Durham Centre for Soft Matter

Biophysical Sciences Institute

Durham University

Surveying Free Energy Landscapes: Applications to Continuum Soft Matter Systems

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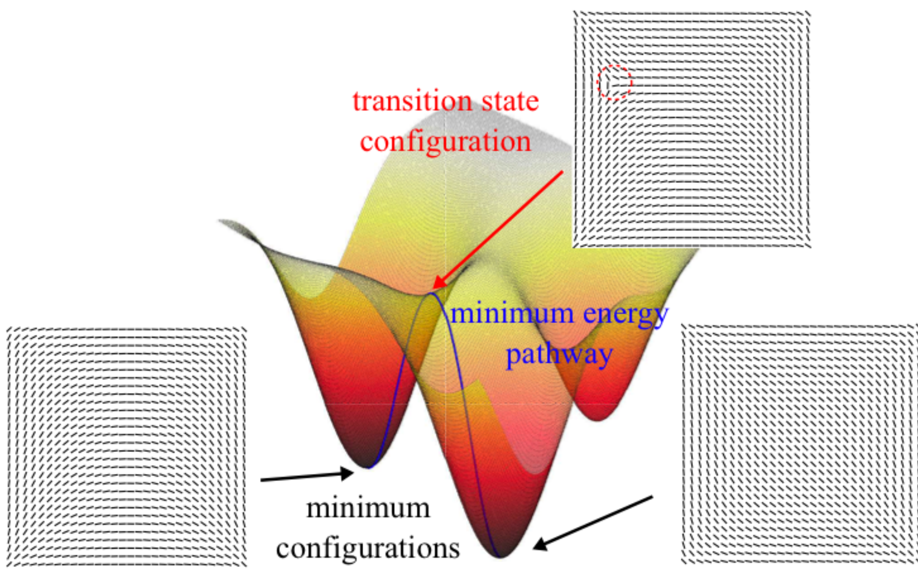
Department of Physics, University of Durham



Acknowledgement

David Wales (Cambridge)

Discussions on various numerical techniques

Apala Majumdar (Bath)

Collaboration on the LC example

On the Menu Today

The Basic Idea

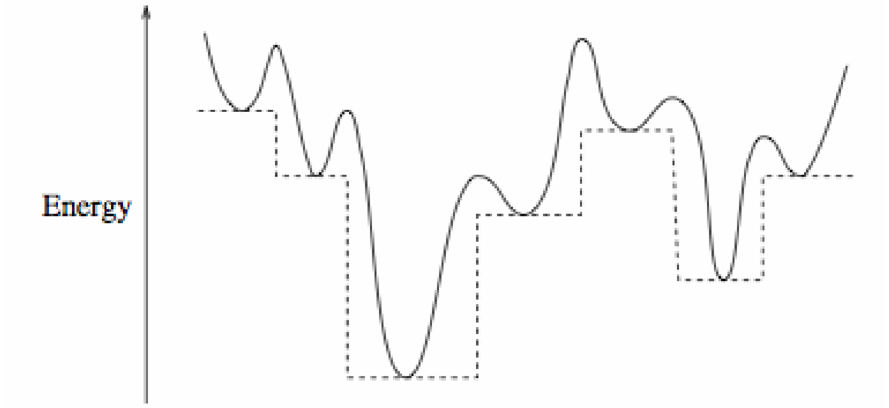
Motivation - Typical questions

Methods - Exploring the free energy landscapes

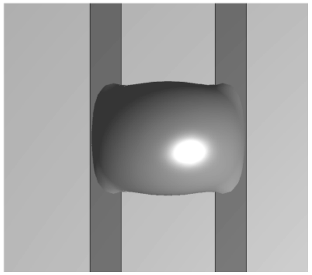
Energy Minimization

Nudged Elastic Band Method

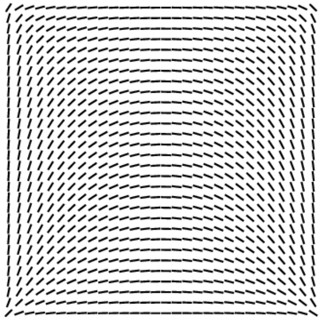
Eigenvector Following



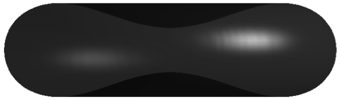
Results - Specific Systems



Wetting on Chemically Striped Surfaces



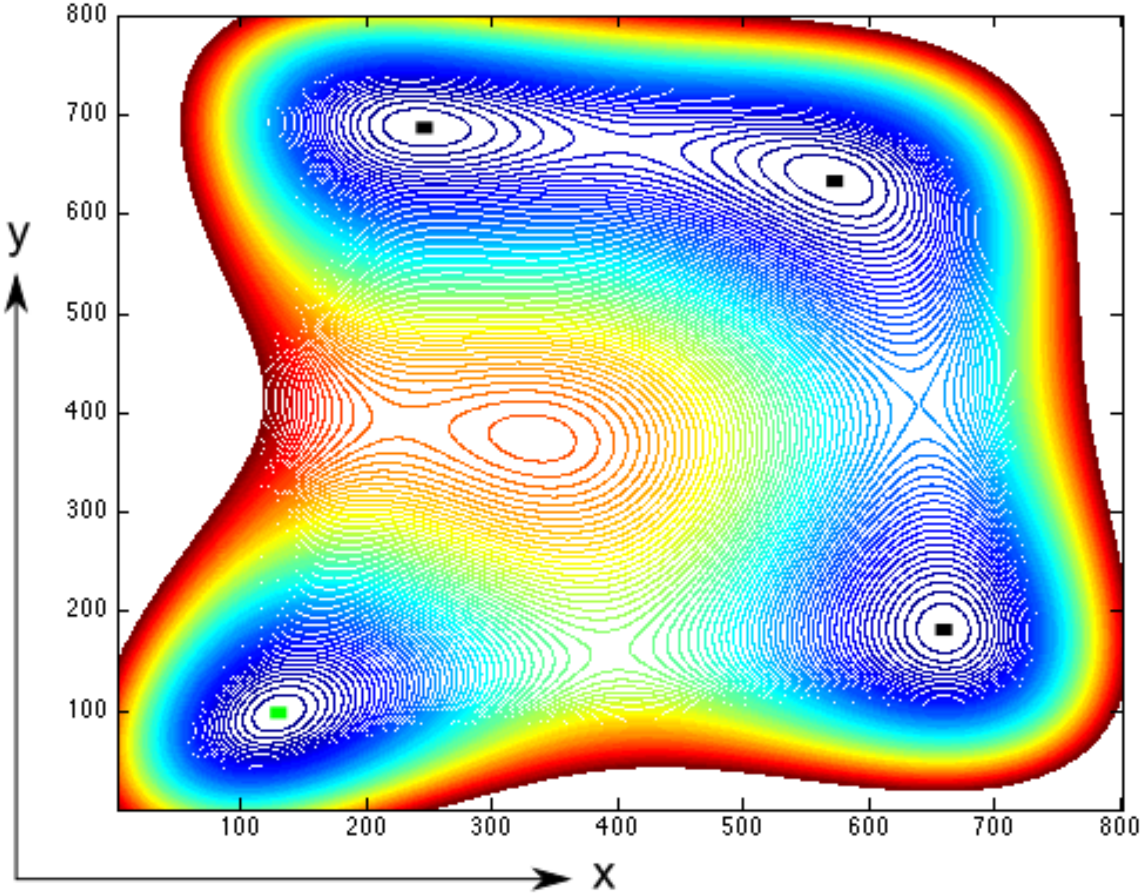
Liquid Crystals



Lipid Vesicles

The Basic Idea

Two-dimensional energy contour plot: F (x, y)

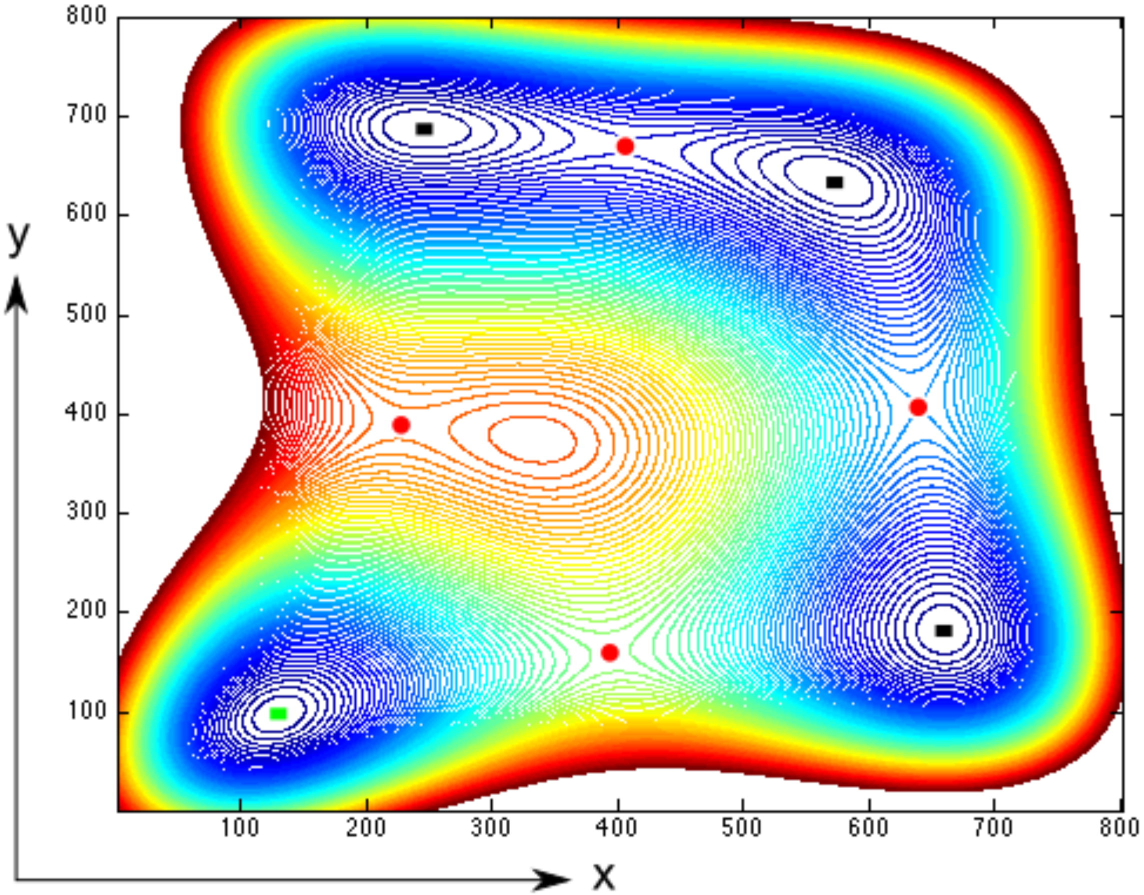


The global minimum

All relevant minima

The Basic Idea

Two-dimensional energy contour plot: F (x, y)



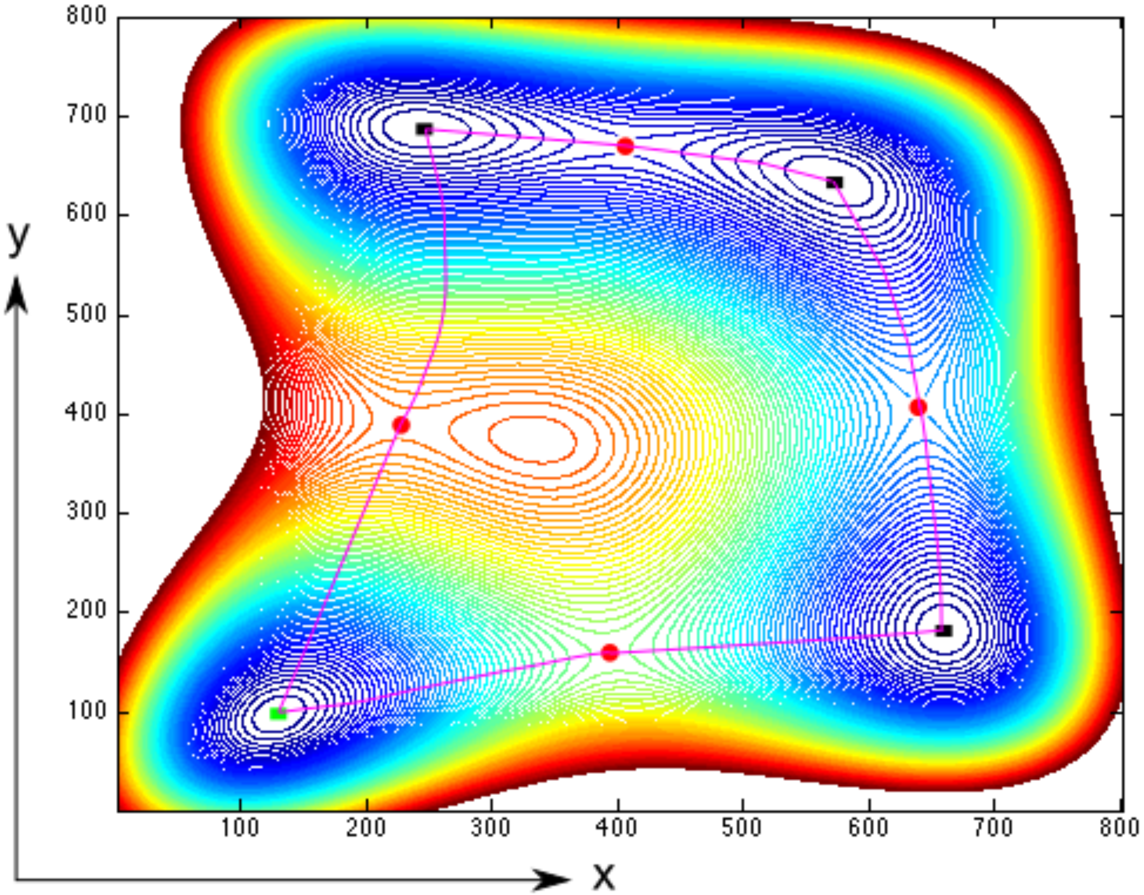
The global minimum

All relevant minima

Saddle point

The Basic Idea

Two-dimensional energy contour plot: F (x, y)



The global minimum

All relevant minima

Saddle point

Minimum Energy Pathway

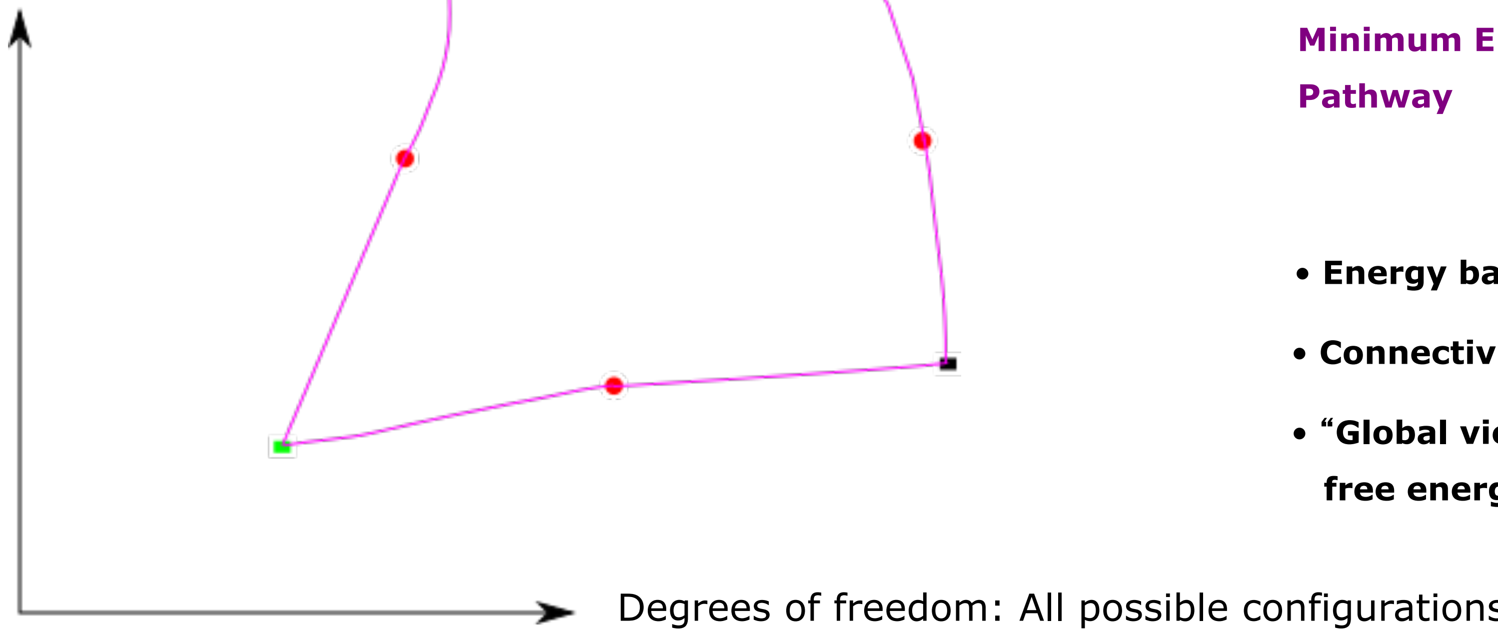
- **Energy barriers**
- **Connectivity**
- **"Global view of the free energy landscape"**

The Basic Idea

Our Goal:

Study the evolution of the ***free energy landscapes*** as function of the system parameters.

The skeleton represents perhaps the most interesting points on the landscape.



