Aperiodic crystals: Phonon and phason

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References on this lecture can be found in:


Introduction to phonon
Phonon

- Equation of motion of atoms: plane wave
- $q$ wavevector = $2\pi/\lambda$, $\lambda$ is the wavelength
- Frequency or energy $\hbar \omega$. Unit: THz or meV
  Phonon E is in the range 0-100 meV
- $e(q,s)$ Polarisation of the wave
- Displacement $u_n(x) = e(q,s) \exp i(qR_n - \omega t)$
1D model

- 1D Chain
- Interaction with first neighbors, spring constant $K$, 2 masses $M$ et $m$.
- $E = E_0 + \frac{1}{2}K\Delta u^2$
- $M = m$. Long wavelength: Acoustic mode and linear dispersion relation.

$$\omega = a \sqrt{\frac{K}{m_{1(2)}}} q$$
Phonons: a simple 1D model

2 atoms with masses $M=\tau m$,

Interaction by a spring $K$.

- Eigen mode: phase opposition
- Eigen mode: in phase

Phonon: wavevector $q=2\pi/\lambda$, energy $E$, eigenmode $e$
2 Atoms: gap opening

Brillouin zone boundary:

Gap opening

Light atom moves

Heavy atom moves

Stationary wave.

Phonon modes are Bragg reflected.
5 atoms in the unit cell

\[ \text{LSLLSLSLLS} \ldots \]

- **5 branches**: 1 acoustic branch and 4 optic one
- 4 gaps
- Some similarity with the 2 atoms case
5 atoms in the unit cell

• 5 branches: 1 acoustic branch and 4 optic one
• 4 gaps
• Some similarity with the 2 atoms case
**Phonons: 13 atoms**

LSLLSLLSLLSLLSL

- 13 ‘Branches’
- New gaps opening
- Large gap around 17 meV + optic ‘bands’
- Smaller gap around 13
- $E < 10$ meV : acoustic character
**Phonons: 13 atoms**

**LSLLSLSSLLSLLSL**

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Aperiodic crystals

- No periodicity: the Bloch theorem is no longer valid
- What is a phonon? Plane wave expansion?
- Phason degree of freedom and phason dynamics.
Measuring phonons

Coherent inelastic neutron (X-ray) scattering

Neutron energy transfer to the crystal: phonon creation or annihilation

Energy analysis of scatt. neutron
\[ \Delta E = \hbar (k_F^2 - k_I^2)/2m \]

\[ Q = k_F - k_I \]

\[ Q = Q_{\text{Bragg}} + q \]

q is the phonon wave-vector
Mesure: $Q$-constant, scan en énergie

\[ q = 0.24 \text{ Å}^{-1} \]

\[ E \text{ (meV)} \]

Counts

\[ 0 \rightarrow 2400 \]

\[ q \rightarrow \]

\[ Q_{\text{Bragg}} \]

\[ Q_x \text{ (rlu)} \]

\[ A2x \]

\[ (3, 5, 0), (6, 0, 0), (10, 0, 0) \]
Coherent inelastic neutron scattering

Triple axis spectrometer
Constant $Q$, Energy scan

Measurement: $S(Q_B+q, E)$ Related to the space and time Fourier transform of the structure

Damped Harmonic Oscillator

- $E(q)$: Dispersion relation
- $\Gamma$ (Width): phonon lifetime
- Intensity: related to the pattern of vibration (eigenvectors)
**Triple axis: Inelastic neutron scattering**

- Incoming neutron energy: 20-100meV
- Resolution of the order 1 meV
- Graphite crystals analyser
- Large single grain sample (1cm³)
Inelastic neutron scattering experiment
Inelastic x-ray scattering

- BL35XU, Spring8
- $E_i = 20$ keV
  (Si 11 11 11)
- Energy resolution 2 meV ($\Delta E/E = 10^{-7}$!!
  1 mK monoc control!!)
- Spot size 0.1*0.1 mm$^2$
- Flux $10^{10}$ photons/s
• Phason modes:
  Hydrodynamic theory
  Microscopical models
  Experimental results
• Phonons
  - Quasicrystal
  - Composites
Introduction to phason modes
Phason modes in aperiodic crystals

The free energy of the system is invariant through a translation of the Epar space along the perpendicular direction.
Phason mode

- Phase shift of the modulation function.
- Equivalent to a translation of the cut space.
- Leads to new excitations: phason.
Phasons modes: modulated phases

- Displacive modulated structure
- A change in the phase of the modulation induces a small change in atomic position.

