Forcing Adsorption of a Tethered Polymer by Pulling

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AUSTRALIAN RESEARCH COUNCIL
Centre of Excellence for Mathematics and Statistics of Complex Systems

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Queen Mary University of London

Walk above a wall

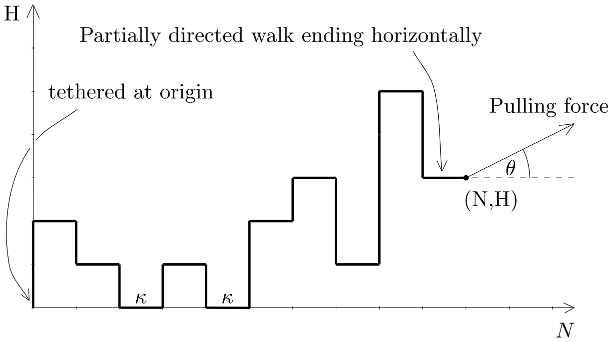

Figure: A walk with weight $x^{10}y^{17}\kappa^2\mu^3$

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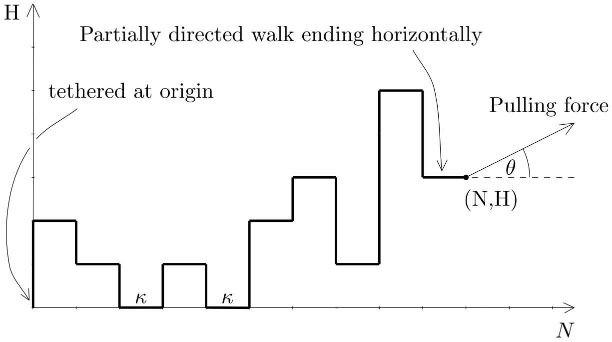

Figure: A walk with weight $x^{10}y^{17}\kappa^2\mu^3$

Generating function G

$$G(x, y, \kappa; \mu) = \sum_{N,M,K,H\geq 0} C_{N,M,K,H} x^N y^M \kappa^K \mu^H$$

Generating function - functional equation

Abbreviate $G(\mu) := G(x, y, \kappa; \mu)$. Then

$$
\begin{aligned}
G(\mu) &= \kappa x && \text{horizontal step at height } 0 \\
&\quad + G(\mu)\Bigg(x && \text{horizontal step at height} > 0 \\
&\quad + \frac{xy\mu}{1 - y\mu} && \text{vertical steps up, then horizontal} \\
&\quad + \frac{x\frac{y}{\mu}}{1 - \frac{y}{\mu}} \Bigg) && \text{vertical steps down, then horizontal} \\
&\quad - \frac{x}{1 - \frac{y}{\mu}} G(y) && \text{minus over-counting; } y \text{ fills to surface} \\
&\quad + \kappa x G(y) && \text{plus contact weights}
\end{aligned}
$$

Kernel Method

- $$\underbrace{\left(1 - \frac{x(1-y^2)}{1 - y(\mu + \frac{1}{\mu}) + y^2}\right)}_{\text{Set } \textit{kernel} = 0;} G(\mu) = \kappa x - x\left(\frac{1}{1-\frac{y}{\mu}} - \kappa\right) G(y)$$

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- Quadratic equation:

$$y\mu^2 - (1 - x + y^2 + xy^2)\mu + y = 0$$

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$$G(y)=\frac{\kappa \cancel{x}}{\left(\frac{1}{1-\frac{y}{\mu_0}}-\kappa\right)\cancel{x}}$$

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$$G(y)=\frac{\kappa \cancel{x}}{\left(\frac{1}{1-\frac{y}{\mu_0}}-\kappa\right)\cancel{x}}$$

