The search for periodons

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The search for periodons

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Abstract. Periodons have been suggested as a mechanism for modulated structures with Q_{IC} near one-third of a reciprocal lattice vector, based on a $-x^2 + x^4$ anharmonic potential. Molecular dynamic simulation is used to look for periodon-like motion in a crystal in thermal agitation. Such motion was never seen, because periodons are very unstable and their phase space input presumably occupies a negligible portion of the total available phase space. No evidence of a phase transition was found.

1. Introduction

Quite a few incommensurate structures have modulations with a wavevector around one-third of a reciprocal lattice vector, say $\boldsymbol{a}^*$. A large class of the A_2BY_4 materials like K_2SeO_4 show this behaviour for example [1].

Bilz proposed a mechanism that specifically gives modulations around $\frac{1}{3}\boldsymbol{a}^*$. The Bilz model has an anharmonic potential $-\alpha w^2 + \beta w^4$ in a normal shell model. The quartic term gives a w^3-term in the force which appears in the equations of motion. If w is proportional to $\exp[\mathrm{i}(kna - \omega t)]$, this third-order term leads to an expression containing $\exp[3\mathrm{i}(kna - \omega t)]$. These exact solutions containing the two terms mentioned above are called periodons and have the interesting property that $\omega(\boldsymbol{k}) \to 0$ as $\boldsymbol{k} \to \frac{1}{3}\boldsymbol{a}^*$. Bilz thought this could lead to soft modes and modulated structures with $\boldsymbol{k}$ around $\frac{1}{3}\boldsymbol{a}^*$. Interaction with other modes in the system can shift the soft mode away from exactly $\frac{1}{3}\boldsymbol{a}^*$.

Let us look at the Bilz *et al* model [2–6] in more detail in its simplest form. All the work in the references was done for one-dimensional systems, but the genralisation to three dimensions is straightforward. The system is governed by the following Hamiltonian for a simple cubic model:

$$H = \sum_{j,k,l} \tfrac{1}{2}M\dot{u}_{jkl}^2 + \tfrac{1}{2}m\dot{v}_{jkl}^2 - \tfrac{1}{2}\alpha w_{jkl}^2 + \tfrac{1}{4}\beta w_{jkl}^4 + \tfrac{1}{2}f[(u_{j+1kl} - u_{jkl})^2 + (u_{jk+1l} - u_{jkl})^2 + (u_{jkl+1} - u_{jkl})^2] + \tfrac{1}{2}f'[(v_{j+1kl} - v_{jkl})^2 + (v_{jk+1l} - v_{jkl})^2 + (v_{jkl+1} - v_{jkl})^2]. \quad (1)$$

In the Hamiltonian u_{jkl} and v_{jkl} are envisaged as the values of two scalar variables per unit cell of the shell and core respectively and $w_{jkl} = u_{jkl} - v_{jkl}$. This Hamiltonian leads to 2N coupled non-linear equations of motion with the following periodon solutions:

$$w_{jkl} = A\sin(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}) \qquad u_{jkl} = B\sin(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}) + C\sin 3(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}) \quad (2)$$

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with

$$\omega^2(\boldsymbol{k}) = \frac{2(f+f')(3-\cos 3k_x a-\cos 3k_y a-\cos 3k_z a)}{9(m+M)}. \tag{3}$$

Also A, B and C are particular functions of $\boldsymbol{k}$ without an arbitrary amplitude factor because of the non-linearity of the equations. The soft mode behaviour around $\frac{1}{3}\boldsymbol{a}^*$ is clear from equation (3); in fact in this model all points (0 or $\pm 2\pi/3a$, 0 or $\pm 2\pi/3a$, 0 or $\pm 2\pi/3a$) give $\omega(\boldsymbol{k}) = 0$.

In the original Bilz model the adiabatic approximation (i.e. $m = 0$) was used for the electron shell, but giving the shell a mass only changes A, B and C somewhat without altering the singularity at $\frac{1}{3}\boldsymbol{a}^*$ as is evident from equation 3. Because computer simulations with a non-zero mass are much easier, we gave the shell a finite mass.

The problem with these solitary solutions is that they are not superposable and thus cannot possibly describe a hot solid. Bilz *et al* [7, 8] therefore imagined a motion that is in some sense periodon-like (periodonish) leading to a self-consistent phonon theory with a soft periodon mode phase transition.

2. Looking for periodons

To see whether such periodonish motion as proposed by Bilz *et al* could in fact occur in practice, we tested this hypothesis using molecular dynamics simulations in a microcanonical ensemble. A $16 \times 16 \times 16$ set of atoms on a cubic lattice was used. In order to recognise the periodinishness, the scattering function, $S(\boldsymbol{k}, \omega)$, was calculated. If the motion is indeed periodonish (with periodon wavevector $\boldsymbol{k}$), one would see two characteristic peaks—one at $\boldsymbol{k}$ and ω (as given by equation (3)) and another at $3\boldsymbol{k}$ and 3ω. The height of the peaks will, among other things, depend on how periodonish the motion is. The peaks are shown in figure 1 for two typical cases.

