Higher Order Morita Approximations for Random Copolymer Adsorption

Workshop
Combinatorial Problems Raised
by Statistical Mechanics

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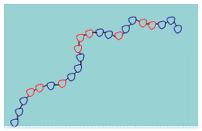
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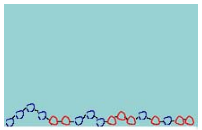
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Introduction and model assumptions

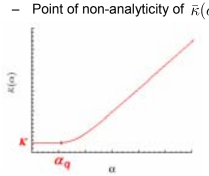
- Dilute solution (polymer-polymer interactions can be ignored).
- System in equilibrium.
- Polymer's conformations: self-avoiding walks, Motzkin paths, Dyck paths.

- Degree of polymerization: n
- Two types of monomers: A and B.
- Monomer sequence (*colouring*) is random.
- χ_i is *colour* of monomer i ($\chi_i = 1 \rightarrow A$)
  - i.i.d. Bernoulli random variables, $P(\chi_i=1) = p$
- $E(\omega|\chi)$: energy of conformation ω for fixed colour χ
- Conformations with same energy are equally likely.

$$Z_n(T|\chi) = \sum_{\omega\in\Omega_n} e^{-E(\omega|\chi)/kT}$$

- In particular, $E(\omega|\chi) = -\alpha\, n_{A,S}$.
- $n_{A,S}$: number of A monomers at the surface.
- $\alpha = -1/kT$
- So $Z_n(\alpha|\chi) = \sum_{n_{A,S}=0}^{n} c_n(n_{A,S}|\chi)\, e^{\alpha n_{A,S}}$
- $c_n(n_{A,S}|\chi)$: number of walks with $n_{A,S}$ vertices coloured A at the surface.

- Intensive free energy at fixed χ : $\kappa_n(\alpha|\chi) = n^{-1}\log Z_n(\alpha|\chi)$
- Quenched average free energy : $\bar\kappa^q_n(\alpha) = \langle n^{-1}\log Z_n(\alpha|\chi)\rangle_\chi$
- Limiting quenched average free energy (exists): $\bar\kappa(\alpha) = \lim_{n\to\infty}\bar\kappa^q_n(\alpha)$
  - Indicates if polymer prefers desorbed or adsorbed phase.
  - Point of non-analyticity of $\bar\kappa(\alpha)$ corresponds to phase transition.



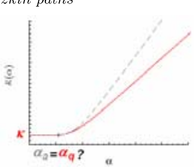
$$\kappa = \begin{cases} \log 2 & \textit{Dyck paths} \\ \log 3 & \textit{Motzkin paths} \end{cases}$$

- As $\alpha\to\infty$, $\bar\kappa(\alpha)$ is asymptotic to a line with slope $\begin{cases} p/2 & \textit{Dyck paths} \\ p & \textit{Motzkin paths} \end{cases}$
- Q: What is the value of α_q ?
- Q: What is $\bar\kappa(\alpha)$ for $\alpha > \alpha_q$?

- Annealed average free energy: $\bar\kappa^a_n(\alpha) = n^{-1}\log\langle Z_n(\alpha|\chi)\rangle_\chi \ \geq\ \bar\kappa^q_n(\alpha)$
- Limiting annealed average free energy: $\bar\kappa^a(\alpha) = \lim_{n\to\infty}\bar\kappa^a_n(\alpha)\ \geq\ \bar\kappa^q(\alpha)$

- So, $\alpha_a = \begin{cases} \log(1+1/p) & \textit{Dyck paths} \\ \log(1+1/2p) & \textit{Motzkin paths} \end{cases} \leq \alpha_q$

- As $\alpha\to\infty$, $\bar\kappa^a(\alpha)$ is asymptotic to a line with slope
$\begin{cases} 1/2 \neq p/2 & \textit{Dyck paths} \\ 1 \neq p & \textit{Motzkin paths} \end{cases}$



The Morita Approximation (Constrained Annealing)

- Consider the constrained annealed average free energy

$$\bar\kappa^{c.a.}_n(\alpha,\lambda) = n^{-1}\log\left\langle Z_n(\alpha|\chi)\, e^{\Lambda(\lambda|\chi)}\right\rangle_\chi$$

with the Lagrangian $\Lambda(\lambda|\chi) = \sum_{C\subseteq[n]}\lambda_C\left[p^{|C|} - \prod_{i\in C}\chi_i\right]$

