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Sliding charge-density waves in periodic and disordered lattices*

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The Frenkel-Kontorova model (which consists of a chain of atoms connected by springs able to slide in a sinusoidal potential well) is applied to the problem of a charge-density wave moving through a periodic lattice under an applied external electric field. Computer experiments are reported for this model which partially support Lee, Rice, and Anderson's result which states that an incommensurate periodic lattice does not pin a charge-density wave. Experiments for a chain of atoms containing impurities partially support the conjectures made by the present author which state that weak random impurities need not pin a charge-density wave. For impurity strengths actually encountered in real systems, however, the charge-density wave most likely will be pinned.

I. INTRODUCTION

The reported observation of a very large peak in the conductivity of the "one-dimensional metallic conductor" tetrathiafulvalinium-tetracyanoquinodimethanide (TTF-TCNQ) at around 60 °K by Coleman, Cohen, Sandman, Yamagishi, Garito, and Heeger[1] has stimulated a good deal of study of this compound. The temperature at which this peak occurs is just above the temperature at which a metal to insulator transition occurs. The insulating phase is believed to be caused by a Peierls distortion.[2] Recent x-ray and neutron-diffraction experiments on both TTF-TCNQ and another one-dimensional compound, potassium cyano-platinide (KCP), have provided evidence for the existence of a Peierls distortion in these compounds.[3,4] Bardeen[5] revived a theory of superconductivity in one dimension due to Frolich,[6] which suggests that the Peierls state should actually be superconducting rather than insulating. Below 60° (in the Peierls phase), however, TTF-TCNQ is an insulator rather than a superconductor; the large conductivity is only observed in the "fluctuation regime" around 60 °K. The Frolich model,[6] being a jellium model, however, does not take into account effects of the periodic lattice or impurities. Lee, Rice, and Anderson[7] found that if the Peierls distortion is incommensurate with the periodic lattice, the electronic charge density will not be pinned; rather, it will be able to slide through the lattice freely, and thus conduct electricity. Leung has found, however, that if twice the Fermi wave vector is *nearly* commensurate with the lattice, the charge density wave will exist in a phase in which it is commensurate with the lattice,[8] even if the resulting wave vector is not $2k_F$. This effect is similar to the "locking in" of a spin density wave to a periodic lattice which is almost commensurate with it[9] (the so-called "commensurability transition"). Lee, Rice, and Anderson[7] have argued that in addition to the electrostatic interaction between charge density waves on the TTF and TCNQ chains, the presence of random impurities and other imperfections in the lattice can result in pinning of the charge density wave, and hence to insulating behavior.

The present author has argued,[10] using perturbation theory, that weak random impurities need not pin the charge-density wave. Nagaoka pointed out that this result, which was only proven for nonsubstitutional impurities, is also true for substitutional impurities.[11] Random impurities can be thought of as a disordered lattice which is certainly incommensurate with the charge-density wave, and thus, should not pin the wave, in the same way that periodic lattice incommensurate with the wave does not pin it. Lee, Rice, and Anderson find a phonon self-energy which diverges as the phonon frequency goes to zero and argue that this implies that a gap must form in the phonon spectrum for the charge-density wave, implying that the wave cannot slide freely. They also argue that if the concentration of impurities is very small, the charge-density wave can always distort so that a crest or a trough lies at each impurity site with little cost in energy necessary to distort either the wave or the lattice to accomplish this. McMillan has also found that dilute impurities lead to a gap in the collective mode spectrum of the charge density wave, which implies some sort of pinning.[12] The present author has argued that the average over impurity distribution of the interaction energy between the wave and random impurities must be independent of the position of the wave relative to the impurities by translational invariance of the average. Since fluctuations usually scale as the square root of the length of the system, whereas the interaction of the wave with an externally applied electric field scales as the length of the system, the wave

will not be pinned in place by random impurities in the thermodynamic limit. The problem with this treatment is that it is not clear that perturbation theory is applicable to such a highly nonlinear problem, in which large distortions can take place under the influence of the impurity potential at very little cost in energy.