Although about 100 or more scattering functions were calculated for different values of the parameters in equation (1), no such peaks were ever observed. Two of the examples are shown in figure 1. Note that there is absolutely no hint of a peak at the expected sites in figure 1(a) and although there is a peak at the right place in figure 1(b), there is no sign of the second accompanying peak necessary to signify periodon motion. We looked especially at temperatures such that the energy in the system is a little larger than that of one periodon, thinking that these conditions would be most likely to result in periodonish motion.

3. The phase space behaviour of periodons

The negative results of the scattering function calculations lead one to ask whether it is possible to show more convincingly that periodonish motion never occurs in practice. Two issues turn out to be of central importance here: the stability of the periodons and the behaviour of the paths in phase space around these solutions.

Let us look at the stability question first. In an analytical approach one puts $u = u_p + \delta u$ as usual where u_p is the pure periodon solution and one linearises the resulting equations in δu and δv. The final result is 2N coupled time-dependent differential equations. Although these equations are now linear, they are still very difficult to solve and one has to resort to numerical methods.

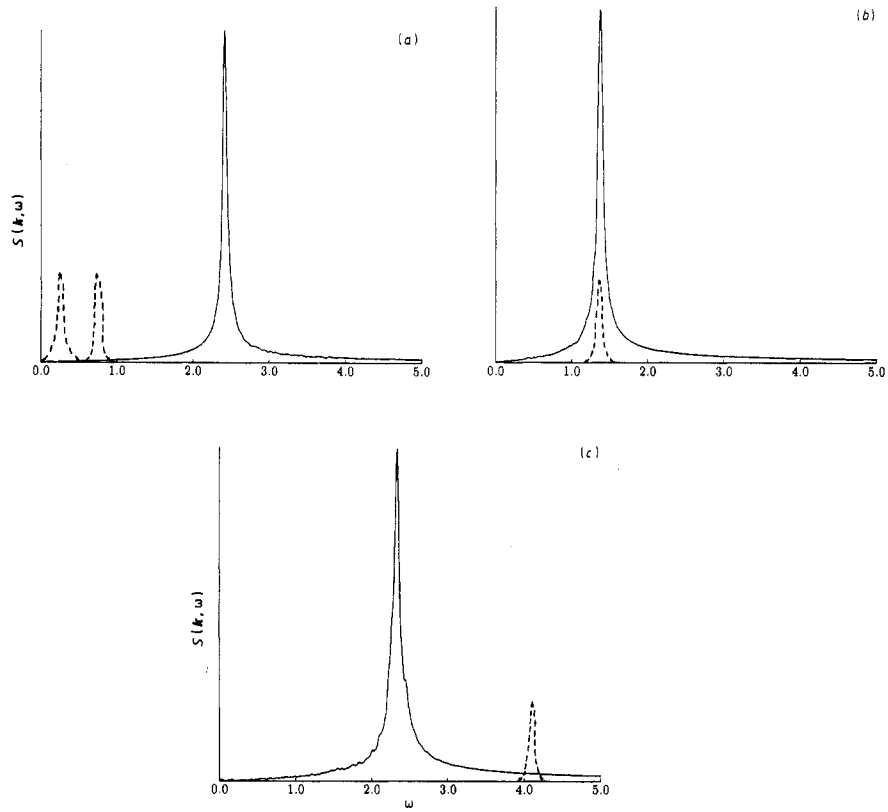


Figure 1. Typical graphs of $S(\boldsymbol{k}, \omega)$ as observed in real simulations (full traces) and the positions where the periodon peaks would have been if they were present (broken traces). In all cases the total energy of the system was chosen a little larger than the periodon energy. In (*a*) $\boldsymbol{k} = (0.5, 0.0, 0.0), f = 0.2, f' = 0.1$ and in (b) and (c) $\boldsymbol{k} = (0.375, 0.375, 0.375), f = 1.5, f' = 0.1$. In both cases $M = 1.0, m = 0.1, \alpha = 1.0$ and $\beta = 1.0$. To get rid of finite-time diffraction effects the function was smoothed out using a Gaussian.

