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FAST TRACK COMMUNICATION

Higher order Morita approximations for random copolymer adsorption

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Abstract

Random linear copolymers are linear polymers with two or more types of monomer where the monomer sequence is determined by some random process. Once determined the sequence is fixed so random copolymers are an example of a system with quenched randomness. Even for simple configurational models the quenched model is too difficult to solve analytically. The Morita approximation is a partial annealing procedure which yields upper bounds on the quenched average free energy. In this paper we consider higher order Morita approximations in which we control correlations to various orders between neighbouring monomers along the polymer chain. We consider different approaches for incorporating correlations and apply these to Motzkin and Dyck path models of the adsorption of a random copolymer at a surface. We also present lower bounds which, along with the Morita bounds, determine the limiting quenched average free energy for adsorption very precisely at low temperatures.

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Consider a linear polymer with two types of co-monomers, A, B. The sequence of As and Bs making up the polymer is determined by a random process, but is then fixed, so that the randomness is quenched. The appropriate free energy for such models is the expectation (over the monomer distribution) of the logarithm of the partition function; this is referred to as the *quenched average free energy*. In this paper we shall be concerned with adsorption of a random copolymer at an impenetrable surface [1]. Even for simple models the quenched system is too difficult to solve analytically [2]; see [3, 4] for corresponding results for the localization problem. To make progress we either have to use numerical methods or an approximation.

One approximation approach which has proved useful is based on an idea introduced by Morita [5] in which the quenched average free energy is replaced by an annealed average subject to constraints on the moments of the monomer distribution. This idea, developed in a series of papers since 1963 [5–7], is based on the following facts: the quenched average free energy is the solution to a constrained optimization problem in which all the moments of the quenched probability distribution are fixed, and relaxing some of the moment constraints in this optimization procedure yields an upper bound on the quenched average free energy [5, 7].

Previous work on random copolymer models using Morita approximation ideas has focused on either an annealed approximation (with no moment constraints) or constraining only the first moment so that the polymer has the correct proportion of As and Bs [1, 2]. One might hope to improve the situation by fixing higher order moments. Caravenna and Giacomin [8] have recently shown that for a set of models, including adsorption, if the annealed free energy equals the quenched average free energy for one region of the phase diagram then the bound on the location of the phase boundary obtained from the annealed approximation will not be improved by introducing further constraints. In contrast, this does not however preclude the bound on the quenched average free energy being improved by introducing further constraints.

In this paper, we investigate the effect of including different types of constraints in a Morita approximation for two directed walk models (Motzkin and Dyck paths) and we use two different methods for obtaining bounds on the quenched average free energy: one is based on a transfer matrix approach while the other relies on a direct application of renewal arguments. The latter approach involves only constraints on the monomer distribution within non-overlapping sequences of consecutive comonomers whereas the transfer matrix approach takes into account constraints involving some overlapping comonomer sequences. In either case, the bound can be expressed in terms of the free energy for a homopolymer problem and this free energy can be obtained using renewal arguments. The upper bounds improve (compared to previous work in [2]) the bounds on the free energy in the interior of the adsorbed phase region. We show that the upper bounds are extremely good at least at low temperatures.

The adsorption model and Morita approximations

A *Dyck path* is a walk in two dimensions which

(i) starts at the origin and ends on the line $y = 0$,
(ii) has no vertices with negative y-coordinate, and
(iii) has steps (of length $\sqrt{2}$) only in the directions $(1, 1)$ and $(1, -1)$.

A *Motzkin path* differs from a Dyck path only by having three kinds of steps, $(1, 1)$, $(1, -1)$ and $(1, 0)$. In the Motzkin and Dyck path [9, 10] models for adsorption, any path ω of length n can be represented by the sequence $\omega = (\omega_0, \omega_1, \ldots, \omega_n)$, where ω_i represents the ith vertex of the path having x-coordinate i and y-coordinate $\omega_i \geqslant 0$. A vertex with $y = 0$ is called a *visit*. Consider a sequence of i.i.d. Bernoulli random variables $\chi = (\chi_1, \chi_2, \ldots, \chi_n)$ and associate it with the path ω by assigning the *colour* $\chi_i \in \{0, 1\}$ to vertex i. ($\chi_i = 1$ corresponds to comonomer A at vertex i.) Let p be the probability that $\chi_i = 1$. Let $\Delta_i(\omega)$ be a function such that $\Delta_i(\omega) = 1$ if $\omega_i = 0$ (visit) and $\Delta_i(\omega) = 0$ otherwise ($\omega_i > 0$); let $\Delta(\omega) = (\Delta_i(\omega), i = 1, \ldots, n)$. The appropriate partition function for a given set, Ω_n, of n-edge paths and for fixed χ, is then

$$Z_n(\alpha|\chi) = \sum_{\omega \in \Omega_n} \exp\left(\alpha \sum_{i=1}^{n} \chi_i \Delta_i(\omega)\right). \tag{1}$$

