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Stability of quasicrystals: energy, entropy and phason modes.

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*Discussion session ICQ9***Stability of quasicrystals: energy, entropy and phason modes.****M. de Boissieu**

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The energy and entropy contribution to the quasicrystal stability is an on-going matter of debate. In that respect phason modes play a particular role since these excitations are characteristic of the quasicrystalline long range order. We present some of the results and list open questions to be focused on during the discussion session.

1. Introduction

The stability of quasicrystals, the way quasiperiodic long range order propagates are still open questions. This is not surprising in view of the complexity of the atomic structure of these phases. It is only recently that a better understanding of the atomic structure by means of structural determination using X-ray or neutron diffraction and High Resolution transmission electron microscopy images has been achieved in a few systems [1-4]. How the structure should be described, whether clusters are entities which have a physical relevance is nevertheless a matter of debate (see W. Steurer, this proceeding).

Concerning the stabilisation mechanism and growth model for quasicrystals, we must admit that we are still relying on very simple models. The two models which are frequently opposed are referred to as the energy and entropy stabilised QC. Their difference relies mainly on the relative weight one is giving to the configurational entropy in the expression of the free energy of the system. This entropy term is related to the phason degree of freedom of the structure.

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4 The energy stabilised scenario considers that a set of well chosen short range
5 interactions should be enough to give a QC ground state at zero K. This is the case of
6 the 'matching rule' model [5, 6], or of the quasi-unit cell model [7] which in some sense
7 is just a rephrasing of the matching rule model. In the latter one, one considers clusters
8 with some overlapping rules [8].
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11 The entropy stabilised scenario considers that the configurational entropy is a
12 dominant term in the stabilisation mechanism [9]. In this scheme the QC is only stable
13 at elevated temperature and should transform into a crystalline state at lower
14 temperature.
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17 Finally, there are a large number of theoretical and experimental studies on the
18 electronic stabilisation of QC by means of a pseudo-gap at the Fermi level.
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22 In this debate phason modes are playing an important role. We give in the following a
23 brief overview of the theory and experiment on phason modes. A detailed presentation
24 of the hydrodynamics theory of quasicrystals is given in [10] and a review on phason
25 modes in aperiodic crystals can be found in [11, 12].
26
27

28 29 30 **2. Hydrodynamic theory of QC and phason modes**

31 Phason modes are common to all *aperiodic crystals*. An aperiodic crystal has a
32 definition in term of its Fourier spectrum, which is 'essentially discrete'. It is indexed
33 by a linear combination of n independent linear indices, where n is larger than 3 for 3D
34 crystals. Generally aperiodic crystals are classified in incommensurately modulated
35 crystals (where the modulation can be of the displacive or the chemical type),
36 composites crystals where two subsystems interact, and quasicrystals which have space
37 groups incompatible with lattice translation [13]. As for any classification scheme, there
38 is some arbitrariness, and there are sometime some ambiguities.
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42 The hydrodynamic theory of aperiodic crystals relies on the analysis of the broken
43 symmetry of the system when going from the high to a lower temperature phase as for
44 instance from the liquid to the solid state for QC [10, 14]. Mode counting arguments
45 and symmetry analysis allows then to predict what are the hydrodynamic modes, i.e.
46 modes for which the frequency goes to zero as a power of the wavevector q .
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50 For *all* aperiodic crystals, the theory predicts that there should be $(n-3)$ *phason modes*,
51 which in the long-wavelength limit are collective *diffusive* modes. For icosahedral
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2 phases this lead to 3 phason modes [10]. Note that the diffusive character of phason
3 modes (i.e. not a propagative mode) is a consequence of the mode counting argument
4 and applies for all aperiodic structures including incommensurately modulated structure
5 [10, 11, 15].
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8 The two hypotheses necessary for this approach to be valid are best expressed in the
9 high dim picture of quasicrystals:
10

- 11 - The free energy of the system is invariant upon a rigid translation of the cut space.
- 12 - The free energy of the system may be expressed as a function of the squared gradient
13 of the 'phonon' and 'phason' strain (or parallel and perpendicular strains).
14

