Three-wave interactions in problems with two length scales: Faraday waves and soft-matter quasicrystals

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R., Silber & Skeldon (2012), *Phys. Rev. Lett.*, **108** 074504

Newton Institute, January 2013

Experimental quasipatterns I

Quasicrystals have orientational but not translational order – interest in these structures originated with the Al-Mn quasicrystal discovered about 25 years ago:

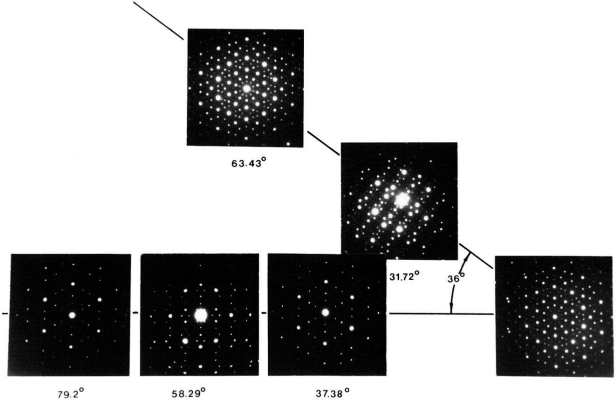


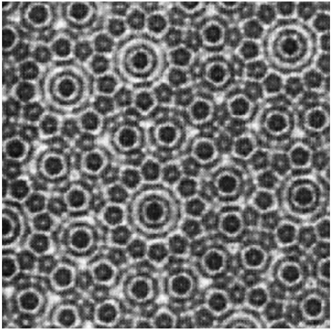
FIG. 2. Selected-area electron diffraction patterns taken from a single grain of the icosahedral phase. Rotations match those in Fig. 1.

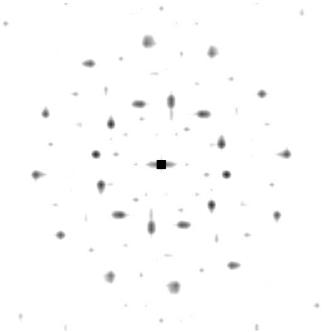
Shechtman et al. (1984)

Experimental quasipatterns II

Since the early 1990's, quasipatterns have been found in a variety of other systems: Faraday waves...

- The rotation symmetry is manifested in the Fourier spectra: 12 peaks with the same wavenumber (two wavenumbers)
- Quasipatterns do not tile the plane, so these wavevectors are the basis of a quasilattice rather than a lattice

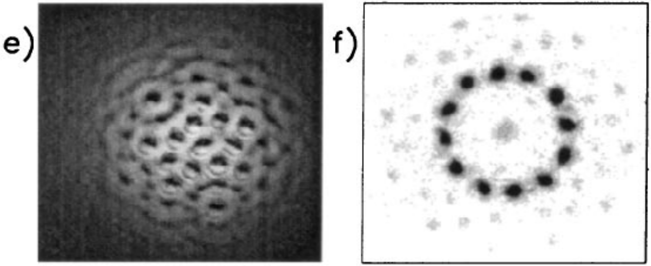




Kudrolli, Pier & Gollub (1998)

Experimental quasipatterns III

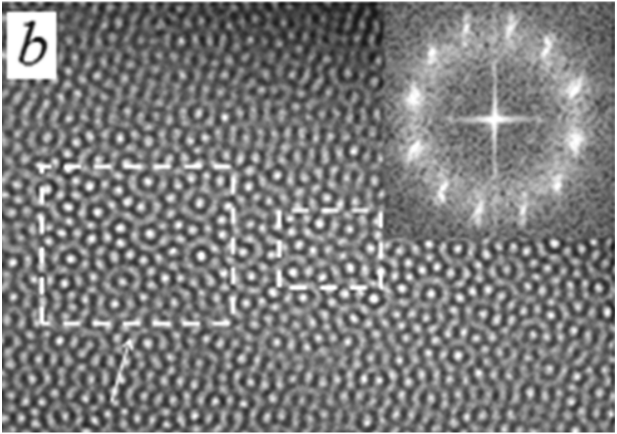
… nonlinear optics (laser with feedback):



Herrero et al. (1999)

Experimental quasipatterns IV

... block copolymers:



Zhang et al. (2012)

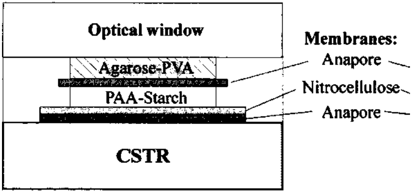
2D 12-fold quasicrystal formed by a poly(styrene-b-isoprene-b-styrene-b-ethylene oxide) tetrablock terpolymer.

Outline

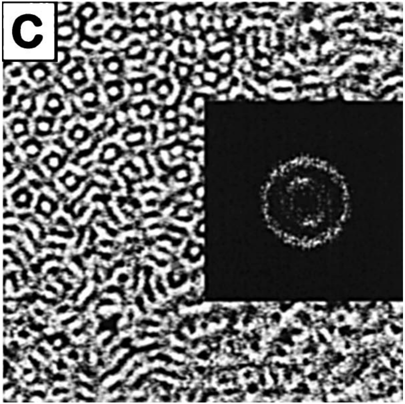
- Do quasipatterns exist as solutions of a pattern-forming PDE? (difficulty associated with small divisors, now resolved?)
- Role of three-wave interactions between two length scales in stabilising quasipatterns and producing spatiotemporal chaos
- Is this idea useful for understanding soft matter quasicrystals?