The corresponding free energy is $\kappa_n(\alpha|\chi) = n^{-1}\log Z_n(\alpha|\chi)$ and it is known that the *limiting quenched average free energy*,

$$\bar{\kappa}(\alpha) = \lim_{n\to\infty}\langle\kappa_n(\alpha|\chi)\rangle \equiv \lim_{n\to\infty}\bar{\kappa}_n(\alpha), \tag{2}$$

exists where the average is taken over the distribution of χ [11]. (The argument given in [11] is for self-avoiding walks but applies *mutatis mutandis* for Motzkin and Dyck paths.) It is also easy to prove that [11]:

- There exist constants κ, $\alpha_q > 0$ such that $\bar{\kappa}(\alpha) = \kappa$ for $\alpha \leqslant \alpha_q$ and is greater than κ otherwise. The constant $\kappa = \log 2$ for Dyck paths and $\kappa = \log 3$ for Motzkin paths.
- As $\alpha \to \infty$, $\bar{\kappa}(\alpha)$ is asymptotic to a line with slope $p/2$ and p respectively for Dyck and Motzkin paths.

For the annealed approximation, the limiting free energy is given by $\lim_{n\to\infty} n^{-1}\log\langle Z_n(\alpha|\chi)\rangle$ and there exists a critical value of α, denoted by α_a, corresponding to an adsorption transition, where $\alpha_a = \log(1+1/p)$ for Dyck paths [2] and $\alpha_a = \log(1+1/2p)$ for Motzkin paths [1]. The limiting annealed free energy is asymptotic to a line with slope $1/2$, 1 as $\alpha \to \infty$ for Dyck and Motzkin paths respectively. Note that this limiting slope differs from that of the quenched average free energy. For a first-order Morita approximation it is natural to constrain $\left\langle\sum_i \chi_i\right\rangle = np$ where all vertices are treated equally. In this case the critical value of α does not change with respect to the annealed approximation however the slope of the asymptote changes to p for both Dyck and Motzkin paths. Note that this is the correct asymptotic slope for Motzkin paths but not for Dyck paths. It is not correct for Dyck paths since the constraint ignores the Dyck path property that only even vertices can lie in $y = 0$. Alternatively, one can fix the first moment for odd and even vertices separately, i.e. $\left\langle\sum_i \chi_{2i}\right\rangle = np/2$ and $\left\langle\sum_i \chi_{2i+1}\right\rangle = np/2$. For this case, the critical value of α does not change but the asymptotic slope for Dyck paths changes to $p/2$. The fact that the critical value is α_a for all the above approximations is consistent with the results in [8]. However, the bound on the limiting quenched average free energy can be improved by adding constraints.

In a general framework for the Morita approximation one considers a set of Lagrange multipliers $\lambda = (\lambda_C, \forall C \subseteq \{1, 2, \ldots, n\}) \in \mathbb{R}^{2^n}$ and the corresponding partition function

$$Z_n(\alpha, \lambda|\chi) = \sum_{\omega\in\Omega_n} \exp\left(\alpha\sum_{i=1}^{n}\chi_i\Delta_i(\omega) + \Lambda(\lambda|\chi)\right), \tag{3}$$

where for each subset C of vertices, $\Lambda(\lambda|\chi)$ is used to impose the correct distribution for the probability that exactly the vertices in C are coloured A. Specifically,

$$\Lambda(\lambda|\chi) = \sum_{C\neq\emptyset}\lambda_C\left[\left(\prod_{i\in C}\chi_i\prod_{i\notin C}(1-\chi_i)\right) - p^{|C|}(1-p)^{n-|C|}\right] \tag{4}$$

