One-dimensional model for a crystal with displacive modulation

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As a model for a crystal with displacive modulation a classical linear chain is discussed with up to third-neighbor interaction. This system has an infinite number of stable equilibrium configurations separated by high barriers. It has a zero-frequency phonon mode, a low-lying phason branch, and an amplitude mode.

In recent years there has been a growing interest in crystals with a displacive modulation, especially incommensurate ones.[1,2] One type consists of systems with two competing periodicities, e.g., composite structures or layers of atoms adsorbed on crystal surfaces. For this type one has obtained much insight into the behavior by the study of one-dimensional models.[3-7] However, these models lack translational invariance and hence do not have a zero-frequency acoustic mode. Therefore, they are not very well adapted as models for another type, namely, the modulated phases of ionic crystals like Na_2CO_3, K_2SeO_4, or Rb_2ZnBr_4, although many characteristics of these models may also apply to these systems. From the theory of magnetism it is known that an intrinsic cause for incommensurate helix structures may be the presence of competing interactions with the nearest and next-nearest neighbors. A similar instability may occur in the displacements of crystal atoms, but here this requires us automatically to take into account more than harmonic forces only.

In this paper we report on a dynamical model that is translational invariant and can give rise to displacive modulation. Moreover, it exhibits in a natural way the presence of a phasonlike mode and an amplitude mode. The model consists of a linear chain with classical particles of equal mass, coupled by nearest-neighbor and next-nearest-neighbor harmonic interaction and a nearest-neighbor anharmonic coupling, which is necessary to stabilize the system. We may write the Hamiltonian as

$$H=\sum_n \left(\frac{p_n^2}{2m}+\frac{\alpha}{2}(u_n-u_{n-1})^2+\frac{\beta}{2}(u_n-u_{n-2})^2 +\frac{\gamma}{4}(u_n-u_{n-1})^4\right), \tag{1}$$

with $\gamma>0$ and where the displacement of the nth particle from its position na in an equidistant array is u_n. The equilibrium positions of the system follow from the condition $\partial V/\partial u_n=0$. Introducing the difference coordinate $x_n=u_n-u_{n-1}$ we get

$$\alpha(x_n-x_{n+1})+\beta(x_{n-1}+x_n-x_{n+1}-x_{n+2}) +\gamma(x_n^3-x_{n+1}^3)=0. \tag{2}$$

Confining ourselves to the most interesting case of $\beta<0$, we may take $\beta=-1$ and $\gamma=1$ in Eq. (2) by rescaling the coordinates of the particles. The absolute minimum of the potential energy V is reached for $\alpha\leq 4$ by the solution

$$u_n=(4-\alpha)^{1/2}n. \tag{3}$$

There are two regimes where the solutions of Eq. (2) can be obtained analytically. For $\alpha\ll -1$ one can neglect in Eq. (2) the term with β. As a result, the potential energy in terms of x_n is that of a collection of uncoupled double-well potentials. The value of x_n can be chosen arbitrarily in either of the two wells. For nonzero β, the coupling will favor energetically periodic solutions, but the values of $|x_n|$ will be nearly constant. The modulation function in x space is very discontinuous, while the function u_n will have a sawtooth form. For the other regime, characterized by $0<4-\alpha\ll 1$, the solution u_n is expected to be a smooth function of n. For this case the continuum limit can be taken and the resulting equations can be solved exactly. The solutions are given by

$$x_n=k\left(\frac{8-2\alpha}{1+k^2}\right)^{1/2}\mathrm{sn}\left[n\left(\frac{4-\alpha}{1+k^2}\right)^{1/2}\right], \tag{4}$$

where $\mathrm{sn}(x)$ is the Jacobi elliptic function with parameter k between 0 and 1. Equation (4) corresponds to a periodic solution in n.

In the discrete case we may also look for solutions of Eq. (2) with a given period N, i.e., $x_n=x_{n+N}$ for all n. The resulting set of equations has been studied extensively on the computer. For every period N a nontrivial solution can be found if $\alpha<4$. However, the solutions are only stable for $N>N_0(\alpha)$, where $N_0(\alpha=0)=4$ and N_0 tends to

increase with increasing α. There are an infinite number of solutions to Eq. (2) which correspond to local minima for the potential energy. Moreover, in addition to the periodic solutions with two nodes per period, there are solutions with $2s$ ($s>1$) nodes per period. We can identify them with solutions with a fractional period N/s. In doing so we find that the potential energy per particle becomes a smooth function of the fractional period, as is shown in Fig. 1. Also, incommensurate phases can readily be realized in our model. We obtain an incommensurate period if we consider a limiting sequence of fractional periods so that the fractions tend to an irrational number. From the above construction we see that such a solution has an infinitely large period N, but finite N/s. Although these solutions cannot be described, in general, by a smooth function with period N/s, they can be considered as periodically distorted structures. In the structure factor, one can indeed distinguish main reflections and satellites.