II. APPLICATION OF THE FRENKEL-KONTOROVA MODEL TO A CHARGE-DENSITY WAVE INCOMMENSURATE WITH THE PERIODIC LATTICE

There exists a model system called the Frenkel-Kontorova model which has been studied extensively as a one-dimensional model suitable for the study of dislocations in solids.[13] This model consists of a periodic chain of masses connected by springs which are situated in a sinusoidal potential well of the same or different periodicity. If we identify the sinusoidal potential as the potential produced by the charge-density wave, this model could be used in the study of the motion of charge-density waves in a periodic lattice. There are, of course, major differences between these models. For one thing, in the case of the charge-density wave, it is precisely the Peierls distortion of the lattice which produces the charge density wave, whereas in the Frenkel-Kontorova model we assume the presence of a sinusoidal potential which is independent of the distortion of the lattice from the start. This is probably not a serious problem because we may simply assume that a Peierls distortion is always present and that distortions of the lattice in our model represent additional distortions. Second, the sinusoidal potential in the Frenkel-Kontorova model is rigid, whereas the charge-density wave is able to distort. Nevertheless, the fact that the charge-density wave's acoustic-phonon velocity (the charge-density wave's acoustic phonon is the so-called "sliding mode" at zero wave vector) found by Lee, Rice, and Anderson is of the order of the electron Fermi velocity, which is much larger than the lattice's acoustic-phonon velocity, indicates that the charge-density wave is much more rigid than the lattice, so that the rigid sinusoidal potential is not a bad approximation.

The potential energy in the Frenkel-Kontorova model is

$$V = 0.5\alpha \sum_{j=1}^{N_a-1} (x_{j+1} - x_j - b)^2 - V_o \sum_{j=1}^{N_a} \cos \frac{2\pi x_j}{a}, \tag{1}$$

where x_j is the position of the jth atom in a chain containing N_a atoms, α is the force constant for the harmonic potential linking a pair of atoms, V_0 is the strength of the sinusoidal potential, and a and b are the periodicities of the sinusoidal potential and chain of atoms, respectively. Whereas in treatments of dislocations in solids the chain and sinusoidal potential are taken to represent adjacent planes of atoms, here the sinusoidal potential will represent the electrical potential interaction of the charge density wave and the chain of atoms, which represents the underlying lattice.

Frank and Van der Merwe,[14] and more recently, Snyman and Van der Merwe[15] have studied this model in connection with epitaxial crystal growth. They find that for

$$l_0[(b-a)/a] < 2/\pi, \tag{2}$$

where $l_0 = (\alpha a^2/4V_0)^{1/2}$, the chain will have absolute minimum energy if it distorts in such a way that each atom lies at a trough of the sinusoidal potential. In such a case, there will clearly be pinning, because if we apply the same sufficiently small force to each atom (this is equivalent to applying a uniform electric field to the ion–charge-density-wave system), there will clearly be a restoring force to oppose it, due to the sinusoidal potential.

For the charge-density-wave problem a chain of atoms with the same periodicity as the sinusoidal potential is the trivial case of no charge-density wave. Thus, since the energy lowering of the system due to the charge-density wave clearly only exists when a charge-density wave is present, this commensurability transition will not occur in this case. For the charge-density-wave problem, the first important case in which commensurability matters is when $a = 2b$. (Similar results can be obtained for $a = Mb$, where M is any interger > 1.) The system will have minimum energy if we place the undistorted chain in a configuration in which every minimum of the sinusoidal potential has two atoms symmetrically placed around it (i.e., one a distance $\frac{1}{4}a$ to the left and one a distance $\frac{1}{4}a$ to the right of the minimum) and then allow the lattice to distort so as to minimize its energy. Elementary calculations show that if l_0^2 is $\gg 1$, the potential energy per atom is approximately given by