The global minimum

All relevant minima

Saddle point

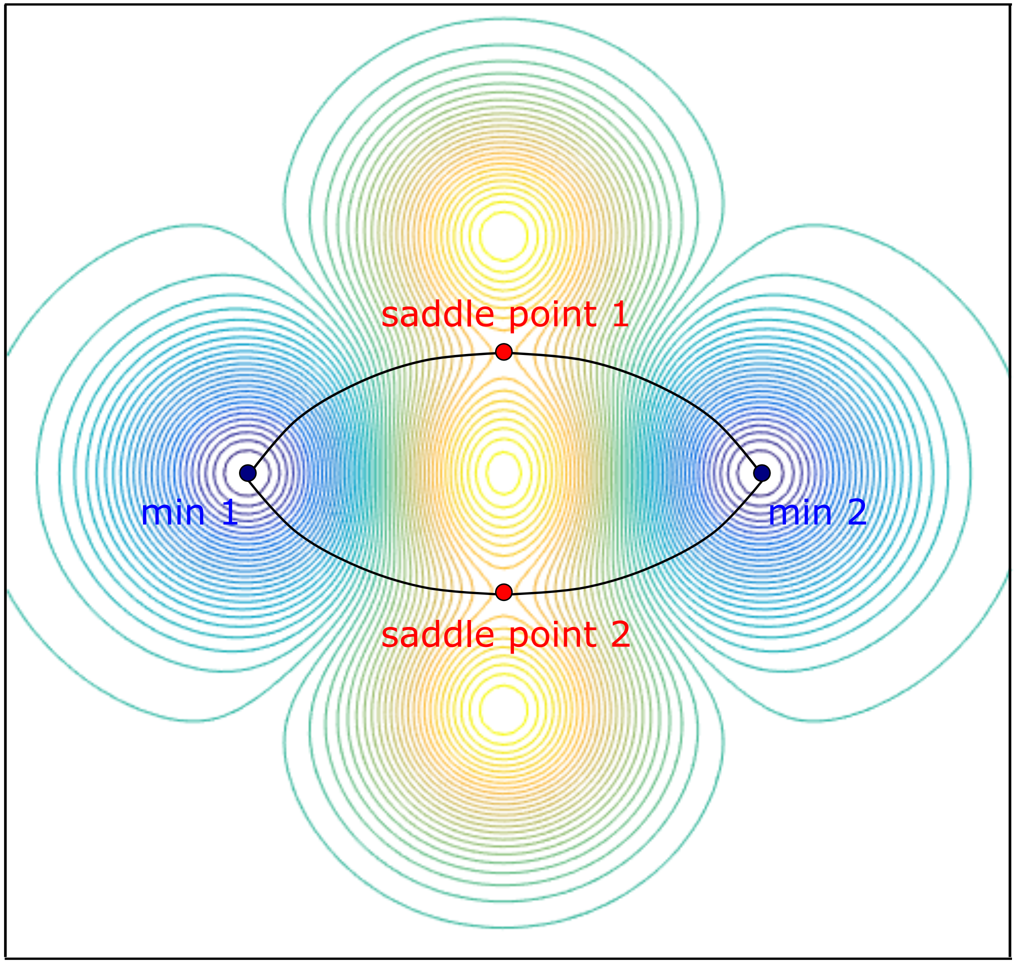
Minimum Energy Pathway

- **Energy barriers**
- **Connectivity**
- **"Global view of the free energy landscape"**

Competing Pathways

More than one possible minimum energy pathways

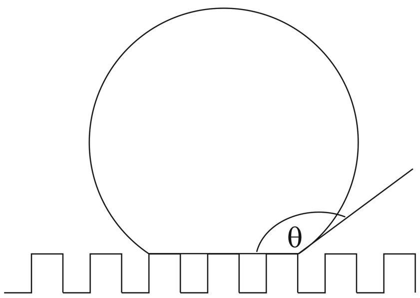
Systematic algorithm to enumerate these pathways?

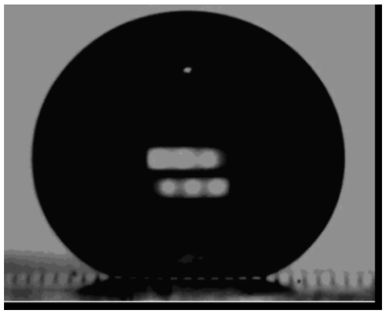


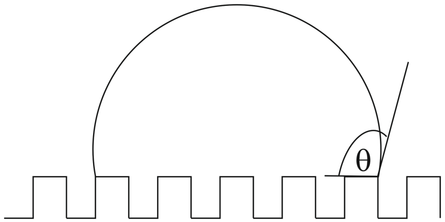
Motivation

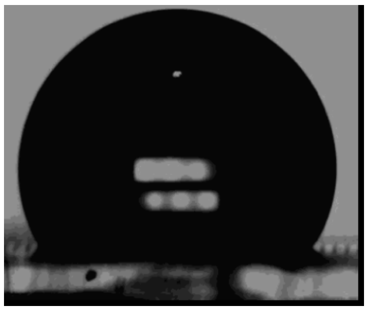
Wetting States

- **Superhydrophobic Surfaces**







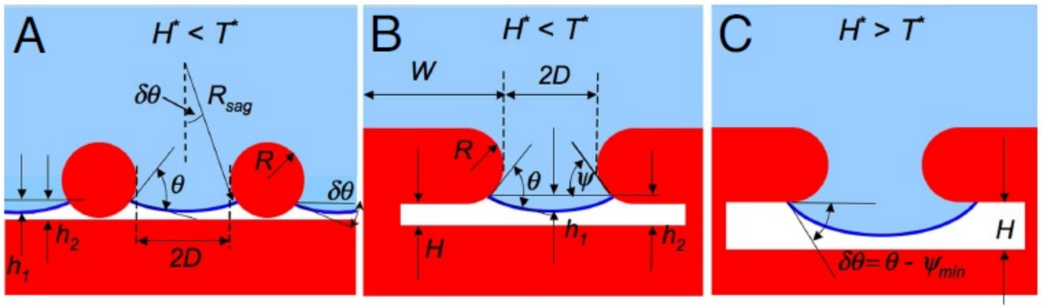


Suspended - ‘Good’

Collapsed - ‘bad’

Reentrant

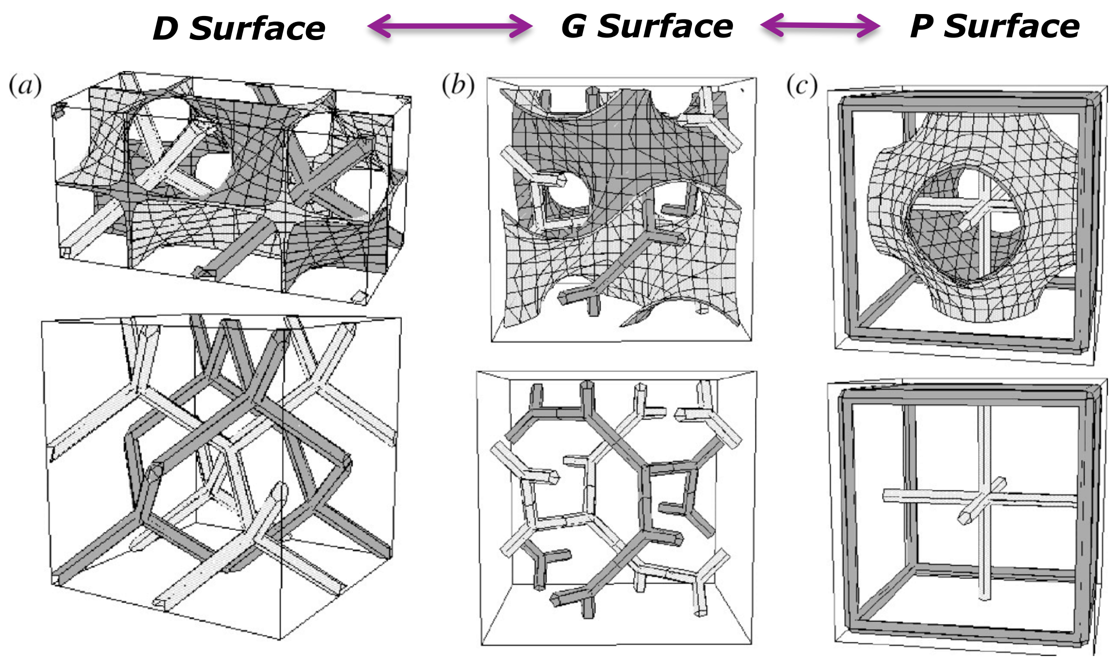
Post Geometry:



Tuteja et al.

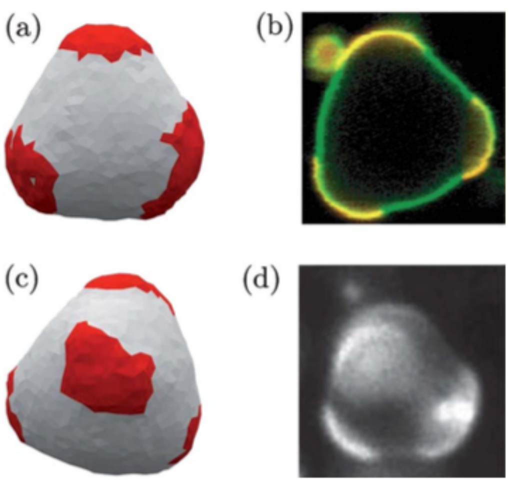
Membranes

- **Cubic Membranes**



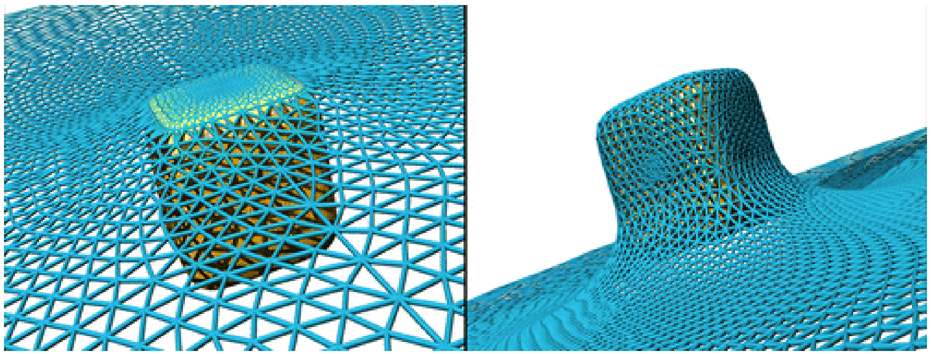
Seddon et al.

- **Multicomponent Membranes**



Hu et al.

- **Encapsulation of Nanoparticles**

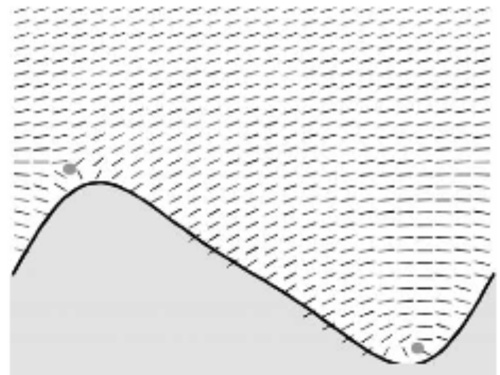


Dasgupta et al.

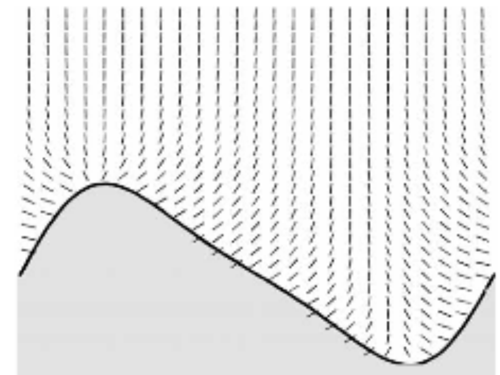
Multistable Liquid Crystal Devices

Zenithal Bistable Display

Spencer et al.

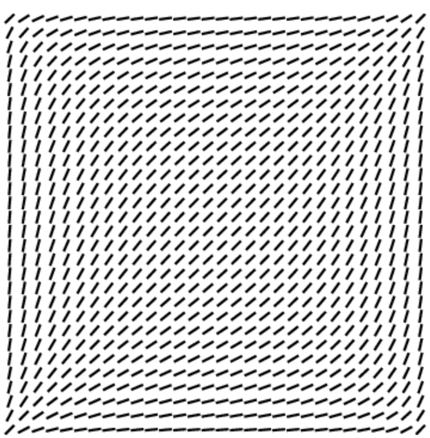


Defect State - bright

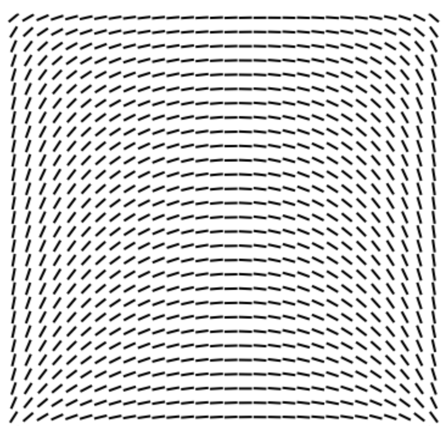


Continuous State - dark

Nematic Liquid Crystal Wells

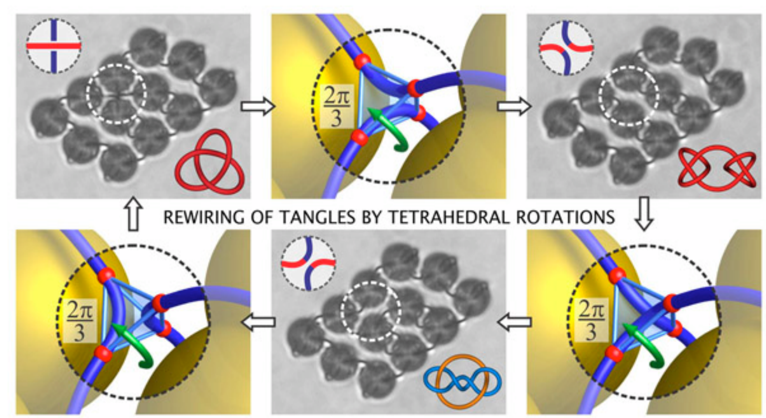


Diagonal State



Rotated State

Liquid Crystal Colloids



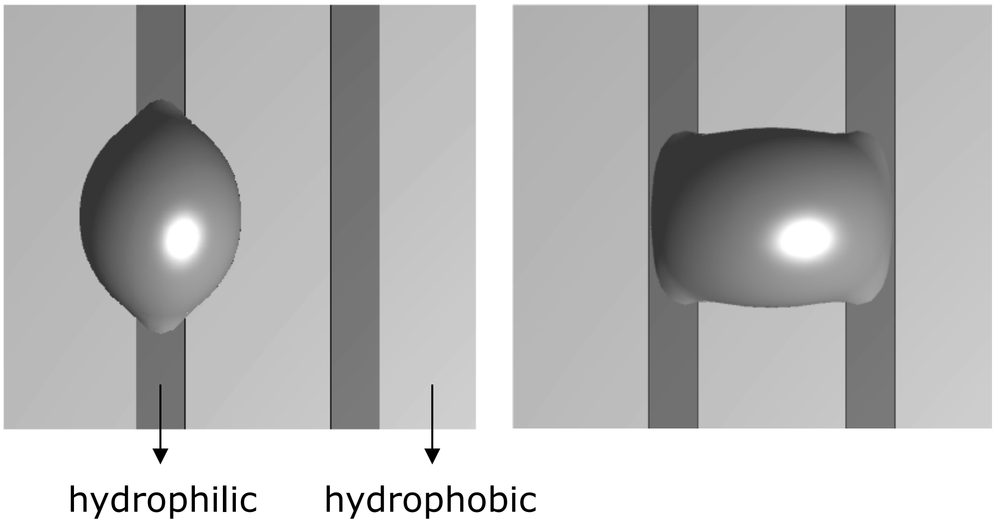
Tkalec et al.

