Partially directed walks and polymer adsorption on striped surfaces

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The physical problem

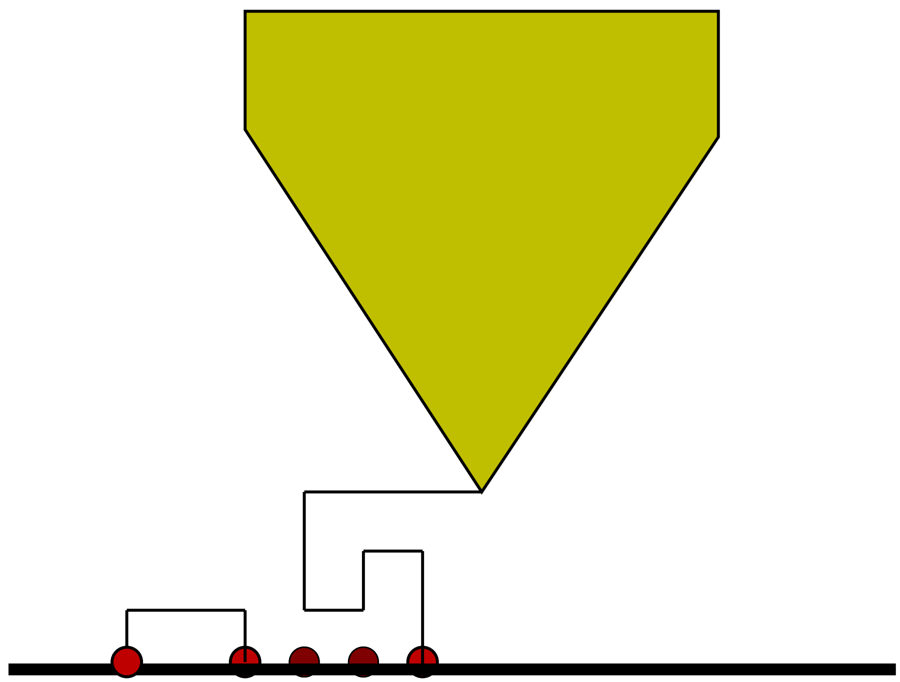
Polymer adsorption

1. A polymer in dilute solution can adsorb at an impenetrable surface

2. For an infinite polymer there will be a phase transition from an adsorbed phase to a desorbed phase at some characteristic temperature

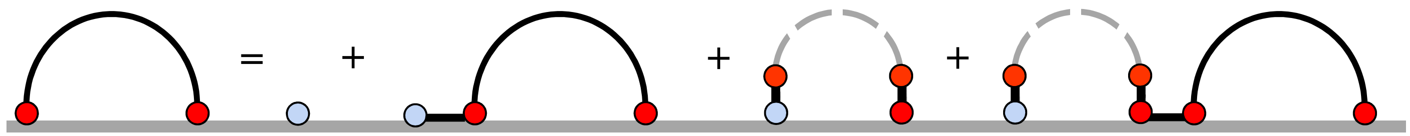
3. For an adsorbed polymer, the polymer can be desorbed by application of a force

The idea behind AFM



Partially directed walks in three dimensions

Vertex weighting

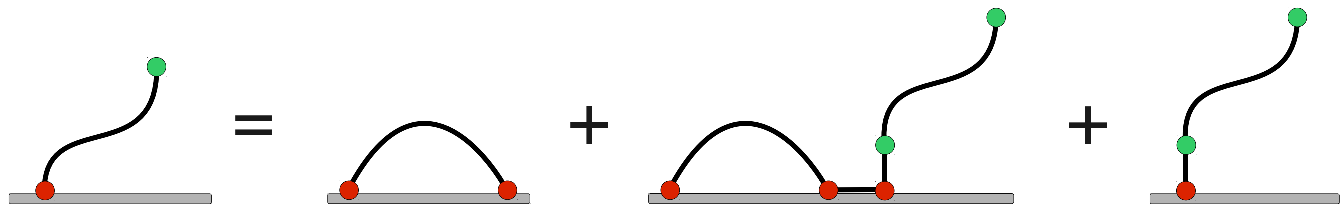


$$P(a,z) = 1 + 2azP(a,z) + az^2(P(1,z) - 1)(1 + 2azP(a,z))$$

$P(a,z)$ has two physically relevant singularities, $z = z_1 = (\sqrt{17} - 3)/4$ and a pole at $z = z_2(a)$. z_1 dominates for small a and $z_2(a)$ dominates for large a.

