Existence of Homoclinic Connections Corresponding to Bilayer Structures in Amphiphilic Polymer Systems

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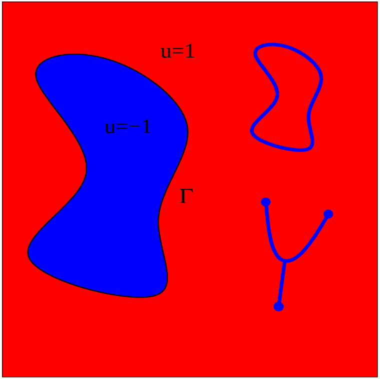
Outline

Introduction to the Functionalized Cahn-Hilliard Energy

Existence of Bilayer (Homoclinic solution) of the Functionalized Cahn-Hilliard Energy by Functional Analytical Approach

Existence of Bilayer by Lin's method for less degenerate class of perturbations

Single Layer versus Bilayer



Single-layer can not:

- open up a pore;
- pearl the interface;

Amphiphilic Mixture

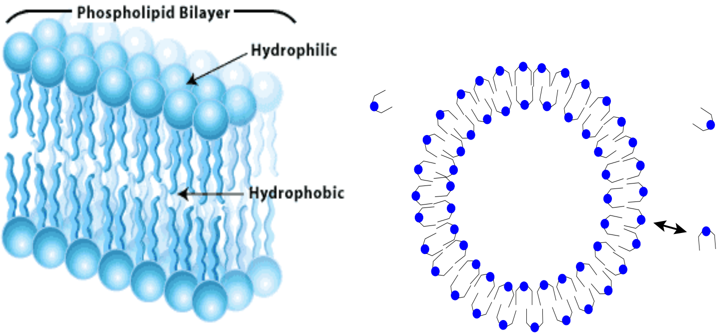


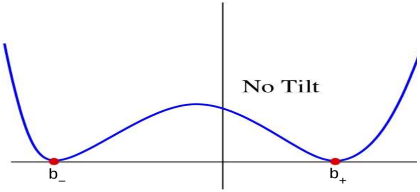
Figure: [K. Promislow, 2013](Left) A typical lipid bilayer with polar head groups exposed and hydrophobic tails point inward toward the center line. (Right) A spherical liposome.

Functionalized Cahn-Hilliard Energy

We define the quadratic functionalization of $\mathcal{F}$ related to the local balance $|\tilde{\eta}| \ll 1$ to be

$$\mathcal{F}(u) = \int_\Omega \frac{1}{2}\left(\frac{\delta \mathcal{E}}{\delta u}\right)^2 dx - \tilde{\eta}\,\mathcal{E}(u)$$
$$= \int_\Omega \frac{1}{2}\left(-\varepsilon^2 \Delta u + W'(u)\right)^2 - \tilde{\eta}\left(\frac{\varepsilon^2}{2}|\nabla u|^2 + W(u)\right) dx$$

over some appropriate subspace of $H^2(\Omega)$. Here $\mathcal{E}$ is the Cahn-Hilliard Energy and W is a double well potential with wells at $b_\pm$.



The long-time evolution of a mass-preserving projection gradient flow of the Functionalized Energy on a periodic domain $\Omega \in \mathbb{R}^d$ for $d \geq 2$,

$$u_t = -\mathcal{G}\frac{\delta \mathcal{F}}{\delta u},$$
$$u(x,0) = u_0(x).$$

where $\mathcal{G}$ is positive, self-adjoint operator whose only kernel is the constant factor 1. Examples include the zero-mass projection Π_0,

$$\Pi_0 f := f - \frac{1}{|\Omega|}\int_\Omega f(x)dx,$$

as well as the negative Laplacian $-\Delta$ subject to some mass-preserving boundary condition.

We are interested in the critical points of above equation,

$$\mathcal{G}\frac{\delta \mathcal{F}}{\delta u} = 0$$
$$\mathcal{G}\left((\varepsilon^2\Delta - W''(u) + \tilde{\eta})(\varepsilon^2\Delta u - W'(u))\right) = 0.$$

We look for flat interface co-dimension one bi-layer solutions Φ_m,

$$(\partial_z^2 - W''(\Phi_m) + \tilde{\eta})(\partial_z^2\Phi_m - W'(\Phi_m)) = \theta.$$

- For $\theta = 0$, there are single-layer heteroclinic solutions seen in the gradient flow of Cahn-Hilliard equation

$$\phi'' - W'(\phi) = 0$$

- But for $0 < |\theta| \ll 1$, the fourth order equation possesses a rich family of homoclinic solutions (bilayer solutions).

