Title: Transition Pathways Connecting Stable and Metastable Phases

Date: Dec 05, 2013 09:35 AM

URL: http://pirsa.org/13120010

Abstract: Phase transitions are ubiquitous in nature. Understanding the kinetic pathways of phase transitions has been a challenging problem in physics and physical chemistry. From a thermodynamics point of view, the kinetics of phase transitions is dictated by the characteristics of the free energy landscape. In particular, the emergence of a stable phase from a metastable phase follows specific paths, the minimum energy paths, on the free energy landscape. I will describe the characteristics of the minimum energy paths and introduce an efficient method, the string method, to construct them. I will use self-assembled phases of block copolymers as examples to demonstrate the power of the method. In particular, I will show how precisely determined transition pathways provide understanding and surprises when we try to connect the different ordered phases of block copolymers.

Transition Pathways Connecting Stable and Metastable Phases

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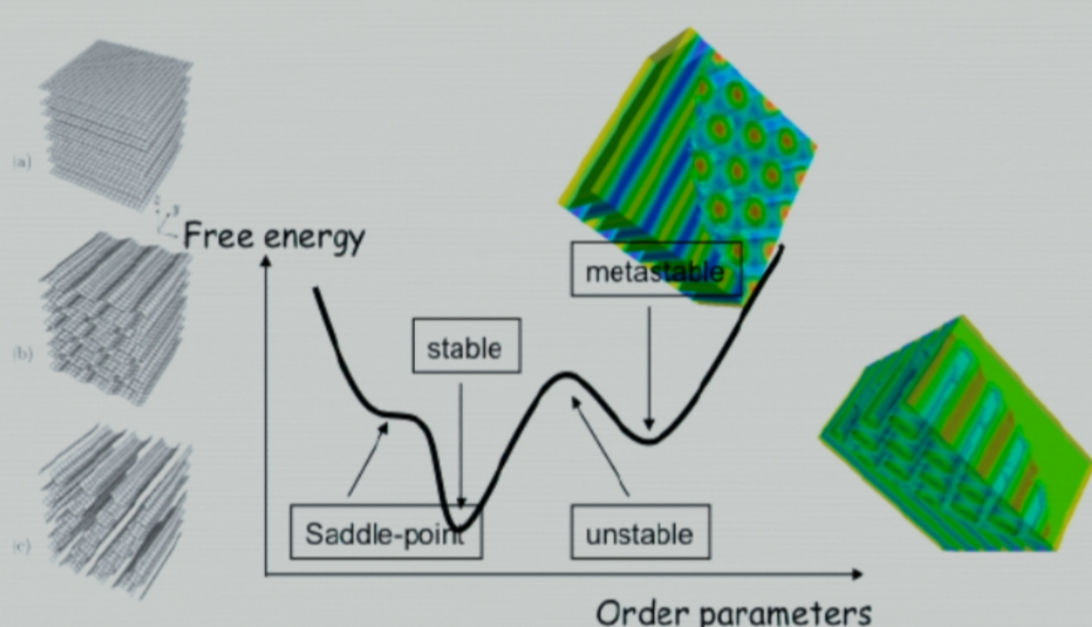
Outline

- Introduction
- String Method
- Case Study: Transitions between diblock copolymer phases
- Summary

