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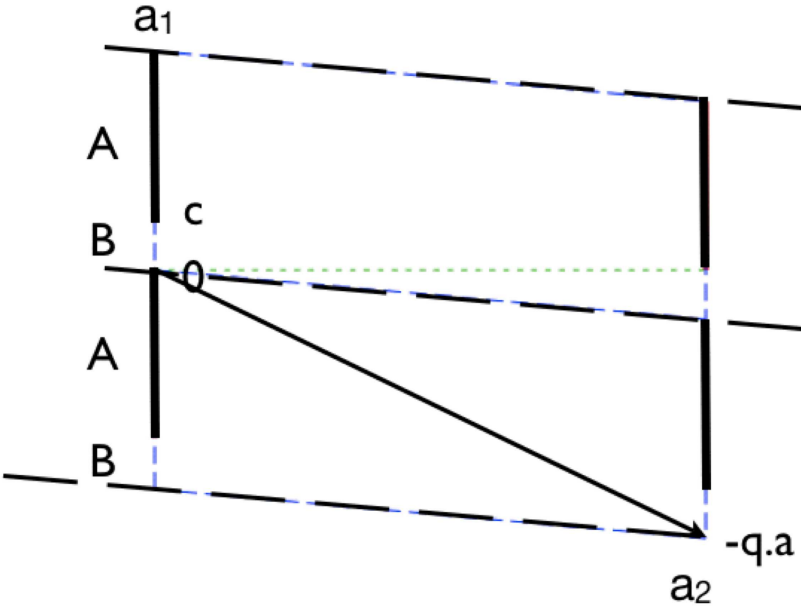


Figure 1
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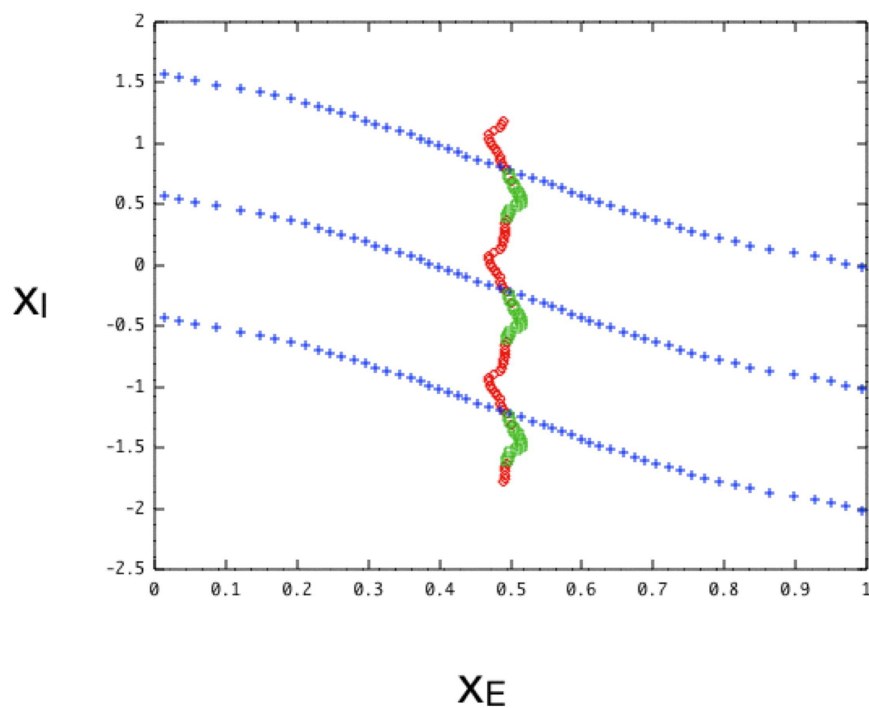