Partially directed walks in three dimensions

Pulling vertically



$$F(a,y,z) = P(a,z)(1+2ayz^2F(1,y,z)) + yzF(1,y,z)$$

$F(a,y,z)$ has three relevant singularities, $z_1 = (\sqrt{17}-3)/4$, and two poles $z_2(a)$ and $z_3(y)$.

The connection to thermodynamics

If we write $w_n(v,h)$ for the number of walks with n edges, $v+1$ vertices in the surface (*visits*) and last vertex at height h then the partition function is

$$Z_n(a,y) = \sum_{v,h} w_n(v,h) a^v y^h$$

where $a = \exp(-\epsilon/kT)$ and $y = \exp(f/kT)$. The limiting free energy

$$\kappa(a,y) = \lim_{n\to\infty} n^{-1} \log Z_n(a,y)$$

exists and

$$F(a,y,z) = \sum_n Z_n(a,y) z^n = \sum_n e^{[\kappa(a,y)n + o(n)]} z^n$$

$$F(a,y,z) = \sum_n e^{[\kappa(a,y)n + o(n)]} z^n$$

which is singular at

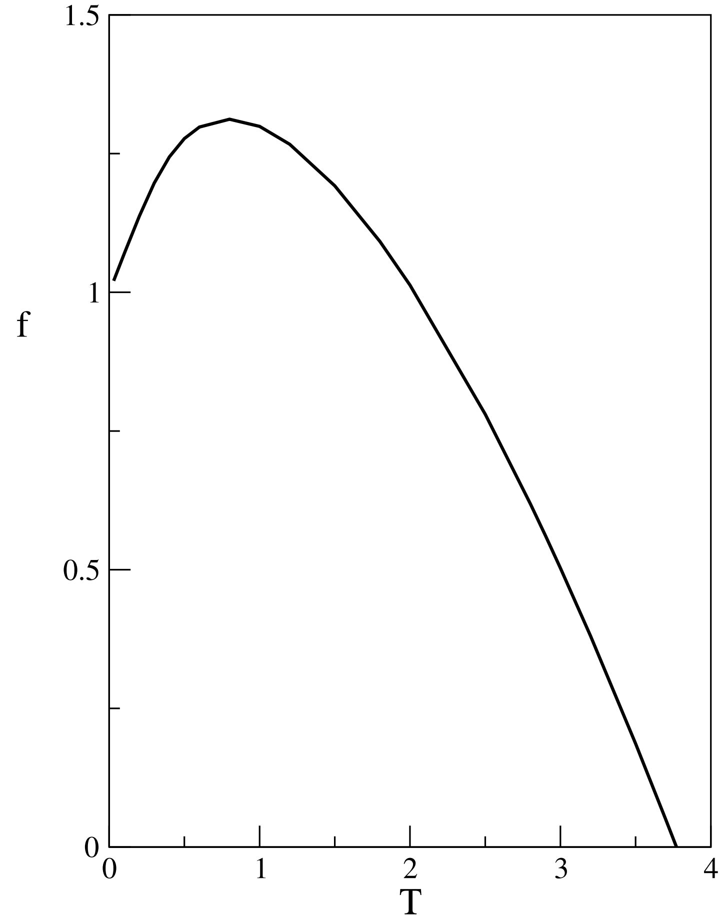
$$z = z_c(a,y) = \exp(-\kappa(a,y))$$

so

$$\kappa(a,y) = -\log z_c$$

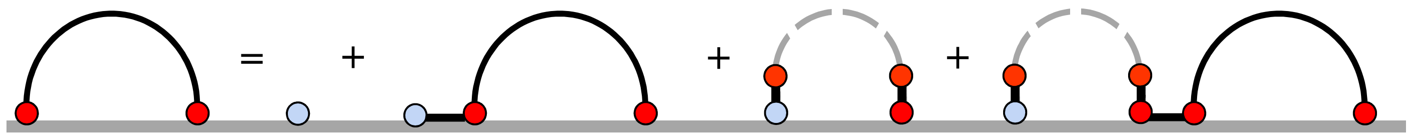
and the singularity structure determines the thermodynamics.

