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Free sliding in lattices with two incommensurate periodicities

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The equilibrium configurations of the Frenkel-Kontorova model have been studied numerically. This model, which consists of a chain of ions connected by springs in the presence of a static sinusoidal potential, can be used to describe sliding charge-density waves in solids, incommensurate chain compounds such as $Hg_{3-\delta}AsF_6$, superionic conductors, and epitaxial crystal growth. If the natural periodicity of the chain is incommensurate with the periodicity of the sinusoidal potential, there exists, in the thermodynamic limit at some critical strength of the sinusoidal potential, a transition from a state in which the chain is pinned in place to a state in which it can accelerate freely when an arbitrarily small force is applied to each ion. The lattice vibration spectrum in the sliding regime exhibits a zero-frequency mode involving ionic vibrations that are more complicated than those found in the continuum limit of this model. Chains with free ends appear to require an activation energy to slide. Comparisons between the exact numerical results and those generated through approximation schemes are made along with an assessment of the validity of these schemes for various problems. The results of this work have direct application to the study of the conductivity, lattice dynamics, and elastic neutron and x-ray scattering of the systems previously mentioned.

I. INTRODUCTION

There has recently been an upsurge of interest in lattices with two incommensurate periods. Spin-density waves in chromium, incommensurate with the underlying lattice, have been studied for years.[1] In the last few years there has also been interest in charge-density waves in psuedo-one-dimensional electrical conductors, caused by the Peierls instability, and also in layered compounds.[2] More recently, the compound $Hg_{3-\delta}AsF_6$ has been found to have chains of mercury atoms incommensurate with the periodicity of the rest of the lattice.[3] Many ionic conductors have a state in which the conducting ions form an ordered structure incommensurate with the rest of the lattice.[4] In particular, the ionic conductor potassium hollandite has one-dimensional channels running through the crystal, containing mobile potassium ions,[5] which form a one-dimensional ordered structure along the channels.

Such systems have no translational invariance because there exists no single translation under which both periods are invariant. This leads to the question of whether there is wave-vector conservation in the optical spectrum of these materials. This question is treated in a separate publication,[6] where it is shown that despite the apparent lack of translational symmetry, such systems always seem to have optical absorption due to phonons not much different from that of systems having only one periodicity (and hence having translational invariance).

Since two rigid incommensurate periodic structures have no favored phase relationship with respect to each other, they are not locked together but are free to slide with respect to each other at no cost in energy. If one or both of the periodic structures can distort so as to conform to the other, then one would expect that the periods might become locked together. This locking or pinning phenomenon was treated for charge-density waves by Lee, Rice, and Anderson who found that incommensurate charge-density waves are not pinned by a rigid lattice.[7] The Frenkel-Kontorova model[8] (which consists of a chain of masses connected by springs interacting with a sinusoidal potential well), used in the study of dislocations and epitaxial crystal growth,[9] was applied by one of us to the problem of pinning of a charge-density wave incommensurate with the underlying lattice.[10]

The question of pinning in the Frenkel-Kontorova and related models was studied by Aubry using the mathematics of Ergodic theory.[11] In his work, he makes use of the fact that the difference equations which give the equilibrium positions of the atoms can be written in the form of a nonlinear operator, operating on a pair of successive atomic positions, which generates all other atomic positions. There exist mathematical theorems which show that this operator admits fixed points, which correspond to commensurate equilibrium configurations. If the operator operates on points in the neighborhood of a type of fixed point called an elliptic fixed point, it moves the original point (positions of the first two atoms measured relative to atomic positions when the springs connecting the atoms are at their natural lengths) along an elliptic curve in the two-dimensional space, consisting of two successive atomic positions, by an angle which is not an integral fraction of 2π. Thus, one gets an incommensurate configuration because as one moves along the chain one finds that the atoms never repeat their original configuration. Because one can start laying out this chain at any point on this ellipse, it follows that the displacement of each atom is a smooth function of the integer which numbers the atoms. From this Aubry was able to show that there exists a zero-frequency lattice mode, which shows that the system is not pinned. Thus, although Aubry was able to show that such incommensurate periodic systems have unlocked configurations, he was not able to give the values of the parameters for which the system is or is not pinned.

In this paper, we present numerical solutions of the equilibrium equations of the Frenkel-Kontorova model. We have found the values of the parameters for which the system first becomes pinned. We have also found the type of atomic motion which occurs in the zero-frequency mode. This motion is much more complicated than that found in the continuum approximation to the Frenkel-Kontorova model by Theodorou and Rice,[12] Sutherland,[13] and McMillan.[14] We have also calculated the static structure factor. Comparison will be made to approximate analytic solutions of the problem to assess their validity.

II. MODEL

Our studies will be based on the Frenkel-Kontorova model which consists of a chain of ions connected by springs interacting with a sinusoidal potential. The potential energy of this model can be written

$$V=\frac{\mu}{2}\sum_{n=1}(x_{n+1}-x_n-b)^2+\frac{W}{2}\sum_{n=1}\left(1-\cos\frac{2\pi x_n}{a}\right), \tag{1}$$

where x_n is the position of the nth marble, b is the unstretched spring length, and a is the period of the sinusoidal potential. One of the authors[10] has applied this model to the study of a charge-density waves in a one-dimensional solid by identifying the sinusoidal potential with the interaction of the ions in the lattice with a charge-density wave whose period is a. This procedure is good if the charge-density wave is much more rigid than the lattice. The fact that Lee, Rice, and Anderson[7] obtain a velocity for phononlike excitations of the charge-density wave much larger than the phonon velocity of the lattice is evidence in support of this picture. In another application, the sinusoidal potential can be taken to represent the periodic potential due to the nonmobile ions in a superionic conductor and the chain of ions, to represent the mobile ions themselves.[5,15]

In a third application, the chain of ions could represent the mercury ions in $Hg_{3-6}AsF_6$ and the sinusoidal potential, the potential due to the rest of the lattice in which the mercury ions sit.