Methods

H. Kusumaatmaja, J. Chem. Phys. **142**, 124112 (2015)

Wetting on Chemically Striped Surfaces

Wetting on Striped Surfaces



Contact Angle

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

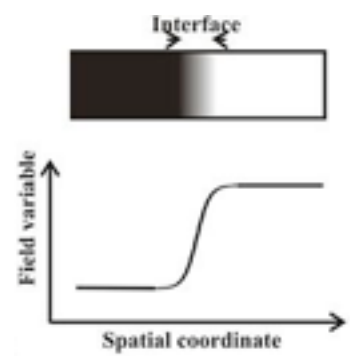
Free Energy Function

Surface Energies $$\Psi = \gamma_{LV} A_{LV} + \gamma_{SV} A_{SV} + \gamma_{SL} A_{SL}$$

Landau Free Energy $$\Psi = \int_V \left(\psi_b + \frac{\varepsilon}{2} |\nabla \phi|^2 \right) dV + \int_A \psi_A \, dA$$

Double well potential $$\psi_b = \frac{1}{4\varepsilon} \left(\phi^2 - 1 \right)^2$$

Surface Energy $$\psi_A = -h \phi_A$$



Continuum vs Discrete

Continuum

$$\Psi = \int_V \left(\psi_b + \frac{\varepsilon}{2} \left| \nabla \phi \right|^2 \right) dV + \int_A \psi_A \, dA$$

Discrete

$$\int_V \psi_b dV = \sum_{ijk} \frac{1}{\varepsilon} \left(-\frac{1}{2} \phi_{ijk}^2 + \frac{1}{4} \phi_{ijk}^4 \right) \Delta x \Delta y \Delta z$$

$$\int_V \frac{\varepsilon}{2} \left| \nabla \phi \right|^2 dV = \sum_{ijk} \frac{\varepsilon}{2} \left| \nabla \phi \right|_{ijk}^2 \Delta x \Delta y \Delta z$$

$$\int_A -h \phi_A dA = \sum_{ijk \in A} -h \phi_{ijk} \, \Delta x \Delta y$$

Minimum/Saddle Points (Continuum)

1st Derivative $$\frac{\delta \Psi}{\delta \phi(\vec{x}_1)} = 0$$

2nd Derivative $$\frac{\delta^2 \Psi}{\delta \phi(\vec{x}_1) \delta \phi(\vec{x}_2)}$$

Minimum/Saddle Points (Discrete)

1st Derivative $$\frac{\partial \Psi}{\partial \phi_{ijk}} = 0$$

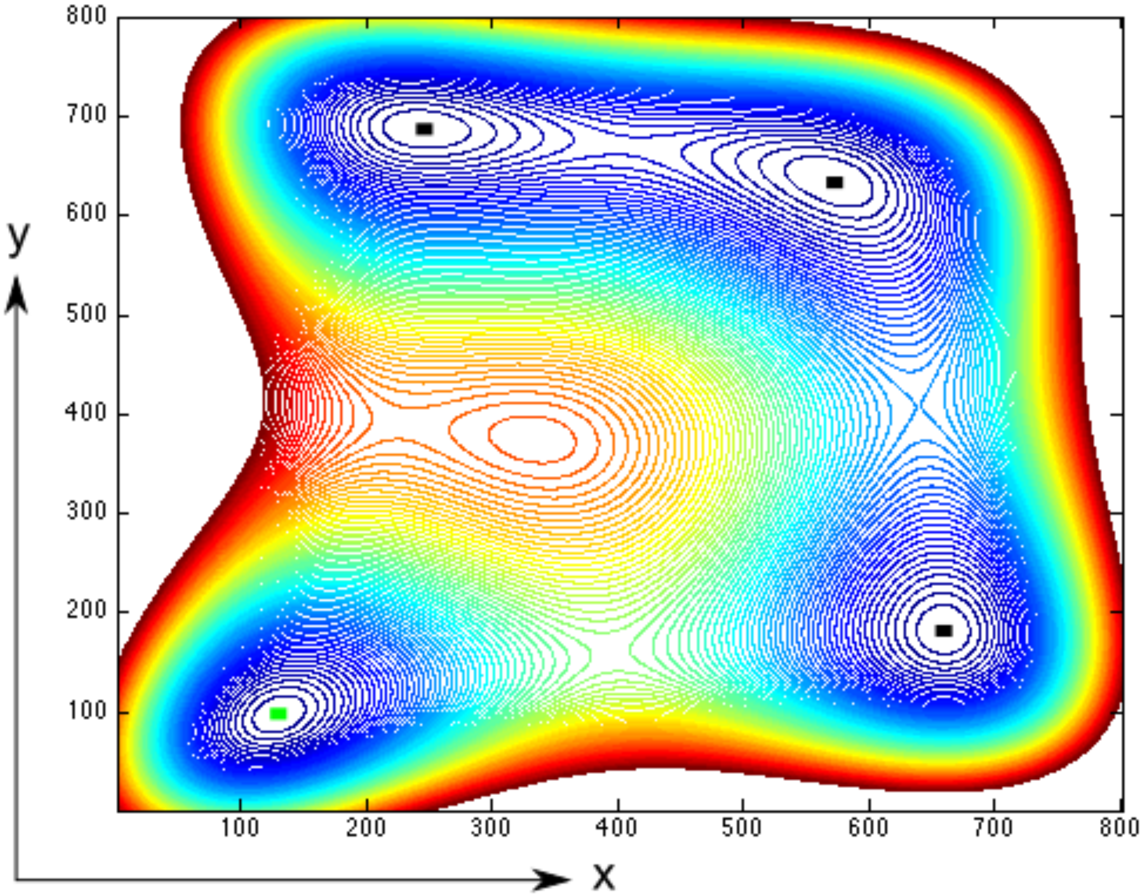
2nd Derivative $$\frac{\partial^2 \Psi}{\partial \phi_{ijk} \partial \phi_{i'j'k'}}$$

All positive eigenvalues *for a* ***minimum***.

One negative eigenvalue, the others are positive for a ***transition state***.

Typically 10^6 degrees of freedom.

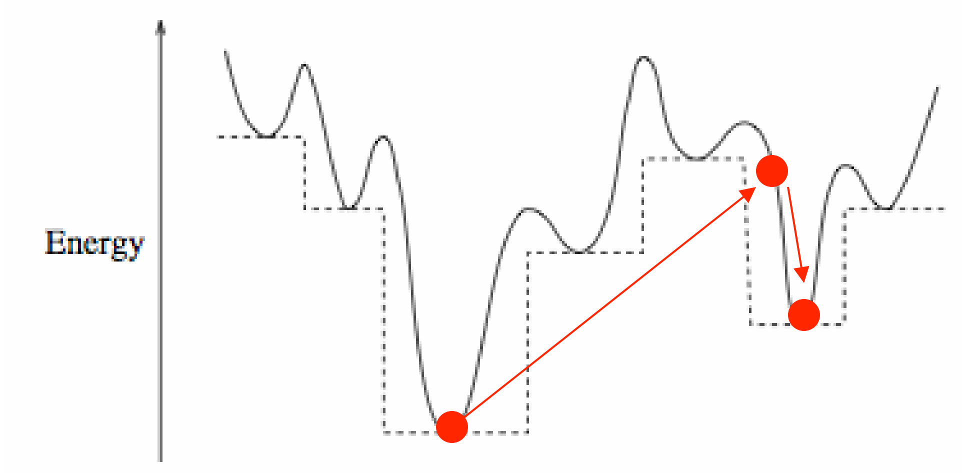
Finding Minimum Free Energy States

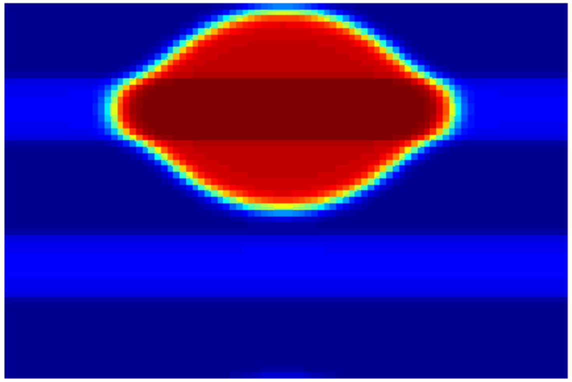


The global minimum

All relevant minima

Basin-Hopping





Three sub-steps:

1. Random perturbations

   Option 1: $\phi_{ijk} \rightarrow \phi_{ijk} + d\,\xi$

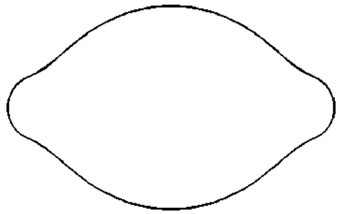
   Option 2: Deform the contour of the shape

2. Minimizations – use LBFGS algorithm (or others)

3. Acceptance criterion

   Option 1: use Metropolis algorithm

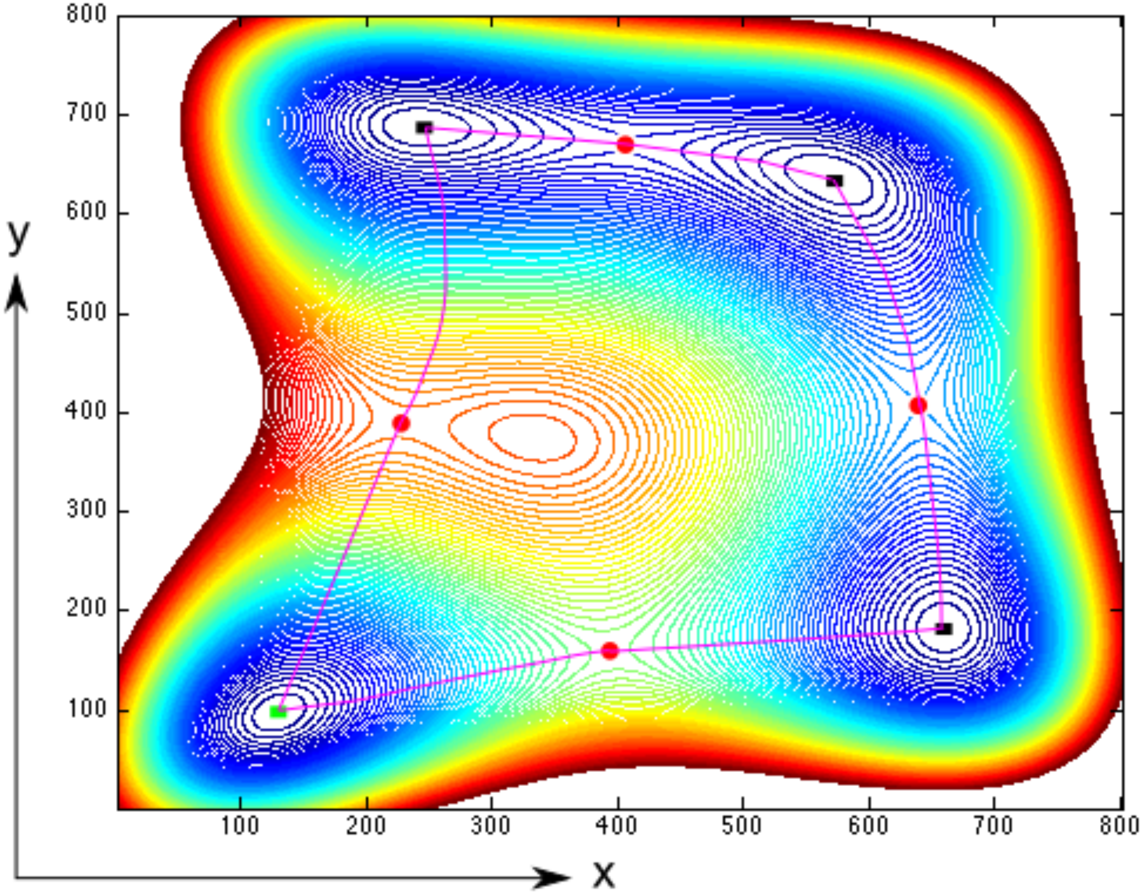
   Option 2: accept all minima (random search)



Finding barriers and pathways

Generally two classes of method:

1. Single ended methods – start from a minimum
2. Double ended methods – start with two minima of interests



The global minimum

All relevant minima

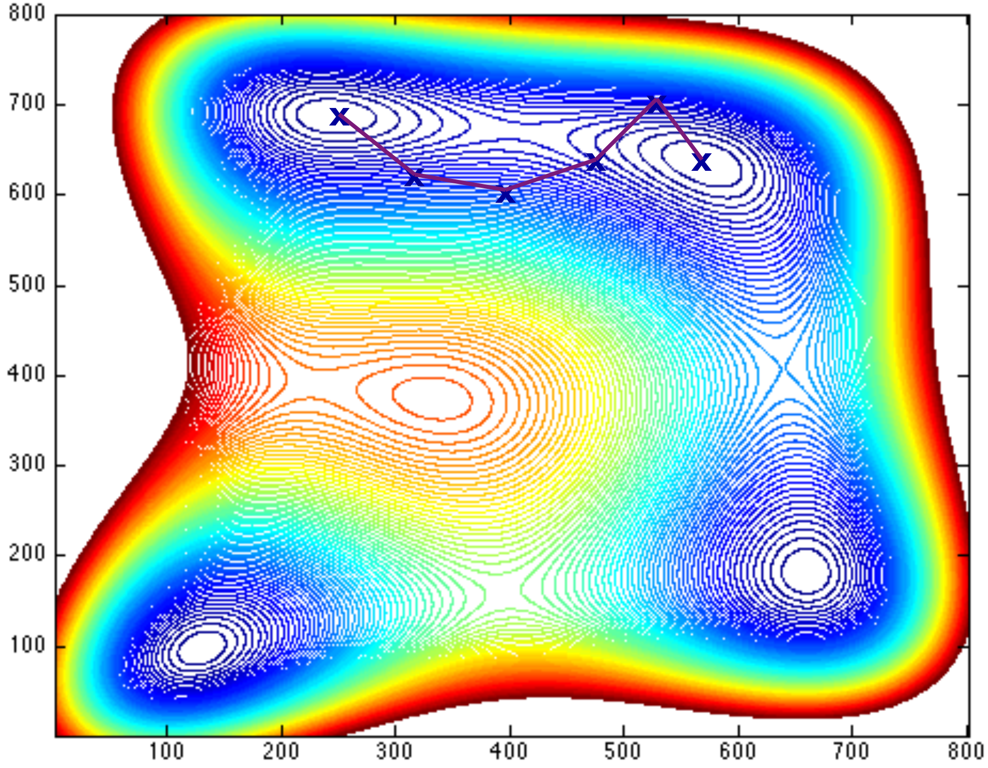
Saddle point

Minimum Energy Pathway

(Doubly-) Nudged Elastic Band

Basic Algorithm:

1. Make an initial guess for a set of images between the two minima

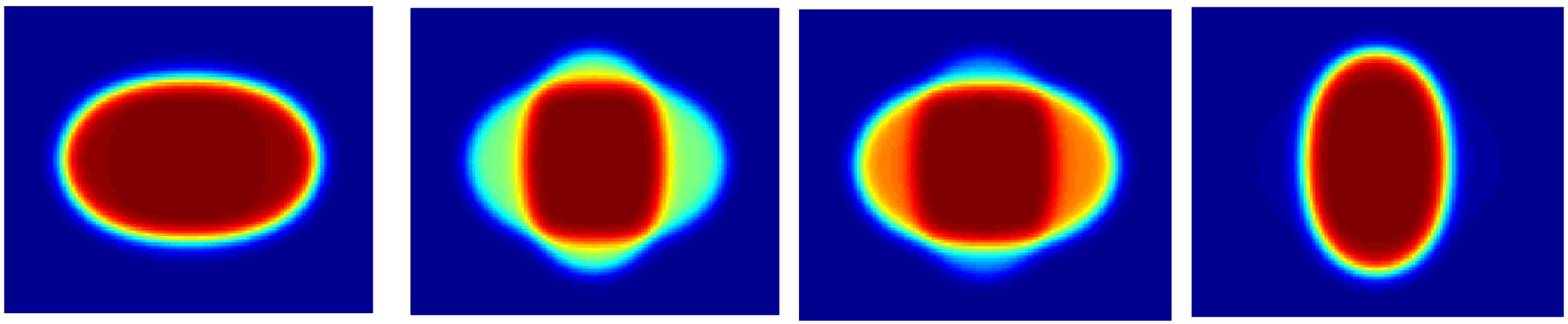


(Doubly-) Nudged Elastic Band

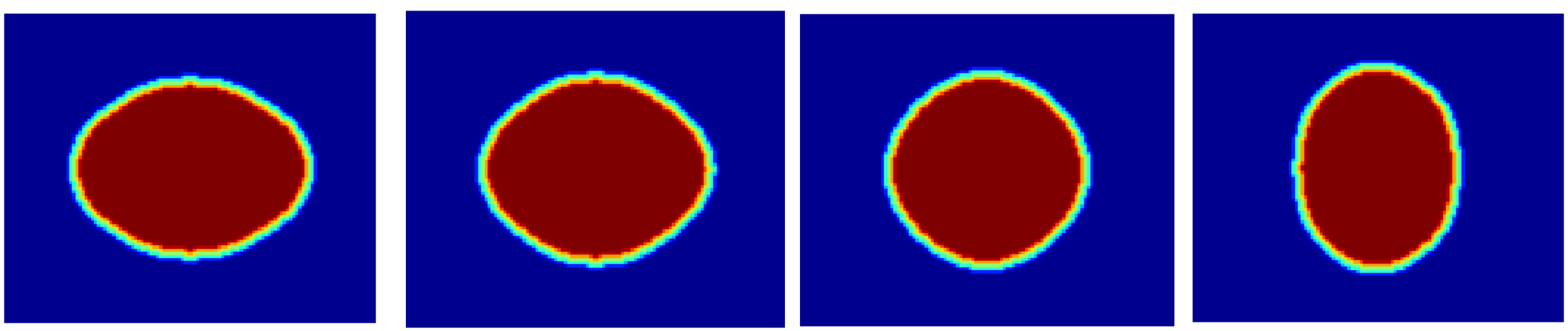
Basic Algorithm:

1. Make an initial guess for a set of images between the two minima

Linear Interpolations - Inefficient



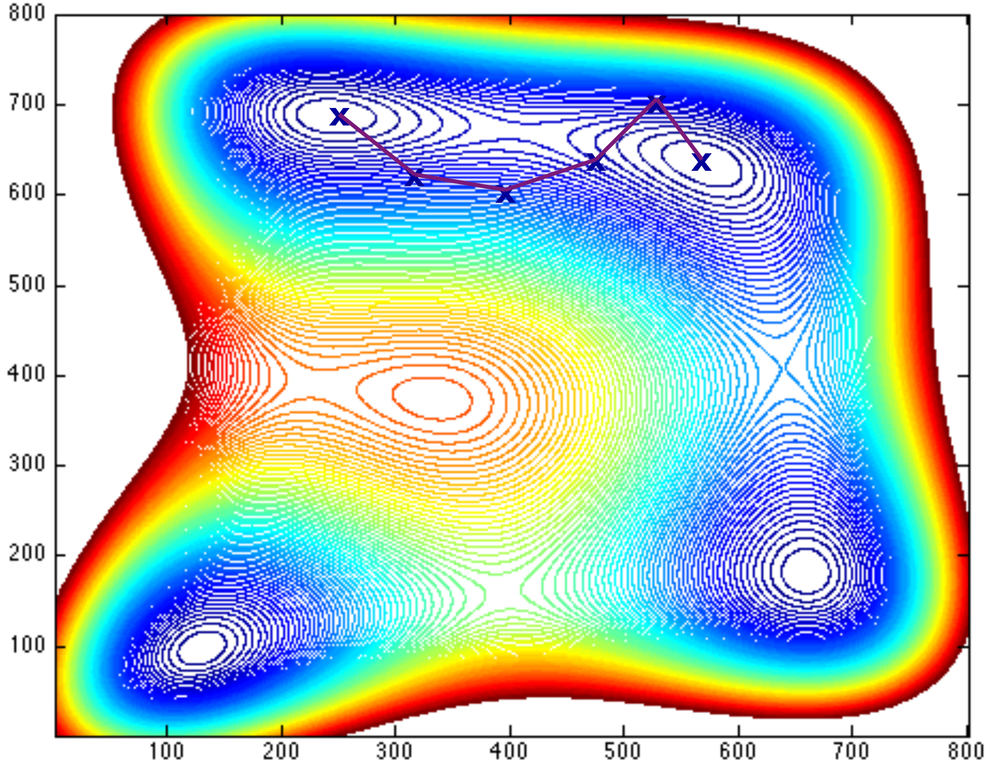
Need to “Morph” the shape



(Doubly-) Nudged Elastic Band

Basic Algorithm:

1. Make an initial guess for a set of images between the two minima
2. Connect these images by springs



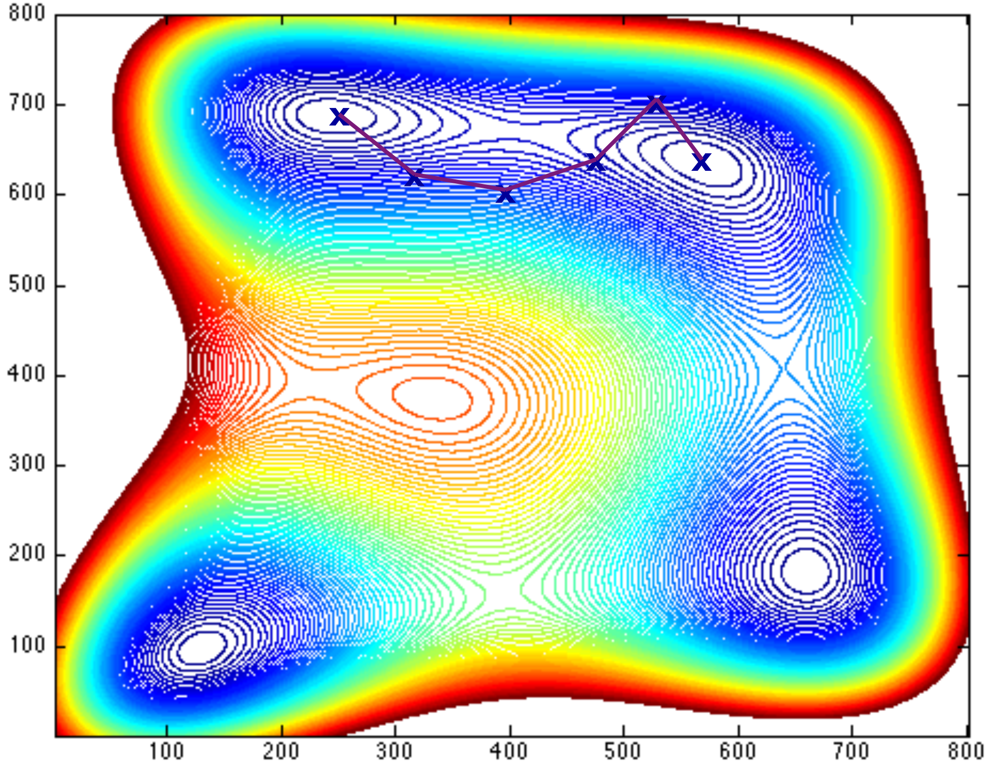
Spring potential energy:

$$V_{spring}^{\alpha} = \frac{k}{2}\left(\left(s^{\alpha,-}\right)^2 - \left(s^{\alpha,+}\right)^2\right)$$

(Doubly-) Nudged Elastic Band

Basic Algorithm:

1. Make an initial guess for a set of images between the two minima
2. Connect these images by springs
3. Relax using projections from the "true gradient" and from the "spring force" component



(Doubly-) Nudged Elastic Band

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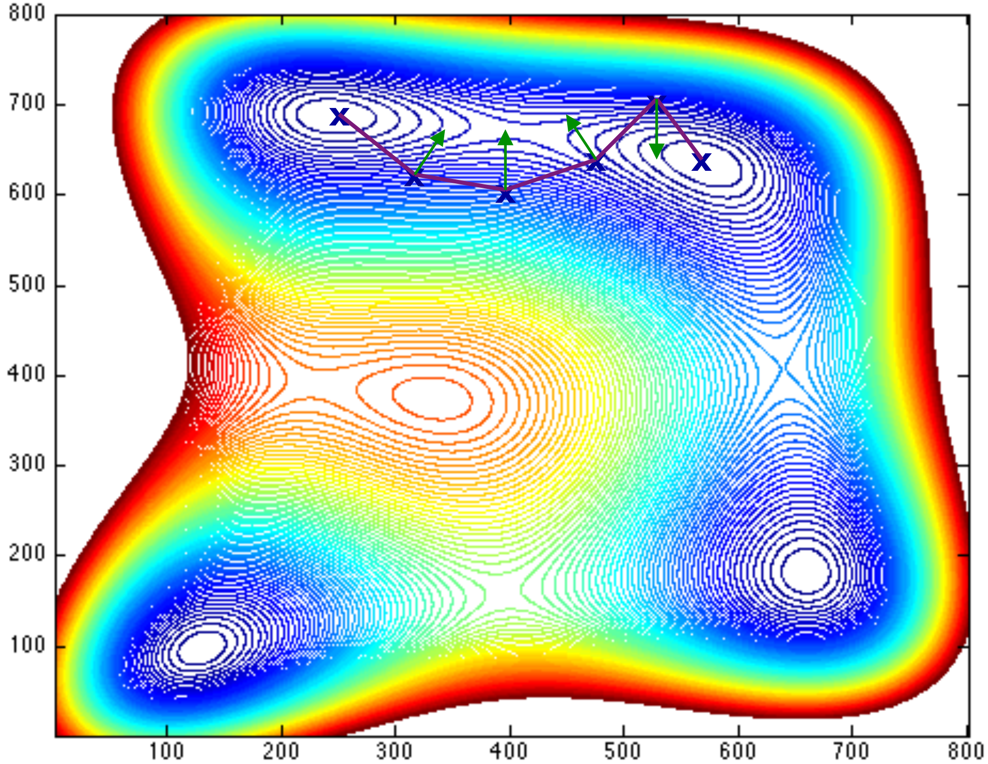


Perpendicular component of the true gradient:

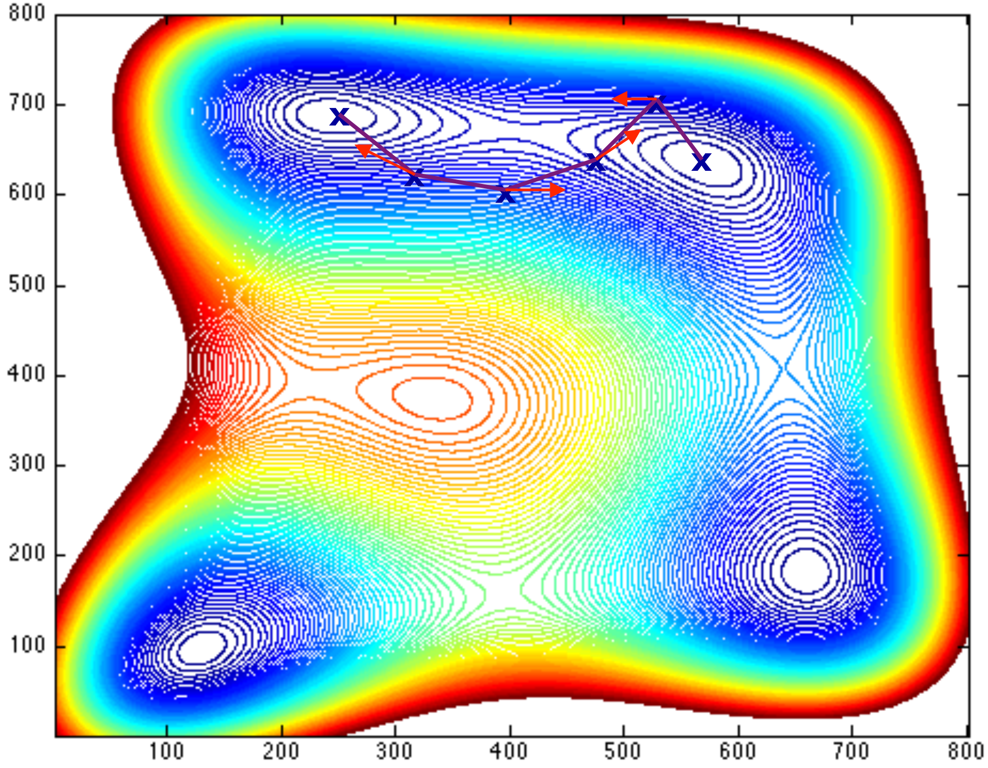
$$g_{\perp}^{\alpha} = g^{\alpha} - \left(g^{\alpha} \cdot \hat{\tau}^{\alpha}\right)\hat{\tau}^{\alpha}$$

Avoid all images collapsing to minima

(Doubly-) Nudged Elastic Band

Basic Algorithm:

1. Make an initial guess for a set of images between the two minima
2. Connect these images by springs
3. Relax using projections from the "true gradient" and from the "spring force" component



Parallel component of the spring force:

$$\tilde{g}_{\perp}^{\alpha} = k\left(s^{\alpha,+} - s^{\alpha,-}\right)\hat{\tau}^{\alpha}$$

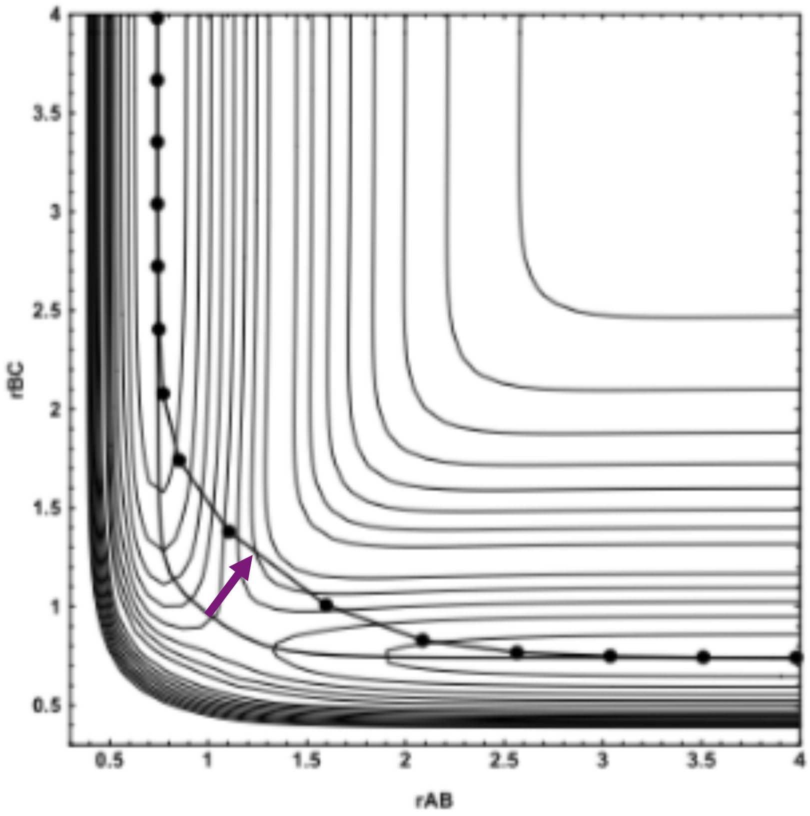
Maintain equal distance between images

Avoid "corner-cutting"

(Doubly-) Nudged Elastic Band

Basic Algorithm:

1. Make an initial guess for a set of images between the two minima
2. Connect these images by springs
3. Relax using projections from the "true gradient" and from the "spring force" component



Parallel component of the spring force:

$$\tilde{g}_{\perp}^{\alpha} = k\left(s^{\alpha,+} - s^{\alpha,-}\right)\hat{\tau}^{\alpha}$$

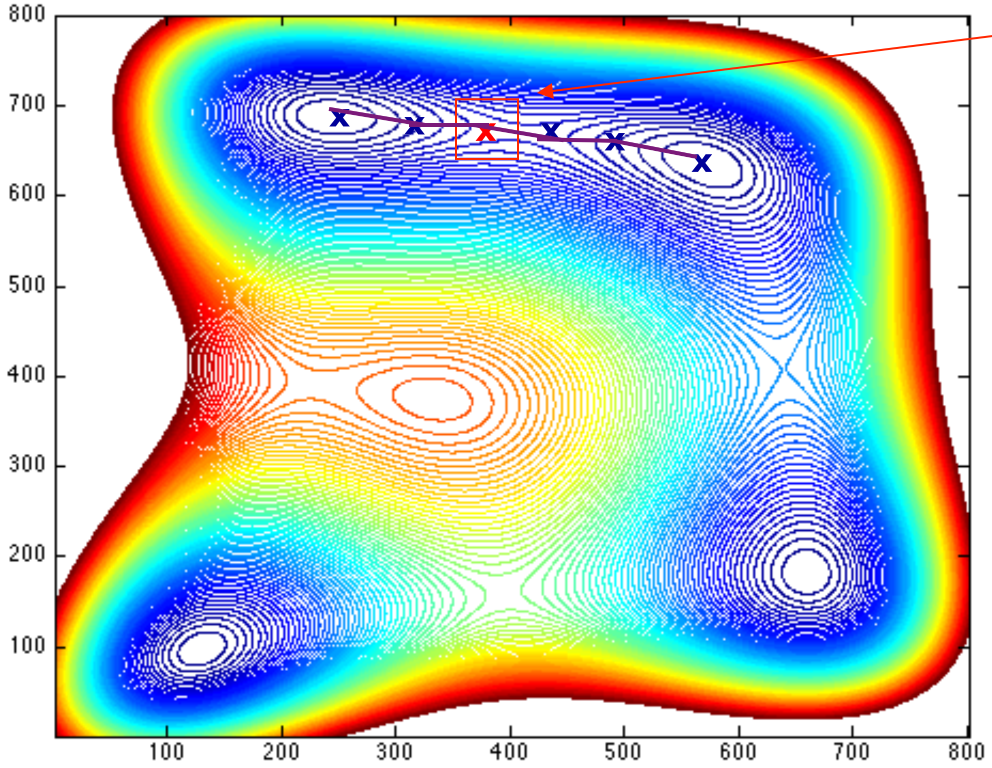
Maintain equal distance between images

Avoid "corner-cutting"

Hybrid Eigenvector-Following

Further optimise using hybrid eigenvector-following:

1. First, remember that we want to find saddle point of index 1
2. Uphill step in one eigendirection
3. Minimization in the tangent space



Candidate for a transition state

Optimize using eigenvector-following

Obtain a “**minimum energy path**”

Keep iterating until all minima and transition states are found!

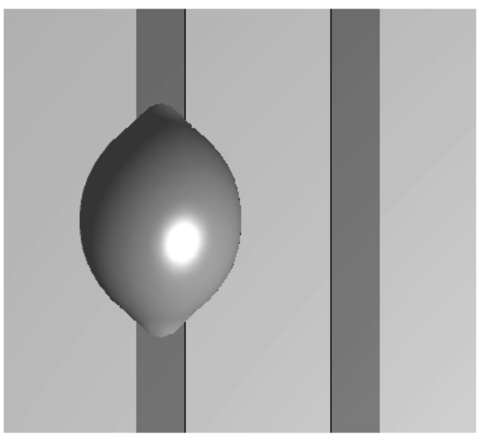
Hybrid Eigenvector-Following

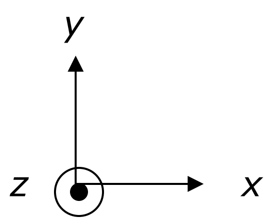
Further optimise using hybrid eigenvector-following:

1. First, remember that we want to find saddle point of index 1
2. Uphill step in one eigendirection
3. Minimization in the tangent space
4. Remove zero eigenvectors

Zero Eigenvectors

Arise when periodic boundary conditions are used



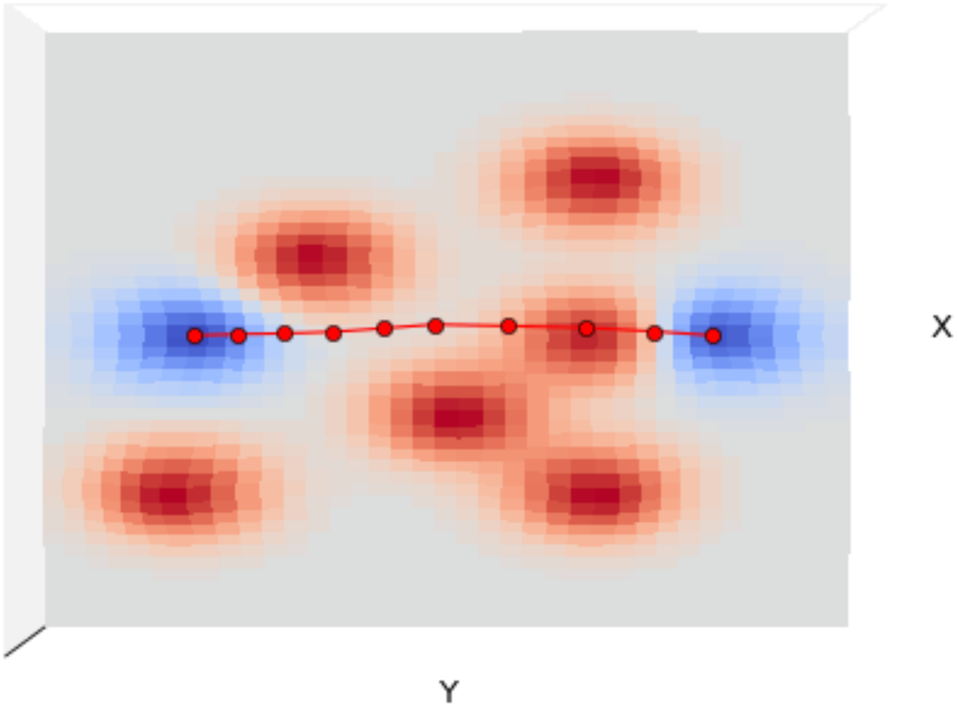


In this example, for the y-direction:

$$\hat{e} = \frac{1}{N}\left(\frac{\partial \phi_{111}}{\partial y} \cdots \frac{\partial \phi_{ijk}}{\partial y} \cdots \frac{\partial \phi_{NxNyNz}}{\partial y} \right)$$