- Back-substitute to solve for $G(\mu)$ in terms of $G(y)$

Explicitly

$$G(x,y,\kappa;\mu) = \kappa x \left(\frac{1 - \left(\frac{\mu-\kappa(\mu-y)}{\mu-y}\right)\left(\frac{\mu_0-y}{\mu_0-\kappa(\mu_0-y)}\right)}{1 - \left(\frac{x(1-y^2)}{1-y\left(\mu+\frac{1}{\mu}\right)+y^2}\right)} \right)$$

where

$$\mu_0 = \frac{(1-x+y^2+xy^2) - \sqrt{-4y^2+(1-x+y^2+xy^2)^2}}{2y}$$

Finite-step partition function

- We're interested in the partition function Z_L for walks of length L

$$G(x = \lambda t, y = t, \kappa; \mu) = \sum_{L \geq 0} t^L Z_L(\lambda, \mu, \kappa)$$

- t : conjugate to *path length*
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- The singularities of G determine the asymptotic growth of Z_L

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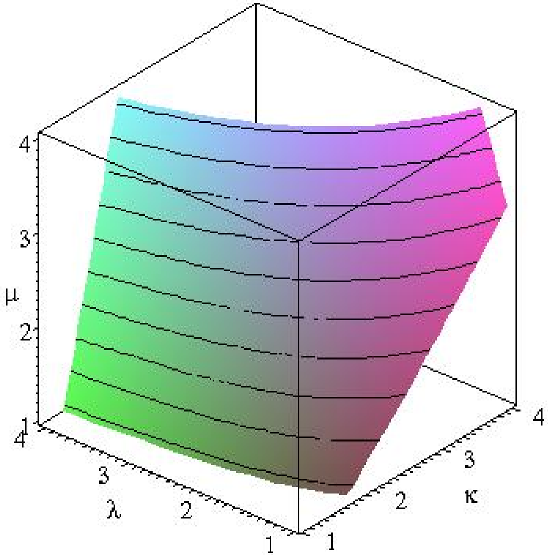
- These poles coincide ("Phase transition") when

$$\lambda = \frac{\kappa\mu(\kappa - 1 - \kappa\mu^2)}{(\kappa-1)[(\kappa-1)^2 - \kappa^2\mu^2]}$$

Phase diagram in (κ, λ, μ)



Physical Variables

- Energy of a configuration:

$$E = KJ - NF_x - HF_y$$

  - $KJ \equiv$ (number of contacts) $\times$ (energy per contact)
  - $NF_x \equiv$ (horizontal distance) $\times$ (horizontal force)
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- Weight of a configuration:

$$\begin{aligned} e^{-\frac{1}{kT}\times E} &= e^{-\frac{1}{kT}\times(KJ-NF_x-HF_y)} \\ &= e^{-\frac{KJ}{kT}}\, e^{\frac{NF_x}{kT}}\, e^{\frac{HF_y}{kT}} \\ &= \kappa^K\, \lambda^N\, \mu^H \end{aligned}$$

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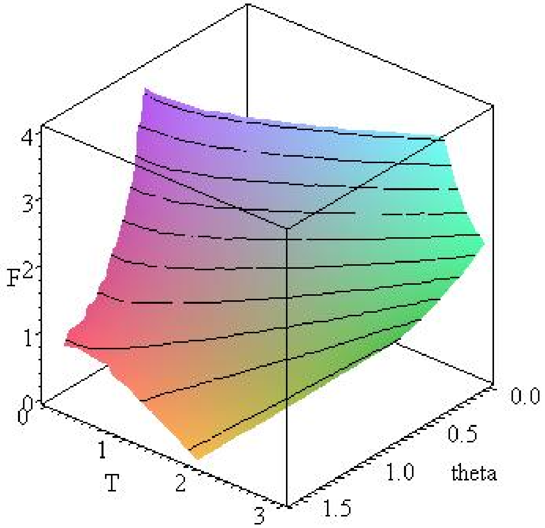
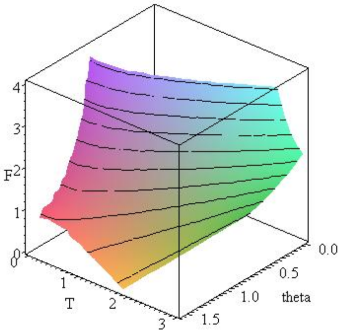
- Normalize (by letting $k = 1$ and choosing $J = -1$):

