Discussion session ICQ9

Stability of quasicrystals: energy, entropy and phason modes.

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Warning: *the document below is only a* ***draft*** *aimed at starting the discussion during the session at the ICQ9 conference. Its purpose is to briefly present a few points and underline some open questions. As such I did include only a few references.*

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. How the structure should be described, whether clusters are entities which have a physical relevance is nevertheless a matter of debate (see the paper by W. Steurer).

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 is mainly 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.

The energy stabilised scenario considers that a set of well chosen short range interactions should be enough to give a QC ground state at zero K. This is the case of the 'matching rule' model, or of the quasi-unit cell model which in some sense is just a rephrasing of the matching rule model. In the latter one, one considers clusters with some overlapping rules.

The entropy stabilised scenario considers that the configurational entropy is a dominant term in the stabilisation mechanism. In this scheme the QC is only stable at elevated temperature and should transform into a crystalline state at lower temperature.

Finally, there are a large number of theoretical and experimental studies on the electronic stabilisation of QC by means of a pseudo-gap at the Fermi level.

In this debate phason modes are playing an important role, some results are briefly given hereafter.

1. Hydrodynamic theory of QC and phason modes

Phason modes are common to all *aperiodic crystals*. An aperiodic crystal has a definition in term of its Fourier spectrum, which is 'essentially discrete'. It is indexed by a linear combination of n independent linear indices, where n is larger than 3 for 3D crystals. Generally aperiodic crystals are classified in incommensurately modulated crystals (where the modulation can be of the displacive or the chemical type), composites crystals where two

subsystems interact, and quasicrystals which have space groups incompatible with lattice translation. As for any classification scheme, there is some arbitrariness, and there are sometime some ambiguities.

The hydrodynamic theory of aperiodic crystals relies on the analysis of the broken symmetry of the system when going from the high to a lower temperature phase as for instance from the liquid to the solid state for QC. Mode counting arguments and symmetry analysis allows then to predict what are the hydrodynamic modes, i.e. modes for which the frequency goes to zero as a power of the wavevector q.

For all aperiodic crystals, the theory predicts that there should be (n-3) *phason modes*, which in the long-wavelength limit are collective diffusive modes. For ico phases this lead to 3 phason modes [1].

The two hypotheses necessary for this approach to be valid are best expressed in the high dim picture of quasicrystals:

- The free energy of the system is invariant upon a rigid translation of the cut space.
- The free energy of the system may be expressed as a function of the squared gradient of the 'phonon' and 'phason' strain.

Whereas the first hypothesis does not lead to much debate, the second one is not obvious a priori. It can only be validate on microscopical models.

In this scheme a phason mode can be represented by a sin wave, with a wavevector **q**, and a time dependence which is decaying exponentially as $\exp(-t/\tau)$ (it is not a propagative mode).

From this theory, prediction on the shape and intensity distribution of the diffuse scattering due to the equilibrium distribution of phason modes can be made.

2. 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 (gradient square of the phason strain in the free energy) and of phason modes ?

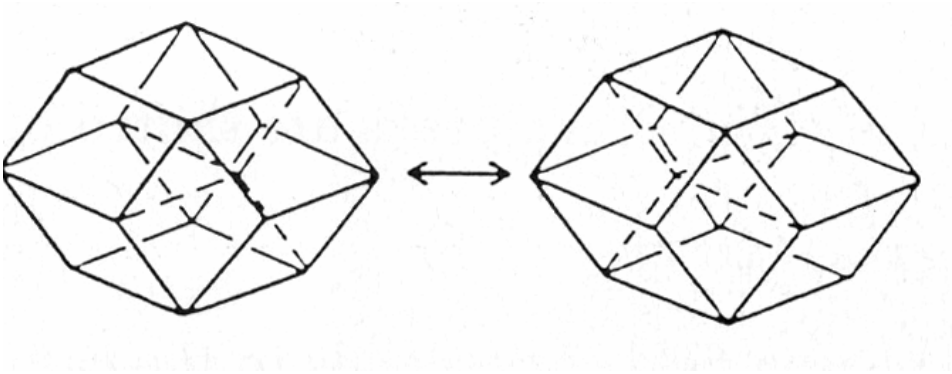
- What is the physics driving the collective diffusive phason modes? Amplitude of phason modes?

The main model developed for quasicrystals is the 'random' tiling model [2]. In this case the local process is a 'configuration flip' sometime called 'phason flip' (see Fig. below): there are two atomic sites, too close to be occupies 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.

Simulations on simple models have shown that:

- 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-arrangmeent; any departure from the ideal QC leads to a decrease of the entropy. Some recent attempts have been made to include an energy part to the model, in which case a chemical driving force might be invoqued (see Trebin talk).



Open question:

- all above plus:

- is a tiling the proper description of the structure?

- Clusters (see W. Steurer).?

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

Note that 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) [3].

3- Experimental results

3-1 Atomic flip, phason flip.

- Quasielestic neutron scattering experiments (Coddens et al.) have shown that a signal is present in icosahedral quasicrystals (AlPdMn and AlCuFe). It is interpreted as the result of assisted jump process involving a few atoms. The length involved in these jumps is of the order 0.3 nm [4].

- 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 correspond to the border of the atomic surfaces in the 5D model. It thus corresponds to a 'flip site' with a distance of the order 0.1-0.2 nm [5].

3-2 Long-wavelength phason modes:

Studies have been mainly carried out by diffuse scattering measurement in the i-AlPdMn phase:

Observed diffuse scattering can be interpreted in the hydrodynamic theory framework.

The diffuse scattering increases as T decreases: this has been interpreted as pre-transitional phason fluctuations [6, 7].

At high T, the collective dynamics is of a diffusive character (see Francoual et al. talk) [8].

In decagonal phases, Edagawa et al. have observed by HREM images in situ 'column' flips on a length scale of 2 nm. The time correlation of these images has been analysed [9].

Recent diffuse scattering experiments in the deca phase have been interpreted as resulting from phason modes [10].

Open questions:

- How reconcile the time scale observed for 'phason 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?)

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

- Experimental results are not in agreement with a tile configuration alone. Is a tiling an appropriate description of the structure?

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

4- Thermodynamics- T stability.

There are very few measurements of macroscopic thermodynamical 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.

T- Stability: almost all QC of reasonable quality for which in situ T measurements of the diffraction pattern have been carried out show, as T is decreased, either:

- A transformation of the QC 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…) in the QC stability, but the origin of the entropic contribution is still not clear: tile configuration, chemical disorder….

Open questions/experiments:

- What other experiments to probe the stability of QC?

- T studies on more QC in particular the CdYb type QC?

- Role of ab-initio calculations? Larger unit cell calculations? EAM potentials?

- Comparison with other fields of research (order/disorder phase transitions in metallic alloys, aperiodic crystals….). For instance a devil's staircase has been observed for IMS but not for QC.

- Importance of the chemical order and disorder.

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