Exact Solution of a Simple Adsorption Model of De-naturating DNA

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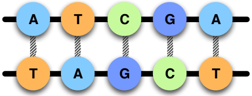
DNA

- DNA is a polymer consisting of four repeating nucleic bases A,C,G,T.
- Two strands entwined with a helix structure
- Denaturation: At high T, strands pulled apart



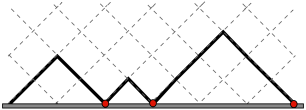
The other physical motivation is the adsorption phase transition where polymers in solution can stick to the surface of a container

- Second order phase transition
- Order parameter is coverage of the surface by the polymer

We use models in two dimensions and lattice models at that — Proven to be insightful and integrable

Adsorption: very simple one directed walk model

- Single Dyck path in a half space
- Energy $-\varepsilon_a$ for each time (number m_a) it visits the surface
- Boltzmann weight $a = e^{\varepsilon_a/k_B T}$



Consider the coverage, our order parameter (indicator for a phase):

$$\mathcal{A}(a) = \lim_{n\to\infty} \frac{\langle m_a \rangle}{n}$$

There exists two phases, desorbed and adsorbed, and a phase transition at a temperature T_a given by $a = 2$ between these:

- For $T > T_a$ (small a) the walk moves away entropically and $\mathcal{A} = 0$
- For $T < T_a$ (large a) the walk is adsorbed onto the surface and $\mathcal{A} > 0$

Adsorption and Unzipping

Previously: *two friendly walks above a sticky wall with single and double interactions* in modelling ring polymers above an absorbing surface interacting with both sides of the ring.

Now we combine adsorption and unzipping:

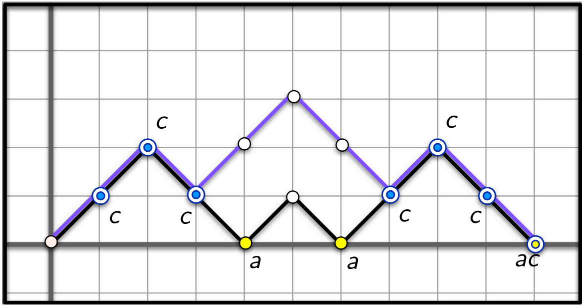
(Our system — Adsorption and Unzipping)

- *double DNA strand in a solvent*
- *near attractive surface*
- *assume aligned base sequence*
- *so expect both adsorption and denaturation (unzipping)*

ALLOWED WALKS

Consider two directed walks along the square lattice.
Let our model contain the class of allowed configs. with n steps as described:

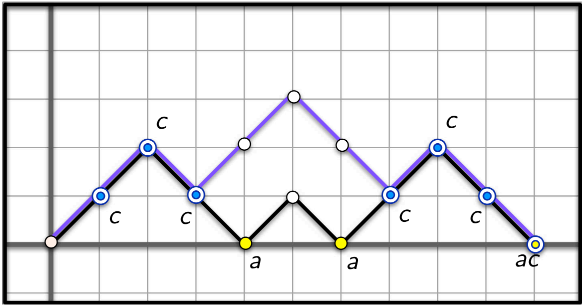
- both walks begin at $(0,0)$, end at $(2n,0)$.
- directed: can only take steps in the $(\pm 1, 0)$ directions.
- (∞) - friendly: walks can share sites, but cannot cross



UNZIPPING ADSORPTION MODEL

Let T be the system temperature, k_B the Boltzmann constant.

- surface visit sites: $a \equiv e^{\varepsilon_a / k_B T}$
- shared site contacts: $c \equiv e^{\varepsilon_c / k_B T}$
- trivial walk consisting of zero steps has weight 1.