Relation with phonon
Phasons modes: modulated phases

- Displacive modulated structure
- A change in the phase of the modulation induces a small change in atomic position.

Relation with phonon
**Composite**

- Sliding modes: relative motion of the guest and host.
QC: Atom ‘flip’

Local distortion of the cut space
Local rearrangement: Same local order

Phason mode: Clear diffusive process. $\tau^{-1} = Dq^2$
QC: Atom ‘flip’

Local distortion of the cut space
Local rearrangement: Same local order

Phason mode: Clear diffusive process. $\tau^{-1} = Dq^2$
• **What is a phason in quasicrystal?**
  Phason jump, phason strain, phason mode....

• **Phasons appear everywhere in QC studies!!**
  - Growth of QC: ‘phason’ entropy/local rules
  - Stability of QC: phason entropy contribution


Decagonal B-Mg-Ru random tiling is stabilised by phason entropy
• **What is a phason in quasicrystal?**
  Phason jump, phason strain, phason mode....
• **Phasons appear everywhere in QC studies!!**
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Decagonal B-Mg-Ru random tiling is stabilised by phason entropy

Hydrodynamic theory

- Symmetry breaking analysis
- Valid for all aperiodic crystals
- Introduction of symmetry and elastic constants.
Hydrodynamic modes

- Continuous symmetry is broken:
  Example: Fluid $\rightarrow$ Crystal
- Continuous translational symmetry is broken.

$\text{Crystal}(R) \neq \text{Crystal}(R+r)$

**But same free energy.**

Continuous degeneracy of the free energy with respect to translation.

Going continuously from $R$ to $R+dR$ has almost zero energy cost

From, James P. Sethna. See also Chaikin and Lubenski book.
Hydrodynamic modes

- Slow, long wavelength degree of freedom and modes for which the frequency vanishes as some power of the wavevector of the mode as $q \to 0$
- Identify the broken symmetry and define an order parameter ($F(Q)$)
- Hydrodynamical variables related to conservation law: particle number, momentum and energy
- Symmetry and mode counting arguments
Hydrodynamic: phonons

- Fluid: 5 hydrodynamic variables: mass and energy conservation (2) + momentum (3)
- Fluid: 5 modes:
  - Longitudinal propagative mode (2),
  - 2 transverse **diffusive** shear waves
  - heat diffusion

Note that the shear waves are not propagative, but diffusive.

A propagative mode counts for 2 (time reversal symmetry)
Hydrodynamic: phonons

- Fluid: 5 modes: Longitudinal propagative mode (2), 2 transverse \textit{diffusive} shear waves, heat diffusion
- Crystal: broken symmetry + Goldstone theorem. \textbf{8 modes instead of 5}
  - Two ‘new’ transverse propagating phonons: Goldstone modes (goes from diffusive to propagative: count for 2)
    \[ \omega = \pm vq \]
  - Vacancy diffusion (diffusive, count for 1)
  + Longitudinal acoustic and heat diffusion
Phason modes: Hydrodynamic theory

A translation of the cut space leads to a new structure indistinguishable from the previous one. Same Fourier spectrum.

Analogy with the treatment of phonon: small translation does not cost any energy. 1 new variable.
**Phason modes**

- Hydrodynamic: in the case of a 1D displacive modulation, predict 1 supplementary mode.

  New variable: Perp translation: 1D, counts for one

  The new phason mode related to phase fluctuation of the modulation is a **Diffusive** phason mode.

  The dispersion relation is:  \(-i\omega = Dq^2\)

  D is a phason diffusion constant, and one has an overdamped mode. This can be expressed in the time domain (FT of \( \omega \))

  \( S(q, t) \) is decaying exponentially.

  \[
g(q, t) = \exp\left(-\frac{2t}{\tau_c(q)}\right) \quad \tau_c^{-1} = Dq^2
  \]
Phason mode and hydrodynamic theory

• The above arguments on diffusive modes hold for all aperiodic crystals case.

• For all aperiodic crystals the hydrodynamic theory predict a phason diffusive mode.

