

Theory and Experiment of Chain Length Effects on the Adsorption of Polyelectrolytes onto Spherical Particles: The Long and the Short of It — Supporting Information

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1 Calculations for the Mean-Field Lattice Model

1.1 Estimating the Number of Configurations

Here is a summary of the notation for the model system from Section 2.2 of the Main Paper.

Our model system has a single sphere in a solution of volume V . The model solution volume is filled by a simple cubic lattice, with the number of lattice sites in this volume denoted by V_{latt} . The surface of the sphere is covered by a two-dimensional lattice with coordination number q (that is, each site on the surface has exactly q neighboring sites). We assume that the distance between lattice sites corresponds to the distance between adjacent

monomers within a polymer. We assume that in equilibrium, every lattice site in the surface is covered by an adsorbed monomer. We also assume that in each polymer, either every monomer is adsorbed or else no monomer is adsorbed.

We assume that our model system has n_L “long” chains, each with $\mathcal{L}_L$ monomers, as well as n_S “short” chains, each with $\mathcal{L}_S$ monomers.

We define $n = \mathcal{L}_L/\mathcal{L}_S$, so that $\mathcal{L}_L = n\mathcal{L}_S$. We also define $B_{SL} = n_s/(n \cdot n_L)$, which represents the ratio of the densities (in g/L, say) of short chains to long chains in the system. It will turn out that the value of B_{SL} has little effect on the tendency for long chains to cover the spheres, unless it differs from 1 by several orders of magnitude.

We let S_{latt} be the number of lattice sites on the surface of one sphere. Then the maximum number of long chains that can adsorb onto the surface is $S_{latt}/\mathcal{L}_L$, which we call a . For simplicity, we assume that a is an integer.

We write $\mathcal{E}_j$ for the set of all configurations (of n_L long chains and n_S short chains) that have exactly j $\mathcal{L}_L$ -mers adsorbed onto the surface. The possible values of j are the integers from 0 to a . For each configuration in $\mathcal{E}_j$, it must be true that:

- (i) the number of $\mathcal{L}_L$ -mers in solution is $n_L - j$;
- (ii) the number of $\mathcal{L}_S$ -mers adsorbed onto the surface is $n(a - j)$; and
- (iii) the number of $\mathcal{L}_S$ -mers in solution is $n_S - n(a - j)$.

The full space of configurations in our model is $\cup_{j=0}^a \mathcal{E}_j$, which we call $\mathcal{E}$.

We also assume that there are many more long chains and many more long chains in the system than are need to cover the surface; i.e. we assume that n_L and n_S/n are each significantly larger than a . This does not conflict with the assumption that both sizes of chains form a dilute solution.

Since the energy of every configuration of $\mathcal{E}$ is exactly the same, the calculation of probabilities of events is equivalent to counting the configurations. In particular, writing $|\mathcal{A}|$ for

the number of configurations in a set $\mathcal{A}$, we have

$$\text{Probability that } j \text{ long polymers are adsorbed} = \frac{|\mathcal{E}_j|}{|\mathcal{E}|}, \quad (j = 0, 1, \dots, a).$$

Thus, to find the most likely number of $\mathcal{L}_L$ -mers (and $\mathcal{L}_S$ -mers) to be adsorbed onto the sphere, we need to find which of the sets $\mathcal{E}_j$ is largest.

In order to better comprehend the model we provide an illustration Figure 1 with much simpler values than what would be considered standard chain lengths in polymer science. We let each lattice point of area of one mer of PAA, be a square on the grid. Suppose a short chain is 25-mers and long chain is 75-mers and the colloid surface has 2025 available single mer sites. In the parameters of this model, we have $S_{latt} = 2025$, $\mathcal{L}_S = 25$, $\mathcal{L}_L = 75$, $n = 3$, and $a = 2025/75 = 27$. For simplicity, the figure shows each short chain filling a 5×5 square of lattice points, and each long chain fills three adjacent 5×5 squares. We can think of the model initially with the colloid surface sites fully covered exclusively by short chains, which in this concrete example requires 81 short chains (a). We then remove 3 short chains and replace them with our first long chain (b). We can think of continuing this process of adding more and more long chains in place of the equivalent number of mers in short chains (c,d,e) until we reach the maximum number of long chains (f).