Figure 2
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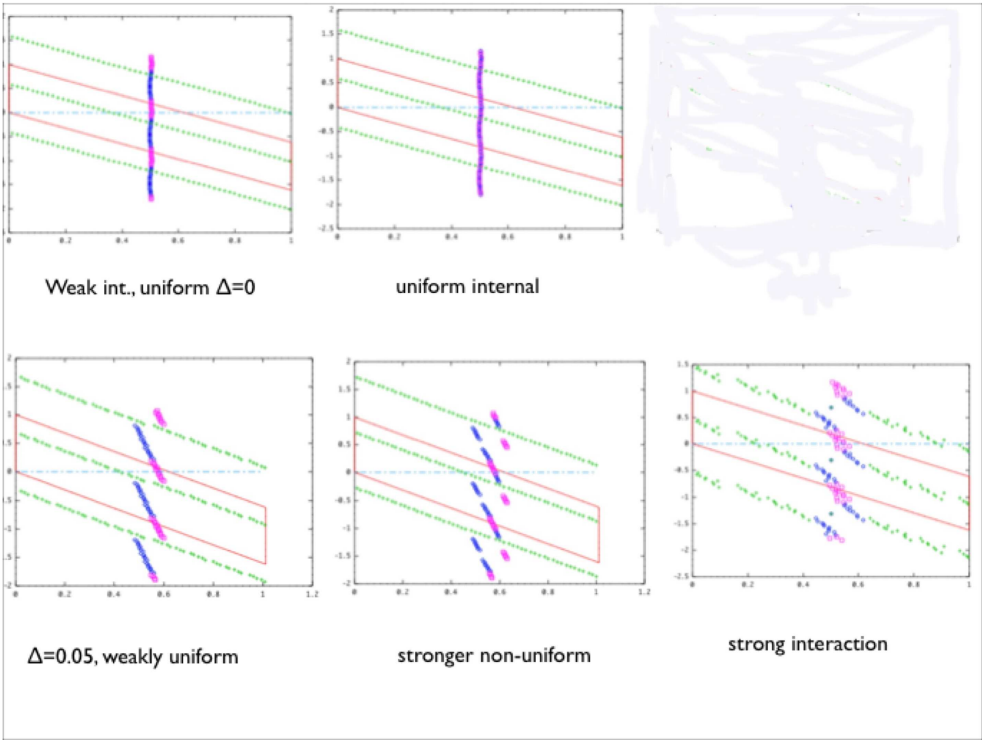


Figure 3
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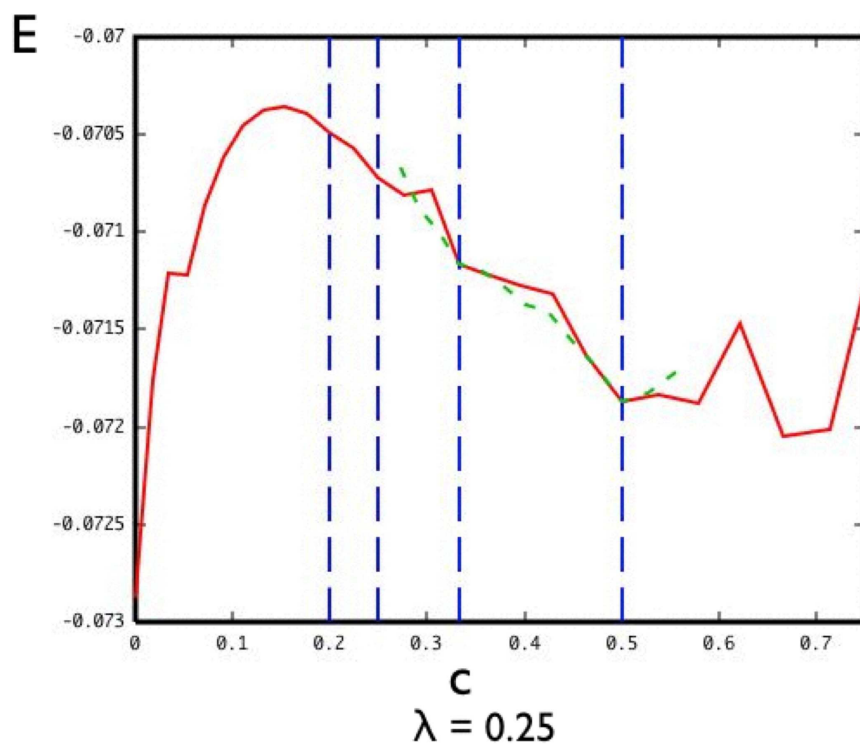


