

S12.A.2. Fluctuations in the Brusselator

Chemical crystals (or **Turing structures**) are stationary chemical concentration patterns (dissipative structures) that emerge far from chemical equilibrium in non-linear reaction-diffusion processes involving highly different diffusion coefficients. It was first realized using the **CIMA** (Chlorite Iodide Malonic Acid) reaction in a 2-D gel.

S12.A.2.1. Equations of Motion & Stability Analysis

Consider rate equations of the Brusselator [see (12.53-4) of §12.D.1],

$$\frac{\partial X}{\partial \tau} = A - (B+1)X + X^2 Y + D_x \nabla_r^2 X \quad (12.53)$$

$$\frac{\partial Y}{\partial \tau} = BX - X^2 Y + D_y \nabla_r^2 Y \quad (12.54)$$

with the equilibrium values

$$X_0 = A \quad \& \quad Y_0 = \frac{B}{A} \quad (12.55)$$

Setting

$$X(\mathbf{r}, t) = A + \delta x(\mathbf{r}, t) \quad Y(\mathbf{r}, t) = \frac{B}{A} + \delta y(\mathbf{r}, t) \quad (12.135a)$$

while introducing the chemical noise concentrations $\xi_x(\mathbf{r}, t)$ & $\xi_y(\mathbf{r}, t)$, we have

$$\begin{aligned} \frac{\partial \delta x}{\partial \tau} &= A - (B+1)(A + \delta x) + (A + \delta x)^2 \left(\frac{B}{A} + \delta y \right) + D_x \nabla_r^2 \delta x + \xi_x \\ &= (B-1) \delta x + \frac{B}{A} (\delta x)^2 + 2A \delta x \delta y + (\delta x)^2 \delta y + D_x \nabla_r^2 \delta x + \xi_x \end{aligned} \quad (12.135)$$

and

$$\begin{aligned} \frac{\partial \delta y}{\partial \tau} &= B(A + \delta x) - (A + \delta x)^2 \left(\frac{B}{A} + \delta y \right) + D_y \nabla_r^2 \delta y + \xi_y \\ &= -B \delta x - A^2 \delta y - \frac{B}{A} (\delta x)^2 - 2A \delta x \delta y - (\delta x)^2 \delta y + D_y \nabla_r^2 \delta y + \xi_y \end{aligned} \quad (12.136)$$

Keeping only linear terms, we get

$$\begin{aligned} \frac{\partial \delta x}{\partial \tau} &= (B-1) \delta x + A^2 \delta y + D_x \nabla_r^2 \delta x + \xi_x \\ \frac{\partial \delta y}{\partial \tau} &= -B \delta x - A^2 \delta y + D_y \nabla_r^2 \delta y + \xi_y \end{aligned}$$

which Fourier transforms

$$\begin{aligned} -i\omega \tilde{x}_k(\omega) &= (B-1) \tilde{x}_k(\omega) + A^2 \tilde{y}_k(\omega) - D_x k^2 \tilde{x}_k(\omega) + \tilde{\xi}_{xk}(\omega) \\ -i\omega \tilde{y}_k(\omega) &= -B \tilde{x}_k(\omega) - A^2 \tilde{y}_k(\omega) - D_y k^2 \tilde{y}_k(\omega) + \tilde{\xi}_{yk}(\omega) \end{aligned}$$

that can be put into matrix form as

$$-i\omega \begin{pmatrix} \tilde{x}_k(\omega) \\ \tilde{y}_k(\omega) \end{pmatrix} - \begin{pmatrix} B-1 - k^2 D_x & A^2 \\ -B & -A^2 - k^2 D_y \end{pmatrix} \begin{pmatrix} \tilde{x}_k(\omega) \\ \tilde{y}_k(\omega) \end{pmatrix} = \begin{pmatrix} \tilde{\xi}_{xk}(\omega) \\ \tilde{\xi}_{yk}(\omega) \end{pmatrix} \quad (12.137)$$

or [c.f. (12.64) of §12.D.2]

$$(-i\omega \mathbb{I} - \mathbb{M}) \begin{pmatrix} \tilde{x}_k(\omega) \\ \tilde{y}_k(\omega) \end{pmatrix} = \begin{pmatrix} \tilde{\xi}_{xk}(\omega) \\ \tilde{\xi}_{yk}(\omega) \end{pmatrix} \quad (12.137a)$$

where

$$\mathbb{M} = \begin{pmatrix} B - 1 - k^2 D_x & A^2 \\ -B & -A^2 - k^2 D_y \end{pmatrix} \quad (12.138)$$