and the sum is over all $C \subseteq \{1, 2, \ldots, n\}$. Minimizing $n^{-1}\log\langle Z_n(\alpha, \lambda|\chi)\rangle$ with respect to the λ_C's yields the quenched average free energy $\bar{\kappa}_n(\alpha)$ for the model and ensures that the colour distribution constraint is satisfied for each subset $C \neq \emptyset$ [1]. A Morita approximation $\kappa_n^M(\alpha)$ for $\bar{\kappa}_n(\alpha)$ is obtained by relaxing some of these constraints (in the annealed case, all the λ_C's are set to zero) and minimizing $n^{-1}\log\langle Z_n(\alpha, \lambda|\chi)\rangle$ with respect to the reduced set λ^M of λ_C's. This yields an upper bound on $\bar{\kappa}_n(\alpha)$ for the model, $\kappa_n^M(\alpha) = \min_{\lambda^M} n^{-1}\log\langle Z_n(\alpha, \lambda|\chi)\rangle \geqslant \bar{\kappa}_n(\alpha)$. The minimization is typically

quite complicated. However, one can also obtain an upper bound $\kappa_U(\alpha)$ on $\bar{\kappa}(\alpha)$ via

$$\begin{aligned}\kappa_U(\alpha) &= \min_{\lambda^M} \lim_{n\to\infty} \frac{1}{n} \log\langle Z_n(\alpha, \lambda^M|\chi)\rangle \\ &= \min_{\lambda^M}\{-\log(r_G(\alpha, \lambda^M))\} \\ &\geqslant \lim_{n\to\infty} \kappa_n^M(\alpha) \geqslant \bar{\kappa}(\alpha) \end{aligned} \tag{5}$$

where $r_G(\alpha, \lambda^M)$ is the radius of convergence of the generating function

$$G(z, \alpha, \lambda^M) = \sum_{n=0}^{\infty} z^n \langle Z_n(\alpha, \lambda^M|\chi)\rangle. \tag{6}$$

For both the annealed and first-order Morita approaches, $G(z, \alpha, \lambda^M)$ can be expressed in terms of a homopolymer generating function which keeps track of the number of visits in the walks. This is an important result because it allows one (in principle) to find the Morita limiting free energy by looking at a re-parametrization of the well known singularity structure of the homopolymer model.

For higher order Morita approximations, by using the methods we describe below, it is still possible to relate $G(z, \alpha, \lambda^M)$ to a homopolymer generating function that however will be a more complicated function of the paths involved. Let $\sigma \geqslant 1 \in \mathbb{N}$ be the *order* (defined below) of the approximation and let $B^{(\sigma)}$ denote the related homopolymer generating function. $B^{(\sigma)}$ can be obtained using standard factorization (renewal) arguments but we leave the details of this to a subsequent paper. Rather here we focus on two methods for relating $G(z, \alpha, \lambda^M)$ to $B^{(\sigma)}$ which depend on the choice of λ^M, and in order to show how the two methods work we will focus on the second-order ($\sigma = 2$) approximation.

Transfer matrix approach

For ease of implementation of the transfer matrix approach, we assume periodic boundary conditions for the colouring, i.e. $\chi_0 = \chi_n$. For a transfer matrix approximation of order σ, we only impose colouring constraints that involve vertices whose labels are at most $\sigma - 1$ apart. With $\lambda = (\lambda_0, \ldots, \lambda_4)$ and even $n \geqslant 0$, the partition function, $Z_n^{(2)}(\alpha, \lambda|\chi)$, for the second-order transfer matrix approximation for Motzkin paths is obtained from equation (3) by replacing $\Lambda(\lambda|\chi)$ by

$$\begin{aligned}\Lambda^{(2)}(\lambda|\chi) = \lambda_0 \sum_{i=1}^{n/2}(\chi_{2i-1} - p) + \lambda_1 \sum_{i=1}^{n/2}(1 - \chi_{2i-1} - (1-p)) + \lambda_2 \sum_{i=1}^{n}(\chi_i\chi_{i-1} - p^2) \\ + \lambda_3 \sum_{i=1}^{n}((1-\chi_i)\chi_{i-1} + \chi_i(1-\chi_{i-1}) - 2p(1-p)) \\ + \lambda_4 \sum_{i=1}^{n}((1-\chi_i)(1-\chi_{i-1}) - (1-p)^2).\end{aligned} \tag{7}$$

This imposes the full set of colouring constraints on each odd vertex and imposes constraints on the distribution of the number of A's in each vertex pair $(i-1, i)$ for $i = 1, \ldots, n$. Note that some of these constraints are redundant (in fact only three constraints are necessary). However, this form gives an indication of how we generalize to higher σ where, for vertex sets including vertices which are at most $\sigma - 2$ apart, we impose the full set of colouring constraints while for other vertex sets we only constrain the distribution of the number of A's. Full details for higher σ and for Dyck paths, where the constraints are defined slightly

differently to take advantage of the fact that only even vertices can visit the surface, will be provided in a subsequent paper.