Patterns with two length scales I

Two-layer Turing patterns:

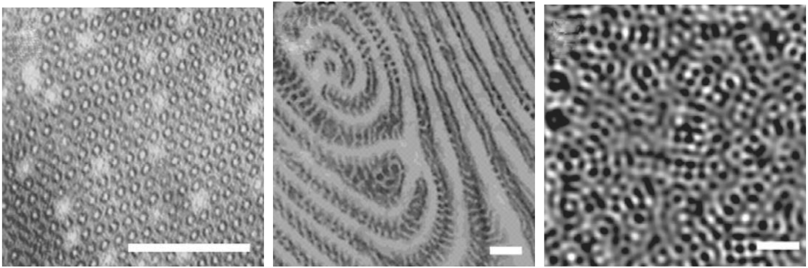


Patterns with different length-scales ($0.46\,\mathrm{mm}$ and $0.25\,\mathrm{mm}$) in the two layers are diffusively coupled



Berenstein et al. (2004)

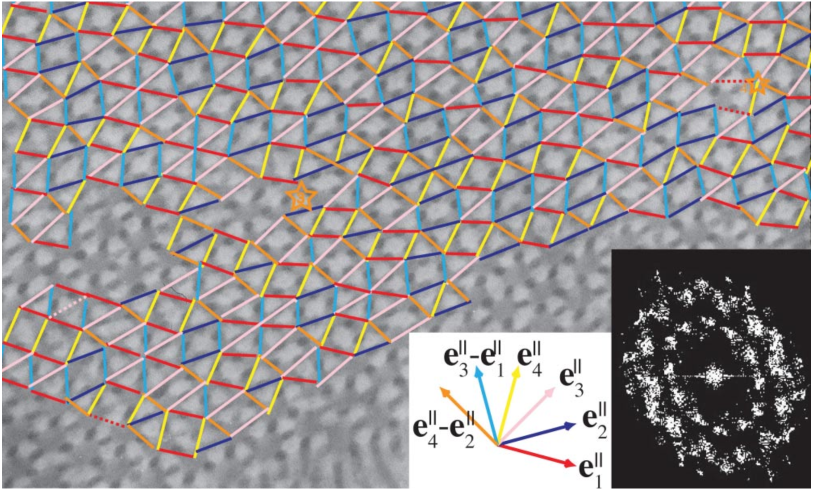
Patterns with two length scales II



Smart et al. (2008)

- Cubic micellar phase formed by poly(ethylene oxide)-poly(ethyl ethylene) in an epoxy network; disordered lamellar phase formed by poly(styrene)-block-poly(butadiene)-block-poly-(methyl methacrylate) in an epoxy network; bicontinuous phase formed by poly(ethylene oxide)-poly(butylene oxide) in water – frozen-in spatio-temporal chaos?

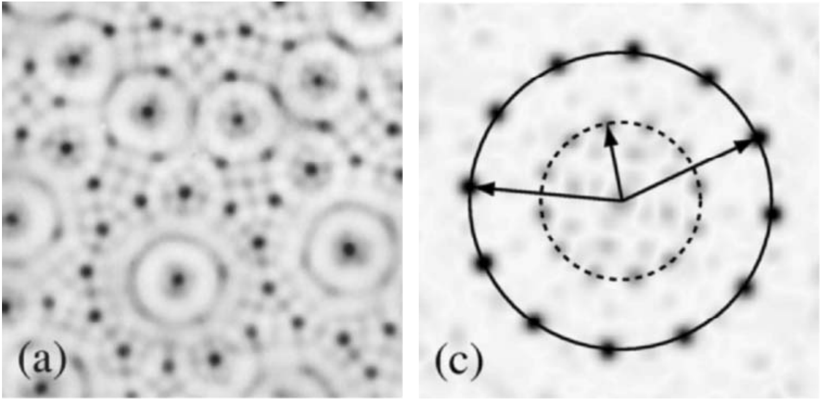
Patterns with two length scales III



Hayashida et al. (2007)

Two-dimensional 12-fold quasicrystal formed by a polyisoprene/polystyrene/poly(2-vinylpyridine) star polymer.

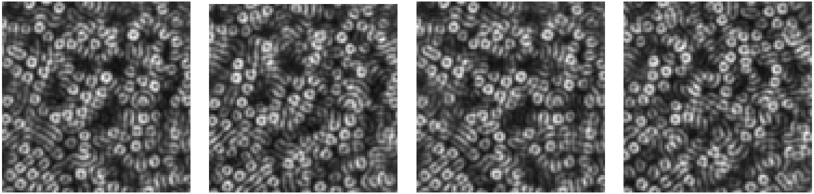
Patterns with two length scales IV



Ding & Umbanhowar (2006)

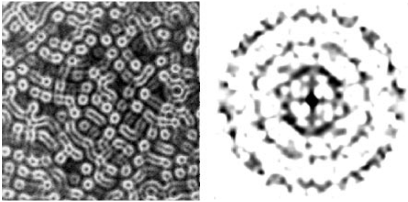
Two length scales are evident in the Fourier transform of this 12-fold quasipattern, and two vectors on the outer circle add up to one on the inner

Patterns with two length scales V



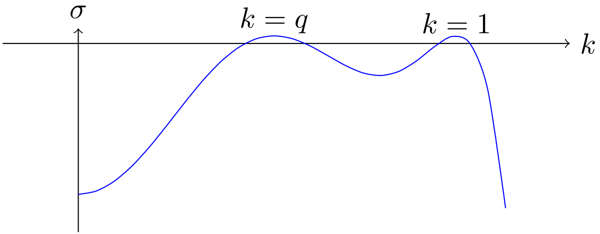
Epstein & Fineberg (2005)

Multiple length scales arise in spatiotemporal chaos: "... continually evolving irregular domains of patterns with differing spatial orientations."