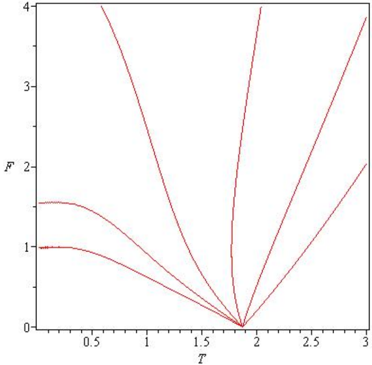
$$\kappa = e^{\frac{1}{T}}\,, \quad \lambda = e^{\frac{F\cos\theta}{T}}\,, \quad \mu = e^{\frac{F\sin\theta}{T}}$$

Phase diagram in (θ, T, F)



Varying the pulling angle





- Thermal desorption at $T = 1/\log(1 + \sqrt{2}/2) \approx 1.87$

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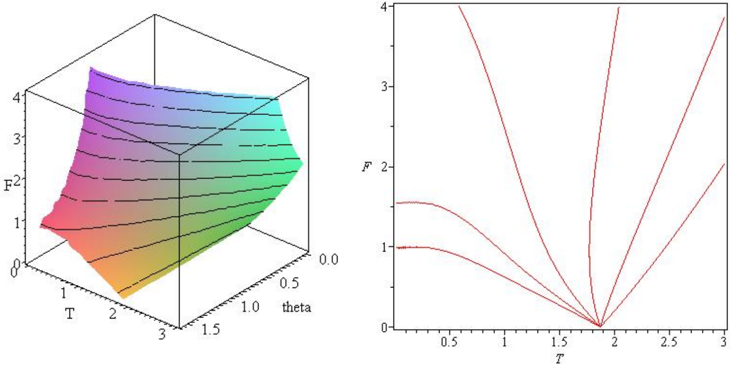

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- Vertical pulling, $\theta = 90^o$ (left curve):
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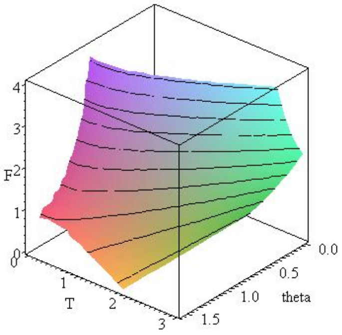

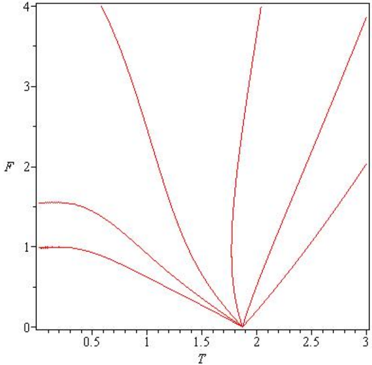

- Thermal desorption at $T = 1/\log(1+\sqrt{2}/2) \approx 1.87$
- Vertical pulling, $\theta = 90^o$ (left curve): Increasing F favours desorption
- Horizontal pulling, $\theta = 0^o$ (right curve): Increasing F disfavours desorption

Critical angles

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$$\theta = \tan^{-1}(1/2) \approx 26.565^o$$

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- Once $\theta \leq 45^o$, no zero-temperature desorption occurs.

Order parameter

- To study transition between desorbed/adsorbed phases, consider the surface coverage

$$\mathcal{C} := \lim_{L\to\infty} \frac{1}{L}\langle K\rangle = \frac{\partial \log t_c}{\partial \log \kappa}$$

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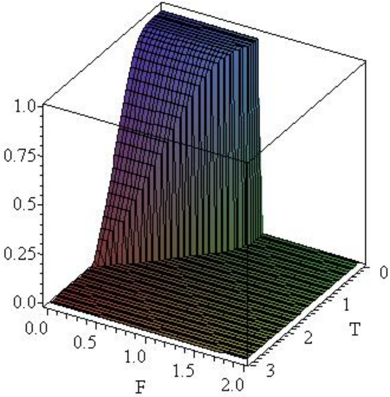
- First-order transition: discontinuity in $\mathcal{C}$