Force–temperature diagram for pulling vertically



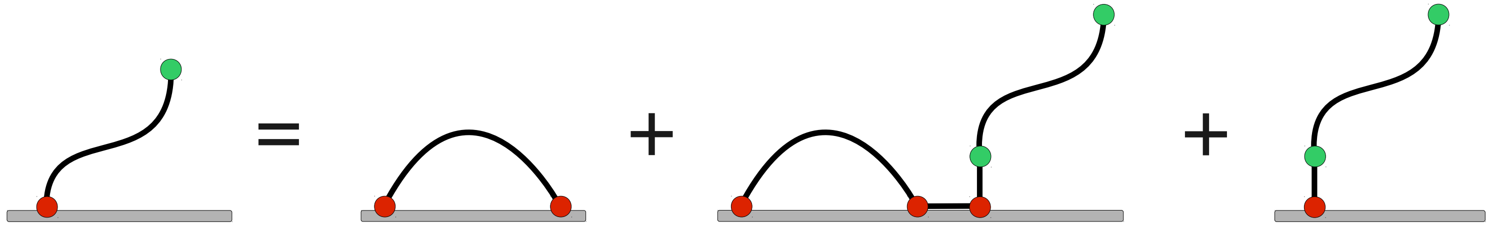
Pulling at an angle

If we want to pull at an angle we have to keep track of all the coordinates of the last vertex to track the response to the applied force.



$$\begin{aligned} P(a, y_1, y_2, z) &= 1 + a(y_1 + y_2)zP(a, y_1, y_2, z) \\ &+ az^2(P(1, y_1, y_2, z) - 1)(1 + a(y_1 + y_2)zP(a, y_1, y_2, z)) \end{aligned}$$

Pulling at an angle



$$F(a, y_1, y_2, y_3, z) = P(a, y_1, y_2, z)(1 + a(y_1 + y_2)y_3z^2F(1, y_1, y_2, y_3, z)) + y_3zF(1, y_1, y_2, y_3, z)$$

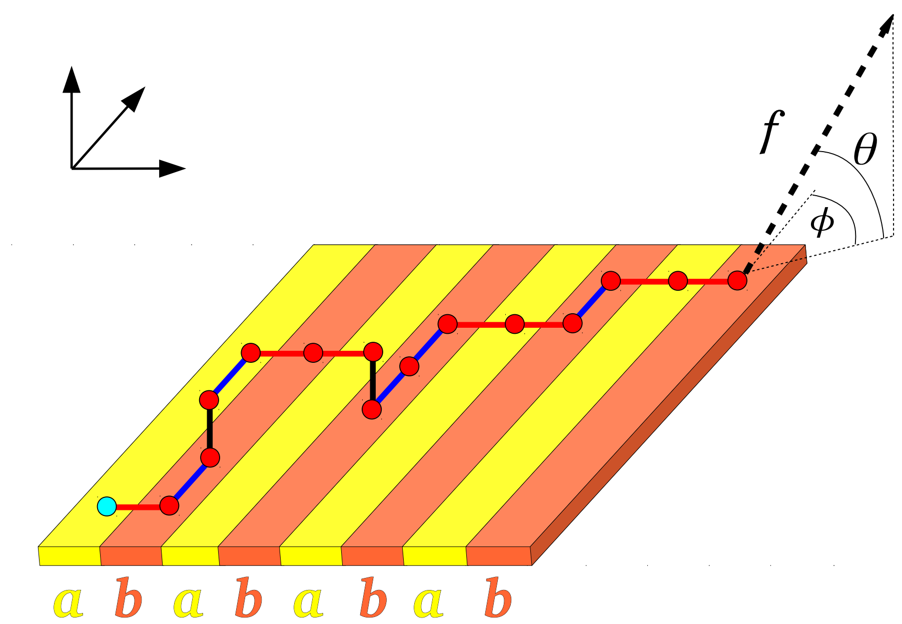
Singularities of $F(a, y_1, y_2, y_3, z)$

- $F(a, y_1, y_2, y_3, z)$ has three relevant singularities, a branch cut $z_1(y_1, y_2)$, and two poles $z_2(a, y_1, y_2)$ and $z_3(y_1, y_2, y_3)$.