Figure 4
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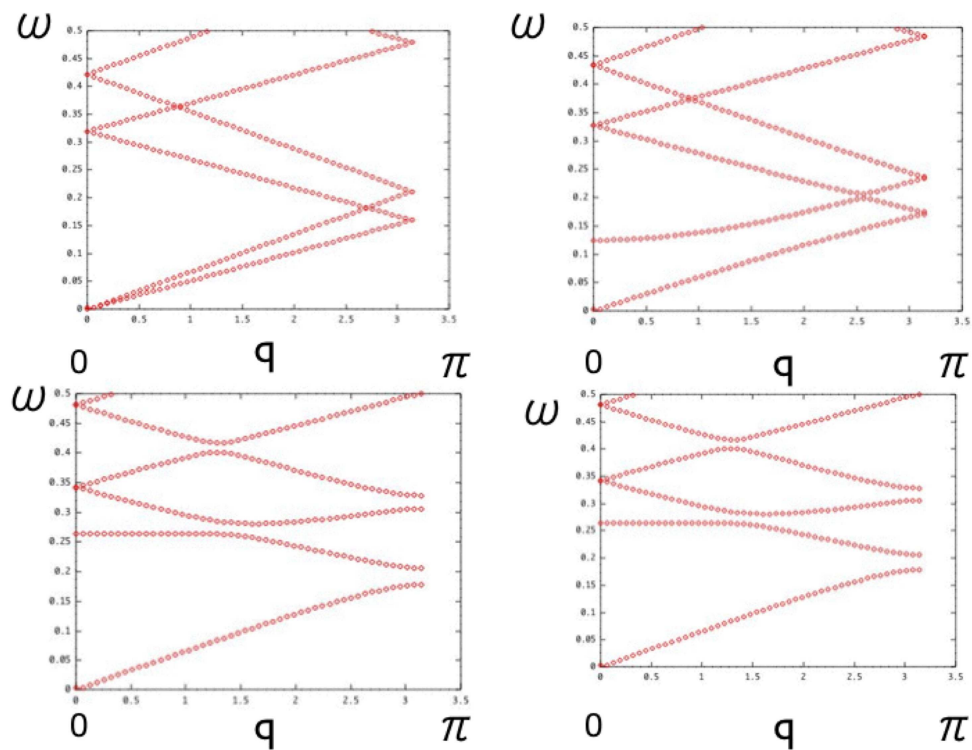


Figure 5
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The Aperiodic Double Chain Model Applied to Composition Flexible Compounds

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A simple model for composition flexible compounds is studied. A discussion is given of the coupling between structure and composition, and of the dynamics.

Introduction

The family of compounds, related to hexagonal perovskites, and with formula $A_{1+x}(A'_xB_{1-x})O_3$ [2, 5] may be described as incommensurate composites. One subsystem consists of incommensurate columns of octahedra and triangular prisms. In between there are chains of atoms. The parameters are the composition c , related to the modulation wave vector q and the height difference 2Δ between an octahedron and a prism. The rank of the system is four: the wave vector of the $(A', B)O_3$ column and the mismatch parameter between the two subsystems are related. The embedding of the structure has finite, disjoint atomic surfaces, which means that the compounds may as well be described as modulated phases with an occupation modulation (with a crenel modulation function) and a displacive modulation (saw-tooth modulation function) [1].

Incommensurate composites have been studied with the Double Chain Model (DCM) [6]. It is a system consisting of two parallel chains at a distance d , where the lattice constant a of the first chain is incommensurate with the lattice constant b of the second. The intra-chain interaction is limited to nearest neighbours. The potential energy is given by

$$V = \sum_n V_1(x_n - x_{n-1}) + \sum_m V_2(y_m - y_{m-1}) + \lambda \sum_{nm} V_i(x_n, y_m). \tag{1}$$

The interactions have been taken to be

$$V_1(x) = \frac{\alpha}{2}(x - a)^2, \quad V_2(y) = \frac{\beta}{2}(y - b)^2,$$

and the inter-chain interaction is given by the Lennard-Jones potential

$$V_i(x, y) = (r^2/[(x - y)^2 + d^2])^6 - 2(r^2/[(x - y)^2 + d^2])^3.$$

The positions of the n_1 particles in the first chain are at $x = x_n$, $y = 0$ and the n_2 particles in the second chain at $x = y_m$, $y = d$. We consider periodic boundary conditions

$$n_1a = n_2b = L; \quad x_{n+n_1} = x_n + L, \quad y_{m+n_2} = y_m + L. \tag{2}$$

The ground state configuration is a pair of incommensurate modulated phases:

$$x_n = x_0 + na + f(na), \quad y_m = y_0 + mb + g(mb); \quad f(x + b) = f(x), \quad g(y + a) = g(y).$$

is incommensurate because a/b is supposed to be irrational, and is approximated by the fraction n_2/n_1 . For this model the ground state and the excitations have been calculated numerically. For the interaction parameter $\lambda = 0$ the chains are unmodulated, for larger values they are modulated, with continuous modulation functions for $\lambda < \lambda_c$ and discontinuous modulation functions if $\lambda > \lambda_c$. For $\lambda < \lambda_c$, there are two vibration modes with frequency equal to zero, an acoustic and a phason mode. In the other case, there is only one such mode, the acoustic mode, and the phason branch has a gap. A generalisation gives the aperiodic double chain model (APDC). In this model one of the subsystems has a quasiperiodic average structure. An example is a harmonic chain in combination with a Fibonacci chain. When there are no special relations between the modulation wave vector and the reciprocal lattice of the second chain, the rank of the Fourier module is three or more. It is similar to a generalised Frenkel-Kontorova model [7].