Define the following 'norm' function:

$$P_k^u(t) = \left(\sum_{jkl} |u_{jkl}(t) - u_{jkl}^{\text{per}_k}|\right) \Big/ \left(\sum_{jkl} \max\{|u_{jkl}(t)|, |u_{jkl}^{\text{per}_k}(t)|\}\right) \tag{4}$$

where $u_{jkl}(t)$ is the observed value of the core displacement at time t and $u_{jkl}^{\text{per}_k}(t)$ that predicted by the periodon solution of wavevector $\boldsymbol{k}$. The same function can obviously be defined for w_{jkl} or v_{jkl}. For pure periodon motion, i.e. $u(t) \equiv u^{\text{per}_k}(t)$ we have $P_k^u(t) \equiv 0$; for $u(t)$ an arbitrary motion bearing no resemblance to periodonish motion, $P_k^u(t)$, will oscillate around 1 with the oscillations becoming smaller as the system grows bigger. The function $P_k^u(t)$ is thus a measure of the periodonishness of a certain motion and can be used to see how quickly and how far the real solutions drift away from the exact periodons. Note that if a periodon differing by a phase factor of $\pi/2$ is tested using $P_k^u(t)$, one gets $P_k^u(t) \equiv 1$. Therefore to test an arbitrary function for periodonishness, it is necessary to calculate $P_k^u(t)$ with two periodon test functions differing by a phase of $\pi/2$.

Using $P_k^u(t)$ in this manner we have shown that periodons are unstable and, more important, that there are no stable orbits in phase space displaying a noticeable amount of periodonishness. Figures 2, 3 and 4 are typical examples of systems that were started off with the displacements and velocities of the atoms as one would expect for perfect periodon solutions, the only perturbations being those due to the discretisation of the differential equations and computer rounding errors. We used double precision and Beeman's method with timesteps roughly 0.01 times a periodon period in our calculations. In all cases the variations in the total energy were less than 0.1%. As can be seen in figure 3, all traces of periodonishness die away extremely quickly. Graphs like these were drawn for a few hundred different sets of parameters and initial conditions and in all cases the periodons die away without leaving any trace. We can thus conclude that no stable orbits exist near the periodon solutions and that periodon solutions are extremely unstable, even on a timescale of one period of a periodon oscillation.

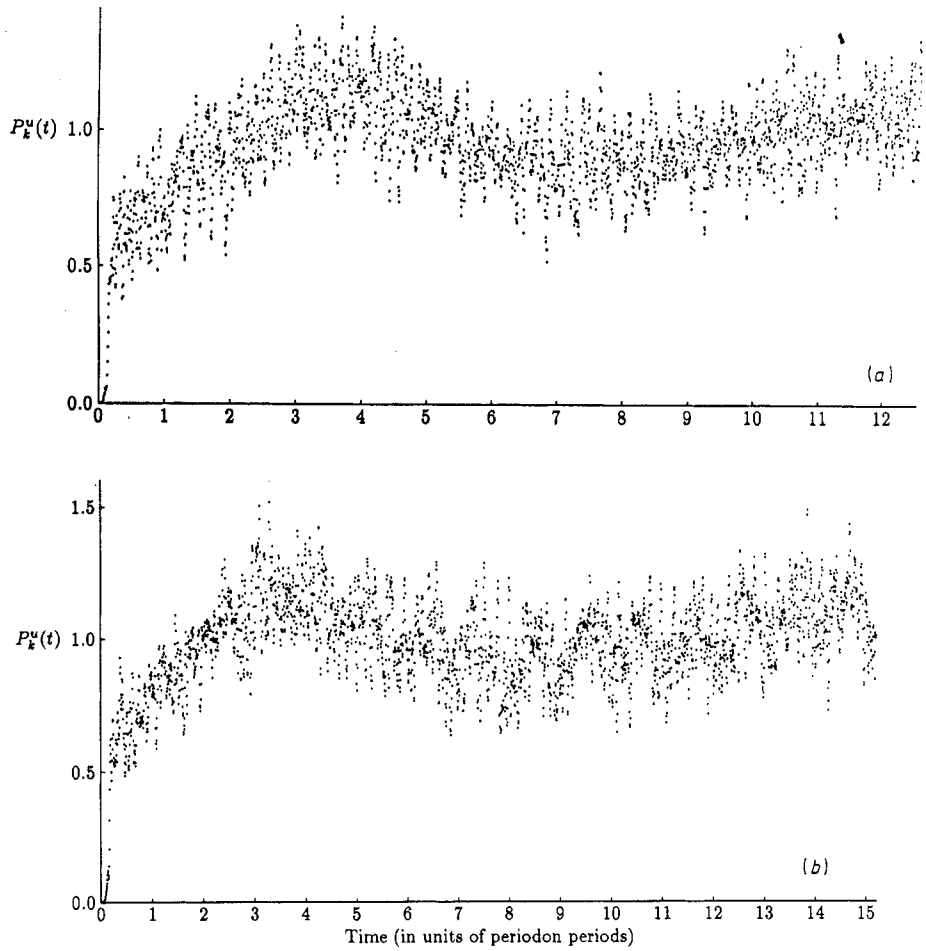


Figure 2. Examples of $P_k^u(t)$ with the system started off as a pure periodon. All parameters except k are the same as in figure 1(*a*). In (*a*) $k = (0.875, 0.0, 0.0)$ and in (*b*) $k = (0.375, 0.0, 0.0)$. The time axis is calibrated in terms of the period of the pure periodon. In all cases the k-vectors are measured in units of π/a.