$$E/(N_a F_0) \cong -\tfrac{1}{8} F_0/\alpha, \tag{3}$$

where N_a is the number of atoms in the lattice and where $F_0 = 2\pi V_0/a$. If the lattice constant of the chain is too small by u_0 to be commensurate, we first stretch each spring by u_0, place the lattice in the configuration described above, and then allow it to distort. (If the lattice constant is too large by u_0 we compress each spring by u_0.) In this case we find that

$$E/N_a \approx -\tfrac{1}{8} F_0^2/\alpha + \tfrac{1}{2}\alpha u_0^2. \tag{4}$$

Thus, we see that if $a = 2b$, the system is pinned

because sliding the chain by about $\frac{1}{4}a$ raises the energy from the above amount to zero. Note that the actual charge-density wave, unlike the sinusoidal potential in the Frenkel-Kontorova model, disappears completely when we displace the wave $\frac{1}{4}a$. Since the above energy is linear in the number of atoms in the chain, the system will be pinned in the thermodynamic limit. We also see that if $u_0 > \frac{1}{2}F_0/\alpha$, there will no longer be a negative pinning energy and thus the system will not be pinned. This is the analogue in the Frenkel-Kontorova model of Leung's result[8] for the locking in of the charge-density wave; namely, if u_0 is less than a critical value the wave will become commensurate.

We will now determine whether or not there will be pinning when the wave is neither commensurate nor nearly commensurate. We will study this by performing a "computer experiment" on the Frenkel-Kontorova model as follows: We apply a force σ to each atom (assumed to be due to the electric field) and *for convenience* we include a damping term proportional to the velocity ($-\gamma\, dx_j/dt$ for the jth atom), which we take to be much larger than the inertial term $m\, d^2x_j/dt^2$ (i.e., the motion of each atom is assumed to be overdamped). Thus, the chain is able to relax to a relative minimum energy state in the sinusoidal potential as it moves, but the high damping prevents the creation of elementary excitations. With the above assumptions we obtain the following first order differential equations of motion:

$$\gamma\frac{dx_1}{dt} = +\alpha(x_2 - x_1 - b) - F_0\sin\frac{2\pi}{a}x_1 + \sigma, \tag{5a}$$

$$\gamma\frac{dx_j}{dt} = -\alpha(2x_j - x_{j-1} - x_{j+1}) - F_0\sin\frac{2\pi}{a}x_j + \sigma \tag{5b}$$

for $j \neq 1$ or N_a;

$$\gamma\frac{dx_{N_a}}{dt} = -\alpha(x_{N_a} - x_{N_a-1} - b) - F_0\sin\frac{2\pi}{a}x_{N_a} + \sigma, \tag{5c}$$

where $F_0 = (2\pi/a)V_0$. These equations can be solved by successive iteration to obtain the position of each atom as a function of time. Each "experiment" is started with the atoms in the lattice placed at their "natural" separation b. The potential energy was calculated from Eq. (1) for each iteration and found to be a periodic function of the position of the center of mass of the chain with periodicity a as expected. The value of the parameter l_0 [defined after Eq. (2)] which was used was 7, the value used by Frank and Van der Merwe[14] and Snyman and Van der Merwe.[15] A convenient value of the force σ equal to $0.1F_0$ was chosen which was generally not varied in successive experiments. A few experiments were repeated for other values of σ, but the results for the energy as a function of center-of-mass position were not changed significantly by varying σ. Experiments were performed for chains of various lengths ranging from 100 to 900 atoms. In Fig. 1, the results for the pinning energy, the difference between the maximum and minimum potential energies per atom, for each chain is plotted as a function of $N_a^{-1/2}$, where N_a is the number of atoms in the chain, for a few different values of the ratio b/a below the critical value of 0.91 at which the chain distorts to be exactly commensurate with the sinusoidal potential. Extrapolation of these curves to the $N_a \to \infty$ limit provides evidence that pinning energy approaches zero in the thermodynamic limit for all the cases considered. Thus, we conclude that if the chain is neither commensurate nor nearly commensurate, it is not pinned, in agreement with Lee, Rice, and Anderson's[7] conclusions. The probable reason that Lee, Rice, and Anderson do not obtain pinning in nearly commensurate case as we do is that they assume that the charge-density wave has periodicity of twice the Fermi wave vector, thus excluding the possibility of the wave locking into the periodicity of the lattice (i.e., they assume that