An allowed configuration of length 10. The overall weight is $a^3 c^7$

Generating function

- Partition function: $Z_n(a,c) = \sum_{\widehat{\varphi} \ni |\widehat{\varphi}|=n} a^{m_a(\widehat{\varphi})} c^{m_c(\widehat{\varphi})}$
- Generating function: $G(a,c) \equiv G(a,c;z) = \sum_{n\geq 1} Z_n(a,c) z^n$
- Reduced free energy:

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

where $z_s(a,c)$ is dominant singularity of G w.r.t. z

Two order parameters:

$$\mathcal{A}(a,c) = \lim_{n\to\infty} \frac{\langle m_a \rangle}{n} \qquad \text{and} \qquad \mathcal{C}(a,c) = \lim_{n\to\infty} \frac{\langle m_c \rangle}{n},$$

Context

No wall/interaction:

- Vicious dir. walks: *Lindström-Gessel-Viennot thm.* ('85), *Essam & Guttmann* ('95), *Guttmann, Owczarek & Viennot* ('98)
- Friendly walks & Osculating walks: *Brak* ('97), *Guttmann & Vöge* ('02), *Bousquet-Mélou* ('06)

With wall (but no interaction)

- Vicious: *Krattenhaler, Guttmann & Viennot* ('00)

With wall (interaction)

- Vicious: *Brak, Essam & Owczarek* ('99, '01)
- Friendly (two walks): *Owczarek, Rechnitzer & Wong* ('12) - last year's talk!

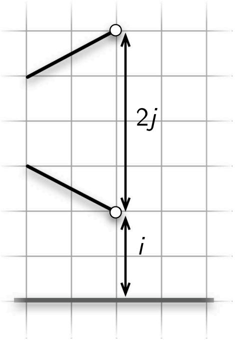
Generalised generating function

We consider walks φ in the larger set, where each walk can end at any possible height.

- To find $G(a, c)$, consider larger class of configs.
- Generalised generating function:

$$F(r, s) \equiv F(r, s, a, c; z) = \sum_{\varphi \in \Omega} a^{m_a(\varphi)} c^{m_c(\varphi)} r^i s^j z^n$$

- $G(a, c) = F(0, 0)$



Establishing a functional equation

- By considering the addition of a single column onto a configuration, and the types of walks obtained, we can find a decomposition of all configurations
- Translating back to generating functions we end up with

$$
\begin{aligned}
K(r,s)F(r,s) &= \frac{1}{ac} + \left(C(c) - \frac{zr}{s}\right) F(r,0) \\
&\quad + \left[A(a) - \frac{z}{r}(s+1)\right] F(0,s) - A(a)C(c)F(0,0)
\end{aligned}
$$

where

$$
A(a) = \frac{a-1}{a}, \quad C(c) = \frac{c-1}{c}
$$

and the kernel $K(r,s)$ is

$$
K(r,s) \equiv K(r,s;z) = \left(1 - z\left[r + \frac{s}{r} + \frac{r}{s} + \frac{1}{r}\right]\right).
$$

Obstinate kernel method

- Equation is written as "bulk = boundary terms" where bulk term is product of kernel and bulk generating function
- Answer needed is one of the boundary generating functions so try to remove bulk by setting the value of a catalytic variable to a value that makes the kernel vanish
- Standard kernel method due to *Knuth* (1968): use values of "catalytic variable' to "kill" kernel
- From ≈ early '00's applied to a number of dir. walk problems
- Sometimes need multiple values of catalytic variable(s): obstinate kernel method
- More than one catalytic variable requires this
- Earliest combinatorial application of the obstinate kernel method due to *Bousquet-Mélou* ('02).
- See Bousquet-Mélou *Math. and Comp. Sci 2* (2002)), Bousquet-Mélou, Mishna *Contemp. Math.* **520** (2010)

Symmetries of the Kernel

The kernel is symmetric under the following two transformations, which are involutions:

$$(r,s) \mapsto \left(r, \frac{r^2}{s}\right), \qquad (r,s) \mapsto \left(\frac{s}{r}, s\right)$$