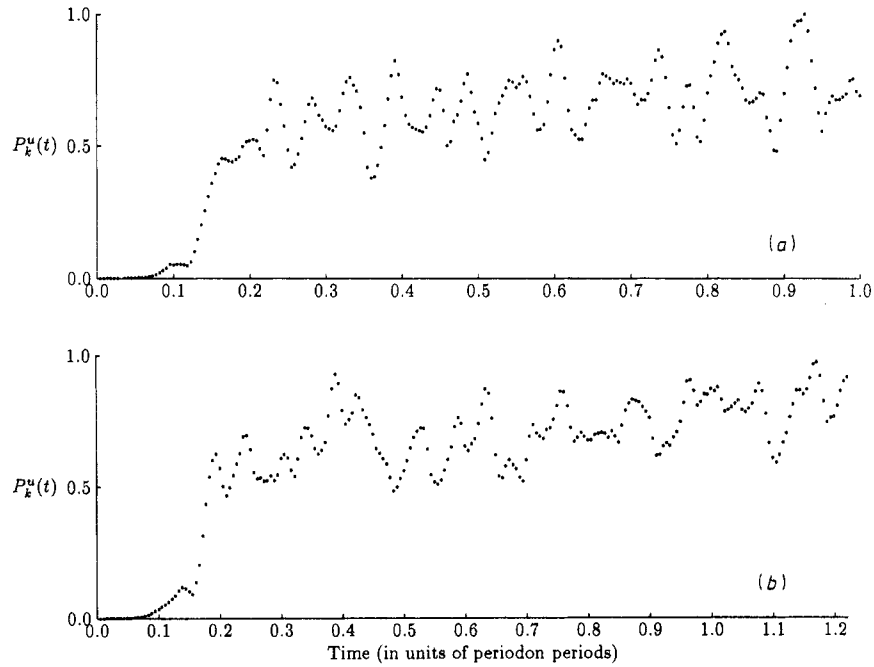


Figure 3. The same graphs as in figure 2 but over a shorter timescale.

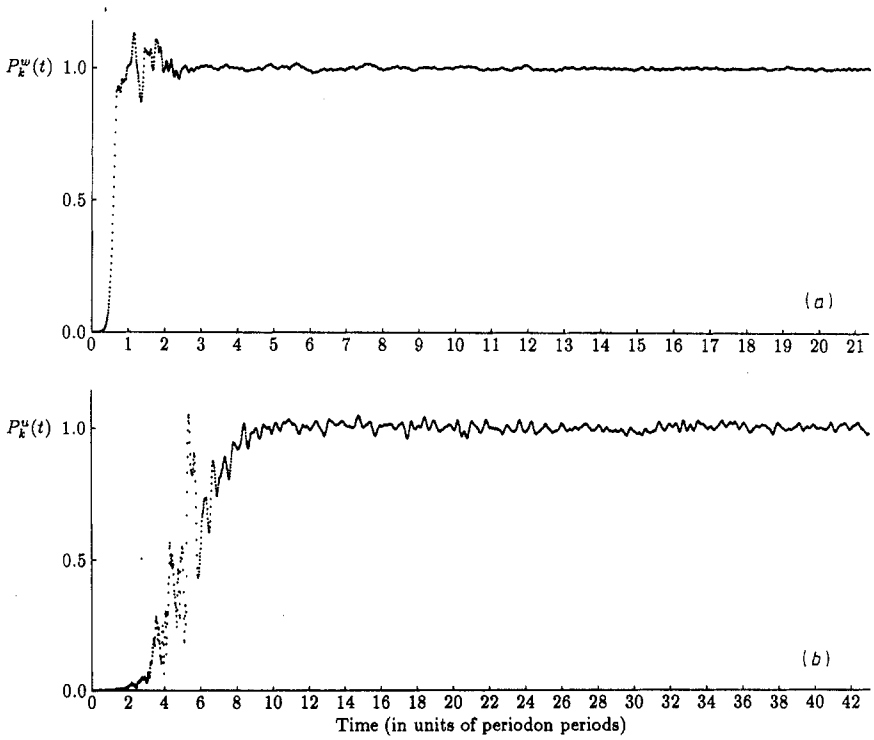


Figure 4. Examples of $P_k^w(t)$ with everything the same as in figure 2, except that $f = 0.8$ and the $\boldsymbol{k}$-vectors and (*a*) and (*b*) are (0.625, 0.625, 0.625) and (0.25, 0.25, 0.25) respectively.

