Self-avoiding walks interacting with a surface and subject to a force

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Joint work with Buks van Rensburg

The physical problem

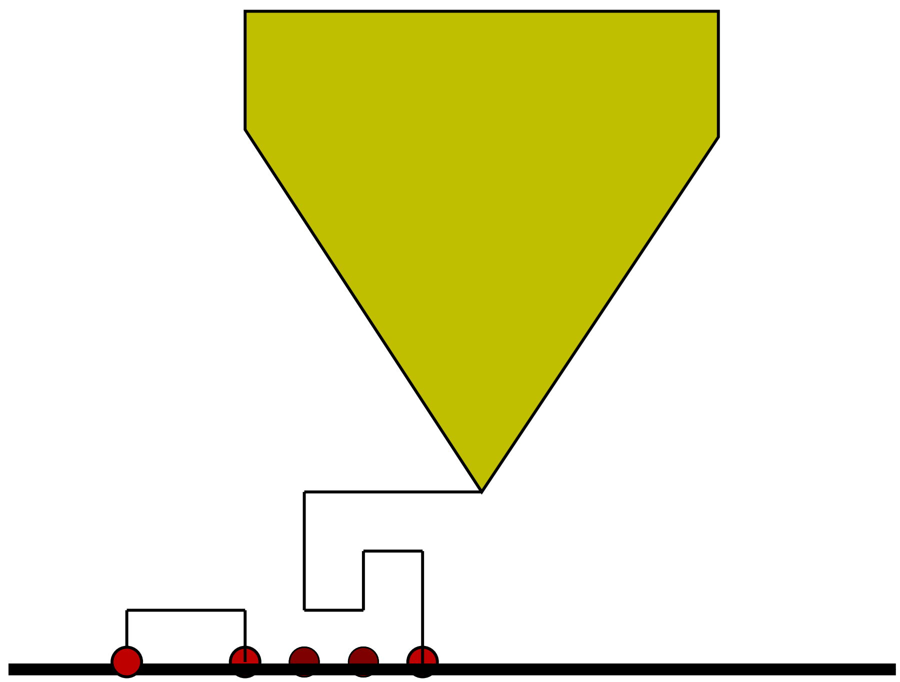
Polymer adsorption

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



Self-avoiding walks on Z^d — Large n behaviour

Suppose that c_n is the number of n-step self-avoiding walks on Z^d.

- The limit $\lim_{n\to\infty} n^{-1} \log c_n \equiv \kappa_d$ exists [Hammersley 1954].

- $\log d \leq \kappa_d \leq \log(2d-1)$

Positive walks

Coordinates of a vertex in Z^d: $(x, y, \dots z)$. The i'th vertex of a walk has coordinates $(x_i, y_i, \dots z_i)$.

A positive walk is a self-avoiding walk on Z^d, starting at the origin and having $z_i \geq 0$ for all i.

Suppose $c_n(v, h)$ is the number of positive walks with n edges, $v + 1$ vertices in $z = 0$ and with $z_n = h$. v counts *visits* to the adsorbing plane. h is the *height* of the walk.

Define the partition function

$$C_n(a, y) = \sum_{v,h} c_n(v, h) a^v y^h.$$

Connection to physical variables

$$C_n(a, y) = \sum_{v,h} c_n(v, h) a^v y^h.$$

$$a = e^{-\epsilon/kT} \quad y = e^{f/kT}$$

Two special cases:

1. No force: $f = 0 \quad y = 1$
2. No surface interaction: $\epsilon = 0 \quad a = 1$

No force, $y = 1$

- The limit $\lim_{n\to\infty} n^{-1} \log C_n(a,1) \equiv \kappa(a)$ exists.

- $\kappa(a)$ is a convex function of $\log a$.

- $\kappa(a) = \kappa(1) = \kappa_d$ for all $a \leq 1$.

- For $a > 1$, $\kappa(a) \geq \max[\kappa_d, \kappa_{d-1} + \log a]$.

- There is a phase transition at $a = a_c$ where $1 < a_c < \exp[\kappa_d - \kappa_{d-1}]$.

- $\kappa(a)$ is asymptotic to $\kappa_{d-1} + \log a$.

No surface interaction, $a = 1$

- The limit $\lim_{n\to\infty} n^{-1} \log C_n(1, y) \equiv \lambda(y)$ exists.

- $\lambda(y)$ is a convex function of $\log y$.

- $\lambda(y) = \lambda(1) = \kappa_d$ for all $y \leq 1$ and $\lambda(y) \geq \max[\kappa_d, \log y]$ for $y > 1$.

- There is a phase transition at $y = y_c = 1$ [Ioffe and Velenik, Beaton].

- $\lambda(y)$ is asymptotic to $\log y$.

General a and y

- The limit $\lim_{n\to\infty} n^{-1} \log C_n(a,y) \equiv \psi(a,y)$ exists and $\psi(a,y)$ is a convex function of $\log a$ and $\log y$.