Let $w_p(\chi_i)$ denote the density function for the random variable χ_i. Averaging over χ gives

$$\left\langle Z_n^{(2)}(\alpha, \lambda|\chi)\right\rangle = \mathrm{e}^{-nq^{(2)}(\lambda)} \sum_{\omega\in\Omega_n} Q^{(2)}(\alpha, \lambda|\omega) \tag{8}$$

where

$$q^{(2)}(\lambda) = \frac{\lambda_0}{2}p + \frac{\lambda_1}{2}(1-p) + \lambda_2 p^2 + 2\lambda_3 p(1-p) + \lambda_4(1-p)^2, \tag{9}$$

$$Q^{(2)}(\alpha, \lambda|\omega) = \int \left(\prod_{i=1}^{n} \mathrm{d}\chi_i\right) \prod_{i=1}^{n/2}\prod_{j=0}^{1} \sqrt{w_p(\chi_{2i-2+j}) w_p(\chi_{2i-1+j})} \times \exp\left[\lambda_{2+N(i,j)} + \frac{\lambda_{1-\chi_{2i-1}} + \chi_{2i-2+j}\Delta_{2i-2+j}(\omega) + \chi_{2i-1+j}\Delta_{2i-1+j}(\omega)}{2}\right], \tag{10}$$

and $N(i, j) = \chi_{2i-2+j} + \chi_{2i-1+j}$ for $j = 0, 1$. The transfer matrix approach now involves finding a sequence of 2×2 real matrices $T^{(i)}(\alpha, \lambda|\omega)$ for $i = 1, \ldots, n/2$ such that

$$Q^{(2)}(\alpha, \lambda|\omega) = \mathrm{Tr}\left(\prod_{i=1}^{n/2} T^{(i)}(\alpha, \lambda|\omega)\right) \tag{11}$$

and so that, using the properties of the trace of a real matrix [12],

$$Q^{(2)}(\alpha, \lambda^M|\omega) \leqslant 2\prod_{i=1}^{n/2} \sqrt{\eta\left(T^{(i)}(\alpha, \lambda|\omega) T^{(i)t}(\alpha, \lambda|\omega)\right)} \tag{12}$$

where $\eta(\cdot)$ denotes the eigenvalue with largest modulus and A^t is the transpose of matrix A. This bound on the trace will be tightest if the matrices are symmetric since $\sqrt{\eta(TT^t)} = |\eta(T)|$ ($|\cdot|$ denotes the modulus) for a real symmetric matrix T. For Motzkin paths, the matrix $T^{(i)}(\alpha, \lambda|\omega) = T^{(i,0)}(\alpha, \lambda|\omega) T^{(i,1)}(\alpha, \lambda|\omega)$, where

$$T^{(i,j)}(\alpha, \lambda|\omega) = \begin{pmatrix} (1-p)\,\mathrm{e}^{\lambda_2 + \frac{\lambda_1}{2}} & \sqrt{(1-p)p}\,\mathrm{e}^{\frac{\alpha\Delta_{2i-1+j}(\omega)}{2} + \lambda_3 + \frac{\lambda_j}{2}} \\ \sqrt{(1-p)p}\,\mathrm{e}^{\frac{\alpha\Delta_{2i-2+j}(\omega)}{2} + \lambda_3 + \frac{\lambda_{1-j}}{2}} & p\,\mathrm{e}^{\frac{\alpha\Delta_{2i-2+j}(\omega)}{2} + \frac{\alpha\Delta_{2i-1+j}(\omega)}{2} + \lambda_4 + \frac{\lambda_0}{2}} \end{pmatrix}. \tag{13}$$

