Self-Assembly

Lecture 2

Models of Self-Assembly

Models of Self-Assembly

- **The aim**: Solving the engineering problems of self-assembly: forward, backward and the yield.
  - understand the feasibility

Modelling helix formation

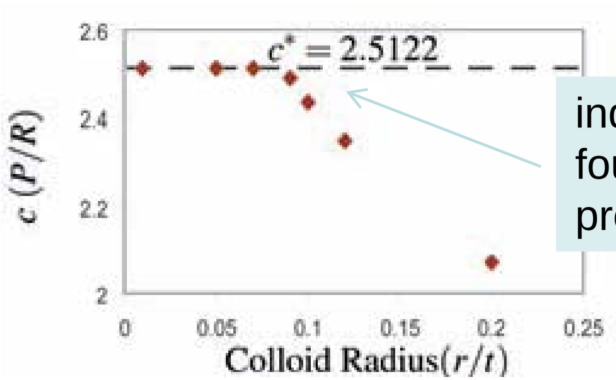
- Many long molecular chain objects self-assemble into helical shapes (DNA, α-helix of a protein).
- Why it happens?
- Is it possible to predict the helix parameters?

Modelling helix formation

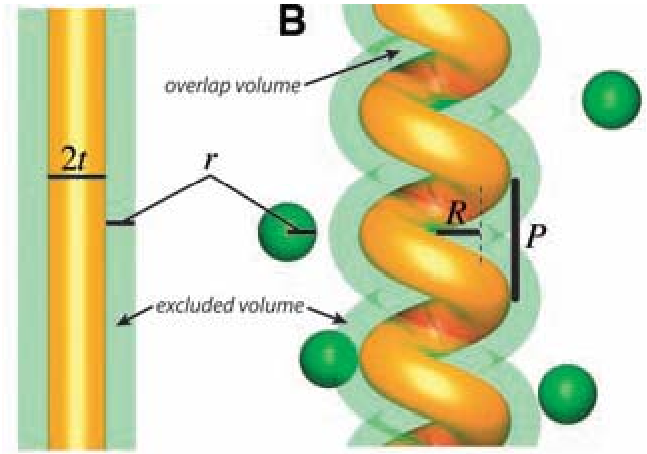
- **Model:** solid elastic rod of length **L**, radius **t** and persistence length $\mathbf{l_p}$ is immersed in the solution of hard spheres (radius **r**, concentration **n**)
- From a pure thermodynamic reason, the energy change upon bending the rod:

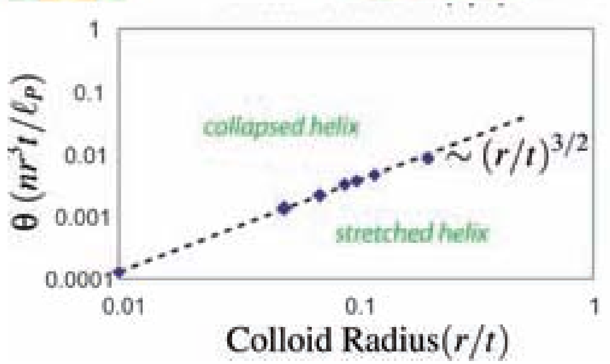
$$\Delta F \propto \frac{1}{2} L l_p \kappa^2 - nV_0$$

In a helix V_0/L is related to κ.
and the optimal helix parameters can be found:



indeed found in proteins





Y. Snir and R. D. Kamien, Science 307, 1067 (2005)

Modelling helix formation

- simple model: a bent rod on a lattice

$$\vec{m} = [m_0, m_1, \ldots, m_N]$$

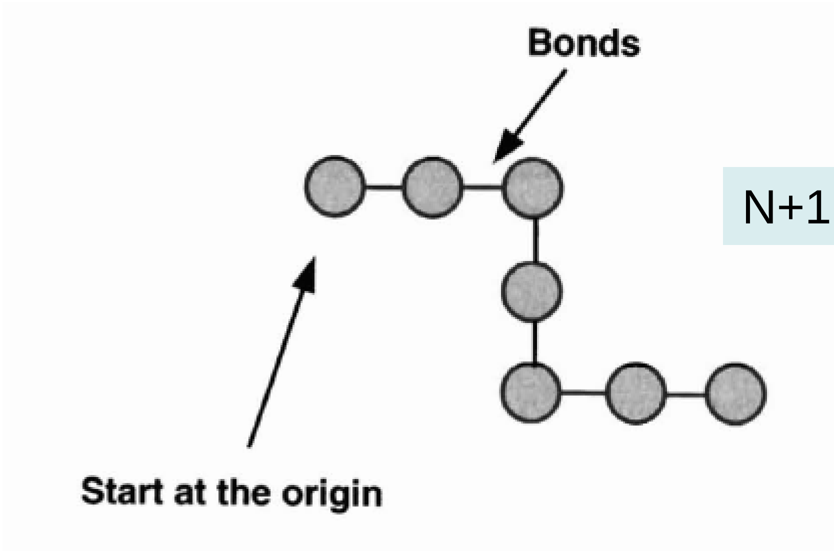
$$\text{Elastic energy} = \alpha \sum_{i=1}^{N} m_i^2$$

straight rod

bent rod

$$\text{Excluded volume energy} = \beta(V_s - V_e) = \beta V(\vec{m})$$

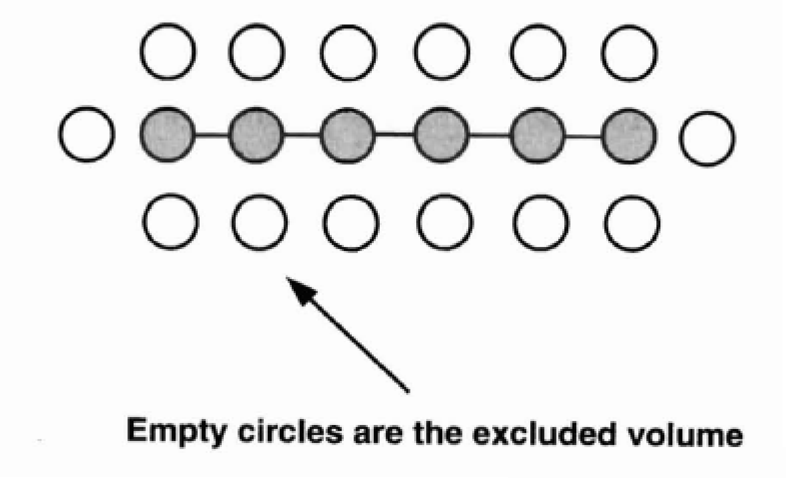
$$E(\vec{m}) = \alpha \sum_{i=1}^{N} m_i^2 - \beta V(\vec{m})$$



