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Phason and amplitudon-like vibrations of one-dimensional incommensurate systems

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Abstract. In this paper we show that phason- and amplitudon-like vibrations can be obtained in one-dimensional incommensurate systems with harmonic interactions between first neighbours only. This is achieved provided a realistic modulation of the force constants is used. The incommensurate systems are approximated by commensurate ones with large unit cells. Several criteria are used to characterise the phason- and amplitudon-like vibrations and we find that these types of vibrations exist, for reasonable values of the amplitude of the modulation, if there is a sufficient number of atoms per modulation period.

1. Introduction

There has recently been great interest in two particular excitations of incommensurate (I) systems: phasons and amplitudons. In an I system the equilibrium atomic positions are modulated with respect to those in a periodic lattice, with a period incommensurate with that of the lattice. Phasons and amplitudons correspond, respectively, to changes in the phase and amplitude of the modulation. These excitations were attributed by many authors (see, for example, Bruce and Cowley 1978) to the interaction between the soft mode at $\boldsymbol{q}_s$ that drives the transition to the I phase and the vibrations of the lattice with wavevectors $\boldsymbol{q}$ close to $\boldsymbol{q}_s$. This interaction, when treated with a Landau Hamiltonian in a quasi-harmonic approximation, gave a splitting of the soft mode into a phason with frequency $\omega_p = |\boldsymbol{q} - \boldsymbol{q}_s|$ and an amplitudon with frequency $\omega_a = [2(T - T_0) + |\boldsymbol{q} - \boldsymbol{q}_s|^2]^{1/2}$ where T_0 is the transition temperature. Therefore, the phason frequency was always lower than that of the amplitudon and at $\boldsymbol{q} = \boldsymbol{q}_s$ it became zero.

A quite different approach is that of Janssen and Tjon (1981, 1982), who studied the vibrational spectra of different models for an I system and tried to identify phasons and amplitudons with particular vibrational modes. In their calculations they approximated the I systems by commensurate (C) ones with large unit cells. In their simplest model of a one-dimensional system the modulation of the atomic positions was assumed to be sinusoidal, only first-neighbour harmonic interactions were considered between atoms and the force constants were also assumed sinusoidally modulated (de Lange and Janssen 1981). Therefore, they considered $u_i = A\cos(q_s i + \phi)$ and $k_i = B\cos(q_s i + \varphi)$ where u_i is the displacement of atom i from its position in the equidistant lattice and k_i the stretching force constant between atoms i and $i - 1$. In this model it was not possible

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to identify two particular vibrations as phasons and amplitudons, as the modes having the adequate number of nodes were still degenerate. They considered later more elaborate models for the I system, with harmonic interactions up to second or third neighbours and first-neighbour anharmonic terms (Janssen and Tjon 1981, 1982). In these cases they obtained, by minimisation of the total energy, several I phases. The vibrations around the corresponding modulated equilibrium positions were studied numerically. Two particular modes could be identified with phasons and amplitudons, as the corresponding eigenvectors described approximately oscillations in the phase and amplitude of the modulation. Also the phason frequency was lower than the amplitudon one and there was a gap between them in the vibrational spectrum. However, only in special cases did the phason frequency become zero.

In this paper we will assume that the equilibrium configuration of the I system is given by a sinusoidal modulation of the atomic positions. We will not study the forces that are responsible for the existence of this I phase but only the vibrational excitations of the I system. For this we will consider only first-neighbour harmonic interactions as in Janssen's first calculation. The difference from his model is that the force constants k_i will not be cosinusoidally modulated with i but will be modulated with a more adequate function. This will produce the splitting of the two degenerate modes and will lead to phason- and amplitudon-like vibrations. Furthermore, we will show via a simple first-order degenerate perturbation theory that a necessary condition for the splitting of the relevant degenerate modes is that the modulation function for k_i should contain even powers if expanded in a power series of cosines.