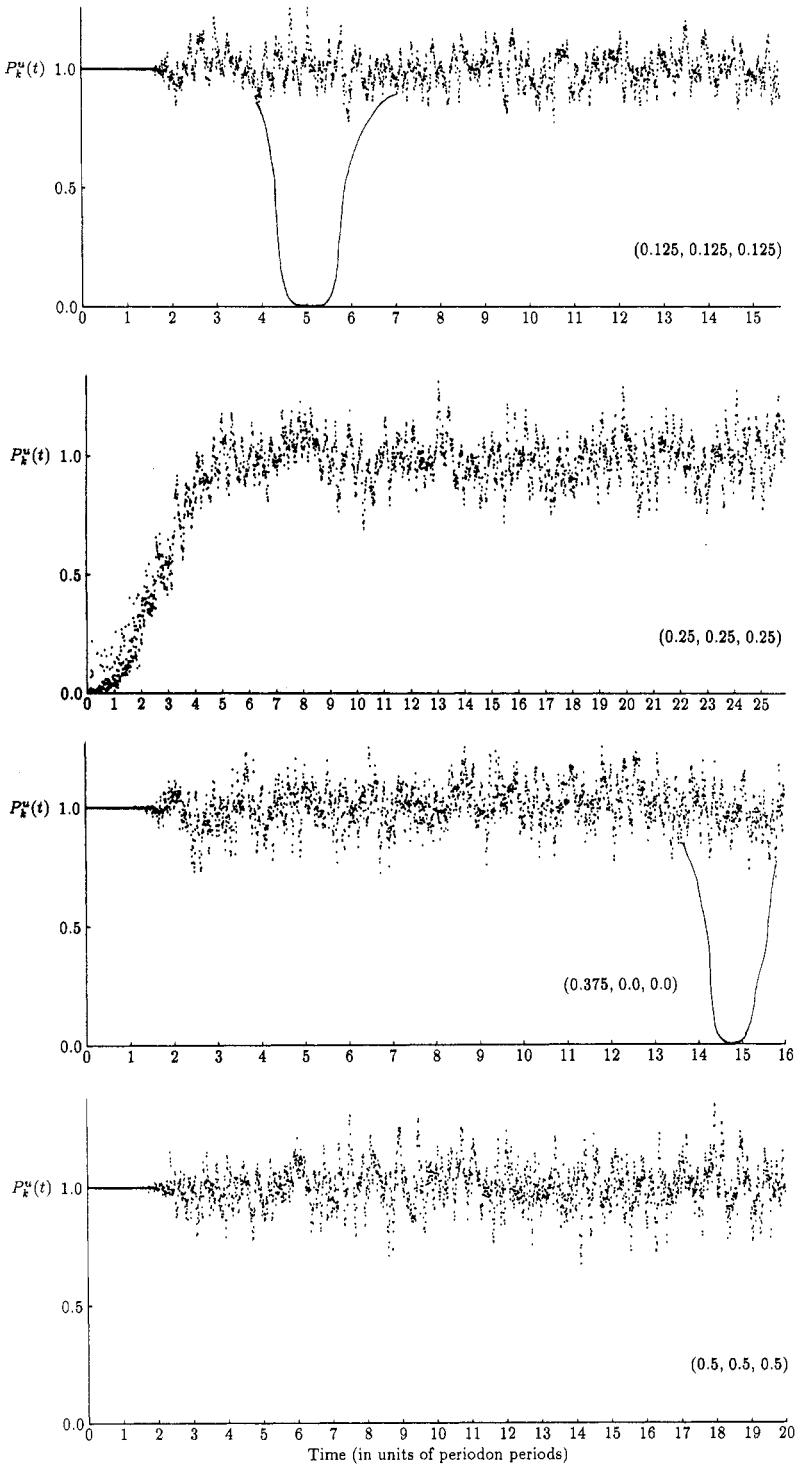
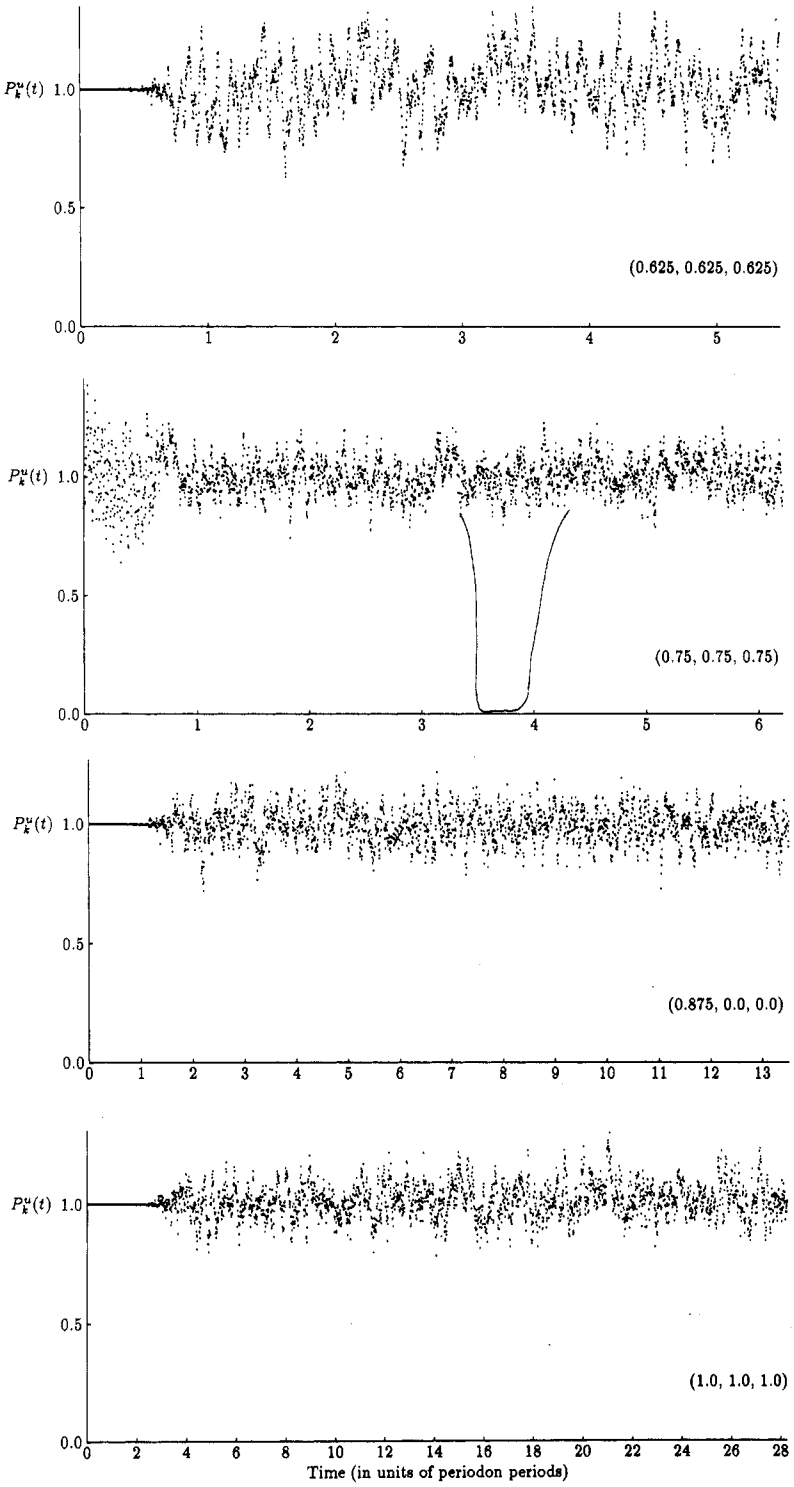