Phase Transitions: Spinodal Decomposition and Nucleation

$\min_{nk}[\lambda_n(\mathbf{k})] < 0$

$\min_{nk}[\lambda_n(\mathbf{k})] > 0$



spinodal decomposition

nucleation

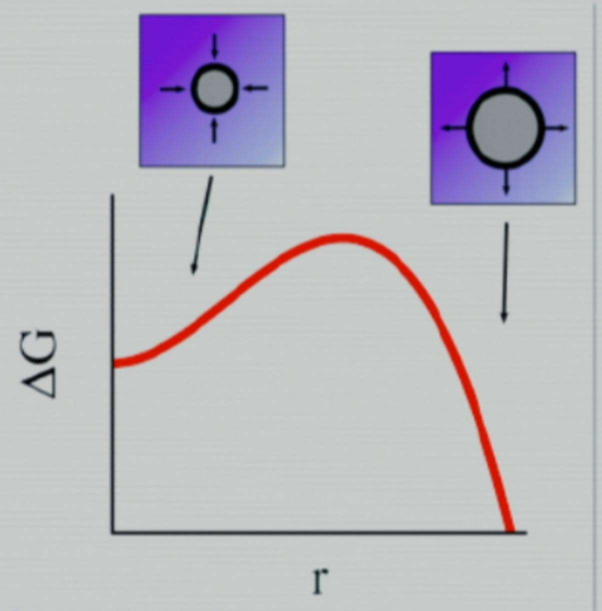
Classical Nucleation Theory

Assume a macroscopic nucleus: Reaction coordinate

Competition between bulk and interfacial free energy

$$\Delta G = -\frac{4\pi}{3} r^3 \Delta f + 4\pi r^2 \sigma$$

$$r_c = \frac{2\sigma}{\Delta f}, \Delta G_c = \frac{2\pi}{3} \frac{(2\sigma)^3}{(\Delta f)^2}$$



Qualitatively correct physical picture

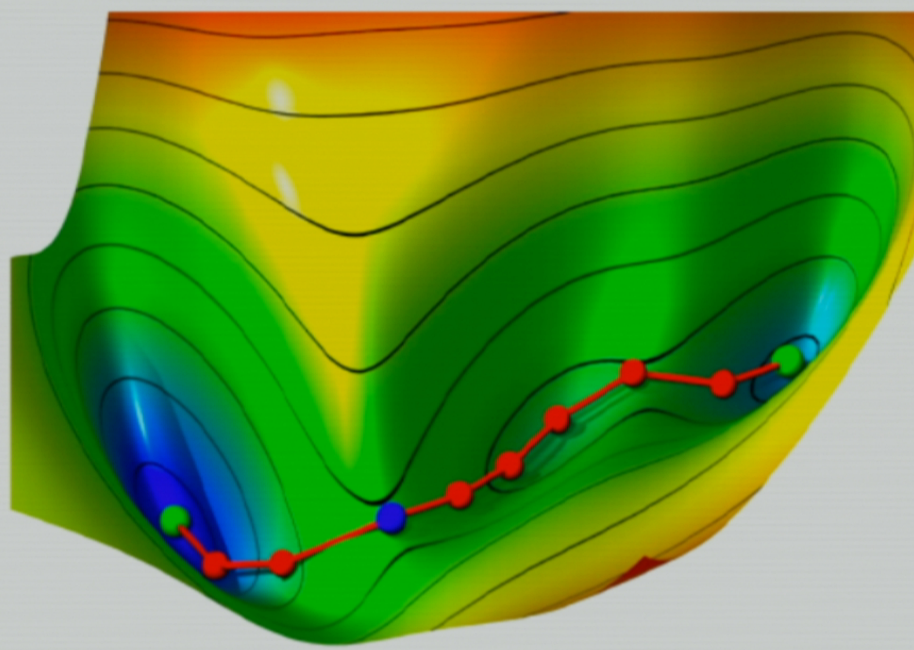
But not all nuclei are large and spherical!

Can we do better?