- Minimization of $\bar\kappa^{c.a.}_n(\alpha,\lambda)$ with respect to λ_C enforces the constraint
$Prob(\text{all the walk vertices in } C \text{ are coloured } A) = \langle\prod_{i\in C}\chi_i\rangle = p^{|C|}$
- Mazo (1963), Morita (1964), and Kuhn (1996) showed that $\bar\kappa^q_n(\alpha)$ can be obtained as the solution to

$$\min_\lambda \bar\kappa^{c.a.}_n(\alpha,\lambda)$$

- Setting some λ's to zero and then minimizing $\bar\kappa^{c.a.}_n\left(\alpha,\hat\lambda\right)$ to obtain $\bar\kappa^{u.b.}_n(\alpha)$ yields an upper bound on $\bar\kappa^q_n(\alpha)$.
  - In particular, we obtain $\bar\kappa^q_n(\alpha)\ \leq\ \bar\kappa^{u.b.}_n(\alpha) \leq\ \bar\kappa^a_n(\alpha)$
  - and so $\bar\kappa^q(\alpha)\ \leq\ \bar\kappa^{u.b.}(\alpha) \leq\ \bar\kappa^a(\alpha)$
  - Minimization to obtain $\bar\kappa^{u.b.}_n(\alpha)$ is quite complex.

Morita approximation of order σ

- Include only constraints involving colours at most σ vertices apart.

$$\underbrace{\chi_1,\chi_2,\dots,\chi_\sigma}_{1}\cdots\underbrace{\chi_{\sigma(i-1)+1},\chi_{\sigma(i-1)+2},\dots,\chi_{\sigma i}}_{i}\cdots\underbrace{\chi_{\sigma(n-1)+1},\chi_{\sigma(k-1)+2},\dots,\chi_{\sigma k}}_{k}$$

- Recall we want to obtain

$$\bar\kappa^{u.b.}(\alpha) = \lim_{k\to\infty}(k\sigma)^{-1}\min_{\lambda^{(\sigma)}}\log\left\langle Z_{k\sigma}(\alpha|\chi)\, e^{\Lambda\left(\lambda^{(\sigma)}|\chi\right)}\right\rangle_\chi$$

- We can upper bound it by

$$\bar\kappa^{(\sigma)}(\alpha) = \min_{\lambda^{(\sigma)}}\lim_{k\to\infty}(k\sigma)^{-1}\log\left\langle Z_{k\sigma}(\alpha|\chi)\, e^{\Lambda\left(\lambda^{(\sigma)}|\chi\right)}\right\rangle_\chi \ \geq\ \bar\kappa^{u.b.}(\alpha)$$

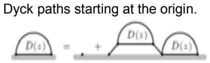
  - This can be obtained by considering the grand canonical partition function

$$G^{(\sigma)}\left(z,\alpha,\lambda^{(\sigma)}\right) = \sum_{k=0}^{\infty} z^{k\sigma} Z_{k\sigma}(\alpha|\chi)\, e^{\Lambda\left(\lambda^{(\sigma)}|\chi\right)}$$

  with radius of convergence $r_G\left(\alpha,\lambda^{(\sigma)}\right)$.
  - We obtain $\bar\kappa^{(\sigma)}(\alpha) = \min_{\lambda^{(\sigma)}}\left\{-\log r_G\left(\alpha,\lambda^{(\sigma)}\right)\right\}$

- G_σ can be written in terms of a homopolymer generating function B_σ.
  - B_σ keeps track of the number of segments ω of the path that have the same sequence of surface touches.
  - B_σ can be obtained via factorization,
    - e.g., d_n: number of n-step Dyck paths starting at the origin.