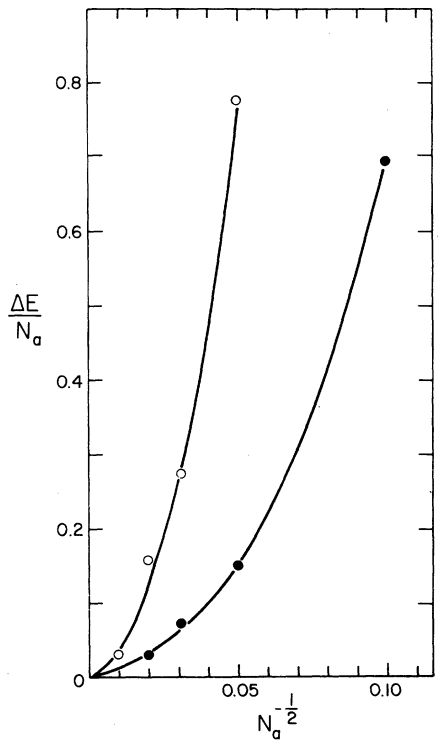

FIG. 1. Pinning energy per atom E/N_a is plotted against $N_a^{-1/2}$ for chains of atoms containing no impurities. ○ represents chains in which $b/a = 0.31416$ (E/N_a is in units of $10^{-3}F_0a$ for these chains) and ● represents chains in which $b/a = 0.89536$ (E/N_a is in units of $10^{-2}F_0a$).

the charge-density wave's potential always mixes electronic states on opposite sides of the Fermi level). Such a state is most likely a metastable state when the system is nearly commensurate.

III. IMPURE LATTICE

Here the case of a lattice containing substitutional impurities will be considered. In order to adapt the Frenkel-Kontorova model to this problem, we choose a set of N_i out of the N_a lattice sites on the chain at random ($c = N_i/N_a$ is the impurity concentration). On each of these sites we place an impurity potential, in addition to the potential of the ions in the pure lattice. Then, if $v(x - x_j)$ is the impurity potential on the jth site, the additional interaction of the impurities with the charge-density wave is [assuming that the charge density of the wave is proportional to $-\cos(2\pi x/a)$] proportional to