- $\psi(a,y) = \max[\kappa(a), \lambda(y)]$

- There is a phase boundary, $y = y_c(a)$, in the (a,y)-plane, for $y \geq 1$, determined by $\kappa(a) = \lambda(y)$.

- The phase boundary is asymptotic to $y = \exp[\kappa_{d-1}]a$ as $a \to \infty$.

- The phase transition is first order except perhaps at $(a_c, 1)$.

Phase diagram in the force-temperature plane

Recall that

$$a = e^{-\epsilon/kT} \quad y = e^{f/kT}$$

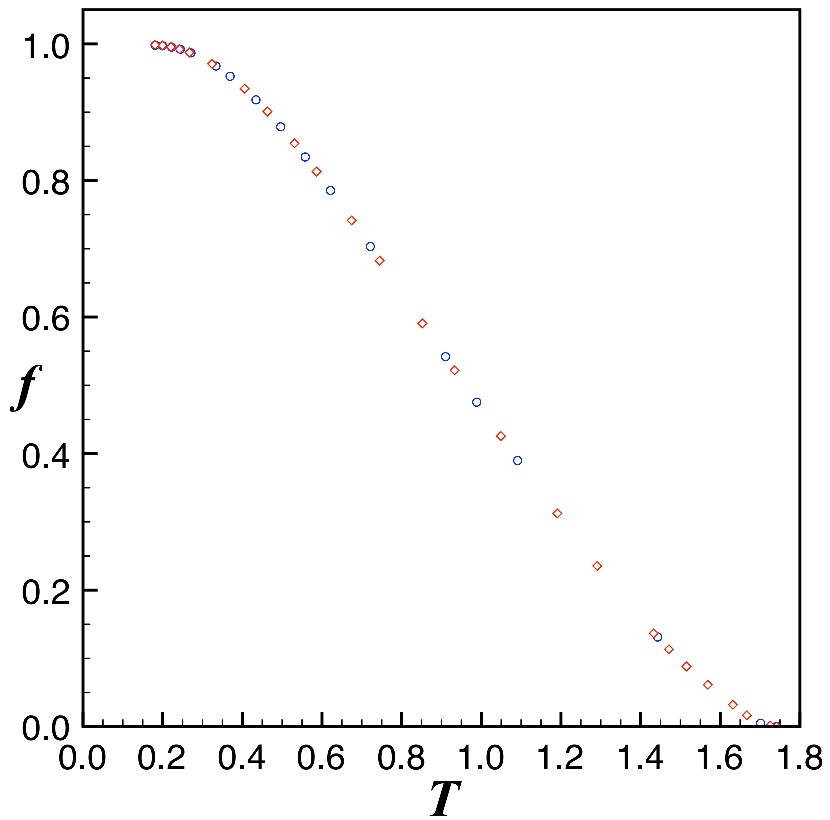
When $d \geq 3$,

$$\lim_{T \to 0} df(T)/dT > 0$$

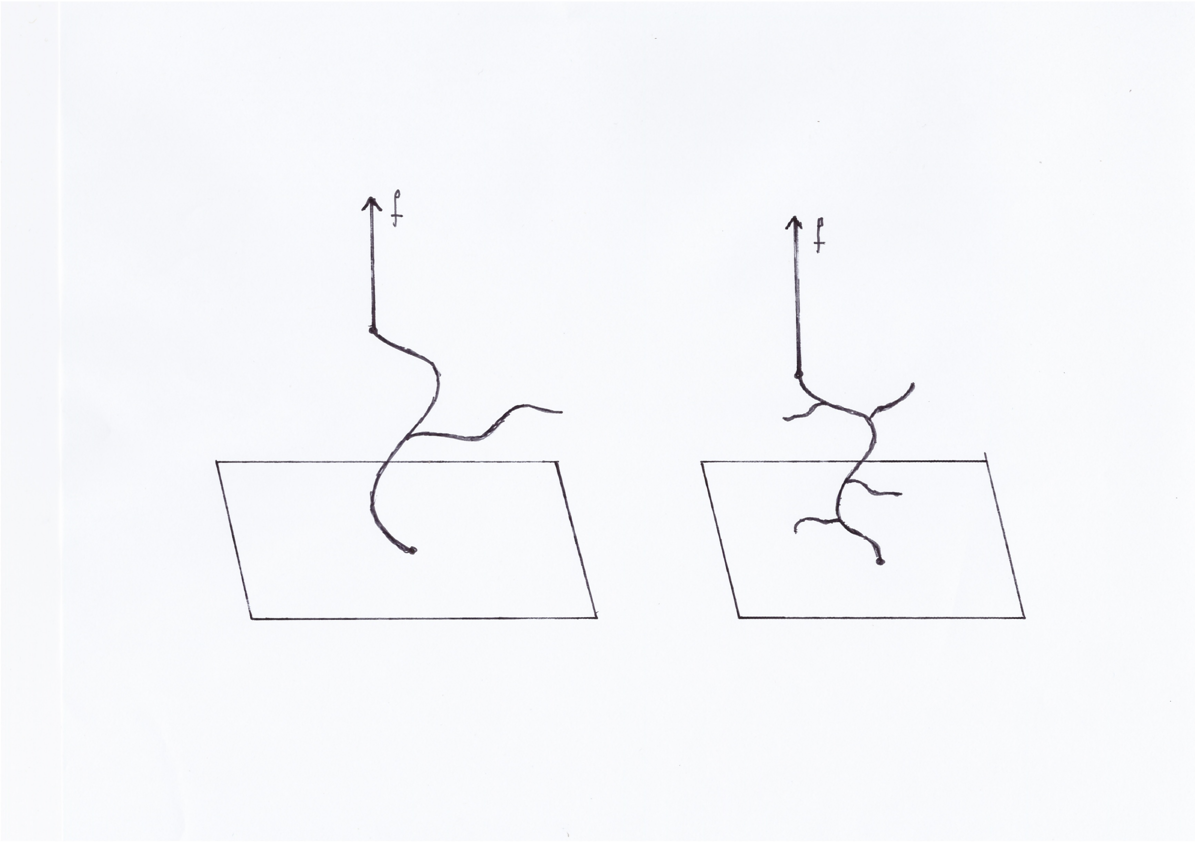
so the phase boundary is reentrant.

