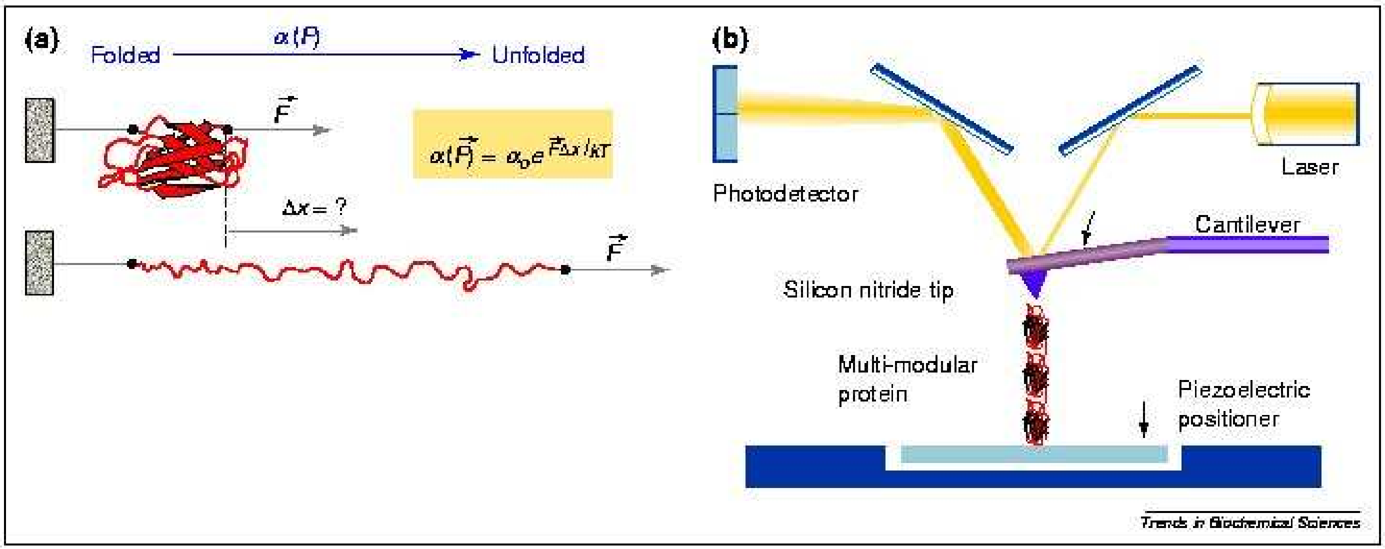
Directed walk models of polymers stretched by a force.



G. Iliev, A. Rechnitzer, M.C. Tesi

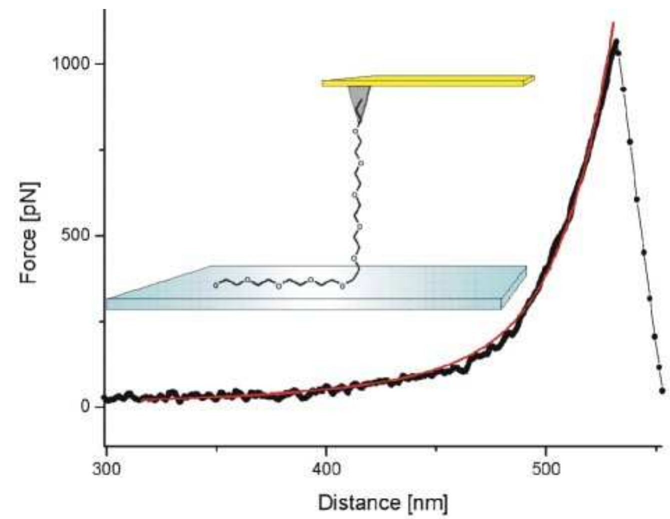
Stu Whittington.

Mechanical desorption of a polymer adsorbed onto a plane.

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

2. In the thermodynamic limit there is a phase transition from an adsorbed phase to a desorbed phase at some critical temperature Tc.

3. In the adsorbed phase the polymer can be desorbed by application of a force.



Which model ?

Different models can be used in order to study the configurational properties of a linear polymer.

Off-lattice models: Freely jointed chain, Gaussian chain, worm like chains etc.

On-lattice models: random walks, self-avoiding walks.

Self-avoiding walks

No clue how to determine rigorously the force-temperature phase diagram.

How about directed walks ?

Dyck paths

Motzkin paths

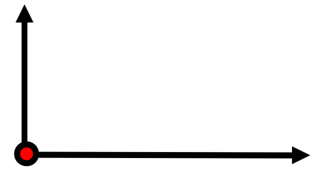
Exact solutions can be obtained
Stretched walks wouldn't be so different from being directed.

Dyck Path

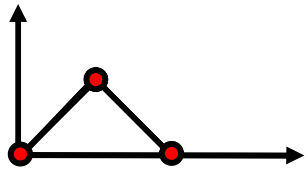
- A Dyck path of length n is a lattice path in the plane from the origin (0,0) to (n,0) consisting of up steps (1,1) and down steps (1,-1) that never run below the x-axis.