Note that if $\Delta_{2i-2}(\omega) = \Delta_{2i}(\omega)$ then $T^{(i,1)} = T^{(i,0)t}$ and so $T^{(i)}$ is symmetric. Note further that $T^{(i)}$ only depends on ω through $\Delta^{(i)} = (\Delta_{2i-2}(\omega), \Delta_{2i-1}(\omega), \Delta_{2i}(\omega))$ (the reference to ω is dropped for convenience). Thus there are eight possible matrices for $T^{(i)}$ which can be indexed by the binary string $\Delta^{(i)}$, and one can rewrite (10) as

$$Q^{(2)}(\alpha, \lambda^M|\omega) = \mathrm{Tr}\left(\prod_{i=1}^{n/2} T_{\Delta^{(i)}}\right) \leqslant \prod_{i=1}^{n/2} \left(\eta\left(T_{\Delta^{(i)}} T^t_{\Delta^{(i)}}\right)\right)^{1/2} = \prod_{j=0}^{7} \left(\eta\left(T_j T_j^t\right)\right)^{n_j(\omega)/2}, \tag{14}$$

where the matrices in the last equality are indexed in base 10 and $n_j(\omega)$ is the number of times the jth binary sequence appears as a $\Delta^{(i)}$ in $\Delta(\omega)$. Hence the averaged partition function (8) becomes

$$\left\langle Z_n^{(2)}(\alpha, \lambda|\chi)\right\rangle = \mathrm{e}^{-nq^{(2)}(\lambda)} \sum_{\omega\in\Omega_n} \mathrm{Tr}\left(\prod_{i=1}^{n/2} T_{\Delta^{(i)}}\right) \leqslant \mathrm{e}^{-nq^{(2)}(\lambda)} \sum_{\omega\in\Omega_n} \prod_{j=0}^{7} \left(\eta\left(T_j T_j^t\right)\right)^{n_j(\omega)/2}. \tag{15}$$

Grouping together all walks with the same sequence of n_j's yields

$$\begin{aligned} G^{(2)}(z,\alpha,\lambda) &= \sum_{n\geqslant 0} z^n \left\langle Z_n^{(2)}(\alpha,\lambda|\chi)\right\rangle \\ &\leqslant \sum_{n\geqslant 0} \left(z\,\mathrm{e}^{-q^{(2)}(\lambda)}\right)^n \sum_{n_0,\ldots,n_7} b_n(n_0,\ldots,n_7) \prod_{j=0}^{7} \left(\eta\left(T_j T_j^t\right)\right)^{n_j/2} \\ &:= B^{(2)}\left(z\,\mathrm{e}^{-q^{(2)}(\lambda)}, w_0,\ldots,w_7\right) \end{aligned} \tag{16}$$

where $w_j = \eta\left(T_j T_j^t\right)^{1/2}$ and $b_n(n_0,\ldots,n_7)$ is the number of walks in Ω_n having n_j segments which have an associated visit string $\Delta^{(i)}$ given by the sequence of bits in j base 2. Thus, the second-order Morita partition function can be bounded above by a homopolymer partition function. (For higher orders σ, $T^{(i,j)}(\alpha,\lambda|\chi)$ is a $2\times(\sigma-1)$ matrix for $j=0$ and a $(\sigma-1)\times 2$ matrix for $j=1$; full details will be provided in a subsequent paper.) The approach is similar for Dyck paths; however, the transfer matrix $T^{(i)}(\alpha,\lambda|\omega)$ can be defined so that it represents the transition from vertex $2i-1$ to vertex $2i+1$ (rather than vertex $2i-2$ to $2i$ as above) and is always symmetric.

Direct renewal approach

The standard factorization (or renewal) arguments for directed paths take advantage of the fact that after the first return to the surface the remaining portion of the path is again a directed path. However, correlation constraints such as $\langle\chi_i\chi_{i+1}\rangle = p^2, i = 1,\ldots,n-1$ are complicated to factor at the location of the first return to the surface. This difficulty can be reduced by considering only colouring constraints on non-overlapping vertex sequences. In fact, given an order σ, for each $i \geqslant 0$, we impose the full set of colouring constraints on the vertices $(i\sigma + j, j = 1,\ldots,\sigma)$. Note that these sequences of vertices do not overlap. This will have the advantage that we can write the partition function almost immediately in terms of a homopolymer partition function. Again we limit our discussion here to the case $\sigma = 2$ and refer to a subsequent paper for the full details and the generalization to higher values of σ.