Coverage

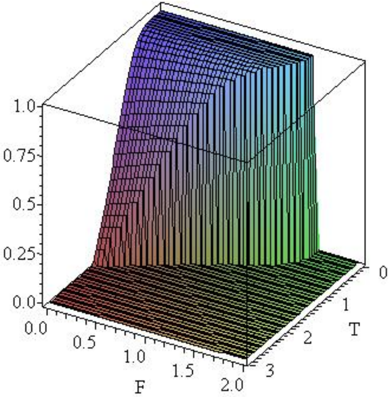
Pulling angle
$\theta = 90^\circ$



A clear first-order transition for $F > 0$

Coverage

Pulling angle
$\theta = 72^\circ$



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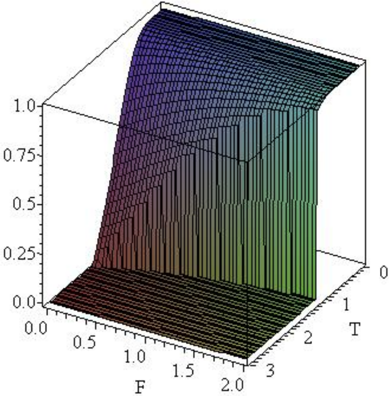
Pulling angle
$\theta = 54^\circ$



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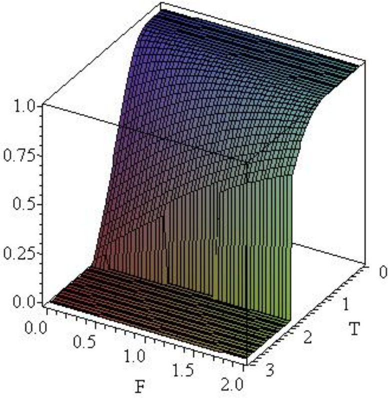
Pulling angle
$\theta = 36^\circ$



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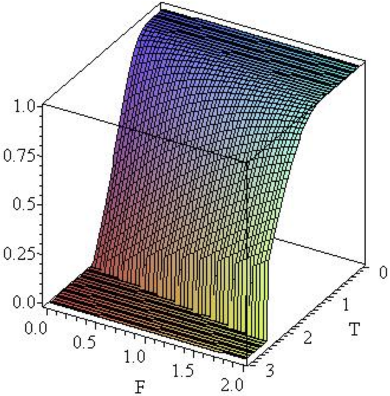
Coverage

Pulling angle
$\theta = 18^\circ$



A clear first-order transition for $F > 0$

Coverage

Pulling angle
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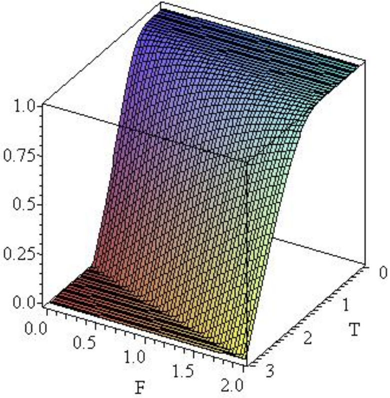


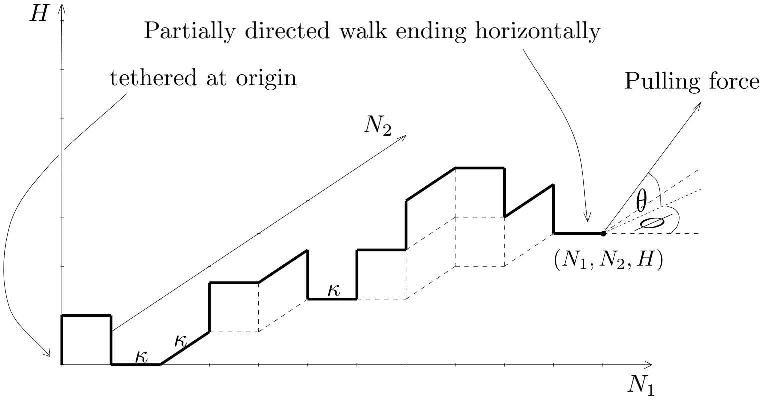
No first order transition because pulling is purely horizontal here