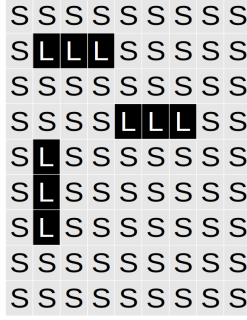
(a) $\mathcal{E}_0$: 0 long & 81 short chains on Colloid Surface



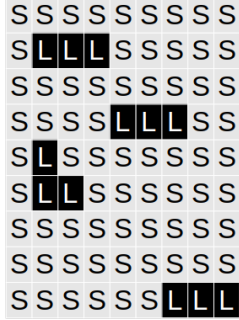
(b) $\mathcal{E}_1$: 1 long & 78 short chains on Colloid Surface



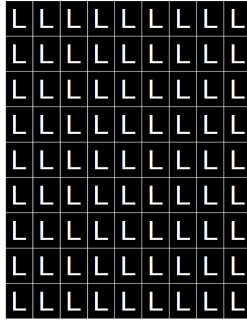
(c) $\mathcal{E}_2$: 2 long & 75 short chains on Colloid Surface



(d) $\mathcal{E}_3$: 3 long & 72 short chains on Colloid Surface



(e) $\mathcal{E}_4$: 4 long & 69 short chains on Colloid Surface



(f) $\mathcal{E}_{27}$: 27 long & 0 short chains on Colloid Surface

Figure 1: Schematic of configurations in $\mathcal{E}_j$ for $j = 0, 1, 2, 3, 4, 27$, with j long chains and $81 - 3j$ short chains adsorbed onto the colloid surface. Each S represents a 5×5 square of lattice points covered by one short chain; similarly, three contiguous L's are covered by one long chain.

In the Main Paper, we found that the number of configurations in $\mathcal{E}_j$ is

$$|\mathcal{E}_j| = \frac{\Psi_L^{n_L-j}}{(n_L-j)!} \frac{\Psi_S^{n_S-n(a-j)}}{(n_S-n(a-j))!} G(j) \quad (1)$$

where

$$\Psi_L = V_{latt} A_3 (\mathcal{L}_L)^{\gamma_3-1} \mu_3^{\mathcal{L}_L}, \quad \Psi_S = V_{latt} A_3 \mathcal{L}_S^{\gamma_3-1} \mu_3^{\mathcal{L}_S}, \quad (2)$$

and $G(j)$ is the number of ways to cover the surface with j $\mathcal{L}_L$ -mers and $n(a-j)$ $\mathcal{L}_S$ -mers. (Here A_3 , γ_3 , and μ_3 are constants related to self-avoiding walks.) Computing $G(j)$ is a hard combinatorial problem, so we use a mean-field approximation of the Flory-Huggins type, which we now explain (see also Section XII.1 of P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953).

For a particular choice of j , we want to know the number of ways to place j $\mathcal{L}_L$ -mers and $a(n-j)$ $\mathcal{L}_S$ -mers on the surface, without overlapping. We place one polymer at a time, starting with the long ones. Let $\tilde{w}_k$ be the number of ways to place the k^{th} $\mathcal{L}_L$ -mer on the surface, given that $(k-1)$ $\mathcal{L}_L$ -mers have already been placed. To begin with, there are $a\mathcal{L}_L - (k-1)\mathcal{L}_L$ available sites for the first monomer. Recall that q is the number of neighbors of each site in the surface lattice. In the absence of other polymers, there would be q choices for the second monomer in the chain, and $q-1$ choices for each monomer after that (here we are using the non-reversed walk model of a polymer instead of the fully self-avoiding model). But the number of choices should on average be reduced by the fraction of the surface that has already been covered. Thus, when we are trying to place the second monomer of our chain, there are $a\mathcal{L}_L - (k-1)\mathcal{L}_L - 1$ unoccupied sites, so each site has probability $[a\mathcal{L}_L - (k-1)\mathcal{L}_L - 1]/[a\mathcal{L}_L]$ of being available. Thus there are $q[a\mathcal{L}_L - (k-1)\mathcal{L}_L - 1]/[a\mathcal{L}_L]$ choices for the second monomer. Similarly, after i monomers of the current chain have been placed ($i \geq 2$), the fraction of the surface that has not been covered is $[a\mathcal{L}_L - (k-1)\mathcal{L}_L - i]/[a\mathcal{L}_L]$, so there are $(q-1)[a\mathcal{L}_L - (k-1)\mathcal{L}_L - i]/[a\mathcal{L}_L]$ choices