Transformations generate a family of 8 symmetries ('group of the walk')

$$(r,s), \left(r, \frac{r^2}{s}\right), \left(\frac{s}{r}, \frac{s}{r^2}\right), \left(\frac{r}{s}, \frac{1}{s}\right), \left(\frac{1}{r}, \frac{1}{s}\right), \left(\frac{1}{r}, \frac{s}{r^2}\right), \left(\frac{r}{s}, \frac{r^2}{s}\right), \text{ and } \left(\frac{s}{r}, s\right)$$

- *We make use of four of these which only involve positive powers of* r.
- *This gives us four equations.*
- *One can eliminate many of the unknown generating functions by a clever choice of adding these equations*

Roots of the Kernel

- The kernel has two roots as function of either r or s
- choose the one which gives a positive term power series expansion in z
- with Laurent polynomial coefficients in s (r):

$$\hat{r}(s;z) \equiv \hat{r} = \frac{s\left(1-\sqrt{1-4\frac{(1+s)^2z^2}{s}}\right)}{2(1+s)z} = \sum_{n\geq 0} C_n \frac{(1+s)^{2n+1}z^{2n+1}}{s^n},$$

where $C_n = \frac{1}{n+1}\binom{2n}{n}$ is a Catalan number.

- *Make the substitution* $r \mapsto \hat{r}$

Finding the solution

Key idea

- Treat K as fn. of r or s to get roots $\hat{r}$ and $\hat{s}$
- Then use subset of $\mathcal{F}$ to get system of eqns. E.g. Using $\hat{r}$:

$(\hat{r}, s)$	$F(\hat{r}, 0)$	$F(0, s)$	$F(0,0)$
$(\hat{r}, \hat{r}^2/s)$	$F(\hat{r}, 0)$	$F(0, \hat{r}^2/s)$	$F(0,0)$
$(\hat{r}/s, \hat{r}^2/s)$	$F(\hat{r}/s, 0)$	$F(0, \hat{r}^2/s)$	$F(0,0)$
$(\hat{r}/s, 1/s)$	$F(\hat{r}/s, 0)$	$F(0, 1/s)$	$F(0,0)$

- Combine these eqns. to get new fn. eqn

$$N_1^\star(s;z)F(0,1/s) + N_2^\star(s;z)F(0,s) = \left[M^\star(s) - c^2 H^\star(s;z)\right]\left(\frac{1}{ac} - ACF(0,0)\right),$$

- Can do the same using $\hat{s}$!
- Nice things happen when $a = 1$ or $c = 1$ to $N_1^\star(s;z)$ etc

SOLUTION FOR $G(a,1)$

Exact solution for $G(a,1)$ is known and can be found using the method described

- Brak, Essam & Owczarek (1998, 2001): Partition fn. using Lindström-Gessel-Viennot Thm.
- Owczarek, Rechnitzer & Wong (2012): Gen. fn calculated by employing same kernel method techniques.

Specifically:

$$G(a,1) = \sum_{n\geq 0} z^{2n} \sum_{k=0}^{n} a^k \frac{k(k+1)(k+2)}{(2n-k)(n+1)^2(n+2)} \binom{2n-k}{n} \binom{2n}{n}.$$

SOLUTION FOR $G(1, c)$

- No known previous solution for $G(1, c)$

We can write functional equation as

$$G(1, c) = F(0, 0, 1, c; z) = [r^1] \frac{\hat{s}\left(r^2 - 1\right)\left[r - cr + cz\left(1 + r^2 - \hat{s}\right)\right]}{(c-1)\left(\hat{s} - c\hat{s} + crz\right)},$$

expanding RHS as power series in c and so obtain, after some work:

$$G(1, c; z) = 1 + c^2 z^2 + c^3 (1 + 2z) z^4$$
$$+ \sum_{i=3}^{\infty} z^{2i} \sum_{m=3}^{2i} c^m \sum_{k=3}^{m} (-1)^{k+1} \frac{k(k-1)(k-2)(2i-k+1)(i-k+2)}{i^2(i-1)^2(i+1)(i-2)} \binom{m}{k} \binom{2i-k}{i-2} \binom{2i-k-1}{i-3}.$$