The eigenvalues of \mathbb{M} are given by (12.67) as

$$-i\omega_{\pm} = \frac{1}{2} \left[C_1 - C_2 \pm \sqrt{(C_1 + C_2)^2 - 4A^2 B} \right] \quad (12.138a)$$

where [see (12.66)]

$$C_1 = B - 1 - D_x k^2 \quad \text{and} \quad C_2 = A^2 + D_y k^2 \quad (12.138b)$$

The critical mode for purely spatial oscillation occurs when one of the real $i\omega$ eigenvalues vanishes.

This happens if [see (12.69)]

$$C_1 C_2 - A^2 B = 0 \quad (12.138c)$$

so that [see (12.70)]

$$\tilde{B}_c = 1 + \frac{D_x}{D_y} A^2 + \frac{A^2}{D_y k^2} + D_x k^2 \quad (12.138d)$$

where

$$k^2 = \frac{n^2 \pi^2}{L^2}$$

The minimum value of \tilde{B}_c occurs at

$$\frac{\partial \tilde{B}_c}{\partial k^2} = 0 = -\frac{A^2}{D_y k^4} + D_x$$

which gives the critical value of k^2 as

$$k_c^2 = \frac{A}{\sqrt{D_x D_y}} \quad (12.138e)$$

Putting this back into (12.138d) gives the critical value

$$B_c = \tilde{B}_c \Big|_{k=k_c} = 1 + \frac{D_x}{D_y} A^2 + 2A \sqrt{\frac{D_x}{D_y}} = \left(1 + A \sqrt{\frac{D_x}{D_y}} \right)^2 \quad (12.138f)$$

The eigenvalues of the critical matrix

$$\mathbb{M}_c = \mathbb{M} \Big|_{\substack{B=B_c \\ k=k_c}} = \begin{pmatrix} B_c - 1 - k_c^2 D_x & A^2 \\ -B_c & -A^2 - k_c^2 D_y \end{pmatrix}$$

are [see §Code]

$$\lambda_s = 0$$

and

$$\lambda_f = A^2 \left(-1 + \frac{D_x}{D_y} + \frac{1}{D_y k_c^2} \right) - D_y k_c^2$$

$$\begin{aligned}
&= A^2 \left(-1 + \frac{D_x}{D_y} + \frac{1}{A} \sqrt{\frac{D_x}{D_y}} \right) - A \sqrt{\frac{D_y}{D_x}} \\
&= A \left(-A + A \frac{D_x}{D_y} + \sqrt{\frac{D_x}{D_y}} - \sqrt{\frac{D_y}{D_x}} \right) \tag{12.139}
\end{aligned}$$

where λ_s is the slow mode with the (unnormalized) left and right eigenvectors [see §Code]

$$\chi_s^c = \left(1 + \frac{1}{A} \sqrt{\frac{D_y}{D_x}}, 1 \right) \quad \psi_s^c = \left(-\frac{A D_y}{A D_x + \sqrt{D_x} \sqrt{D_y}}, 1 \right) \tag{12.140}$$

and

$$\chi_s^c \cdot \psi_s^c = 1 - \frac{D_y}{D_x}$$

In general, the diffusion coefficients for chemical reactions in fluids are of the same order of magnitude. Hence, $D_x \approx D_y$, so that $\lambda_f \approx 0$. There is no separation of time scales so that no Turing structure occurs. This is remedied by placing the CIMA reaction in a gel so that the diffusion coefficients can be changed and separated in value.