Two length scales: linear theory I

Consider waves with wavenumbers $k = 1$ and $k = q$ $(q < 1)$ becoming unstable, with growth rates μ and ν respectively:

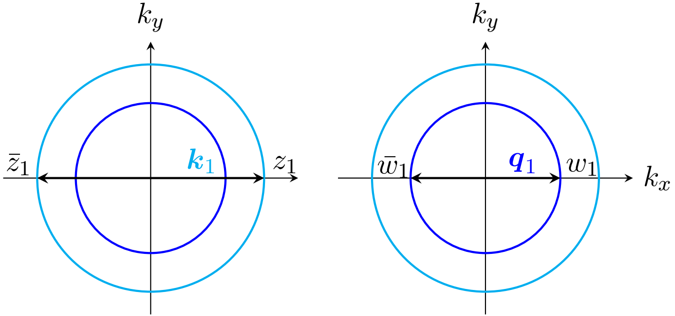


At onset, the pattern will contain an arbitrary combination of eigenfunctions: Fourier modes $e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$ with $|\boldsymbol{k}| = 1$ or $|\boldsymbol{k}| = q$:

$$\sum_{|\boldsymbol{k}_j|=1} z_j(t)e^{i\boldsymbol{k}_j\cdot\boldsymbol{x}} + \sum_{|\boldsymbol{q}_j|=q} w_j(t)e^{i\boldsymbol{q}_j\cdot\boldsymbol{x}}$$

Two length scales: linear theory II

From the multitude, focus on one wave from each of the two circles: $z_1 e^{i\boldsymbol{k}_1\cdot\boldsymbol{x}}$ and $w_1 e^{i\boldsymbol{q}_1\cdot\boldsymbol{x}}$, as well as complex conjugates:

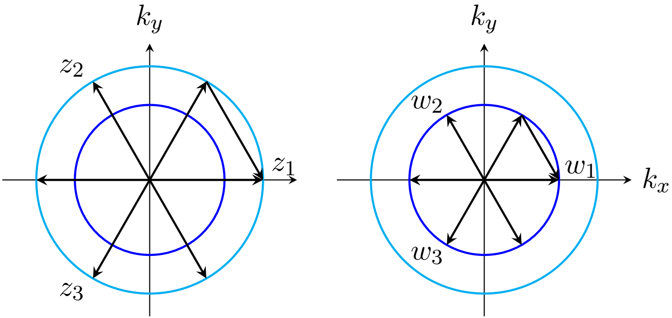


and the evolution of the amplitudes z_1 and w_1 will governed by:

$$\dot{z}_1 = \mu z_1, \qquad \dot{w}_1 = \nu w_1$$

Two length scales: nonlinear theory I

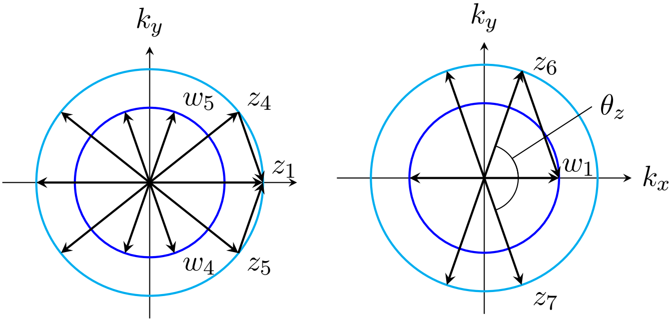
Products of waves lead to sums of wave vectors. Expanding in a power series in the small amplitude of the waves, at second order, there will be contributions from all possible three-wave interactions. The simplest interations involve modes at 60°:



$$\dot{z}_1 = \mu z_1 + Q_{zh}\bar{z}_2\bar{z}_3, \qquad \dot{w}_1 = \nu w_1 + Q_{wh}\bar{w}_2\bar{w}_3$$

Two length scales: nonlinear theory II

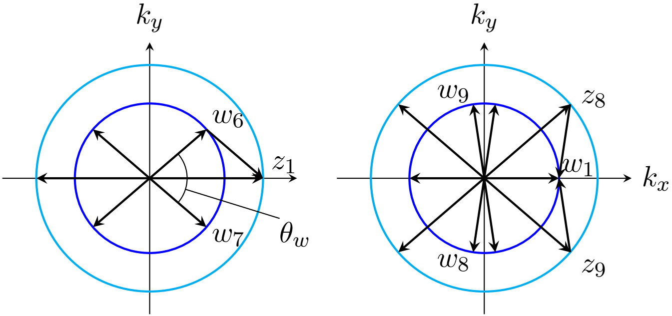
Two waves on the outer circle can couple to a wave on the inner circle: $\boldsymbol{k}_6 + \boldsymbol{k}_7 = \boldsymbol{q}_1$, defining $\theta_z = 2\arccos(q/2)$.



$$\dot{z}_1 = \cdots + Q_{zw}(z_4 w_4 + z_5 w_5), \qquad \dot{w}_1 = \cdots + Q_{zz} z_6 z_7$$

Two length scales: nonlinear theory III

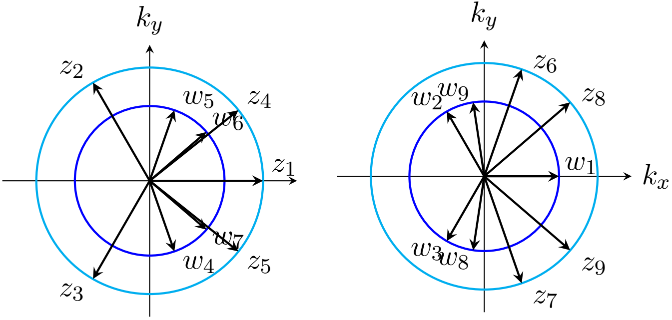
Two waves on the inner circle can couple to a wave on the outer, provided $q \geq \frac{1}{2}$: $\boldsymbol{q}_6 + \boldsymbol{q}_7 = \boldsymbol{k}_1$, defining $\theta_w = 2\arccos(1/2q)$.