SOLUTION FOR $G(1, c)$

- While we have an explicit solution for $G(1, c)$ it is advantageous for analysis to directly read off the singularities
- Alternative — find differential equation satisfied by generating function
- Use Zeilberger-Gosper algorithm: Maple: DETools package, Zeilberger hyperexp. implementation
- Result: DE for $G(1, c)$ is order 6 with poly. coeff of $\deg_z = 12$

FORTUNATE DECOMPOSITION OF $G(a, c)$

Using various combinatorial relationships between the generating functions we can re-write $G(a, c)$ in terms of $G(a, 1)$ and $G(1, c)$:

$$G(a,c) = \frac{1}{(a-1)(c-1)} + \frac{p_1(a,c,z)}{p_2(a,c,z) + p_3(a,c,z)G(a,1) + p_4(a,c,z)G(1,c)}$$

where p_i are polynomials in a, c and z: quadratics in z^2.

Key point: With solutions to $G(a, 1)$ and $G(1, c)$ we additionally have solved for $G(a, c)$.

SINGULARITIES OF $G(a,1)$ & $G(1,c)$

- Recall, free energy $\kappa(a,c) = \log z_s(a,c)$
- For $G(a,1)$, prev. known:

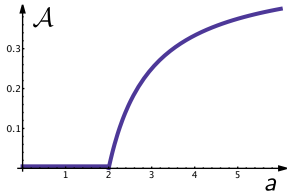
$$z_s(a,1) = \begin{cases} z_b \equiv 1/4, & a \leq 2 \\ z_a \equiv \frac{\sqrt{a-1}}{2a}, & a > 2 \end{cases}$$

- For $G(1,c)$, we use the DE (roots of leading poly. coeff.):

$$z_s(1,c) = \begin{cases} z_b \equiv 1/4, & c \leq 4/3 \\ z_c \equiv \frac{1-c+\sqrt{c^2-c}}{c}, & c > 4/3 \end{cases}$$

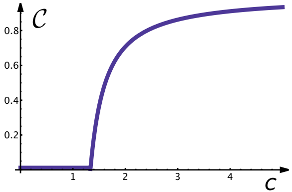
TRANSITIONS OF $G(a,1)$ & $G(1,c)$

- For $G(a,1)$: the order parameter associated with the phase transition is the surface coverage



$$\mathcal{A}(a,1) = \begin{cases} 0, & a \le 2 \\ \frac{a-2}{2(a-1)}, & a > 2 \end{cases}$$

- For $G(1,c)$: the order parameter associated with the phase transition is the shared site density



$$\mathcal{C}(1,c) = \begin{cases} 0, & c \le 4/3 \\ \frac{c-2+\sqrt{c(c-1)}}{2(c-1)}, & c > 4/3 \end{cases}$$

- Second-order adsorption and zipping phase trans. resp.

SINGULARITIES AND PHASES

This leads us to associate the singularities of $G(a,1)$ and $G(1,c)$ with the phases as

- $z_b = 1/4$ with a desorbed phase where $\mathcal{A} = 0$ and $\mathcal{C} = 0$
- $z_a = \frac{\sqrt{a-1}}{2a}$ with an adsorbed phase where $\mathcal{A} > 0$
- $z_c = \frac{1-c+\sqrt{c^2-c}}{c}$ with a zipped phase where $\mathcal{C} > 0$

Order parameters for the full model

Four possible phases:

- Desorbed: $\mathcal{A} = \mathcal{C} = 0$
- Adsorbed: (a-rich) $\mathcal{A} > 0, \mathcal{C} = 0$
- Zipped: (c-rich) $\mathcal{A} = 0, \mathcal{C} > 0$
- Zipped & Adsorbed: (ac-rich) $\mathcal{A} > 0, \mathcal{C} > 0$