"Three dimensions for the price of two"

The solution extends to 3 dimensions

via a substitution

From walks above a line to walks above a slab



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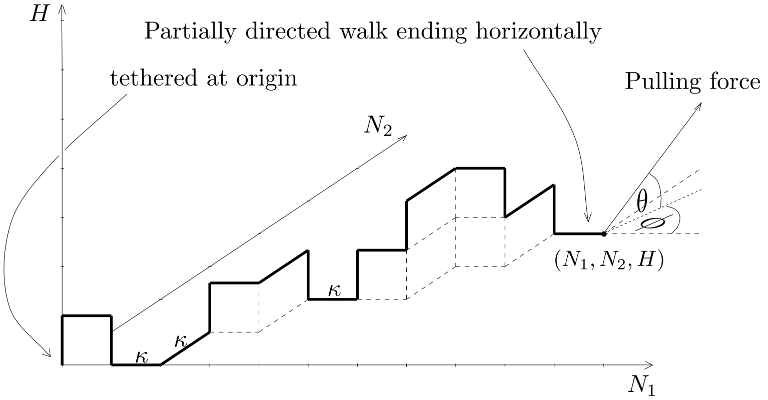

Substitution

$$x \leftarrow \lambda_1 t + \lambda_2 t$$

Walks above a slab

The *same* generating function G as for the two-dimensional case!

$$\sum_{L\geq 0} t^L Z_L(\lambda_1, \lambda_2, \mu, \kappa) = G(x = \lambda_1 t + \lambda_2 t, y = t, \kappa; \mu)$$

- t : conjugate to *path length*
- λ_i : conjugate to *horizontal positions*
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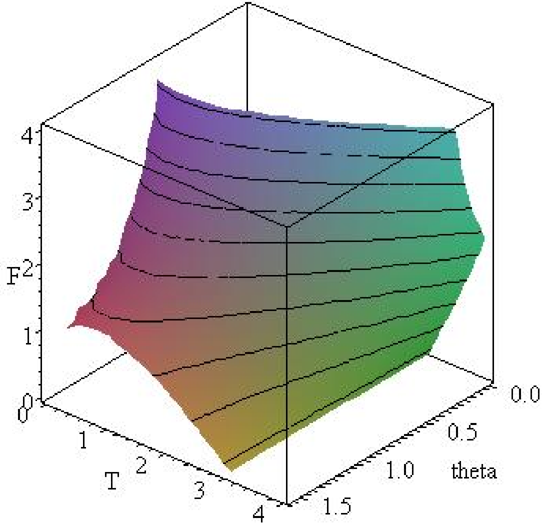
Physical variables

$$\kappa = e^{\frac{1}{T}}\,, \quad \lambda_1 = e^{\frac{F\cos\theta\cos\phi}{T}}\,, \quad \lambda_2 = e^{\frac{F\cos\theta\sin\phi}{T}}\,, \quad \mu = e^{\frac{F\sin\theta}{T}}$$

where ϕ is the horizontal pulling angle

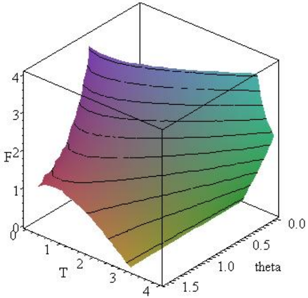
Phase diagram in (θ, T, F) for diagonal pulling

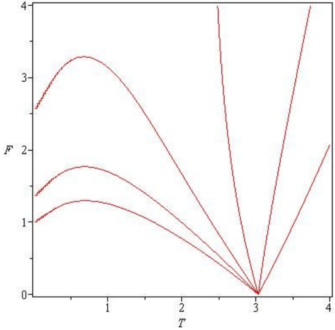
$\phi = 45^o$



Varying the vertical pulling angle

$\phi = 45^o$





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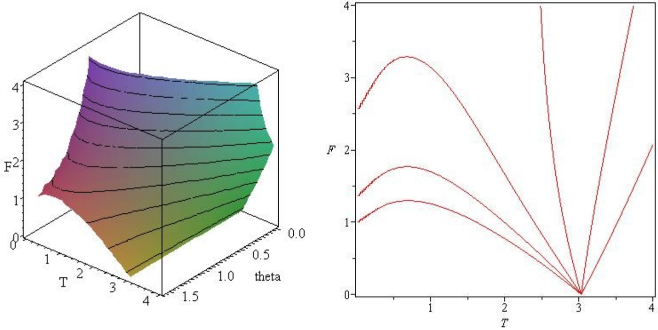