Although it is appropriate to use free-end boundary conditions for the problem of epitaxial crystal growth, to which this model was originally applied,[9] we feel that for the applications described in the preceding paragraph it is better to use periodic boundary conditions. That is, we assume that x_n is periodic in n with period N, the number of ions in the crystal, i.e.,

$$x_{n+N}=x_n+La. \tag{2}$$

The reason for this choice of boundary conditions for charge-density waves is that the mean interionic spacing is fixed by the length of the lattice. For the superionic conductors and mercury compounds, the number of ions in a given length of lattice is fixed, which fixes the mean lattice constant. Later on, however, we will report some calculations for the free-end case in order to discuss the crystal growth applications of the model.

The physics of the system, in the thermodynamic limit, may then be deduced from the study of a single unit cell containing N ions. Due to the boundary conditions, the unit cell may be viewed as a ring whose circumference is necessarily equal to Nb. The periodic chain is then an infinite commensurate system, i.e.,

$$La=Nb, \tag{3}$$

where L and N are integers. It is important to emphasize that, unlike a chain with free ends, the periodic chain can neither expand nor contract; the "dislocation density" is fixed by b/a. This feature will be seen to be crucial in understanding the existence of a zero-frequency excitation (sliding mode) which arises in the incommensurate limit (b/a an irrational number).

The equilibrium positions are solutions of the following nonlinear difference equations, obtained by setting the derivative of V with respect to x_n equal to 0:

$$\begin{aligned}&x_{n+1}=2x_n-x_{n-1}+\lambda\sin(2\pi x_n/a), \quad n=2,3\ldots,N+1\\&x_{N+1}=La+x_1,\\&x_{N+2}=La+x_2,\end{aligned} \tag{4}$$

where

$$\lambda/a=\pi W/\mu a^2. \tag{5}$$

The presence of the nonlinear sine term precludes the possibility of finding a general analytic solution which is valid for all values of N and b/a. One can, for certain values of the parameters, make valid approximations which render the problem tractable. These approximate methods will be discussed in Sec. IV. To obtain exact solutions for any values of the parameters, one must solve the equations numerically.

The numerical solution of Eq. (4), which is nontrivial, can be simplified by exploiting the symmetries of the system. The periodic chain, unlike the chain with free ends studied numerically by Snyman and Van der Merwe,[9] always has a center of symmetry. As a consequence, there can, in general, be only three types of symmetry configurations. These are classified (up to a shift in origin) by the position of the first ion:

$$\left.\begin{aligned}&\text{Type (i)}\ \ x_1=0\,,\\ &x_{2+k}+x_{N-k}=La\,,\quad k=0,1,2,\ldots\end{aligned}\right] \tag{6a}$$

$$\left.\begin{aligned}&\text{Type (ii)}\ \ x_1=\tfrac{1}{2}a\,,\\ &x_{2+k}+x_{N-k}=(L+1)a\,,\quad k=0,1,2,\ldots\end{aligned}\right] \tag{6b}$$

$$\left.\begin{aligned}&\text{Type (iii)}\ \ x_1+x_2=0\,,\\ &x_{3+k}+x_{N-k}=La\,,\quad k=0,1,2,\ldots\end{aligned}\right] \tag{6c}$$

The existence of these symmetries reduces the numerical problem to a *one-parameter* search.

We will now show from Eq. (6) that only two of these three configurations are distinct for a given chain. Assume that L and N are relatively prime integers. (i) Suppose N is an even integer. Then L is necessarily odd. The $(x_1=0)$ configuration has its center of symmetry passing through an ion located on a crest, whereas the $(x_1=\frac{1}{2}a)$ configuration has its center of symmetry passing through an ion located in a trough. By translating the origin and relabeling the ions, types (i) and (ii) are seen to be equivalent. (ii) Suppose N is an odd integer. If L is odd, then the type (ii) $(x_1=\frac{1}{2}a)$ and type (iii) $(x_1+x_2=0)$ configurations are equivalent. Alternately, if L is even, the type (i) $(x_1=0)$ and type (iii) $(x_1+x_2=0)$ configurations are equivalent. Hence, there are only two distinct configurations for a given N.

There are other symmetries in the problem worth mentioning. As in the model with free ends, one need only consider values of b/a in the interval $[\frac{1}{2},1]$. The equilibrium positions and energies associated with any value of b/a outside this interval can be obtained from those within the interval by a point transformation. (i) Suppose $b/a=L/N+m$. The coordinate transformation $x_n=y_n+m(n-1)a$ maps the set $\{x_n|b/a=L/N+m\}$ onto the set $\{y_n|b/a=L/N\}$ leaving the energy unchanged. (ii) Suppose $b/a=0.5-L/N$, where $0\leq L/N\leq 0.5$. The transformation $y_n=na-x_n$ maps the set $\{x_n|b/a=0.5-L/N\}$ onto the set $\{y_n|b/a=0.5+L/N\}$ leaving the energy unchanged. The energy is thus a periodic function of b/a (with period one) and is symmetric about the values $b/a=\frac{1}{2}(2m+1)$.