• Polarization of the mode in perp space

• Characterized by a phason diffusion constant

• Of course the value of this phason diffusion constant will depend on the nature of the aperiodic crystal.
Hydrodynamic theory of icosahedral QC

- It has been much developed for quasicrystal
- Importance of the symmetry
- Lead to a generalized elasticity theory for QC.
Phason modes in QC right after the QC discovery:
V. Elser 1986
Hydrodynamics theory of aperiodic crystals

- **Hypothesis:**
  Infinetesimal translation along $E_{\text{perp}}$ does not cost energy. Problem in some cases. For incommensurate modulated structure, breaking of the analyticity of the atomic surface shape (Aubry, Janssen) induces a $q=0$ phason gap.

- **Generalised elasticity**
  How does the system respond to a strain?

  $$F = \alpha |\nabla u_{\text{par}}|^2 + \beta |\nabla u_{\text{per}}|^2$$

  *Phonon and phason strain.*

  *Elastic constants, phonon, phason and phonon-phason coupling.*
Phason strain and phason modes

Phason strain distribution
Diverging fluctuations
Bragg peak broadening

Long wavelength fluctuations
Phason modes. Non diverging.
Bragg peak + diffuse scattering
Elasticity of icosahedral phase

- From the hydrodynamic theory one can derive a generalized elasticity. (Kalugin et al., Back, Lubenski):
  - Continuum theory.
  - Free energy density: squared gradient of phason strain.

- Ico phase: 5 elastic constants.
  Phonon: isotropy of icosahedral symmetry: 2 phonons constant (1 longitudinal one transverse)
  Phasons 2 constants: K1 and K2
  Phonon/phason coupling term: K3
Elasticity of icosahedral phase

- Influence on diffraction spectrum:
  Thermal equilibrium phonon and phason fluctuation (Jaric, Ishii, Widom):
  - In 3D, fluctuations are bounded: Bragg peak remain
  - Phonon give rise to a Debye-Waller (Bragg peak decrease) and diffuse scattering
  - In the same way phason fluctuation lead to diffuse scattering whose shape depends on K1 and K2 (see herafter).
DIFFUSE SCATTERING

Phonon

Phason

TDS CONTRIBUTION

PHASON CONTRIBUTION $k_2/k_1 = -0.6$
Summary

• Hydrodynamic theory applies to all aperiodic crystal
• Phason mode, in the long wavelength limit, are diffusive mode or overdamped harmonic oscillator.
• Mode polarised in the perpendicular space
• ‘Dispersion relation’: $\tau_c^{-1} = D(q)q^2$
• In quasicrystal, phason elastic constant have been derived. Used for diffuse scattering.
Microscopic models and phason modes

- Hydrodynamic theory is only a long wavelength, phenomenological theory
- Connection with microscopic models:
  1. Frenkel-Kontorova model
  2. DIFFOUR
  3. Double chain
  4. Amman 3D icosahedral tiling
• a/b is an irrational number
• \( \lambda \) coupling param
• Weak and strong coupling
• Weak coupling: smooth modulation
• Strong coupling: the modulation function is discontinuous.
Analyticity breaking (Aubry)

- If the modulation function is smooth: phason branch is such that it goes to zero as $q$ goes to zero.
- Strong coupling: discontinuous atomic surfaces. There is a phason gap, i.e. $E$ of the phason branch is not zero as $q$ goes to zero: Energy to overcome...
Incommensurate modulation: the DIFFOUR model

First and second neighbours interaction:

**FRUSTRATION**

(T. Janssen et al.)

Gray color: incommensurate phase

Succession of phase is reproduced, with the correct dynamics

The incommensurate phase is stabilized by phason entropy

Phason seen as a mode with a polarisation in perp space.
• A phason gap appears, when the discontinuity appears (T. Janssen): \( E(q=0) \) is non zero.
Composites

Low-frequency structural dynamics in the incommensurate composite crystal \( \text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta} \)

J. Etrillard\(^1\), L. Bourgeois\(^1\), P. Bourges\(^1\), B. Liang\(^3\), C. T. Lin\(^3\) and B. Keimer\(^3\)
Composites

- The two sublattice react independently
- Two sound velocity
- Sliding modes?
Are phason hydrodynamic modes in QC?

*Simulation on a 3D ‘Toy model’:* 3D Penrose tiling (or Ammann tiling) and the random tiling (Elser, Henley, Tang).

High T Monte-Carlo simulation (all configurations are equivalent).