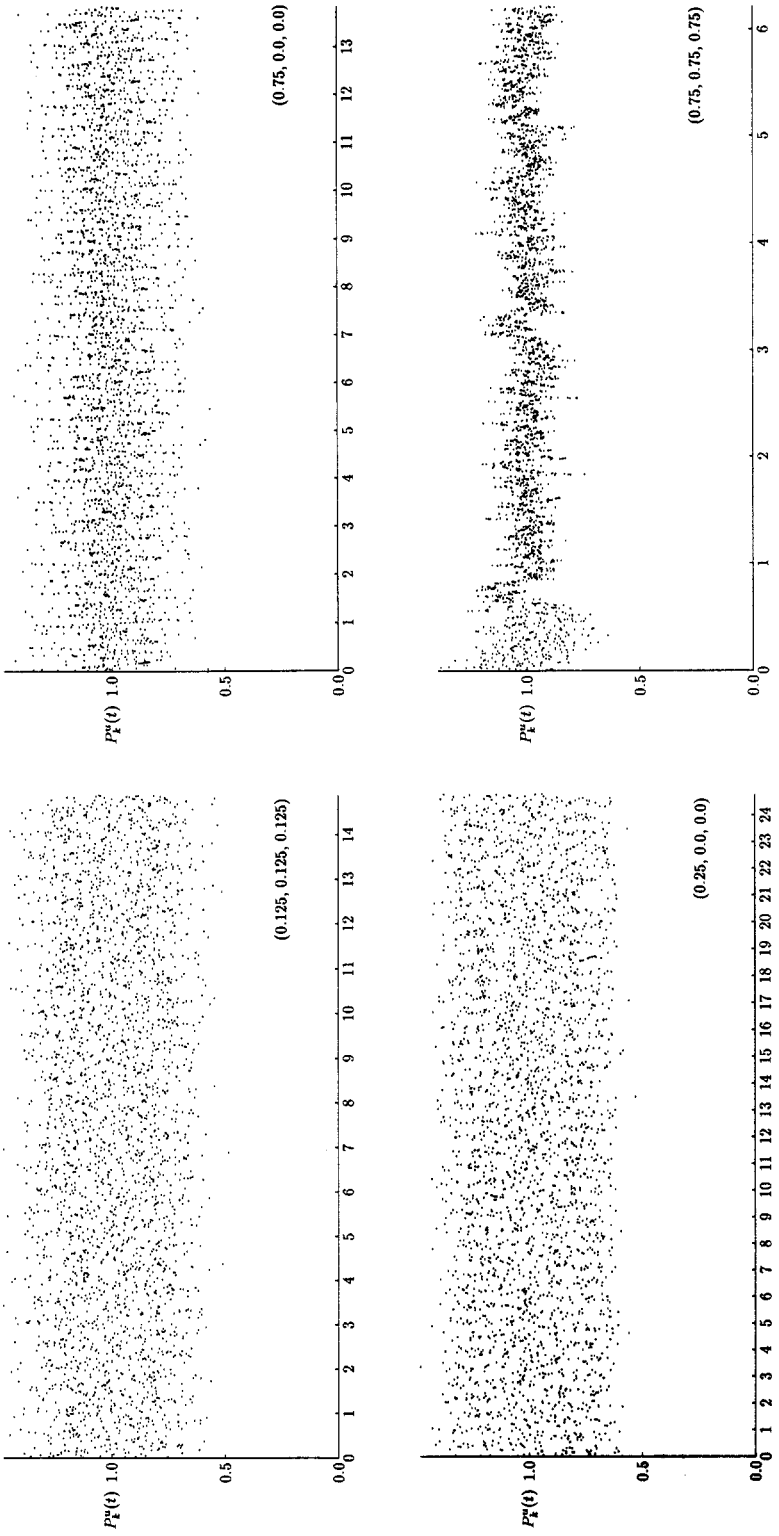