Modern Nucleation Theory: String Method

The most probable kinetic pathway: Minimum Energy Path

MEP can be viewed as a string in configuration space and it can be found by solving a relaxation equation



http://www.theochem.uni-stuttgart.de/~kaestner/images_large/nudged_elastic_band_big.jpg

Transition Pathways: String Method

The most probable kinetic pathway: Minimum Energy Path

MEP found by solving a relaxation equation: large-scale computations

The string is discretized into N+1 point $(\psi_k)_i,\ 0 \le i \le N$

with two ends fixed $(\psi_k)_0 = u_0, (\psi_k)_N = u_1$

The rest N-1 points are evolved according to

$$\frac{d}{dt}\psi_i = -(\nabla F)(\psi_i) + r\hat{\tau}_i$$

MEP is obtained when steady state solution is found. The maximum along the MEP corresponds to the critical transition state.

$$\Delta F = F(u_s) - F(u_0)$$

E et al. 2002, 2007; Cheng et al. 2010

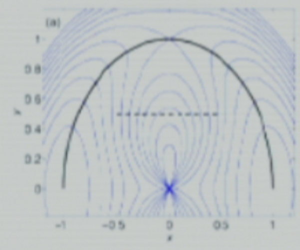
Transition Pathways: The String Method

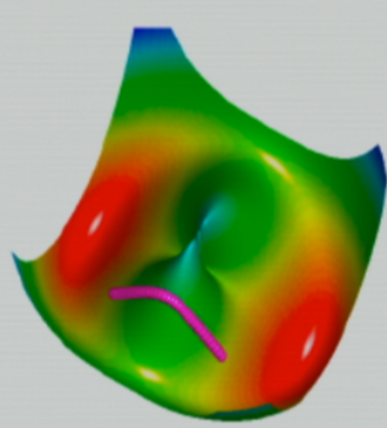
Minimum Energy Path can be obtained by a two-step procedure

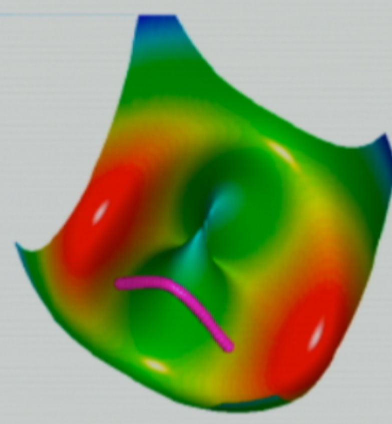
Step 1: Evolution of the images $\frac{d}{dt}\psi_i = -(\nabla V)(\psi_i)$

Step 2: Interpolation/reparametrization of the string

$V(x,y) = (1-x^2-y^2)^2 + \frac{y^2}{x^2+y^2}$







Simple method for any physical energy landscapes

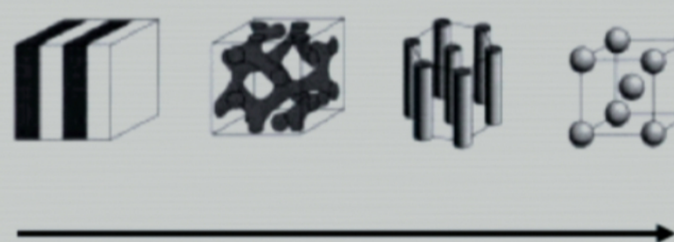
E, Ren & Vaden-Eijnden. 2002, 2007, Animation by Weihua Li

Diblock Copolymers: Self-Assembly

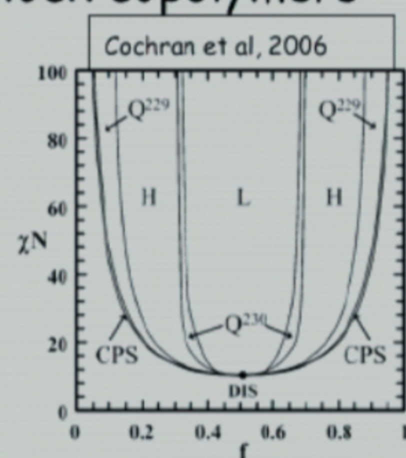
Competition between entropy and energy

$R_G \sim N^{1/2}$ $\quad$ $T \downarrow (\chi \uparrow)$ $\quad$ $d \sim \chi^{1/6} N^{2/3}$