Many Ways to Rome

With Joao Louis Carabetta

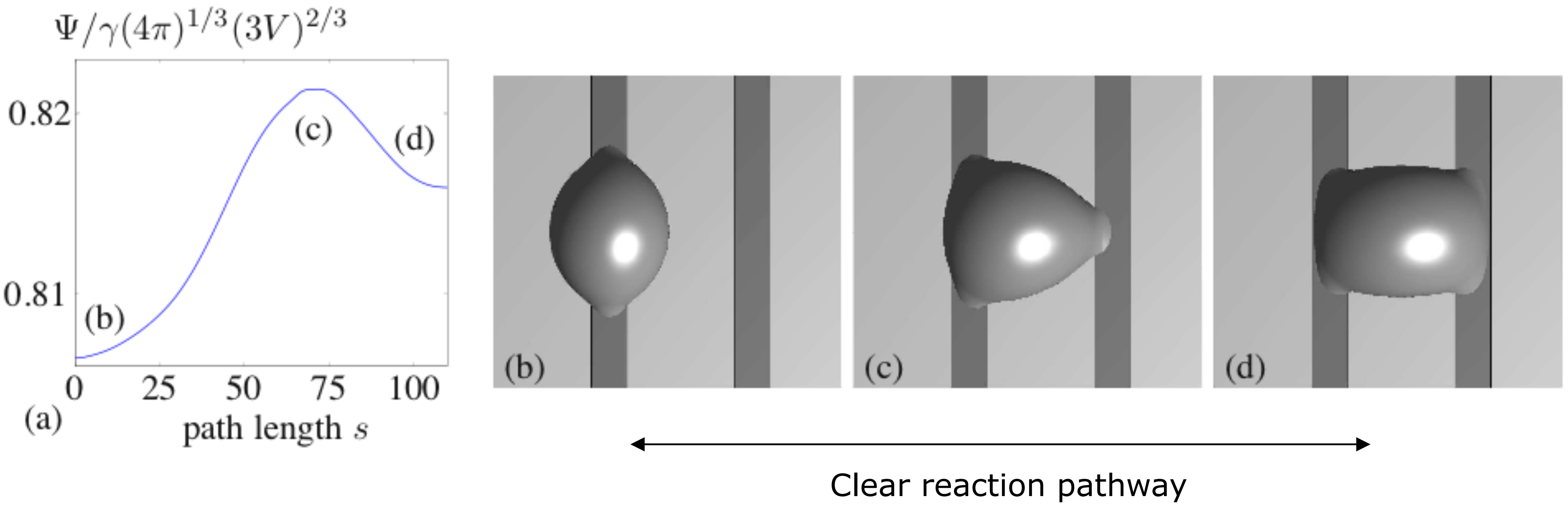


Results

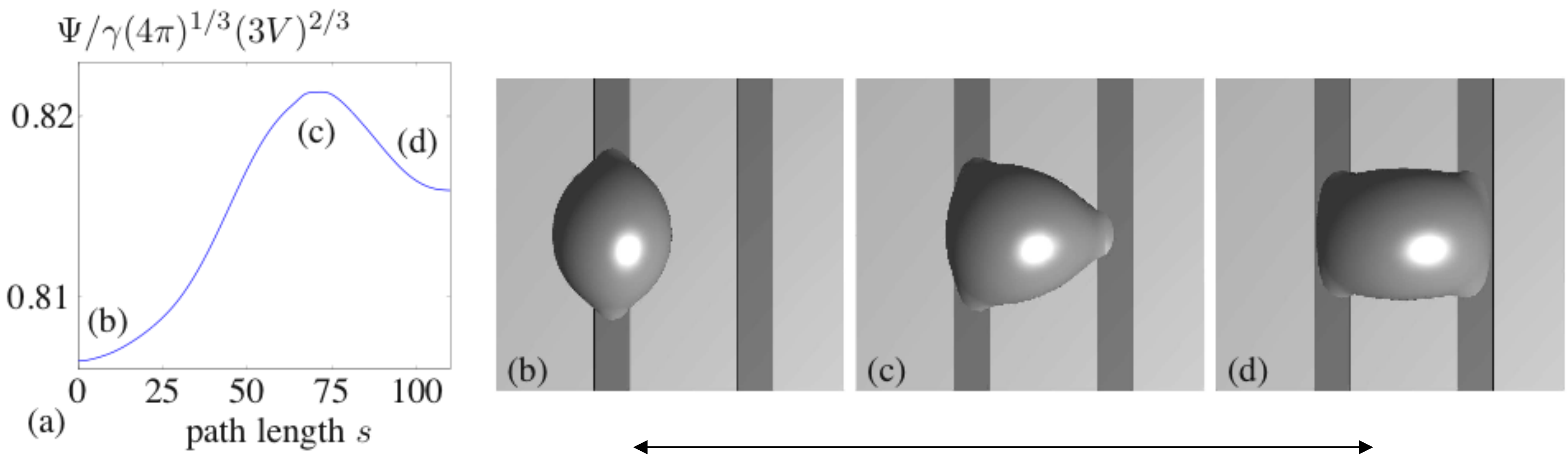
Wetting on Chemically Striped Surfaces

Surface Energies $$\Psi = \gamma_{LV} A_{LV} + \gamma_{SV} A_{SV} + \gamma_{SL} A_{SL}$$

Contact Angle $$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

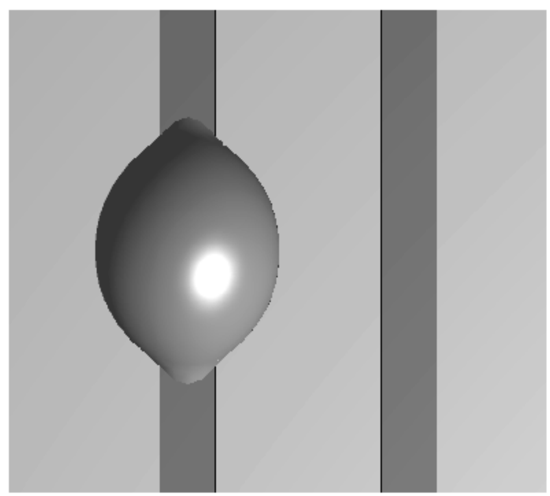


Wetting on Chemically Striped Surfaces



Clear reaction pathway

Minimum Energy Path



Vesice Shapes I

Helfrich Free Energy

$$\Psi = \int_A \frac{\kappa}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 dA \quad + \quad PV \quad + \quad \gamma A$$

Curvature Energy Volume Conservation Area Conservation

Energy scales for bending:

e.g. for a vesicle of size 1 micron.

$$F \sim \kappa_b\left(\frac{1}{R^2}\right)A \sim \kappa_b \approx 10-20\ k_BT$$

Energy scales for shearing: ~0.

This is a consequence of membrane fluidity. For example, when where there is a spectrin (cytoskeleton) network (e.g. red blood cells), this contribution is non-zero and can be important.

Energy scales for stretching:

e.g. for a vesicle of size 1 micron to be stretched by 1%.

$$F \sim \kappa_s A\left(\frac{\Delta A}{A}\right)^2 \approx 60\frac{k_BT}{\text{nm}^2}\times(1000\text{nm})^2\left(\frac{1}{100}\right)^2 \approx 6000\ k_BT$$

For this reason, the membrane area is also assumed to be constant, when considering vesicle shapes that arise due to bending energy.

Vesicle Shapes I

Helfrich Free Energy

$$\Psi = \int_A \frac{\kappa}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 dA \quad + \quad PV \quad + \quad \gamma A$$

Curvature Energy | Volume Conservation | Area Conservation

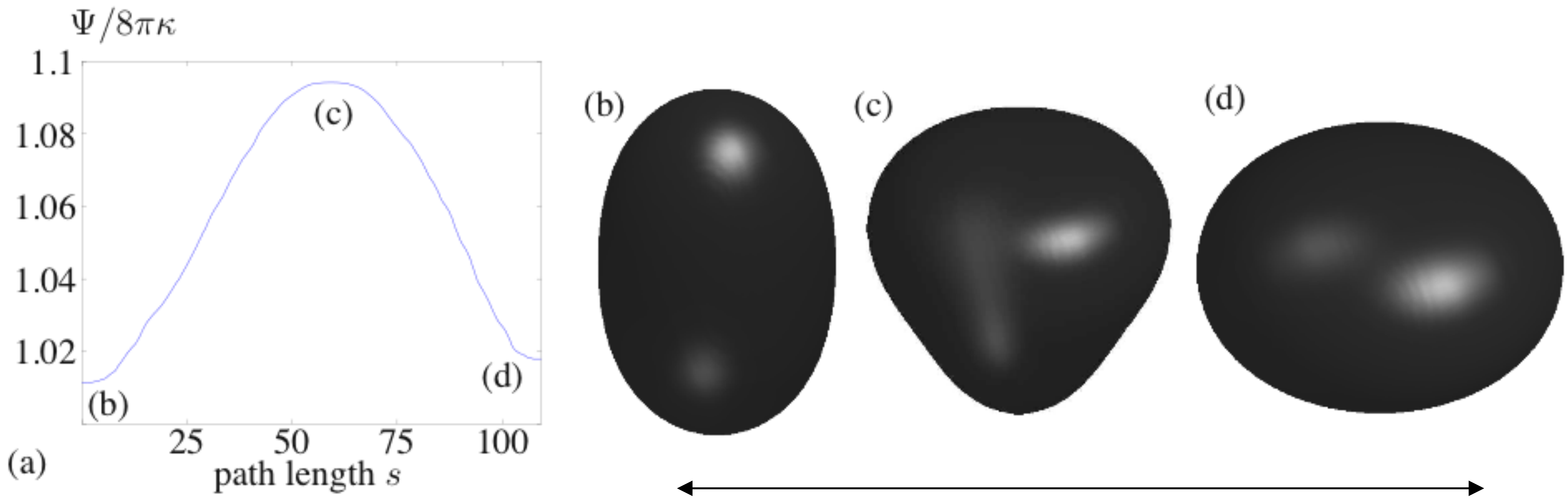
Landau Free Energy

[Du et al. (2004)]

$$\Psi = \int_V \frac{\kappa\varepsilon}{2}\left(\Delta\phi - \frac{1}{\varepsilon^2}\left(\phi^2 - 1\right)\phi\right)^2 dV + \frac{1}{2}k_V\left(V - V_0\right)^2 + \frac{1}{2}k_A\left(A - A_0\right)^2$$

Reduced volume

$$\nu = \frac{V_0 / (4\pi/3)}{\left(A_0/4\pi\right)^{3/2}} = 0.987$$



Reaction pathway unclear

Vesicle Shapes I

Helfrich Free Energy

$$\Psi = \int_A \frac{\kappa}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 dA \quad + \quad PV \quad + \quad \gamma A$$

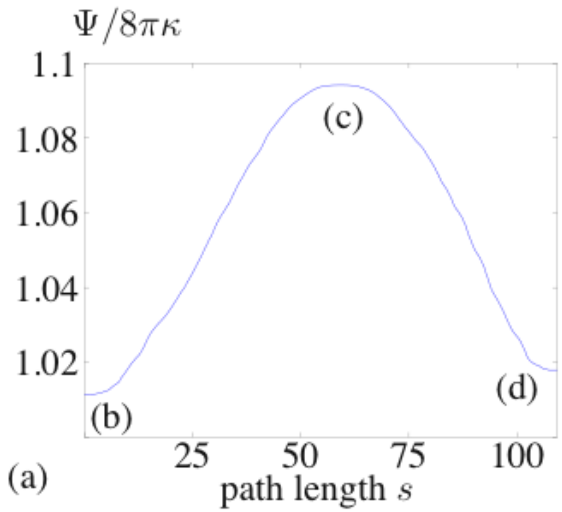
Curvature Energy | Volume Conservation | Area Conservation

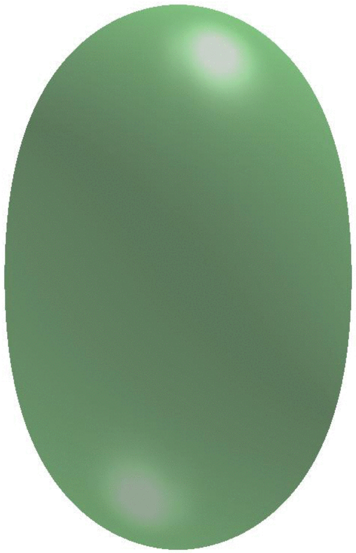
Landau Free Energy

$$\Psi = \int_V \frac{\kappa\varepsilon}{2}\left(\Delta\phi - \frac{1}{\varepsilon^2}\left(\phi^2 - 1\right)\phi\right)^2 dV + \frac{1}{2}k_V\left(V - V_0\right)^2 + \frac{1}{2}k_A\left(A - A_0\right)^2$$

Reduced volume

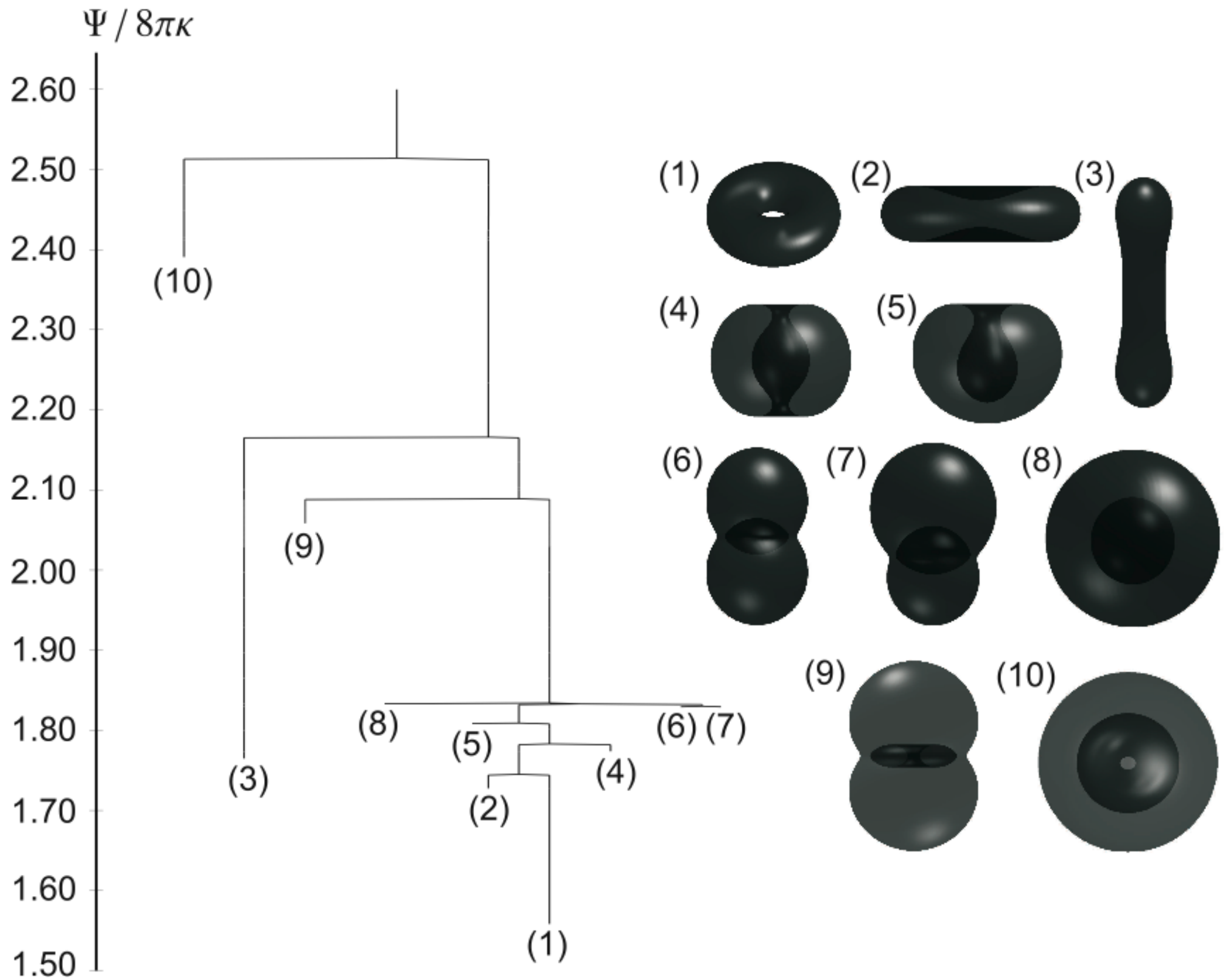
$$v = \frac{V_0/(4\pi/3)}{\left(A_0/4\pi\right)^{3/2}} = 0.987$$