N+1 bonds

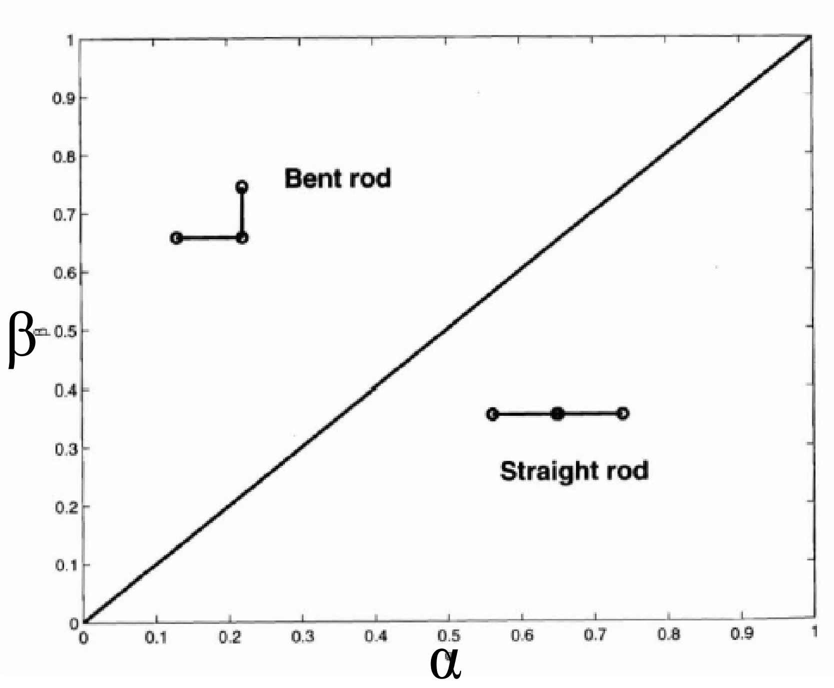
Modelling helix formation

- The excluded volume in a lattice model:



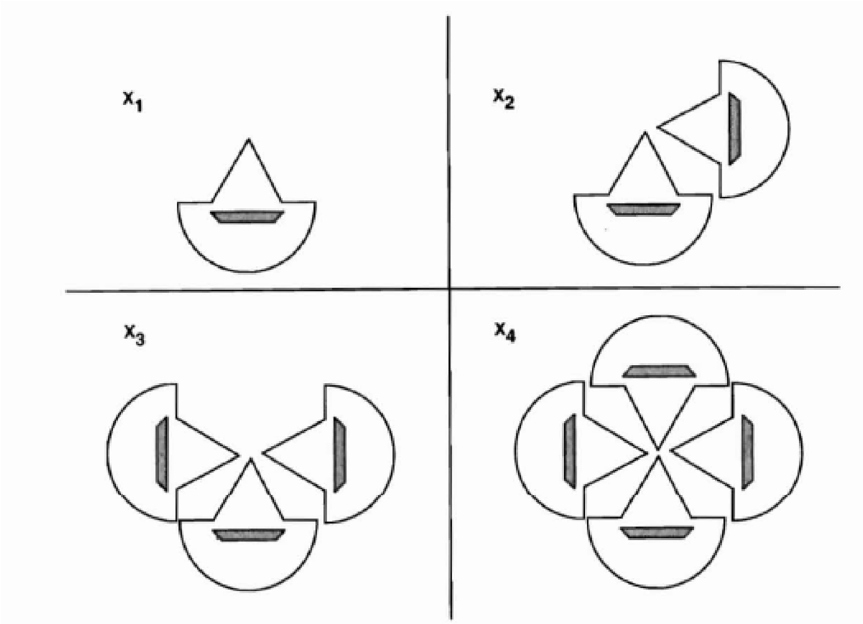
- For N=1

$$E[1,0]=0$$
$$E[1,1]=\alpha-\beta$$



Chemical kinetics model

- In Hosokawa experiment there are 4 possible configuration of tiles:



possible reactions:

$$2X_1 \rightarrow X_2$$
$$X_1 + X_2 \rightarrow X_3$$
$$X_1 + X_3 \rightarrow X_4$$
$$2X_2 \rightarrow X_4$$

- The state of the system can be described

$$\vec{x}(t) = \left[x_1(t), x_2(t), x_3(t), x_4(t)\right]^T$$

Chemical kinetics model

- The evolution of the system can be described as

$$\vec{x}(t+1) = \vec{x}(t) + AP\left(\vec{x}(t)\right)$$

possible reactions:

$$2X_1 \rightarrow X_2$$
$$X_1 + X_2 \rightarrow X_3$$
$$X_1 + X_3 \rightarrow X_4$$
$$2X_2 \rightarrow X_4$$