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12. The model

For the composition flexible compounds we may use this APDC as well. The chain corresponding to the system of octahedra and prisms has an incommensurability which has its origin in the coupling to the other chain. However, there are two types of incommensurability here. One is the sequence of prisms and octahedra, which is a discrete sequence, and one is the displacements wave induced by the interaction. For given sequence of building blocks this may be modelled by the APDC model.

The second chain now represents the atoms between the stacks of octahedra and prisms. They form a modulated chain with average distance b . The first chain represents the stacks and is composed of n_{11} intervals of length a_1 and n_{12} intervals of length a_2 . The length, the difference between the average positions \bar{x}_n and \bar{x}_{n-1} , corresponds to the value of a spin variable σ_n such that

$$\bar{x}_n - \bar{x}_{n-1} = a + \sigma_n \Delta. \quad (3)$$

There are n_{11} spins up, and n_{12} spins down, with $n_{11} + n_{12} = n_1$. The relations for the periodic boundary conditions become

$$n_2 b = n_{11} a_1 + n_{12} a_2 = n_{11} (a + \Delta) + n_{12} (a - \Delta) = L. \quad (4)$$

The concentration c is defined as

$$c = n_{11} / n_1. \quad (5)$$

From this follows that

$$L = n_2 b = n_1 (c(a + \Delta) + (1 - c)(a - \Delta)).$$

Notice that, for $\Delta=0$, we recover the original DCM.

The potential energy of the systems becomes

$$V = \sum_n V_1(x_n - x_{n-1}, \sigma_n) + \sum_m V_2(y_m - y_{m-1}) + \lambda \sum_{n,m} V_i(x_n, y_m). \quad (6)$$

Here $V_1(x, \sigma) = \alpha(x - a - \sigma\Delta)^2/2$ and $V_2(y) = \beta y^2/2$. In principle the interaction V_i also depends on σ . This is taken into account by considering as variation parameter the discrete set of spin configurations σ . The influence of σ on the inter-chain interaction (intervals of different length correspond actually to different atoms) is neglected here. By the interaction the second chain becomes displacively modulated, the first chain has an aperiodic average structure which also becomes modulated by the interaction. The average distance of the first chain depends on the concentration c .

$$\bar{a} = c a_{11} + (1 - c) a_{12} = n_2 b / n_1. \quad (7)$$

Below we show that there is a relation between the value of \bar{a}/b and the concentration. This implies that the rank of the system two and not three (periods \bar{a} and b and the incommensurability in σ). The incommensurate composite may then be embedded in two-dimensional space in the usual way. The Fourier module of the system is spanned by the points $1/\bar{a}$ and $1/b$. These are the projections of the basis vectors $(1/\bar{a}, 0)$ and $(1/b, 1)$. The corresponding basis for the direct lattice consists of $(\bar{a}, -\bar{a}/b)$ and $(0, 1)$. The incommensurability is given by $\bar{a}/b = n_2/n_1$.

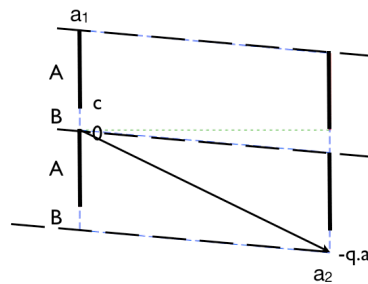


Figure 1. Embedding of the system, and closeness condition. The vertical lines correspond to spin up of chain 1, the gaps to spin down. The dashed line corresponds to the positions of chain 2. The vectors \mathbf{a}_1 and \mathbf{a}_2 span the unit cell. The upper end of the spin up part in one atomic surface corresponds to the lower end in a neighbouring atomic surface.

The above mentioned relation between the modulation wave vector q and the concentration c is given by the so called closeness condition. The closeness condition says that the projection of the boundary of an atomic surface should coincide with that of another atomic surface. The term is usually used in the description of quasicrystals, but it is a general concept for quasiperiodic systems.