Gradient flow of functionalized energy

$$u_t = -\mathcal{G}\frac{\delta \mathcal{F}}{\delta u},$$
$$u(x,0) = u_0(x).$$

Here $\mathcal{G} = \frac{-\Delta}{1-\Delta}$.

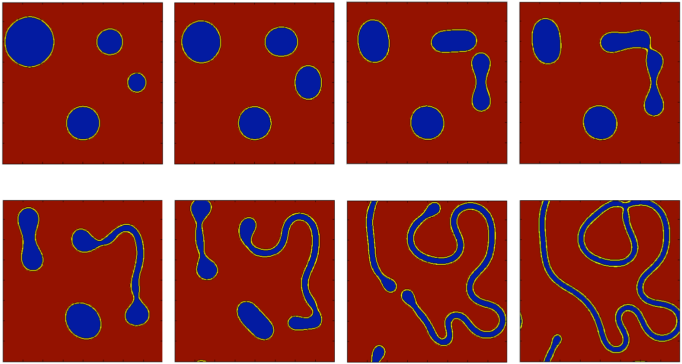


Figure: [N. Gavish, G. Hayrapetyan, K. Promislow, L. Yang, 2010] Numerical Simulation for the evolution of the $\mathcal{G}$ FCH gradient flow

Pearling interface for Amphiphilic Mixture

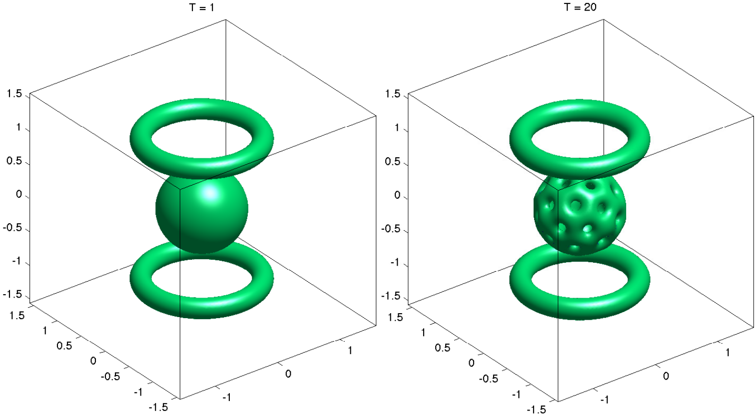


Figure: [J. Jones, 2013]Numerical simulation for the evolution of the $\mathcal{G}$ FCH gradient flow (Left) $T = 1$ (Right) $T = 20$

Qualitative Comparison to Data

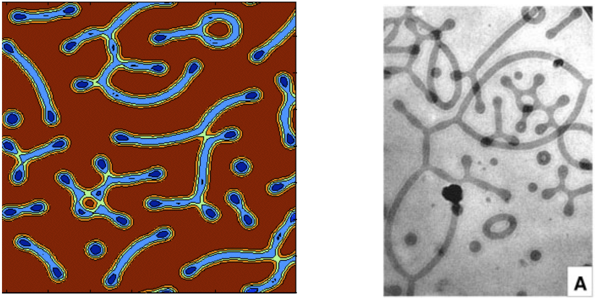


Figure: (Left)[N. Gavish, G. Hayrapetyan, K. Promislow, L. Yang, 2010] A 2D simulation of the FCH gradient flow with periodic boundary conditions for an 80% polymer (white) 20% solvent (dark) mixture starting from random initial data; (Right)[S. Jain, F. Bates, 2003] Amphiphilic di-block co-polymer mixtures of Polyethylene oxide and Polybutadiene.

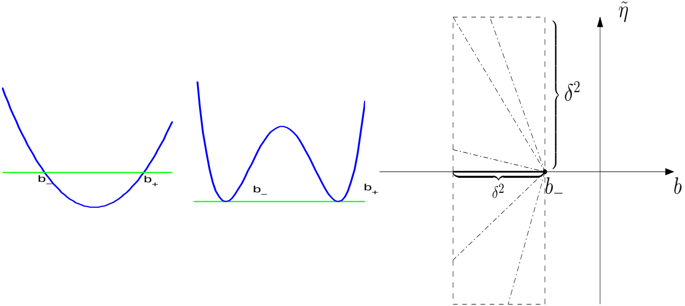
Assumption and Scaling for Functional Analytical Approach

(H1) The well potential W is a smooth double well $W = P^2$ where P is a convex function with transverse zeros at $b_\pm$ with $b_- < b_+$, $W(b_\pm) = W'(b_\pm) = 0$ and $\mu_\pm := W''(b_\pm) > 0$.