2. Calculation of the force constants

We consider a one-dimensional incommensurate chain of identical atoms i, whose equilibrium positions are

$$x_i = i + u_i \tag{1a}$$

with

$$u_i = A\cos(q_s i + \phi). \tag{1b}$$

That is, u_i measures the equilibrium displacement along the chain of each atom i from its position in an equidistant lattice of unit distance between first neighbours (the high-temperature phase).

To study the vibrations of the I system, whose equilibrium positions are given by equations (1), we assume first-neighbour harmonic interactions only. This implies that the system is simply a collection of springs along the direction of the chain and, as the atoms are identical but their equilibrium positions are modulated, the force constants of the different springs must be different. This idea is supported by the fact, well known from the study of molecules (see, for example, Wilson *et al* 1955), that the bond length and the stretching-force constant of a particular pair of atoms (bond) differ slightly from one molecule to another due to the differences in the environments of the corresponding bonds. From equations (1) the equilibrium distance between atoms i and $i-1$ is

$$r_i = 1 + A'\cos(q_s i + \phi') \tag{2}$$

where

$$A' = -2A \sin(q_s/2)$$

$$\phi' = \phi - q_s/2 - \pi/2.$$

In real I systems where the atomic positions have been determined experimentally the amplitude of the modulation varies between a few parts per thousand and a few parts per hundred of the interatomic distances. In our calculations we will assume that r_i varies in a range of, at most, 0.9 to 1.1.

From (2) it follows that a linear dependence of k_i on the equilibrium distance r_i implies that there is a cosinusoidal modulation of the force constants. As mentioned in § 1 this particular model does not lead to phason- and amplitudon-like vibrations. Furthermore, when studying the dependence of the force constant k_i on the equilibrium distance r_i of the bond, one would expect that for $r_i = 1 + |\Delta r|$ the force constant will decrease in Δk from the value at $r_i = 1$, but for $r_i = 1 - |\Delta r|$ the force constant will certainly increase in $\Delta k' > \Delta k$ due to the large repulsion produced by the overlapping of the electronic charge clouds of the atoms on approaching each other. The harmonic interactions are an approximation to the more realistic representation of the interaction between identical atoms, such as the Lennard-Jones, Morse and Buckingham potentials. These are all asymmetric and, for example, the Lennard-Jones potential $v(r) = (r^{-12} - 2r^{-6})/72$ (with unit equilibrium distance and unit force constants) has its second derivative equal to 0.03 for $r = 1.1$ and 6.9 for $r = 0.9$. If we take as a first approximation to the force constants k_i the second derivative of the Lennard-Jones potential at r_i it is clear that k_i will vary in a very non-linear way with r_i (see figure 2). The second approximation to the calculation of the force constant of a bond that is not at its isolated equilibrium length $r_e = 1$ must take the external field into account explicitly. Because in this paper we are not concerned with the specific external field that produces the incommensuration we will only consider simple external fields produced by further-neighbour atoms of the single bond studied. We shall choose a few one- and two-dimensional configurations of atoms, so that the equilibrium length of the bond studied is in the range of the r_i of the I system. In figure 1 we show the configurations used; for each configuration the total potential energy V is taken as the sum of all pairwise first- and second-neighbour interactions. We take the central bond as the only variable distance r and the rest of the first-neighbour distances fixed at a value r'. From the condition $\partial V/\partial r = 0$ we obtain the equilibrium distance of the central bond r_e, which depends on the parameter r'. The corresponding force constant is $k(r_e) = (\partial^2 V/\partial r^2)_{r=r_e}$. By adequately varying r' and the depth of the Lennard-Jones potentials for some of the second-neighbour bonds we were able to cover the range of interest. Therefore the inclusion of second-neighbour interactions as an external field leads to

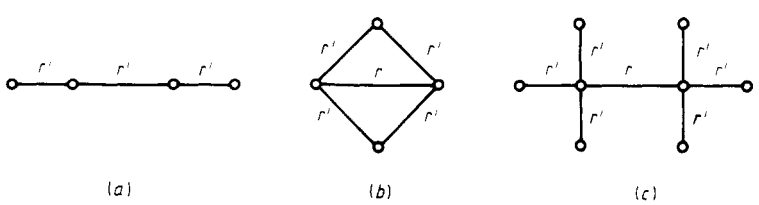

Figure 1. Different external fields used for the determination of r_e and $k(r_e)$ of the central bond.