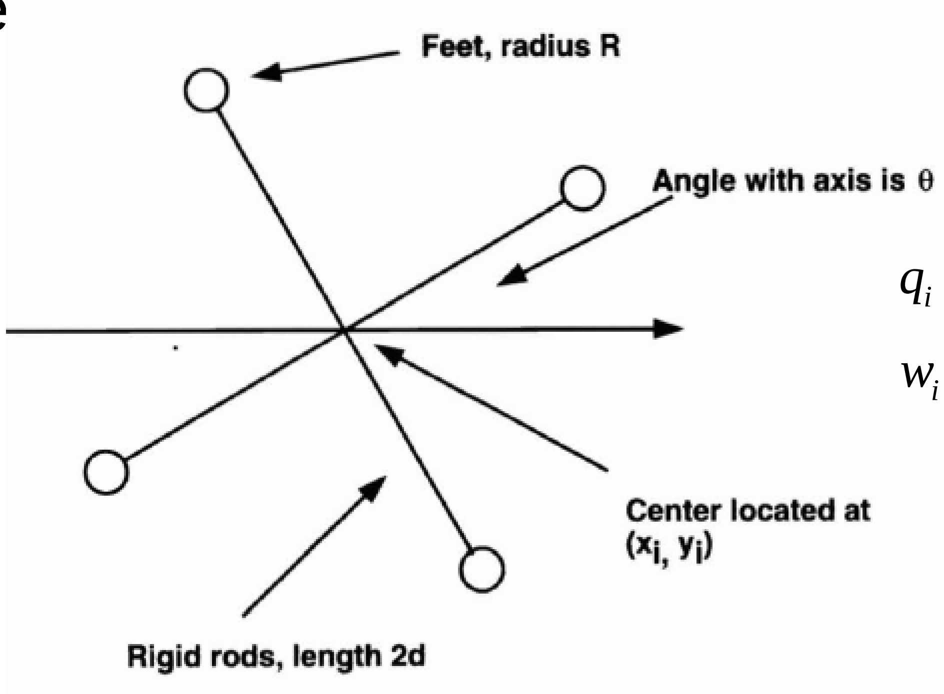
$$A = \begin{bmatrix} -2 & -1 & -1 & 0 \\ 1 & -1 & 0 & -2 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & 1 \end{bmatrix}$$

$$P\left[\vec{x}(t)\right] = \frac{1}{S^2}\left[P_{11}x_1^{\ 2}, 2P_{12}\,x_1x_2, 2P_{13}x_1x_3, P_{22}x_2^{\ 2}\right]^T$$

probability of bond formation

The Waterbug model

- The model is motivated by the capillary force driven assembly but can be reformulated for magnetic and electrostatic force as we''



$$q_i = [x_i, y_i, \theta_i]$$

$$w_i = [u_{i,j}, v_{i,j}]; u_{i,j} = x_i + d\cos\theta_i$$

- The state of the system can be described as:

$$q = [q_1, q_2, \ldots, q_N]$$

The Waterbug model

- The energy can be calculated as a sum of potential energy (e.g. due to surface tension) and kinetic energy.

$$u(q_i, q_k) = -\sum_{j=1}^{4}\sum_{l=1}^{4} c_{ijkl} K_0(\rho||w_{i,j} - w_{k,l}||).$$

$$c_{ijkl} = 2\pi\gamma Q_{ij} Qkl.$$

$$U(q) = \sum_{1 \le i \neq k \le n} u(q_i, q_k).$$

$$K_i = \frac{m}{2}(\dot{x}_i^2 + \dot{y}_i^2 + d^2\dot{\theta}_i^2)$$

$$K = \sum_{i=1}^{n} K_i.$$

- Equating the Langrangian to the friction forces and minimizing

$$8m\ddot{x}_i + \sum_{k=1, k\neq i}^{2} \frac{\partial}{\partial x_i} u(q_i, q_k) = -4k_f \dot{x}_i$$

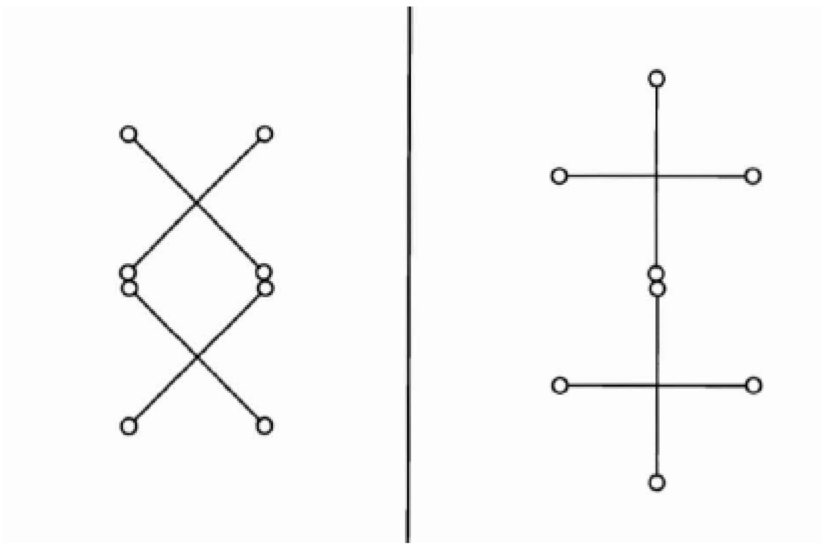
$$8m\ddot{y}_i + \sum_{k=1, k\neq i}^{2} \frac{\partial}{\partial y_i} u(q_i, q_k) = -4k_f \dot{y}_i$$

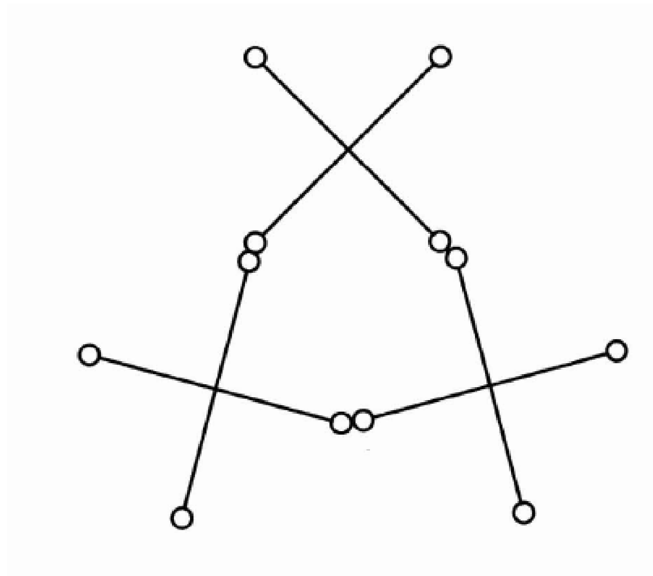
$$8md^2\ddot{\theta} + \sum_{k=1, k\neq i}^{2} \frac{\partial}{\partial \theta_i} u(q_i, q_k) = -4k_f d^2 \dot{x}_i.$$

can be solved numerically

The Waterbug model

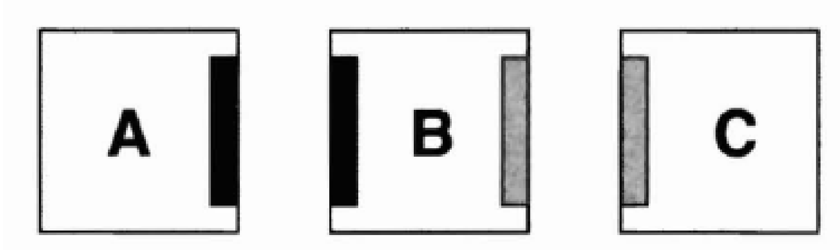
- The model can predict stability of the systems
- Demonstrate what wettability control can do to eliminate defects and to construct finite structures