Tang has shown that this maximally random tiling behaves as predicted by the hydrodynamic: **PHASON ELASTIC CONSTANT**

*Restoring force: configurational entropy: Entropy is maximal for QP state and varies quadratically with phason strain.*

See also chemical effect (Koschella et al.)
Diffuse scattering in the 3D random Penrose tiling.

( From M. Mihalkovic)

- Diffuse scattering in agreement with elasticity theory. $K_2/K_1$ is related to the tile and phason flip geometry.

- Intensity decrease of the Bragg peak intensity proportional to $Q_{perp}$: perpendicular Debye-Waller factor.
Quasicrystal: analyticity?

- In quasicrystal discontinuous atomic surfaces.
- Jeong and Steinhardt have shown that there is a breaking down of hydrodynamic in a model system with a $T=0$ QC as a ground state
  - Hydrodynamic behavior only above $T_c$
- The ‘continuous’ parameter is not related to the shape of the atomic surface but to the fluctuations of the cut space (number of tile flip).
Quasicrystal: analyticity?

- Hydrodynamic behavior only above Tc
  
  • The ‘continuous’ parameter is not related to the shape of the atomic surface but to the fluctuations of the cut space (number of tile flip).

Entropic model.
‘Entropic’ elasticity.
Summary

• Atomistic models also predict phason modes
• Regime of wavevector were phason modes are damped propagative modes (incommensurately modulated phases)
• Longer wavelength modes are diffusive
• Quasicrystals: always diffuse modes
• Phason modes in quasicrystal might be interpreted as an entropy term leading to a restoring force
Phason modes: example
Displacive modulation: ThBr4
Displacive modulation: ThBr$_4$

$q_s = 0.31 \ c^*$

$T<95K$ Incommensurate modulation along $c$.

Above $T_c$: Soft mode transition
ThBr4: propagative phason mode

Inelastic neutron scattering: $T<T_c$

Near the satellite reflection: new zone center

The ‘acoustic’ like excitation is not an acoustic phonon: phason mode

$L. Bernard et al$

T=85K
Phason mode: ThBr₄
Dispersion slope is different from the acoustic one

$q_s = 0.31 \ c^*$
ThBr4: Phasons / Amplitudons eigenvectors

Phason $q \neq 0$

Amplitudon $q = 0$

Amplitudon $q \neq 0$

Phason $q = 0$
Phason modes: ThBr4

- In fact the hydrodynamic theory predicts only one mode: why two propagative phason and not a diffusive mode?
- Need to introduce lifetime: *Lifetime is finite* as q goes to zero. Phason has a finite width.
- Two ‘half’ hydrodynamic modes are equivalent to a diffusive mode.

\[ \Gamma = 0.3 \text{ meV for ThBr4} \]

Mean free pass \( \sim \) a few 10 nm.

Mode with \( \lambda > \) mean free pass, do not propagate.
NaNO$_2$ orientational disorder
Order-disorder phase transition

\[ T > T_i \quad \text{and} \quad T < T_c \]

\[ T_c < T < T_i \]

\[ \text{modulation period} = 9.22a \]
NaNO$_2$: diffusive phason mode

Modulation function is smooth but is an occupation probability: diffusive phason mode.

$\tau^{-1}(q) \propto \frac{1}{\sqrt{T-T_i}}$

$T<T_i \quad \tau^{-1}=Dq^2 \ ? \ Hydrodynamic \ modes \ ?$

Quasicrystals: Long-wavelength Phasons modes

- Long-wavelength phason modes: collective diffusive modes
- Phason Mode: $q$ and polarisation in perp space
- $-i\omega = D_{\text{phason}} q^2$ (‘dispersion’)
- $\exp(-t/\tau) \quad \tau = D_{\text{phason}} q^2$
- Frozen at room $T$

Measuring long-wavelength phasons: diffuse scattering

Elasticity theory: calculation of diffuse scattering (similar to TDS). Two parameters: $K2$ and $K1$ the phason elastic constants.
Diffuse scattering

- Structure = Ideal structure + fluctuations

If fluctuations are bounded then

$$S(Q) = S_{\text{Bragg}}(Q) + S_{\text{Diff}}(Q)$$

Bragg FT  \[ \langle \rho(R) \rangle \]

Diffus FT

\[ \langle \rho(r_i) \rho(r_j) \rangle - \langle \rho(r) \rangle^2 \]
**Phason modes in quasicrystal**