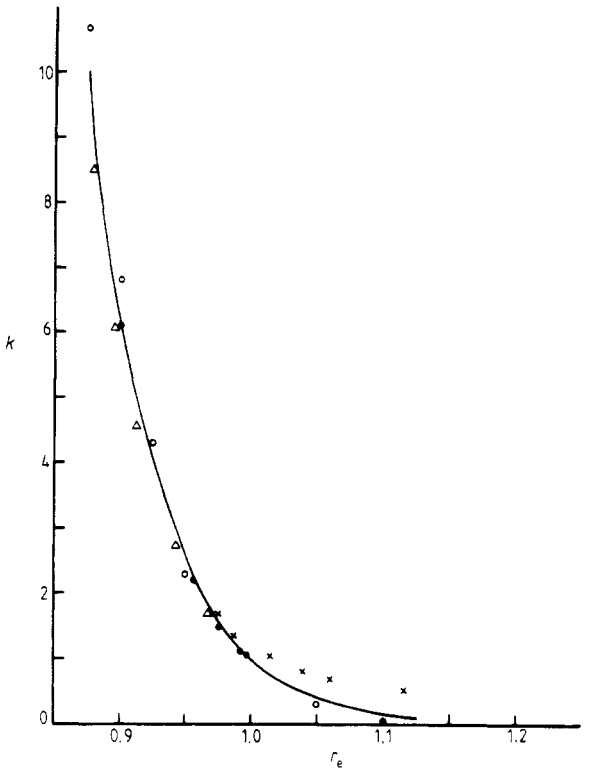

Figure 2. Force constants as a function of distance for a single bond. ○ Second derivative of a single Lennard-Jones potential (called the first approximation in the text). ● Configuration (*a*). × Configuration (*b*). △ Configuration (*c*). The full curve corresponds to $k(r_e) = \exp[17.9\,(1 - r_e)]$ which is chosen because it gives a good fit for the large force constants. The units are such that the isolated bond has $r_e = 1$ and $k(r_e) = 1$.

changes in the equilibrium distance of the central bond of about $\pm 10\%$. However, the corresponding changes in the force constants are much larger. For the calculation of these force constants the effect of second neighbours is about 10% of the leading term, which is the second derivative of the Lennard-Jones potential at r_e. Thus, the results for both the first approximation and the different models for the external field in the second approximation all fit approximately the single-exponential dependence of $k(r_e)$ on r_e shown in figure 2:

$$k(r_e) = \exp[\alpha(1 - r_e)] \qquad \text{with } \alpha = 17.9. \tag{3}$$

By identifying r_e with r_i of (2) we obtain

$$k_i = \exp[-\alpha A' \cos(q_s i + \phi')]. \tag{4}$$

3. Calculations and results

We approximate the vibrational spectra of the I system by that of C systems with sufficiently large unit cells (Janssen and Tjon 1981, 1982, Sokoloff 1980). This is a

common approximation, although it is not known whether truly I systems with $q_s/2\pi$ irrational constitute the limit of a sequence of C systems with unit cells becoming larger and larger (where $q_s/2\pi = M/N$, M and N being integers). The distinction between an I system and a C one with a large unit cell is only mathematical, as a real physical system is always finite. Also, from experiments, the values of the discommensurations are usually given with few significant figures and thus it is not possible to discriminate between systems with very large C unit cells and I systems. With $q_s/2\pi = M/N$ in equation (4) the force constants repeat themselves every N atoms and within each unit cell the cosine function in (1*b*), (2) and (4) has $2M$ nodes. Calculations were performed by the diagonalisation of $N \times N$ dynamical matrices.