Setting

$$B = B_c + \delta B \quad k^2 = k_c^2 + \delta k$$

we can expand (12.138) near the critical point. Keeping only terms $O(\delta B)$ and $O(\delta k)^2$, we get

$$\begin{aligned}
\delta \mathbf{M} &= \mathbf{M} - \mathbf{M}_c \\
&= \begin{pmatrix} \frac{(A^2 D_x + D_y) \delta B + A \left[(-1 + \delta k) \delta k + 2 \delta B \right] \sqrt{D_x D_y}}{D_y} & 0 \\ -\frac{(A^2 D_x + D_y) \delta B + A \left[2 \delta B + (\delta k)^2 \right] \sqrt{D_x D_y}}{D_y} & -\frac{A D_y \delta k}{\sqrt{D_x D_y}} \end{pmatrix}
\end{aligned}$$

The eigenvalue of the slow mode near the critical point is therefore [see (12.122e) of §S12.A.1]

$$\begin{aligned}
\lambda_s &\approx \frac{1}{\chi_s^c \cdot \psi_s^c} \chi_s^c \cdot \delta \mathbf{M} \cdot \psi_s^c \\
&= -\left(\left(\sqrt{D_y} \left\{ \left(A^2 D_x + D_y + 2 A \sqrt{D_x D_y} \right) \delta B + A \sqrt{D_x D_y} (\delta k)^2 \right\} \right) / \left(\left(A \sqrt{D_x} + \sqrt{D_y} \right) (D_x - D_y) \right) \right) \\
&= -\frac{1}{\sqrt{B_c} (D_x - D_y)} \left[D_y B_c \delta B + D_x D_y k_c^2 (\delta k)^2 \right] \\
&= -\frac{1}{\sqrt{B_c} (D_x - D_y)} \left[D_y (B - B_c) + \frac{D_x D_y}{k_c^2} (k^2 - k_c^2)^2 \right] \\
&= -\frac{1}{\sqrt{B_c} (D_x - D_y)} \left[D_y (B - B_c) + \frac{(D_x D_y)^{3/2}}{A} (k^2 - k_c^2)^2 \right]
\end{aligned}$$

$$= -\frac{1}{A\sqrt{B_c}(D_x - D_y)} \left[A \sqrt{\frac{D_y}{D_x}} (B - B_c) + D_x D_y (k^2 - k_c^2)^2 \right] \quad (12.141)$$

Code

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M =  $\begin{pmatrix} c1 & A^2 \\ -B & -c2 \end{pmatrix}$ 
{{c1, A^2}, {-B, -c2}}

subC = {c1 → B - 1 - k^2 Dx, c2 → A^2 + k^2 Dy};
subB = {B → 1 +  $\frac{Dx}{Dy} A^2 + \frac{A^2}{Dy k^2} + Dx k^2$ };

subk = {k →  $\sqrt{\frac{A}{\sqrt{Dx Dy}}}$ } // PowerExpand;

M1 = M /. subC;
M1 // MatrixForm
 $\begin{pmatrix} -1 + B - Dx k^2 & A^2 \\ -B & -A^2 - Dy k^2 \end{pmatrix}$ 

(* eigenvalues & right eigenvectors *)
{λ, evR} = Eigensystem[M]
{{ $\frac{1}{2} \left( c1 - c2 - \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2} \right)$ ,  $\frac{1}{2} \left( c1 - c2 + \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2} \right)$ },
{{ $-\frac{c1 + c2 - \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2}}{2 B}$ , 1}, {- $\frac{c1 + c2 + \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2}}{2 B}$ , 1}}}

(* eigenvalues & left eigenvectors *)
{λ, evL} = Eigensystem[M^T]
{{ $\frac{1}{2} \left( c1 - c2 - \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2} \right)$ ,  $\frac{1}{2} \left( c1 - c2 + \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2} \right)$ },
{{ $-\frac{-c1 - c2 + \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2}}{2 A^2}$ , 1}, {- $\frac{-c1 - c2 - \sqrt{-4 A^2 B + c1^2 + 2 c1 c2 + c2^2}}{2 A^2}$ , 1}}}