From the previous symmetry considerations several conclusions may be drawn about the system when λ is "small" (strong-spring-weak-potential limit). First of all, if these symmetries represent the only solutions, there are two energies in the problem. Secondly, by translating the origin and relabeling the ions, it is seen that the first ion is allowed precisely $2N+1$ equilibrium locations within the interval $|x_1|\leq\frac{1}{2}a$. Thirdly, these allowed locations will alternate sequentially between the two symmetry types and thus alternate between the two energies. The system, in the incommensurate limit ($N\to\infty$, L/N finite and irrational), might then be capable of supporting a zero-frequency sliding mode. As the chain becomes more incommensurate with the underlying periodic potential, the allowed equilibrium positions of the first ion become dense along the line. Being that the periodic chain can neither expand nor contract (unlike the chain with free ends), the allowed equilibrium positions of all the ions become dense along the line. Since the differences between the positions of the ions in two sequential configurations become infinitesimal, one might expect the difference between the two energies (the "pinning" energy) to vanish. Thus, in the incommensurate limit there would exist an infinite number of equilibrium configurations, all with the same energy. This degeneracy should give rise to a zero-frequency mode. Thus, there exists a continuum of infinitesimal displacements $\{u_n\}$ which translate the chain through successive equilibrium configurations; the chain will then slide, i.e., an infinitesimal constant force placed on each ion will cause the chain to accelerate. One sees from the equilibrium equations that the chain cannot be translated rigidly; the infinitesimal displacements for each ion are necessarily different. The zero-frequency mode, therefore, cannot be the usual zero wave-vector acoustical mode.

It should be emphasized that these conclusions are only valid for sufficiently small λ, for which the system only admits the two possible equilibrium states which we have discussed.

III. NUMERICAL RESULTS

The equilibrium positions for the Frenkel-Kontorova model with periodic boundary conditions have been computed for various values of $l_0'=a(a\pi/2\lambda)^{1/2}$ and b/a using a one-parameter search as dictated by the symmetry considerations of Sec. II. Even with simplifications afforded by symmetry, the numerical problem is nontrivial in that the function, whose roots are to be determined, can be extremely pathological. To cope with such functions, one uses double precision arithmetic (good to, at worst, 1 part in 10^{25}) and three different numerical techniques—grid, bisection, and Newton's method.

The equilibrium energy per particle found in this way $\bar{E}$ as a function of b/a is displayed in Fig. 1. The energy is seen to be a smooth function of b/a (except for cusps at multiples of $\frac{1}{2}$) which is periodic with period one and symmetric about $b/a = \frac{1}{2}$. Being that b/a gives the dislocation density for periodic boundary conditions, it is instructive to compare this plot with Snyman and Van der Merwe's[9] plot of the equilibrium energy per particle versus dislocation density for the discrete Frenkel-Kontorova model with free ends. One finds that the two plots are equivalent when the free-end chains approach the thermodynamic limit. Furthermore, in this limit, the positions predicted by these two models agree. One also notes that if l_0 is "sufficiently" large, positions (and energies) predicted by these two models will agree with those of Frank and Van der Merwe's continuum model. Thus, a periodic chain of *finite length* can, in certain cases, be used to deduce properties of chains of infinite length.

The point here is that if the periodic model has but the two equilibrium solutions required by symmetry, the study of a single period of the chain is equivalent to the study of an infinite chain. Longer chains which are composed of integer multiples of this unit chain contain no new information. However, as l_0 is decreased so that a registry transition should occur, we have found, along with Snyman and Van der Merwe,[9] that each distinct symmetry configuration allows multiple equilibrium solutions. Thus a long chain composed of several unit chains can support many configurations since each unit chain has several allowed equilibrium states. The existence of such multiple solutions in this regime is a reflection of the fact that a periodic chain can neither expand nor contract to accomodate registry. It must, therefore, develop dislocations when the registry transition occurs. Most of these solutions are not the ground state, however. In the actual ground state, the dislocations form a periodic lattice incommensurate with the sinusoidal potential.[16]

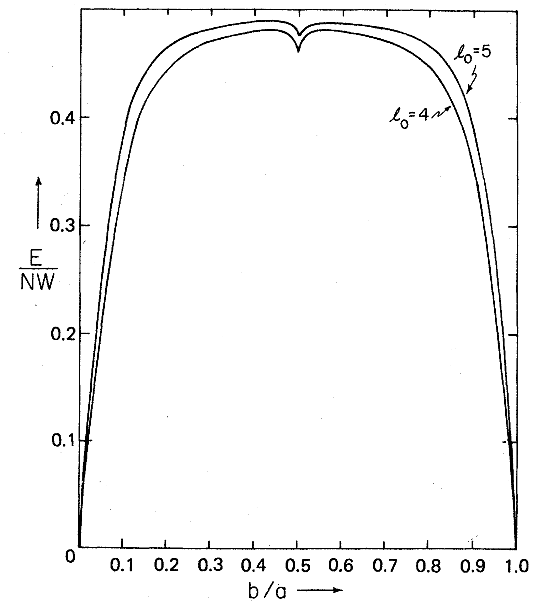

FIG. 1. Energy per atom (in units of W) as a function of b/a for two values of l_0 for a periodic chain (in units of a).

It was argued in Sec. II that, for l_0 sufficiently large, the difference in equilibrium energy per particle between the two allowed symmetry configurations, $\Delta F(l_0)$, should vanish in the incommensurate limit. One might expect to see this occur as l_0 is increased beyond some critical value which defines the registry transition. In that a sequence of commensurate chains of increasing order of commensurability are to be used to simulate an incommensurate chain, two points must be kept in mind. First, the pinning energy of *any* periodic chain can be made arbitrarily small by choosing l_0 sufficiently large (rigid-spring–zero-potential limit). An incommensurate (sliding) transition is said to occur if ΔE drops dramatically with a small increase in l_0 beyond a critical value. Second, if the periodic model is to be of any practical use in locating the registry transition, the desired effect must be observable in relatively short chains.