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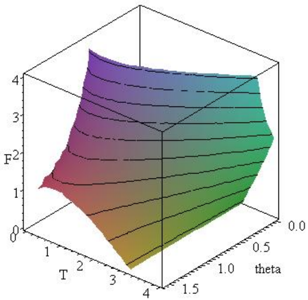
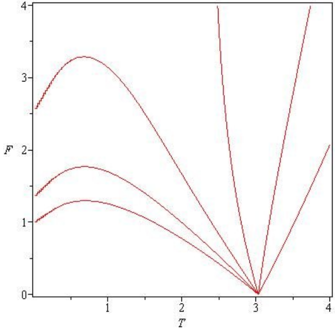
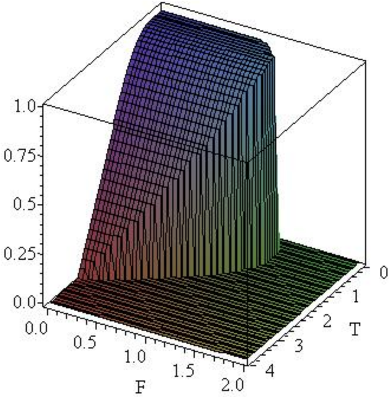




- Thermal desorption at $T = 1/\log(7/8 + \sqrt{17}/8) \approx 3.03$
- Reentrance phenomenon in three dimensions (due to non-zero entropy of an adsorbed walk)

Coverage

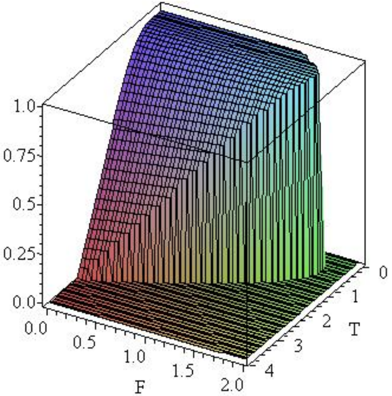
$\phi = 45^\circ$
$\theta = 90^\circ$



A clear first-order transition for $F > 0$

Coverage

$\phi = 45°$
$\theta = 72°$



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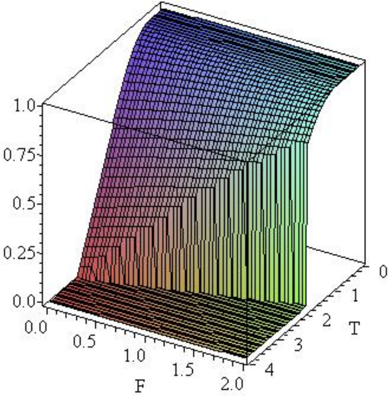

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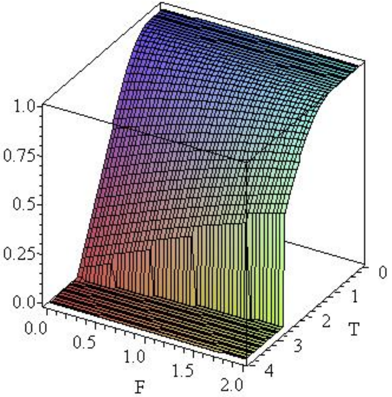

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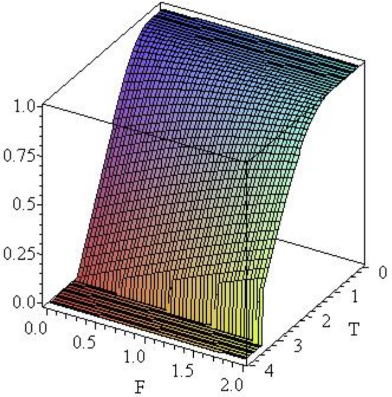
$\theta = 18^\circ$