- Hydrodynamics theory and elasticity. For icosahedral phases, K1, K2 phason elastic constant K3 phonon-phason coupling (Jaric; Ishii; Widom)

Phason modes lead to **diffuse scattering** (similar to TDS) which can be computed using the hydrodynamic matrix C(K1,K2,K3,q)

- Thermal equilibrium phonon and phason fluctuations
- Scattered intensity in : \( Q = H_{\text{Bragg}} + q \)

\( Q = H_{\text{Bragg}} \)  Bragg intensity + **Par and Perp Debye-Waller factor**

Fluctuations are limited in par and perp space

\[
S_{\text{Bragg}}(H_{\text{par}}) = S_{\text{Ideal}}(H_{\text{par}}) \exp(-\langle u^2_{\text{par}} \rangle H_{\text{par}}^2). \exp(-\langle u^2_{\text{per}} \rangle H_{\text{per}}^2)
\]
Phason modes in quasicrystal

- **Diffuse scattering**, $K3$ negligible: phonon and phason part

$$S_{Diffus}(H_{par} + q) = S_{Bragg}(H_{par}) \left< H_{par} \left| C_{par,par}^{-1}(q) \right| Q_{par} \right>$$

$$+ S_{Bragg}(H_{par}) \left< H_{per} \left| C_{per,per}^{-1}(q) \right| H_{per} \right>$$

**Three main characteristics** of phason diffuse scattering

- $S(Q+q)$ decays as $1/q^2$

- Intensity is proportional to $I_{Bragg} Q_{per}^2$

- Shape anisotropy depends on $K2/K1$ and $K3$

- For Bragg peak along the same axis, and for weak $K3$

$$I(Q+q) = \alpha(q) \ I_{Bragg} Q_{per}^2 / q^2$$

$\alpha(q)$ depends only on the $q$ direction
DIFFUSE SCATTERING

Phonon modes: 3 polarisation, longitudinal and transverse

Phason modes: 3 polarisation $e_{\text{per}}$. ‘Selection rule’ $e_{\text{per}}H_{\text{per}}$
**DIFFUSE SCATTERING**

Selection rule: perpendicular
Component are almost orthogonal

Phason modes: 3 polarisation $e_{\text{per}}$. ‘Selection rule’ $e_{\text{per}} H_{\text{per}}$
i-AlPdMn: Neutron diffraction

- Analyser: no TDS contribution
- The diffuse scattering around Bragg reflections is anisotropic
- Phason contribution to the diffuse scattering: 15/24 and 16/24 reflections

Simulation with a single parameter: $K2/K1=-0.52$
Neutron data

- Absolute scale measurement.
- \(1/q^2\) fit along several directions.
- \(K_1/k_B T = 0.1\) atom\(^{-1}\)
- \(K_2/k_B T = -0.052\) atom\(^{-1}\)
- Good agreement with experimental data measured around 11 reflections and 4 directions. \(R=0.2\)
Absolute scale X-ray data (ESRF, D2AM)

- $K_1/k_B T = 0.06 \text{ atom}^{-1}$  $K_2/k_B T = -0.03 \text{ atom}^{-1}$

- Absolute scale measurement allows comparison between different sample and quasicrystals.
Phason fluctuations explains 90% of the observed diffuse scattering

Measurement (rotating anode)  Simulation
Stability: Two competing (simple) models

Phason fluctuations
Increase with T

Perfect QC
Ground state
energy stabilised

Random tiling
QC is stabilised by entropy from phason

Crystalline state
i-AlPdMn. Temperature neutron diff study

Diffuse scattering diminishes when $T$ increases.

High Q per Bragg peaks intensity increases.

Phason softening when $T$ decreases.

close to a 3-fold instability.
i-AlPdMn quasicrystal. In situ T study

T evolution of the diffuse Scattering

FROM 750°C to 500°C

In situ X-ray.

The diffuse scattering is due to pre-transitional fluctuations (3-fold), with a phason softening

Agreement with the random-tiling scenario
3-fold instability: $K2/K1 = -0.75$  
5-fold instability: $K2/K1 = 0.75$

- Experimentally $K2/K1 = -0.52$ at RT and $-0.4$ at 700°C
- Consistent with a softening of the phason mode:

*Phason diffuse scattering can then be interpreted as pre-transitional fluctuations.*

Consistent with the random tiling scenario
Phason dynamics

- HRTEM observed at 1123 K in d-AlCuCo (Edagawa et al., PRL, 8, 1676, 2000)
- Local ‘phason Jump’, involving atoms columns.
- Time scale : 10 sec
**Long-wavelength phason dynamics**

- **Collective diffusive mode**: exponential time decay of the correlations. Time scale? Too slow for inelastic neutron scatt.

