# Some problems in the statistical mechanics of polymers

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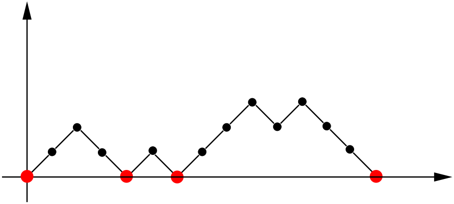
Eindhoven, June 21, 2007

# Motivation

- viewpoint: combinatorics and asymptotic enumeration
- compute limit laws of parameters of random polymer models
- qualitative change of limit law w.r.t. temperature indicates phase transition
- rule of thumb: away from phase transitions: concentrated distributions (microscopic fluctuations)
  at phase transitions: non-concentrated distributions (macroscopic fluctuations)

# Dyck paths with surface interaction

(..., Fisher 84, ...)



Dyck paths are ordered sequences of arches

arches are elevated Dyck paths

length, contact number additive w.r.t. decomposition description with ordinary generating function

$$G(z,u) = \sum_{m,k} d_{m,k} z^m u^k$$

$d_{m,k}$ number of Dyck paths of length $2m$ with $k$ contacts

functional equation

$$G(z,u) = \frac{u}{1 - uzG(z,1)}$$

explicit solution

$$G(z,u) = \frac{2u}{2 - u + u\sqrt{1-4z}}$$

analyticity structure: $u = 2$ special point

$\mathcal{C} = \mathcal{C}(u)$ random variable of contacts

$$\mathbb{P}_m[\mathcal{C} = k] = \frac{d_{m,k} u^k}{\sum_k d_{m,k} u^k}$$

limit laws for $\mathcal{C}(u)$

$u > 2$ (absorbed phase)

$$\mathbb{E}_m[\mathcal{C}] \sim \frac{1}{2} \frac{u-2}{u-1} 2m \qquad (m \to \infty)$$

concentrated distribution $(\sqrt{\mathbb{V}_m}/\mathbb{E}_m \to 0)$

$u = 2$ (phase transition)

$$\mathbb{E}_m[\mathcal{C}^k] \sim M_k m^{k/2} \qquad (m \to \infty)$$

moment generating function

$$\mathbb{E}_m[\exp(-x\mathcal{C}/\sqrt{m})] \sim 1 - xe^{\frac{x^2}{\pi}} \operatorname{erfc}\left(\frac{x}{\sqrt{\pi}}\right)$$

probability density

$$\frac{\pi s}{2} e^{-\frac{\pi s^2}{4}}$$

Rayleigh distribution

bijection to bilateral Dyck paths (bridges)

$0 < u < 2$ (desorbed phase)

$$\mathbb{P}_m(\mathcal{C} = k) = \frac{k-1}{2^k} u^{k-2}(u-2)^2 \qquad (m \to \infty)$$

exact finite size expressions via Lagrange inversion

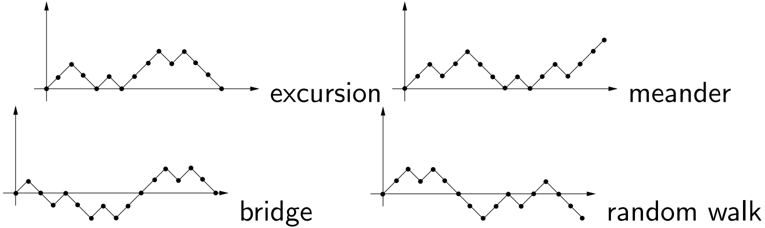
discrete limit distribution

mean number of contacts

$$\mathbb{E}_m[\mathcal{C}] = \frac{4}{2-u}$$

typical Dyck path ($u = 1$) consists of three arches!

- Variants:




excursion ≡ Dyck path, bridge ≡ bilateral Dyck path

- different critical contact activity
- limit distributions at criticality and in the absorbed/desorbed phases?

dependence on step set and on interaction strength?

- stochastic approach for models with continuous step sizes (Deuschel, Giacomin, Zambotti 05)
  desorbed phase: asymptotically described by excursion
  phase transition: asymptotically described by |bridge|
  absorbed phase: asymptotically described by concentrated measure
- analogous results for meanders, bridges and random walks with contacts
- discrete case?