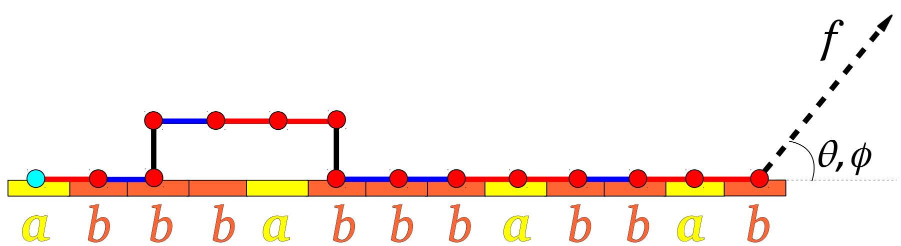
- $z_2(a, y_1, y_2)$ controls the adsorbed phase and $z_3(y_1, y_2, y_3)$ controls the desorbed phase in the presence of a force that can desorb the walk.

- The phase boundary is determined by the condition $z_2 = z_3$.

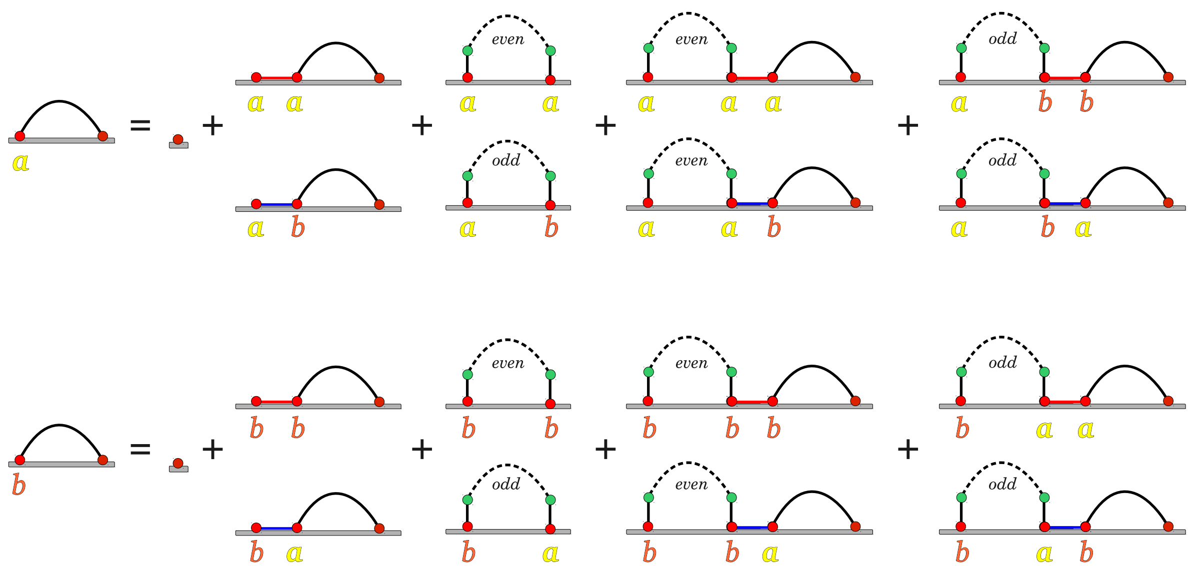
Pulling on a striped surface



Mapping to a bicoloured PDW