(S) Fix $\eta \in \mathbb{R}$ and $\beta < 0$. Then our standard scaling is

$$\tilde{\eta} = \eta\delta^2, \quad b = b_- + \delta^2\beta, \quad \text{for } 0 < \delta \ll 1.$$

where b is the background state of the homoclinic pulse.



Functional Analytical Approach

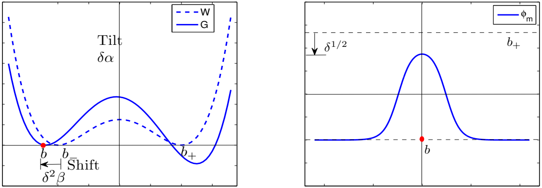
The functional analytical approach is based upon the Newton type contraction mapping argument.

Basic Idea: It constructs the homoclinic solution Φ_m of the full system in the neighborhood of ϕ_m, which is the homoclinic solution of a particular second-order differential equation,

$$\phi_m'' = G'(\phi_m),$$

where

$G(u;\alpha,b) = W(u) - W(b) - W'(b)(u-b) - \tilde{\eta}/4(u-b)^2 - \tilde{\eta}\alpha g(u;b)$, a perturbation of the equal-depth double-well potential W.



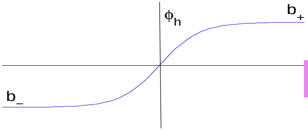
Degeneracy of the problem

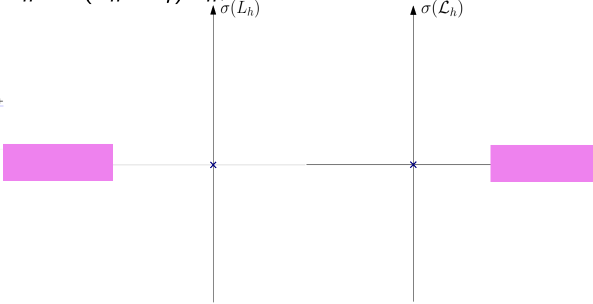
Difficulty: the linearization of the full system about ϕ_m is degenerate.

Let ϕ_h the heteroclinic solution of

$$\phi_h'' = W'(\phi_h),$$

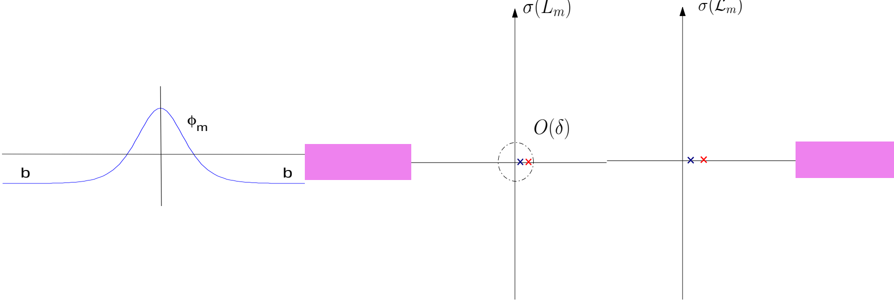
which connects the two minima $b_\pm$ of W. Linearizing the full system around ϕ_h yields $\mathcal{L}_h := (L_h + \tilde{\eta})\, L_h$, where $L_h := \partial_z^2 - W''(\phi_h)$.





Degeneracy of the problem

Linearizing the full system around ϕ_m yields $\mathcal{L}_m := (L_m + \tilde{\eta})\, L_m$, where $L_m := \partial_z^2 - W''(\phi_m)$.



The degeneracy is related to the small eigenvalue. Removing this degeneracy is the main effort of the contraction mapping construction.