- **Experimental study**: coherent X-ray scattering (ID20, ESRF)

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**Incoherent scattering**

**Coherent scattering**
Experimental set up: ESRF ID20

- Slits: S1 60x60 μm; Circular pinhole D=10 μm
- CCD: Directly illuminated (photon counter); pixel 22x22 μm; Δq = 5.10⁻⁵Å⁻¹ ; Total area: 2.10⁻²Å⁻¹
- Partial coherence 11% ; Flux 10⁹ photon/s
• Measurement around the 7/11 5-fold reflection (1, t, 0)
• Along the direction of maximum intensity: (t, -1, 0)
• The diffuse scattering intensity presents a **speckle pattern**

Time dependence of the speckle pattern in the diffuse scattering

→ Time dependence of phason fluctuations.

**Intensity correlation= f(t)**
Time dependence of the speckle pattern

\( T=650^\circ C \)

- Intensity correlation as a function of time
- Exponential decay fit:
  
  \[
  F_{\text{correl}} = 1 + \beta \cdot \exp(-t/\tau)
  \]

- Such a decay is expected for a diffusive process.

- \( \tau \) should be proportional to \( q^{-2} \)

Phason fluctuations: a diffusive process

- \( D_{\text{phason}} = 1/q^2 \tau \)
- \( D_{\text{phason}} = 2.2 \times 10^{-18} \text{ m}^2\text{s}^{-1} \)
- Phason ‘dispersion curve’

\( q_{\text{phason}} = (-\tau, 1, 0) \), slow direction

\( D_{\text{phason}} \) is anisotropic (3 values)


Analogous to sound velocities
Phason fluctuation: Activated process

- Strong variation with temperature
- Activation energy $\sim 3$ eV
  
  $D_{\text{phason}} = 2.2 \times 10^{-18}$ m$^2$s$^{-1}$

- Comparison with atomic diffusion:
  
  Mn is a slow diffuser
  
  $T=650^\circ C$  $D_{\text{Mn}} = 10^{-14}$ m$^2$s$^{-1}$
  
  $H \sim 2$ eV.

(H. Mehrer et al.)
Mechanical properties

- Dislocation in quasicrystal:
  Elastic field + Phason field
- Plasticity: phason ‘wall’
  (from Caillard et al.)
HREM Images: Phason walls
(Feuerbacher et al.; Wang et al.; Caillard et al.)

Relaxation at high T through phason fluctuations
**Dilaocation motion: Relaxation of phason walls (Caillard et al.)**

*Time scale compatible with phason diffusion.*

![Image](image_url)

**Figure 1.** Dislocation motion in a twofold plane at 700°C. Note the fringe contrast behind the moving dislocation in (a) and (b), which has disappeared in (c). The crosses indicate fixed points in the sample.
i-AgInYb and i-ZnMgSc

- i-ZnMgSc (Ishimasa), very small diffuse scattering intensity (PRL, 2005, 95, 105503). High Qperp Bragg: Qper = 7

2-fold Q-scan

- i-AgInYb absolute scale and rescaled for Bragg peak power
- *More diffuse scattering in i-AgInYb QC than in i-ZnMgSc*
- High Qper Bragg have disappeared. Qper max = 5
Diffuse scattering in QC and approximant

- Long wavelength phason fluctuations are a consequence of the long range aperiodic order
- A priori no phason diffuse scattering in periodic approximant
- Only one study: 1/1 Zn$_6$Sc as compared to i-ZnMgSc (S. Francoual, T. Ishimasa)

1/1 Zn$_6$Sc approximant:
- Only phonon diffuse scattering
- No phason diffuse scattering

$Q_{\text{per}} = 0.51$

*PRL, 2005, 95, 105503*
Summary

- Phason modes are propagative modes in incommensurately modulated phases, but with a finite width. Diffusive mode in the low q, long wavelength limit.
- Composites. Sliding modes?
- Quasicrystal:
  - Phason modes observed by diffuse scattering
  - i-AlPdMn PDS due to pre-transitional fluctuations
  - Phason dynamics is diffusive as measured by x-ray
  - Different QC, present different PDS
PHONONS