The pinning energy as a function of l_0 has been investigated for various values of b/a. Five of these are displayed in Fig. 2. The transition is seen to occur in some chains which have a relatively low degree of incommensurability. In fact, for certain chains a small increase in l_0 produces a decrease in ΔE of 20 orders of magnitude. It was observed in this study that the "strength" of the transition varies substantially with the natural spring length and the number of ions in the unit chain. For very short chains or for values of b/a very near $\frac{1}{2}$ or 1, the transition is "weak" or nonexistant as expected.

It has been shown that one feature of the incommensurate limit, $\Delta E(l_0) \to 0$, can be *simulated* by a relatively short chain. This leads one to speculate as to whether or not a relatively short chain, for which ΔE vanishes, can simulate a zero-frequency sliding mode. The answer to this question is a "qualified" yes. To begin with, one recalls that all commensurate chains slide in the rigid-

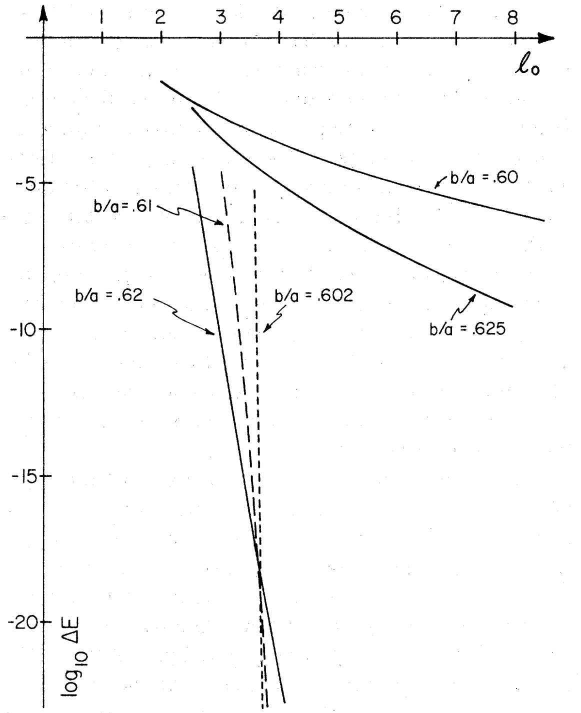

FIG. 2. Log_{10} ($\Delta E/NW$) dimensionless as a function of l_0 (in units of a) for a few values of b/a for a periodic chain. It should be noted that b/a determines the length of the unit cell of the periodic chain, so that for $b/a = 0.61$, the unit cell is 100 atoms long, for $b/a = 0.62$ it is 50 atoms long, 500 atoms long for $b/a = 0.602$, 5 atoms for 0.6, and 8 atoms for 0.625.

spring–zero-potential limit ($l_0 \to \infty$). On the other hand, for finite l_0, no short chain can really support such a mode since the equilibrium locations are not dense along the line. If a relatively short chain is to simulate sliding, then the sliding mechanism must necessarily involve certain nonequilibrium configurations. One may conjecture that the energies of two consecutive equilibrium configurations bound, from above and below, the energies of those nonequilibrium configurations whose ions are restricted to lie in intervals defined by the consecutive equilibrium locations. Since these nonequilibrium configurations evolve naturally into real equilibrium configurations in the incommensurate limit, they may be suitable to simulate the sliding.

To investigate these configurations, one might place the ions randomly in the allowed intervals and monitor the energy. Since one is seeking to identify the equal energy configurations, this general procedure is of little use. There is an alternate approach which is more fruitful. Recall that the periodic model has two boundary conditions. If one were to ignore the symmetry of the model, then the problem of determining equilibrium positions would require the use of a two-parameter search. If a two-parameter search is applied to chain whose pinning energy is known to be *numerically* equal to 0 (say to 1 part in 10^{26}), an interesting effect is observed. Given *any* x_1, one can find a unique x_2 such that the configuration generated by (x_1, x_2) satisfies both boundary conditions to, say, 1 part in 10^{24}. Thus, any x_1 can be considered *numerically* to be an equilibrium location of the first ion. Furthermore, it was found that the energies associated with these pseudoequilibrium configurations differ among themselves and from the true equilibrium energy by no more than 1 part in 10^{25}.

It must be emphasized that these configurations in a finite chain are strictly numerical in origin and arise solely from the limitations of the computer. The minimum value of l_0 which defines the onset of these configurations is then somewhat arbitrary. If the boundary condition tolerance is set to a value approximately one order of magnitude larger than $\Delta E(l_0)$, then these configurations will always exist. Due to the limitations of the available double precision arithmetic package $\Delta E \approx 10^{-24}$ W has been chosen to define the critical value of l_0.

From a study of these pseudoequilibrium configurations, one concludes that a relatively short chain can simulate a zero-frequency sliding mode. There exist configurations in which the ions are located arbitrarily close to real equilibrium positions. The infinitesimal displacements from equilibrium extracted from these configurations define the zero-frequency eigenvector of the dynamical matrix. Thus, the system can support a zero-frequency mode. Furthermore, a continuum of these infinitesimal displacements (which are not constant) can be generated which translate the chain through successive equilibrium configurations without changing its energy. Thus the chain can slide.