Leads to <u>microphase</u> separation of diblock copolymers



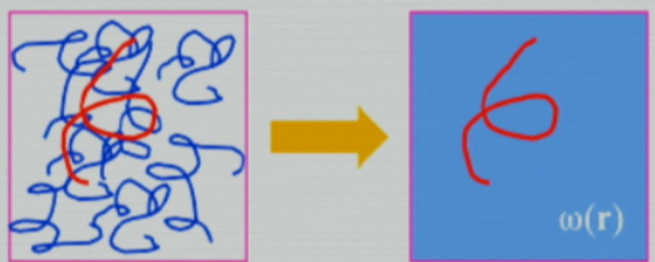
f



Free Energy Landscape: Self-Consistent Field Theory

Simple theoretical framework

- Chain statistics and polymer density $\rho(\mathbf{r})$ determined by $\omega(\mathbf{r})$
- Mean field $\omega(\mathbf{r})$ determined self-consistently by $\rho(\mathbf{r})$
- Flexible framework, applies to many systems



Many-body interaction   Fluctuating field

$$\phi_\alpha(\vec{r}) = \frac{1}{Q_c}\int_0^{f_\alpha} ds\, q_\alpha(\vec{r},s)\, q_\alpha^{+}(\vec{r}, f_\alpha - s),$$

$$\omega_\alpha(\vec{r}) = \chi N\left[\phi_\beta(\vec{r}) - f_\beta\right] + \eta(\vec{r}),$$

$$\phi_A(\vec{r}) + \phi_B(\vec{r}) = 1.$$

$$Q_c = \frac{1}{V}\int d\vec{r}\, q_A^{+}(\vec{r}, f_A)$$

$$\frac{\partial}{\partial s} q_\alpha(\vec{r},s) = \sigma_\alpha^2 \nabla^2 q_\alpha(\vec{r},s) - \omega_\alpha(\vec{r})\, q_\alpha(\vec{r},s)$$

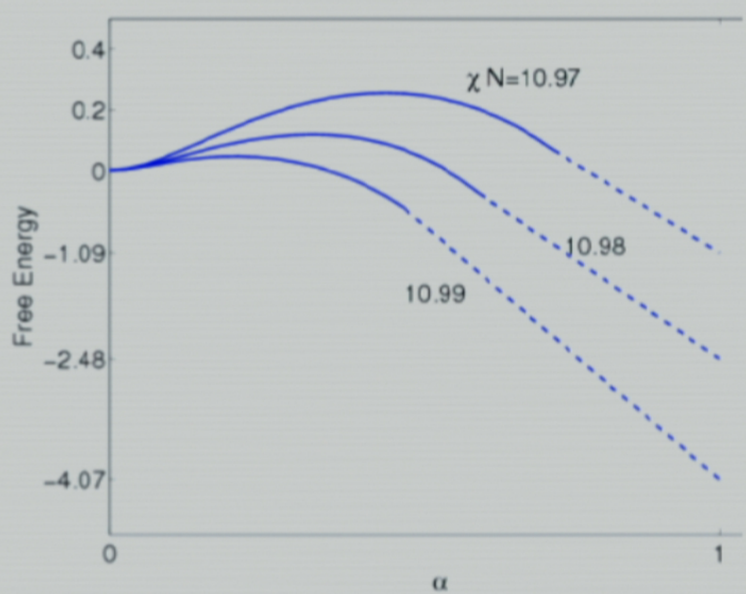
$$q_\alpha(\vec{r},0) = 1$$

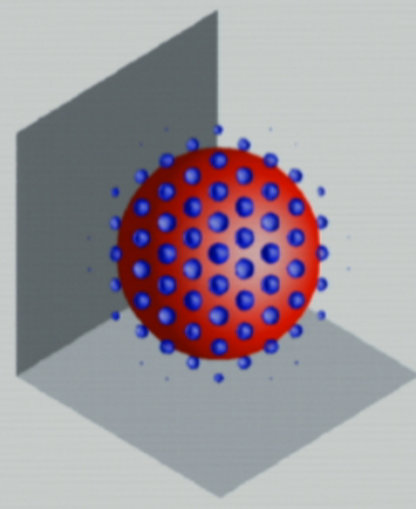
$$\frac{N}{\rho_0 R_g^3 V} F = \frac{1}{V}\int d\vec{r}\left[\chi N\, \phi_A(\vec{r})\phi_B(\vec{r}) - \sum_\alpha \omega_\alpha(\vec{r})\phi_\alpha(\vec{r})\right] - \ln Q_c(\{\omega_\alpha\}).$$