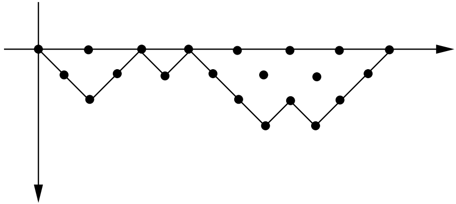
Possible extensions:

- $r$ vicious walkers interacting with a wall
  (Brak, Essam, Owczarek 98, Krattenthaler 06, ...)
  first moment for all $r$ in absorbed phase,
  critical moment gf for $r = 1, 2$ known
- $r$ vicious walkers interacting with two walls
  ($r = 1$: this workshop)
- models of copolymer absorption
- models of DNA denaturation

self-avoiding walk models in dimension $d \geq 2$

- self-avoiding meanders and general SAW (Hammersley, Thorrie, Whittington 82)
- existence of free energy for $0 < u < \infty$
- existence of phase transition ($u_c$ not known)
- exact enumeration data ($m \leq 21$ in $d = 2$, $m \leq 14$ in $d = 3$)
- limit distributions in the absorbed and desorbed phases may be analysed numerically

# Dyck droplet at a surface



- $d_{m,n}$ number of Dyck paths of perimeter $2m$ and area $n$
- equivalent to staircase polygons by perimeter and area resp.

  directed compact percolation (Essam 89)
- area additive w.r.t. arch decomposition

- generating function

$$D(z,q) = \sum_{m,n} d_{m,n} z^m q^n$$

- functional equation via arch decomposition

$$D(z,q) = \frac{1}{1 - zqD(zq^2, q)}$$

linearisation leads to explicit expression for $D(z,q)$

- $\mathcal{L} = \mathcal{L}(z)$ random variable of length

$$\mathbb{P}_n[\mathcal{L} = m] = \frac{d_{m,n} z^m}{\sum_m d_{m,n} z^m}$$

- limit law for $\mathcal{L}(z)$ at phase transition $z_c = 1/4$?

$$\frac{\mathbb{E}_n[\mathcal{L}^k]}{k!} \sim \frac{\Gamma(\beta_0)}{\Gamma(\beta_k)} \frac{b_k}{b_0} C^k n^{2k/3} \qquad (n \to \infty)$$

$\beta_k = 2k/3 - 1/3$, $C > 0$ some constant

- $b_k$ related to Airy function $\mathrm{Ai}(z) = \frac{1}{\pi} \int_0^\infty \cos(t^3/3 + tz)\mathrm{d}t$

$$F(s) = -\frac{\mathrm{d}}{\mathrm{d}s} \log \mathrm{Ai}(s) = \sum_{k \geq 0} b_k s^k$$

moment gf? density?

- compare: area law at criticality determined by coefficients of $F(s)$ in the asymptotic expansion about $s = \infty$, with exponents $\gamma_k = (3k/2 - 1/2)$ (excursion area)
- expect Gaussian limit laws away from phase transition.

- gravitation can be included:

  potential energy $\sim$ sums of squares of heights

- $d_{m,n,l}$ number of Dyck paths of perimeter $2m$, area $n$ and sum of squares of heights $l$

  parameters additive w.r.t. arch decomposition

- generating function

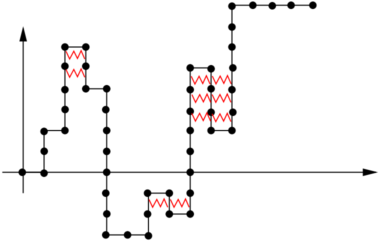
$$D(z,q,p) = \sum_{m,n,l} d_{m,n,l} z^m q^n p^l = \frac{1}{1 - zqpD(zq^2p^2, qp^2, p)}$$

  no linearisation possible

- asymptotic analysis can be performed ...

# IPDSAW

- Brak, Guttmann, Owczarek, Prellberg, Whittington, ... 90-93



- $p_{m,n,k}$ number of walks with $m$ horizontal steps, $n$ vertical steps and $k$ nearest-neighbour contacts

$$P(x, y, w) = \sum_{m,n,k} p_{m,n,k} x^m y^n w^k$$

- exact solution:

$$1 + P(x, y, w) = \frac{1 - y}{(1 - x)(1 - y) - 2xyH(y, yw, xy(w - 1))}$$

- functional equation for $H(y, q, t)$

$$H(y, q, t) = \left[ 1 - \frac{t}{(1 - y)(1 - qy)} \left[ 1 - \frac{q^2 yt}{(1 - qy)(1 - q^2 y)} H(q^2 y, q, qt) \right]^{-1} \right]^{-1}$$

- isotropic model $x = y$:

  critical point $w_c = 0.295597\ldots$ satisfies $w_c^3 + w_c^2 + 3w_c - 1 = 0$

- limit law of interaction strength can be extracted at $w_c$. Same as that of absolute area under a Brownian bridge!