Examples

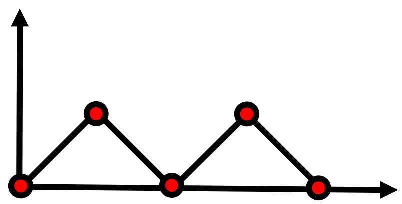
•n=0

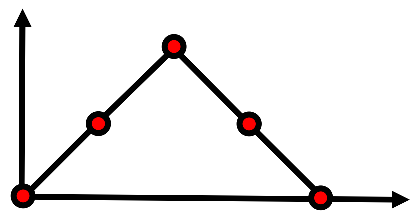


•n=2

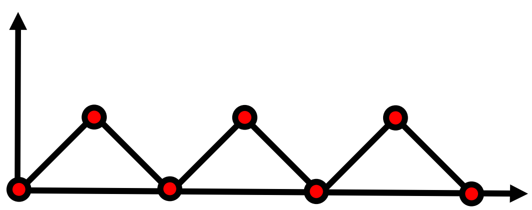


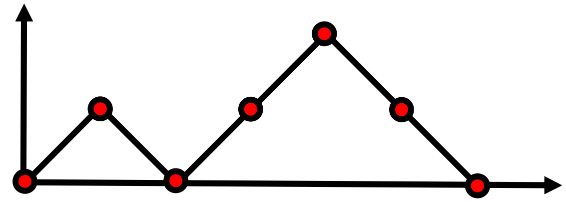
•n=4

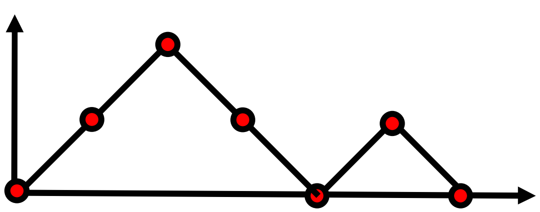


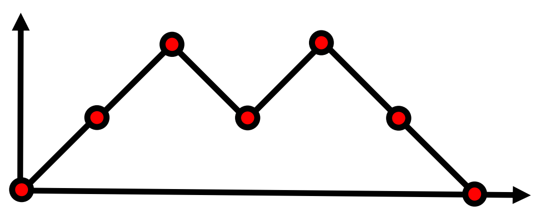


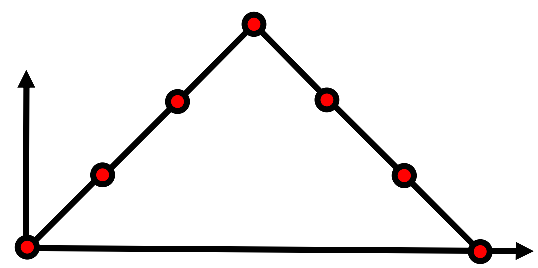
•n=6









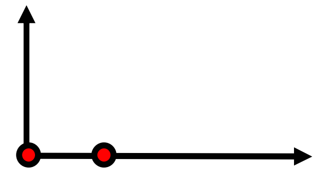


Motzkin Path

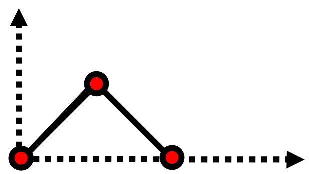
- A Motzkin path of length n is a lattice path in the plane from the origin (0,0) to (n,0) consisting of up steps (1,1), down steps (1,-1) and horizontal steps (1,0) that never run below the x-axis.

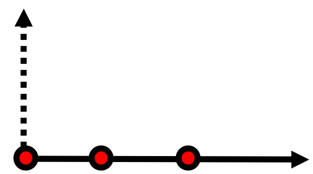
Examples

- n=1

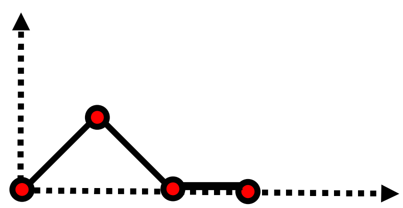


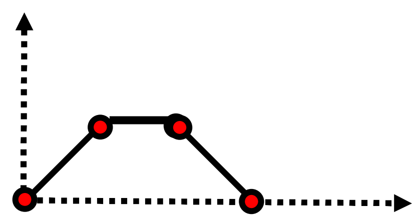
- n=2

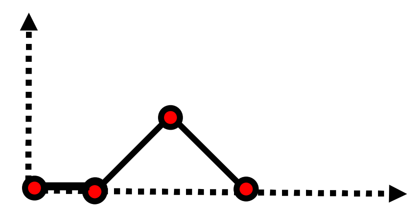


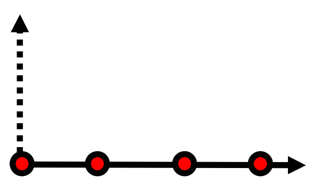


- n=3



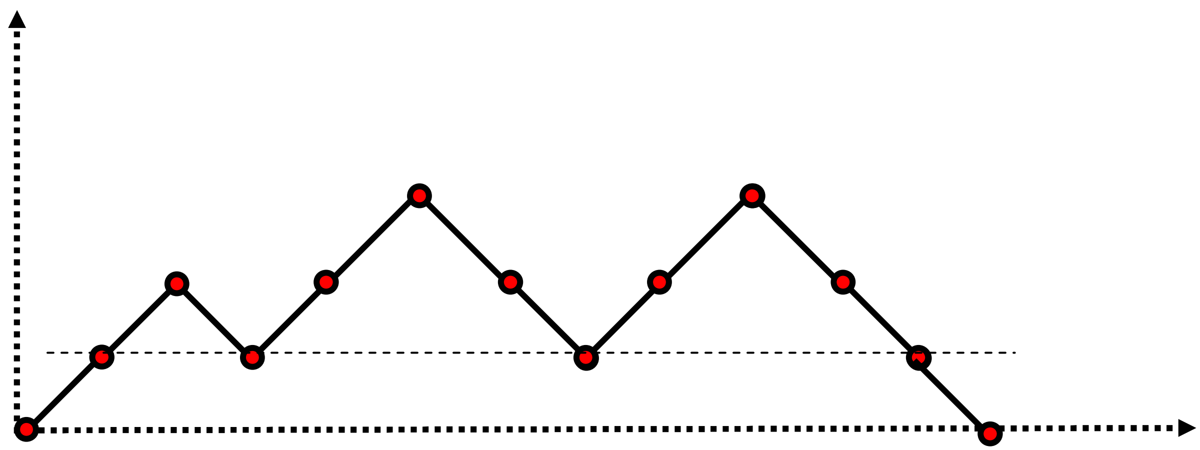






Dyck Excursion

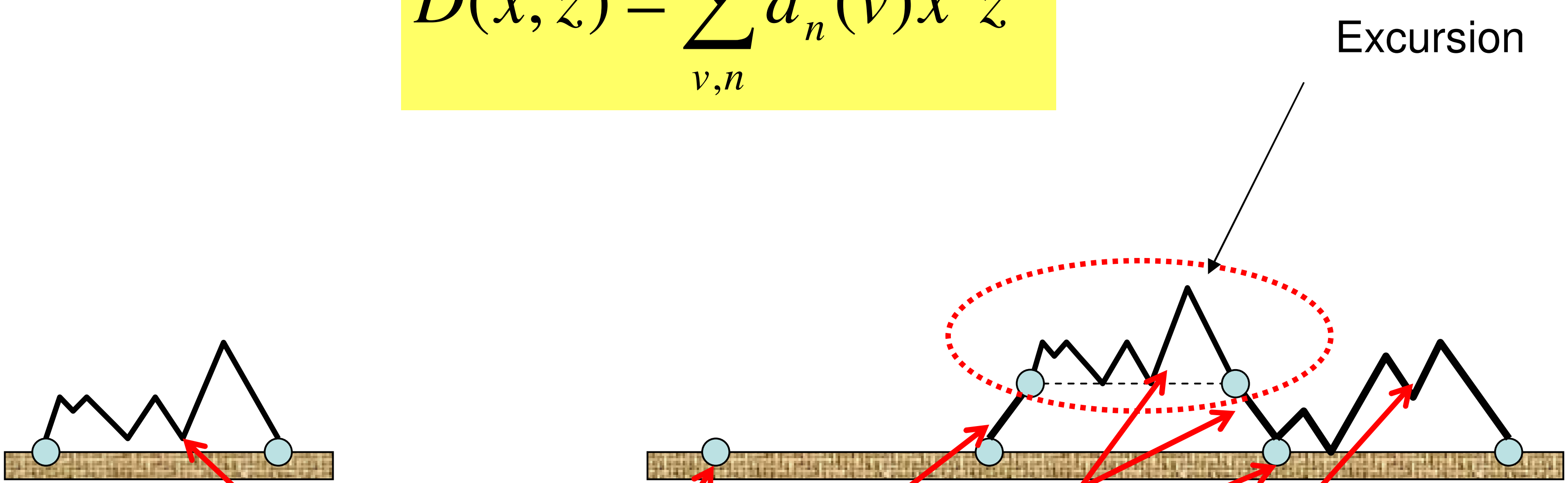
- A Dyck excursion of length n is a Dyck path Where $y(i) > 0$ for all i except $i=1,n$