With $\lambda = (\lambda_0,\ldots,\lambda_3)$ and even $n \geqslant 0$, the partition function for the second-order approximation is now given by

$$Z_n^{(2)}(\alpha,\lambda|\chi) = \mathrm{e}^{-nq^{(2)}(\lambda)} \sum_{\omega\in\Omega_n} \exp\left(\alpha\sum_{i=1}^{n}\chi_i\Delta_i(\omega) + \sum_{i=1}^{n/2}\lambda_{C(i)}\right) \tag{17}$$

where $C(i)$ is the lexicographic order of the subcolouring (χ_{2i-1}, χ_{2i}), and now

$$q^{(2)}(\lambda) = \tfrac{1}{2}(\lambda_3 p^2 + \lambda_2 p(1-p) + \lambda_1(1-p)p + \lambda_0(1-p)^2). \tag{18}$$

Thus

$$\begin{aligned} \left\langle Z_n^{(2)}(\alpha,\lambda^M|\chi)\right\rangle = \mathrm{e}^{-nq^{(2)}(\lambda)} \sum_{\omega\in\Omega_n}\prod_{i=1}^{n/2}[&p^2\mathrm{e}^{\alpha(\Delta_{2i-1}(\omega)+\Delta_{2i}(\omega))+\lambda_3} + p(1-p)\,\mathrm{e}^{\alpha(\Delta_{2i-1}(\omega))+\lambda_2} \\ &+ (1-p)p\,\mathrm{e}^{\alpha(\Delta_{2i}(\omega))+\lambda_1} + (1-p)^2\mathrm{e}^{\lambda_0}]. \end{aligned} \tag{19}$$

The term in the square brackets depends only on the sequence $(\Delta_{2i-1}(\omega), \Delta_{2i}(\omega))$ and hence can be determined from $\Delta^{(i)} = (\Delta_{2i-2}(\omega), \Delta_{2i-1}(\omega), \Delta_{2i}(\omega))$ (as defined previously). Hence, by grouping together all the walks that have the same sequence of n_j's one now obtains

$$G^{(2)}(z,\alpha,\lambda) = \sum_{n\geqslant 0} z^n\left\langle Z_n^{(2)}(\alpha,\lambda|\chi)\right\rangle = B^{(2)}\left(z\,\mathrm{e}^{-q^{(2)}(\lambda)}, w_0,\ldots,w_7\right) \tag{20}$$

where $B^{(2)}$ is the generating function (16), and where for $i = 0, \ldots, 3$

$$w_i = w_{i+4} = p^2\, \mathrm{e}^{\alpha(s_1+s_0)+\lambda_3} + p(1-p)\, \mathrm{e}^{\alpha s_1+\lambda_2} + (1-p)p\, \mathrm{e}^{\alpha s_0+\lambda_1} + (1-p)^2 \mathrm{e}^{\lambda_0} \tag{21}$$

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

Finding the Morita approximation free energy

For a given order σ, the two approaches described above give the possibility of computing from equation (5) the upper bound $\kappa_U^{(\sigma)}(\alpha)$ in terms of the singularities of the generating function $B^{(\sigma)}$ (for $\sigma = 2$, see equation (16) for the transfer-matrix approach and equation (20) for the renewal method). Indeed the radius of convergence of $G^{(\sigma)}(z, \alpha, \lambda)$ will satisfy the inequality

$$r_G(\alpha, \lambda) \geqslant \mathrm{e}^{q^{(\sigma)}(\lambda)} \min\{|z_1|, |z_2|, \ldots, |z_{1+n_r}|\} \tag{22}$$

where $z_2, z_3, \ldots, z_{1+n_r}$ are the poles of $B^{(\sigma)}$, while z_1 is the branch cut governing the desorbed phase. The z_i's are functions of α and λ. Therefore from equation (5), the upper bound $\kappa_U^{(\sigma)}(\alpha)$ becomes

$$\kappa_U^{(\sigma)}(\alpha) = \max_{\lambda}\{q^{(\sigma)}(\lambda) + \min\{\log|z_1|, \log|z_2|, \ldots, \log|z_{1+n_r}|\}\}. \tag{23}$$

Closed form expressions for the z_i's are available for $\sigma = 1$ for Motzkin paths and $\sigma = 2$ for Dyck paths. For these choices of σ it is possible to determine $\kappa_U^{(\sigma)}$ either exactly or by numerical optimization, depending on the value of α. In particular, it is still possible to determine the desorbed phase boundaries. For higher values of σ, determining $z_2, \ldots, z_{1+n_r}$ involves finding the roots of a polynomial of degree greater than seven for Motzkin paths and greater than five for Dyck paths. Hence the roots can only be determined numerically for specific choices of λ, α and thus the optimization must also be done numerically.