$$\dot{z}_1 = \cdots + Q_{ww} w_6 w_7, \qquad \dot{w}_1 = \cdots + Q_{wz}(w_8 z_8 + w_9 z_9)$$

Two length scales: nonlinear theory IV

Putting it all together: there are 8 modes that couple to each of z_1 and w_1:

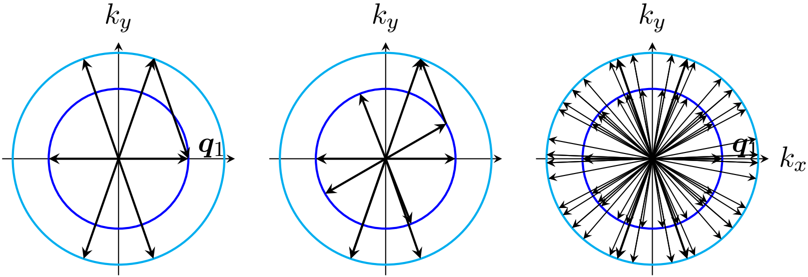


$$\dot{z}_1 = \mu z_1 + Q_{zh}\bar{z}_2\bar{z}_3 + Q_{zw}(z_4 w_4 + z_5 w_5) + Q_{ww} w_6 w_7,$$

$$\dot{w}_1 = \nu w_1 + Q_{wh}\bar{w}_2\bar{w}_3 + Q_{zz} z_6 z_7 + Q_{wz}(w_8 z_8 + w_9 z_9)$$

Two length scales: nonlinear theory V

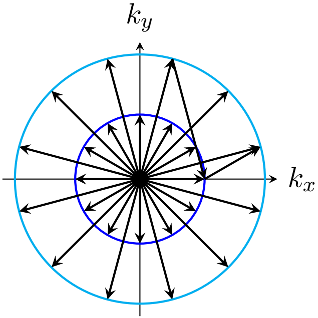
However, each z mode we've introduced couples to 8 other modes, and each w mode we've introduced couples to 8 other modes, and so on: an infinite number of modes can be generated:



Here, $q = 0.66$, $\theta_z = 141.4^\circ$, $\theta_w = 81.5^\circ$.

At cubic order, all modes couple to all other modes.

Two length scales: nonlinear theory VI



In fact, there is one value of $q = \frac{1}{2}(\sqrt{6} - \sqrt{2})$ ($\theta_z = 150^\circ$, $\theta_w = 30^\circ$) that leads to a finite number of waves, corresponding to 12-fold quasipatterns.

Is this the only q for which a finite number of waves will form a closed set under three-wave interaction? How about in three dimensions?

Three-wave interactions I

How to make progress? Pull out one of the basic three-wave interactions, two outer vectors coupling to an inner:

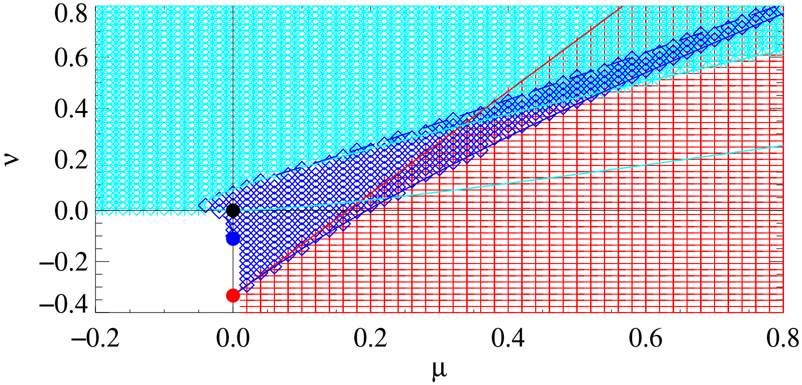
We illustrate using:

$$\begin{aligned}
\dot{z}_1 &= \mu z_1 + Q_{zw}\bar{z}_2 w_1 - (3|z_1|^2 + 6|z_2|^2 + 6|w_1|^2) z_1 \\
\dot{z}_2 &= \mu z_2 + Q_{zw}\bar{z}_1 w_1 - (6|z_1|^2 + 3|z_2|^2 + 6|w_1|^2) z_2 \\
\dot{w}_1 &= \nu w_1 + Q_{zz} z_1 z_2 - (6|z_1|^2 + 6|z_2|^2 + 3|w_1|^2) w_1
\end{aligned}$$

The outcome depends on the product of quadratic coefficients $Q_{zw}Q_{zz}$. Typically (Cf Porter & Silber 2004):

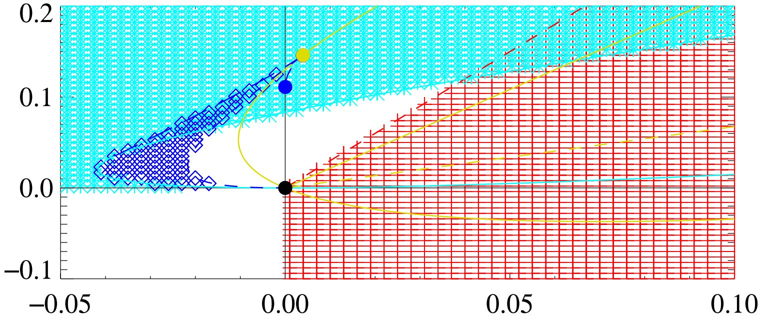
- Positive $Q_{zw}Q_{zz}$: stable steady stripes, or stable rhombs (mixed z and w);
- Negative $Q_{zw}Q_{zz}$: stable steady stripes, or time-dependent competition between z and w modes.
- Same conclusion for any of the three-wave interactions.

Three-wave interactions II



Positive $Q_{zw}Q_{zz}$: stable steady z (red) or w (cyan) stripes, or stable rhombs (blue), which are mixed z and w.