• Incommensurately modulated phases
  new dynamic related to phason modes.
• Composites
• Quasicrystals
In aperiodic crystals, the Bragg peaks of the two sublattices never superimpose, but in zero. The Bragg peaks do not define anymore a Center of Zone, since there are no more Brillouin Zone.
Composites

Low-frequency structural dynamics
in the incommensurate composite crystal Bi$_2$Sr$_2$CuO$_{6+\delta}$

J. Etrillard$^{1,2}$, L. Bourgeois$^1$, P. Bourges$^1$, B. Liang$^3$, C. T. Lin$^3$ and B. Keimer$^3$

![Graphs showing neutron counts vs. frequency for different Q values](image)
Composites

- The two sublattice react independently
- Two sound velocity
- Sliding modes?
Phonons in quasicrystals
**Phonons: 13 atoms**

**LSLLSLLSLLSLLSL**

- 13 ‘Branches’
- New gaps opening
- Large gap around 17 meV + optic ‘bands’
- Smaller gap around 13
- E< 10 meV : acoustic character
Phonon: 1D quasicrystal

- Long wavelength: acoustic modes.
- Infinity of gap opening and self similarity

From Lu, Odaki and Birman, PRB, 1986, 33, 4809
Phonon: 1D quasicrystal

Higher energy: **modes are critical**: neither localised, nor extended. The eigenvector decays with a power law and recursion around similar environment.

From Lu, Odaki and Birman, PRB, 1986, 33, 4809
**Inelastic neutron scattering: Fibonacci chain**

*(From Benoit and Poussigue)*

- **Acoustic mode**: \( S(Q+q) \sim I_B Q^2 / E^2 \); Norme = \( S(Q+q) \times E^2 = \text{cte} \)

- Fibonacci chain: **Strong Bragg=Zone center** (\( \Gamma \)); Pseudo zone boundary (PZB)
3D QC Systems

- Acoustic mode
- Pseudo-zone boundary (Niizeki)
- Critical modes?

AlLiCu 5/3 approximant simul.
(Krajci et al.)

Critical modes: Neither localised nor delocalised.
i-AlPdMn phase

Pseudo Brillouin Zone Boundary Map (Niizeki)

2-fold diffraction pattern

Around each strong Bragg peak (zone center): stacking of PZB. At the PZB: stationary mode (Bragg reflected wave)
Acoustic mode

- In the long wavelength limit (continuum), there are acoustic phonons. Because of the icosahedral symmetry, there is an isotropy: 2 sound velocities, one transverse and one longitudinal.

Inelastic neutron scattering intensity. $Q=G+q$

$$I(G+q, \omega_q) \sim I_b(Q.e_{T(L)})^2/\omega_q^2$$

$I_b$: Bragg peak intensity; $q$ phonon wavevector; $\omega_q$ Phonon energy, $e_{T(L)}$ Phonon polarisation. **SELECTION RULE**

- For an acoustic branch: $I_{ph} \omega^2 = \text{cte}$ this define the acoustic regime
**Phonons in i-ZnMgSc and c-ZnSc Quasicrystal specific?**

- System isostructural to CdYb
- i-Zn$_{80.5}$Mg$_{4.2}$Sc$_{15.3}$ QC and Zn$_{86}$Sc$_{14}$ 1/1 approximant
- Respective influence of local order (clusters) and long range periodic or quasiperiodic
- Study by inelastic neutron and x-ray scattering on single grain samples.
**Quasicrystal structure**

- **Clusters** packing with well defined chemical order: *94% of atoms*
- Hierarchical packing of the clusters in the QC (Periodic packing in 1/1 approximant)
ZnSc: Comparison 1/1 approxt and QC

\[ \text{Zn}_6\text{Sc 1/1 app Crystal} \]

\[ \text{i-ZnMgSc Quasicrystal} \]

Same clusters: effect of local order and long range periodic or QP order.
Experimental transverse phonon

- Pseudo gap observed in both QC and approximant
- Pseudo gap is larger in the approximant
- Related to the distribution of Brillouin zone and PBZ
Inelastic neutron scattering close to a strong Bragg peak: Transverse modes

Well defined acoustic modes

Abrupt broadening

Very similar in both cases

Optic modes are better defined in the 1/1 crystal
Acoustic mode broadening rate

**i-ZnMgSc**

• *Abrupt broadening* \( q > 0.30 \text{ Å}^{-1} 

• \( q = 0.31 \text{ Å}^{-1} \): \( \lambda = 20 \text{ Å} \); mean free path \( <l> \sim 160 \text{ Å} \)

• \( q = 0.53 \text{ Å}^{-1} \): \( \lambda = 12 \text{ Å} \); mean free path \( <l> \sim 20 \text{ Å} \)

• **Intensity:** Norme increases : mode mixing.