From all the vibrations of the incommensurate system we expect to be able to identify two modes with phasons and amplitudons. These excitations correspond respectively to small changes in the phase ϕ and in the amplitude A in equation (1*b*). That is, the instantaneous displacements of all the atoms in the crystal from the positions in the equidistant lattice would become for phasons and amplitudons, respectively,

$$u_i + \delta u_i^{\mathrm{p}} = A \cos(q_s i + \phi + \delta\phi) \simeq u_i - A\delta\phi \sin(q_s i + \phi) \tag{5a}$$

$$u_i + \delta u_i^{\mathrm{a}} = (A + \delta A) \cos(q_s i + \phi) = u_i + \delta A \cos(q_s i + \phi). \tag{5b}$$

These types of displacements are obtained from the diagonalisation of the dynamical matrix for zero wavevector, as in this case the corresponding eigenfunctions do not change phase from one unit cell to the next one.

To characterise fully phasons and amplitudons let us recall that both must correspond to vibrations with $2M$ nodes and that the eigenvectors corresponding to the phason (amplitudon) mode should have sinusoidal (cosinusoidal) behaviour as a function of position (see equation (5)). Deviations of the calculated eigenvectors from the above functional form are studied using the inverse participation ratio, P_μ (Cohan and Weissmann 1979):

$$P_\mu = \left(\sum c_{i\mu}^4\right) \Big/ \left(\sum c_{i\mu}^2\right)^2 \tag{6}$$

where $\mu = 1, 2, \ldots, N$ characterise the eigenvectors and P_μ is a measure of the localisation. If the eigenvectors are localised in one atom of each unit cell $P_\mu = 1$ and if they are extended $P_\mu \simeq 1/N$. For a sinusoidal or cosinusoidal eigenfunction in a continuous system with $2M$ nodes per unit cell the inverse participation ratio becomes:

$$P_{\mathrm{c}} = \frac{2\pi M}{N} \int_0^{2\pi M} \sin^4 x \, \mathrm{d}x \Big/ \left(\int_0^{2\pi M} \sin^2 x \, \mathrm{d}x\right)^2 = \frac{3}{2N}. \tag{7}$$

We consider phasons and amplitudons to be present if the ratios $D_{2M} = P_{2M}/P_{\mathrm{c}}$ and $D_{2M+1} = P_{2M+1}/P_{\mathrm{c}}$ do not differ significantly from unity. Also, from some experiments (Zumer and Blinc 1981) as well as from mean-field theory (Bruce and Cowley 1978), as mentioned in § 1, both phasons and amplitudons arise from the softening and splitting of the high-temperature mode at q_s. Therefore we expect the phason frequency ω_{p} to be lower than that of the amplitudon ω_{a} and also lower than $\omega_s = 2(k/m)^{1/2} \sin(\pi M/N)$, the frequency of the equidistant lattice at q_s. Furthermore, mean-field theory predicts $\omega_{\mathrm{p}} = 0$ at q_s and a gap between the phason and the amplitudon frequencies.

In table 1 we show results, for $A = 0.05$ and $A = 0.1$, of equation (1*b*). These amplitudes for the modulation were used because they give reasonable variations in the distances r_i. The C unit cells used contained between 20 and 50 atoms. In fact, the

Table 1. Results for the $2M$ and $2M+1$ modes obtained from diagonalisation of the dynamical $N \times N$ matrix for zero wavevector. The second column is simply $p = N/M$ and gives the average number of atoms per modulation period. $\omega_s = 2\sin(\pi M/N)$ is the frequency of the system with one atom per unit cell and $q_s = 2\pi M/N$. Also $\Delta\omega = (\omega_{2M+1} - \omega_{2M})/\omega_s$. All frequencies are measured in units such that $k = m = 1$ for the system with one atom per unit cell.