Three-wave interactions III



Negative $Q_{zw}Q_{zz}$: stable steady z or w stripes, some stable rhombs (blue), or time-dependent competition between z and w modes (empty area). (Cf Porter & Silber 2004.)

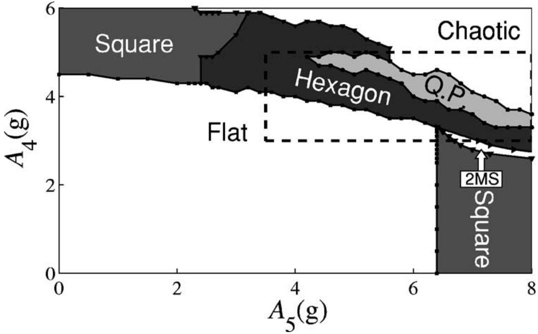
Three-wave interactions IV

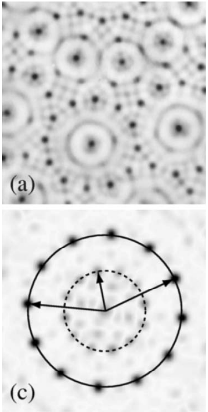
With multiple three-wave interactions, we hypothesise (wth $q > \frac{1}{2}$):

- We expect to find steady complex patterns or spatiotemporal chaos, according to the signs of $Q_{zw}Q_{zz}$ and $Q_{wz}Q_{zz}$.
- If $Q_{zw}Q_{zz}$ and $Q_{wz}Q_{zz}$ are both negative, we expect to see greater time dependence.
- These effects will be more pronounced for larger values of the products.
- With $q = \frac{1}{2}(\sqrt{6} - \sqrt{2}) = 0.5176$ we expect steady or time-dependent 12-fold quasipatterns, according to the signs of $Q_{zw}Q_{zz}$ and $Q_{wz}Q_{zz}$.

More detailed investigation is under way.

Experimental patterns I

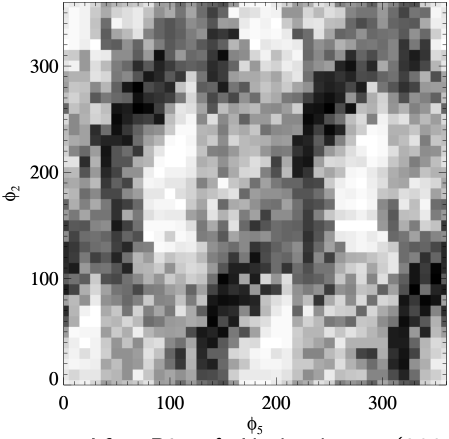




Ding & Umbanhowar (2006)

$$f(t) = a_4 \cos(4\omega t) + a_5 \cos(5\omega t + \phi_5) + a_2 \cos(2\omega t + \phi_2)$$

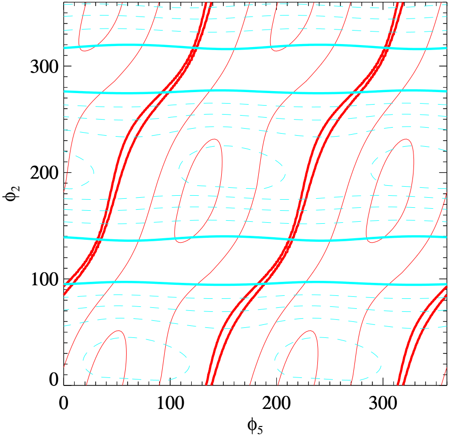
Comparison with experimental results: $q = 0.52$ I



After Ding & Umbanhowar (2006)

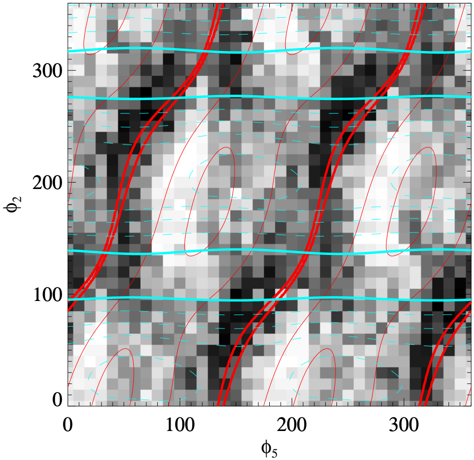
Dependence of the pattern on the phases ϕ_5 and ϕ_2, with $4 : 5 : 2$ forcing. The grey-scale is the angular autocorrelation function at 30°: white represents 12-fold quasi-patterns, black represents spatiotemporal chaos.

Comparison with experimental results: $q = 0.52$ II



Contours of $Q_{zz}Q_{zw}$ (red) and $Q_{ww}Q_{wz}$ (cyan), calculated from the Navier–Stokes equations using the methods of Skeldon & Guidoboni (2007): $Q_{zz}Q_{zw} > 0$ apart from between the thick line; $Q_{ww}Q_{wz} < 0$ apart from between the thick lines.

Comparison with experimental results: $q = 0.52$ III



Regions of 12-fold quasi-patterns correlate extremely well with regions of positive $Q_{zz}Q_{zw}$. Conversely, when $Q_{zz}Q_{zw}$ is small or negative, STC is seen.

The extra structure where the dark stripes broaden horizontally is aligned with changes in $Q_{ww}Q_{wz}$ although our expectation would be for enhanced STC where $Q_{ww}Q_{wz}$ is negative.

Model PDE I

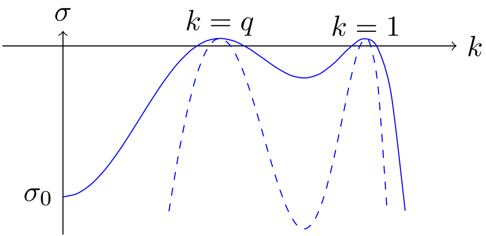
In order to explore these mode interactions in more detail, we have devised a model PDE, based on the Swift–Hohenberg equation, in which two wavenumbers can be excited:

$$\frac{\partial U}{\partial t} = \mathcal{L}(\mu, \nu, q)U + Q_1 U^2 + Q_2 U \nabla^2 U + Q_3 |\nabla U|^2 - U^3$$

Muller (1994), Frisch & Sonnino (1995) and Lifshitz & Petrich (1997) have written down similar models.