Figure 5. A few examples of $P_k^u(t)$ calculated for several different k-vectors (given within each panel) simultaneously for a subsystem of 16 atoms. Pure periodon initial conditions with k-vector (0.25, 0.25, 0.25) were used and $M = 1.0$, $m = 1.0$, $f = 0.5$, $f' = 0.1$, $\alpha = 1.0$



and $\beta = 1.0$. The units on the time axis are the period of periodon (a) in all cases. The dotted traces show the kind of 'dips' one would observe for a system moving from periodon to periodon: they were never seen.


(0.75, 0.0, 0.0)
(0.75, 0.75, 0.75)
(0.125, 0.125, 0.125)
(0.25, 0.0, 0.0)
$P_k^w(t)$

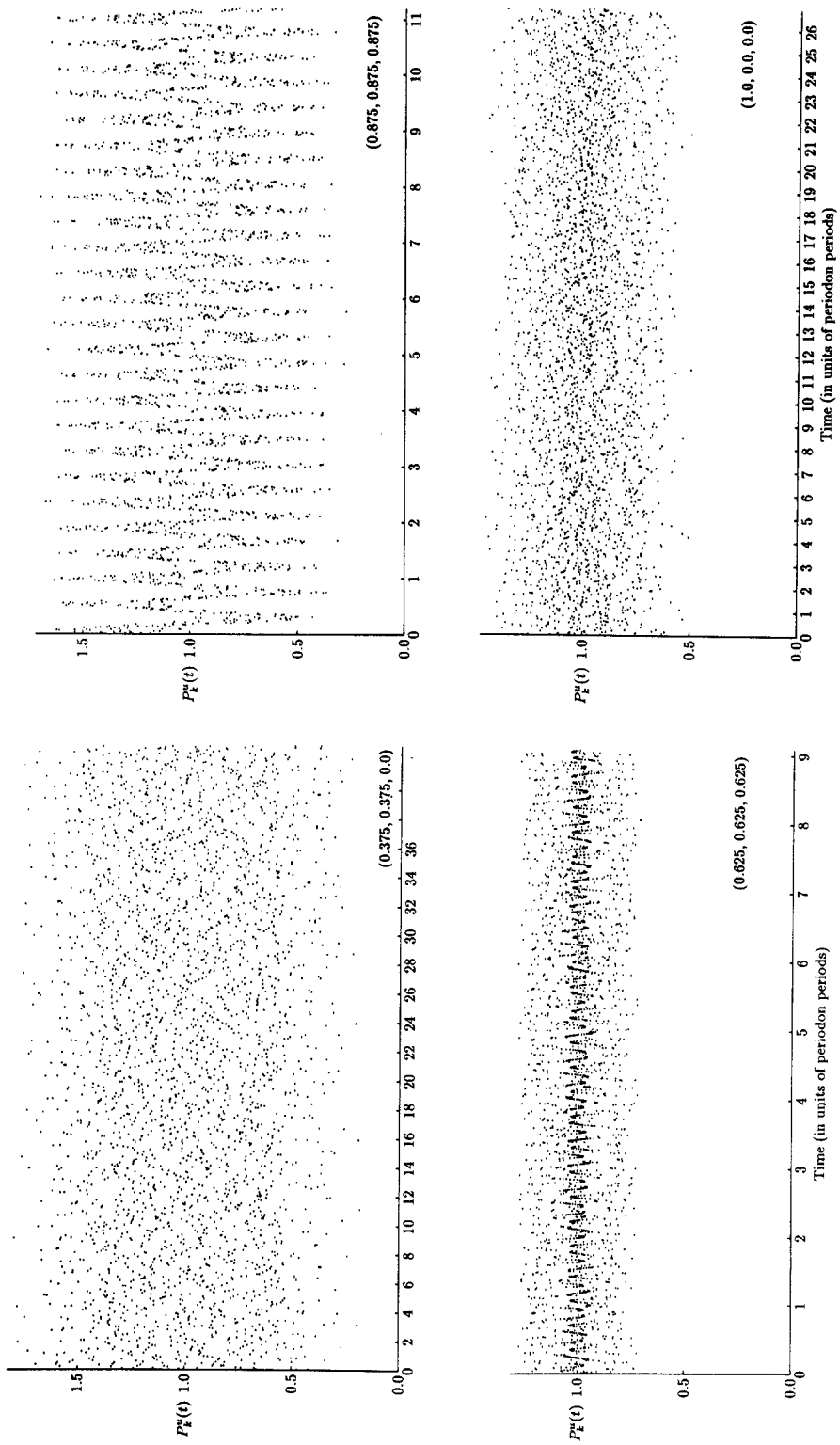


Figure 6. Typical graphs of $P_k^w(t)$ for a subsystem of four atoms for various k (given within each panel). The same parameters as in figure 4 were used and the same timescales as in figure 2. The initial conditions were random with an average slightly bigger than the largest periodon energy.

Let us now turn to the second issue. It is conceivable that a periodon orbit is a saddle-type instability, and hence that some nearby orbits are first attracted to it and then repelled. The path leaving a certain periodon orbit may thus get attracted to another periodon orbit before it is repelled only to end up at or near yet another periodon solution. Does one in this way get periodonish motion even though every single orbit in the vicinity of the periodon orbit is unstable?

It is possible to use the 'norm' function $P_k^u(t)$ to answer this question. We calculated $P_k^u(t)$ for 20 different $\boldsymbol{k}$-vectors simultaneously. If the phase space orbit of the system moves from periodonish orbit to periodonish orbit, one should see something like that indicated by the full trace in figure 5. No such 'dips' for any $\boldsymbol{k}$-vector were ever observed showing that once a periodon orbit has been left, the system never returns to it or to another periodon orbit or even very near to some periodon orbit. In technical terms one can say that the phase space inputs of periodon orbits are of a much lower dimension than the rest of phase space.