(* eigenvalues at critical point *)
(λ /. c1 → A^2 B / c2) // Simplify // PowerExpand // Simplify
{ $\frac{A^2 B}{c2} - c2, \theta$ }

Bc = B /. subB
1 +  $\frac{A^2 Dx}{Dy} + \frac{A^2}{Dy k^2} + Dx k^2$ 

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B /. subB /. subk // Simplify

$$\frac{(A \sqrt{Dx} + \sqrt{Dy})^2}{Dy}$$

$\lambda c = ((\lambda /. subC) /. subB) // Simplify // PowerExpand // Simplify$

$$\{A^2 \left(-1 + \frac{Dx}{Dy} + \frac{1}{Dy k^2}\right) - Dy k^2, \theta\}$$

$\lambda c /. subk // Simplify // PowerExpand // Simplify // Expand$

$$\left\{-A^2 + \frac{A^2 Dx}{Dy} + \frac{A \sqrt{Dx}}{\sqrt{Dy}} - \frac{A \sqrt{Dy}}{\sqrt{Dx}}, \theta\right\}$$

eq = (c1 c2 == A^2 Bc /. subC) /. B → Bc // Simplify

True

(evL[[1]] /. subC) /. subB // Expand // Simplify // PowerExpand // Simplify // Expand

$$\left\{\frac{Dx}{Dy} + \frac{1}{Dy k^2}, 1\right\}$$

evLc = (((evL[[1]] /. subC) /. subB) /. subk) // Expand // Simplify // PowerExpand // Simplify // Expand

$$\left\{1 + \frac{\sqrt{Dy}}{A \sqrt{Dx}}, 1\right\}$$

evRc = (((evR[[1]] /. subC) /. subB) /. subk) // Expand // Simplify // PowerExpand // Simplify // Expand

$$\left\{-\frac{A Dy}{A Dx + \sqrt{Dx} \sqrt{Dy}}, 1\right\}$$

(* Normalization constant *)

NN = evLc.evRc // Simplify

$$1 - \frac{Dy}{Dx}$$

Mc =

$$\left(\left(M /. subC\right) /. subB\right) /. k \rightarrow \sqrt{k2c} // Expand // Simplify // PowerExpand // Simplify // Expand$$

$$\left\{\left\{\frac{A^2 Dx}{Dy} + \frac{A^2}{Dy k2c}, A^2\right\}, \left\{-1 - \frac{A^2 Dx}{Dy} - \frac{A^2}{Dy k2c} - Dx k2c, -A^2 - Dy k2c\right\}\right\}$$

MM = (M1 //. {B → Bc (1 + δB), k → √k2}) /. {k2 → k2c (1 + δk)} // Simplify

$$\left\{\left\{\left(\left(1 + Dx k2c (1 + \delta k)\right) \left(A^2 (1 + \delta B) + Dy k2c \delta B (1 + \delta k)\right)\right) / \left(Dy k2c (1 + \delta k)\right), A^2\right\}, \left\{-\left(\left(1 + \delta B\right) \left(1 + Dx k2c (1 + \delta k)\right) \left(A^2 + Dy k2c (1 + \delta k)\right)\right) / \left(Dy k2c (1 + \delta k)\right), -A^2 - Dy k2c (1 + \delta k)\right\}\right\}$$

(* perturbed term δM *)

(MMp = (((MM + O[δk] ^ 3) // Normal) + O[δB] ^ 2) // Normal) // MatrixForm

(δM = MMp - Mc) // Expand // Simplify // MatrixForm

$$\left(\begin{array}{cc} \frac{A^2 + A^2 D_x k_{2c} - A^2 \delta k + A^2 \delta k^2}{D_y k_{2c}} + \frac{\delta B (A^2 + A^2 D_x k_{2c} + D_y k_{2c} + D_x D_y k_{2c}^2 - A^2 \delta k + D_x D_y k_{2c}^2 \delta k + A^2 \delta k^2)}{D_y k_{2c}} & \\ -\frac{A^2 - A^2 D_x k_{2c} - D_y k_{2c} - D_x D_y k_{2c}^2 + A^2 \delta k - D_x D_y k_{2c}^2 \delta k - A^2 \delta k^2}{D_y k_{2c}} + \frac{\delta B (-A^2 - A^2 D_x k_{2c} - D_y k_{2c} - D_x D_y k_{2c}^2 + A^2 \delta k - D_x D_y k_{2c}^2 \delta k - A^2 \delta k^2)}{D_y k_{2c}} & -A^2 - D_y k_{2c} \end{array} \right)$$