Counting Dyck paths keeping track of vertices in the surface

Define the generating function

$$D(x,z) = \sum_{v,n} d_n(v) x^v z^n$$



$$D(x,z) = \quad 1 + z^2 \, x \quad D(1,z) \quad D(x,z)$$

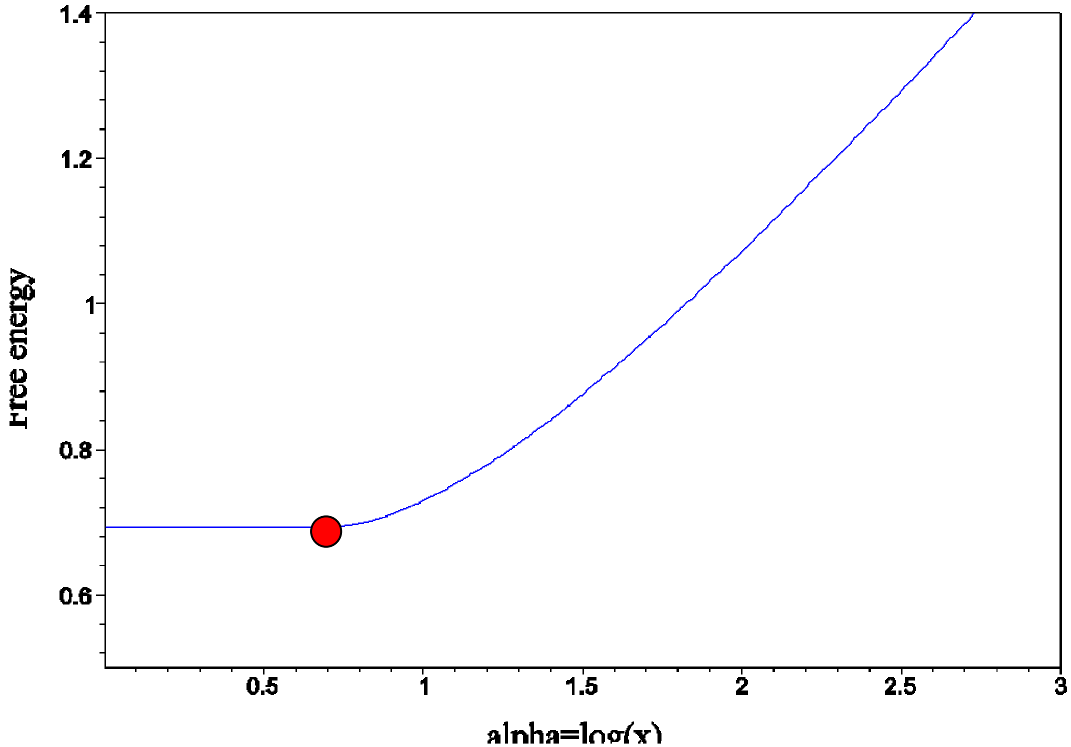
Singularity structure of *D(x,z)*

$$D(x,z) = 1 + x\,z^2\,D(1,z)\,D(x,z)$$

$$D(x,z) = \frac{2}{2 - x\,(1 - \sqrt{1 - 4\,z^2}\,)}$$

$$D(x,z) = \frac{2}{2 - x(1 - \sqrt{1 - 4z^2})}$$

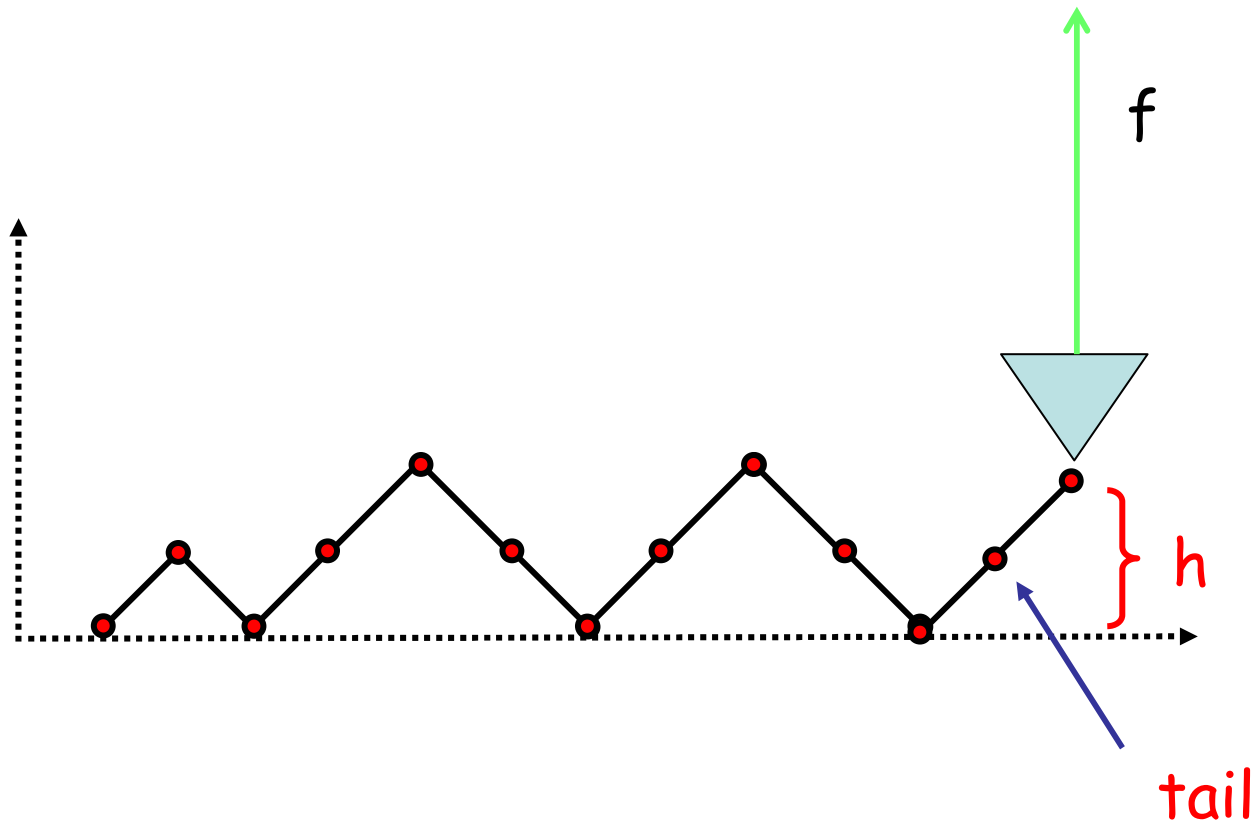
D(x,z) has a square root singularity at $z = z_1 = 1/2$ which dominates for $x < 2$ and a pole at $z = z_2(x)$ which dominates for $x > 2$.