Lower bound

We also explored a lower bound on the quenched average free energy which we expect to be best for large values of α. For a given χ we only include those paths which have visits at vertices where $\chi_i = 1$, i.e., for Motzkin paths we calculate

$$\kappa_{L^*}^{(\sigma)}(\alpha) = \alpha p + \sigma^{-1}\langle \log d_\sigma^*(\chi)\rangle \leqslant \bar{\kappa}_\sigma(\alpha) \leqslant \sup_\sigma \bar{\kappa}_\sigma(\alpha) = \bar{\kappa}(\alpha) \tag{24}$$

where $d_\sigma^*(\chi)$ is the number of σ-edge paths which have visits at vertices where $\chi_i = 1$ and the last equality can be proved following arguments in [11]. At infinite α, the only contribution to the quenched average free energy will be from paths with visits at the vertices where $\chi_i = 1$ so that $\lim_{\alpha\to\infty}[\bar{\kappa}_\sigma(\alpha) - \alpha p] = \kappa_{L^*}^{(\sigma)}(\alpha) - \alpha p$, which is independent of α. Combinatorial arguments lead to

$$\kappa_{L^*}^{(\sigma)}(\alpha) = \alpha p + \frac{(1-p)^\sigma}{\sigma}\log d_\sigma + \frac{p}{\sigma}\sum_{i=0}^{\sigma-1}(1-p)^i(\log d_i + \log d_{i+1}) + \frac{p^2}{\sigma}\sum_{j=0}^{\sigma-2}(\sigma - 1 - j)(1-p)^j \log d_{j+1} \tag{25}$$

where d_n is the number of Motzkin paths of length n. An explicit formula for d_n can be determined from the Motzkin path generating function $M(z) = \sum_n d_n z^n = \frac{1-z-\sqrt{1-2z-3z^2}}{2z^2}$ (see [1]).

Table 1. Bounds on $\bar{\kappa}(\alpha)$ at $\alpha = 2, 4, \ldots, 10$ listed by the method used (bnd) and the order (σ). (a) For Motzkin paths: upper bounds are for $\sigma = 1, 2, 4$ and, as indicated, based on results of [2], direct renewal (DR) via equation (20) or transfer matrix (TM) via equation (16); and lower bounds (LB) are for order $\sigma = 398$ and based on equation (25). (b) For Dyck paths: upper bounds are for $\sigma = 1, 2, 4, 6, 8, 12$ and, as indicated, based on the results of [2], direct renewal (DR) or transfer matrix (TM); and lower bounds (LB) are for $\sigma = 400$.

	(a) Motzkin path bounds					(b) Dyck path bounds				
σ^{bnd}	$\alpha = 2$	4	6	8	10	$\alpha = 2$	4	6	8	10
$1^{[2]}$	1.457 98	2.379 63	3.369 25	4.367 85	5.367 66	0.788 47	1.225 01	1.717 01	2.215 93	2.715 79
2^{DR}	1.457 50	2.378 99	3.368 60	4.367 20	5.367 01	0.788 47	1.225 01	1.717 01	2.215 93	2.715 79
2^{TM}	1.457 17	2.378 62	3.368 24	4.366 84	5.366 65	0.788 47	1.225 01	1.717 01	2.215 93	2.715 79
4^{DR}	1.457 03	2.378 30	3.367 88	4.366 47	5.366 28	0.787 79	1.223 31	1.715 14	2.214 05	2.713 90
4^{TM}	1.456 88	2.378 18	3.367 77	4.366 36	5.366 17	0.787 79	1.223 31	1.715 14	2.214 05	2.713 90
6^{DR}						0.787 47	1.222 61	1.714 38	2.213 27	2.713 12
8^{DR}						0.787 29	1.222 26	1.713 99	2.212 87	2.712 72
12^{DR}						0.787 10	1.221 91	1.713 61	2.212 49	
σ^{LB}	1.364 45	2.364 45	3.364 45	4.364 45	5.364 45	0.710 24	1.210 24	1.710 24	2.210 24	2.710 24

Results for $p = 1/2$

Since the Morita approximations will yield the same limiting free energy for all $\alpha \leqslant \alpha_a$, the annealed critical point, we confine our discussion of the upper bounds to the region $\alpha > \alpha_a$ ($= \log 2$ and $\log 3$ for Motzkin and Dyck paths respectively). By [8], the Morita approximation bounds all exhibit critical points at α_a. This does not prohibit the transfer matrix bounds, which are upper bounds on Morita approximations, from having a critical point smaller than α_a. However, the transfer matrix bounds presented here do have critical points at α_a. The upper and lower bounds for various values of σ are shown for Motzkin paths in table 1 (a) and for Dyck paths in table 1 (b). It is interesting to note that, at least for $\sigma = 2, 4$, the transfer matrix upper bound is better than the corresponding direct renewal upper bound in the case of Motzkin paths, whereas for Dyck paths the two bounds are apparently (at least to nine decimal places) the same. The latter result is expected to be because the transfer matrix only overlaps at odd vertices for Dyck paths and these vertices cannot visit the surface. For Dyck paths the first-order moment Morita approximation in which even and odd vertices are distinguished (see [1, 2]) is exactly the same as the second-order direct renewal Morita approximation since the sets of constraints involved end up being equivalent.