It has been mentioned in Sec. II that a sliding mode cannot be strictly the usual zero wave-vector acoustical mode since the chain cannot be translated rigidly while remaining in equilibrium. A few successive equilibrium positions for the sliding chain are illustrated in Fig. 3. One sees that a small translation of the first ion, originally at the bottom of its potential well, to the next equivalent equilibrium position will allow another ion further down the chain to move into the bottom of the potential well in which it lies. If the origin of coordinates is moved from the first ion to this ion, the new equilibrium configuration looks the same as the original configuration. This explains the origin of the high degeneracy of the ground

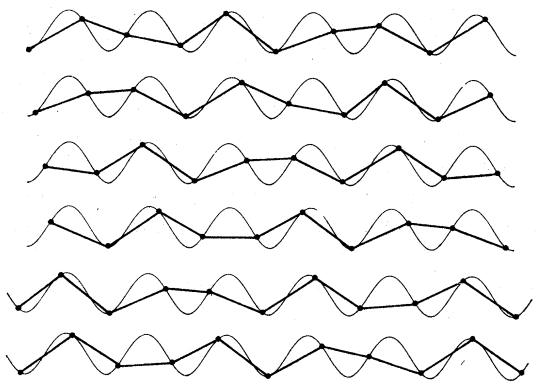

FIG. 3. Successive equilibrium positions (i.e., the motion that occurs for the sliding mode) for a chain of atoms with $b/a = 0.62$ and $l_0 = 5$ (in units of a). We have shown the sinusoidal potential for reference.

state. As the repeat distance of the periodic chain approaches infinity (i.e., the chain approaches the incommensurate limit), the allowed equilibrium positions become infinitesimally close together because when the first ion is translated on arbitrarily small distance there will always exist an ion further down the chain which will move into the bottom of its potential well. Thus, the actual ionic motion which occurs in the zero-frequency (sliding) mode is much more interesting than that found in the continuum (i.e., large l_0) limit in Refs. 12–14. It is not simply a rigid translation of dislocations as occurs in the continuum limit. When l_0 is made larger, however, the zero-frequency mode when viewed from a distance, as illustrated in Fig. 4 (which shows several consecutive equilibrium configurations), does look like a rigid motion of dislocations if we do not look in detail at the motion of the individual atoms.

We will now demonstrate that unlike the case of a periodic chain that we have discussed up to this point, a chain of atoms with free ends in a sinusoidal potential need not have a zero-frequency sliding mode. The reason for this is that unlike a chain of fixed length, the chain with free ends is able to expand and contract in order to lower its potential energy in the sinusoidal potential well (at the expanse of its own distortional potential energy). These chains differ from the periodic chains in a fundamental way. As observed by Snyman and Van der Merwe, free chains need not have a center of symmetry. In their analysis of ground-state properties they discard these nonsymmetric configurations by arguing (correctly) that a nonsymmetric configuration cannot be the state of lowest energy. (This is not to say that all nonsymmetric configurations have higher energies than all symmetric configurations.) It might then be expected that a free-end chain of finite length (and finite l_0) is necessarily pinned.

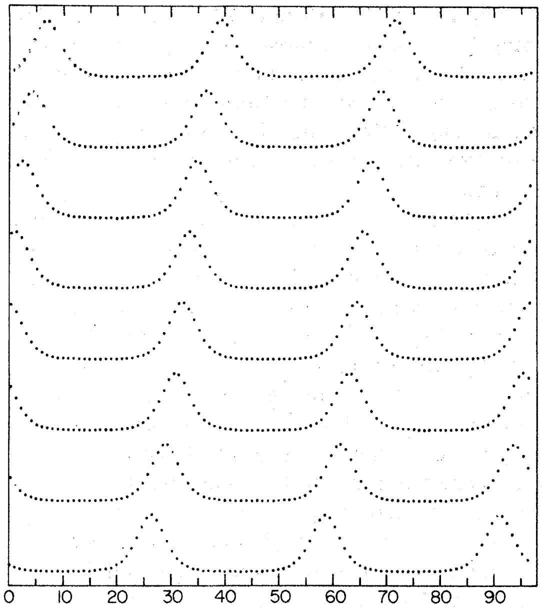

FIG. 4. Successive equilibrium positions for a chain of atoms with $b/a = \frac{97}{100}$ and $l_0 = 12$ (in units of a). The ordinate gives the contribution to the potential energy of an atom due to the sinusoidal potential and the abscissa gives the location of the atoms in units of a (remember that the sinusoidal potential energy increases as the atoms are displaced away from the minima of the sinusoidal potential well).

In order to test this conjecture, we have solved the equilibrium difference equations [Eq. (4)] for free ends. The difference equations for the end atoms become in this case

$$x_2 - x_1 - b = \lambda \sin[(2\pi/a)x_1] , \tag{7a}$$

$$x_{N-1} - x_N + b = \lambda \sin[(2\pi/a)x_N] . \tag{7b}$$

To solve, choose x_1, use Eq. (7a) to find x_2, iterate the set of equilibrium difference equations [Eq. (4)] to obtain x_N, and check to see if Eq. (7b) is satisfied. Thus, we are doing a one-parameter search for the value of x_1 which generates a value of x_N which satisfies Eq. (7b). Several free-end chains were studied in this way. In all cases, the energy per particle was found to oscillate smoothly with x_1 with an amplitude which did not decrease as the chain length was increased. For example, for a chain with $b/a = 0.31416$ and $l_0 = 7a$, the amplitude of the oscillation in the energy per particle ΔE (i.e., the pinning energy) was found to be 0.02 W, which did not vary significantly with chain length, despite the fact that chains with number of atoms ranging from 100 to 100 000 were studied! The same type of behavior was found for chains with $l_0 = 20\,000a$ (i.e., very stiff chains), with N

varying up to 2000. Although ΔE falls off with increasing l_0, it does not abruptly drop to zero at a critical value of l_0. In our studies, we have observed a direct correlation between chain energy and chain length, implying that this pinning effect is likely to be due to expansions and contractions of the chain.