Transition Pathways: String Method on SCFT

Disordered phase to sphere transition

MEP and critical transition state





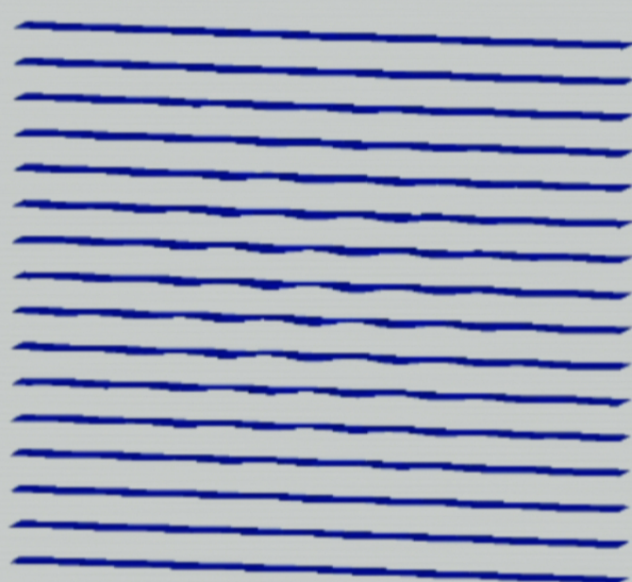
$f = 0.42, \chi N = 10.98$

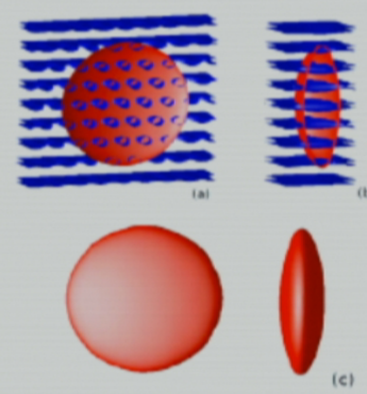
Cheng et al. 2010

Transition Pathways: String Method on SCFT

Lamella to cylinder transition

Lens-like nucleus





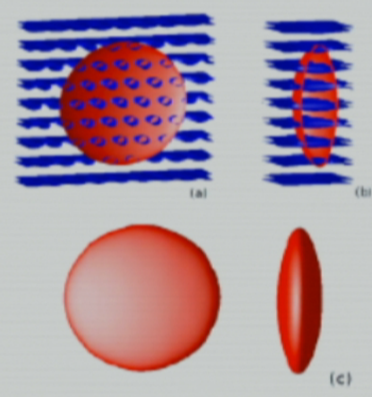
Consistent with previous CNT by Wickham et al.

Cheng et al. 2010

Transition Pathways: String Method on SCFT

Lamella to cylinder transition

Lens-like nucleus



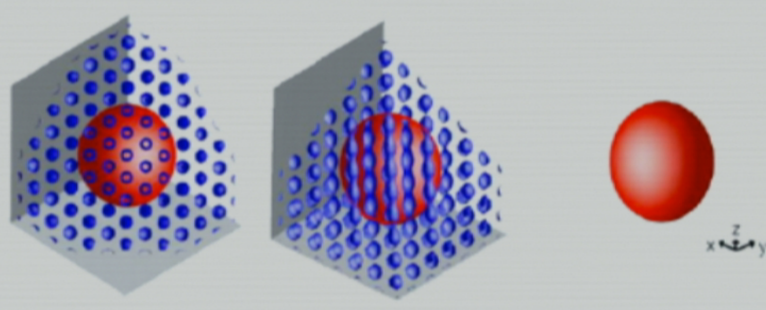
Consistent with previous CNT by Wickham et al.