Adsorption point

$$x_c = 2$$

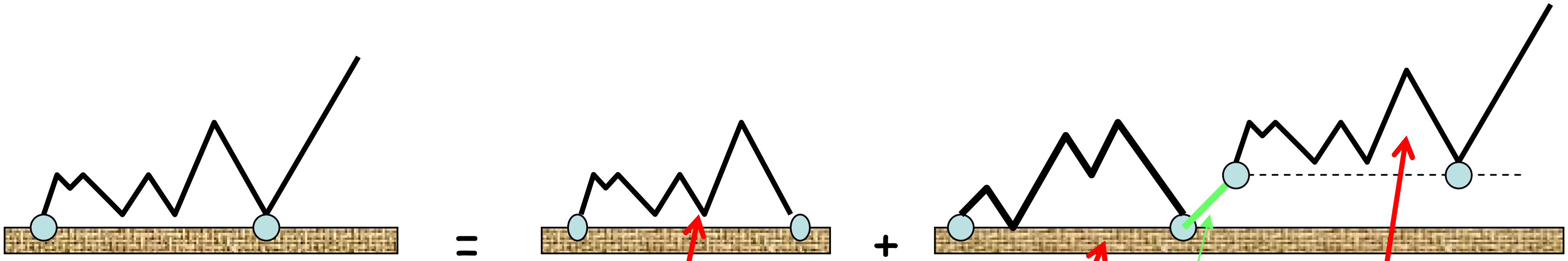
Now let us apply a lifting force acting on the last vertex of the walk………



New generating function

$$F(x,y,z)=\sum_{v,h,n} d_n(v,h)\,x^v y^h z^n$$

$y \longleftrightarrow \exp(f / k_B T)$



$$F(x,y,z) = D(x,z) + D(x,z)\; y\, z\; F(1,y,z)$$

$$F(x,y,z) = \frac{4z}{\left(2 - x + x\sqrt{1-4z^2}\right)\left(2z - y + y\sqrt{1-4z^2}\right)}$$

N.B. One pole depends on x and the other on y

$$F(x,y,z)=\frac{4z}{\left(2-x+x\sqrt{1-4z^2}\right)\left(2z-y+y\sqrt{1-4z^2}\right)}$$

Square root singulariry $z = \frac{1}{2}$ control the desorbed phase

Two poles:
$$\begin{cases} z_c^{(1)}=\dfrac{\sqrt{x-1}}{x} \\ z_c^{(2)}=\dfrac{y}{y^2+1} \end{cases}$$

Phase boundary for $z^{(1)}_c=z^{(2)}_c$

$$y_c(x)=\sqrt{x-1}$$

Changing to physical variables

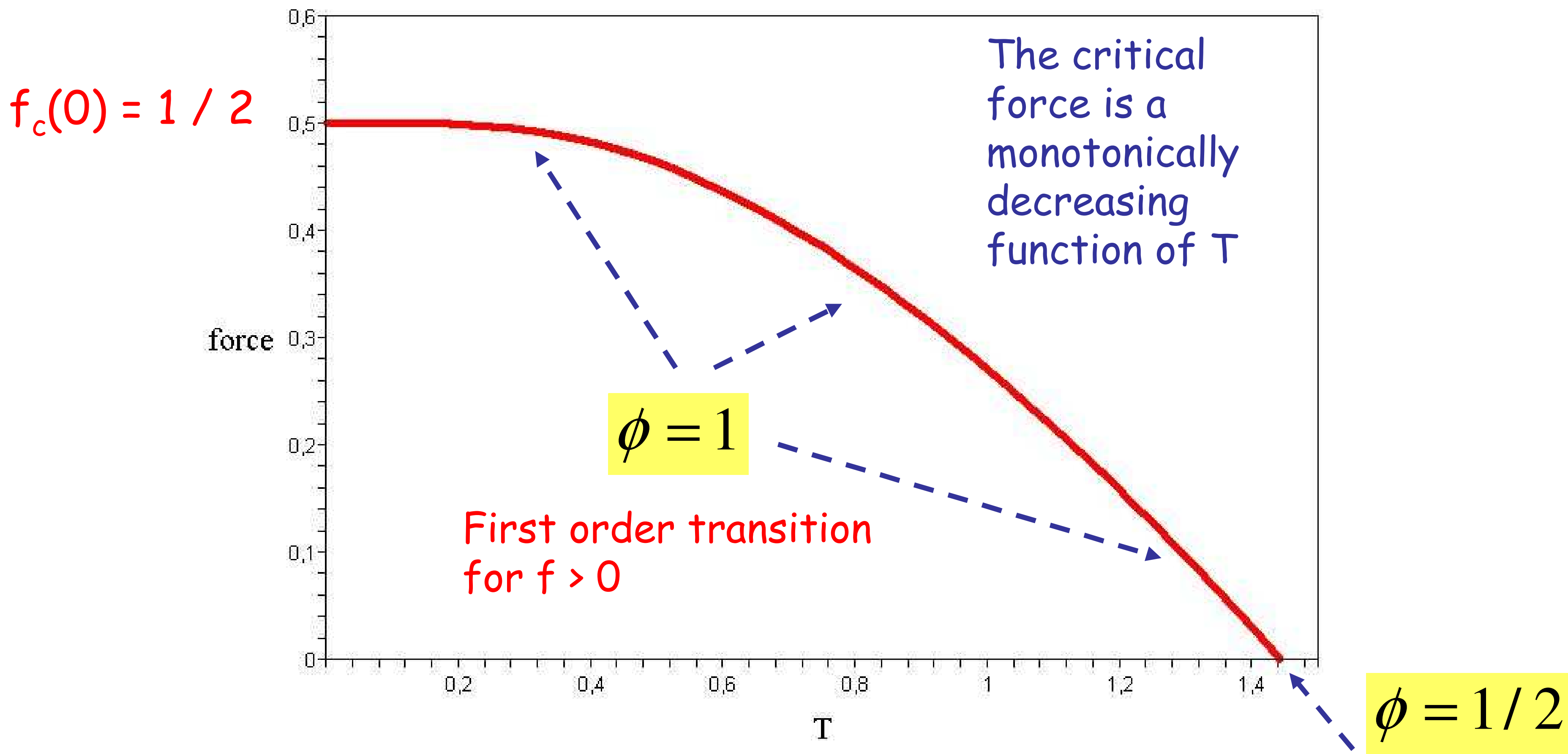
$y \longleftrightarrow \exp(f / k_B T)$

$x \longleftrightarrow \exp(1 / k_B T)$

$$f_c(T)=\frac{k_B T}{2}\log\left(e^{1/k_B T}-1\right)$$

Force-Temperature relation

$$f_c(T) = \frac{k_B T}{2} \log\left(e^{1/k_B T} - 1\right)$$



Similar phase diagram for Motzkin paths: $f_c(0) = 1$

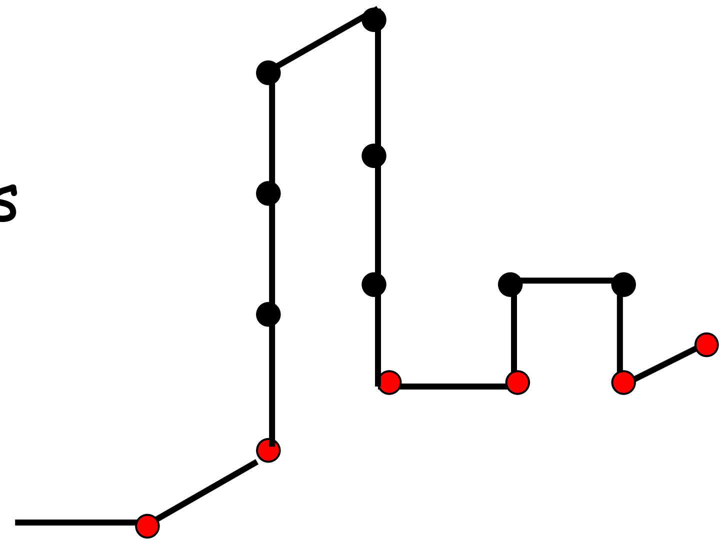
Adsorption on a plane: partially directed walks in three dimensions.