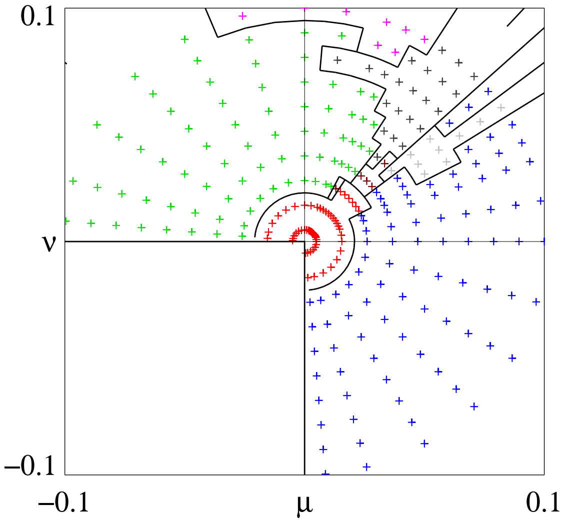
The linear operator $\mathcal{L}$ defined by its dispersion relation: $\mathcal{L}(e^{ikx}) = \sigma(k)e^{ikx}$.

Model PDE II



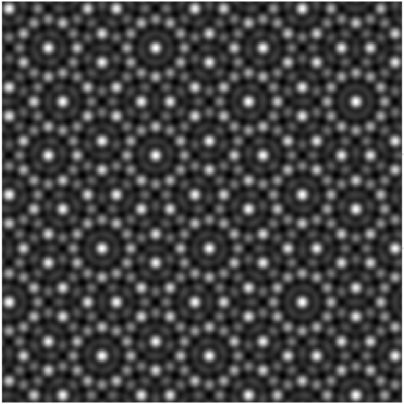
- $\sigma(1) = \mu$ and $\sigma(q) = \nu$, so the growth rates of the two modes of interest are directly controllable.
- $\sigma'(1) = 0$ and $\sigma'(q) = 0$, so the growth rates are maxima at $k = 1$ and $k = q$.
- $\sigma(-k) = \sigma(k)$, so $\mathcal{L}$ can be written in terms of Laplacians.
- The depth of the minimum between $k = 1$ and $k = q$, and the width of the bands of excited modes, are controlled by $\sigma(0) = \sigma_0 < 0$.

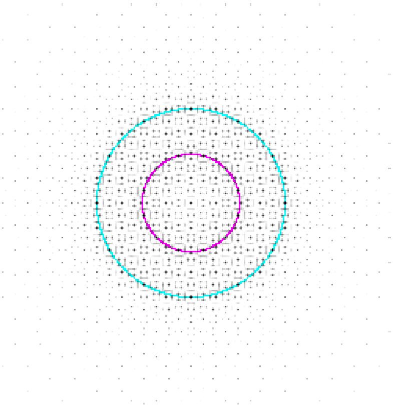
Model PDE III



$q = 0.5176,\ Q_{zz}Q_{zw} > 0,\ Q_{ww}Q_{wz} > 0$

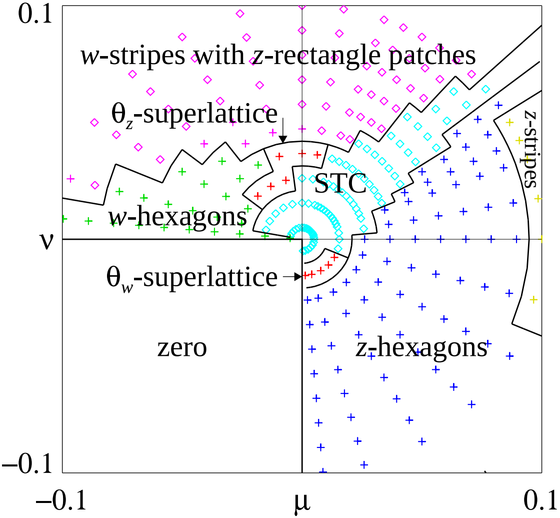
Model PDE IV





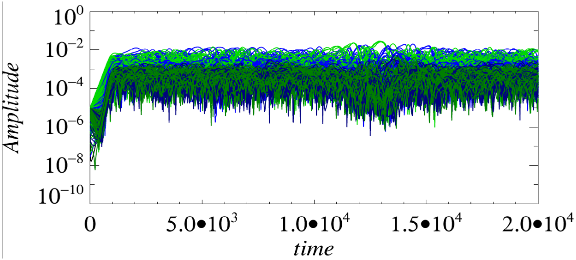
$q = 0.5176,\ Q_1 = 0.3,\ Q_2 = 0,\ Q_3 = 0,\ \sigma_0 = -10$
$\mu = \nu = 0.0035355.$

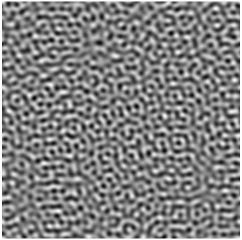
Model PDE V

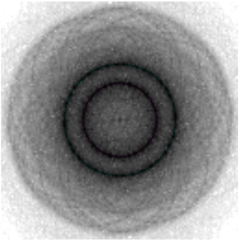


$q = 0.66,\ Q_{zz}Q_{zw} < 0,\ Q_{ww}Q_{wz} < 0$

Model PDE VI







Typical example of STC, with $q = 0.66$, $\sigma_0 = -2$, $Q_1 = 0.3$, $Q_2 = 1.3$, $Q_3 = 1.7$ (so $Q_{zz}Q_{zw} < 0$ and $Q_{ww}Q_{wz} < 0$), and $\mu = \nu = 0.00707$. The two critical circles are clearly seen in the power spectrum. The correlation length is about 1–2 wavelengths.