**c-ZnSc**

• Similar broadening, but larger mean free path.
• This abrupt broadening is observed in all other quasicrystals

• i-ZnMgY: abrupt cross-over between the acoustic regime and mixing of several states.

• Acoustic limit: MEAN FREE PATH ~24 Å
  Cluster diameter Dcl ~ 12 Å
  Wavelength Dcl; mean free path 2Dcl

• i-AlpdMn: crossover for the same wavelength, but the mean free path is smaller ~ Dcl
Phonons: i-AlPdMn

- Dispersion relation and Pseudo Brillouin Zones
- Abrupt broadening of acoustic excitations
Simulations: ZnSc

- Ab initio limitations to ~ 100 atoms/cell.
- Adapted Hamiltonian is necessary: oscillating pair potentials.
- Allows to study large cells up to several 1000 atoms.
- Pair potentials fitted on a DFT data base (VASP) containing all simple phases in ZnSc. Fitting on E and Forces
Oscillating pair potential

M. Mihalkovic, C. Henley et al.

Phase diagram determination.
Simulations: atomic model

- 1/1 Approximant and 3/2 approximant for the QC
- Based on canonical cell model
- **Problem:** Cd orientation/correlation and disorder of the inner tetrahedron.
Simulations

Tetrahedron orientation induces *cluster distortion*. *Crucial in the simulation*

- 1/1 approximant: Super-cell containing 8 clusters. *Molecular dynamics at 300C to have a solution for relative orientation then quenched.*
- 3/2 approximant contains 32 clusters. Based on canonical cell model. a=3.6 nm. 2984 atoms per unit cell (2528 Zn, 456 Sc). *Molecular dynamics at 300C for the tetrahedra orientation followed by a quench.*

- Lattice dynamic: Harmonic: inversion of the dynamical matrix.
Simulated diffraction pattern in good agreement with experiment

1/1 Approximant

Quasicrystal

Data

Simulation
Comparison simulation-measurement
Transverse modes

1/1 approximant Zn-Sc

Quasicrystal

Good agreement. Differences QC and 1/1 are well reproduced.

Intensity distribution: comparison simulation-experiment.

TA- c-ZnSc

TA i-ZnMgSc

• Energy is slightly too small in transverse geometry.

• Good reproduction of the overall intensity distribution SENSITIVE TEST.

• Broadening is due to mode mixing. Equivalent to finite lifetime.

Blue curve: simulation

Longitudinal modes (Inelastic X-ray scattering)

Very good agreement. The 6 meV low energy mode is well reproduced. Differences are also reproduced. Link with BZB
Longitudinal modes: Intensity distribution.

Blue curve: simulation

• The simulation is thus in very good agreement with the experiment.
• The QC and 1/1 approximant differences are reproduced.
• One can use this simulation with confidence to analyse the vibrational properties of he QC and 1/1 approximant.
• Cluster modes?
• Nature of the modes?
Partial density of vibrational states

- Tetrahedra shows low energy mode, especially in 1/1 approximant

- Related to the 1/1 ordering phase transition? (Tamura et al.)

- Strong distortion of the dodecahedron both in 1/1 and 3/2 approximant.

- Consistant with Ishimasa structure at low T.
Conclusion

Phonon in QC:
Acoustic mode at low energy
Abrupt broadening, length scale $\sim$ cluster size
Notion of quasi-Brillouin zone boundary
Modeling in good agreement

Are mode critical?
Cluster modes? Plane wave description?
CONCLUSION

• Dynamic of aperiodic crystals shows distinct features.
• Most prominent effect are the phason modes:
  Phason mode are diffusive mode in the very long wavelength limit.
  Damped propagating modes in a few incommensurately modulated systems.
• Lattice dynamics of quasicrystals: Notion of QZB, abrupt broadening and characteristic length scale.
  Critical modes?