The calculated minima corresponding to the periodic solutions have a higher energy than the one given by Eq. (3), but energetically they are well separated by high barriers. This has important consequences for the thermodynamic behavior of such a system. Actually, the equilibrium position problem is very similar to that of a model studied by Aubry,[8] but the dynamics of his (nontranslational invariant) model is quite different from ours, as can already be seen from the fact that for the present model there is always a zero-frequency translational mode. Under the simplifying assumption that the barriers between the various local minima are infinitely high, the thermodynamic properties for each period can be related in a good approximation to the eigenvibrations around the (stable) equilibrium positions. The latter form a modulated crystal. Since the number of particles in the unit cell may be very large, in principle there is a great number of gaps in the frequency spectrum. Actually, for $4-\alpha>1$ the spectra are complicated, but there are also features which depend more on the fractional period than on the actual period as is shown in Fig. 2, where the spectra are plotted as a function of the former. Such a feature is the broad band linking the lowest gaps in the spectra for the integer periods. For $4-\alpha \ll 1$ the spectra resemble more those of a modulated spring model with a simple modulation.[9]

The acoustic branch in the phonon dispersion starting from the zero-frequency acoustic mode determines the sound velocity in the modulated crystal. Again, the sound velocity is a smooth function of the fractional period, except in the neighborhood of odd integer periods (Fig. 3). For these cases the sound velocity is very low. The same feature is reflected in the specific heat, which is exceptionally large there.

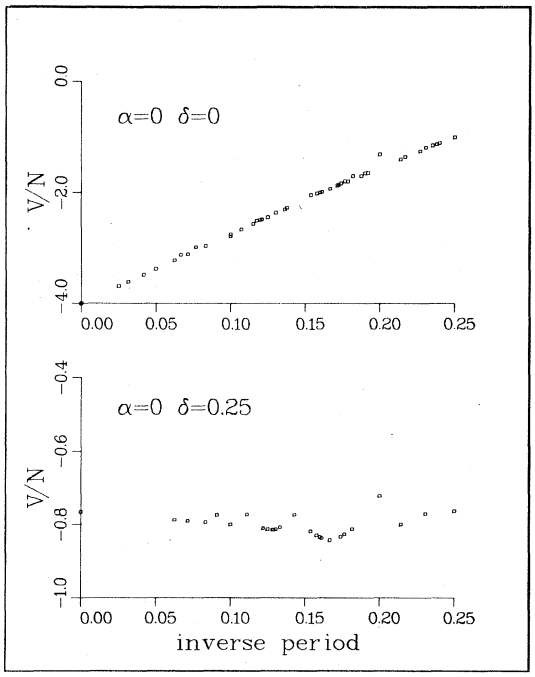

FIG. 1. Potential energy per particle versus inverse of the fractional period.

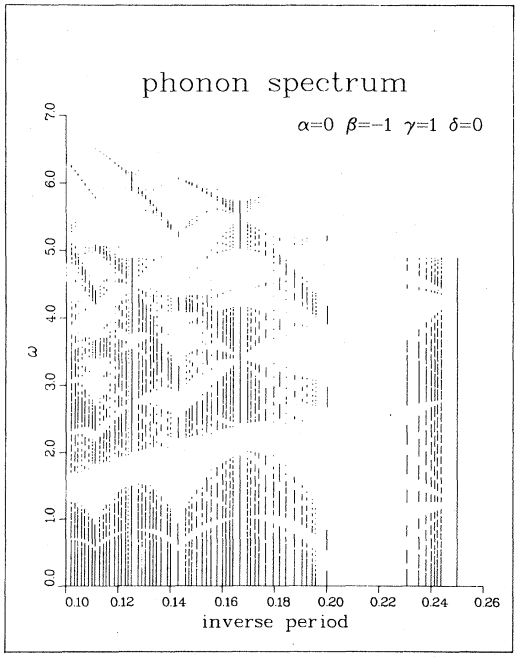

FIG. 2. Spectra of the eigenvibrations for various fractional periods.