One might conjecture that the pinning energy may decrease as the number of ions increase. However, this was not found to be the case except in the rigid-spring (zero-potential) limit. Although the equilibrium locations for the first ion in the interval $|x_1| \leq \frac{1}{2}a$ do become dense along the line (like a periodic chain) as N increases, the equilibrium locations of the last ion do not. A small change in x_1 can produce sizable changes in length which alter the energy and the dislocation density.

Some insight into the previous remarks can be gained by examining the rigid-spring case where the chain can be made to slide. Here equilibrium can be maintained in two nontrivial ways, both of which require a center of symmetry. For general b, a, L, N equilibrium is achieved only if the center of mass (center of symmetry) is located on a peak or in a trough. Here there are two energies in the problem which become equal only in the limit $N \to \infty$. This being the case, one could hardly expect a free chain of finite length to slide at finite l_0. Equilibrium may also be achieved in the rigid-spring limit by requiring $b/a = L/N$ (i.e., fixed length) whereupon it is found that the equilibrium energy is independent of x_1 for all N. Since this condition is reminiscent of the periodic chain, it is worthwhile to examine the effects of this constraint upon the free chain equations with $\lambda \neq 0$. (Of course, the fixed length constraint requires that there be forces on the end atoms in general.) If the length is fixed at La, the chain satisfies the condition

$$x_N = x_1 + La - b\ . \tag{8}$$

If Eq. (7b) is written

$$b = x_N - x_{N-1} + \lambda \sin[(2\pi/a)x_N]$$

and if x_N is added to both sides, we obtain

$$x_N + b = 2x_N - x_{N-1} + \lambda \sin[(2\pi/a)x_N] = x_{N+1}\ . \tag{9}$$

Substituting from Eq. (8) for x_N gives

$$x_{N+1} = x_1 + La\ . \tag{10}$$

If Eq. (7a) is written

$$x_2 = x_1 + b + \lambda \sin[(2\pi/a)x_1]$$

and if La is added to both sides of the equation and La is added to x_1 in the argument of the sine, we have, using Eq. (10),

$$\begin{aligned} x_2 + La &= 2(x_1 + La) - (x_1 + La - b) + \lambda \sin[(2\pi/a)x_{N+1}] \\ &= 2x_{N+1} - x_N + \lambda \sin[(2\pi/a)x_{N+1}] = x_{N+2}\ . \end{aligned}$$

Thus, the boundary conditions for a free-end chain constrained to be of fixed length are identical to those for the periodic chain, and hence, we expect such a chain to exhibit a zero-frequency sliding mode (i.e., this chain is not pinned). With this result in mind, it is easy to understand why Ying[17] found such a sliding mode for a chian with apparently free ends. Ying assumes that

$$x_n = nb + u_n\ ,$$

where the small equilibrium displacements from uniform ionic spacing u_n are assumed small and satisfy

$$\sum_n u_n = 0\ ,$$

which is equivalent to requiring an infinity long chain to have fixed length.

Our conclusion, at least for noninfinite chains, is that with free ends the system is pinned, in contradiction to Ying.[17] Aubry has also found that boundary conditions can drastically affect the nature of the registry transition.[11] Although microscopic expitaxially grown crystallites have been observed by electron microscopy to be quite mobile,[18] we must conclude that this motion is thermally activated with an activation energy proportional to the number of atoms in the crystallite, and in the limit of weak substrate potential, proportional to the depth of a substrate potential well in which an atom in the crystallite sits. For $l_0/a = 7$, the value used by Frank and Van der Merwe for films, we have estimated this activation energy per crystallite atom (i.e., the pinning energy found earlier) to be about 1% of the well depth.

One of the authors[10] studied the motion of some chains with free ends under an applied field (i.e., the same external force on each atom) as a function of chain length. The fluctuation in the chain potential energy per atom was found to extrapolate to zero in the infinite chain limit, which was taken to imply that in the thermodynamic limit, the chains were not pinned. Although the fluctuations in the energy found for a chain as it slides under a field are considerably smaller than the fluctuations in the equilibrium energies that we have found here, it should be noted that when the chain slides under a force it need not be in a state in which each atom is in equilibrium at all times. The correct limiting procedure to consider for studying the question of pinning for a chain in the thermodynamic limit is to first take the thermodynamic for a small nonzero applied field and then consider the limit as the field approaches zero.

This procedure was not followed here nor in Ref. 10. Although it is clear that in the limit as the field approaches zero any finite chain will settle into one of the equilibrium positions that we have found, it is not obvious that this will happen if the thermodynamic limit is taken first. It should be pointed out that for the chain sliding under an applied field, the chain length fluctuates by around 0.1%, which is considerably smaller than the fluctuation in chain length among the equilibrium states that we have found in this paper. This is quite likely the physical reason that the energy fluctuations found in the sliding chain problem are so much smaller than the fluctuation among the equilibrium-state energies.

One can use the equilibrium positions that we have found to study the effects of incommensurability on the elastic structure factor at zero temperature,

$$S(Q)=\delta_{Q,\,2\pi m/La}\left|\frac{1}{N}\sum_{l}e^{-iQx_l}\right|^2 . \qquad (11)$$

Given that there are two competing periodicities in the system it is useful to express the wave vector as

$$Q=n_a(2\pi/a)+n_b(2\pi/b) . \qquad (12)$$

The choice of (n_a,n_b) for any Q is not unique but can be made so by applying suitable restrictions (see Sec. IV). The strengths of the peaks in $S(Q)$ will clearly depend upon b/a and l_0. For large values of l_0 (strong spring–weak potential), one finds that for the periodic chains the major peaks occur near $Q=n_b(2\pi/b)$ (see Fig. 5). The satellite peaks corresponding to nonzero values of n_a are seen to decrease in intensity as n_a increases. The families of satellite peaks with n_a fixed are seen to first increase and then decrease with increasing Q, following a damped quasi-periodic function. As l_0 is decreased, the intensity of the peaks at $Q=n_b(2\pi/b)$ decreases while the intensities of the satellite peaks increase. The families of peaks appear to "contract" with l_0. For small values of l_0, the roles of a and b are reversed if the chain is close to natural registry. Nothing unusual happens at the value of l_0 for which the transition from the free sliding to the pinned regime occurs.