$$D(z) = \sum_{n\geq 0} d_{2n} z^{2n}$$



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

- The radii of convergence are related by $r_G\left(\alpha,\lambda^{(\sigma)}\right) = r_B\cdot e^{q^{(\sigma)}\left(\lambda^{(\sigma)}\right)}$
- where
  - $r_B = \min\{|z_1|,|z_2|,\cdots,|z_{1+n_r}|\}$
  - z_1: branch cut from the desorbed phase (square root singularity)
  - the other z_i's are the n_r poles from the adsorbed phase.
  - $\Lambda(\lambda|\chi) = \sum_{C\subseteq[n]}\lambda_C\left[p^{|C|} - \prod_{i\in C}\chi_i\right] = q^{(\sigma)}\left(\lambda^{(\sigma)}\right) - \sum_{C\subseteq[n]}\lambda_C\prod_{i\in C}\chi_i$

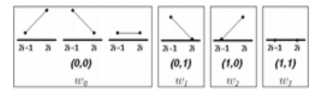
Direct Renewal approach

- Consider only colouring constraints on sequences of **non-overlapping** vertices.

$$\underbrace{\chi_1,\chi_2,\dots,\chi_\sigma}_{1}\cdots\underbrace{\chi_{\sigma(i-1)+1},\chi_{\sigma(i-1)+2},\dots,\chi_{\sigma i}}_{i}\cdots\underbrace{\chi_{\sigma(n-1)+1},\chi_{\sigma(k-1)+2},\dots,\chi_{\sigma k}}_{k}$$

- As an example, consider the case $\sigma = 2$ for Motzkin paths. Then
  - $\lambda^{(2)} = (\lambda_0,\dots,\lambda_3)$
  - $\left\langle Z_{2k}(\alpha|\chi)\, e^{\Lambda(\lambda^{(2)}|\chi)}\right\rangle = e^{-2kq^{(2)}(\lambda^{(2)})}\sum_{\omega\in\Omega_{2k}}\prod_{i=1}^{k}\Big[p^2 e^{\alpha(\Delta_{2i-1}(\omega)+\Delta_{2i}(\omega))+\lambda_3}$
    $+p(1-p)e^{\alpha(\Delta_{2i-1}(\omega))+\lambda_2} + (1-p)pe^{\alpha(\Delta_{2i}(\omega))+\lambda_1} + (1-p)^2 e^{\lambda_0}\Big]$
  - $q^{(2)}\left(\lambda^{(2)}\right) = \frac{1}{2}\left(\lambda_3 p^2 + \lambda_2 p(1-p) + \lambda_1(1-p)p + \lambda_0(1-p)^2\right)$
  - $\Delta_i = 1$ if vertex i is at surface.
  - Term in square brackets depends only on sequence $(\Delta_{2i-1}(\omega),\Delta_{2i}(\omega))$

$(\Delta_{2i-1}(\omega),\Delta_{2i}(\omega))$



- Then $G^{(2)}\left(z,\alpha,\lambda^{(2)}\right) = B^{(2)}\left(ze^{-q^{(2)}(\lambda^{(2)})}, w_0,\dots,w_3\right)$

where
  - $B^{(2)}(z,w_0,\dots,w_3) = \sum_{n\geq 0} z^n \sum_{n_0,\dots,n_3} b_n(n_0,\dots,n_3)\prod_{j=0}^{3} w_j^{n_j}$
  - $b_n(n_0,\dots,n_3)$ is the number of Motzkin paths of length n with n_j segments with the sequence $(\Delta_{2i-1}(\omega),\Delta_{2i}(\omega))$ as the sequence of bits in j base 2.
  - $w_j = p^2 e^{\alpha(s_1+s_0)+\lambda_3} + p(1-p)e^{\alpha s_1+\lambda_2} + (1-p)pe^{\alpha s_0+\lambda_1} + (1-p)^2 e^{\lambda_0}$

  with the sequences $s_1 s_0$ given by the bits in i base 2.