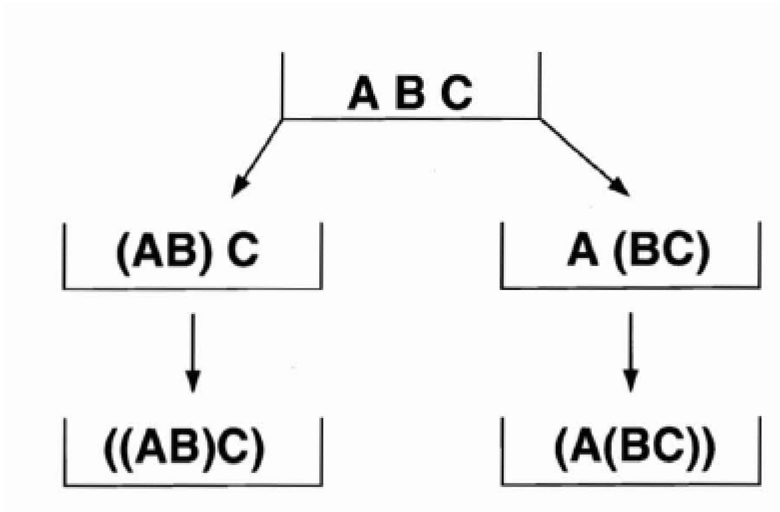


Conformational switching model

- Let’s consider a system of 3 particles A,B,C that can form bonds:



$$\begin{aligned} A + B &\longrightarrow AB \\ B + C &\longrightarrow BC \\ AB + C &\longrightarrow ABC \\ A + BC &\longrightarrow ABC. \end{aligned}$$

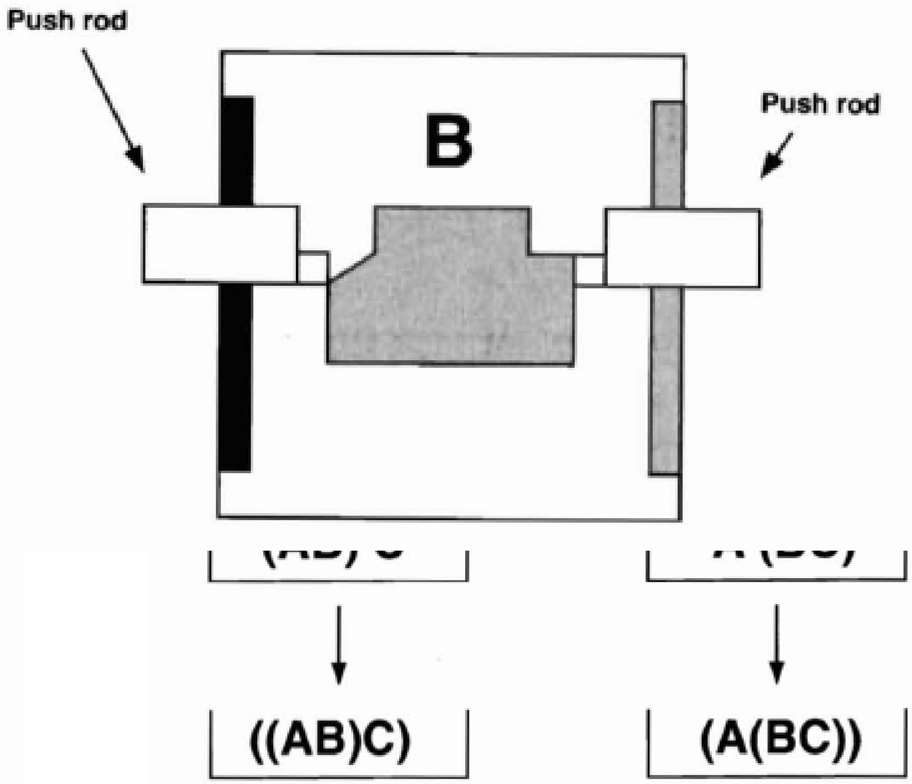


- How a preferred route of self-assembly can be created?

Conformational switching model

- We can introduce a conformational switch in the B-tile ("minus switch")

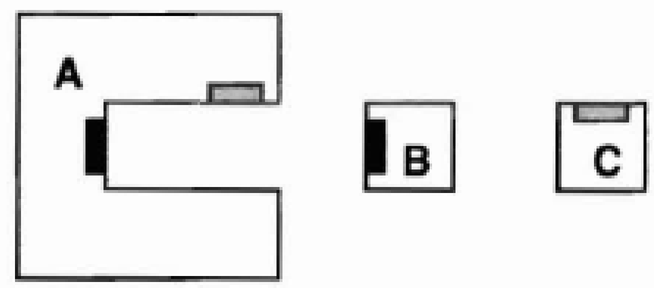
$$A + B \longrightarrow AB'$$
$$AB' + C \longrightarrow AB'C.$$
$$A + B \longrightarrow AB$$
$$B + C \longrightarrow BC$$
$$AB + C \longrightarrow ABC$$
$$A + BC \longrightarrow ABC.$$



- How a preferred route of self-assembly can be created?

Conformational switching model

- Let's consider a different system:



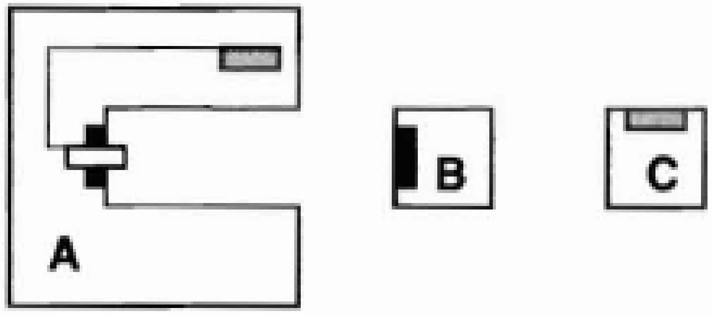
- Tile C here can block access to tile B preventing the desired structure formation

$$A + B \longrightarrow AB$$
$$AB + C \longrightarrow ABC$$
$$A + C \longrightarrow AC.$$

- How a preferred route of self-assembly can be created?