M/N	p	ω_s^2	$A = 0.05$					$A = 0.1$				
			ω_{2M}^2	ω_{2M+1}^2	$\Delta\omega$	D_{2M}	D_{2M+1}	ω_{2M}^2	ω_{2M+1}^2	$\Delta\omega$	D_{2M}	D_{2M+1}
2/29	14.5	0.185	0.179	0.186	0.019	1.05	1.02	0.164	0.187	0.064	1.19	1.08
2/25	12.5	0.247	0.237	0.249	0.025	1.07	1.03	0.210	0.250	0.084	1.26	1.12
3/29	9.67	0.408	0.380	0.410	0.037	1.12	1.05	0.312	0.404	0.121	1.44	1.22
3/25	8.33	0.542	0.493	0.544	0.048	1.18	1.07	0.379	0.518	0.141	1.63	1.32
4/29	7.25	0.705	0.621	0.704	0.061	1.26	1.09	0.442	0.621	0.147	1.94	1.81
3/19	6.33	0.906	0.764	0.892	0.074	1.41	1.12	0.490	0.684	0.133	2.23	2.77
7/44	6.29	0.919	0.772	0.902	0.074	1.42	1.12	0.491	0.681	0.130	2.18	3.19
17/107	6.29	0.916	0.771	0.900	0.074	1.42	1.12	0.491	0.682	0.131	2.18	3.56
5/29	5.80	1.063	0.866	1.028	0.080	1.40	1.29	0.558	0.756	0.119	2.19	5.74
6/29	4.83	1.465	1.132	1.369	0.088	1.36	1.91	0.792	1.025	0.101	3.85	8.20
11/45	4.09	1.930	1.278	1.424	0.045	3.01	4.23	1.017	1.153	0.047	10.40	10.20
12/41	3.42	2.530	2.044	2.366	0.068	6.57	8.12					
16/49	3.06	2.925	2.420	2.577	0.029	4.54	6.30					

characteristics of the two modes that we are studying do not change appreciably with the size of the C unit cell used to approximate the I system. In particular for the irrational number represented by the following continued fraction:

$$q_s/2\pi = 1/[\![6 + 1/\{3 + 1/[2 + 1/(2 + 1/\ldots)]\}]\!]$$

the first four approximations to $q_s/2\pi$ are $\frac{1}{6}$, $\frac{3}{19}$, $\frac{7}{44}$ and $\frac{17}{107}$ and we see from the table that the results are similar for the last three approximations. We also verified that the sizes of the C unit cells used are large enough for the results to be independent of the phase ϕ in equation (1*b*).

We notice that for $A = 0.05$, D_{2M} and D_{2M+1} increase monotonously for decreasing p up to $p \simeq 5$ where they increase abruptly and their behaviour becomes erratic. By inspection of the shape of the eigenvectors we find that mode $2M$ behaves as a phason and mode $2M + 1$ as an amplitudon when $p > 5$, but for $p < 5$ the eigenvectors become localised within each unit cell. Also from the table we see that the frequency of the phason is always lower than that of the amplitudon and also lower than ω_s. To prove the existence of a gap between the two levels, calculations were performed for values of the wavevector different from zero up to the border of the Brillouin zone. We find that for $p > 5$ the phason energy corresponds to the top of an energy band and the amplitudon to the bottom of the next one. For $p < 5$ they belong to extremely narrow bands. The dependence of the frequencies on wavevector decreases with the increasing size of the C unit cell used to approximate the I system. It is interesting to note that the normalised energy gap $\Delta\omega = (\omega_{2M+1} - \omega_{2M})/\omega_s$ also changes its behaviour with decreasing p at about the same values of p as do the other properties. For $A = 0.1$ all the above considerations apply again and phason- and amplitudon-like vibrations exist for a somewhat larger value of p, $p > 6$. Figure 3 shows a typical example of these vibrations in a case where equations (5) are already reasonably well satisfied.