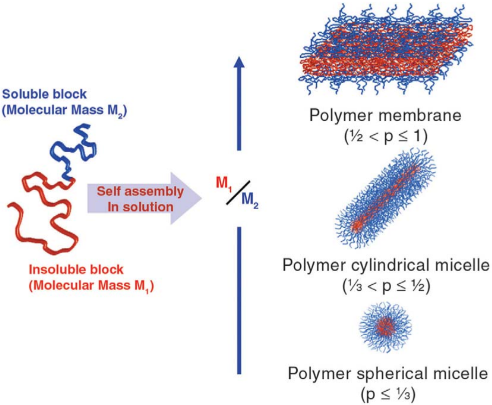
R, Silber & Skeldon (2012)

Conclusions (part I)

- If the ratio of wavenumbers q is between $\frac{1}{2}$ and 2, mode interactions in both directions must be taken in to account.
- Most values of q in this range lead to the possibility of generating an infinite number of interacting waves. The exceptions is $q = \frac{1}{2}(\sqrt{6} - \sqrt{2})$ associated 12-fold quasipatterns. In fact, this is by far the most common 2D quasipattern.
- The outcome of the mode interactions will be influenced by the signs of the quadratic coefficients, with time-dependence (and spatiotemporal chaos) most likely in the case of (both pairs of) quadratic coefficients with opposite sign.
- These ideas align with the experiments of Ding & Umbanhowar (2006) and in a model PDE (further investigation in progress).
- How to deal with a fully occupied circle of waves?

Application to soft-matter quasicrystals I

- Micelles formed from (for example) branched polymers or block co-polymers can make a stiff inner hydrophobic polymer core surrounded by a corona of hydrophillic polymer chains with a varying degree of flexibility.



Smart et al. (2008)

Application to soft-matter quasicrystals II

- Colloids made from micelles can self-assemble into crystalline and quasicrystalline structures.
- The idea that having micelles with two length scales may be responsible for stabilising soft-matter quasicrystals was been proposed by Lifshitz & Diamant (2007) and by Engel & Trebin (2007), but the connection (from the physics of the polymers to pattern formation) has not been made quantitative.
- A possible route to a quantitative connection is through Density Functional Theory (DFT) and Phase Field Crystals (PFC), well suited to the study of freezing and crystallisation of liquids and colloids.

Density Functional Theory I

- A Helmholtz free energy $\mathcal{F}$ is defined as a functional depending on the density $\rho(\boldsymbol{x})$ of the particles, which interact via a pair potential $V(r)$:

$$\mathcal{F} = kT\int \rho(\boldsymbol{x})\left(\log\rho(\boldsymbol{x}) - 1\right)\, d\boldsymbol{x} + \frac{1}{2}\iint \rho(\boldsymbol{x})V(|\boldsymbol{x}-\boldsymbol{x}'|)\rho(\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}',$$

  where T is temperature, k is Boltzmann's constant.
- The first term is the ideal-gas (entropic) contribution and the second term arises from the interactions between particles.
- The task is to find the density distribution that minimises the grand potential $\Omega = \mathcal{F} - \mu\int\rho(\boldsymbol{x})d\boldsymbol{x}$, where μ is the chemical potential.
- This is equivalent to performing a minimisation on $\mathcal{F}$, subject to the constraint that the number of particles $N = \int\rho(\boldsymbol{x})d\boldsymbol{x}$ in the system is fixed.

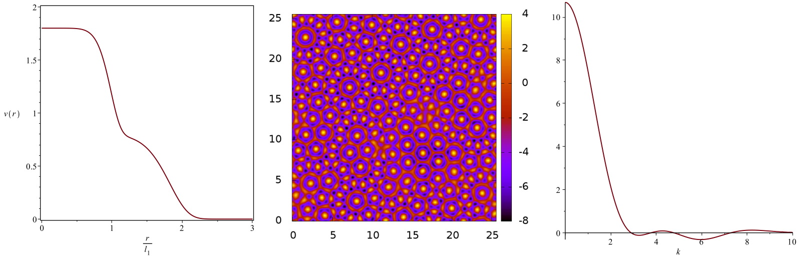
Density Functional Theory II

- There is also Dynamic Density Functional Theory (DDFT):

$$\frac{\partial \rho}{\partial t} = M \nabla \cdot \rho \nabla \frac{\delta \mathcal{F}}{\delta \rho},$$

  where $\frac{\delta \mathcal{F}}{\delta \rho}$ is the functional derivative of $\mathcal{F}$, so equilibrium states will correspond to extrema of $\mathcal{F}$ and where M is the particle mobility.
- In the fluid state, the density $\rho(\boldsymbol{x})$ that minimises the free energy takes a uniform constant value ρ_0.
- As the temperature is lowered, there is a transition to $\mathcal{F}$ being minimised by different crystalline (or quasicrystalline) density distributions.

Density Functional Theory III



- Left: potential $V(r)$ with two length scales:

$$V(r) = V_1 e^{-(r/l_1)^8} + V_2 e^{-(r/l_2)^8},$$

  with $V_1 = 1$, $V_2 = 0.8$, $l_1 = 1$, $l_2 = 1.855$. Centre: density $\rho(x, y)$ (log scale) that minimises $\mathcal{F}$, with an average density $\rho_0 = 3.5$. Right: Fourier transform $\hat{V}(k)$.
- This type of potential may be appropriate as a simple model for soft matter.