Functional Analytical Approach

After integration by parts, shifting the potential and adding the tilt, we obtain the shifted energy,

$$\mathcal{H}(u) = \int_\Omega \frac{1}{2}\left(\varepsilon^2 \Delta u - G_0'(u)\right)^2 + p(u)\ dx.$$

where $G_0(u) = W(u) - W(b) - W'(b)(u-b) - \tilde{\eta}/4(u-b)^2$.
Relation: $\frac{\delta \mathcal{H}}{\delta u} = \frac{\delta \mathcal{F}}{\delta u} - \theta$, where $\theta = W'(b)(W''(b) - \tilde{\eta})$.
We introduce a "tilt" parameter (Modica-Mortola parameter) α that tunes the shape of the potential,

$$G(u;\alpha,b) = G_0(u;b) - \delta\alpha g(u;b),$$

where $g(u;b) = \int_b^u \sqrt{W(t-b+b_-)}dt$.Then $\mathcal{H}$ can be written,

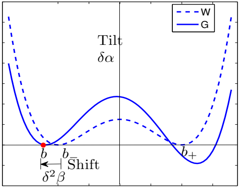
$$\mathcal{H}(u) = \int_\Omega \frac{1}{2}\left(\varepsilon^2 \Delta u - G'(u) - \delta\alpha g'(u)\right)^2 + p(u)\ dx.$$

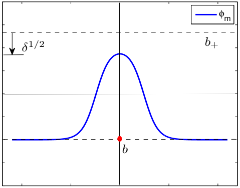
Reduced problem and Full problem

$\phi_m = \phi_m(z;\alpha)$ is the homoclinic solution of the second-order differential equation,

$$\phi_m'' = G'(\phi_m;\alpha),$$

which is homoclinic to b and symmetric about $z = 0$.





$\Phi_m = \Phi_m(z;\delta,\eta,\beta)$ is the homoclinic solution of the fourth-order differential equation,

$$\frac{\delta\mathcal{H}}{\delta u}(\Phi_m) = 0.$$

Relation: $\Phi_m = \phi_m(z;\alpha_*(\delta;\beta,\eta)) + O(\delta^2)$ in H^4

Main Theorem

Theorem 1

Let the potential W satisfying $(H1)$ be given. Let $\tilde{\eta}$, β be given by the scaling (S) and η, β satisfy

$$(H_2) \qquad \left|A_1^h \beta + A_2^h \eta\right| > \nu\, \delta^{\omega},$$

for some $\nu > 0$, $\omega > 0$ independent of δ only depends on W. The constants A_1^h and A_2^h depend only upon the heteroclinic orbit ϕ_h,

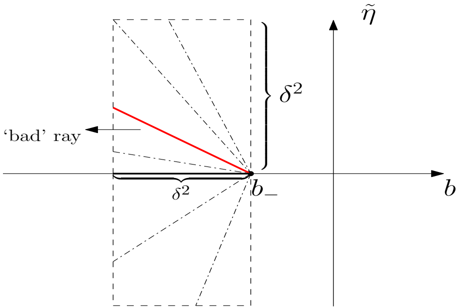
$$\begin{aligned} A_1^h &:= -\frac{9}{2}\mu_+^{\frac{5}{2}}(b_+ - b_-) + 3\left(W'''(\phi_h)(\phi_h - b_-), (\phi_h')^2\right)_2, \\ A_2^h &:= \left(W'''(\phi_h)(\phi_h - b_-), (\phi_h')^2\right)_2. \end{aligned}$$

Then there exists a solution Φ_m of full system admits the following expansion

$$\Phi_m = \phi_m(z; \alpha_*(\delta; \beta, \eta)) + O(\delta^2),$$

in H^4 where ϕ_m is the corresponding solution of the second-order differential equation with $\alpha_* = \alpha_*(\delta; \beta, \eta)$.

Main Theorem



- Conjecture : High order Melnikov integral A_1^h, A_2^h is related to an orbit-flip condition in the fourth-order system.
- α_* has the expression

$$\alpha_*(\delta; \beta, \eta) = \sqrt{-\frac{\mu_+^{\frac{3}{2}}(b_+ - b_-)\beta}{\sqrt{2}\, g(b_+)}} + O(\sqrt{\delta}).$$

Outline of Proof of Main Theorem

We want to show that for δ small enough, we can generate a solution of the Euler-Lagrange via a modified Newton's method initiated at ϕ_m, where ϕ_m is the homoclinic solution of the second order problem. We define the Newton map,

$$N(u) = u - \mathcal{L}_\alpha^{-1}(F(u)),$$

where

$$\mathcal{L}_\alpha = \frac{\delta^2 \mathcal{H}}{\delta u^2}(\phi_m(z;\alpha)), \quad F(u) = \frac{\delta \mathcal{H}}{\delta u}.$$