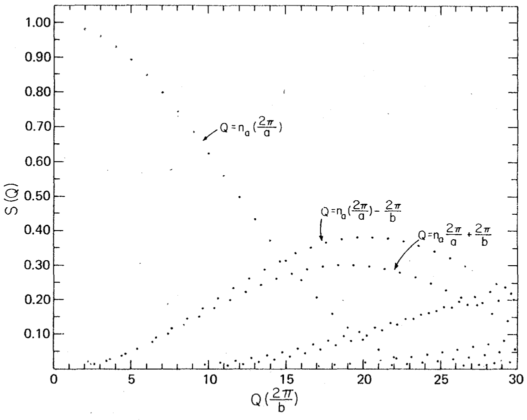

FIG. 5. Calculated static structure factor as a function of wave vector in dimensionless units in which $s(0)=1$. The scattering wave vector Q is in units of $2\pi/b$.

It should be pointed out that these are zero-temperature structure factors. As the temperature is raised, the one-dimensional nature of the system comes into play and some of the peaks are broadened into diffuse scattering. In particular, Widom has found that only the satellite peaks due to the sinusoidal potential do not broaden.[19]

IV. COMPARISON WITH APPROXIMATION SCHEMES

Many of the effects observed in the numerical analysis of this problem can be demonstrated analytically using approximate solutions of the equilibrium equations. Since λa is often small in many applications of the model, x_n varies slowly with n. Successive displacements differ from the natural-spring length by amounts of order λa. Therefore, the continuum approximation of Frank and Van der Merwe[9] and the linearization-iteration scheme of Ying[17] should be applicable.

In the continuum approximation the second-order difference in Eq. (4) is replaced by a second derivative yielding the "sine-Gordon equation," which is integrable. One finds (in units of $a\equiv 1$) that the displacements are periodic functions of n,

$$x_n=\tfrac{1}{2}+(1/\pi)\mathrm{am}\{[\pi(n-1)/l_0k]-F[\pi(\tfrac{1}{2}-x_1)]\} , \qquad (13)$$

where "am" is the amplitude of an elliptic function of the first kind, $F(\phi)$. The period can be set to L by requiring

$$L/N=\pi/[2l_0kK(k)] , \qquad (14)$$

which uniquely defines k. With this restriction it follows that the displacements in the continuum model have the symmetries of the discrete chain. When l_0 is large ($\lambda/a\ll 1$) the displacements predicted by this model are in reasonable agreement with the exact displacements computed numerically. If these displacements are used to approximate the *discrete* positions of the ions in the numerical calculation of the energy, then many effects discussed previously regarding pinning will be obtained. However, if one wishes to have analytic expressions for the quantities of interest, one must evaluate these quantities in the continuum limit where sums are replaced by integrals. Then, all lattice-dependent effects disappear. For example, the equilibrium energy for the periodic chain,

$$E = Wl_0^2\{[4E(k)/\pi l_0 k] - 2(1-k^2)[K(k)/\pi l_0 k] - b\}, \quad (15)$$

is independent of x_1 regardless of the degree of incommensurability. In this approximation the chain can always support a zero-frequency sliding mode. This is the acoustical mode discussed by Sutherland,[13] McMillan,[14] and Theodorou and Rice.[12]

The approximation scheme of Ying[17] is well suited for an analytic description of certain lattice-dependent effects when λ is small. In this iteration procedure, a power series in λ is generated by linearizing at each step,

$$x_{n+1}^{(m)} - 2x_n^{(m)} + x_{n-1}^{(m)} = \lambda \sin[(2\pi/a)x_n^{(m-1)}]. \quad (16)$$

The resultant displacements are periodic functions of n with the proper symmetries so the method is well suited to the problem at hand. One finds to first order

$$\begin{aligned} x_n = {} & x_1^{(0)} + (n-1)b \\ & - \lambda \sin\{(2\pi/a)[x_1^{(0)} + (n-1)b]\}/[4\sin^2(\pi b/a)] \\ & + O(\lambda^2). \end{aligned} \quad (17)$$

The problem with this approach is that the series in λ will ultimately diverge for any commensurate chain since the denominators in the expansion go as $\sin^2(n\pi b/a)$. Nevertheless, a numerical study shows that when $\lambda/4\sin^2(\pi b/a) \ll 1$, the first-order term approximates the displacements rather well (to two or three decimal places). These first-order displacements should then be adequate in analyzing certain lattice-dependent effects.

Consider the equilibrium energy per particle. For finite chains it is easily shown that the energy depends upon the position of the first ion through a series of terms which are Bessel functions of small argument $[\pi\lambda/2\sin(2\pi b/a)]$ and large order (multiples of N). These terms provide a pinning energy which decreases *rapidly* as the system becomes more incommensurate. In the incommensurate limit, the pinning energy vanishes, rendering the equilibrium energy independent of the position of the first ion. Thus the system, in the approximation, is seen to support a zero-frequency sliding mode. Again, this is not the usual zero wave-vector acoustical mode in which all the ionic lattice moves rigidly.