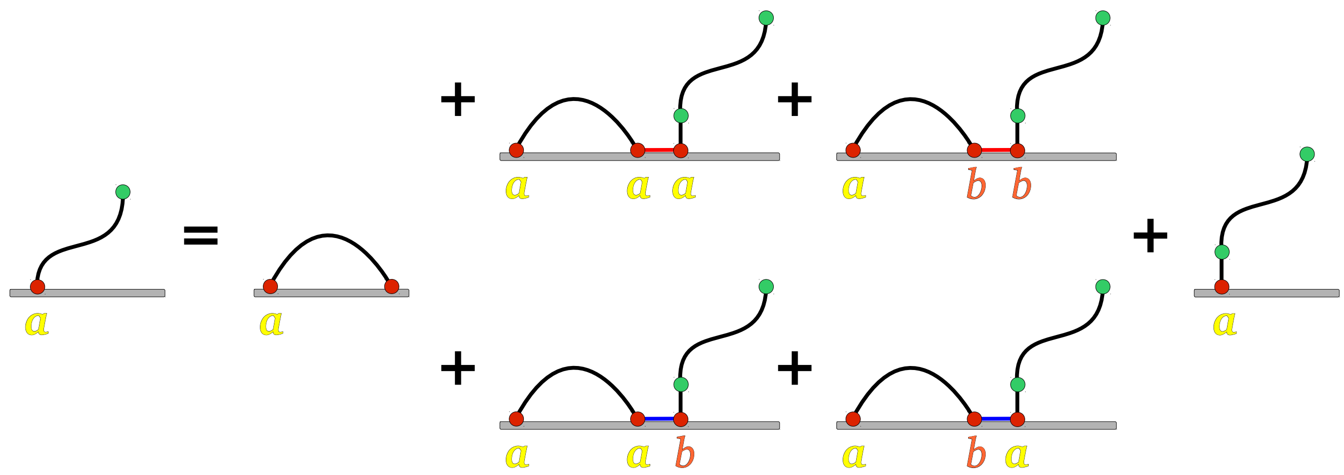


Factorization scheme for a striped surface

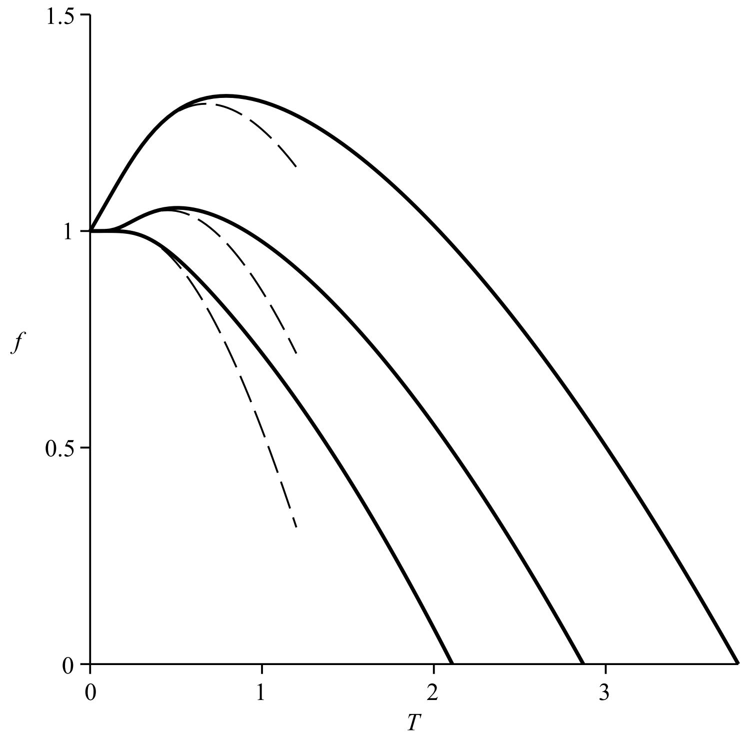


This requires keeping track of the parity of the number of steps parallel to the surface, in the direction perpendicular to the stripe direction, since we need to know if we have followed a stripe or crossed from one stripe to another.