$$-v\left(\frac{2\pi}{a}\right)\sum_j \cos\frac{2\pi}{a}x_j ,$$

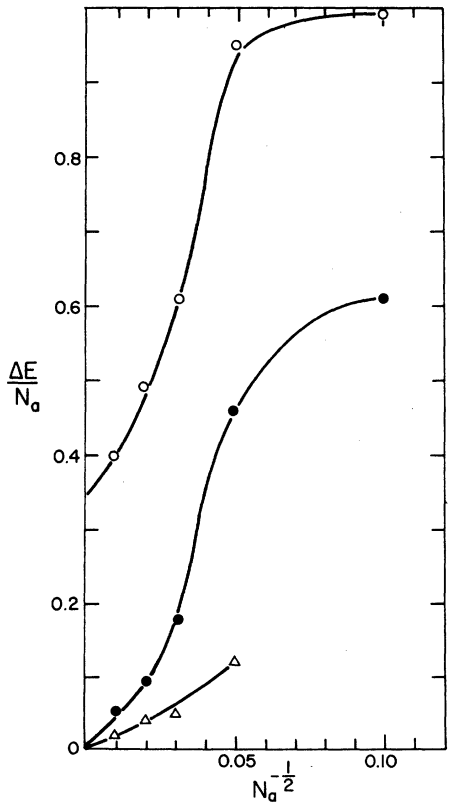

FIG. 2. Pinning energy is plotted as a function of $N_a^{-1/2}$ for chains with $b/a = 0.314\,16$ containing substitutions/impurities. ○ denotes an impurity potential strength of $0.5V_0$ with a 50% impurity concentration and ● denotes an impurity potential strength of $0.2V_0$ and a 50% impurity concentration. △ denotes a $0.2V_0$ impurity strength and a 5% impurity concentration.

where $v(k)$ is the Fourier transform of $v(x)$ and j is summed over those sites containing impurities [if $v(x - x_j)$ is an even function of $x - x_j$]. Thus, the effect of having an impurity on a site is to add a potential $V_{\text{imp}} = v(2\pi/a)$ to the potential V_0 for that site in Eq. (1).

We will now consider what happens when a force is applied to each atom, using the methods described in the Sec. II for a few impurity concentrations. Experiments have been performed with chains of length varying from 100 to 10 000 atoms. In these calculations the ratio of the perfect lattice potential strength V_0 to the spring constant α for the perfect lattice is taken to be the same as that used in the calculation of Sec. II. In Fig 2, a plot is made of pinning energy per atom as a function of $N_a^{-1/2}$ for a lattice with a 50% concentration of impurities with an impurity potential strength of $0.5V_0$. The curve clearly shows no sign of extrapolating to zero as N_a approaches infinity. We interpret this to mean that the system is pinned. Detailed behavior of a pinned lattice is further illustrated for another lattice in Fig. 3, in which the energy and the positions of the first ten atoms are given as a function of number of iterations. Locat-

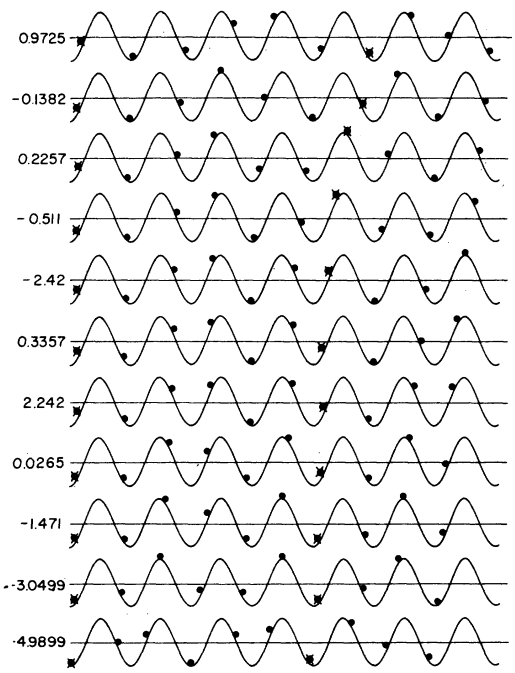

FIG. 3. Plots of the energy and positions of the first 10 atoms of a chain at successive time intervals (earliest time is the lowest plot in the figure) in an experiment in which there was an impurity concentration of 5.3%, the impurity potential strength was $5.0V_0$, $b/a = 0.64$, and $N_a = 100$. The first and seventh atoms (denoted by ×) contained impurities. The potential energy of the chain is also listed in units of F_0a to the left of each plot.

ions of impurities are also indicated in the figure. We see that at the first energy minimum, the impurities lie at minima of the potential. At the first energy maximum they lie further away from the minima, and on further iterations some impurities lie at potential minima and some at potential maxima and some lie in between. Of course, since there are 100 atoms in this lattice but we are only seeing the first 10, we do not see the locations of all the impurities which contribute to the energy. Clearly, in this case, the relevant pinning energy is the energy difference between the first energy maximum and minimum, which was plotted in Fig. 2.