In figure 1 we show how the lower bound on $\bar{\kappa}(\alpha)$ improves as σ increases, for Dyck paths at $\alpha = 6$. Similar behaviour is observed for Motzkin paths. In figure 2 we show our best upper and lower bounds on $\bar{\kappa}(\alpha)$ for the two models as a function of α.

We notice that the difference between the upper and lower bounds is extremely small at large α. For instance, for Dyck paths at $\alpha = 8$, $2.210\,24 \leqslant \bar{\kappa}(\alpha) \leqslant 2.212\,87$. This identifies the free energy very precisely, and much more precisely than one could hope to do by Monte Carlo or exact enumeration methods alone. The lower bound becomes less useful at smaller α, and especially as we approach α_a. The higher order Morita approximations improve only modestly over the first-order Morita upper bound but, at least for large α, this is because the first-order Morita approximation is already very good. For Dyck paths, for $\alpha \geqslant 6$, the higher order Morita approximation halves the gap between the upper and lower bounds, and we do almost as well for Motzkin paths.

For situations where the first-order Morita approximation is less effective (e.g. for the localization problem, deep inside the localized phase [2]) we expect that higher order Morita approximations will give a substantial improvement. This will be explored in a later paper.

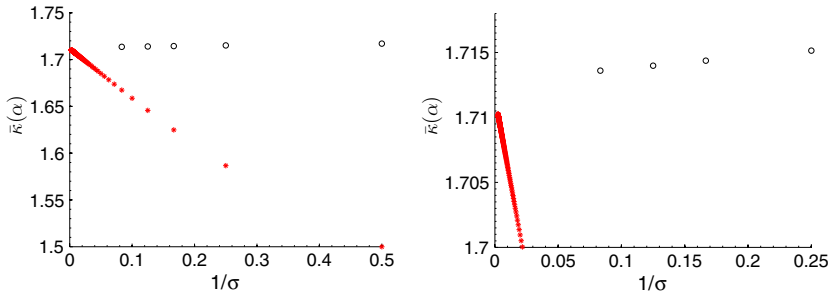

Figure 1. Dyck path upper bounds, $\kappa_U^{(\sigma)}(\alpha)$ ($\circ$) (from direct renewal) for $\sigma = 2, 4, 6, 8, 12$, and lower bounds, $\kappa_{L^*}^{(\sigma)}(\alpha)$ ($*$) for $\sigma = 2, 4, \ldots, 400$, on $\bar{\kappa}(\alpha)$ at $\alpha = 6$. A closer view is shown on the right. The lower bound becomes quite close to the upper bound as $\sigma \to \infty$, although at $\alpha = 6$ they need not have the same limiting value.

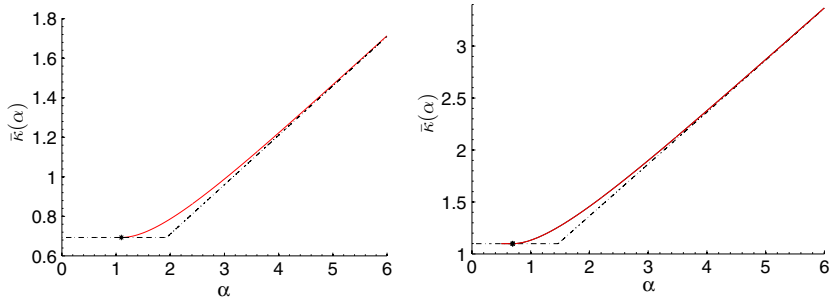

Figure 2. Comparison of best available upper (solid line) and lower (dashed line) bounds on $\bar{\kappa}(\alpha)$ as a function of α for Dyck paths (on the left with $\sigma = 8$ (DR) and $\sigma = 400$ (LB)) and Motzkin paths (on the right with $\sigma = 4$ (TM) and $\sigma = 398$ (LB)). The bounds are equal for $\alpha \leqslant \alpha_a$ ($*$).

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