Since the first-order perturbation theory displacements are reasonable approximations of the exact displacements ($\lambda \ll 1$) some insight into the behavior of $S(Q)$ can be gained by using these approximate positions to compute $S(Q)$ analytically. Consider the Fourier transform of the density

$$\rho_N(Q) = \frac{1}{N} \sum_l e^{iQx_l} \quad (18)$$

(where $\{x_l\}$ denote the atomic positions in one period), whose modulus squared is equal to $S(Q)$. From Eq. (11) it follows using the standard expansion in Bessel functions[20] that

$$\begin{aligned} \rho_N(Q) = {} & e^{iQx_1^{(0)}} \sum_{k=\infty}^{\infty} J_k(Q\gamma_1) \\ & \times \left(\frac{1}{N} \sum_{n=0}^{N-1} e^{i(Q-2\pi k/a)(x_1^{(0)}+nb)} \right), \end{aligned} \quad (19)$$

where

$$\gamma_1 = \lambda/[4\sin^2(\pi b/a)]. \quad (20)$$

The sum over n will vanish unless

$$(Q - 2\pi k/a)b = 2\pi m, \quad m = 0, \pm 1, \ldots. \quad (21)$$

Since the allowed Q values for a Bragg peak to occur are given by $Q = 2\pi n/La$, the solution of this equation is nontrivial, since it is a Diophantine equation.[21] However, Q can always be represented as $Q = n_a(2\pi/a) + n_b(2\pi/b)$ [although (n_a, n_b) are not unique]. The values of n_a and n_b are given by $n_a = \alpha n + sN$ and $n_b = \beta n - sL$, where α, b, and s are integers and s have any value $0, \pm 1, \pm 2$, etc. Because these are the general solutions to the following Diophantine equation obtained when we set $2\pi n/La = n_a(2\pi/a) + n_b(2\pi/b)$,

$$n = Ln_a + Nn_b. \quad (22)$$

It follows that

$$\begin{aligned} \rho_N = {} & e^{iQx_1^{(0)}} \\ & \times \sum_{k=-\infty}^{\infty} J_{n_a+kN}[Q\gamma_1] e^{i2\pi(n_b-Lk)x_1^{(0)}/b}. \end{aligned} \quad (23)$$

In the incommensurate limit, the elastic structure factor is then

$$S(Q) = J_{n_a}^2[Q\gamma_1]. \quad (24)$$

This result qualitatively explains the behavior of $S(Q)$ shown in Fig. 5. Here $N = 50$, so it is not unreasonable to neglect the highest-order terms for moderate Q. One sees that the intensities of the families of peaks (n_a fixed) display the damped, oscillating behavior of Bessel functions. The predominant peaks (J_0^2) correspond to $Q = n_b(2\pi/b)$, whereas the major satellite (J_1^2) correspond to $Q = n_b(2\pi/a) \pm 2\pi/a$. From this analysis one expects these two satellites to have similar functional dependence on Q. One notices, however, that as Q increases, there is a discrepancy between the behavior of the two. The source of this discrepancy is that the first-order displacements which produce an $S(Q)$ are accurate only up to some maximum value of Q. If the second-order displacements,

$$x_n = x_1^{(0)} + (n-1)b - \gamma_1 \sin\{(2\pi/a)[x_1^{(0)} + (n-1)b]\} + \gamma_2 \sin\{(4\pi/a)[x_1^{(0)} + (n-1)b]\}, \tag{25}$$

where

$$\gamma_2 = \pi\lambda^2/16a \sin^2(\pi b/a)\sin^2(2\pi b/a)$$

are used, one finds the density to be

$$\rho_N(Q) = e^{iQx_1^{(0)}} \sum_{k,q} J_{n_a+kN+2q}[Q\gamma_1]J_q[Q\gamma_2] \times \exp^{[i2\pi(n_b-Lk)x_1^{(0)}/b]}, \tag{26}$$

so that in the incommensurate limit,

$$S(Q) = \left(\sum_q J_{n_a+2q}[Q\gamma_1]J_q[Q\gamma_2] \right)^2. \tag{27}$$

From this expression one sees that for values of Q where $Q\gamma_2 \ll 1$, the principal satellites exhibit similar behavior with Q. As Q is increased, however, the functional behavior of the two satellites changes.

V. CONCLUSIONS

From numerical studies on finite chains of atoms in the Frenkel-Kontorova model with periodic boundary conditions, we have concluded that as the coupling of the chain of atoms to the sinusoidal potential in the model decreases below a critical value, a transition occurs for an infinite chain to a state in which the chain will freely accelerate under an arbitrarily small applied electric field (assuming the atoms to be electrically charged). This implies the existence of a zero-frequency "free-sliding" phonon mode of the chain. Our studies show, however, that this mode is not the usual zero wave-vector acoustical mode in which the chain of atoms moves rigidly. Neither is it simply the rigid motion of a lattice of dislocations as found by several people,[12-14] although in the rigid-chain (weak sinusoidal potential) limit this picture is a good discription of the motion if one does not pay much attention to the details of the individual atomic motions. Studies of finite chains with free-end boundary conditions, however, show that in the long chain limit, the pinning energy of the chain is a smoothly oscillating function of the location of the first atom in the chain (the period is the period of the sinusoidal potential) with amplitude which does not decrease with increasing chain length. The conclusions regarding free sliding under a field for this case are still unclear, however. Nevertheless, our results do imply that in epitaxial crystal growth, the mobility observed for small crystallites[18] must be thermally activated.

The static structure factor was calculated and it was found that in the sliding regime, most of its features could be accounted for by using a perturbation theory expression for the equilibrium atomic positions.

Although applications of this model to charge-density waves and to the compound $Hg_{3-6}AsF_6$ probably only require the weak-coupling limit for which the continuum model[9] and perturbation theory[19] are probably adequate for most purposes, stronger coupling theory is important for hollandite, for which displacements of atoms around a vacancy are as large as 25% of a lattice constant.

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