A plot is also made in Fig. 2 of pinning energy per lattice site as a function of $N_a^{-1/2}$ for an impurity potential strength of $0.2V_0$. In this case the pinning energy per lattice site appears to extrapolate to zero as N_a approaches infinity, indicating that the system is not pinned for this impurity strength, in agreement with Ref. 10 which predicts, that for a sufficiently weak impurity potential the system is not pinned. From a comparison with the corresponding pure lattice in Fig. 1, we can see that any pinning which occurs for the impure lattices is due to the impurities.

As was mentioned earlier, according to Lee, Rice, and Anderson's argument for pinning, which says that the wave (and) or lattice distorts to put each impurity at a minimum in the sinusoidal potential, a dilute concentration of impurities should be more effective in pinning than a higher concentration. For example, for a 5% concentration of impurities, there are on the average 20 springs between each pair of impurities to share any distortion which places both impurities at potential minima. A simple calculation of the distortion energy necessary to place a pair of atoms at potential minima (i.e., a calculation in which the required distortion is shared over the springs which exist between the impurities) shows it to be of the order of the impurity potential strength (about $0.2\ V_0$). Thus, we might think that there exists a greater tendency for pinning for a lattice containing a smaller concentration of impurities. Nevertheless, a plot of pinning energy per lattice site versus $N_a^{-1/2}$ for a lattice containing a 5% concentration of impurities for impurity potential strength equal to $0.2V_0$ (see Fig. 2) does not give any indication of there being pinning as N_a goes to infinity.

IV. CONCLUSIONS AND COMPARISON WITH OTHER WORK

Our calculations support the result of Lee, Rice, and Anderson[7] that the periodic lattice does not pin a charge-density wave if it is incommensurate with it, at least away from the nearly commensurate case. We also conclude, however, in agreement with Leung's result,[8] that when the wave is nearly commensurate, the system distorts in such a way that the lattice and wave become commensurate. The range of values of the lattice constant over which the lattice "locks-in" to being commensurate with the sinusoidal potential due to the charge density wave increases as the force constant of the interatomic potential decreases or the strength of the interaction between chain and sinusoidal potential increases.

Our results for impure lattices support the conclusions of Ref. 10, in that the charge-density wave is not pinned by sufficiently weak random impurities. If the impurity potential is sufficiently strong, however, the system does get pinned.

The force constant K for a TTF or TCNQ chain can be estimated from $K = M\omega_D^2$, where ω_D is the Debye frequency and M is the molecular mass (for TTF-TCNQ we assume a Debye temperature of about 100 °K). In the calculations of this paper we have taken the ratio $Ka^2/2\pi V_0 = 33$ from which we estimate that $V_0 \approx 2\times10^{-2}$ eV. Thus, an impurity potential of $0.2V_0$ (at which the system is not pinned) corresponds to 4×10^{-3} eV. Since the impurity potential must be so weak for the system not to be pinned, it is quite likely that the TTF-TCNQ charge density waves are pinned by random impurities, but if the effect of impurity potentials could be reduced in a one-dimensional conductor by having highly polarizable molecules to screen the impurity potential, the charge-density waves might not be pinned and we could possibly get the large collective conductivity that people have speculated about.

The probable reason that McMillan[12] obtains a gap in the collective mode spectrum for a charge-density wave in a lattice containing substitutional impurities, independent of the strength of the impurities is that his long wavelength "phase excitations" involve a rigid sliding of the charge-density wave as a whole relative to the lattice, and there is always a restoring force for such rigid translation of the charge-density wave from its equilibrium configuration relative to the impurities. It has been shown,[16] however, for weak interaction between the charge-density wave and the lattice that such rigid sliding motion decays into phonon excitations in lowest order and therefore is not a well-defined excitation. Thus, we would expect damping of McMillan's zero wave-vector mode which could wipe out the gap in the excitation spectrum.

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