the phonon coordinate—one for the A sublattice $w_A(x)$ and one for the B sublattice $w_B(x)$. The order parameter for the charge-density-wave phase is defined to be

$$\Delta(T) = g \int dx [w_A(x) - w_B(x)]x, \quad (3)$$

which measures the average difference in the phonon coordinate between the A and B sublattices multiplied by the deformation potential.

In Fig. 1, we show a plot of this charge-density-wave order parameter as a function of temperature. The plots include three cases, all at the maximum value of T_c for a given value of g and arbitrary α_{an} . The parameters chosen are $g = 2$, $\alpha_{an} = 0.16$, which has $T_c = 0.1277$; $g = 1.5$, $\alpha_{an} = 0.03$, which has $T_c = 0.1326$; and $g = 1.19$, $\alpha_{an} = 0$, which has $T_c = 0.1340$. The curves are normalized by the maximal gap value calculated at $T \approx T_c/8$, which is very close to the $T = 0$ value, and by T_c . Note that rather than approaching one, there is a small decrease in $\Delta(T)/\Delta_{max}$ at the lowest temperatures. This is an accuracy issue with our calculations (which are performed with a fixed number of 5000 Matsubara frequencies for the energy cutoff). We estimate that our error in the $T = 0$ gap is no larger than about 1%. These curves have the correct generic behavior that we expect for mean-field systems: the order parameter increases like $\sqrt{T_c - T}$ away from the transition temperature and then rapidly saturates. We see no significant difference in the shape of these curves for different values of the anharmonicity. Inset into this figure is a plot of $\langle x_A \rangle$ upper curves and $\langle x_B \rangle$ lower curves. Note how the anharmonic systems are both shifted upwards and have narrower spreads in the average phonon coordinate, but that the curves are symmetric be-

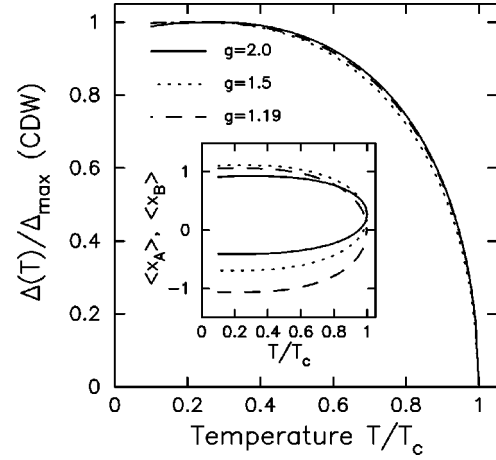


FIG. 1. Charge-density-wave order parameter as a function of temperature for three cases of anharmonicity (all chosen to be at the maximal T_c) (i) $g=2$, $\alpha_{an}=0.16$, $T_c=0.1277$ (solid line); (ii) $g=1.5$, $\alpha_{an}=0.03$, $T_c=0.1326$ (dashed line); and (iii) $g=1.19$, $\alpha_{an}=0$, $T_c=0.1340$ (dotted line). The figure is renormalized to plot $\Delta(T)/\Delta_{max}$ and T/T_c . Inset is a plot of the average phonon coordinate on the A and B sublattices. Note that all the curves are symmetric, but their average value moves away from zero for the anharmonic cases.

tween the A and B sublattices, so the particle-hole asymmetry only affects the midline of the phonon coordinate, not its distortion in the ordered phase.

In summary, we can accurately estimate the value of the $T=0$ gap by performing calculations at $T=T_c/10$ and the shape of the order parameter (as a function of T) is not too strongly dependent on the strength of the anharmonicity. In addition, we find that the main effect of the anharmonic interaction is to change the average of the phonon coordinate values on each sublattice $(\langle x_A \rangle + \langle x_B \rangle)/2$ and shrink the magnitude of the distortion. This does not mean that the gap is reduced by as much, though, because systems that share the same approximate value of T_c will have different values of both g and α_{an} . The reduction in the distortion of the phonon coordinate can be compensated by a correspondingly larger value of g .