Conformational switching model

- To avoid it we can introduce a switch:



- Then the possible reactions are:

$$A + B \longrightarrow A'B$$
$$A'B + C \longrightarrow A'BC$$

Conformational switching model

- Imagine we have to form (AB) complex in a system with a large excess of A

- The process will be very slow and within the finite time we will not get high concentration AB.

- We can introduce a different type of conformational switch in the A-tile ("plus switch")

$$A + A \longrightarrow AA'.$$

$$AA' + B \longrightarrow A + AB.$$

- This will reduce the concentration of A and increase the yield

Conformational switching model

- Now let's consider 4 particle system

$$\begin{aligned} A + B &\longrightarrow AB \\ B + C &\longrightarrow BC \\ C + D &\longrightarrow CD \\ AB + C &\longrightarrow ABC \\ ABC + D &\longrightarrow ABCD \\ B + CD &\longrightarrow BCD \\ A + BCD &\longrightarrow ABCD \\ AB + CD &\longrightarrow ABCD. \end{aligned}$$

- We have 5 possible assembly sequences:
  (((AB)C)D); ((AB)(CD)), (A((BC)D), (A(B(CD))), (A(BC)D)
- Can we do it with a "minus device" again? – No.

Conformational switching model

- Saitou and Jakiela proved that in a general case of self-assembling automation (SA), defined as a pair of a finite set of components and a finite set of rules of the form:

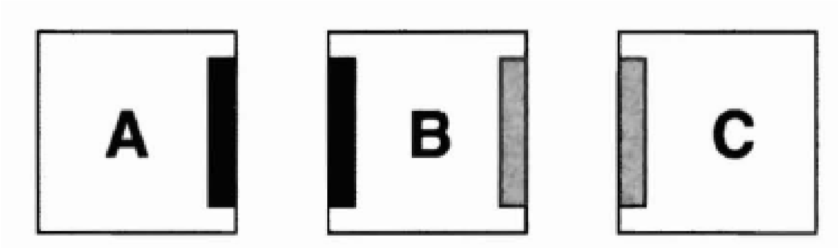
$$a^{\alpha} + b^{\beta} \rightarrow a^{\gamma}b^{\delta}.$$

$$a^{\alpha}b^{\beta} \rightarrow a^{\gamma}b^{\delta}.$$

- any assembly sequences can be encoded with just 3 conformational state per particle.

Graph Grammar (E.Klavins)

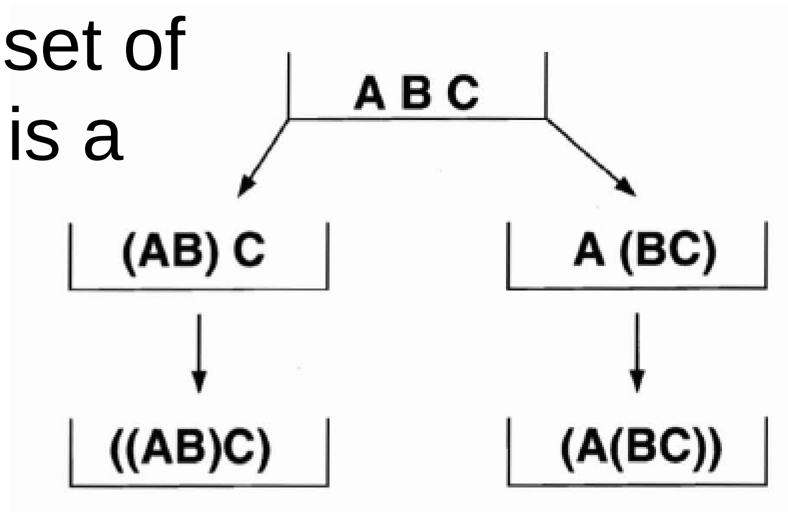
- Is it possible to incorporate conformational switching into graph approach?



- Assume we have tiles A, B,C, but now we want to form AB and CC.
  AB – **unstable** complex, ABC – **stable** complex, CC – **unreachable** complex.

Graph Grammar (E.Klavins)

- Formally, **graph G** over an **alphabet** Σ is a triple G(V,E,l) where V is set of vertices, E – set of edges and l is a labelling function
- In addition, we need to attach a set of **rules** to the graph



example of **constructive rules**

$$\begin{array}{ll} a & a \longrightarrow b - b \\ a & b \longrightarrow b - c \\ b & b \longrightarrow c - c. \end{array}$$