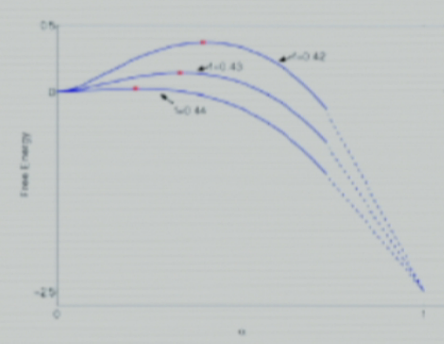
Cheng et al. 2010

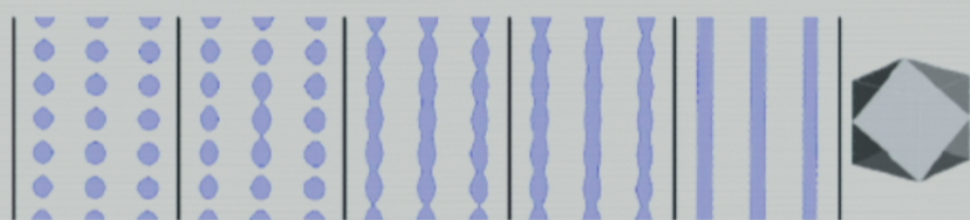
Transition Pathways: String Method on SCFT