for the $(i + 1)^{th}$ monomer in this chain. We conclude that

$$\begin{aligned}
\tilde{w}_k &= [a\mathcal{L}_L - (k - 1)\mathcal{L}_L] \times q \left(\frac{a\mathcal{L}_L - (k - 1)\mathcal{L}_L - 1}{a\mathcal{L}_L} \right) \times \\
&\quad \prod_{i=2}^{\mathcal{L}_L-1} (q - 1) \left(\frac{a\mathcal{L}_L - (k - 1)\mathcal{L}_L - i}{a\mathcal{L}_L} \right) \\
&= \frac{[a\mathcal{L}_L - (k - 1)\mathcal{L}_L]!}{[a\mathcal{L}_L - k\mathcal{L}_L]!} q \frac{(q - 1)^{\mathcal{L}_L-2}}{(a\mathcal{L}_L)^{\mathcal{L}_L-1}} \\
&= \frac{[a\mathcal{L}_L - (k - 1)\mathcal{L}_L]!}{[a\mathcal{L}_L - k\mathcal{L}_L]!} a\mathcal{L}_L \frac{q}{(q - 1)^2} \left(\frac{q - 1}{a\mathcal{L}_L} \right)^{\mathcal{L}_L}. \tag{3}
\end{aligned}$$

Similarly, let $\tilde{u}_\ell$ be the number of ways to place the ℓ^{th} $\mathcal{L}_S$ -mer on the surface, given that $\ell - 1$ $\mathcal{L}_S$ -mers (or a total of $(\ell - 1)\mathcal{L}_S$ monomers) have already been placed. The same argument as for $\tilde{w}_k$ gives

$$\begin{aligned}
\tilde{u}_\ell &= \frac{[an\mathcal{L}_S - (\ell - 1)\mathcal{L}_S]!}{[an\mathcal{L}_S - \ell\mathcal{L}_S]!} q \frac{(q - 1)^{\mathcal{L}_S-2}}{(an\mathcal{L}_S)^{\mathcal{L}_S-1}} \\
&= \frac{[an\mathcal{L}_S - (\ell - 1)\mathcal{L}_S]!}{[an\mathcal{L}_S - \ell\mathcal{L}_S]!} an\mathcal{L}_S \frac{q}{(q - 1)^2} \left(\frac{q - 1}{an\mathcal{L}_S} \right)^{\mathcal{L}_S}. \tag{4}
\end{aligned}$$

We can now express the combinatorial quantity $G(j)$ in Equation (1) as

$$G(j) = \frac{\tilde{w}_1 \tilde{w}_2 \cdots \tilde{w}_j}{j!} \frac{\tilde{u}_{nj+1} \tilde{u}_{nj+2} \cdots \tilde{u}_{an}}{(n(a - j))!}. \tag{5}$$

To determine which value of j maximizes $|\mathcal{E}_j|$, we look at ratios of consecutive terms,

using Equations (1–5):

$$\begin{aligned}
\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|} &= \frac{\left(\frac{\Psi_L^{n_L-j-1}}{(n_L-j-1)!}\right) \cdot \left(\frac{\Psi_S^{n_S-n(a-j-1)}}{(n_S-n(a-j-1))!}\right)}{\left(\frac{\Psi_L^{n_L-j}}{(n_L-j)!}\right) \cdot \left(\frac{\Psi_S^{n_S-n(a-j)}}{(n_S-n(a-j))!}\right)} \frac{\tilde{w}_{j+1}}{\tilde{u}_{nj+1} \cdots \tilde{u}_{n(j+1)}} \\
&\quad \times \frac{j!(na-nj)!}{(j+1)!(na-nj-n)!} \\
&= \frac{\Psi_S^n}{\Psi_L} \frac{\tilde{w}_{j+1}}{\tilde{u}_{nj+1} \cdots \tilde{u}_{n(j+1)}} \left(\frac{n_L-j}{j+1}\right) \\
&\quad \times \frac{(na-nj) \cdots (na-nj-n+1)}{(n_S-na+nj+1) \cdots (n_S-na+nj+n)}. \tag{6}
\end{aligned}$$

From now on, we replace $\mathcal{L}_L$ by $n\mathcal{L}_S$. By Equation (2), we have

$$\frac{\Psi_S^n}{\Psi_L} = \frac{(V_{latt} A_3 \mathcal{L}_S^{\gamma_3-1})^{n-1}}{n^{\gamma_3-1}}. \tag{7}$$

From Equations (3) and (4), we find

$$\begin{aligned}
\frac{\tilde{w}_{j+1}}{\tilde{u}_{nj+1} \cdots \tilde{u}_{n(j+1)}} &= \left(\frac{(q-1)^2}{qan\mathcal{L}_S}\right)^{n-1} \times \frac{\frac{(an\mathcal{L}_S-jn\mathcal{L}_S)!}{(an\mathcal{L}_S-(j+1)n\mathcal{L}_S)!}}{\prod_{\ell=0}^{n-1} \frac{(an\mathcal{L}_S-(nj+\ell)\mathcal{L}_S)!}{(an\mathcal{L}_S-(nj+\ell+1)\mathcal{L}_S)!}} \\
&= \left(\frac{(q-1)^2}{qan\mathcal{L}_S}\right)^{n-1} \times 1. \tag{8}
\end{aligned}$$