example of **destructive rules**

$$b - b \longrightarrow a \qquad a$$

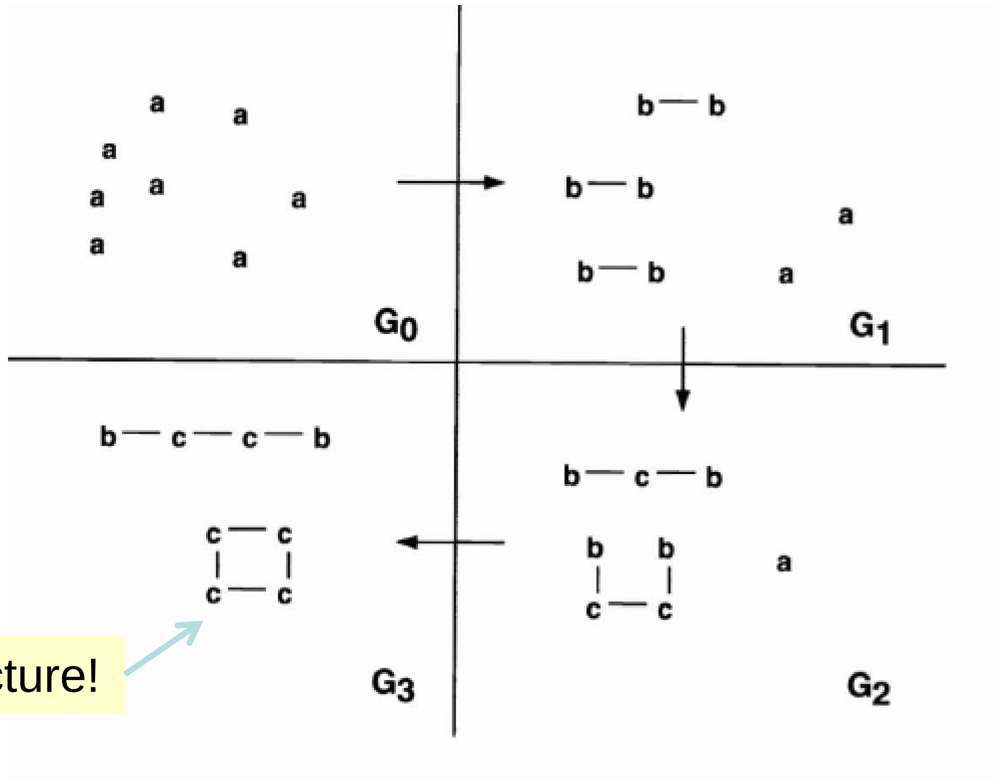
example of **relabelling rules**

$$b - b \longrightarrow a - c.$$

Graph Grammar (E.Klavins)

- Let's look how our rules work on a graph:

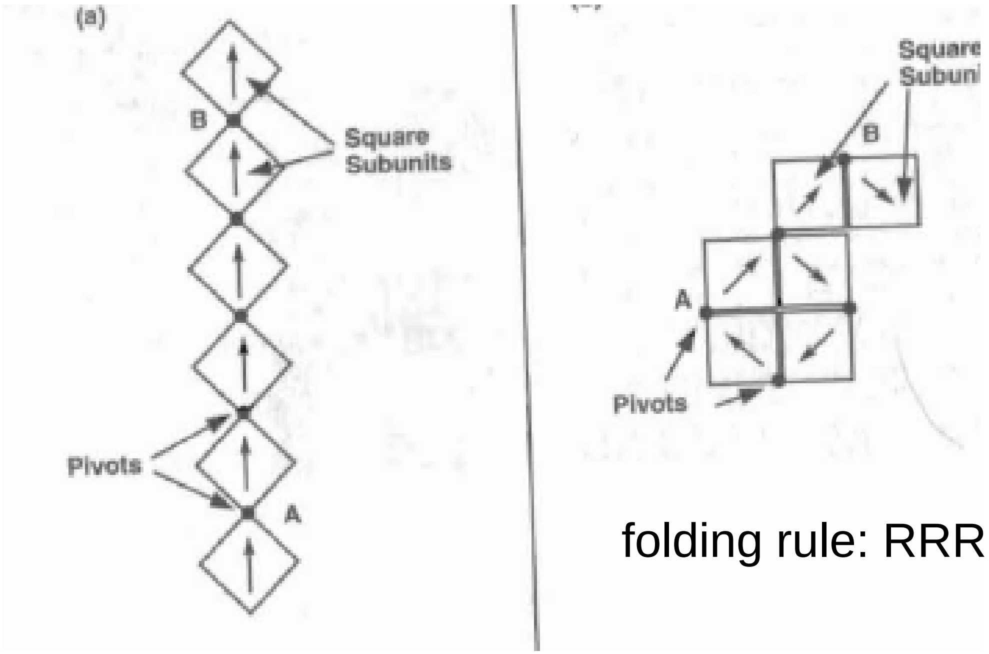
$$
\begin{array}{lll}
a & a & \longrightarrow b - b \\
a & b & \longrightarrow b - c \\
b & b & \longrightarrow c - c.
\end{array}
$$



the only stable structure!

Assembly by folding

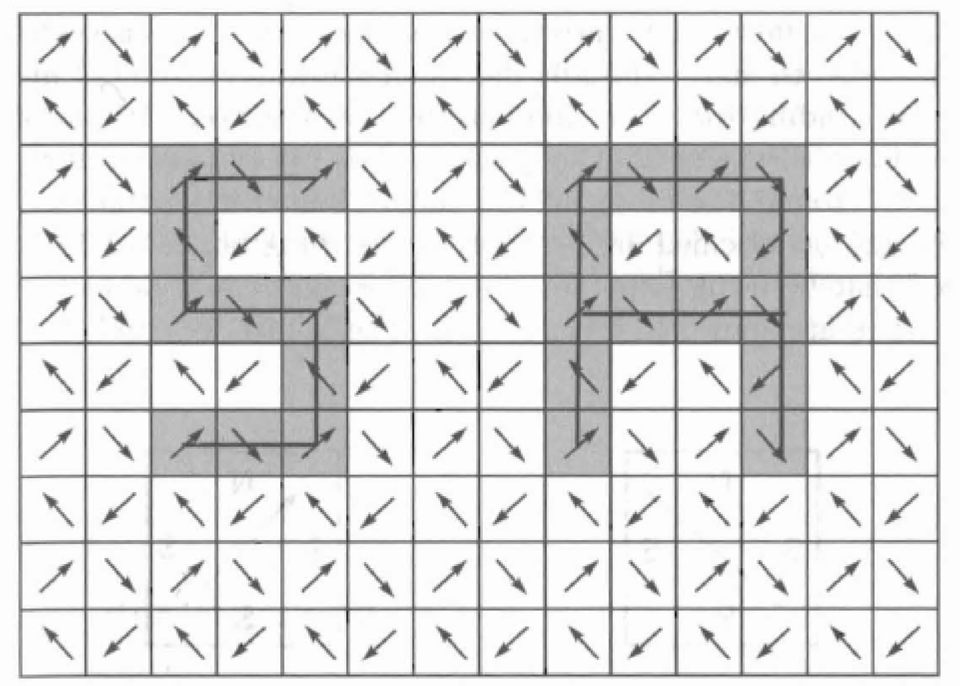
- Let’s make a mechanical model of a protein:



folding rule: RRRLR

Assembly by folding

- From this model we can define topological construction possible or impossible to reach by folding:



- impossible constructions can be made possible by increasing thickness.