Sphere to cylinder transition

Egg-like nucleus





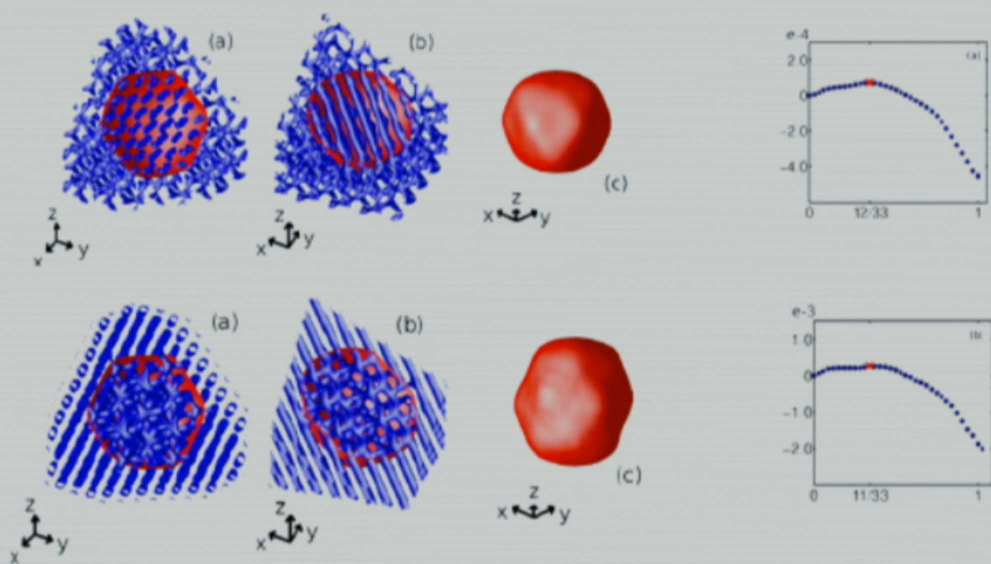


Cheng et al. 2010

Transition Pathways: String Method on SCFT

Gyroid <-> Cylinder Transitions

Anisotropic shaped nucleus

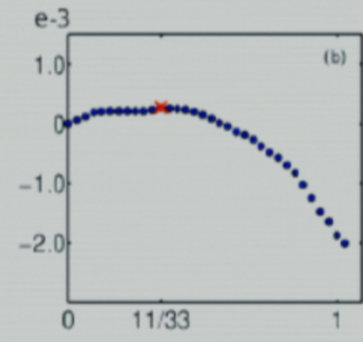


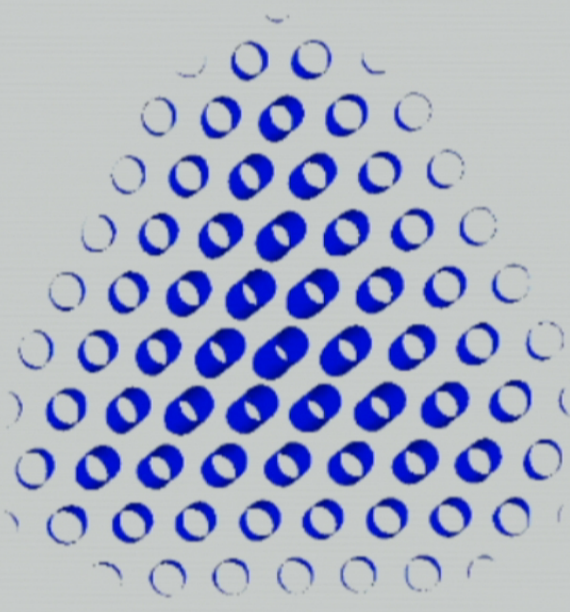
Cheng et al. 2010

Transition Pathways: String Method on SCFT

Cylinder to gyroid transition

Anisotropic shaped nucleus



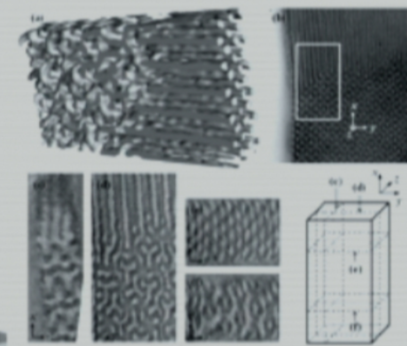


Cheng et al. 2010

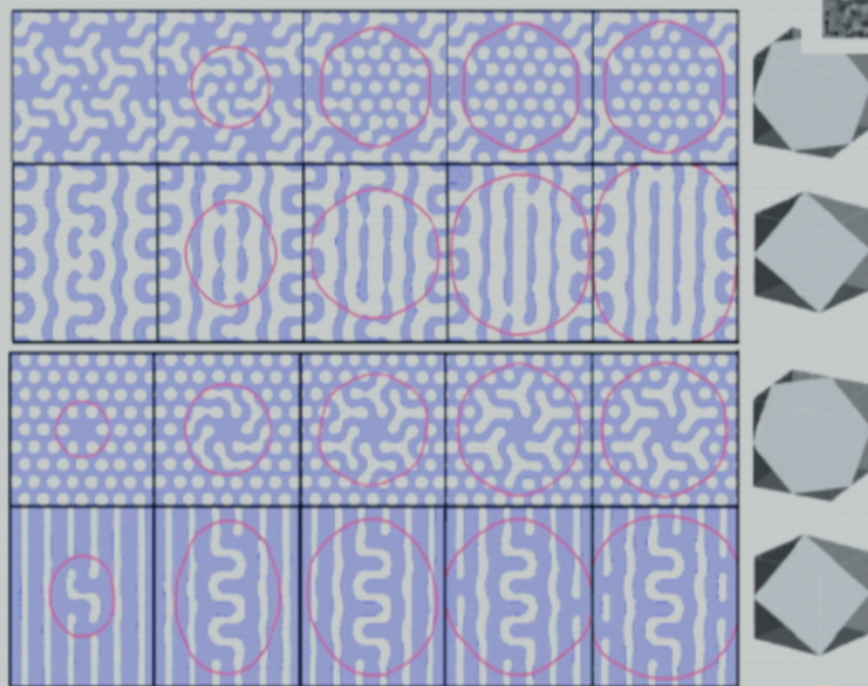
Transition Pathways: String Method on SCFT