We now present results for the charge-density-wave gap as a function of the anharmonicity. The most reasonable way to present these results is to plot the gap versus a measure of the anharmonic potential energy in equilibrium. We can determine what the equilibrium phonon coordinate $\bar{x} = x^*$ is for the atomic problem [determined by Eq. (1) with $t_{ij}=0$ and $\langle n \rangle = 1$] and then plot results versus $\alpha_{an}x^{*4}$. These results are summarized in Fig. 2. Note that this measure of the anharmonic potential energy is double valued when g is large, since it approaches 0 in both the small and large α_{an} limits. The general shapes of these curves are quite similar, but the scales change with the coupling strength and the stronger coupled cases show more curvature (and eventually a double valuedness).

We can examine the static Holstein model in both a strong-coupling¹⁵ and a weak-coupling¹⁶ limit. In the strong-coupling limit, the transition temperature approaches zero as $1/(2g[x_0 - x_2])$, while the zero temperature gap becomes

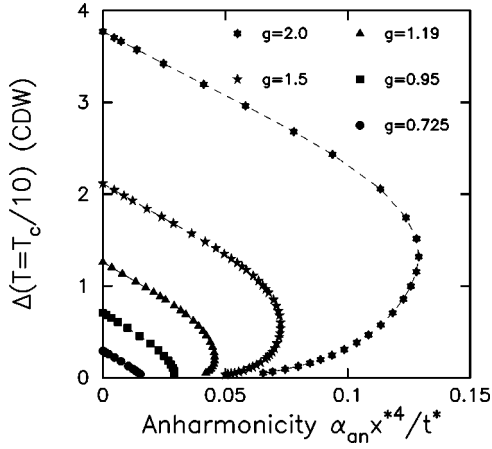


FIG. 2. Charge-density-wave gap calculated at $T_c/10$ plotted versus the anharmonic “energy” $\alpha_{an}x^{*4}$ determined from the average value of the phonon coordinate for the atomic problem. Note how the different curves ($g=0.725, 0.95, 1.19, 1.5,$ and 2.0) have the same general shape, which become double valued for the strongest coupling cases shown here.

large as $g(x_0 - x_2)/2$, and hence, the ratio can diverge [$2\Delta/(k_B T_c) = 2g^2(x_0 - x_2)^2$]. Here, x_i satisfies

$$g(i-1) + \kappa x_i + 3\beta_{an}x_i^2 + 4\alpha_{an}x_i^3 = 0. \quad (4)$$

This ratio becomes infinite as the coupling strength increases, hence, there is no limit to the magnitude of the gap ratio. Note that this result is also true for the superconducting order, when one includes the effect of a nonconstant density of states, since the strong-coupled T_c will approach zero there as well. This result comes entirely from the fact that the phonon-coordinate distortion grows linearly with g in strong coupling, but the transition temperature decreases as $1/g^2$ due to the strong-coupling physics.

We can also investigate the possibility of universal behavior in strong coupling. Since the system consists of empty sites and preformed pairs, the self energy has a low-energy pole and takes the form $\Sigma(\omega) = \alpha/(\omega + i\delta) + O(\omega^0)$ for small $|\omega|$ with $\alpha > 0$. Plugging this form into the self-consistent equations for the Green’s function yields $\alpha = -1/2 + g^2|x_0||x_2|$ (which is larger than zero for g large enough). Defining the wave-function renormalization parameter by a scaling along the imaginary axis¹¹

$$Z = 1 - \left\{ \frac{3}{2} \frac{\text{Im}\Sigma(i\omega_0)}{\omega_0} - \frac{1}{2} \frac{\text{Im}\Sigma(i\omega_1)}{\omega_1} \right\}, \quad (5)$$

with $i\omega_j = i\pi T(2j+1)$, yields

$$Z = 1 - \frac{13}{18} \frac{1}{\pi^2 T^2} + \frac{13}{9} \frac{g^2|x_0||x_2|}{\pi^2 T^2}. \quad (6)$$

Since Z is a function of x_0 and x_2 and $2\Delta/(k_B T_c)$ is a function of $x_0 - x_2$, we don’t expect universal behavior at extremely strong coupling for the anharmonic case. But, in the harmonic case we have $|x_0| = |x_2|$, so we expect deviations from universality only when $|x_0|/|x_2|$ deviates far from unity.