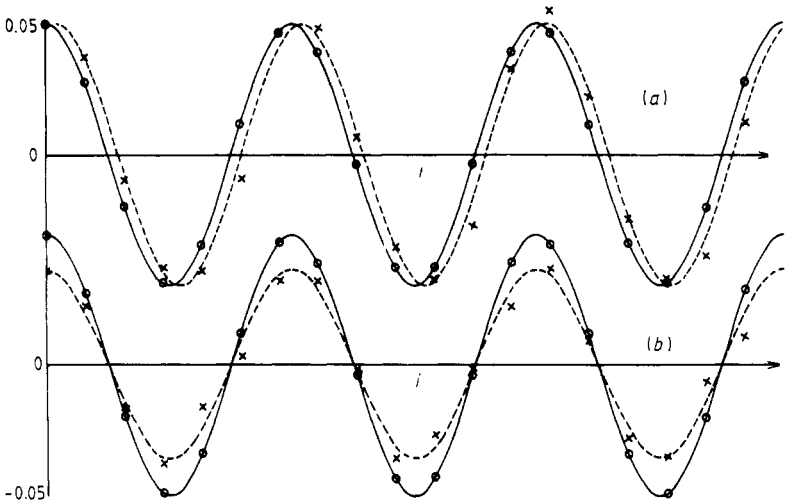

Figure 3. Phason- and amplitudon-like vibrations for $M/N = \frac{8}{19}$ and $A = 0.05$. In (*a*) and (*b*) the full curves and the points marked on them represent the equilibrium displacements of the 19 atoms, the u_i of equation (1*b*). In (*a*) the broken curve is the displacement $u + \delta u^{\mathrm{p}}$ of (5*a*) and the crosses are the results obtained by adding to each u_i an arbitrary fraction of the coefficient c_{i6} of the normalised eigenvector of the 6th mode. In (*b*) the broken curve is $u + \delta u^{\mathrm{a}}$ of (5*b*) and the crosses are similarly obtained by adding to u_i an arbitrary fraction of c_{i7}. In the broken curves $\delta\varphi$ and δA are chosen so that one of the crosses lies exactly on each curve.

For $A = 0.05$ and $p > 5$ the exponent $\alpha A'$ in equation (4) is such that $|\alpha A'| < 1$ and for $A = 0.1$, such that $|\alpha A'| < 2$. If $|\alpha A'|$ is large an approximation to equation (4) by a series expansion is not adequate, but if $|\alpha A'| \ll 1$ a perturbation approach can be used. We will show in the next section that, even in this case, phasons are obtained if more than one term in the expansion is considered. De Lange and Janssen also used a modulation for the force constants with more than one cosine and found an increase in the number of gaps (figure 9 of that paper), but they did not identify the splitting associated with phasons and amplitudons.

4. Perturbation approach

It is known that with a cosine modulation of the force constants there is no gap at $\omega = \omega_s$ for large C systems (de Lange and Janssen 1981). Thus the degeneracy of the two vibrations with $2M$ nodes is not removed and phasons and amplitudons do not appear. Janssen proved that this degeneracy is not removed using degenerate perturbation theory with an extra coordinate arising from the incommensuration. We give below the conditions under which this degeneracy is removed; also these were obtained using degenerate perturbation theory, but for an ordinary commensurate system.