ANALYSING $G(a,c)$

Recall

$$G(a,c) \sim \frac{p_1(a,c,z)}{p_2(a,c,z) + p_3(a,c,z)G(a,1) + p_4(a,c,z)G(1,c)}$$

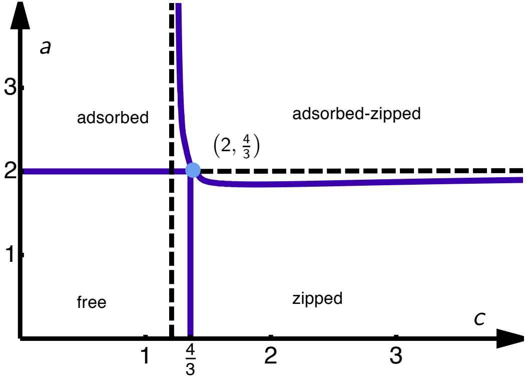
- $\Rightarrow$ Singularities: Look at $G(a,1)$, $G(1,c)$ and root of above denom.
- root of denominator is associated with the zipped-adsorbed phase

The dominant singularity $z_s(a,c)$ of the generating function $G(a,c;z)$ is one of four types associated with the four phases

$$z_s(a,c) = \begin{cases} z_b \equiv 1/4, & a \le 2, c \le 4/3 \\ z_a(a) \equiv \frac{\sqrt{a-1}}{2a}, & a > 2, c \le \alpha(a) \\ z_c(c) \equiv \frac{1-c+\sqrt{c^2-c}}{c}, & a \le \gamma(c), c > 4/3 \\ z_{ac}(a,c), & a > \gamma(c), c > \alpha(a) \end{cases}$$

- $\alpha(a)$ is boundary between adsorbed and zipped-adsorbed phases
- $\gamma(c)$ is the boundary between zipped and zipped-adsorbed phases

Phase diagram



All transitions found to be second order

Low-temp argument gives

- $c \to \infty, \gamma(c) \to 2$
- $a \to \infty, \alpha(a) \to \sqrt{5} - 1$

Asymptotics

Table : The growth rates of the coefficients $Z_n(a,c)$ modulo the amplitudes of the full generating function $G(a,c;z)$ over the entire phase space.

phase region	$Z_n(a,c) \sim$
free	$4^n n^{-5}$
free to adsorbed boundary	$4^n n^{-3}$
free to zipped boundary	$4^n n^{-3}$
$a = 2, c = 4/3$	$4^n n^{-3}$
adsorbed	$z_a(a)^{-n} n^{-3/2}$
zipped	$z_c(c)^{-n} n^{-3/2}$
adsorbed to adsorbed-zipped boundary $(\alpha(a))$	$z_a(c)^{-n} n^{-1/2}$
zipped to adsorbed-zipped boundary $(\gamma(c))$	$z_c(c)^{-n} n^{-1/2}$
adsorbed-zipped	$z_{ac}(a,c)^{-n} n^{-1}$

CONCLUSION

- Simple model of DNA as two friendly walks near a boundary
- Used combinatorial decomposition to obtain linear functional equation
- Used obstinate kernel method to solve functional equations (using symmetries to provide sufficient information)
- Explicit series solutions for $G(a,1)$ and $G(1,c)$
- Combined these equations to relate $G(a,c)$ to both $G(a,1)$ and $G(1,c)$
- Also used Zeilberger-Gosper algorithm to find linear DE for $G(1,c)$
- Full analysis of asymptotics and phase diagram
- R. Tabbara, A. L. Owczarek and A. Rechnitzer, *J. Phys. A.: Math. Theor*, **47**, 015202 (34pp), 2014

FUTURE WORKS

- Consider three walks with multiple unzipping interactions: work in progress – maybe next year's talk!
- Combine single, double surface and unzipping interactions: work in progress
- Also in progress is work in a slit