# ISAW

Self-avoiding walks with nearest-neighbour interaction in $d$ dimensions

- Tesi et al 96, Yu et al 97 ($d = 3$):
  free energy exists for $0 < u \leq 1$ (repulsive regime)
- exact enumeration and Monte-Carlo:
  reliable estimation of critical point and exponent needs very long walks

# Extracting limit distributions at phase transitions

- $p_{m,n}$ number of objects of size $m$ and additional parameter $n$
- Discrete random variable $\widetilde{X}_m$ of additional parameter in a uniform ensemble (wlg)

$$\mathbb{P}[\widetilde{X}_m = n] = \frac{p_{m,n}}{\sum_n p_{m,n}}$$

- Aim: extract limiting distribution from generating function

$$P(x,q) = \sum_{m,n} p_{m,n} x^m q^n$$

- moment method: moments uniquely define limit distribution (typically entire gf)
- factorial moment generating functions

$$
\begin{aligned}
p^{(k)}(x) &= \frac{1}{k!} \left. \frac{\partial^k P(x,q)}{\partial q^k} \right|_{q=1} \\
&= \frac{1}{k!} \sum_m \left( \sum_n (n)_k p_{m,n} \right) x^m \\
&= \frac{1}{k!} \sum_m \mathbb{E}[(\widetilde{X}_m)_k] \mathbb{E}[\widetilde{X}_m] x^m
\end{aligned}
$$

$(a)_k = a \cdot (a-1) \cdot \ldots \cdot (a-k+1)$ lower factorial

- asymptotic behaviour of $\mathbb{E}[(\widetilde{X}_m)_k]$ reflected in singular behaviour of $p^{(k)}(x)$
- assumption (phase transition): $p^{(k)}(x)$ algebraic such that

$$p^{(k)}(x) \sim \frac{f_k}{(1-x/x_c)^{\gamma_k}} \implies [x^m]p^{(k)}(x) \sim \frac{f_k}{\Gamma(\gamma_k)} x_c^{-m} m^{\gamma_k - 1}$$

$\gamma_k = (k-\theta)/\phi$ where $\phi > 0$

- we obtain for the (factorial) moments

$$\frac{\mathbb{E}[(\widetilde{X}_m)_k]}{k!} \sim \frac{\Gamma(\gamma_0)}{\Gamma(\gamma_k)} \frac{f_k}{f_0} m^{\frac{k}{\phi}} \sim \frac{\mathbb{E}[\widetilde{X}_m^k]}{k!} \qquad (m \to \infty)$$

- normalised random variable

$$X_m = \frac{\widetilde{X}_m}{m^{\frac{1}{\phi}}}, \qquad X_m \xrightarrow{d} X$$

- moments of $X$

$$\frac{\mathbb{E}[X^k]}{k!} = \frac{\Gamma(\gamma_0)}{\Gamma(\gamma_k)} \frac{f_k}{f_0}$$

- Watson's lemma

$$\int_0^\infty e^{-st} \mathbb{E}[e^{-t^{1/\phi} X}] \frac{1}{t^{1-\gamma_0}} \mathrm{d}t \sim \frac{\Gamma(\gamma_0)}{f_0} \sum_{k \geq 0} (-1)^k f_k s^{-\gamma_k} \qquad (s \to \infty)$$

- "generating series" for coefficients $f_k$

$$F(s) = \sum_{k \geq 0} (-1)^k f_k s^{-\gamma_k}$$

- $F(s)$ appears in the generating function $P(x,q)$. Heuristics:

$$
\begin{aligned}
P(x,q) &= \sum_{k\geq 0}(-1)^k p^{(k)}(x)(1-q)^k \\
(\text{near } x_c) &\approx \sum_{k\geq 0}(-1)^k \frac{f_k}{(1-x/x_c)^{\gamma_k}}(1-q)^k \\
&= (1-q)^\theta \sum_{k\geq 0}(-1)^k f_k \left(\frac{1-x/x_c}{(1-q)^\phi}\right)^{-\gamma_k} \\
&= (1-q)^\theta F\left(\frac{1-x/x_c}{(1-q)^\phi}\right)
\end{aligned}
$$

- Can sometimes be interpreted as first term in asymptotic expansion of $P(x,q)$ at $(x_c, 1)$ with "scaling function" $F(s)$.
- has a meaning as formal series, e.g. if all $p^{(k)}(x)$ are algebraic with above singular behaviour!