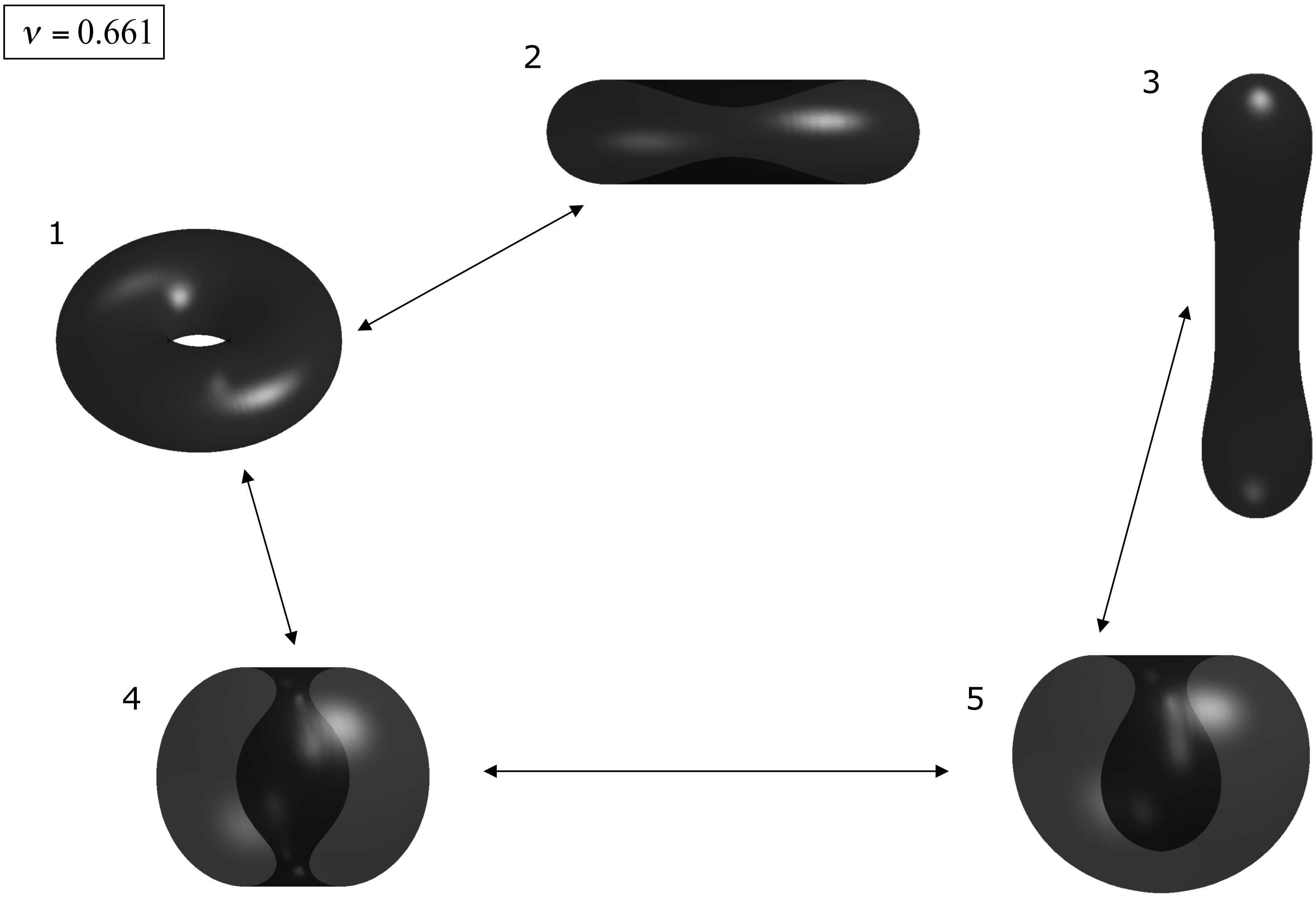


Vesicle Shapes II

$\nu = 0.661$

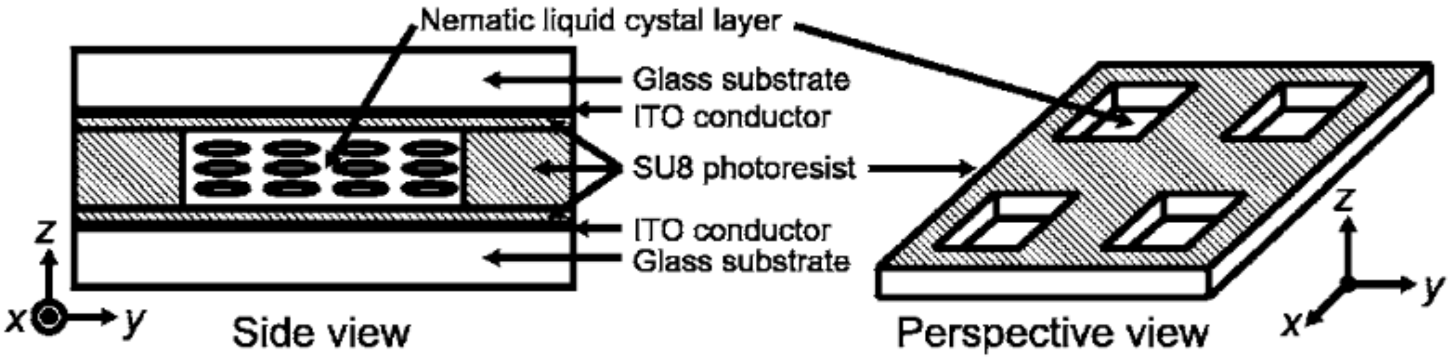


Vesicle Shapes II

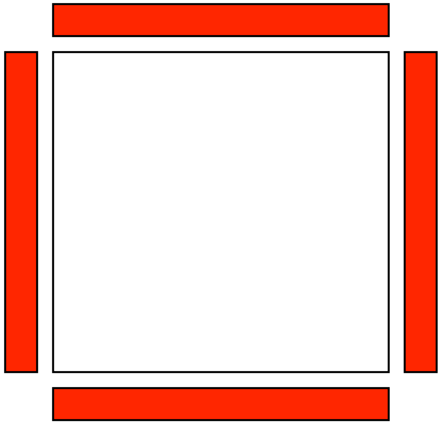


Liquid Crystals

Experimental Setup – Tsakonas et al., APL 90, 111913 2007



+ surface anchoring



Liquid Crystals

H. Kusumaatmaja and A. Majumdar, Soft Matter **11**, 4809 (2015)

Landau-de Gennes Free Energy

$$\Psi = \int_A \frac{\kappa_{el}}{2}\left|\nabla \mathbf{Q}\right|^2 dA + \int_A \left[-\alpha \mathrm{Tr}\mathbf{Q}^2 - \frac{b^2}{3}\mathrm{Tr}\mathbf{Q}^3 + \frac{c^2}{4}\left(\mathrm{Tr}\mathbf{Q}^2\right)^2\right] dA$$

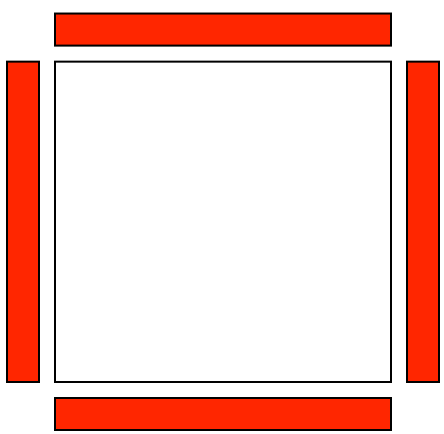
Bending Energy — Bulk Energy

Where the **Q**-tensor is defined as $\mathbf{Q} = \begin{bmatrix} Q_{11} & Q_{12} \\ Q_{12} & -Q_{11} \end{bmatrix} = s\left(2\mathbf{n}\otimes\mathbf{n} - \mathbf{I}\right)$ in two dimensions.

Dimensionless form $\tilde{\Psi} = \int_{\tilde{A}} \tilde{\kappa}_{el}\left[\left|\tilde{\nabla}\tilde{Q}_{11}\right|^2 + \left|\tilde{\nabla}\tilde{Q}_{12}\right|^2\right] d\tilde{A} + \int_{\tilde{A}} \left(\tilde{Q}_{11}{}^2 + \tilde{Q}_{12}{}^2 - 1\right) d\tilde{A}$

As for a scalar order parameter $\Psi = f\left(\left\{Q_{11}, Q_{12}\right\}_{ijk}\right)$

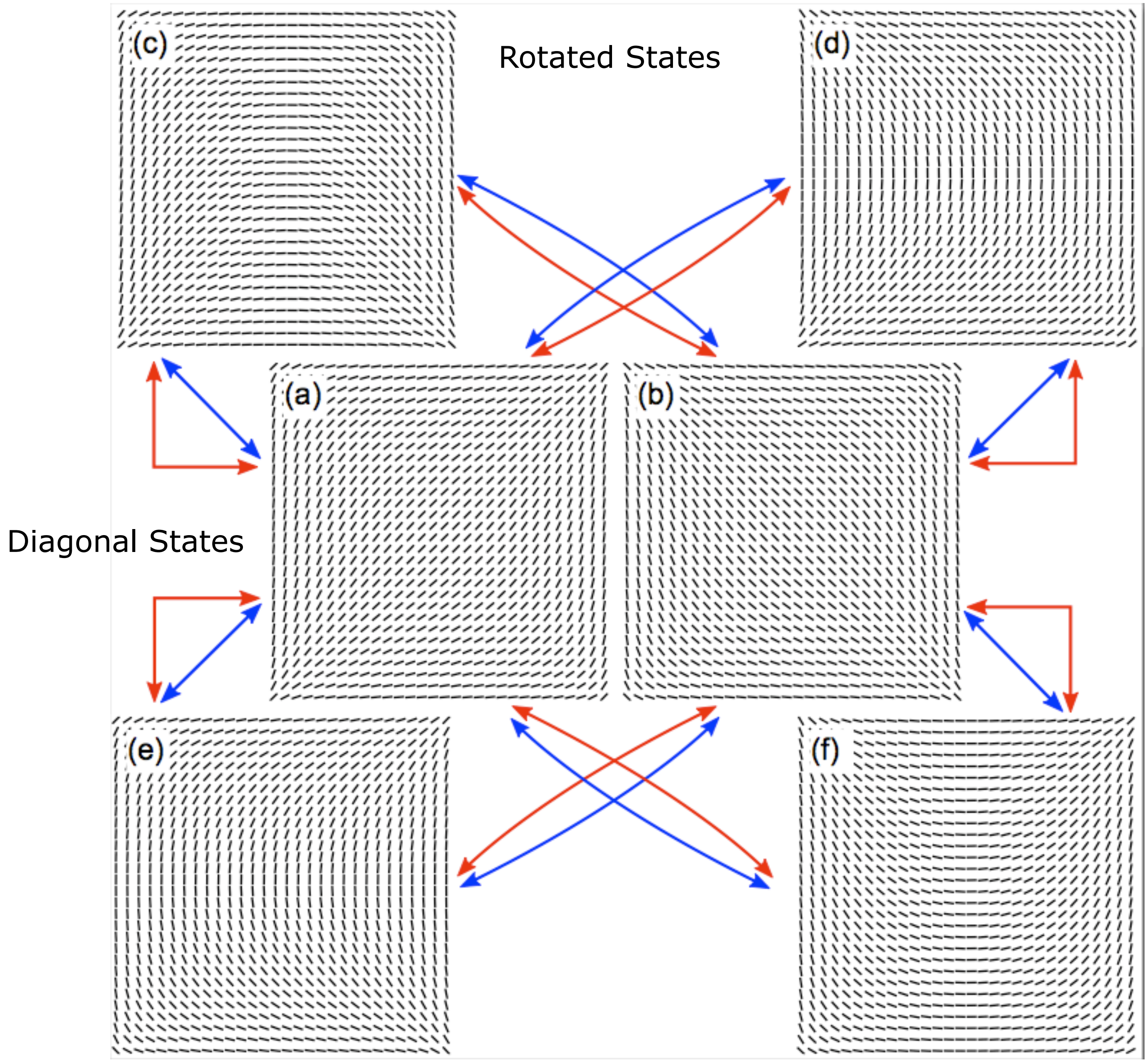
+ surface anchoring



$$\int_{\partial A} W\left(\tilde{Q} - \tilde{Q}_{wall}\right)^2 dl$$

Anchoring Strength *W*

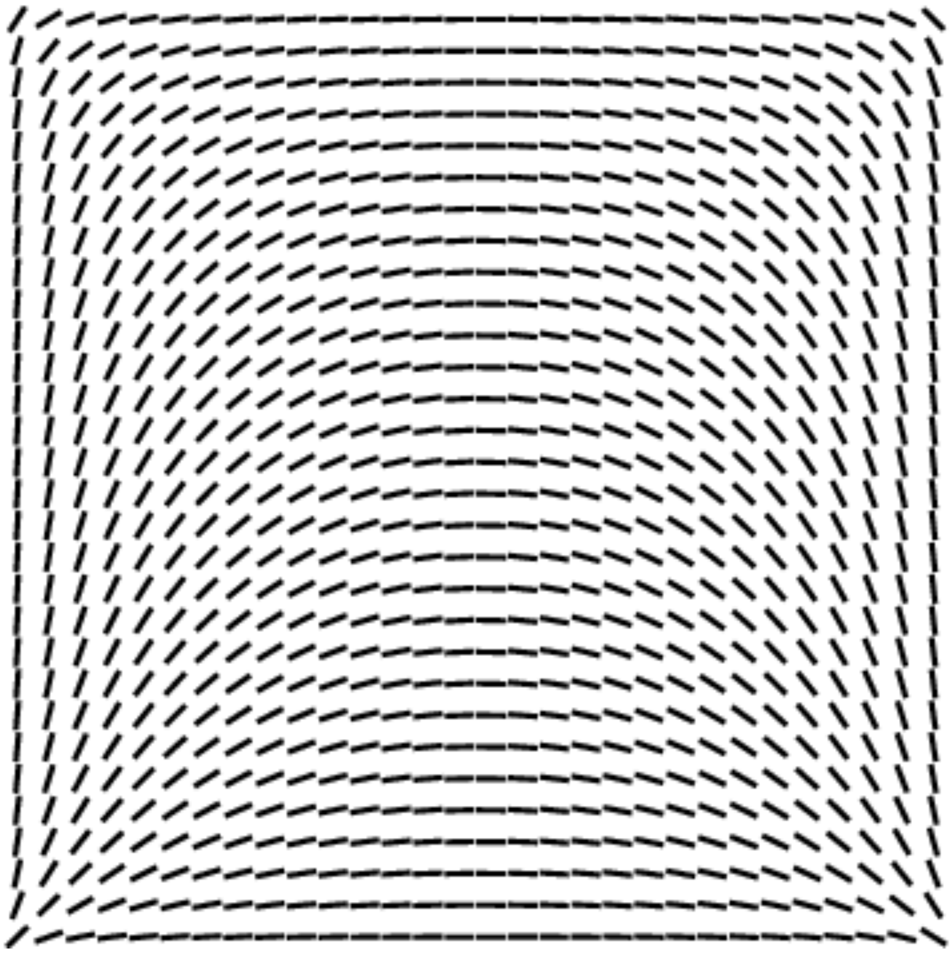
Rotated and Diagonal States



Beyond the minimizers:

1. Pathways and barriers
2. Competing pathways?
3. Connectivity
4. Stability of Minima

One Possible Pathway



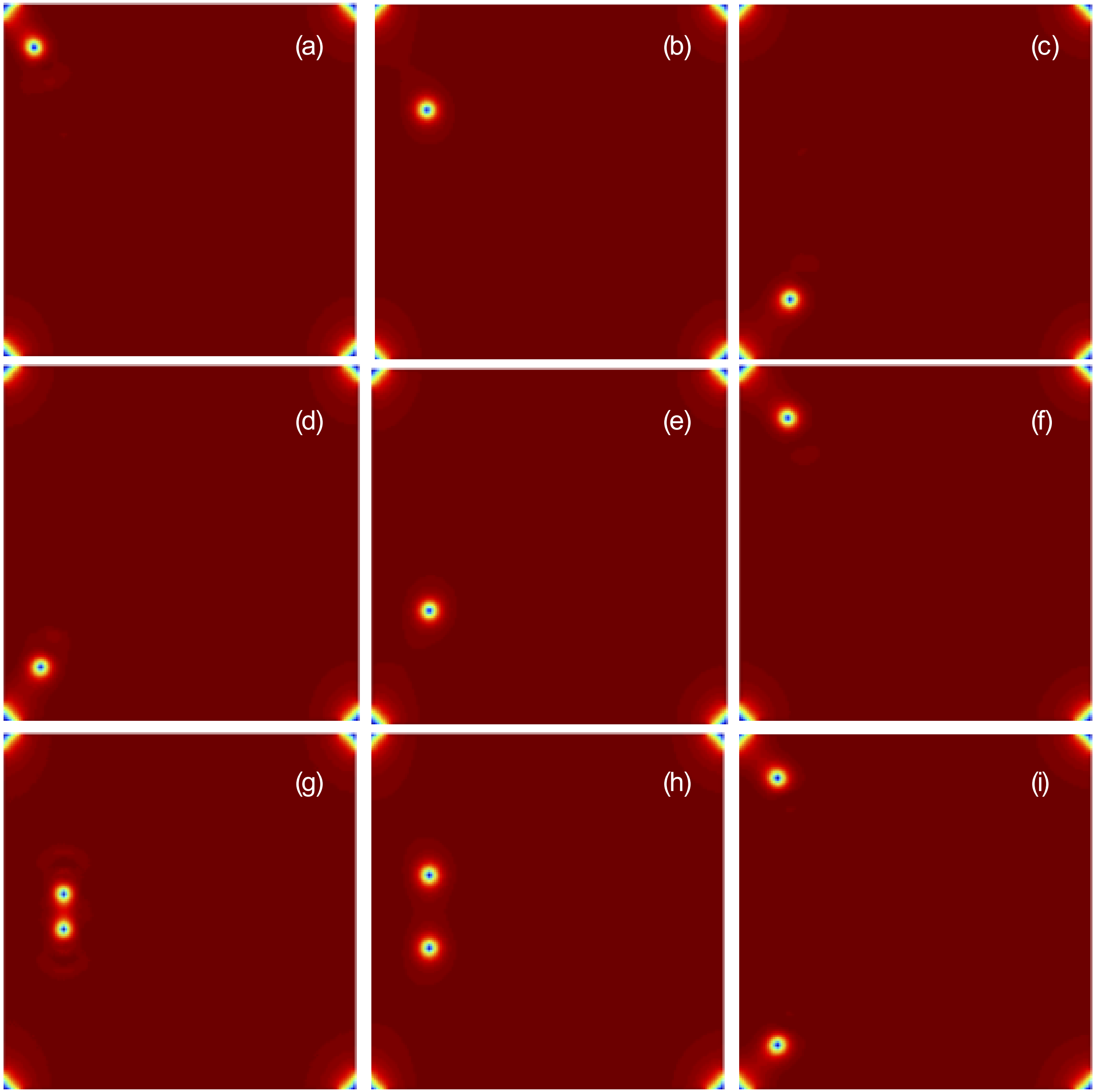
Strong Anchoring Pathways

- ½ defect

+ ½ defect

Pair of defects

Order Parameter *s*



- ½ defect

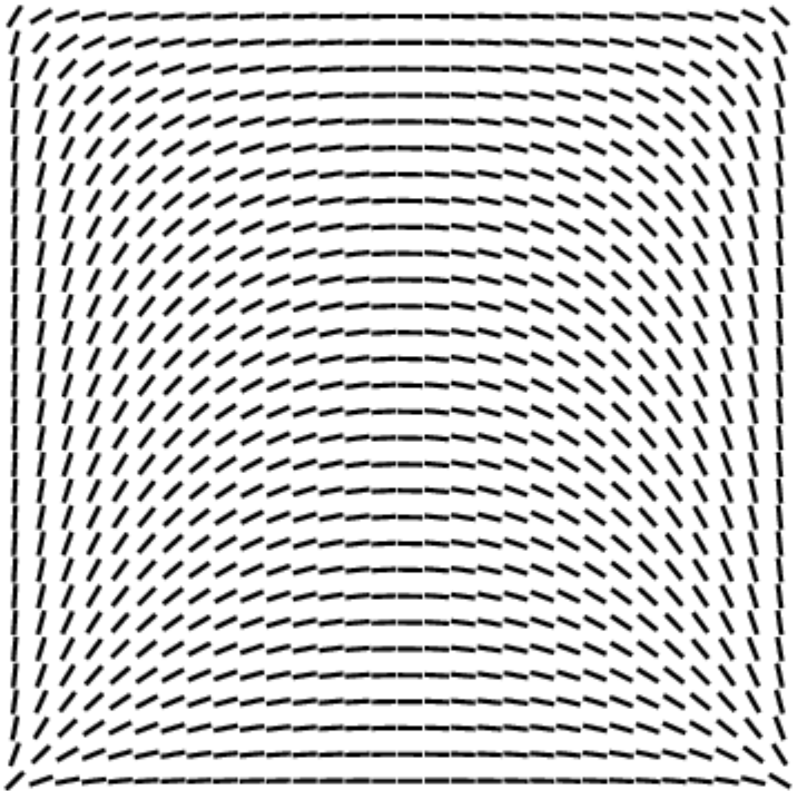
Remember that:

$$\mathbf{Q} = s\left(2\mathbf{n} \otimes \mathbf{n} - \mathbf{I}\right)$$

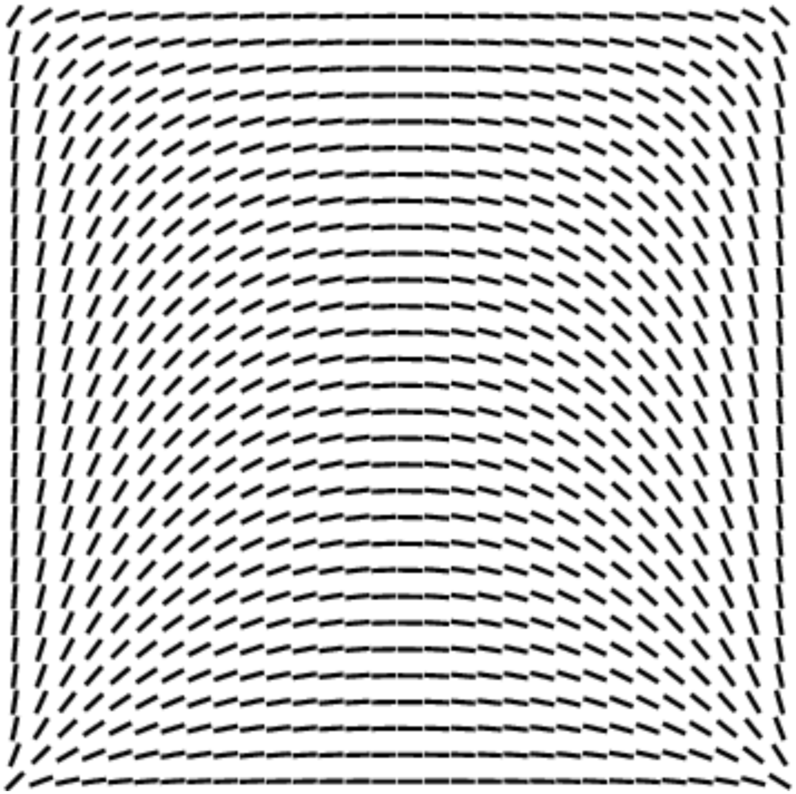
+ ½ defect

Pair of defects

Strong Anchoring Pathways



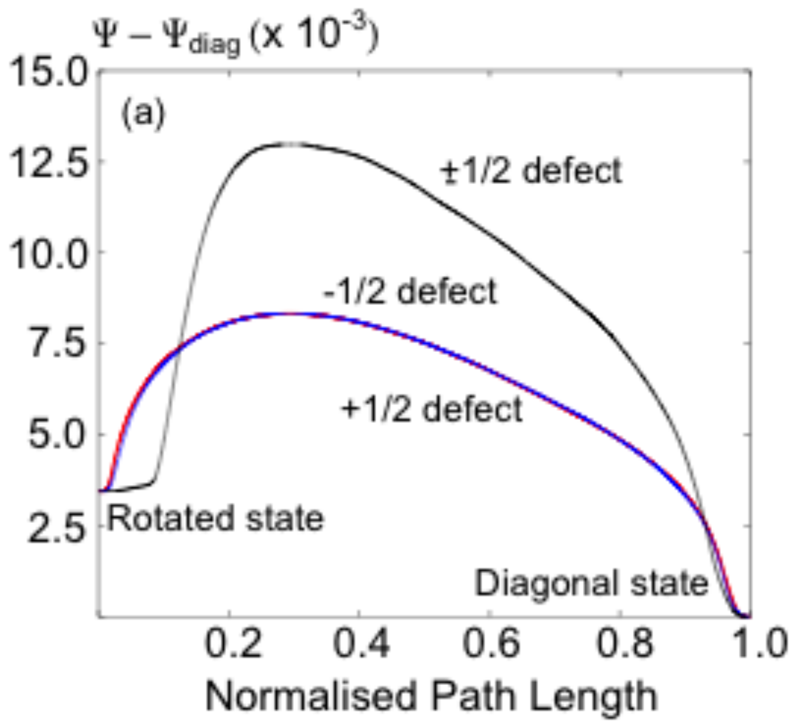
+ ½ defect



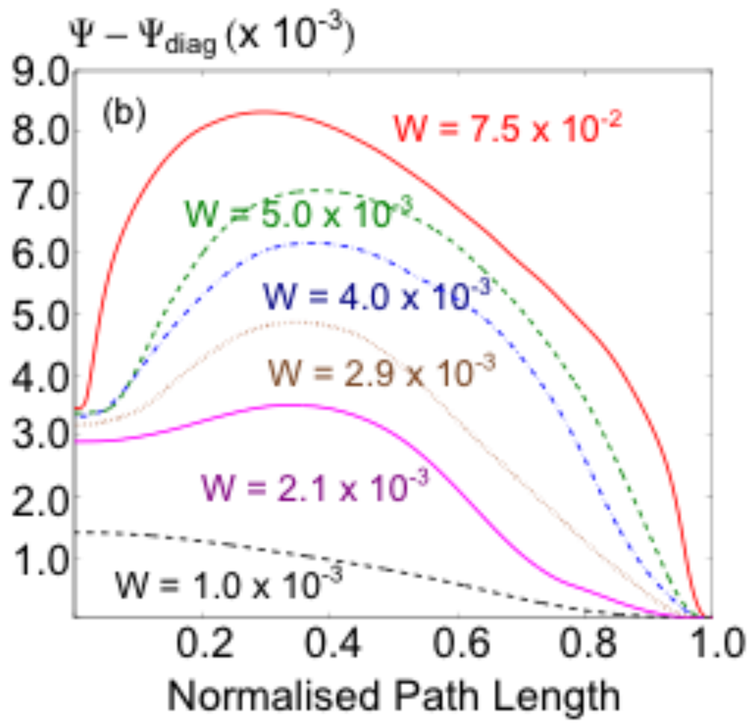
Pair of defects

Energy Profiles

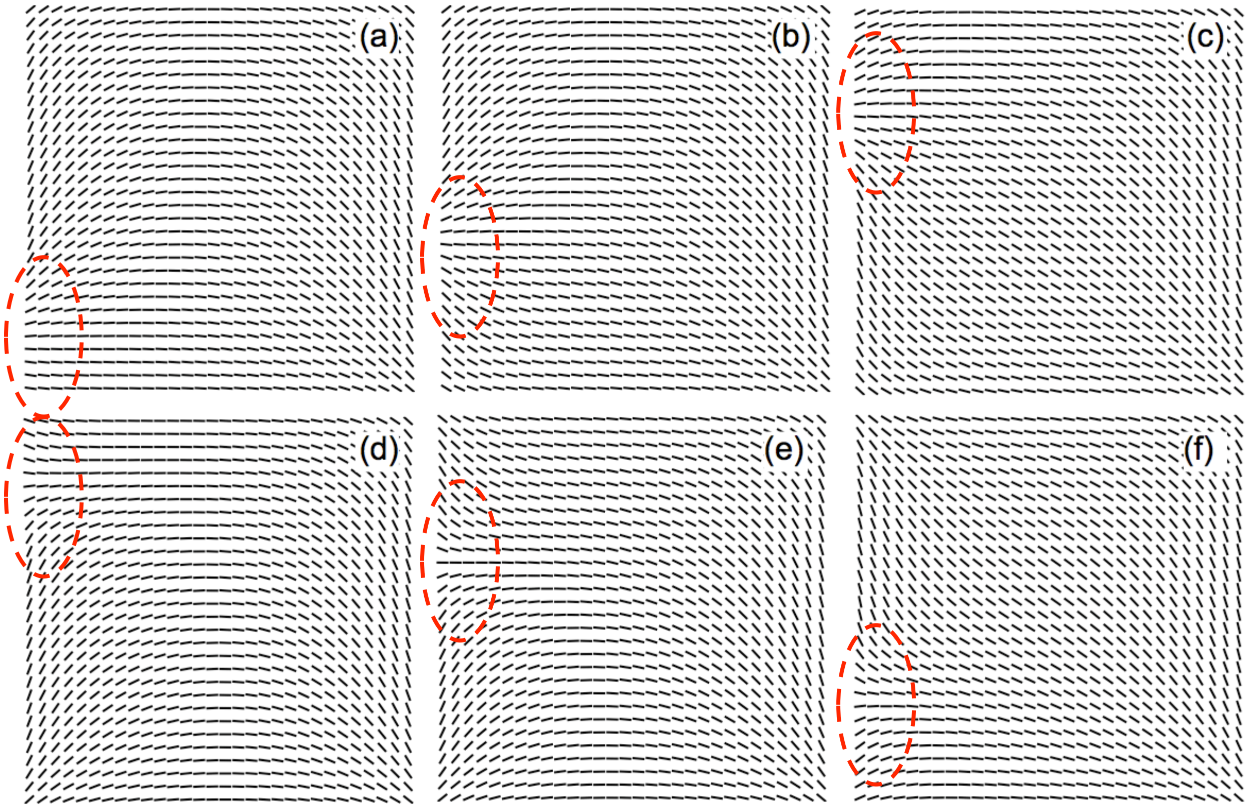
Strong Anchoring



Varying Anchoring Strengths

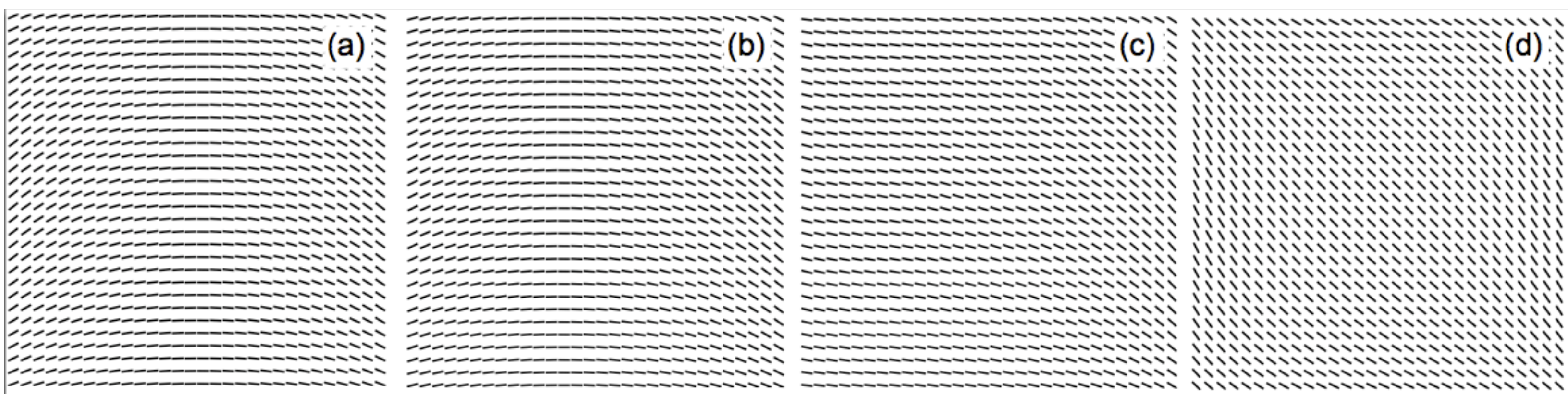


Pathways Depend on Anchoring Strengths



Medium Anchoring Strength

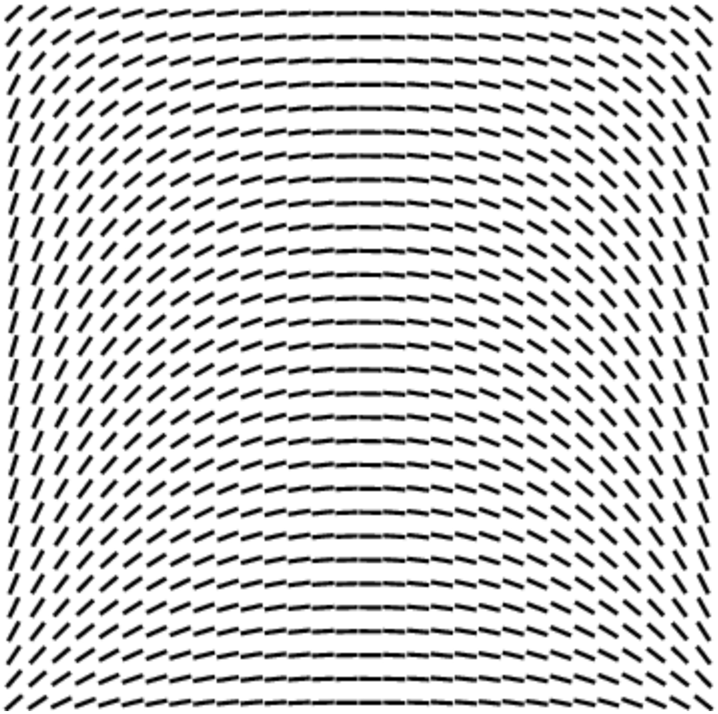
Two Degenerate Pathways

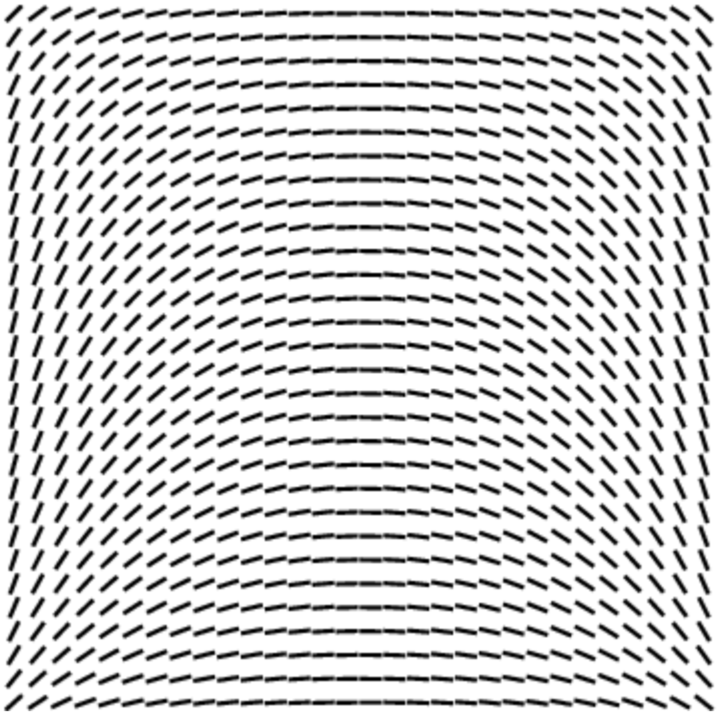


Weak Anchoring Strength

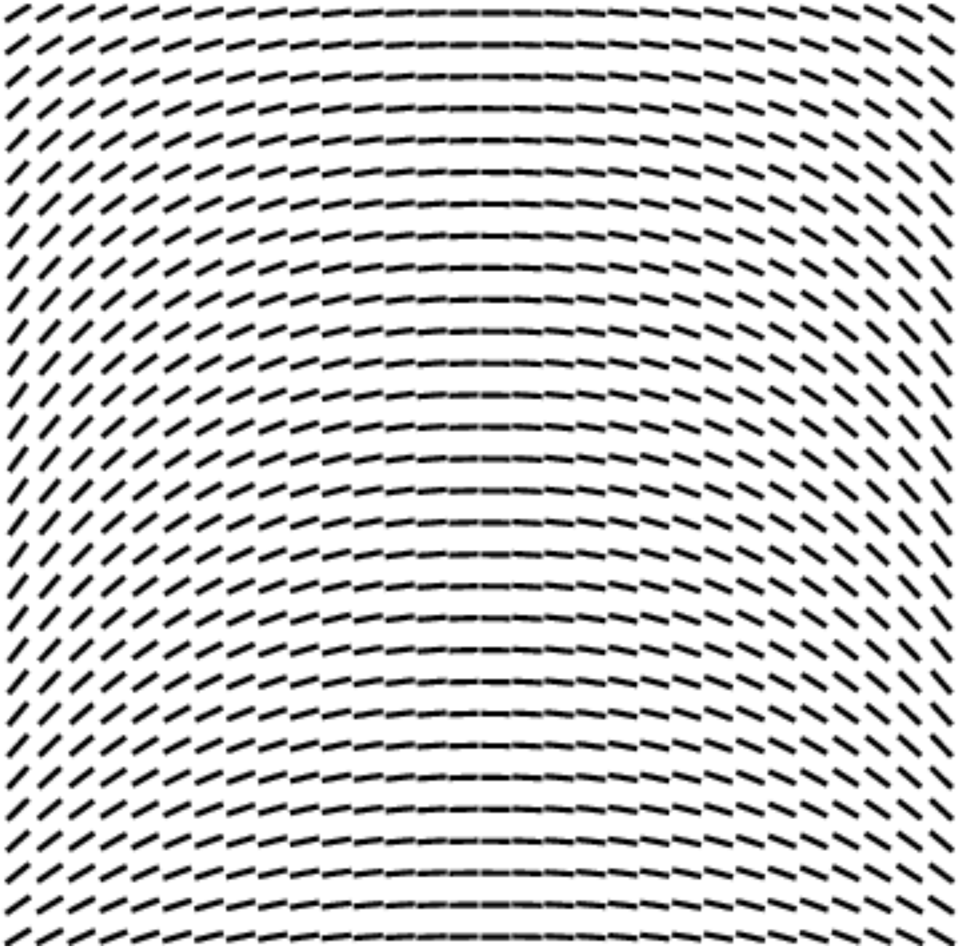
Medium Anchoring

Two Degenerate Pathways



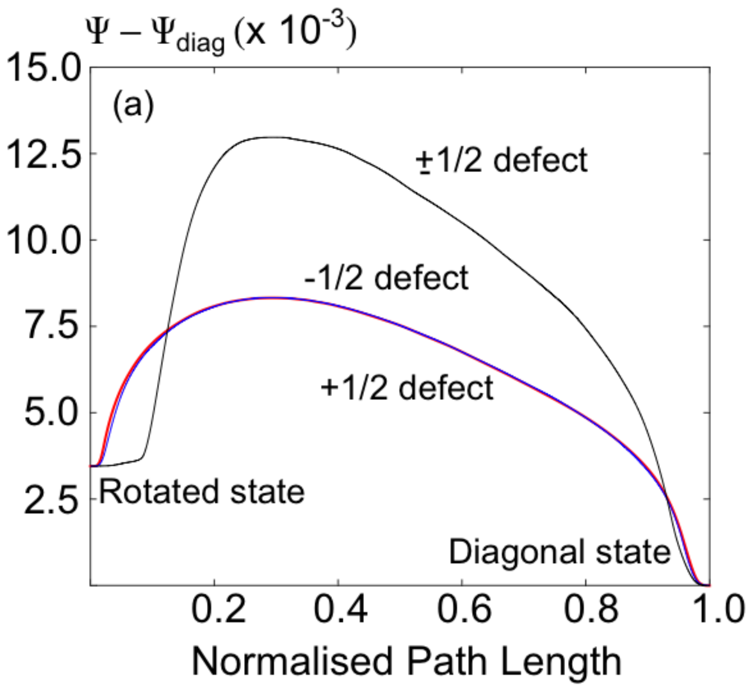


Weak Anchoring

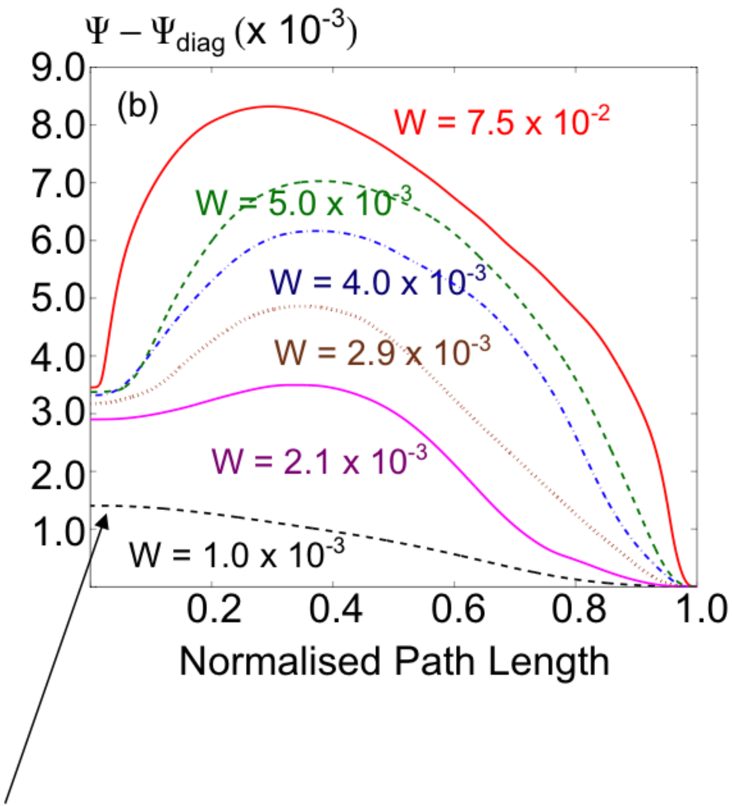


Energy Profiles

Strong Anchoring



Varying Anchoring Strengths

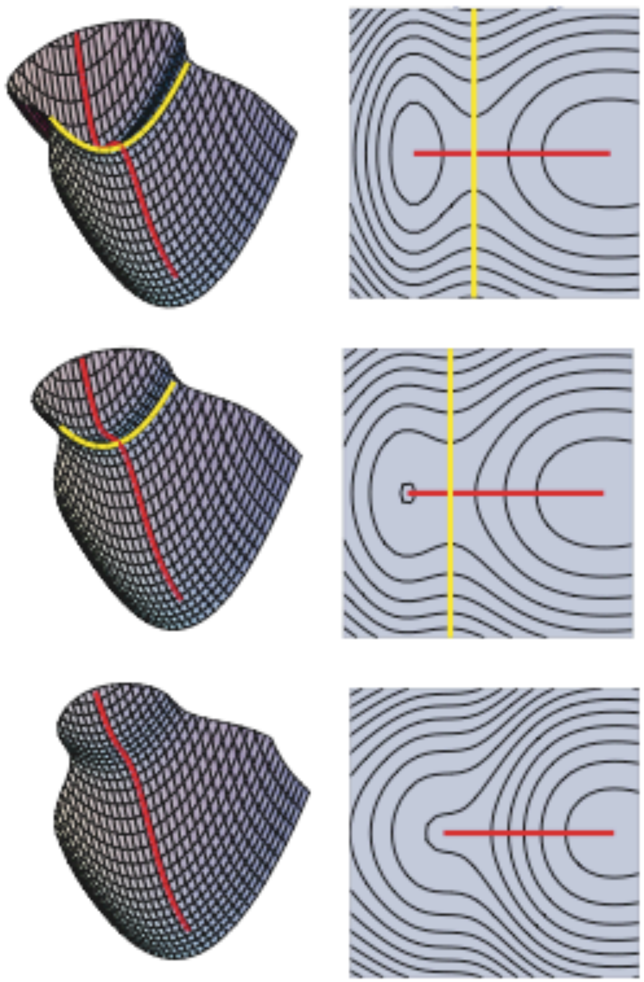


Disappearance of minima

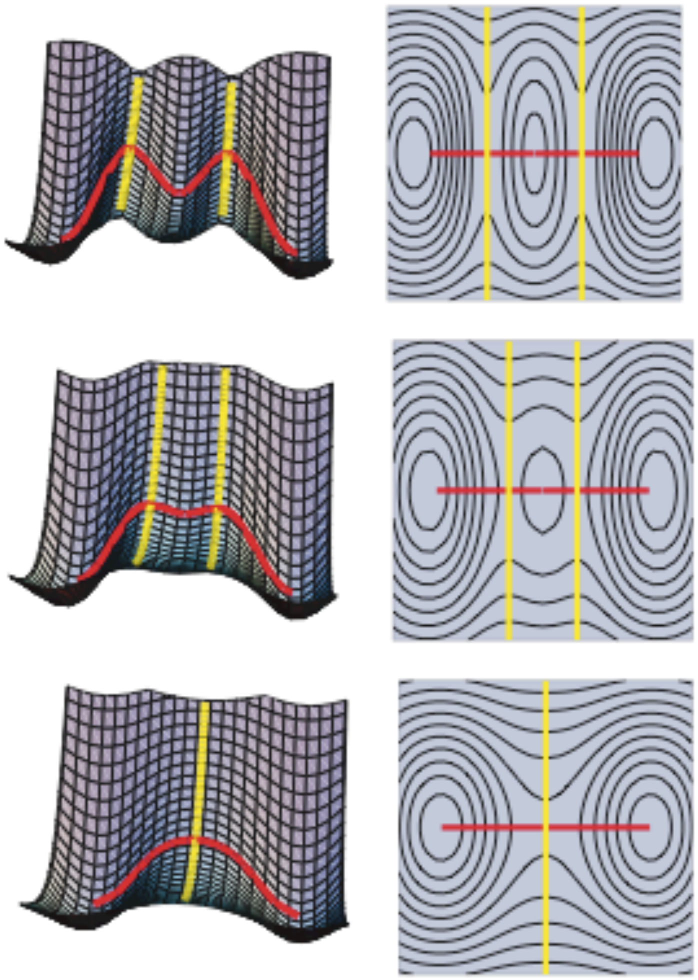
(Catastrophe event)

Catastrophe Events

Fold Catastrophe



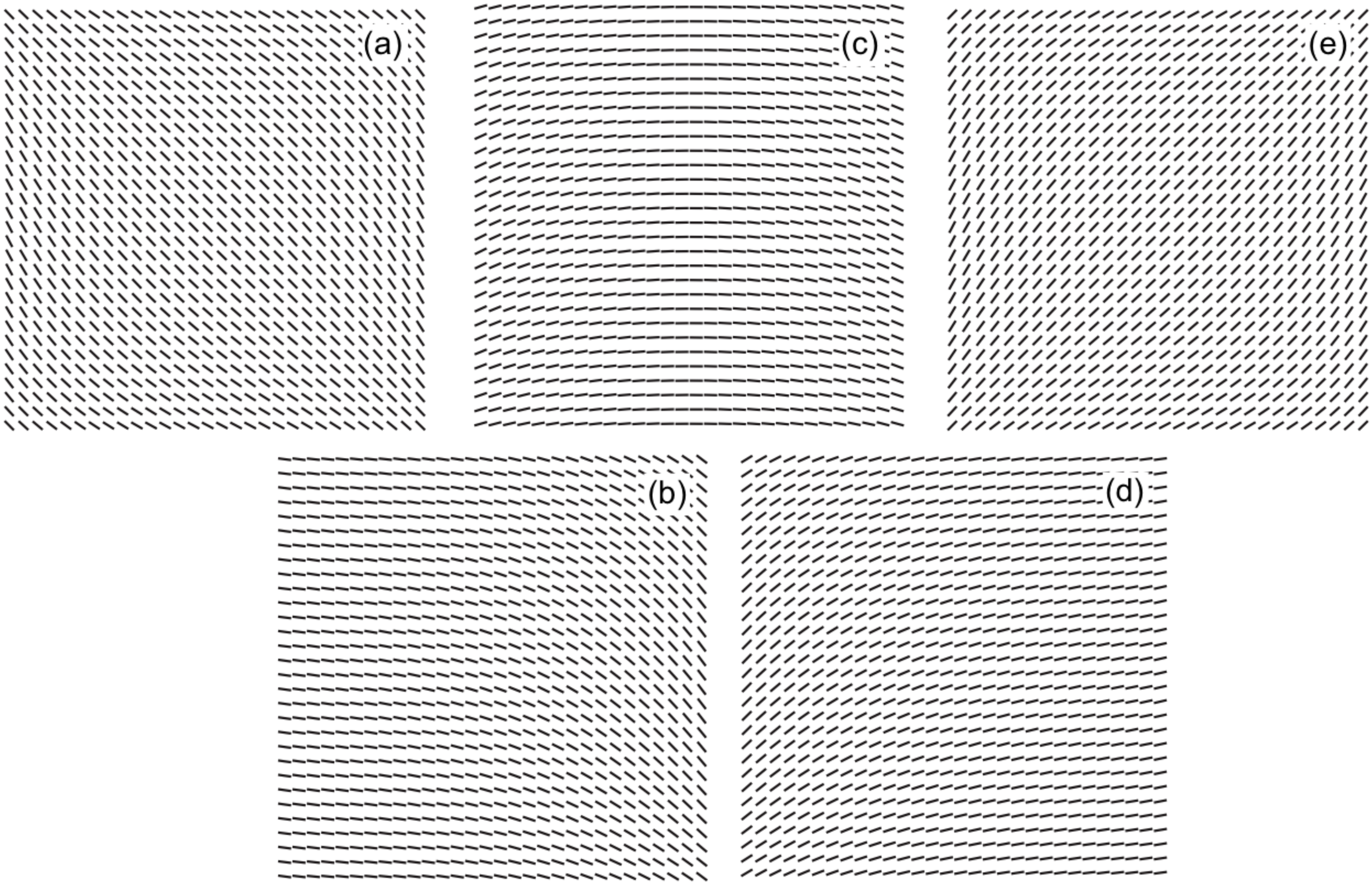
Cusp Catastrophe



Only Diagonal States Are Stable

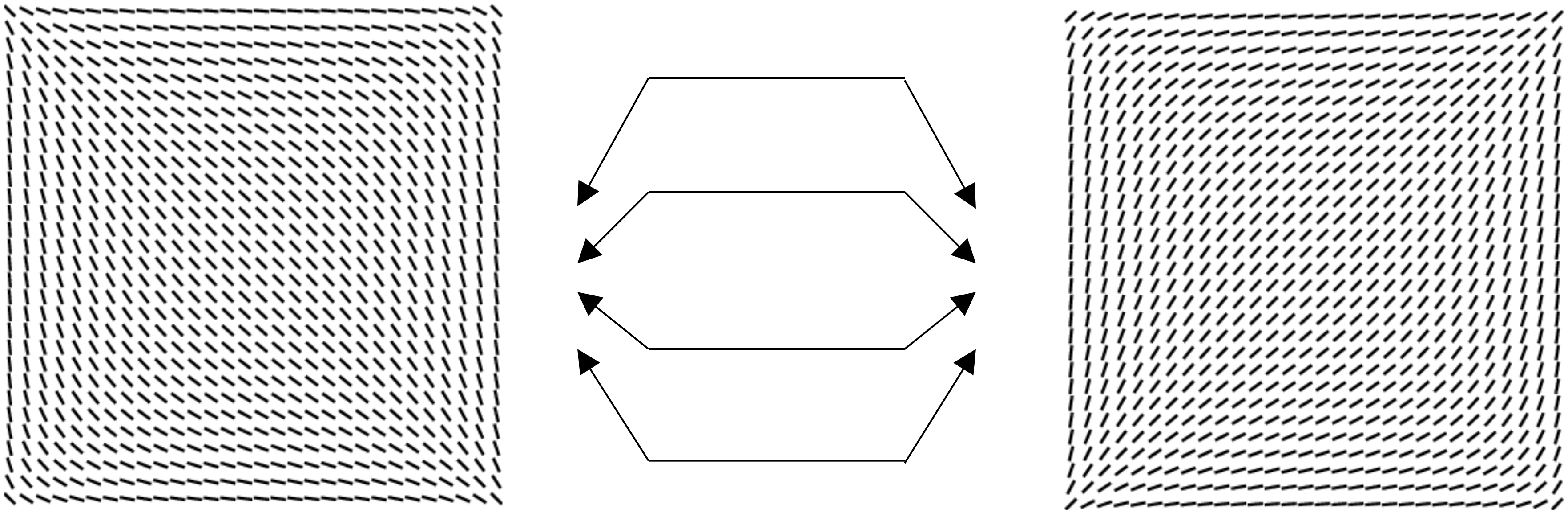
Reminiscent of Rotated State

Minimum | **Transition State** | **Minimum**



Only Diagonal States Are Stable

Four equivalent pathways



Take Home Messages

1. Tools to **survey the free energy landscapes** of Landau models in details, including how they **vary with system parameters, boundary conditions, and external perturbations**.
   - Most, if not all, relevant minima
   - Most, if not all, transition states and competing minimum energy paths
   - Connectivity of the landscapes
   - “Catastrophe” events/phase transitions

2. **Cannot do dynamics**. However, the descriptions and discretizations of the functionals are fully **compatible with other methods**.

3. Can take advantage of schemes already developed for handling **complex boundaries** (corrugations, curved boundaries, etc) from other methods.

4. **Scalar, vector, and tensor** fields can be treated on **equal footing.**

   Landau free energies are very popular in physics, chemistry, and materials science.

   We are interested in testing the limits of the methods.

5. Relatively **inexpensive** (especially compared to atomistic calculations).

   Typical minimization runs take O(minutes).
   Typical pathway runs take O(1 hour).
   } Run in parallel

Thank you for listening!