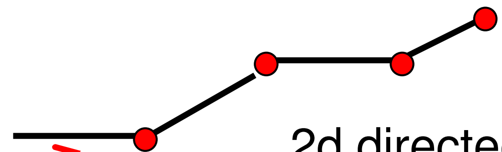
- A n steps partially directed walk in three dimensions confined into the half plane z >= 0 is a walk that

1) starts at the origin
2) with no steps in the negative x and negative y
3) never run below the z-axis.

n = 14 steps

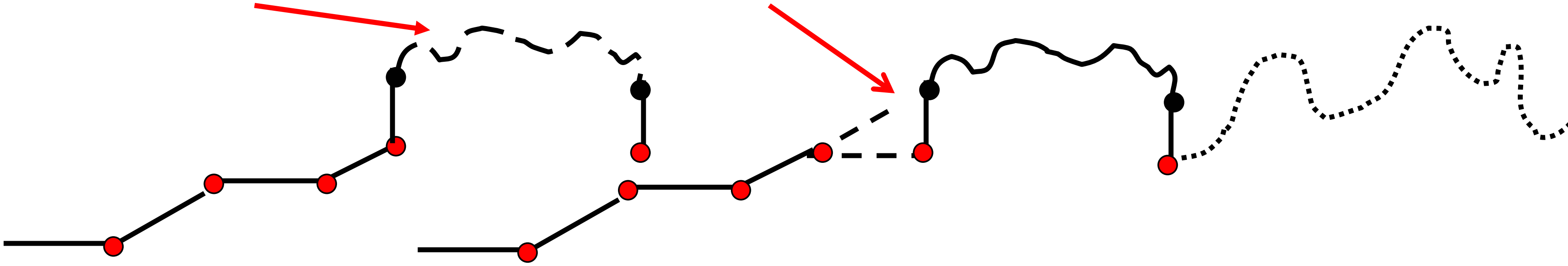
v = 6 visits



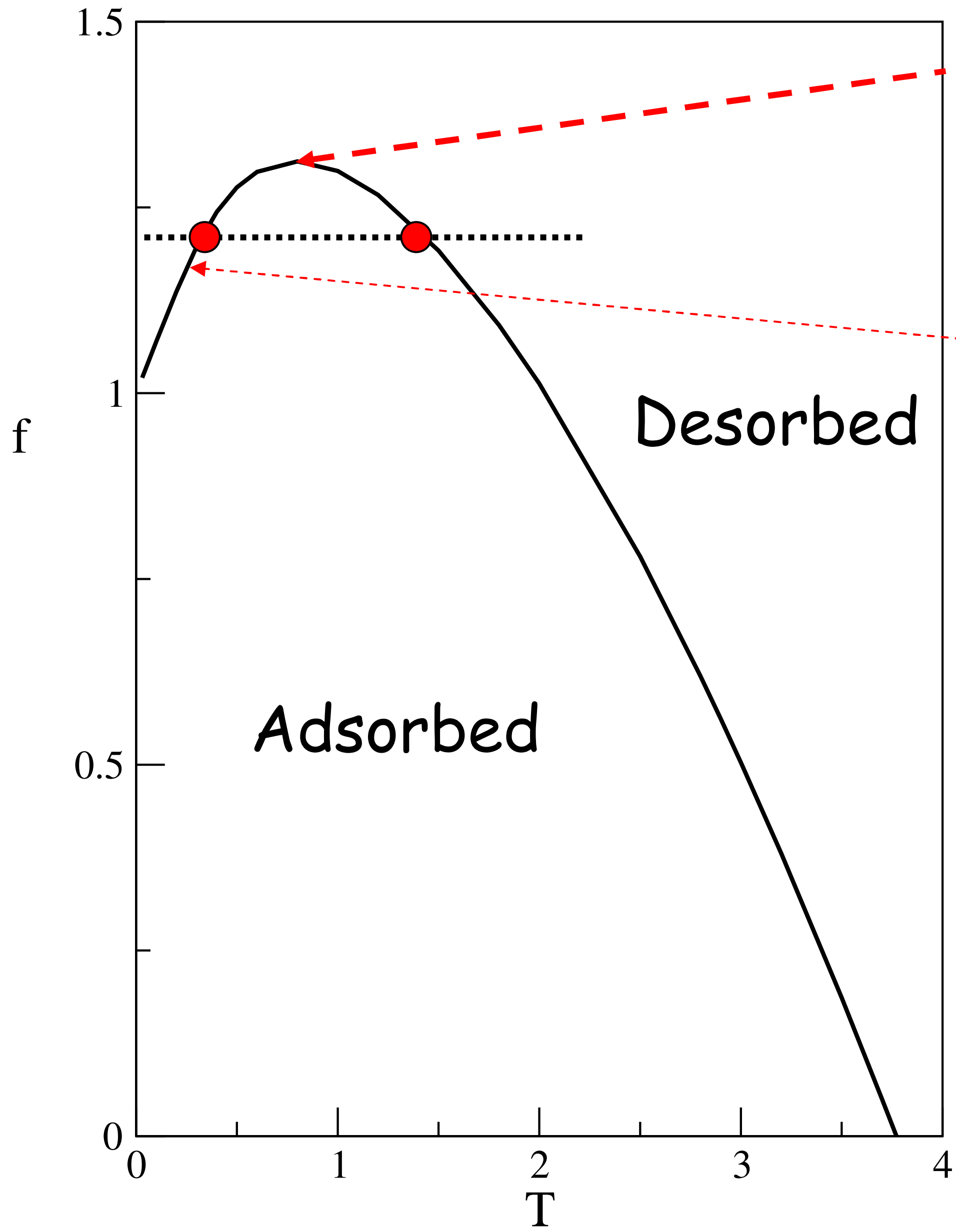


2d directed walks.

$$G(x,z) = \left(1 + 2xz + 4x^2z^2 + \ldots 2^p x^p z^p + \ldots\right)$$
$$\times\left[1 + xz^2\left(G(1,z)-1\right) + 2x^2z^3\left(G(1,z)-1\right)G(x,z)\right]$$



Partially directed walks in three dimensions



The force goes through a maximum as T varies.

Re-entrant transition.

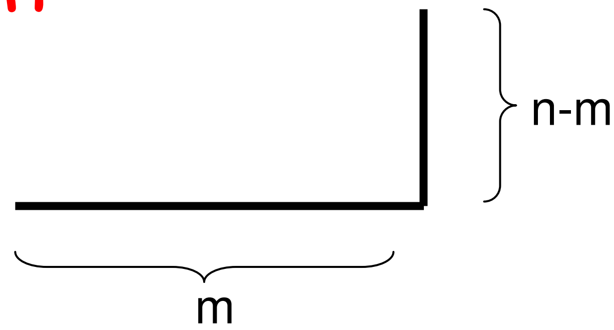
Why a re-entrant transition at low T for partially directed walks (and SAWs) and not for Dyck or Motzkin paths?

⇓

Entropic contribution (extensive in n) of the adsorbed configurations.