15 Whereas the first hypothesis does not lead to much debate, the second one is not
16 obvious a priori and can only be validated on realistic atomistic models and/or by
17 experimental studies.
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21 In this scheme a phason mode can be represented by a sin wave, with a wavevector
22 \mathbf{q}_{par} in the parallel (physical) space and a polarisation \mathbf{e}_{per} in the perpendicular space (In
23 the case of icosahedral phases, there are three phason polarisation vectors associated
24 with each \mathbf{q}_{par}) (Fig. 1). The 'dispersion' relation of the *diffusive* phason mode is given
25 by $-i\omega = D_{\text{phason}}q^2$, which leads to an exponential time decay of the phason mode as
26 $\exp(-t/\tau)$, where $\tau^{-1} = D_{\text{phason}}q^2$ and D_{phason} is the phason diffusion constant (see S.
27 Francoual et al., this proceeding).
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32 **[Insert Fig. 1 about there]**
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34 From the hydrodynamic theory, prediction on the shape and intensity distribution of
35 the diffuse scattering due to the equilibrium distribution of phason modes can be made
36 [16-18].
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40 At this point it might be useful to comment on the phason terminology which is used
41 with three quite different meanings in the quasicrystal community: 'phason jump',
42 'phason strain' and phason modes. I suggest that we should keep the term phason for
43 *phason modes only* as already proposed by T. Janssen [13]. Indeed it is the only one
44 *characteristic* of the quasicrystalline (or aperiodic) long range order. It arises from a
45 general definition valid for *all aperiodic systems* in the hydrodynamic theory: these are
46 long-wavelength *collective* excitations with a *diffusive* character. The term 'phason
47 jump' refers to the local rearrangement process at the atomic scale in quasicrystals: it is
48 a single atom process and should be named 'atom flip' or tile flip if one uses a tiling
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description. Note that this process *is not characteristic* of the quasicrystalline state since it can be found in 1/1 crystalline approximants. The term ‘phason strain’ refers to a perpendicular shear strain of the periodic space, somehow equivalent to a change of the slope of the cut space. I suggest naming it ‘perpendicular’ strain (or ‘internal’ strain if one uses the aperiodic community terminology).

3. Microscopic models

The hydrodynamic theory is a continuum theory which does not deal with the microscopic interpretation of phason modes. There are several questions which arise, most of them still open:

- *What is the atomic realisation of a phason mode?*
- *Is the free energy always ‘analytic’ as a function of phason strain?*
- *What is the origin of the ‘restoring’ force (related to the gradient square dependence of the perpendicular strain in the free energy) and of phason modes ?*
- *What is the physics driving the collective diffusive phason modes? Can we evaluate the amplitude of phason modes?*

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Answering these questions requires simulations or modelling at the atomic level. The main model developed for quasicrystals is the ‘random’ tiling model [9]. In this case the local process is a ‘tile flip’ inside a rhombic dodecahedron in the case of the 3D Penrose tiling (see Fig. 2): there are two atomic sites, too close to be occupied simultaneously. In this approach, realistic structures are constructed with clusters on the nodes of the tiling: the ‘cluster flip’ is obtained by rearranging only a few atoms because in real structure incomplete clusters are interpenetrating.

[Insert Fig. 2 about here]

Simulations on simple models have shown that [19, 20]:

- The free energy is analytic for some T range (hydrodynamic theory is valid)
- The restoring force is of pure entropy origin: the QC has the largest possibility of configurational re-arrangement; any departure from the ideal QC leads to a decrease of the entropy.

In the case of ‘matching rules’ model, there is a critical T above which the hydrodynamic theory apply [6].

Note that the above models only consider simple Hamiltonian on tilings. (See also Trebin, this proceeding for a 1D model). A more realistic Hamiltonian allowed a simulation of elastic constants as a function of T [21]. The role of the chemistry (stoichiometry and energy of local environments) and its influence on the free energy when a perpendicular strain is applied has been studied on 2D models ([22, 23]): it was shown that the system still has a phason elasticity described by the hydrodynamic theory, the 'restoring force' being more similar to a chemical potential in this case. The calculation of phason elastic constants on a realistic 3D atomic structure remains however a difficult problem to be solved.

Open question:

- all above plus:

- *What is the difference in phason modes for tiling models and cluster models if any?*

Deleted: - is a tiling the proper description of the structure?¶
- Clusters and phason modes (see W. Steurer)?¶

More elaborated models have been developed in the field of incommensurately displacive modulated structure (DIFFOUR model for instance). In this case there is a rather complete understanding of the physics of phason modes and of the mechanism leading to an incommensurate phase: it is a competition between first and second neighbours interaction leading to a frustration. There is a competition between entropy and energy terms leading to the succession of phases as T decreases: High symmetry phase, incommensurately displacive modulated phase, 'locked' in phase (equivalent to a rational approximant) [12].