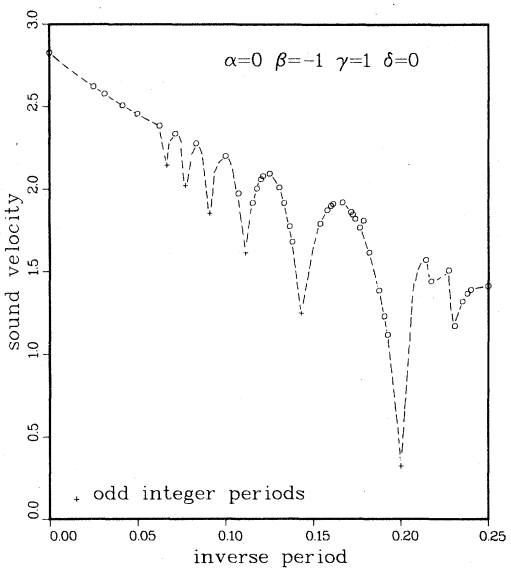

FIG. 3. Sound velocity versus inverse of the fractional period.

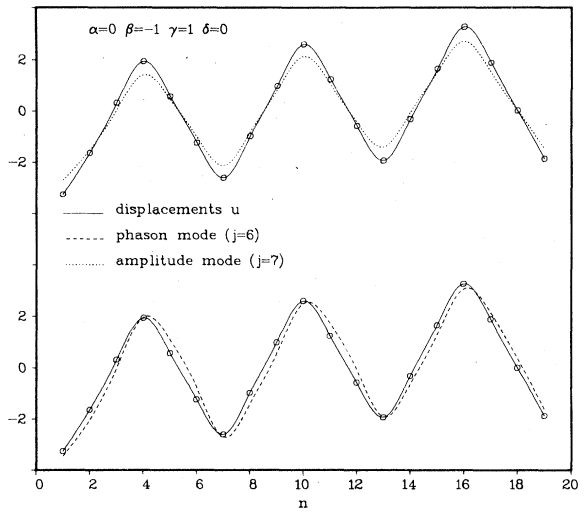

FIG. 4. Displacements u_n for a solution with $N=19$ and $s=3$ to Eq. (2) together with displacements in the phason mode (6th mode for $k=0$) and in the amplitude mode (7th mode).

For a given integer period N the first nonzero-frequency mode with wave vector $k=0$ has an eigenvector which corresponds to a rigid displacement of the modulation wave: This mode resembles what is called a phason mode. A corresponding mode occurs for fractional periods. It is the one belonging to the last branch of the spectrum just below the broad gap in Fig. 2. For $4-\alpha>1$ the frequency of this mode is high for small N/s and decreases only slowly with increasing fractional period, so even for a nearly incommensurate period there is no zero-frequency phason mode. This is contrary to what is usually suggested in the literature and in agreement with the fact that a zero-frequency phason has never been seen experimentally.[10] The explanation is the discontinuous character of the modulation wave. The situation is different in the region $4-\alpha \ll 1$. Here the modulation wave is much smoother and there is a phasonlike mode with frequency decreasing rapidly with increasing period or decreasing $4-\alpha$. Moreover, this mode is separated by a substantial gap from higher frequencies. For the mode corresponding to the upper boundary of this gap we find for $k=0$ an eigenvector with the same node structure as the modulation wave. This mode is the amplitude mode. As an example we show in Fig. 4 the equilibrium positions for the case of $\alpha=0$, $N=19$, and $N/s=6\frac{1}{3}$ together with the phase and amplitude modes at wave vector $k=0$. In general, they correspond, respectively, to the $2s$th and $(2s+1)$th mode a $k=0$.

The configuration (3) with absolutely minimal potential energy for H as given in Eq. (1) has an infinite period. This changes if one takes into account a coupling to the third nearest neighbor. For the Hamiltonian,

$$H' = H + \frac{\delta}{2} \sum_n (u_n - u_{n-3})^2 , \tag{5}$$

where H is given by Eq. (1), there is still a solution given by Eq. (3), when α is replaced by $\alpha+9\delta$, but this may have a higher potential energy than a solution with a finite period. Again the potential energy per particle is a smooth function of the fractional period as is shown in Fig. 1, but now the ground state has a modulated structure.

To summarize, we have presented an anharmonic model for a crystal which exhibits the interesting possibility of having modulated structures as stable equilibrium states. Their origin lies in the interparticle forces, in the interplay between an instability and the nonlinear interaction. The modulation is not forced upon from the outside. Phenomena, like incommensurability and the presence of phase and amplitude modes, can appropriately be interpreted in the model. Although the calculations have been performed in a one-dimensional system, qualitatively the same properties are expected to hold for such a model in higher dimensions.

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