The 'Allosteron' Model for Entropic Allostery of Self-Assembly: Supplementary Information

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In the main text we have shown that the distribution of polymer chains can be calculated using the equilibrium constant

$$K_N = \sqrt{\frac{w^{N-1}}{\det \hat{H}_N(K_\mathrm{c})}} \tag{1}$$

The crucial properties of this equilibrium constant that we used in the main text are the asymptotic limits

$$w \equiv \lim_{N\to\infty} K_{N+1}/K_N = \frac{1}{2} + K_\mathrm{c} + \frac{1}{2}\sqrt{1+4Kc}, \tag{2}$$

and

$$\lim_{K_\mathrm{c}\to\infty} K_N \propto \frac{1}{N}. \tag{3}$$

In this Supplementary Information we calculate K_N analytically, and show that these limits indeed hold. We finalise this section by providing an alternative expression for K_N that has the advantage of numerical stability.

Central in this derivation is the determinant $\det \hat{H}_N(K_\mathrm{c})$, which we calculate from the Hamiltonian of the chain of length N. This Hamiltonian is defined in the main text, and is in matrix notation given by

$$\mathcal{H} = \frac{1}{2}\kappa \mathbf{x}^\mathrm{T} \hat{H}_N \mathbf{x} - \epsilon(N-1), \tag{4}$$

with $\hat{H}_N$ is a $N \times N$ tridiagonal matrix given by [1]

$$\hat{H}_N \equiv \begin{pmatrix} 1+K_\mathrm{c} & -K_\mathrm{c} & 0 & \dots & \dots & 0 \\ -K_\mathrm{c} & 1+2K_\mathrm{c} & -K_\mathrm{c} & & & \vdots \\ 0 & -K_\mathrm{c} & 1+2K_\mathrm{c} & \ddots & & \vdots \\ \vdots & & \ddots & & -K_\mathrm{c} & 0 \\ \vdots & & & -K_\mathrm{c} & 1+2K_\mathrm{c} & -K_\mathrm{c} \\ 0 & \dots & \dots & 0 & -K_\mathrm{c} & 1+K_\mathrm{c} \end{pmatrix}. \tag{5}$$

In this equation κ is the internal spring constant of the monomer and K_c is a dimensionless coupling parameter that couples the monomers in the chain.

The determinant of this tridiagonal matrix may be calculated using the set of recurrence relations [2, 3]

$$p_1 = 1 + K_\mathrm{c}, \tag{6}$$

$$p_2 = 1 + 3K_\mathrm{c} + K_\mathrm{c}^2, \tag{7}$$

$$p_n = (1 + 2K_\mathrm{c})p_{n-1} - K_\mathrm{c}^2 p_{n-2}, \text{ for } 2 < n < N, \tag{8}$$

$$\det \hat{H}_N = (1 + K_\mathrm{c})p_{N-1} - K_\mathrm{c}^2 p_{N-2}, \tag{9}$$

and obeys the polynomial form

$$\det \hat{H}_N = \sum_{l=1}^{N+1} d_l^N K_\mathrm{c}^{l-1}, \tag{10}$$

of which the coefficients d_l^N we calculate below.

In order to do so, we also write p_n in a polynomial form

$$p_n = \sum_{l=1}^{n+1} c_l^n K_\mathrm{c}^{l-1}, \tag{11}$$

which after insertion into the recurrence relations above gives

$$p_n = c_1^{n-1} + (c_2^{n-1} + 2c_1^{n-1})K_\mathrm{c} + \sum_{l=3}^{n}(c_l^{n-1} + 2c_{l-1}^{n-1} - c_{l-2}^{n-2})K_\mathrm{c}^{l-1} + (2c_n^{n-1} - c_{n-1}^{n-2})K_\mathrm{c}^n, \tag{12}$$

for $2 < n < N$. The first three and last two coefficients are given by

$$c_1^n = 1, \;\; c_2^n = 2n - 1, \;\; c_3^n = (2n-3)(n-1), \tag{13}$$

and by

$$c_n^n = n(n+1)/2, \;\; c_{n+1}^n = 1. \tag{14}$$

Finally, we insert the so-obtained coefficients in Eq. (9) and obtain the determinant

$$\det \hat{H}_N = c_1^{N-1} + (c_2^{N-1} + c_1^{N-1})K_\mathrm{c} + \sum_{l=3}^{N}(c_l^{N-1} + c_{l-1}^{N-1} - c_{l-2}^{N-2})K_\mathrm{c}^{l-1} + (c_N^{N-1} - c_{N-1}^{N-2})K_\mathrm{c}^N. \tag{15}$$

Comparing this relation to Eq. (10) yields the polynomial coefficients we were after. We summarise these in Table I. Note that $c_{n+1}^n = 1$ for all n and hence that the term of order K_c^N vanishes. Since the other terms are finite, this confirms the limit $K_N \propto N^{-1}$ for large K_c in Eq. (3).