Consider the embedding of the system into 2D. The atomic surface in the unit cell (the interval $[0,1]$) consists of a portion c of spin up particles and a portion $(1-c)$ of spin down particles. Take the first in the interval $[0,c]$ and the second in the interval $[c,1]$. At the

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average position \bar{a} , the value of the second coordinate ξ_2 of the top of the interval is $-q\bar{a} + 1$. The closeness condition requires (Fig.1) that

$$-q\bar{a} + 1 = -c.$$

Since $q = 1/b$ it follows that

$$\frac{\bar{a}}{b} = 1 + c \rightarrow n_2/n_1 = 1 + c. \tag{8}$$

The physical reason for this condition is a condition on the charge. Because A atoms in the aperiodic chain are divalent and the B atoms monovalent, charge neutrality requires that

$$2n_1c + n_1(1 - c) = n_2 \rightarrow 1 + c = n_2/n_1. \tag{9}$$

The concentration c is the parameter x in the chemical formula $A_{1+x}(A'_xB_{1-x})O_3$. Therefore, the charge condition leads to the closeness condition, which has a simple interpretation in the superspace picture.

For periodic systems, this implies a rational value of c , but for an aperiodic system the approximants n_2/n_1 tend to $1+c$.

Ground state

The ground state of the system corresponds to the minimum of the potential energy V . This may be calculated numerically for finite approximants, using a relaxation procedure. The initial configuration then may be of importance, and should be varied with respect to number of parameters. For the spin wave which determines the distribution of the long intervals in chain 1, we take

$$\sigma_n = \text{Sign}[\sin(2\pi mc\,n + \phi) - \cos(\pi c)],$$

where ϕ determines the starting point of the spin distribution and m the number of sign changes. The value $m = 1$ corresponds to a distribution of spins on the atomic surface which consists of a connected region with value $+1$ and its complement with value -1 . This gives a most non-uniform distribution of spins in the internal space, but the distribution in physical space is then as uniform as possible. On the other hand, a spin wave with one harmonic in physical space (non-uniform in this space) gives a spin distribution on the atomic surface which is very uniform. The value of ϕ determines the position of the spin wave with respect to the two chains. Special points would be $0, \pi/2, \pi$ and $3\pi/2$, because then the number of spins up could be extremal.

The potential energy minima give the ground states for values of n_1 and n_2 such that n_2/n_1 is an approximation to c . These are then embedded into two-dimensional space using the customary procedure. The 2D lattice coordinates ξ_1 and ξ_2 are given by

$$\xi_1 = (x, 0) \cdot (1/a, 0) = x/a, \quad \xi_2 = (x, 0) \cdot (1/b, 1) = x/b. \tag{10}$$

The point in physical space gives an infinite number of embedded points

$$(M_1 + \xi_1)(a, -a/b) + (M_2 + \xi_2)(0, 1) = ([M_1 + \xi_1]a, M_2 + \xi_2 - [M_1 + \xi_1]a/b). \quad (M_1, M_2 \text{ integers})$$

For small values of λ the atomic surfaces are smooth. For larger values of the interaction the atomic surfaces become discontinuous. For still stronger interaction (and $\Delta \neq 0$) the result is a modulated phase with one average lattice constant, and a fractal atomic surface.

For $\Delta=0, \lambda=0$ the atomic surfaces are straight lines parallel to the one of the two basis vectors. For the choice of basis made here, the particles of chain 1 fall on lines parallel to V_I . The atomic surface corresponding to chain 1 consists of alternative regions for the 2 types of particles. Maximal separation in V_I means that particles with spin up fall on $0 < \xi_2 < c$ and those with spin down on $c < \xi_2 < 1$. In direct space this distribution corresponds to a uniform distribution of spins. This means the following. If we have n_{11} spins up, and n_{12} spins down, we can plot the distribution on a square grid by going from $(0,0)$ to (n_{11}, n_{12}) increasing the first coordinate one when there is a spin up, and the second coordinate when there is a spin down. The uniform distribution corresponds to the path that follows the straight line between begin and end point as closely as possible. The other extreme is obtained when n_{11} spins up are followed by n_{12} spins down. On the grid this gives a path consisting of two straight lines (one vertical, the other horizontal), and in internal space it gives a uniform distribution of spins. Varying the distribution by varying the number of harmonics in the spin wave numerical calculations lead to the conclusion that always the lowest energy per particle corresponds to the uniform distribution in real space, although the energy differences are small.

A second parameter is the relative phase of spin wave and modulation. The lowest energy is obtained for $\phi = \pi/2$ if $\lambda > 0$ and $\phi = 3\pi/2$ if $\lambda < 0$. For negative λ this means that the closeness condition is satisfied, or in other words that the spin wave is uniform in physical space. Again the energy differences are small.

For $\Delta=0, \lambda \neq 0$ the lines are no longer straight, but a modulation of the chains sets in. For small values of the interaction parameter the modulation is smooth. For larger values the atomic surface is split into disjoint parts.