Low T argument

For T close to zero one can assume:



$$F_n = -f\,(n-m) - m\,\varepsilon \;-\; m\,T \log \mu$$

$\log \mu$: conformational entropy per monomer in the adsorbed state

The minimum of F_n is given for the critical force

$$\boxed{f_c(T) = \varepsilon + T \log \mu}$$

$$\boxed{f_c(T) = \varepsilon + T \log \mu}$$

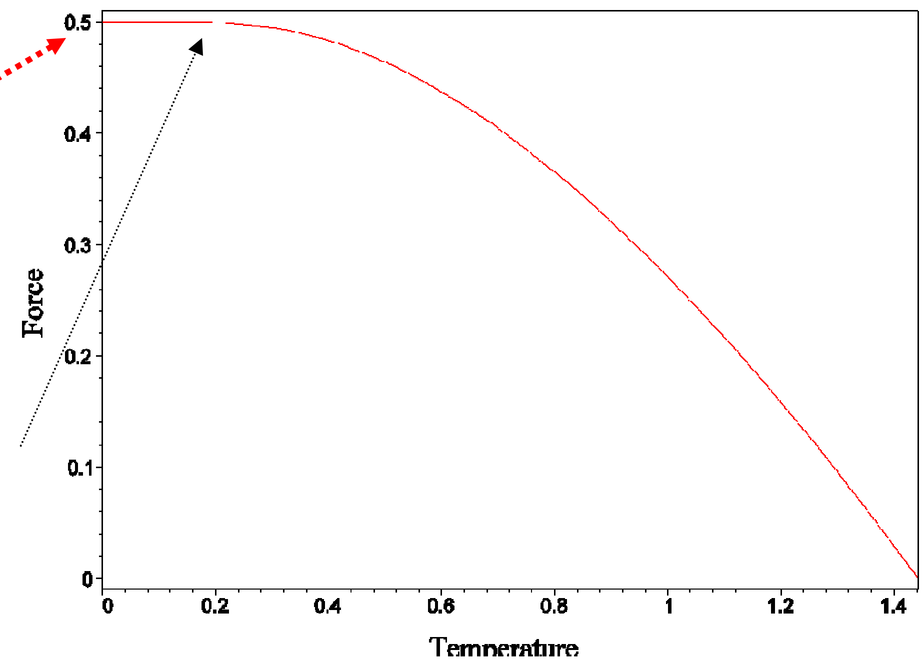
Dyck paths

$\varepsilon = \frac{1}{2}$: only half of the monomers can sit on the line

$\mu = 1$: only one completely adsorbed configuration

$$\boxed{f_c(0) = 1/2}$$

$$\boxed{df_c(T)/dT\,|_{T=0} = 0}$$



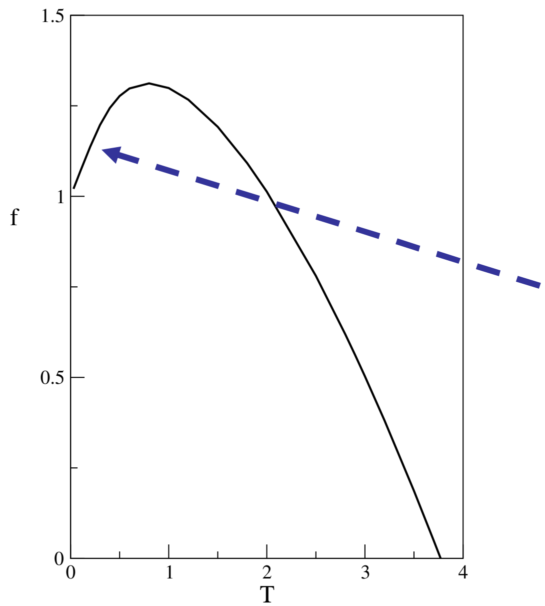
N.B. For SAWs in 2D $\mu = \mu_{1D} = 1$

$f_c(T) = \varepsilon + T \log \mu$

Partially directed walks in 3D

figurations on the plane)

$f_c(0) = 1$

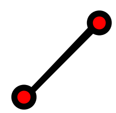


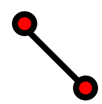
$(T)/dT\,|_{T=0} = \log 2$

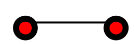
N.B. For 3D SAWs adsorbing on a plane ($\mu = \mu_{2D} = 2.6381\ldots$)
the re-entrant phase diagram was found by Monte Carlo simulations
(J. Krawczyk et al J. Stat. Mech 2004)

Directed walks and 1D random walks

Mapping between a directed walk and a 1D random walk:

 → +1   Step on the right with prob.   p/2

 → -1   Step on the left with prob. p/2

 → 0   Stay at the previous site with prob. q

$$p + q = 1$$

Dyck path --à   random walk with p=1 and q=0

Motzkin path --à   random walk with p=2/3 and q=1/3

Number of visits: --à   number of times the random walk is at the origin.

For a general (p,q) 1D random walk
the reentrance takes place for $p < 2/3$

(Giacomin and Toninelli 2006)

$\boxed{f_c(T) = \varepsilon + T \log \mu}$ $\qquad \mu = 2q/p$

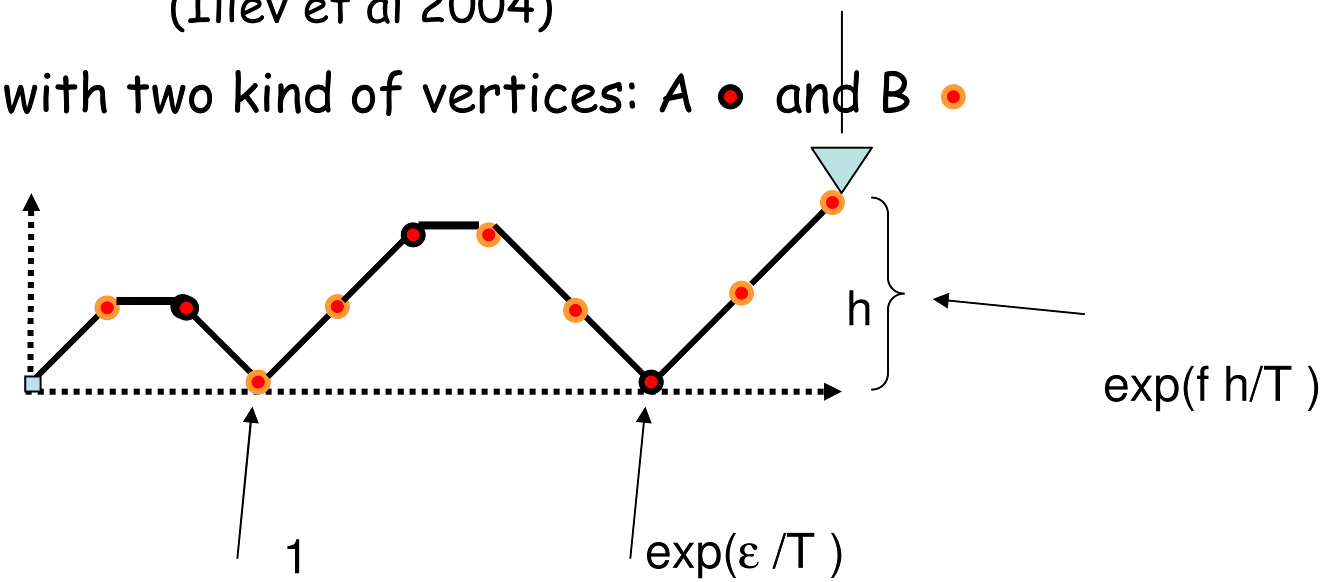
Motzkin path --à (2/3,1/3) random walk à $\mu = 1$