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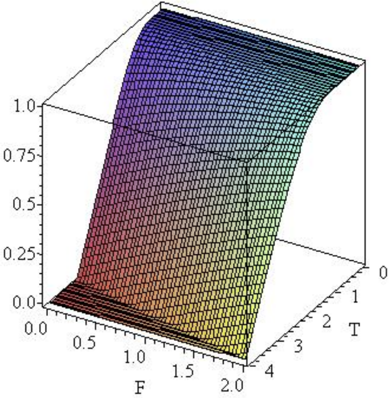

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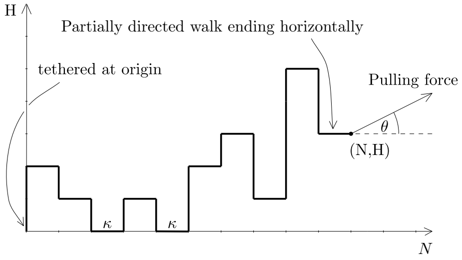
An alternative 3-dim walk model

Recall the 2-dimensional model



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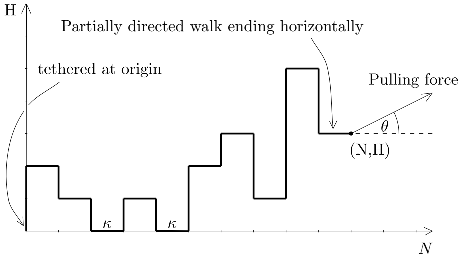

Before each x/y-step, allow steps in z-direction

$$t \leftarrow t\left(1+2t+2t^2+2t^3+\ldots\right)=\lambda t\frac{1+t}{1-t}$$

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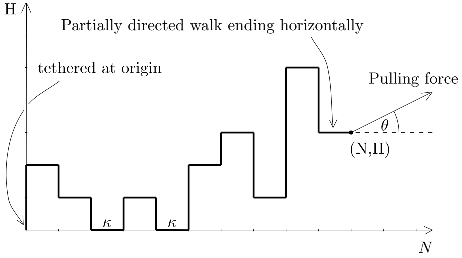

Before each x/y-step, allow steps in z-direction

$$t \leftarrow t\left(1 + 2t + 2t^2 + 2t^3 + \ldots\right) = \lambda t \frac{1+t}{1-t}$$

Adjust interaction weights accordingly for steps in the surface

Walks above a slab II

Again, a simple substitution into the two-dimensional generating function G

$$\sum_{L\geq 0} t^L Z_L(\lambda,\mu,\kappa) = G(x = \lambda t\tfrac{1+t}{1-t}, y = t\tfrac{1+t}{1-t}, \kappa\tfrac{1-t}{1+t}\,\tfrac{1+\kappa t}{1-\kappa t}; \mu)$$

- t : conjugate to *path length*
- λ : conjugate to *horizontal position*
- μ : conjugate to *vertical position*

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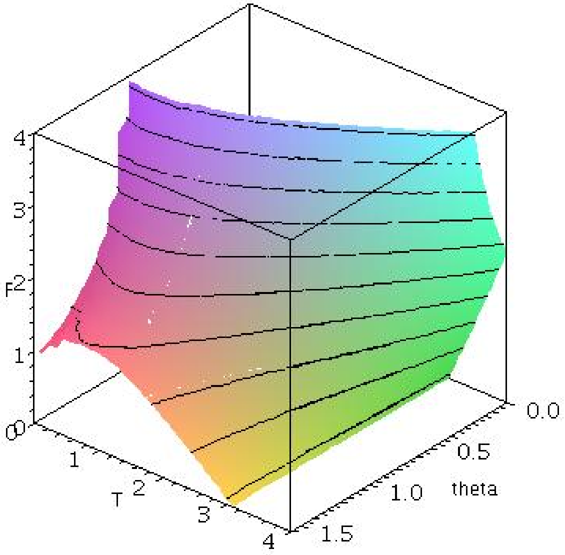
Physical variables

$$\kappa = e^{\frac{1}{T}}\ , \quad \lambda = e^{\frac{F\cos\theta}{T}}\ , \quad \mu = e^{\frac{F\sin\theta}{T}}$$