If $\Delta \neq 0$, then the atomic surface consists of disjoint parts already from $\lambda = 0$. There is an average slope of the pieces. For $\lambda = 0$, this slope is completely determined by the value of Δ . For $\lambda \neq 0$ discontinuities in the disjoint parts set in. For large values of λ the atomic surfaces of both chains merge. The resulting structure is a modulated structure with displacive and occupation modulation. The embedding shows parallel atomic surfaces, with discontinuities and alternative regions of particles of both chains.

Because the energy differences between uniform and non-uniform distributions are small, there are many metastable states. The non-uniform distributions correspond to atomic surfaces with an increasing number of gaps if the number of harmonics in the spin wave increases. Nevertheless, the gaps in one atomic surface correspond to pieces in the atomic surfaces of the neighbours, but the closeness condition is no longer satisfied.

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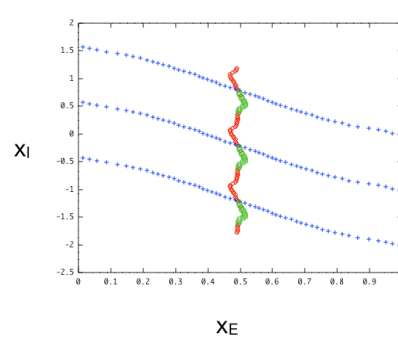


Figure 2. Embedding of a solution with $\lambda=-1.2$, $\Delta=0$.