Partially directed walk $\mu = 2$ --à (1/2,1/2) random walk

Extension to random copolymers

(Iliev et al 2004)

Motzkin paths with two kind of vertices: A ● and B ●



Colour variable χ_i: χ_i = 1 if mon =A and χ_i = 0 if mon = B

Colour configuration: $\{\chi\}_{i=1,n} = \{\chi_1, \chi_2, \chi_3, \cdots, \chi_n\}$

$$H(\omega, f|\chi) = \sum_{i=1}^{n} \varepsilon \Delta_i(\omega)\chi_i - f\ h$$

$$Z(T, f|\chi) = \sum_{\{\omega\}} \exp\left(\left(\Delta_i(\omega)\chi_i + f\ h\right)/T\right)$$

$\Delta_i(\omega) = 1$ if z_i = 0 $\quad \Delta_i(\omega) = 0$ otherwise

Random copolymers

The χ_i's are iid random variables
prob(χ_i=1) = p , prob(χ_i=0)=1-p

$$Z_n(T,f|\chi)=\sum_{\{\omega\}}\exp\left(\left(\Delta_i(\omega)\,\chi_i+f\ h\right)/T\right)$$

Function of random variables

quenched

$$F^q(T,f)=\lim_{n\to\infty} n^{-1}\left\langle \log\left[Z_n(T,f|\chi)\right]\right\rangle_\chi$$

annealed

$$F^a(T,f)=\lim_{n\to\infty} n^{-1}\log\left\langle Z_n(T,f|\chi)\right\rangle_\chi$$

where:

$$\langle O(\chi)\rangle_\chi=\sum_{\{\chi\}} p^{|A(\chi)|}(1-p)^{n-|A(\chi)|}\,O(\chi)$$

First order Morita approximation

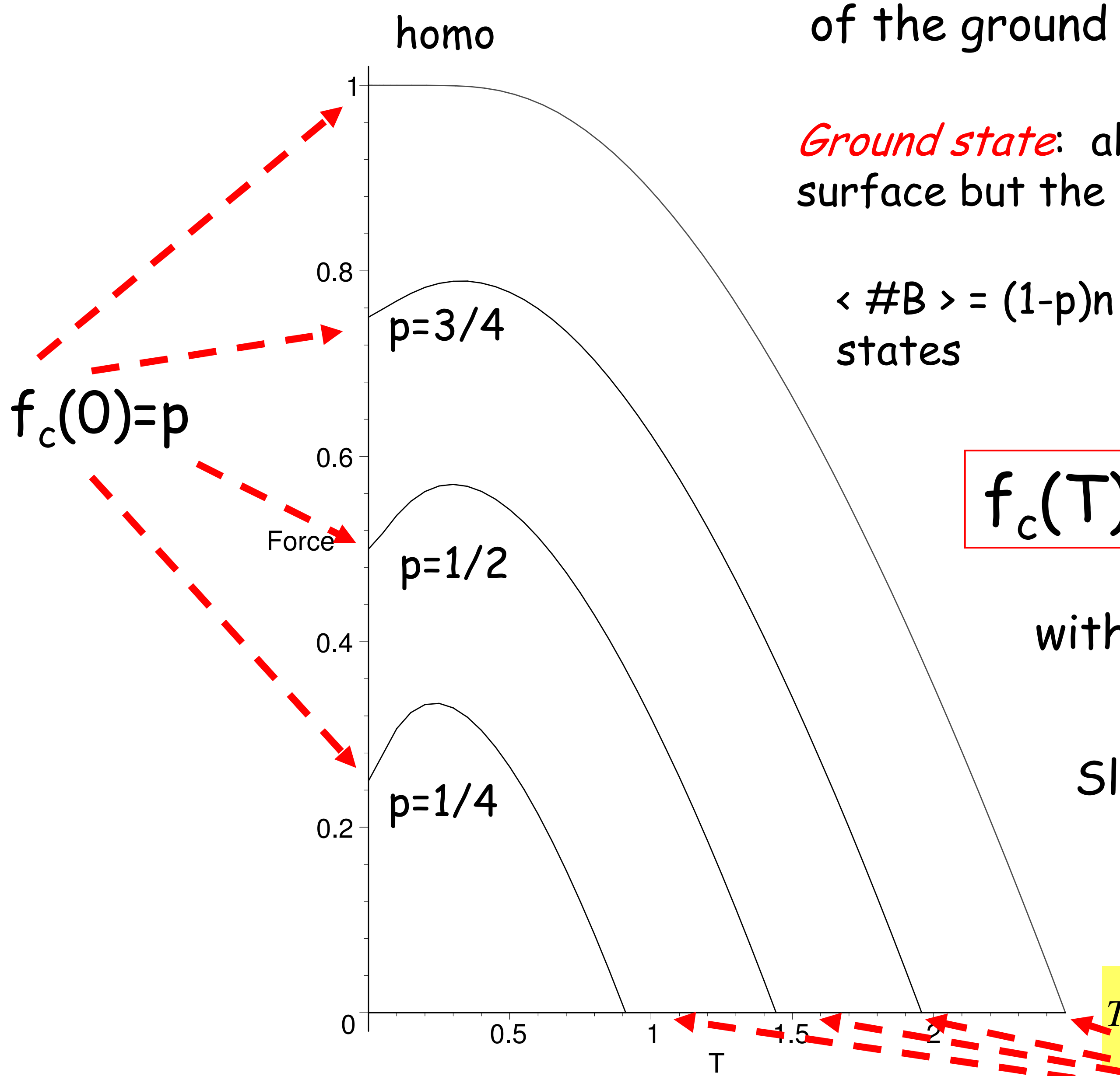
$$F^{1st}(T,f|p)=\lim_{n\to\infty} n^{-1}\log\left\langle Z_n^{1st}(T,f|\chi)\right\rangle_{\chi}$$

$$Z_n^{1st}(T,f,\lambda|\chi)=\sum_{\{\omega\}}\exp((\Delta_i(\omega)\chi_i+f\ h)/T)\exp\left(\lambda\left(\sum_i \chi_i - pn\right)\right)$$

λ chosen such that $\left\langle \sum_{i=1}^{n} \chi_i \right\rangle = pn$

The generating function needs to keep track also of the number of vertices in the bulk.

$$f_c^q(T) \le f_c^{1st}(T)$$



Reentrance due to the degeneracy of the ground state.

Ground state: all the A are at the surface but the B can be everywhere.