Computing with tiles

- Rothemund's tiles:

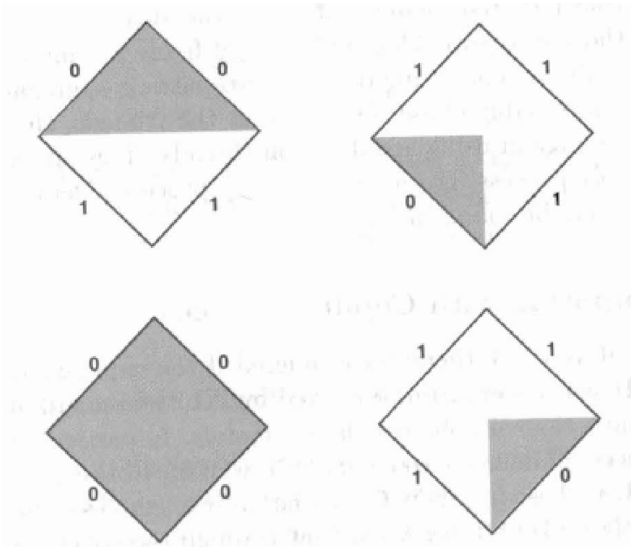
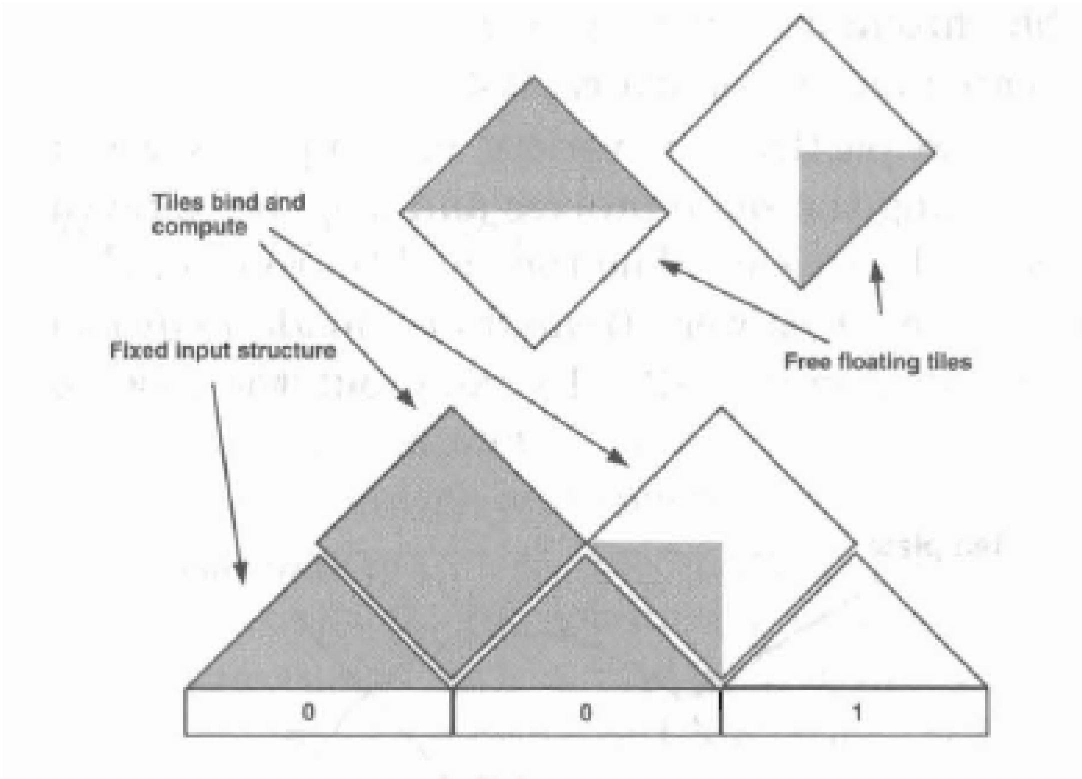


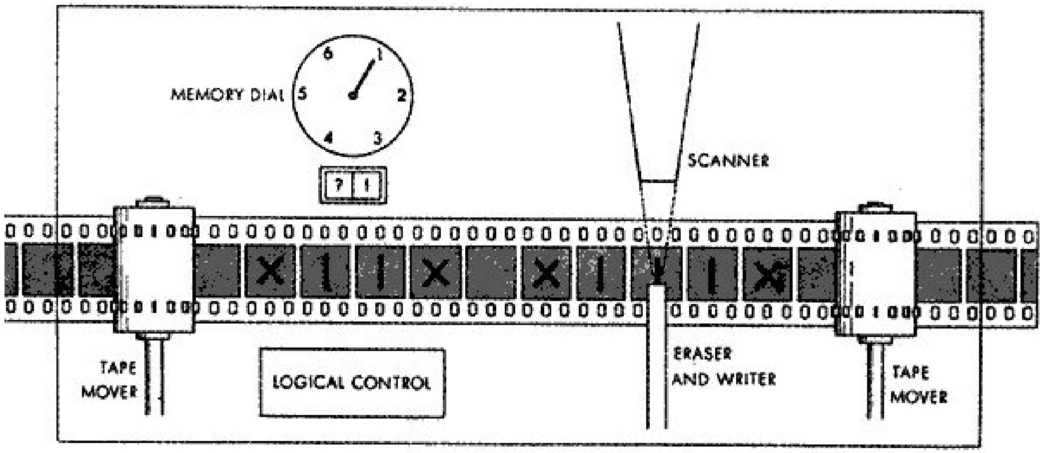
TABLE 6.1: The Logical Operation XOR

Input	Output
0 0	0
0 1	1
1 0	1
1 1	0



Tile assembly model

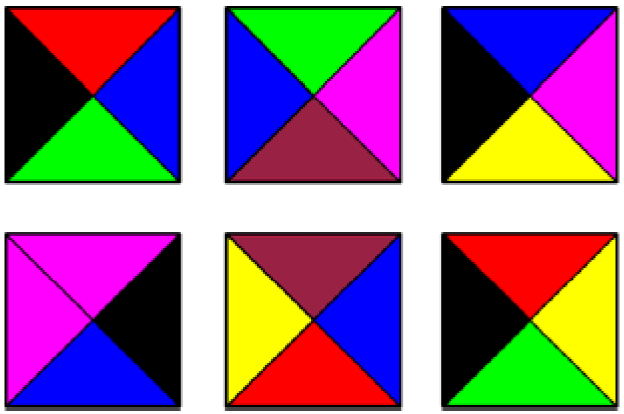
- Turing machine (introduced by Alan Turing in 1936)



- Action of Turing machine:
- A read/write head hovers above a tape where each square can either be left blank, or can contain a zero or a one.
- This read-write head can erase a symbol, write a symbol, and advance the tape one square in either direction.
- The decision is made based on the internal state of a head. The head has a finite number of states and a look-up table that dictates how it should behave once it reads the tape.
- If a special halting state where the Turing Machine stops all operation.