TABLE I: Values of coefficients d_N^i.

1	2	3	4	5	6	…	N
1	1	1	1	1	1	…	$d_N^1 = 1$
	2	4	6	8	10	…	$d_N^2 = 2N - 2$
		3	10	21	36	…	$d_N^3 = (2N-3)(N-2)$
			4	10	56	…	$\vdots$
				5	35	…	$\vdots$
					6		$\vdots$
						$\ddots$	d_N^i
							$\vdots$
							$d_N^N = N$

The next task is to show that in the long-chain limit Eq. (2) holds. We do this through a normal-mode analysis in which we express x_n as the discrete Fourier transform [4]

$$x_n = N^{-1/2} \sum_{p=0}^{N-1} X_p \mathrm{e}^{i2\pi pn/N}, \tag{16}$$

and insert it into the Hamiltonian of Eq. (4). The Hamiltonian then reads $\mathcal{H} = \sum_n \kappa x_i^2 + \sum_n \kappa_\mathrm{c}(x_i - x_{i-1})^2 + (N-1)\epsilon$, where the square term becomes

$$\sum_n |x_n|^2 = \sum_n N^{-1} \sum_{p,q} X_p X_q \mathrm{e}^{i2\pi(p+q)n/N} = \sum_{p,q} X_p X_q \delta_{pq} = \sum_p |X_p|^2. \tag{17}$$

In the last equality we make use of the fact that $x_{-p} = X_p^*$ for real functions, with X_p^* the complex conjugate of X_p. Similarly, we find that the square-gradient term becomes

$$\sum_n |x_n - x_{n-1}|^2 = \sum_n N^{-1} \sum_{p,q} X_p X_q \mathrm{e}^{i2\pi(p+q)n/N} \left(1 - \mathrm{e}^{-i2\pi pn/N}\right)\left(1 - \mathrm{e}^{-i2\pi qn/N}\right), \tag{18}$$

$$= \sum_p |X_p|^2 \left(1 - \mathrm{e}^{-i2\pi pn/N}\right)\left(1 - \mathrm{e}^{i2\pi pn/N}\right) \tag{19}$$

$$= 2\sum_p \left(1 - \cos\left(\frac{2\pi p}{N}\right)\right) |X_p|^2. \tag{20}$$

Hence, the long-chain limit of the Hamiltonian is given by

$$\mathcal{H} \approx \sum_{p=0}^{N-1} \kappa \left(1 + 2K_\mathrm{c}\left(1 - \cos\left(\frac{2\pi p}{N}\right)\right)\right) |X_p|^2. \tag{21}$$

In order to find the long-chain limit of the determinant, $\det \hat{H}_N$, we calculate the partition function $\mathcal{Z}$ from the Hamiltonian $\mathcal{H}$ and equal it to $\mathcal{Z} = \mathcal{Z}_1^N (\det \hat{H}_N)^{-1/2}$. Following these steps, we find

$$\det \hat{H}_N \approx \prod_{p=0}^{N-1} \left[1 + 2\left(1 - \cos\left(\frac{2\pi p}{N}\right)\right) K_\mathrm{c} \right]. \tag{22}$$

After taking the natural logarithm at both sides

$$\ln(\det \hat{H}_N) = \sum_{p=0}^{N-1} \ln \left[1 + 2\left(1 - \cos\left(\frac{2\pi p}{N}\right)\right) K_\mathrm{c} \right], \tag{23}$$

and after approximating the summation by an integral, we find

$$\ln(\det \hat{H}_N) \approx \frac{N-1}{2\pi} \int_0^{2\pi} \mathrm{d}x \ln\left[1 + 2(1-\cos(x))K_\mathrm{c}\right] = (N-1)\ln w. \tag{24}$$

From this relation we confirm Eq. (2), in which $w = 1/2 + K_\mathrm{c} + (1/2)\sqrt{1+4K_\mathrm{c}}$.

Now that we have shown that K_N has all asymptotic properties that we have claimed in the main text, we note that the expression in the main text to calculate K_N is numerically instable. This is caused by the fact that we have to take the products of exponentially big with exponentially small numbers. We remedy this by rephrasing the expression for the mass action as given in the main text into

$$X(\phi, T; \epsilon, K_\mathrm{c}) = \frac{a}{(1-a)^2}\sigma + \sum_{N=1}^{\infty} N(K_N - \sigma)a^N, \tag{25}$$

where $a \equiv \exp(-\beta\tilde{\mu})$ and where the series in the right-hand side of this equation converges for $N \gg \sqrt{K_\mathrm{c}}$. For those large values of N, K_N asymptotically decreases from unity to the constant cooperativity factor σ. Finally, we calculate the equilibrium constant as

$$K_\mathrm{N} = \left(\frac{w}{K_\mathrm{c}}\right)^{\frac{N-1}{2}} \left[\sum_{i=1}^{N} d_N^i K_\mathrm{c}^{i-N}\right]^{-1/2}. \tag{26}$$

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