Analysis of the operator $\mathcal{L}_\alpha$

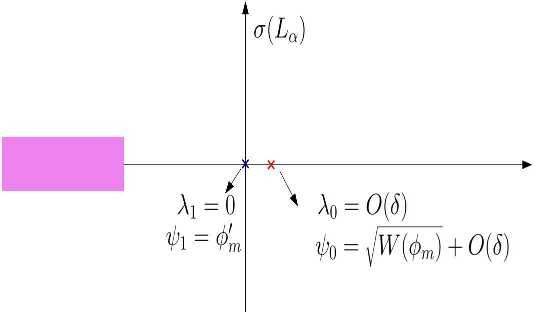
Expand $\mathcal{L}_\alpha$,

$$\begin{aligned}\mathcal{L}_\alpha &= L_\alpha^2 + \delta\,\alpha\left(G'''(\phi_m)g'(\phi_m) - g''(\phi_m)L_\alpha - L_\alpha g''(\phi_m)\right)\\ &\quad +\delta^2\left(\alpha^2 g'''(\phi_m)g'(\phi_m) + \alpha^2 g''(\phi_m)^2 + p_2''(\phi_m)\right).\end{aligned}$$

where

$$L_\alpha = \partial_{zz} - G''(\phi_m).$$

In order to know spectrum of $\mathcal{L}_\alpha$, we need to know the spectrum of L_α first.



Analysis of the operator $\mathcal{L}_\alpha$

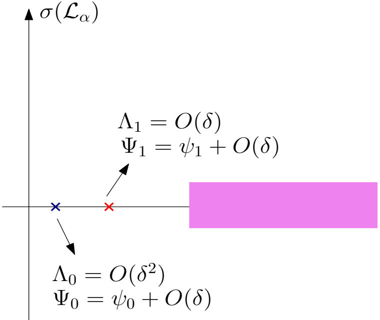
$\mathcal{L}_\alpha$ is an $O(\delta)$, relatively compact perturbation of the operator L_α^2, it has two small eigenvalues, which we denote

$$\Lambda_0 = \underbrace{\lambda_0^2 + O(\delta^2)}_{O(\delta^2)},\ \Lambda_1 = O(\delta),$$

with eigenfunctions

$$\Psi_0 = \psi_0 + O(\delta),\ \Psi_1 = \psi_1 + O(\delta).$$

Ψ_0 is even about $z = 0$ and Ψ_1 is odd about $z = 0$.



Conditioning of the Newton map

$\mathcal{L}_\alpha$ has two eigenvalues near zero. In order to invert $\mathcal{L}_\alpha$ for Newton map, we need a tuning parameter, α, Modica-Mortola parameter.

- For $\Lambda_1 = O(\delta)$ with eigenfunction Ψ_1
  Since Ψ_1 is odd function, then by even-odd symmetry,
  $$(F(\phi_m), \Psi_1)_2 = 0.$$
- For $\Lambda_2 = O(\delta^2)$ with eigenfunction Ψ_0
  Does there exist tilt $\alpha_* = \alpha_*(\delta; \beta, \eta)$,
  $$(F(\phi_m(., \alpha_*)), \Psi_0(., \alpha_*))_2 = 0?$$
  Answer: Yes.

Sketch of Proof of Main Theorem

- There exists $\alpha_* = \alpha_*(\delta; \beta, \eta)$ such that $\phi_m^* := \phi(\cdot, \alpha_*)$ satisfies

$$(F(\phi_m^*), \Psi_0(., \alpha_*))_2 = 0.$$

  Introduce

$$B_\rho^* = \left\{ u - b \in H_e^4(\mathbb{R}) \Big| \|u - (\phi_m^* - \xi_*)\|_{H^4} \leq \rho\delta^{5/2} \right\},$$

  where

$$\xi_* = \mathcal{L}_{\alpha^*}^{-1} F(\phi_m^*) = O(\delta^2).$$

- There exists ρ_1, $\rho_2 > 0$ such that for any $u \in B_{\rho_1}^*$ there exists a unique $\alpha = \alpha(u; \beta, \eta)$ satisfying $|\alpha - \alpha_*| < \rho_2\delta^2$ such that

$$(F(\phi_m(., \alpha)), \Psi_0(., \alpha))_2 = 0.$$

- Newton map $N(u) = u - \mathcal{L}_\alpha{}^{-1}(F(u))$ is a contraction mapping on B_ρ^*.