- If $P(x, q)$ explicitly known and simple, $F(s)$ can be extracted.
- If functional equation for $P(x, q)$ is known and simple, differential equation for $F(s)$ can be mechanically extracted
- method works e.g. for models of Dyck paths, meanders, bridges, random walks, counted by length and area (and generalisations)
- $F(s)$ appears in Feynman-Kac formula for corresponding stochastic objects!
- Works also for corrections to the asymptotic behaviour. These can be mechanically extracted.

# $q$-functional equations

- method has been applied to $q$-difference equations

$$P(x, q) = F(P(x, q), P(qx, q), x, q)$$

- Under generic assumptions on $F$: dominant singularity of $P(x, 1)$ is square-root singularity, like Dyck paths, limit distribution area under a Dyck path
- Extension to $q$-functional equations with area generalisations, obeying limit laws $\int_0^1 e^k(t)\mathrm{d}t$, $\int_0^1 m^k(t)\mathrm{d}t$, ...
- absorption transition may be studied similary

# Gaussian limit laws

Limit theorem for sequences $(X_n)$ of random variables: (Hwang 98)

Laplace transforms $M_n(s) = \mathbb{E}[e^{sX_n}]$ analytic for $|s| < \rho$ for some $\rho > 0$,

$$M_n(s) = e^{\beta_n U(s) + V(s)} \left(1 + \mathcal{O}(\kappa_n^{-1})\right)$$

$\beta_n, \kappa_n \to \infty$, and $U(s), V(s)$ analytic in $|s| < \rho$. If $U''(0) \neq 0$, then

$$\mathbb{E}[X_n] = \beta_n U'(0) + V'(0) + \mathcal{O}(\kappa_n^{-1})$$
$$\mathbb{V}[X_n] = \beta_n U''(0) + V''(0) + \mathcal{O}(\kappa_n^{-1})$$

limit distribution Gaussian with speed of convergence $\mathcal{O}(\kappa_n^{-1} + \beta_n^{-1/2})$

- has been used for models with explicit expressions for generating functions to prove Gaussian limit laws
- applies to Dyck droplets in the uniform ensemble $z = 1$
- has been used to study models satisfying certain functional equations (e.g. some linear DE, Flajolet)
- application to $q$-difference equations?
- assumption: $U(s)$ analytic (free energy)

# Limiting free energy

- finite-size free energy (no of contacts)

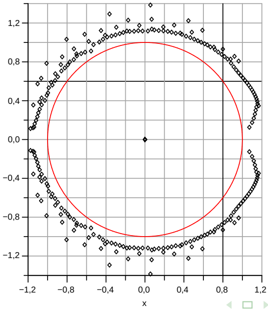
$$f_m(u) = \frac{1}{m} \log \left( \sum_k d_{m,k} u^k \right)$$

Does the limit $m \to \infty$ exist?

- existence on positive real line usually follows from combinatorial arguments (concatenation, subadditive inequalities)
- analyticity questions generally difficult to analyse. Sometimes existence of non-analyticities can be proved, sometimes they can be located.

- Vitali's theorem from complex analysis:

  $(f_m)_{m\in\mathbb{N}}$ sequence of functions analytic in domain $G$, convergent in $C \subseteq G$ with accumulation point in $G$. If $(f_m)$ is locally bounded in $G$, then limit exists and is analytic in $G$.
- Study zeros of partition function (SAP by area, $m = 66$)



# Discussion

- combinatorics: effective methods to extract limit distributions from functional equations
- such distributions may also appear in unsolved models (e.g. SAPs: area resp. perimeter limit laws)
- stochastics: insights into underlying processes ("universality")
- SAW models: analyticity of free energy in certain regimes? (compare: SAP in the inflated regime) Limit laws away from phase transitions?