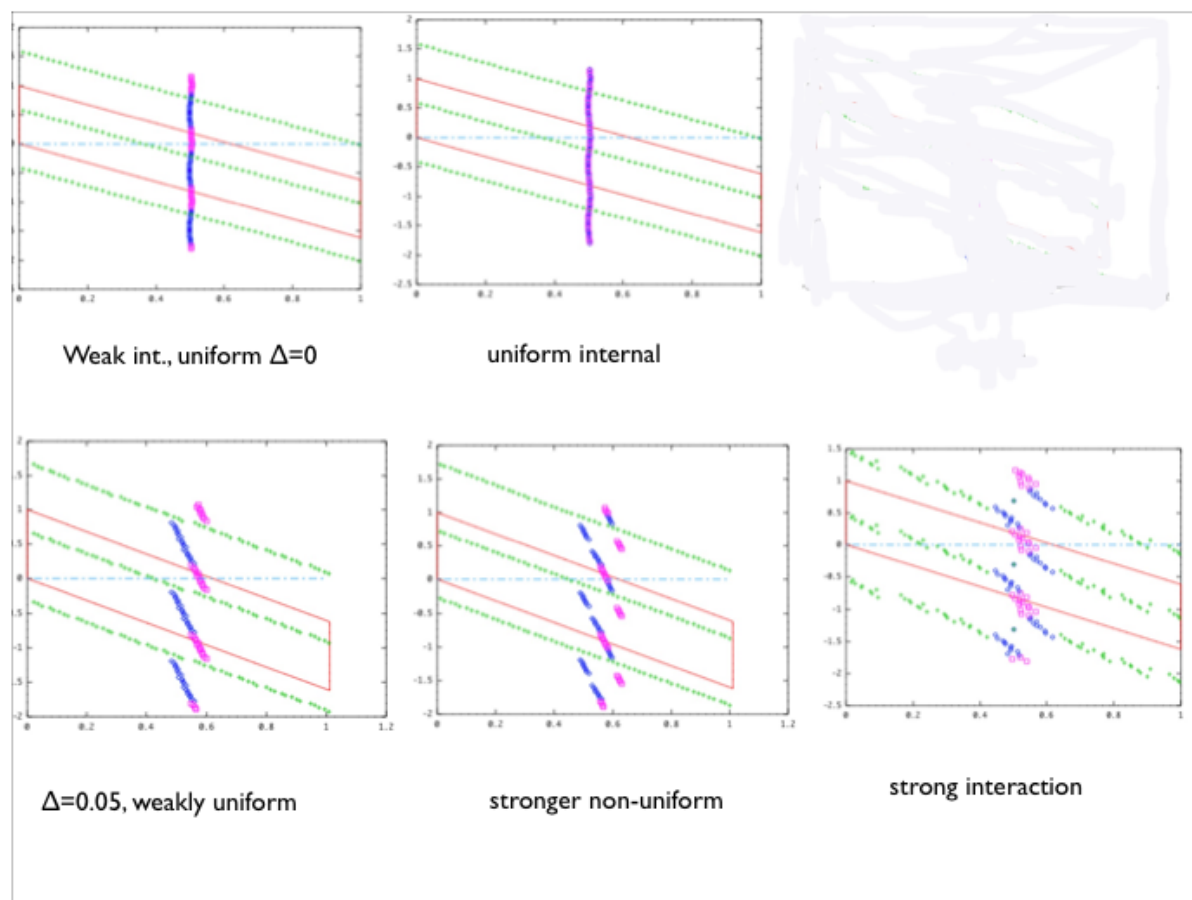


Figure 3. Embedding of 5 solutions. In the first row the pictures give the difference between uniform spin distributions in physical and internal space. For strong coupling λ the atomic surfaces will become discontinuous for $\Delta=0$ as well. For $\Delta > 0$ there is always a discontinuity (frame 4). In the second row the changes in the atomic surfaces are shown if the spin wave is taken to be weakly or strongly uniform, and when the coupling λ becomes large. In the latter case the atomic surface is no longer smooth. On the average there remains one modulated system with a displacive and an occupation modulation. Values of the parameters: $\alpha=1.0$, $\beta=1.5$, $\bar{a}/b=34/55$.

Comparing the energy per particle for the ground states for varying values of the composition c shows a smooth dependence. There is no sign of lock-in terms in the the energy. However, when the interaction parameter λ becomes stronger, there is a weak lock-in effect for $c = 0.5$. (Cf. Fig.4)

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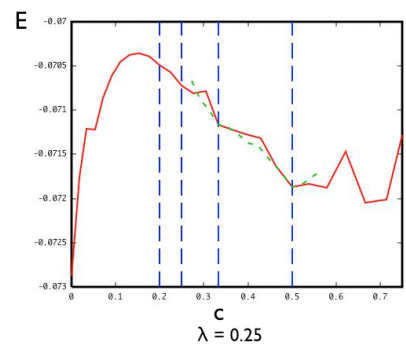


Figure 4. Energy per particle for the ground state as function of the composition c . $\lambda=0.25$, $\Delta=0.05$, $n_2=84$. The vertical lines correspond to simple fractions.

Dynamics

The vibrational spectrum of an aperiodic system may be obtained from the dispersion curves of its approximants. For an approximant the frequencies are the roots of the eigenvalues of the equations

$$m_n \omega^2 u_i = \sum_j \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_{\text{eq}} u_j. \tag{11}$$

For the APDC there is always a zero frequency vibrational mode, because of translation invariance. For an incommensurate phase in the DCM there may be a second such mode as well, if the modulation function is smooth. This corresponds to smoothly connected atomic surfaces. This happens for the APDC only when $\Delta=0$. One expects that for the latter case, there is a zero frequency phason mode as long as the modulation is smooth. And for $\Delta \neq 0$, one expects always a phason gap. This is confirmed by the calculations. If $\Delta \neq 0$, there is only a single mode with zero frequency, and there is always a phason gap as soon as $\lambda \neq 0$ [3].

For $\lambda = 0$ the eigenmodes are limited to one of the chains. If $\lambda \neq 0$, then still eigenmodes may be concentrated on one of the chains, but there are excitations involving both chains in a substantial way. An example is given by the zero frequency mode. If $\lambda = 0$ there are two of such modes, and every linear superposition of the two is an eigenmode. If $\lambda \neq 0$, then this degeneracy is broken. The superposition of the two modes in the separate chains which has an equal displacement for every particle remains with zero frequency. Another combination describes a relative shift of both chains, and has non-zero frequency. This situation occurs again for every crossing point of the dispersion curves of the separate chains, in the extended zone scheme.

The phason mode with wave vector zero is the phonon mode for which the displacement of the centres of mass of the two subsystems, with respect to each other, is maximal. The eigenvector of this phason mode, when there is a phason gap, has maximal displacements of the atoms near the discontinuity of the modulation function. This has been found also in the DIFFOUR (discrete frustrated ϕ^4) model for incommensurate phases [4].

A shift of the subsystems with respect to each other, which may also be described as a change of the internal coordinate in superspace, connects ground states of the same energy. This is, however, not a harmonic excitation, because it involves jumps of atoms between positions. These jumps, in quasicrystals called phason jumps, are actually non-linear excitations. It has been shown for the DCM that such a shift of one system with respect to the other does not cost energy if the atomic surfaces are continuous AND the velocity is below a certain threshold [3]. In this case, however, the atomic surfaces are discontinuous, which means that a phason shift is dissipative.

Concluding remarks

A simple model has been presented for a class of composition flexible compounds. It is a generalisation of the double chain model for incommensurate composites. Although there is an additional length scale, the rank of the system remains two, because of charge neutrality. The embedding in superspace consequently is two-dimensional.