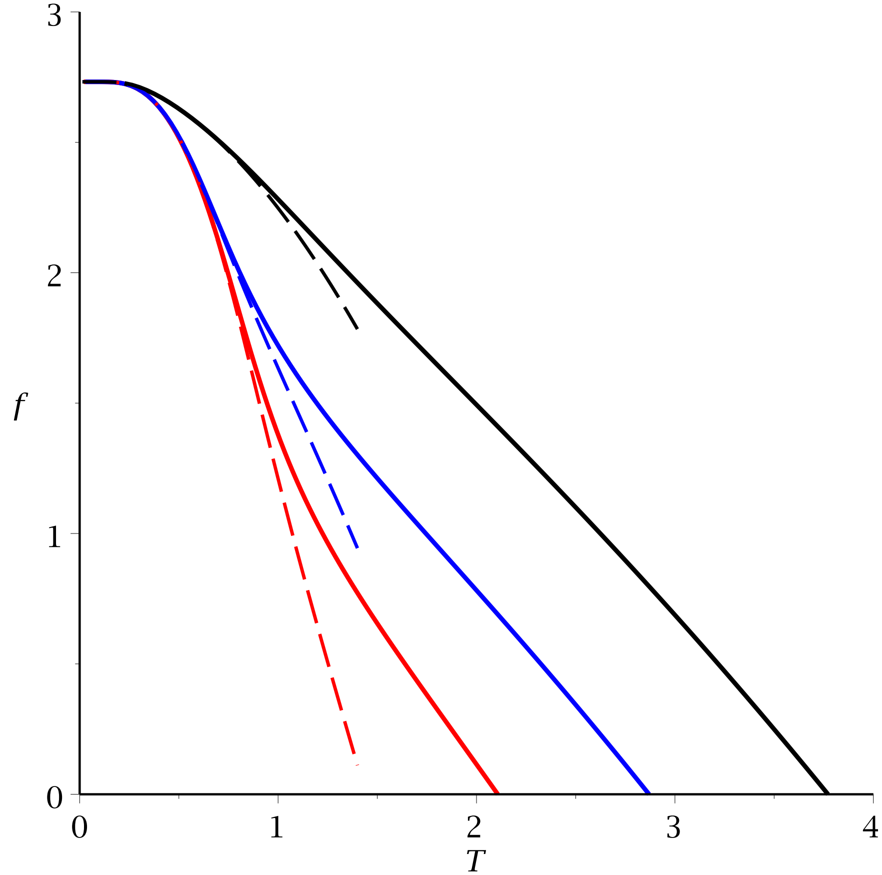
Factorization scheme for a striped surface