Dynamical Systems Approach (Lin's method)

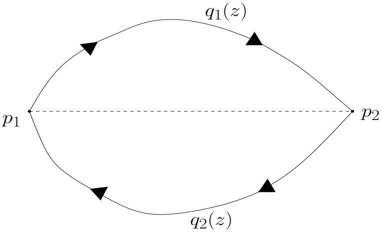
In the view of dynamical system way, we rewrite our problem as a one-parameter family of vector fields

$$\dot{x} = f(x, \theta),$$

where $x = (u, u', u'', u''')^T$ and $f : \mathbb{R}^4 \times \mathbb{R} \to \mathbb{R}^4$ is smooth. For $\theta = 0$ we have the heteroclinic connections between two equilibriums $p_1 = (b_-, 0, 0, 0)^T$ and $p_2 = (b_+, 0, 0, 0)^T$.

$$\lim_{z\to-\infty} q_1(z) = p_1, \lim_{z\to\infty} q_1(z) = p_2,$$
$$\lim_{z\to-\infty} q_2(z) = p_1, \lim_{z\to\infty} q_2(z) = p_1.$$

The system is reversible, that is symmetric under the transformation $z \mapsto -z$.



For $\theta = 0$

$$q_1(z) = (\phi_h(z), \phi_h'(z), \phi_h''(z), \phi_h'''(z))^T,$$

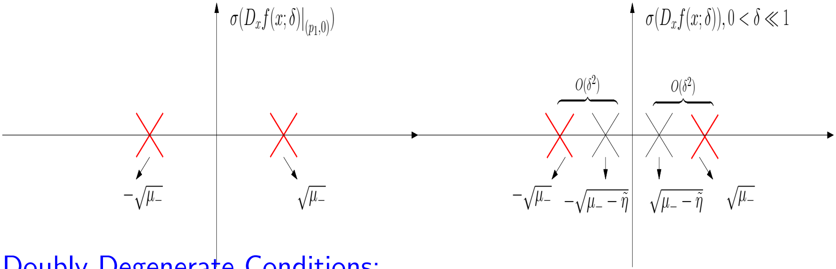
where ϕ_h is the heteroclinic solution of the second order problem $\phi'' = W'(\phi)$. Symmetrically there is another heteroclinic connection

$$q_2(z) = (\phi_h(-z), -\phi_h'(-z), \phi_h''(-z), -\phi_h'''(-z))^T.$$

Spectrum of $D_x f(p_i, \theta)$ under scaling (S)

(S) Fix $\eta \in \mathbb{R}$ and $\beta < 0$. $\tilde{\eta} = \eta\delta^2$, $b = b_- + \beta\delta^2$, for $0 < \delta \ll 1$.

$$\begin{aligned} \theta &= (W''(b) - \tilde{\eta})W'(b), \\ &= \mu_-(\mu_- - \tilde{\eta})\beta\delta^2 + O(\delta^3). \end{aligned}$$



Doubly Degenerate Conditions:

- Jordan Block Structure of the eigenvalue of $D_x f(p_i, \theta)$ for $\delta = 0$;
- for $\delta \neq 0$ Jordan Block unfolds smoothly in δ forming real eigenvalues which perturb at $O(\delta^2)$.

Orbit Flip Condition

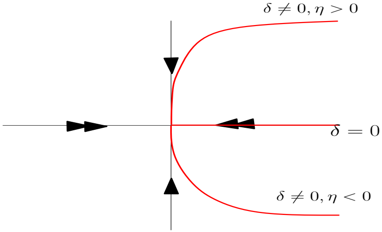
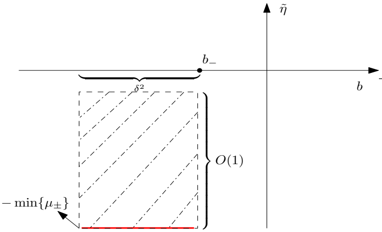


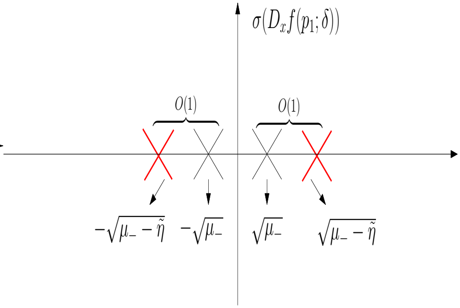
Figure: Depiction of the stable manifold of the equilibrium of a homoclinic orbit under an orbit flip bifurcation.