4- Experimental results

4-1 Atomic flip

- Quasielectric neutron scattering experiments (Coddens et al.) have evidenced a signal, whose intensity is increasing with the temperature above 600°C, in icosahedral quasicrystals (AlPdMn and AlCuFe). It is interpreted as the result of assisted jump process involving a few (2 or 3) atoms. The length involved in these jumps is of the order 0.3 nm [24].

- Abe et al. have observed an anomalous Debye Waller factor by Z contrast images in the deca phase. The atomic sites where the anomalous Debye Waller is observed

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2 correspond to the border of the atomic surfaces in the 5D model. It thus corresponds to a
3 'flip site' with a distance of the order 0.1-0.2 nm [3].
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5 *4-2 Long-wavelength phason modes:*
6

7 Studies on phason modes in quasicrystals have been mainly carried out by diffuse
8 scattering measurements. This experimental approach is completely analogous to the
9 one used for the study of phonons in crystals by Laval, Olmer, Currien and Walker in
10 the 40-50° [25-28]
11

12 Most of the results have been obtained in the i-AIPdMn phase for which a complete
13 study has been carried out.
14

15 At room temperature there is a large amount of diffuse scattering whose intensity
16 distribution can be interpreted in the hydrodynamic theory framework, using only two
17 phason elastic constants K_1 and K_2 [29, 30]. Their absolute value has also been
18 determined and shown to be independent on the sample annealing treatment [31]. The
19 in situ temperature study shows that the diffuse scattering intensity increases as T goes
20 from 770°C to 500°C: this evolution is fully accounted for by a softening of one of the
21 phason elastic constant, a signature of pre-transitional fluctuations [32]. Finally the
22 diffusive collective character of phason modes has been experimentally evidenced in
23 situ using X-ray photon correlation spectroscopy (see Francoual et al., this proceeding)
24 [33]. There is thus a good agreement with the hydrodynamic theory for the i-AIPdMn
25 phase.
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28 Studies for i-AIPdMn with small chemical composition changes [34, 35] (F2 and F2M
29 phase) and on closely related icosahedral phases (i-AlCuFe [36] or i-AIPdRe [37],
30 which are iso structural), all point to the importance of the chemistry and its link with
31 phason fluctuations. It is most likely that the observed phason elasticity is not only
32 connected to a tile configuration, but also to the detailed chemical order/disorder taking
33 place in the quasicrystal. Indeed, if one considers the net effect of a phason mode onto
34 the real structure, this leads to correlated 'atom flip', but also to correlated 'atom specie'
35 exchange (for instance Al/Pd or Al/Mn) with respect to the 'ideal' structure. The
36 'chemical potential' is thus an important ingredient to be taken into account in any
37 realistic simulation of the observed phason elasticity.
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49 The applicability of the hydrodynamic theory on real decagonal phases has been
50 tackled only recently. Indeed, the diffuse scattering intensity distribution (in the
51 quasiperiodic Bragg layer and in between them) is quite complex in most of the
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decagonal phases and has been interpreted as the result of short range order (see the review by Steurer and reference therein [4]). In situ study of the diffuse scattering in the d-AlNiCo phase have been interpreted in term of phason modes and perpendicular strain distributions [38, 39]. Recently, the X-ray diffuse scattering intensity, measured in the quasicrystalline plane of the decagonal AlNiCo phase has been interpreted as resulting from phason modes [40].

Finally, Edagawa et al. have observed by HREM images in situ 'column' flips on a length scale of 2 nm [41]. The time correlation of these images has been analysed [42]. Although the validity of the hydrodynamics has not been checked, the observed process involves a move of a large number of atoms since the sample thickness is large.

Open questions:

- How reconcile the time scale observed for 'atom flip' and the one observed for collective diffusive phason modes? (The jump process observed by Coddens is much faster than the collective diffusive modes. Are the two observations related to the same process?)

- What is the role of the chemistry and/or chemical disorder in this mechanism? It is most likely a key point in the understanding of phason modes and for the QC stability.