Transfer Matrix approach

- Consider the following colouring constraints:

$$\chi_0,\chi_1,\dots,\chi_{\sigma-1},\chi_\sigma,\chi_{\sigma+1},\dots,\chi_{2\sigma-1},\chi_{2\sigma},\dots,\chi_{\sigma(k-1)},\chi_{\sigma(k-1)+1},\dots,\chi_{\sigma k-1},\chi_{\sigma k}$$

- As an example, consider $\sigma = 2$ for Motzkin paths. Then
  - $\lambda^{(2)} = (\lambda_0,\dots,\lambda_4)$
  - $\left\langle Z_{2k}(\alpha|\chi)\, e^{\Lambda(\lambda^{(2)}|\chi)}\right\rangle = e^{-2kq^{(2)}(\lambda^{(2)})}\sum_{\omega\in\Omega_{2k}} Q^{(2)}\left(\alpha,\lambda^{(2)}|\omega\right)$
  - $q^{(2)}\left(\lambda^{(2)}\right) = \frac{\lambda_0}{2}p + \frac{\lambda_1}{2}(1-p) + \lambda_2 p^2 + 2\lambda_3 p(1-p) + \lambda_4(1-p)^2$

$$Q^{(2)}(\alpha,\lambda^{(2)}|\omega) = \int\left(\prod_{i=1}^{2k} d\chi_i\right)\prod_{i=1}^{k}\prod_{j=0}^{1}\sqrt{w_p(\chi_{2i-2+j})w_p(\chi_{2i-1+j})}$$

$$\times\exp\left[\lambda_{2+N(i,j)} + \frac{\lambda_{1-\chi_{2i-1}} + \chi_{2i-2+j}\Delta_{2i-2+j}(\omega) + \chi_{2i-1+j}\Delta_{2i-1+j}(\omega)}{2}\right]$$

- Need to find a sequence of 2×2 real matrices $T^{(i)}(\alpha,\lambda^{(2)}|\omega)$ such that

$$Q^{(2)}(\alpha,\lambda^{(2)}|\omega) = Tr\left(\prod_{i=1}^{k} T^{(i)}(\alpha,\lambda^{(2)}|\omega)\right)$$

- Using the properties of the trace of a real matrix

$$Q^{(2)}(\alpha,\lambda^{(2)}|\omega) \leq 2\prod_{i=1}^{k}\sqrt{\eta\left(T^{(i)}(\alpha,\lambda^{(2)}|\omega)T^{(i)}(\alpha,\lambda^{(2)}|\omega)^t\right)}$$

where $\eta(\cdot)$ denotes the eigenvalue with largest modulus.

- Let $T^{(i)}(\alpha,\lambda|\omega) = T^{(i,0)}(\alpha,\lambda^{(2)}|\omega)T^{(i,1)}(\alpha,\lambda^{(2)}|\omega)$

where $T^{(i,j)}(\alpha,\lambda^{(2)}|\omega) =$

$$\begin{pmatrix} (1-p)e^{\lambda_2+\frac{\lambda_1}{2}} & \sqrt{(1-p)p}e^{\frac{\alpha\Delta_{2i-1+j}(\omega)}{2}+\lambda_3+\frac{\lambda_j}{2}} \\ \sqrt{(1-p)p}e^{\frac{\alpha\Delta_{2i-2+j}(\omega)}{2}+\lambda_3+\frac{\lambda_{1-j}}{2}} & pe^{\frac{\alpha\Delta_{2i-2+j}(\omega)}{2}+\frac{\alpha\Delta_{2i-1+j}(\omega)}{2}+\lambda_4+\frac{\lambda_0}{2}} \end{pmatrix}$$

- $T^{(i)}$ only depends on ω through sequence $\Delta^{(i)} = (\Delta_{2i-2}(\omega),\Delta_{2i-1}(\omega),\Delta_{2i}(\omega))$
- Index the 8 possible matrices $T^{(i)}$ by the binary string $\Delta^{(i)}$ in base 10.
- Then, $Q^{(2)}(\alpha,\lambda^{(2)}|\omega)\ \leq\ \prod_{j=0}^{7}\left(\eta(T_j T_j^t)\right)^{n_j(\omega)/2}$
- and $G^{(2)}\left(z,\alpha,\lambda^{(2)}\right)\ \leq\ \hat B^{(2)}\left(ze^{-q^{(2)}(\lambda^{(2)})}, w_0,\dots,w_7\right)$
- with $w_j = \eta(T_j T_j^t)^{1/2}$
- The matrix $T^{(i)}$ is symmetric if $\Delta_{2i-2} = \Delta_{2i}$.