Conjecture: condition (H2) is equivalent to the orbit-flip condition. It is precisely when the second-order system is different to the fourth-order system. We avoid this via Lin's method by changing the scaling.

Spectrum of $D_x f(p_i, \theta)$ under scaling (S')

(S') Fix $\tilde{\eta}$, β such that $-\min\{\mu_\pm\} < \tilde{\eta} < 0$ and $\beta < 0$. $b = b_- + \beta\delta^2$, for $0 < \delta \ll 1$. $\tilde{\eta}$, β are independent of δ and $\tilde{\eta}$ is not small.





$$
\begin{aligned}
\sigma(D_x f(p_1, \delta)) &= \{\pm\sqrt{\mu_-}, \pm\sqrt{\mu_- - \tilde{\eta}}\}, \\
\sigma(D_x f(p_2, \delta)) &= \{\pm\sqrt{\mu_+}, \pm\sqrt{\mu_+ - \tilde{\eta}}\}.
\end{aligned}
$$

For $\theta = 0$, the stable and unstable manifolds $W^s(p_i)$ and $W^u(p_i)$, $i = 1, 2$ for our system are two-dimensional. Moreover

$$\begin{aligned} T_{q_1(0)} W^u(p_1) \cap T_{q_2(0)} W^s(p_2) &= span\{\dot{q}_1(0)\}, \\ T_{q_2(0)} W^u(p_2) \cap T_{q_1(0)} W^s(p_1) &= span\{\dot{q}_2(0)\}. \end{aligned}$$

Introduce the subspace Z_i such that

$$\begin{aligned} \mathbb{R}^4 &= Z_1 \oplus \left(T_{q_1(0)} W^u(p_1) + T_{q_1(0)} W^s(p_2) \right), \\ \mathbb{R}^4 &= Z_2 \oplus \left(T_{q_2(0)} W^u(p_2) + T_{q_2(0)} W^s(p_1) \right). \end{aligned}$$

Remark that $dim(Z_i) = 1$. We construct the section planes Σ_i which are transverse to $q_i(z)$ at some point $q_i(0)$.

Lin's heteroclinic orbit construction

- (Step One) Construct the perturbed heteroclinic orbits $q_i^{\pm}$ near q_i that solves the full system up to the jump in Σ_i along Z_i . Moreover, it satisfies

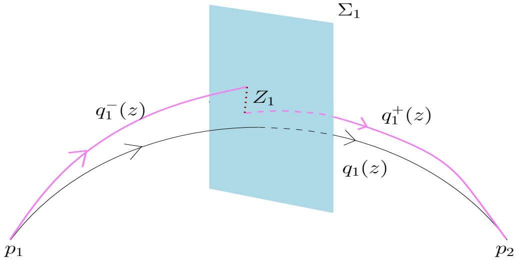
(Q1) $q_i^{\pm}(z;\theta)$ are close to $q_i(z)$.

(Q2) $\lim_{z\to\infty} q_1^{+}(z;\theta) = p_2$, $\lim_{z\to-\infty} q_1^{-}(z;\theta) = p_1$.

(Q3) $\lim_{z\to\infty} q_2^{+}(z;\theta) = p_1$, $\lim_{z\to-\infty} q_2^{-}(z;\theta) = p_2$.

(Q4) $q_i^{\pm}(0;\theta) \in \Sigma_i$.

(Q5) $\xi_i^{\infty}(\theta)\psi_i := q_i^{+}(0;\theta) - q_i^{-}(0;\theta) \in Z_i$.