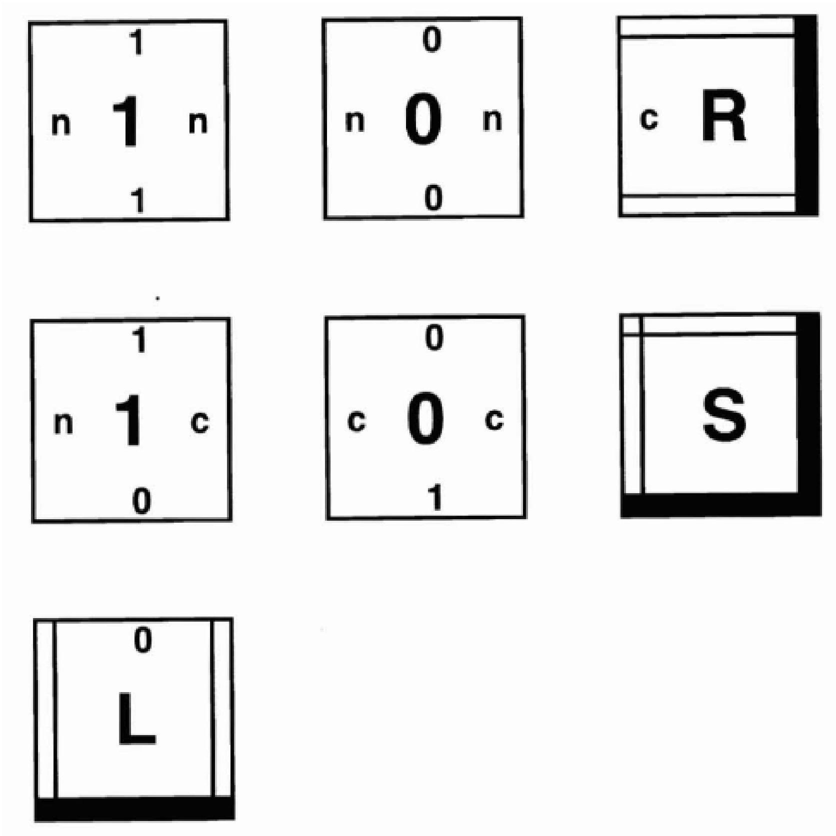
Tile assembly model

- Turing proved that this machine provides a model of computation and this model is universal.
- Other universal models of computation can be created but if they are equivalent to the **Universal Turing Machine**.
- As was shown Hao Wang in 1961, a model known as **Wang Tiles** is equivalent to the Turing Universal Machine
  - Square tiles on a square grid.
  - Tiles have four colored faces
  - Tiles must not be rotated
  - Abuttant faces have to have the same color



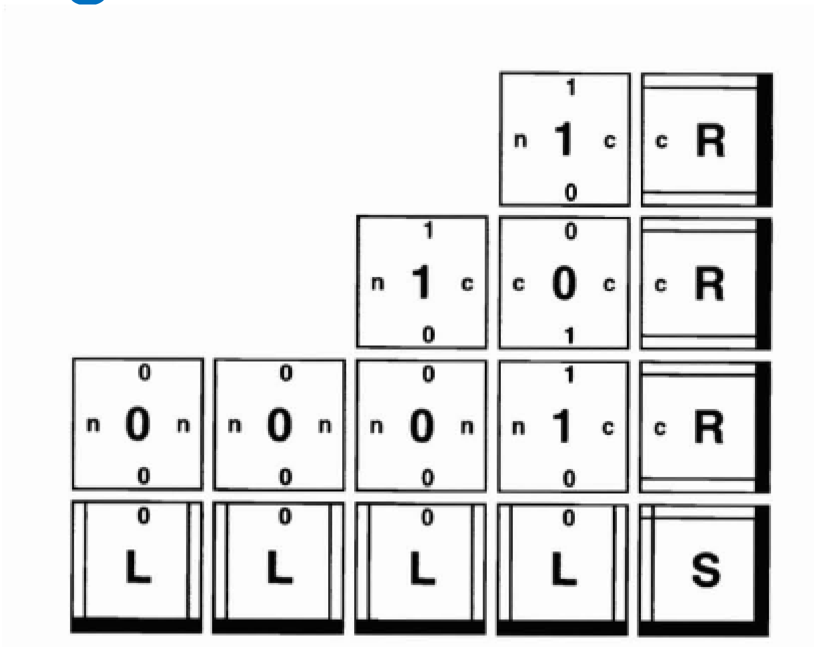
Tile assembly model

- Erik Winfree suggested to model self-assembly with tiles using instead of colours **binding domains**, assigning the **bond strength** and the **temperature**



Tile assembly model

- Temperature means that only bonds of given strength “survives”. This leads to **cooperative bonding**.



T=2

Complexity of a System

Kolmogorov's definition of complexity:

- *For a given bit string the complexity can be defined as the length of the shortest computer program required to produce a string on a Universal Turing Machine*

1111111111 | for i=1..10 write 1 end

1011001110 | write 1; write 0; write 1; write 1; write 0; for i=1..3 write 0 end; write 0

- Problems with the Kolmogorov's definition:
  - Proving that given program is the shortest possible
  - Random string are the most complex according to the definition

Complexity of systems

- Complexity can be defined in terms of tiles required to self-assemble a given bit string

1111111111 — 1 tile

1010101010 — 2 tiles

- What complexity is required to assemble a square of NxN?
  - Complexity is $\sim N^2$ at T=1
  - but ~log(N) at T=2

Problems

- (7) For a lattice model of a rod with N=2, compute possible configurations and sketch a phase diagram
- Home:
  - (9) Hosokawa model simulation.