$$\left(\begin{array}{cc} \frac{D_y k_{2c} \delta B (1 + D_x k_{2c} (1 + \delta k)) + A^2 ((-1 + \delta k) \delta k + \delta B (1 + D_x k_{2c} - \delta k + \delta k^2))}{D_y k_{2c}} & \theta \\ -\frac{D_y k_{2c} (\delta B + D_x k_{2c} \delta B + D_x k_{2c} \delta k + D_x k_{2c} \delta B \delta k) + A^2 ((-1 + \delta k) \delta k + \delta B (1 + D_x k_{2c} - \delta k + \delta k^2))}{D_y k_{2c}} & -D_y k_{2c} \delta k \end{array} \right)$$

δM /. {Dx → D_x, Dy → D_y, k2c → k_c²} // MatrixForm

$$\left(\begin{array}{cc} -\frac{A^2 D_x}{D_y} - \frac{A^2}{D_y k_c^2} + \frac{A^2 - A^2 \delta k + A^2 \delta k^2 + A^2 D_x k_c^2}{D_y k_c^2} + \frac{\delta B (A^2 - A^2 \delta k + A^2 \delta k^2 + A^2 D_x k_c^2 + D_y k_c^2 + D_x D_y k_c^4 + \delta k D_x D_y k_c^4)}{D_y k_c^2} & \\ 1 + \frac{A^2 D_x}{D_y} + \frac{A^2}{D_y k_c^2} + D_x k_c^2 + \frac{-A^2 + A^2 \delta k - A^2 \delta k^2 - A^2 D_x k_c^2 - D_y k_c^2 - D_x D_y k_c^4 - \delta k D_x D_y k_c^4}{D_y k_c^2} + \frac{\delta B (-A^2 + A^2 \delta k - A^2 \delta k^2 - A^2 D_x k_c^2 - D_y k_c^2 - D_x D_y k_c^4 - \delta k D_x D_y k_c^4)}{D_y k_c^2} & \end{array} \right)$$

δM /. {Dx → D_x, Dy → D_y, k2c → $\frac{A}{\sqrt{D_x D_y}}$ } // FullSimplify // MatrixForm

$$\left(\begin{array}{cc} \frac{A^2 \delta B D_x + \delta B D_y + A ((-1 + \delta k) \delta k + \delta B (2 + \delta k^2)) \sqrt{D_x D_y}}{D_y} & \theta \\ -\frac{A^2 \delta B D_x + \delta B D_y + A (2 \delta B + (1 + \delta B) \delta k^2) \sqrt{D_x D_y}}{D_y} & -\frac{A \delta k D_y}{\sqrt{D_x D_y}} \end{array} \right)$$

$\lambda_s = \frac{1}{NN} \text{evLc} . \delta M . \text{evRc}$ /. k2c → $\frac{A}{\sqrt{D_x D_y}}$ // FullSimplify

$$- \left(\left(\sqrt{D_y} \left(A^2 D_x \delta B + D_y \delta B + A \sqrt{D_x D_y} (\delta k^2 + \delta B (2 + \delta k^2)) \right) \right) / \left(\left(A \sqrt{D_x} + \sqrt{D_y} \right) (D_x - D_y) \right) \right)$$

λ_s /. {Dx → D_x, Dy → D_y}

$$- \left(\left(\sqrt{D_y} \left(A^2 \delta B D_x + \delta B D_y + A (\delta k^2 + \delta B (2 + \delta k^2)) \sqrt{D_x D_y} \right) \right) / \left(\left(A \sqrt{D_x} + \sqrt{D_y} \right) (D_x - D_y) \right) \right)$$

(* correction to λ_s due to δB *)