Lower bounds

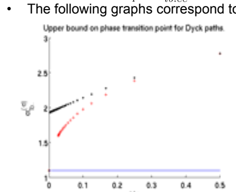
- We can obtain a lower bound using the fact that $Z_{k\sigma}(\alpha|\chi) \geq (Z_\sigma(\alpha|\chi))^k$
so that $\bar\kappa(\alpha)\ \geq\ \sigma^{-1}\langle\log Z_\sigma(\alpha|\chi)\rangle_\chi\ :=\ \bar\kappa^{(\sigma)}_{lb.ee}(\alpha)$
- Another lower bound can be obtained from

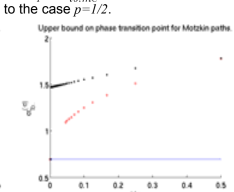
$$Z_\sigma(\alpha|\chi)\ \geq\ c_{\sigma,E_{min}}e^{-E_{min}/kT}\ =\ c_\sigma(n_{A,S}|\chi)e^{\alpha n_{A,S}}$$

so that $\bar\kappa(\alpha)\ \geq\ \alpha\sigma^{-1}\langle n_{A,S}\rangle + \sigma^{-1}\langle\log c_\sigma(n_{A,S}|\chi)\rangle\ :=\ \bar\kappa^{(\sigma)}_{lb.me}(\alpha)$

Results for Q: What is the value of α_q ?

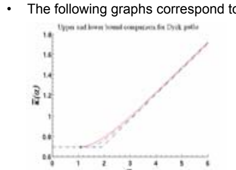
- Know that $\alpha_a \leq \alpha_q$.
- Is $\alpha_a = \alpha_q$ or $\alpha_a < \alpha_q$?
- Know that $\alpha_a \leq \alpha^{(\sigma)} \leq \alpha_q$. *(for direct renewal only)*
  - Is $\alpha_a < \alpha^{(\sigma)}$ for σ large enough?
  - Caravenna and Giacomin show that $\alpha_a = \alpha^{(\sigma)}$ for all finite σ.
- Also know that $\alpha_q \leq \alpha^{(\sigma)}_{lb.ee}$ and that $\alpha_q \leq \alpha^{(\sigma)}_{lb.me}$.
- The following graphs correspond to the case $p=1/2$.

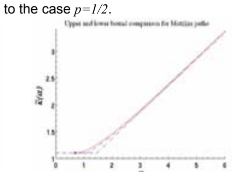




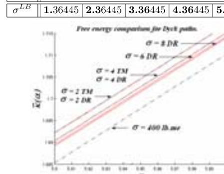
Results for Q: What is $\bar\kappa(\alpha)$ value $\alpha > \alpha_q$?

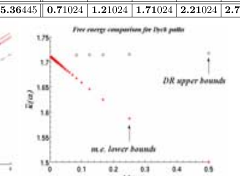
- The following graphs correspond to the case $p=1/2$.





	a) Motzkin path bounds					b) Dyck path bounds				
σ^{bnd}	$\alpha = 2$	4	6	8	10	$\alpha = 2$	4	6	8	10
$1^{[2]}$	1.45798	2.37963	3.36925	4.36785	5.36766	0.78847	1.22501	1.71701	2.21593	2.71579
2^{DR}	1.45750	2.37899	3.36860	4.36720	5.36701	0.78847	1.22501	1.71701	2.21593	2.71579
2^{TM}	1.45717	2.37862	3.36824	4.36684	5.36665	0.78847	1.22501	1.71701	2.21593	2.71579
4^{DR}	1.45703	2.37830	3.36788	4.36647	5.36628	0.78779	1.22331	1.71514	2.21405	2.71390
4^{TM}	**1.**45688	**2.37**818	**3.36**777	**4.36**636	**5.36**617	0.78779	1.22331	1.71514	2.21405	2.71390
6^{DR}						0.78747	1.22261	1.71438	2.21327	2.71312
8^{DR}						0.78729	1.22226	1.71399	2.21287	**2.71**272
12^{DR}						**0.7**8710	**1.2**2191	**1.71**361	**2.21**249	
σ^{LB}	**1.**36445	**2.36**445	**3.36**445	**4.36**445	**5.36**445	**0.7**1024	**1.2**1024	**1.71**024	**2.21**024	**2.71**024





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