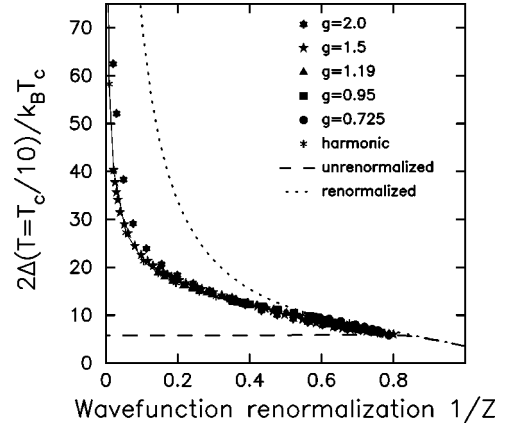


FIG. 3. Ratio of twice the charge-density-wave gap (calculated at $T_c/10$) to the charge-density-wave transition temperature T_c plotted versus the wave-function renormalization parameter. The harmonic limit is connected by a thin solid line (with g ranging from 0.625 to 2), while the renormalized (dotted) and unrenormalized (dashed) weak-coupling approximations are also included. Note how the anharmonic systems generically lie close to the harmonic results for a wide range of parameters.

The weak-coupling limit is much more complicated. There are many approaches that can be taken,^{16,17} but none produce good agreement with the transition temperature over a wide range of coupling strengths (but the zero-temperature gap is approximated well). Here we will concentrate on just two different strategies (for the harmonic case only): (i) the renormalized phonon method¹⁶ where a certain class of vertex correction terms can be neglected from the analysis, but one needs to work with renormalized phonons (renormalized by the electron-hole bubble diagrams) and (ii) a similar approximation¹⁷ that employs the identical set of diagrams, but does not renormalize the phonons.

In Fig. 3, we show the results for the gap ratio in the harmonic case, five different anharmonic cases, and the two approximation schemes described above. In order to check for universal behavior, we plot the results as a function of the wave-function renormalization parameter¹¹ Z [which is evaluated as in Eq. (5)]. One can see some striking behavior in this plot. First, we find that the gap ratio can become as large as one would like as the coupling strength gets bigger and bigger. Furthermore, the gap ratio rises very rapidly above the weak-coupling limit of 3.52, so even Z factors of 1.25 (which would correspond to very weak electron-phonon coupling) would have a gap ratio larger than six. We find that the calculated results lie in between the two different weak-coupling schemes indicating that phonon renormalization is important, but the summation of the bubble diagrams renormalizes the phonons too strongly in the general case.¹⁸ Finally, we notice that except for the case of very strong coupling ($g=2$), the gap ratio is modified by at most about 20% from the harmonic case. This finding is most surprising, but can be explained in relatively simple terms. As the anharmonic potential increases, the effective coupling strength becomes weaker, because the anharmonic potential prevents the phonon coordinate from deviating far from the origin. In the limit of very weak effective coupling, the transition is

dominated by a nesting instability that can be described within a BCS-like format. Hence, all results must agree in the strong anharmonic limit (if one properly identifies the net strength of the attractive interaction). Furthermore, when the system has small anharmonicity, the anharmonic effects can be treated perturbatively, and the system remains close to the harmonic limit there as well. Since the curves are pinned to be close to the harmonic limit for small anharmonicity and for large anharmonicity, we find that they generically do not stray far from the harmonic curve in the intermediate regime. As the coupling strength increases, so this intermediate regime becomes larger, the deviations can also become significant, as we see for the $g=2.0$ case. But we find it surprising that there is such a wide range of parameter space where the results for the anharmonic system remain so close to the harmonic system.

Contrary to the simple arguments about anharmonicity, we find that generically anharmonic phonons are described well by an equivalent harmonic limit, even in the ordered

phase, where one would expect the effects of the anharmonicity to be felt more strongly. Hence, we find that the analysis given for the large gap ratio in the harmonic electron-phonon problem remains essentially unchanged as anharmonicity is introduced except in the limit of extremely strong electron-phonon coupling (which may be so unphysically large that it is not attained in any real material). The reason why this holds is essentially a continuity argument: for small and large anharmonicity, the system must be close to the harmonic results—hence, it remains close for intermediate values as well. We do not expect these results to be changed much for small phonon frequencies, because we know that T_c follows a universal form for low frequency, and we expect the gap value will not change much if the phonon frequency is small.

We would like to acknowledge stimulating discussions with Andy Millis. This work was supported by the National Science Foundation under Grant No. DMR-9973225.

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