When $d = 2$, $\lim_{T\to 0} df(T)/dT = 0$.

Phase diagram in the force-temperature plane when $d = 2$ (Guttmann and Jensen)



Star and comb homeomorphism types



3-stars in Z^3

The free energy is given by

$$\sigma^{[3]}(a,y) = \max\left[\kappa(a), \frac{2\lambda(y)+\kappa_3}{3}, \frac{2\kappa(a)+\lambda(y)}{3}\right].$$

so we have a mixed phase as well as an adsorbed phase and a ballistic phase.

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The phase boundary between the mixed and adsorbed phases is at the solution of

$$\lambda(y) = \kappa(a)$$

and between the mixed and ballistic phases at

$$\lambda(y) = 2\kappa(a) - \kappa_3.$$

Asymptotics

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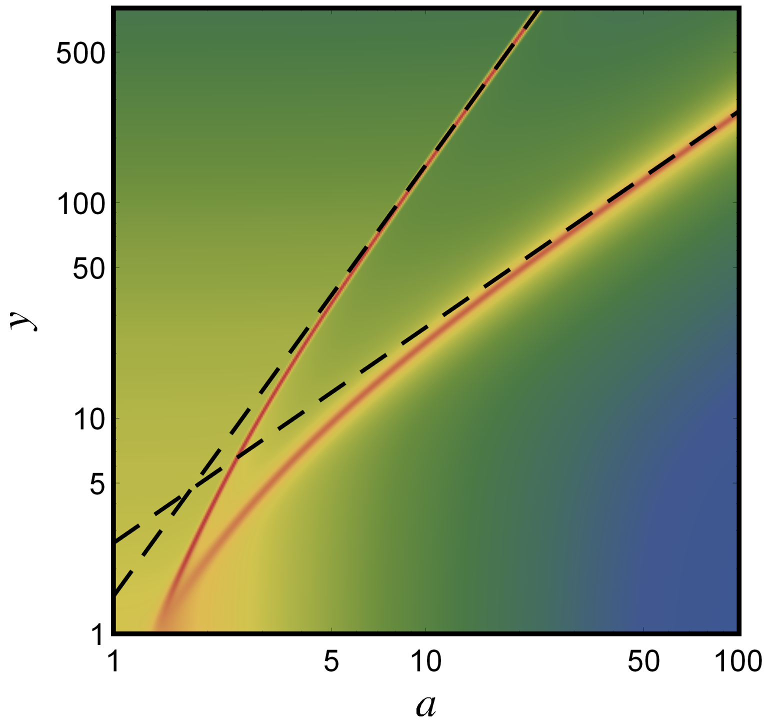
Asymptotically (large a) the boundaries approach

$$y = \exp[\kappa_2]a$$

and

$$y = \exp[2\kappa_2 - \kappa_3]a^2.$$

Asymptotics and Monte Carlo



Monte Carlo work by Chris Bradly and Aleks Owczarek.

Combs with t teeth in Z^3

The free energy is given by

$$\zeta^{[t]}(a,y) = \max\left[\kappa(a), \frac{(t+1)\lambda(y)+t\kappa_3}{2t+1}, \frac{\lambda(y)+2t\kappa(a)}{2t+1}\right].$$

and we have adsorbed, ballistic and mixed phases, independent of the number of teeth. Increasing the number of teeth does not increase the number of phases.