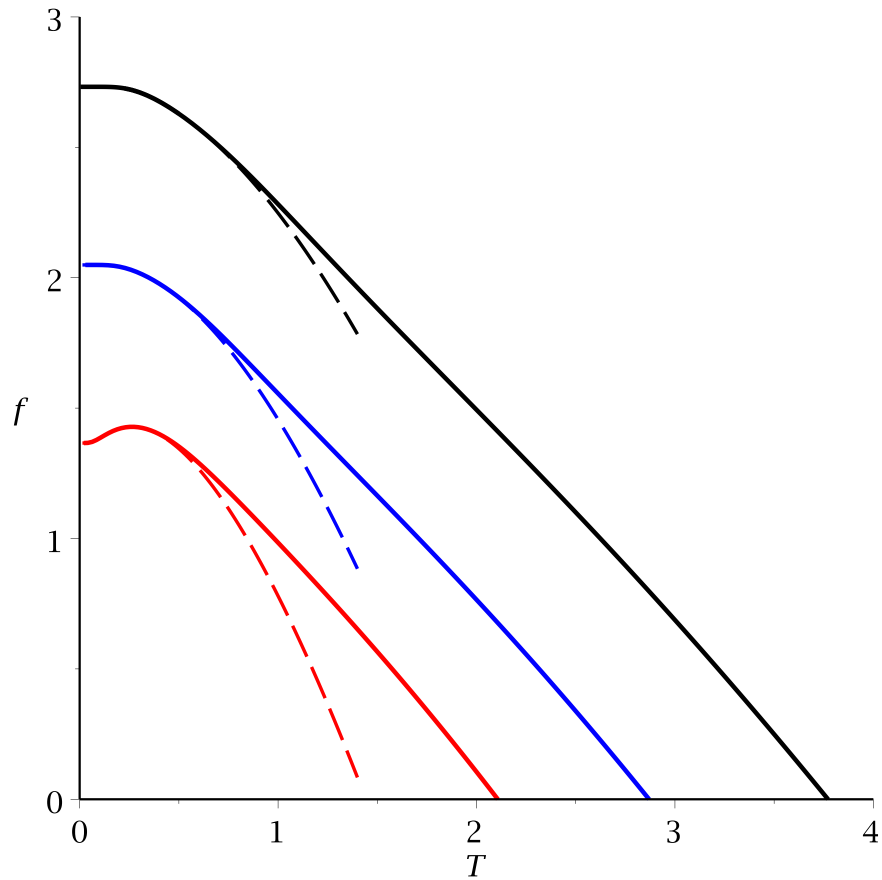
Homopolymer on a striped surface



Pulling normal to surface – top curve is for a homogeneous surface

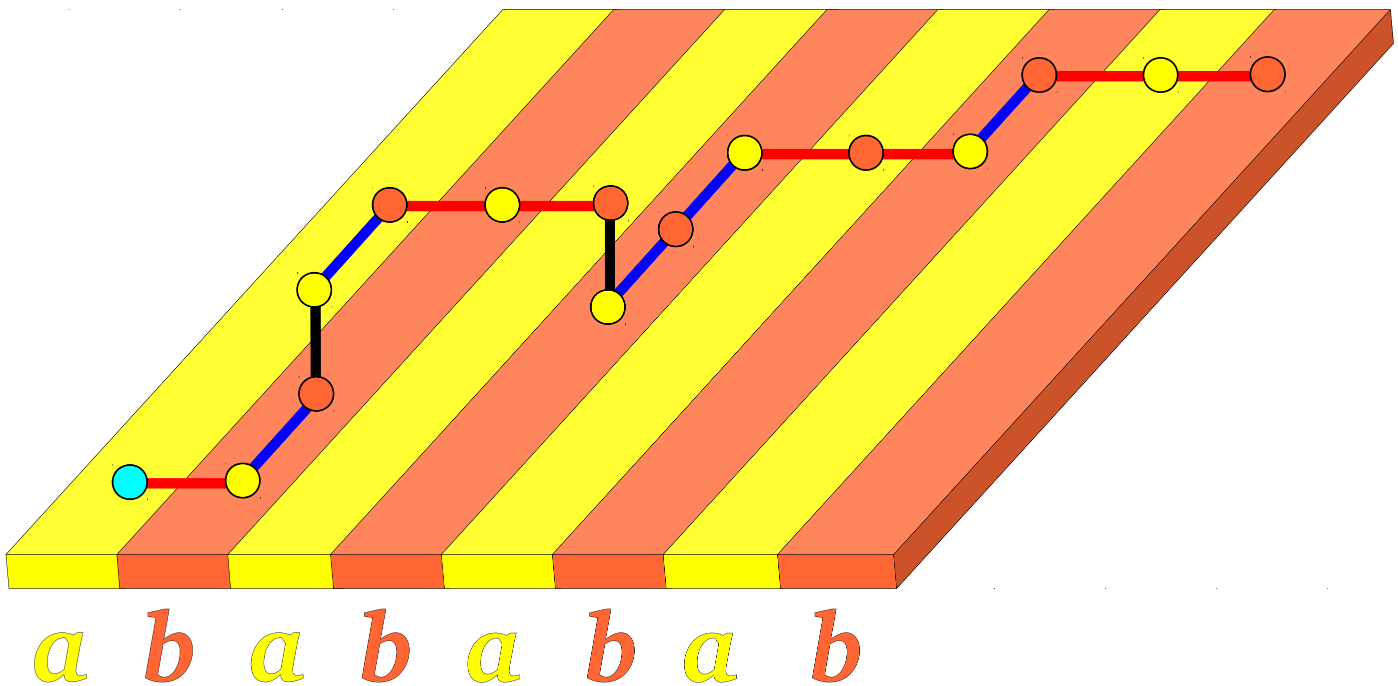


$\theta = \pi/3,\ \phi = 0$



$\theta = \pi/3, \ \phi = \pi/2$

Alternating copolymers on a striped surface



Alternating copolymers on a striped surface

- Now we have inhomogeneity in both the polymer and the surface. We also have to keep track of the parity of the number of edges in the walk. This introduces new complications but can be handled.

- Inhomogeneity in both the polymer and the surface gives a crude model of recognition.