If the value of the parameter Δ is non-zero, the embedding is always discontinuous. In the dynamics this leads to the presence of a phason gap. There is no dissipationless motion of one subsystem with respect to the other. The motion is pinned.

The model shows a transition from a simple composite system (for $\Delta = 0$) to a system that is more easily described as a combination of displacive and occupation modulation, with non-crossing atomic surfaces. This is another proof that modulated phases and composites are not fundamentally different. The fact that for $\Delta \neq 0$ the atomic surfaces are bounded, and the system becomes similar to a quasicrystalline structure. The three classes (modulated phases, composites and quasicrystals) are not mutually exclusive.

There is no indication for a preference for commensurate compositions. The energy per particle is a smooth function, without sharp minima, of the concentration. The lowest energy is obtained for an alteration of prisms and octahedra which is as homogeneous as possible.

A straightforward generalisation to two dimensions consists of an array of parallel chains. Particles with spin of type A have an unmodulated basis structure with positions

$$x_{n,\ell} = x_{n-1} + a + \sigma_n \Delta, \quad y_{n,\ell} = \ell c, \tag{12}$$

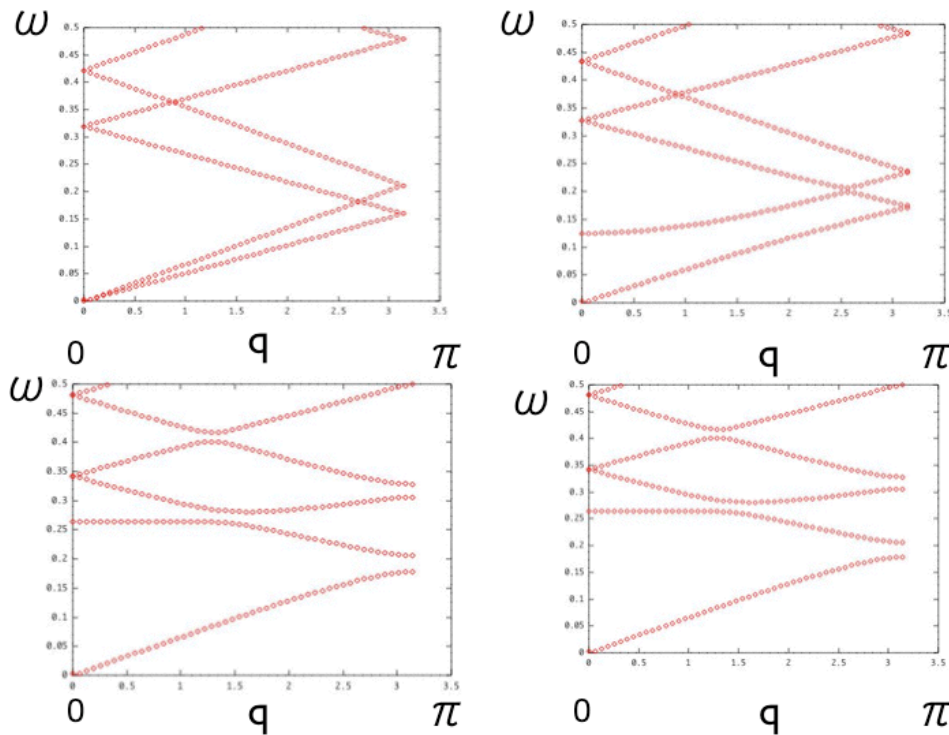


Figure 5. Dispersion curves in the Brillouin zone of the approximant structure, for $\Delta \neq 0$, for 4 values of λ . Upper row, left: $\lambda = 0$: there are 2 modes with frequency zero. For increasing values of λ the phason gap opens. Simultaneously gaps open at the Brillouin zone boundary.

and the particles in subsystem 2 have basic structure positions

$$x_{m,\ell} = mb, \quad y_{m,\ell} = \left(\ell + \frac{1}{2}\right)c. \quad (13)$$

The potential energy may be taken to be

$$V = \sum_{n,\ell,n',\ell'} V_1(\mathbf{r}_{n,\ell} - \mathbf{r}_{n',\ell'}, \sigma_n, \sigma_{n'}) + \sum_{m,\ell,m',\ell'} V_2(\mathbf{r}_{m,\ell} - \mathbf{r}_{m',\ell'}) \\ + \lambda \sum_{n,\ell,m,\ell'} V_i(\mathbf{r}_{n,\ell} - \mathbf{r}_{m,\ell'}, \sigma_n). \quad (14)$$

This higher-dimensional model is under investigation.

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