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- Experimental results on diffuse scattering and phason elasticity do not seem to be in complete agreement with an entropy term arising from a tile configuration alone. Is a tiling an appropriate description of the structure?

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- Some phason modes are propagative in incommensurate structures, why not in QC?

5- Thermodynamics- T stability.

There are very few calorimetric measurements of thermodynamic quantities such as heat of formation, heat of mixing.... The systems in which coexist an approximant and a QC are particularly favourable in that respect. There is a need of such comparative measurements which can then be plugged into phase diagram calculations.

T- Stability: The question of the stability of QC (is there a quasicrystalline ground state ?) will certainly be an on going question for a long time and might turn to be just a theoretical one. Experimentally, almost all QC of reasonable quality for which in situ T

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measurements of the diffraction pattern have been carried out show, as T is decreased, either:

- A transformation of the QC state into a lower symmetry phase (most of the time large periodic approximant)

- An increase of the diffuse scattering intensity as T is decreased.

These two results point to the importance of entropy terms (chemical disorder, configuration, defects ...) in the QC stability, but the origin of the entropic contribution is still not clear: tile configuration, chemical disorder....

Note that in that respect X-ray or neutron diffuse scattering measurements are extremely sensitive tools, since they allow probing the two-body correlation function, which is strongly connected to the interatomic potential.

Open questions/experiments:

- *What other experiments should be carried out to probe the stability of QC?*

- *In situ temperature studies on more QC, in particular the CdYb icosahedral type would be very useful to address the QC stability problem.*

- *A comparison with other fields of research (order/disorder phase transitions in metallic alloys, aperiodic crystals....) would certainly be useful. For instance, some incommensurately modulated phases display a succession of phases as a function of temperature, which can be understood on the basis of physical models [12].*

- *The local chemical order and disorder, certainly plays a key role in stabilising the QC. These point should be addressed both experimentally and theoretically with ab-initio calculation (but up to now limited to a few hundred of atoms), or using adapted potential (such as EAM potentials) for simulation on large size systems.*

In conclusion, we have seen that long wavelength phason modes have been observed experimentally and have a dynamics in agreement with the hydrodynamic theory. All in-situ temperature studies of the diffraction pattern (including diffuse scattering), point to the importance of an entropy term in quasicrystal stabilisation and to a relation with phason modes. However a detailed description of these phenomena at the atomic level is still lacking. The problems of the quasicrystal stability and of the propagation of the quasiperiodic long range order remain fascinating questions to be solved.

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Fig. 1: Simple illustration of a phason mode in the case of a 1D quasicrystal. It is a sinusoidal mode, with a wavevector along the parallel space, and a polarisation of the mode along the perpendicular space. It is not a propagative mode, i.e. its time dependence will be of the form $\exp(-t/\tau)$.

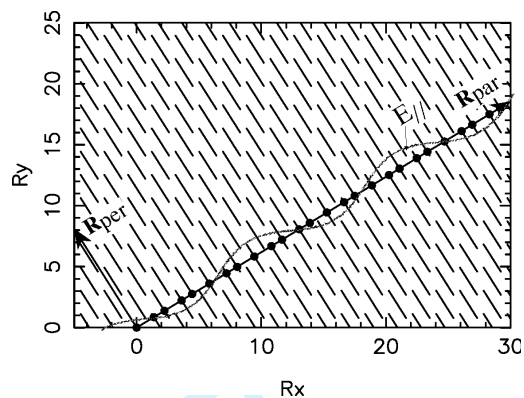
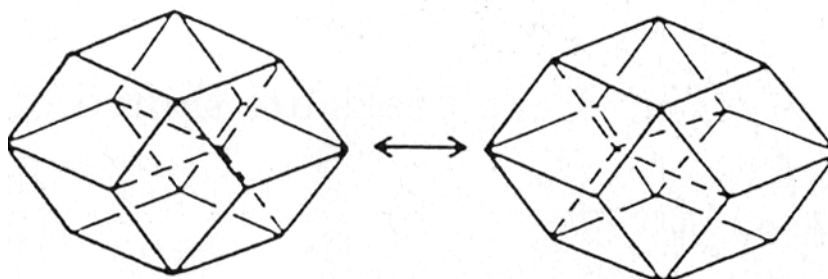


Fig. 2: Illustration of the tile flip used in the 3D random Penrose tiling. The two sites inside the rhombic dodecahedron are related by mirror symmetry.



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