Next we use the approximation $(c+1)(c+2) \cdots (c+m) \approx (c + \frac{m}{2})^m$ (essentially, replacing the geometric mean by the arithmetic mean) to obtain

$$\frac{(na-nj) \cdots (na-nj-n+1)}{(n_S-na+nj+1) \cdots (n_S-na+nj+n)} \approx \frac{[na-(j+\frac{1}{2})n]^n}{[n_S-na+nj+\frac{n}{2}]^n}. \tag{9}$$

Now, putting Equations (7–9) back into (6), we obtain

$$\begin{aligned}
\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|} &\approx [h(j)]^n \frac{n}{Kn^{\gamma_3-1}} \left(\frac{n_L-j}{j+1}\right), \quad \text{where} \tag{10} \\
K &= \frac{V_{latt}}{a\mathcal{L}_S} \frac{A_3 \mathcal{L}_S^{\gamma_3-1} (q-1)^2}{q} \quad \text{and} \quad h(j) = \frac{K(a-j-\frac{1}{2})}{n_S-n(a-j-\frac{1}{2})}.
\end{aligned}$$

For now, we ignore the sub-exponential terms in (10), and assume $|\mathcal{E}_{j+1}|/|\mathcal{E}_j|$ is well approximated by $h(j)^n$; the validity of this step is checked at the end of this subsection. Let j^* be the smallest value of j for which $h(j)$ is less than 1. As explained in the main paper, the quantity $|\mathcal{E}_j|$ is maximized at $j = j^*$, and j^* satisfies $h(j^*) \approx 1$, which can be rewritten as

$$a - j^* - \frac{1}{2} \approx \frac{n_S}{K + n}. \quad (11)$$

We observe that $K \gg n$; indeed, $V_{latt}/a\mathcal{L}_S n = V_{latt}/S_{latt} \gg 1$. Thus we can replace $K + n$ by K in the above, and omit the small term $\frac{1}{2}$, resulting in the approximation

$$1 - \frac{j^*}{a} \approx \left(\frac{n_S \mathcal{L}_S}{V_{latt}} \right) \left(\frac{q}{A_3 \mathcal{L}_S^{\gamma_3-1} (q-1)^2} \right). \quad (12)$$

Observe that the ratio $n_S \mathcal{L}_S / V_{latt}$ gives the concentration of monomers in solution corresponding to those appearing on the short chains only. The quantity in the second set of parentheses in Equation (12) is not large, since $q < (q-1)^2$ and $\gamma_3 > 1$. Assuming that the solution is fairly dilute, then we see that the right (and hence the left) side of (12) is small. That is, the value of j^* is close to a . See the Main Paper for further discussion and interpretation of Equation (12).

Notice that n_L does not appear in Equation (12). This is because in the approximation (10) for $|\mathcal{E}_{j+1}|/|\mathcal{E}_j|$, the variable n_L only appears outside the term that is exponential in n , and thus was omitted from our calculation. To check whether this omission could be significant, we return to the full approximation (10) and ask whether the true maximizing j could be significantly less than our j^* . To do this, we consider (10) at $j = j^* - 1$.

Since $h'(j) = -Kn_S/[n_S - n(a-j-\frac{1}{2})]^2$, equation (11) leads to

$$h'(j^*) \approx -\frac{(K+n)^2}{Kn_S} \approx -\frac{K}{n_S}$$

(using $K \gg n$ for the last step), which approximately equals the reciprocal of (11). The

values from Table 1 in the main paper produce $K/n_S = 1.0 \times 10^7/5562 = 1.8 \times 10^3$. More generally, from our argument following (12) that $a - j^* \ll a$, one finds that $|h'(j^*)| \gg 1/a$; for moderate values of a (order 10^1 in our case), this indicates that

$$h(j^* - 1) \approx h(j^*) - h'(j^*) \approx 1 + \frac{K}{n_S}$$

which is significantly greater than 1. Next, since j^* is close to a and since n_L is significantly larger than a , and recalling $B_{SL} = n_S/(n \cdot n_L)$, equation (10) at $j = j^* - 1$ becomes

$$\frac{|\mathcal{E}_{j^*}|}{|\mathcal{E}_{j^*-1}|} \approx \left(1 + \frac{K}{n_S}\right)^n \frac{n}{K n^{\gamma_3-1}} \left(\frac{n_L}{a}\right) \approx \left(1 + \frac{K}{n_S}\right)^n \frac{n_S}{K} \cdot \frac{1}{B_{SL} a n^{\gamma_3-1}}$$