< #B > = (1-p)n $\Rightarrow$ > $2^{(1-p)n}$ degenerate states

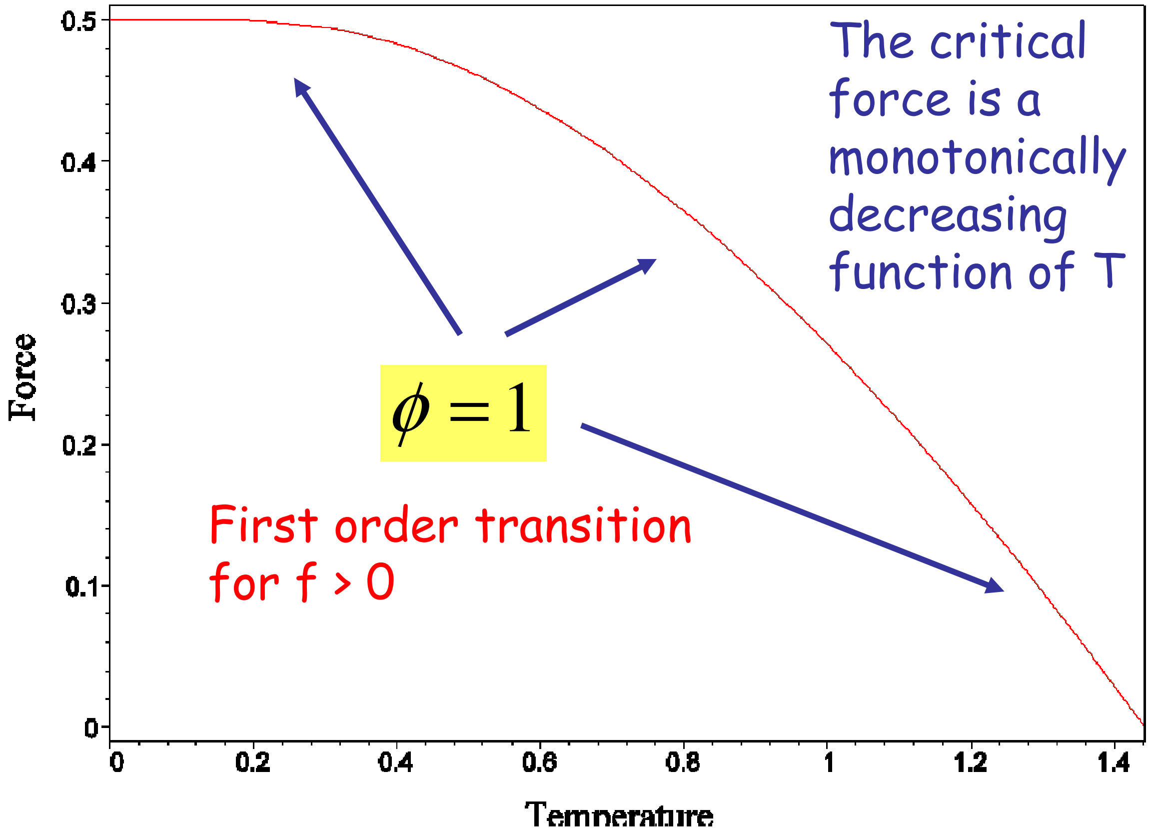
$$\boxed{f_c(T)= \varepsilon + T \log \mu}$$

with $\log \mu$ > (1-p)log 2

Slope > (1-p)log 2

$$T(f=0) \equiv T_c = \frac{1}{\log(2p+1) - \log(2p)}$$

$$f_c(T) = \frac{k_B T}{2} \log\left(e^{1/k_B T} - 1\right)$$



$\phi = 1/2$

Similar phase diagram for Motzkin path: at T=0 f=1

Singularity structure of *D(x,z)*

$$D(x,z) = 1 + x\,z^2\,D(1,z)\,D(x,z)$$

$$D(x,z) = \frac{2}{2 - x\,(1 - \sqrt{1 - 4\,z^2}\,)}$$

where

$$D(1,z) \equiv D(z) = \frac{1 - \sqrt{1 - 4\,z^2}}{2\,z^2} = \sum_{n \geq 0} C_n x^n$$

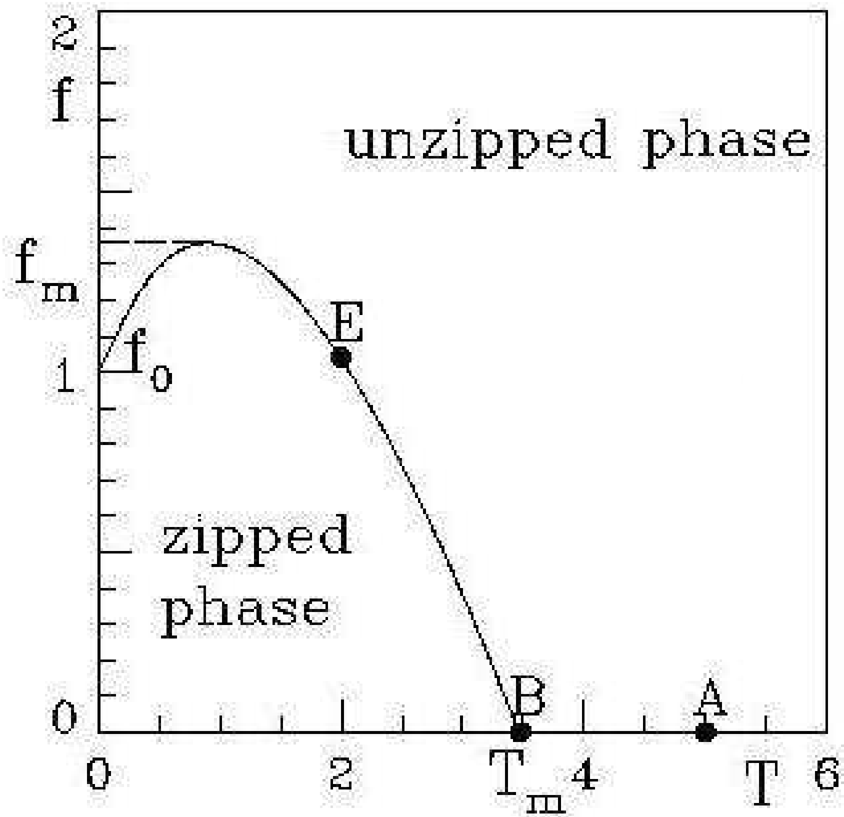
Catalan numbers

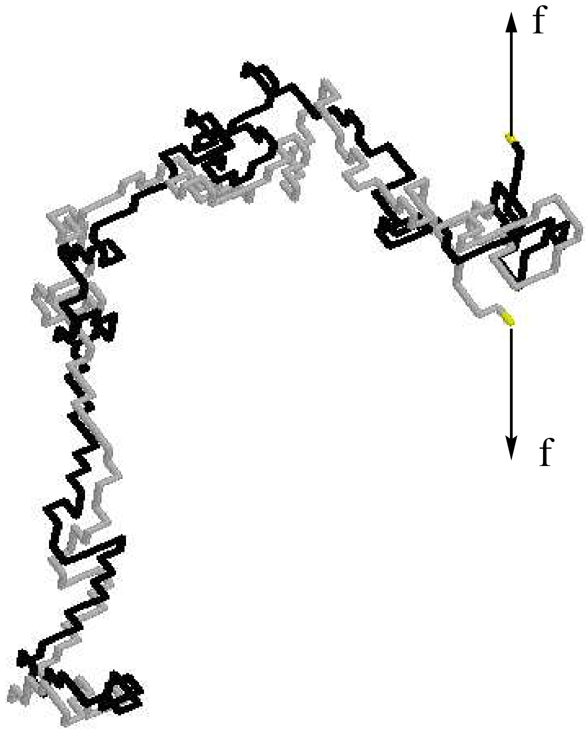
$$C_n = \frac{1}{(n+1)}\binom{2n}{n}$$

For x=1 we get the generating function of unweighted Dyck paths

Mechanical denaturation of DNA

E.O. et al 2001, D. Marenduzzo et al 2002





N.B. The directed DNA model can be mapped
onto a Bicoloured Motzkin path (Janse van Rensburg 2000, Iliev et al. 2006)