the jump estimate $\xi_i^\infty(\theta)$ have the expression

$$\xi_i^\infty(\theta) = M_i\theta + O(\theta^2),$$

where the Melnikov integral M_i is defined

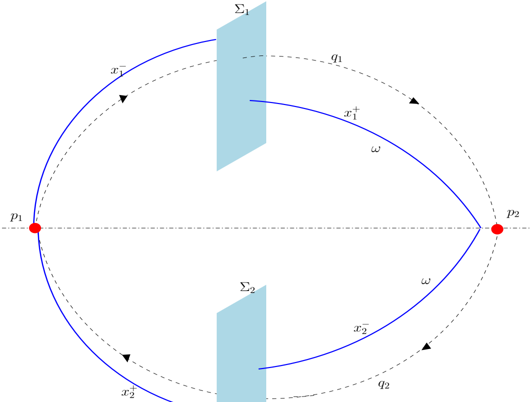
$$M_i := \int_{\mathbb{R}} \psi_i(s)\, D_\theta f(q_i(s), 0)\, ds \neq 0.$$

where $\psi_i(z) = T_i^*(z, 0)\psi_i$. Here $T_i(z, s)$ denotes the transition matrix of $\dot{v} = D_x f(q_i(z), 0)v$ and ψ_i spans Z_i.

Lin's homoclinic orbit construction

- (Step Two) Construct the Lin's orbits $x_i^{\pm}$ near $q_i^{\pm}$ and it solves the full system up to the jump. These orbits have the prescribed flying time 2ω from Σ_1 to Σ_2. Moreover, it satisfies

  (L1) $x_i^{\pm}(z;\theta)$ are close to $q_i^{\pm}$.
  (L2) $x_i^{+}(0;\theta) - x_i^{-}(0;\theta) \in Z_i$.
  (L3) $x_1^{-}(-\infty) = x_2^{+}(\infty)$ and $x_1^{+}(\omega) = x_2^{-}(-\omega)$.



Estimates for the Jump

We derive an expression for the jump

$$\begin{aligned} \xi_i(\theta,\omega) &:= &< \psi_i, x_i^+(\theta,\omega)(0) - x_i^-(\theta,\omega)(0) >, \\ &= &\xi_i^\infty(\theta) + \xi_i^\omega(\theta), \quad i = 1, 2. \end{aligned}$$

- heteroclinic jump has the expansion

$$\xi_i^\infty(\theta) = M_i\theta + O(\theta^2).$$

- difference between the heteroclinic jump and homoclinic jump

$$\xi_i^\omega(\theta) = \xi_i(\theta,\omega) - \xi_i^\omega(\theta).$$

Solving the Bifurcation Equation

To obtain the homoclinic orbit, we require the jumps to be zero, i.e., $\xi_1(\theta, \omega) = 0$ which by the symmetry property of the system also implies $\xi_2 = 0$.
We also derive the leading order term of $\xi_1(\omega, \theta)$

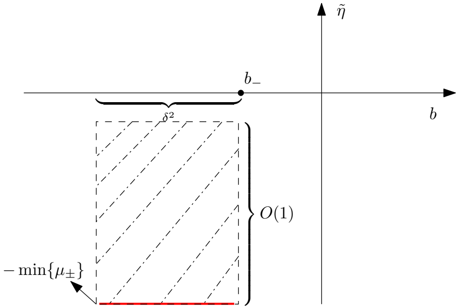
$$\xi_1(\omega, \theta) = M_1\theta + c^u(\theta)e^{-2\omega\lambda_2^u(\theta)} + o(e^{-2\omega\lambda_2^u(\theta)}),$$

where $\lambda_2^u(\theta) = \sqrt{\mu_+}$ and the function $c^u(\cdot)$ is smooth and $c^u(0) \neq 0$. Solving the bifurcation equation $\xi_1 = 0$ we have at the leading order

$$\omega = -\frac{\ln\left(\frac{-M_1\theta}{c^u(0)}\right)}{2\lambda_2^u(0)} + o(\omega).$$

In order to make $-M_1\theta/c^u(0) > 0$ we have to choose $\beta < 0$.

Main Theorem



Theorem 2

Let η, b and double well W be given and satisfy (H1) and (S').
Then there exists $\delta_0 > 0$ such that for all $0 < \delta < \delta_0$, there exists a homoclinic solution Φ_m which is homoclinic to b.

Connection between these two methods

Functional Analysis Method

- sharp characterization of the homoclinic solution of full system in terms of the homoclinic solution of second order problem
- indentifies a nondegeneracy condition (H2) – (Orbit Flip?)
- Contraction Mapping argument

Dynamical System Method

- existence of homoclinic solution in the neighborhood of the heteroclinic chain of full problem
- we didn't permit $\tilde{\eta}$ to scale with δ.
- Lin's method based upon Lyapunov-Schmidt method

Conclusion and Thanks

- Introduction to the Functionalized Cahn-Hilliard Energy
- Existence of the homoclinic solution proved by two approaches
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