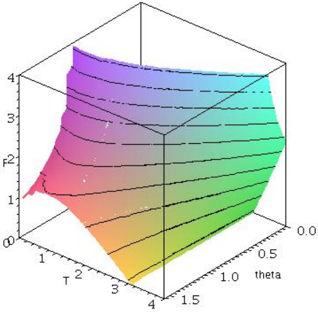
Phase diagram in (θ, T, F) for diagonal pulling

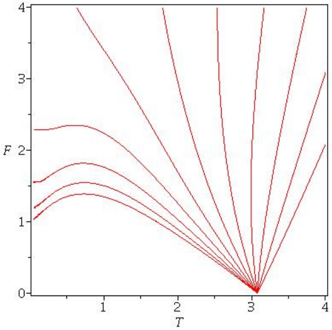
$\phi = 45^o$



Varying the vertical pulling angle

$\phi = 45^o$





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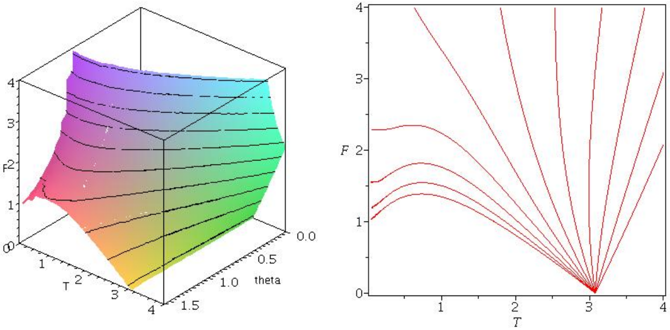
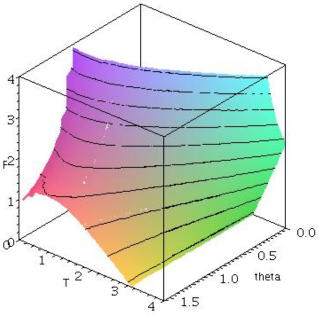
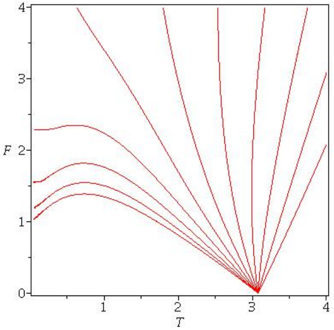


- Thermal desorption at $T \approx 3.07$

Varying the vertical pulling angle

$\phi = 45^o$





- Thermal desorption at $T \approx 3.07$
- Here, the reentrance phenomenon is present but vanishes if pulling is sufficiently shallow!

Summary

- Pulling tethered polymers

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- Walk models — Kernel method

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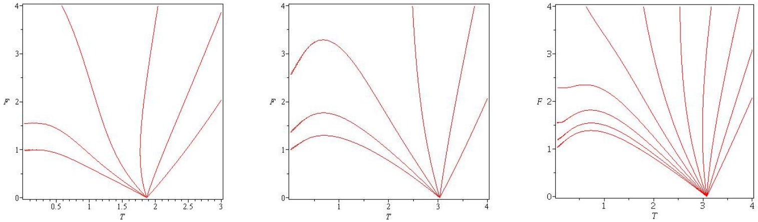
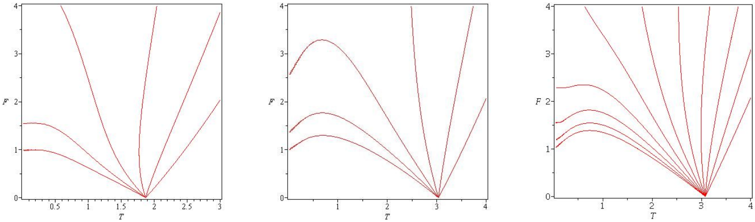


Summary

- Pulling tethered polymers
- Walk models — Kernel method
- Re-entrance phenomena



Shallow pulling or increasing T can favour adsorption

THE END