With K/n_S and n both being large, we see that the only way that the above expression can be less than 1 is if B_{SL} is exponentially large in n . Hence, unless the density of short chains is orders of magnitude greater than the density of long chains, we conclude that $|\mathcal{E}_{j^*}|/|\mathcal{E}_{j^*-1}|$ is much bigger than 1, i.e. that $|\mathcal{E}_{j^*}| \gg |\mathcal{E}_{j^*-1}|$, which confirms that j^* as initially calculated is indeed a valid approximation for the most likely number of long chains adsorbed.

1.2 Interpretations about $|\mathcal{E}_j|$ from ratio $\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|}$

Figure 2 graphically portrays that as one increases the number of adsorbed long chains in a scenario of full surface coverage of the colloid, the ratio of probabilities decreases and eventually crosses the threshold of being equal to one ($\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|} = 1$). This threshold is representative of two consecutive configurations being equal in value and thus the divided differences of $|\mathcal{E}_{j+1}|$ and $|\mathcal{E}_j|$ being equal to zero for $j = j^*$. The fact that ratio is decreasing tells us that the differences $|\mathcal{E}_{j+1}| - |\mathcal{E}_j|$ are positive when $j < j^*$ and are negative when $j > j^*$. These statements indicate the existence of a maximal critical point at j^* .

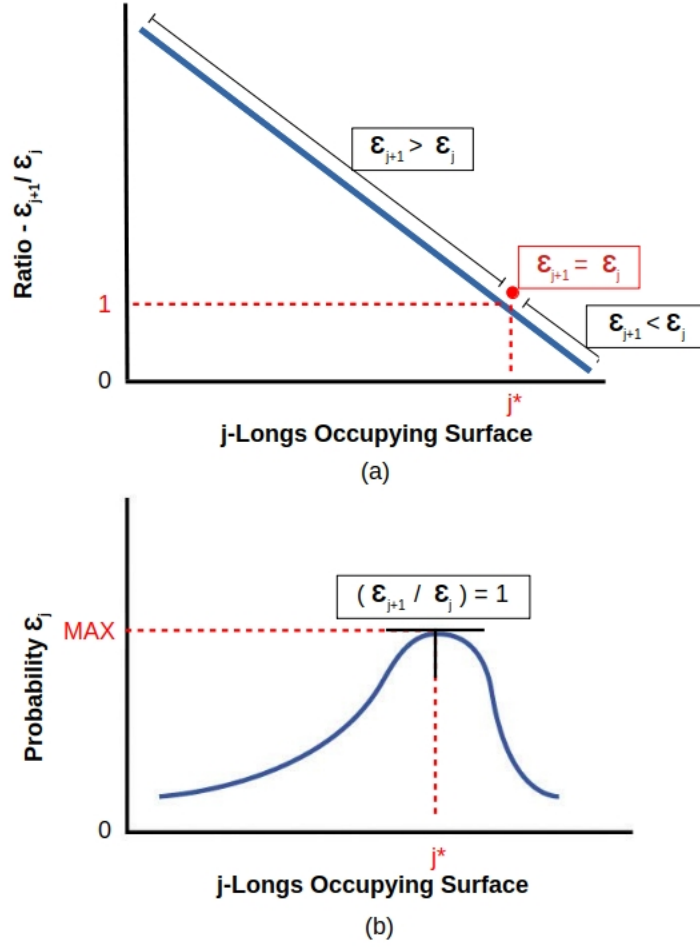


Figure 2

1.3 Derivation of Boltzmann Entropy from Ratio Approximation

Initially, we take the natural logarithm of our ratio $\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|}$. Then we expand the expression using known logarithmic properties and multiply the whole expression by the Boltzmann Constant.

$$\begin{aligned}
 k_B \cdot \log \left(\frac{|\mathcal{E}_{j+1}|}{|\mathcal{E}_j|} \right) &= k_B \cdot (\log |\mathcal{E}_{j+1}| - \log |\mathcal{E}_j|) \\
 &= (k_B \cdot \log |\mathcal{E}_{j+1}|) - (k_B \cdot \log |\mathcal{E}_j|)
 \end{aligned}$$

This is evidently just the difference of Boltzman entropies of j and $j + 1$,

$$= S_{j+1} - S_j = \Delta S_{j \rightarrow j+1}.$$