Phase Field Crystals I

- The connection between DDFT and pattern formation is made through a Phase Field Crystal (PFC) model.
- These models may be derived by making a Taylor expansion around the uniform fluid in powers of $\Delta\rho(\boldsymbol{x}) = \rho(\boldsymbol{x}) - \rho_0$:

$$\mathcal{F}(\rho(\boldsymbol{x})) = \mathcal{F}(\rho_0) - \frac{kT}{2} \iint \Delta\rho(\boldsymbol{x}) C^{(2)}(\boldsymbol{x}, \boldsymbol{x}') \Delta\rho(\boldsymbol{x}') d\boldsymbol{x} d\boldsymbol{x}' + \mathcal{O}(\Delta\rho^3)$$

- In this expansion, the nth term involves the n-point direct correlation functions $C^{(n)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n)$.
- The $n = 1$ term can be absorbed into the chemical potential term in Ω.
- The $n = 2$ term involves $C^{(2)}(\boldsymbol{x}, \boldsymbol{x}')$, which is the pair direct correlation function, whose Fourier transform is simply related to the fluid static structure factor. The theory is often truncated after this term.

Phase Field Crystals II

- In situations with one length scale l_1, the 2-point correlation function $C^{(2)}$ will be peaked when $|\boldsymbol{x} - \boldsymbol{x}'| \approx l_1$, and the Fourier transform of this will be peaked at $k_1 = 2\pi/l_1$.
- Expanding about this peak in Fourier space results in writing

$$C^{(2)}(\boldsymbol{x}, \boldsymbol{x}') = -(\hat{C}_0^{(2)} + \hat{C}_2^{(2)}\nabla^2 + \hat{C}_4^{(2)}\nabla^4 + \dots)\delta(\boldsymbol{x} - \boldsymbol{x}'),$$

  where the coeficients are often assumed to be constants.
- The evolution equation becomes (after further scaling)

$$\frac{\partial U}{\partial t} = -\nabla^2 \left(\mu U - \left(1 + \nabla^2\right)^2 U + Q_1 U^2 - U^3\right) + \\ + Q_2 \nabla \cdot \left(U \nabla \left(1 + \nabla^2\right)^2 U\right)$$

  where $U(\boldsymbol{x}, t)$ is proportional to $\rho - \rho_0$, and μ, Q_1 and Q_2 are related to constants and coefficients defined above.

Phase Field Crystals III

- The classic PFC model (Elder et al. 2002) is recovered by asserting that the term proportional to Q_2 is formally higher order and can be dropped.
- This model is equivalent to the negative Laplacian of the one of the archetypal models of pattern formation, the Swift–Hohenberg equation:

$$\frac{\partial U}{\partial t} = \mu U - (1 + \nabla^2)^2 U + Q_1 U^2 - U^3,$$

  a model with one length scale that produces steady stripes and hexagons when solved in two dimensions.
- PFC models are faster to solve than analagous DDFT models and their analysis is easier.
- The drawbacks of PFC models relate to the approximations made in the expansions, but do seem to be good for some soft matter systems.

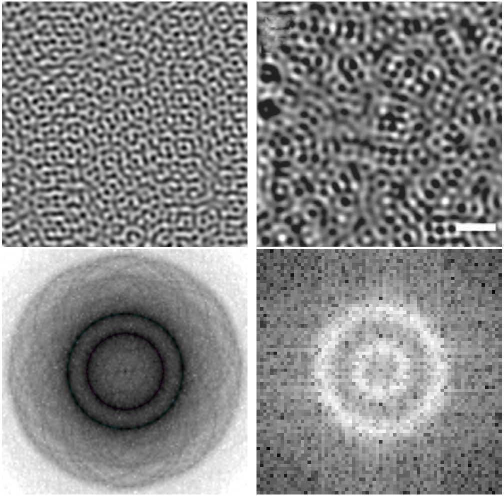
Phase Field Crystals IV

- Two length scales can be introduced in DDFT through a complex potential $V(r)$ (as above) or by having two different-sized components with densities ρ_A and ρ_B and corresponding potentials V_{AA}, V_{AB} and V_{BB}.
- In both cases, a proper reduction to a PFC model has not been made.
- Even before carrying out a proper reduction, we expect that potentials with two length scales will produce PFC models where two wavenumbers might be linearly unstable or weakly damped (Barkan, Diamant & Lifshitz 2011).
- Expanding $C^{(2)}$ in derivatives up to 8th order, the linear part of such a model could look like:

$$\frac{\partial U}{\partial t} = -\nabla^2(q^2 + \nabla^2)^2(1 + \nabla^2)^2 U$$

where the two neutrally stable wavenumbers are q and 1.

Phase Field Crystals V



- Left: model PDE; right: block copolymer bicontinuous phase
- Two length scales might come from the core and corona?

Phase Field Crystals VI

- Filling in all the missing steps should allow a quantitative connection to be made from DFT to the pattern formation analysis that can help understand why certain arrangements (quasicrystals or frozen-in spatio-temporal chaos) are stable.
- The Random Phase Approximation gives potentials that accurately describe flexible polymers that obey Gaussian chain statistics (Leibler 1980), and it is already known that potentials with two length scales can be found (Nap & ten Brinke 2002).
- This could involve treating the micelles as particles, or working directly with the polymer.

Conclusions (part II)

- Ideas from pattern formation with two length scales may be useful in understanding soft-matter quasicrystals.
- The connection between physics (DFT) and mathematics (pattern formation models) is made through the expaning densities and gradients about the homogeneous liquid state.
- The analysis would involve (for example) computing the quadratic coefficients that govern three-wave interactions in problems with two length scales.
- Extension to three dimensions.
- In soft-matter quasicrystals, the two length scales are associated with the core and corona of the micelles; in turn these set by the polymer architecture.
- In metallic quasicrystals, the two length scales could come from the different sizes of the atoms that make up the quasicrystalline alloy.