In fact, let us first write the eigenfunctions for a 1D system of equidistant identical atoms:

$$\psi_{\pm q} = L^{-1/2} \sum_{j=0}^{L-1} \exp(\pm iqj)\chi_j \qquad -\pi \leqslant q \leqslant \pi \tag{8}$$

where χ_j is the displacement of the jth atom and L is the number of atoms in the crystal. We now consider the same system but represented by L/N (integer) unit cells of N atoms per cell. Then the corresponding wavevector is $-\pi/N \leq q' \leq \pi/N$ and the eigenfunctions for $q' = 0$ are, obviously,

$$\psi_{\pm m,0} = L^{-1/2} \sum_{l=0}^{L/N-1} \sum_{j=0}^{N-1} \exp(\pm 2i\pi mj/N)\chi_{j+lN} \qquad m = 0, 1, 2, \ldots, N-1. \tag{9}$$

To study the removal of the degeneracy we have to calculate

$$P_m = |\langle \psi_{m,0}|H|\psi_{m,0}\rangle|^2. \tag{10}$$

Then, using the standard form of the dynamical matrix elements for $q' = 0$ and force constants k_j between first neighbours,

$$\begin{aligned}
&\langle \chi_{0+lN}|H|\chi_{0+lN}\rangle = k_1 + k_N \\
&\langle \chi_{0+lN}|H|\chi_{N-1+lN}\rangle = -k_N \\
&\langle \chi_{i+lN}|H|\chi_{i+lN}\rangle = k_i + k_{i+1} \qquad i = 1, 2, \ldots, N-1 \\
&\langle \chi_{i-1+lN}|H|\chi_{i+lN}\rangle = -k_i \qquad i = 1, 2, \ldots, N-1
\end{aligned} \tag{11}$$

we obtain, after a little algebra

$$P_m = \frac{4}{N^2}\left(1 - \cos\frac{2\pi m}{N}\right)^2 \sum_{j=1}^{N}\sum_{l=1}^{N} k_j k_l \cos\frac{4\pi m(j-l)}{N}. \tag{12}$$

If the force constants have a cosine-type modulation:

$$k_j = k + A\cos(2\pi Mj/N + \varphi) \qquad M = 0, 1, \ldots, N-1 \tag{13}$$

we obtain

$$\begin{aligned}
P_m = \frac{4}{N^2}\left(1 - \cos\frac{2\pi m}{N}\right)^2 A^2 \Bigg\{ &\left[\sum_{j=1}^{N} \cos\left(\frac{2\pi Mj}{N} + \varphi\right)\cos\frac{4\pi mj}{N}\right]^2 \\
&+ \left[\sum_{j=1}^{N} \cos\left(\frac{2\pi Mj}{N} + \varphi\right)\sin\frac{4\pi mj}{N}\right]^2 \Bigg\}
\end{aligned} \tag{14}$$

as the terms in k^2 and kA vanish. For $m = M$ both summations in (14) become zero (for $N > 3$) due to symmetry and thus $P_M = 0$. However if $m = M/2$, then $P_{M/2} \neq 0$. These two results have already been obtained by Janssen and we show here that they are due to the symmetry properties of the force constants.

If the force constants do not have the simple cosine dependence of equation (13) the degeneracy at $m = M$ will, in general, be removed. In fact, any periodic function for k_j (with period $2\pi M/N$) can be expanded in powers of the cosine, that is, of the displacements u_j, and provided that there is one non-zero even power we obtain, from (12), $P_M \neq 0$. In particular this is what happens with the law used by us in (4).

5. Conclusions

We studied the vibrations of an incommensurate system with first-neighbour harmonic interactions only and a realistic modulation of the force constants. Phason- and

amplitudon-like vibrations are obtained for reasonable values of the modulation parameter A if there is a sufficient number of atoms p per period of the modulation (more than about five or six). This implies that the eigenvectors obtained from the diagonalisation of the dynamical matrix correspond approximately to changes in the phase and amplitude of the atomic modulation, that the frequency of the phason is lower than that of the amplitudon and that there is a gap between them. The fact that these excitations appear only for relatively large values of p and the non-zero phason frequency are the only results of the present work that do not agree with mean-field theory. We also show, by perturbation theory, that the splitting of the degeneracy at $\omega = \omega_s$ of the high-temperature phase will always occur if the force constants in the incommensurate system contain even powers of the atomic displacements u_i.

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