Coefficient[λ_s , δB] /. $\delta k \rightarrow \theta$ /. {Dx → D_x, Dy → D_y} // Simplify

$$-\frac{\sqrt{D_y} \left(A^2 D_x + D_y + 2 A \sqrt{D_x D_y} \right)}{\left(A \sqrt{D_x} + \sqrt{D_y} \right) (D_x - D_y)}$$

(* correction to λ_s due to δk^2 *)

Coefficient[λ_s , δk^2] /. $\delta B \rightarrow \theta$ /. {Dx → D_x, Dy → D_y} // Simplify

$$-\frac{A \sqrt{D_y} \sqrt{D_x D_y}}{\left(A \sqrt{D_x} + \sqrt{D_y} \right) (D_x - D_y)}$$

Bc /. subk // Simplify

$$\frac{(A \sqrt{D_x} + \sqrt{D_y})^2}{D_y}$$

$\mathbb{I} = \text{IdentityMatrix}[2];$

evLc. (-i \omega \mathbb{I} - M1). {xk, yk} /. subB /. subk // Simplify

$$-\frac{i (\sqrt{D_y} x_k + A \sqrt{D_x} (x_k + y_k)) \omega}{A \sqrt{D_x}}$$

S12.A.2.3. Correlation Function for the critical Eigenmode

Left-multiplying (12.137a) with the left eigenvector χ_s^c of M_c gives, near the critical point,

$$(-i\omega \mathbb{I} - \lambda_s) \chi_s^c \cdot \begin{pmatrix} \tilde{x}_k(\omega) \\ \tilde{y}_k(\omega) \end{pmatrix} = \chi_s^c \cdot \begin{pmatrix} \tilde{\xi}_{xk}(\omega) \\ \tilde{\xi}_{yk}(\omega) \end{pmatrix} \quad (12.142a)$$

where λ_s is given by (12.141). Setting

$$\begin{aligned} \tilde{u}_k(\omega) &= \chi_s^c \cdot \begin{pmatrix} \tilde{x}_k(\omega) \\ \tilde{y}_k(\omega) \end{pmatrix} = \left(1 + \frac{1}{A} \sqrt{\frac{D_y}{D_x}}\right) \tilde{x}_k(\omega) + \tilde{y}_k(\omega) && [(12.140) \text{ used.}] \\ &= \left(1 + \frac{1}{k_c^2 D_x}\right) \tilde{x}_k(\omega) + \tilde{y}_k(\omega) && (12.143) \\ &= \text{amplitude of the critical mode} \end{aligned}$$

$$\begin{aligned} \tilde{\eta}_k(\omega) &= \chi_s^c \cdot \begin{pmatrix} \tilde{\xi}_{xk}(\omega) \\ \tilde{\xi}_{yk}(\omega) \end{pmatrix} = \left(1 + \frac{1}{A} \sqrt{\frac{D_y}{D_x}}\right) \tilde{\xi}_{xk}(\omega) + \tilde{\xi}_{yk}(\omega) \\ &= \left(1 + \frac{1}{k_c^2 D_x}\right) \tilde{\xi}_{xk}(\omega) + \tilde{\xi}_{yk}(\omega) && (12.144) \\ &= \text{amplitude of the chemical noise} \end{aligned}$$

(12.142a) becomes

$$(-i\omega \mathbb{I} - \lambda_s) \tilde{u}_k(\omega) = \tilde{\eta}_k(\omega) \quad (12.142)$$

which is the same as (1c) of Ex.12.4 in §12.A.1.3, if we set $\lambda_k = \lambda_{-k} = -\lambda_s$.

Note: (12.141) indicates that λ_s is real & negative for $\delta B > 0$.

(8) of Ex.12.4 then gives

$$\langle \tilde{\eta}_{k_1}(\omega_1) \tilde{\eta}_{k_2}(\omega_2) \rangle = -4 \pi \delta(\omega_1 + \omega_2) \delta_{k_1, -k_2} \lambda_s C_{uu}(\mathbf{k}_1, -\mathbf{k}_1; 0) \quad (12.145)$$

Read Reichl's §S12.A.3.