Finally, although periodons on the scale of the whole system (our simulation used 4096 atoms) never occur, it may be that they do occur on a smaller scale of a few atoms. The motion of the whole system can perhaps be thought of as approximating different periodonish motions over different small regions, each region's periodonish motion corresponding to a different $\boldsymbol{k}$-vector. To test this idea we looked for periodonishness on smaller and smaller scales. In figure 6 results analogous to those in figure 5 are shown, but this time for a subsystem consisting of only four atoms. The variations in $P_k^u(t)$ are now much bigger than previously, but are just what one would expect for 'random' motion (i.e. motion bearing no resemblance to periodonic motion) on such a small scale. The periodic variations observed at certain $\boldsymbol{k}$ in figures 5 and 6 are due to phonon-like motion in the system with $\omega_{\text{phonon}}(\boldsymbol{k})$ roughly of the same order as $\omega(\boldsymbol{k})$ given by equation (3).

4. Conclusion

It is of course only possible to look at a finite number of sets of parameters and initial conditions using computer simulations. Parameter space is constrained, however, by the fact that ω, A, B and C must all be real and the initial conditions by the assumption that measurable periodonic effects will occur only in regions where the total energy is of the same order as the periodon energies. With these ideas kept in mind, it seems as though we covered the set of possible sets of parameters and relevant initial conditions reasonably densely in our periodon simulations. Since none of the simulations showed any sign of spontaneous development of periodonish motion and since all periodons seem to be unstable, we conclude that there is no evidence that periodonish motion on any scale will ever occur in nature. A soft periodon phase transition as a mechanism for incommensurates around $\frac{1}{3}\boldsymbol{a}^*$ thus seems unlikely.

Acknowledgments

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