Cylinder <-> gyroid transition

Phase transition pathways



Park et al, 2009

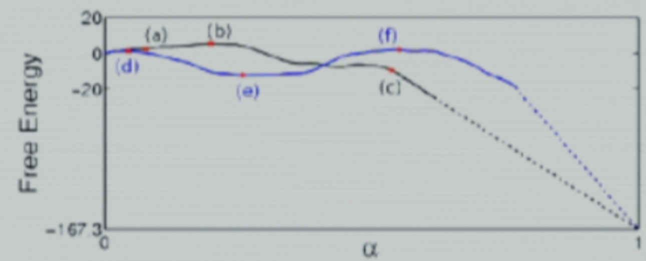


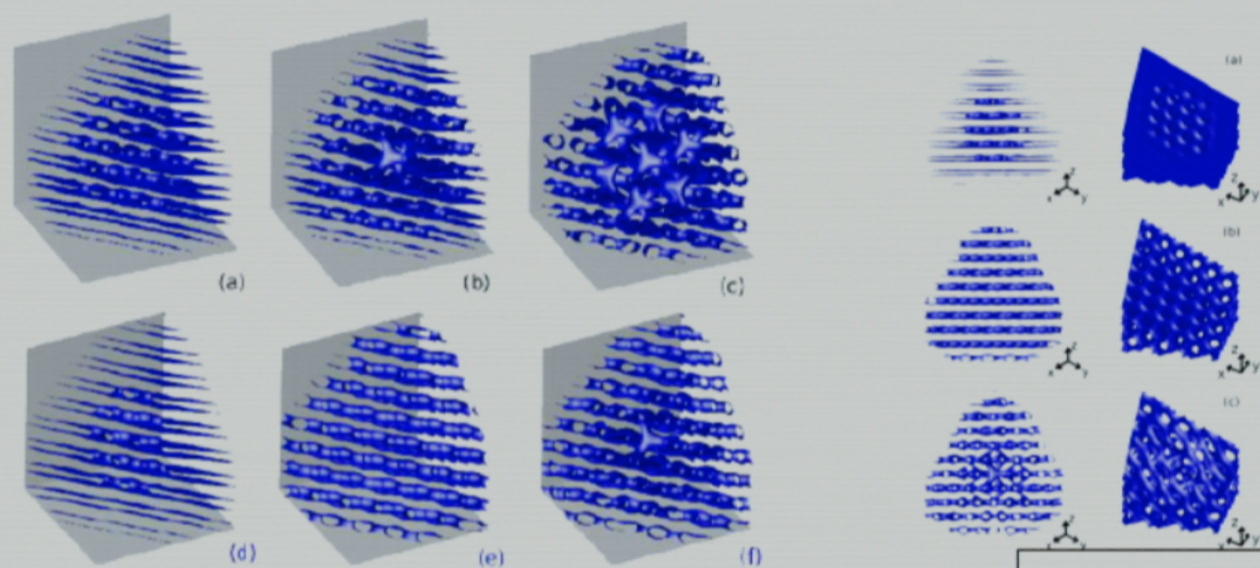
Cheng et al. 2010

Transition Pathways: String Method on SCFT

Lamella to gyroid transition

Two phase transition pathways





Cheng et al. 2010

Summary

Stable and metastable phases correspond to local minima on the free energy landscape

Most probable phase transition pathways correspond to minimum energy path (MEP) on free energy landscape

Transition pathways can be obtained using the string method

- Size and shape of critical nuclei, free energy barrier of nucleation
- disk-to-vesicle transition: emergence and stability of open intermediates
- Order-order transitions in diblock copolymers: anisotropic critical nucleus, free energy barrier
- Gyroid from lamellae: multi-pathways
- Many applications to a wide range of problems