

Supporting Material: Monte Carlo Simulation and Molecular Theory of Tethered Polyelectrolytes

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1 Monte Carlo Chain Regrowth Move in a Finite Geometry

Before beginning this study, it was hypothesized that very strong counterion condensation would necessitate the use of a specialized move for the chain regrowth. If the counterions are strongly condensed there is a high local density in the region where the chain is to be regrown, complicating regrowth. Though overlap may be avoided with Rosenbluth biasing, there is still a tendency for the chain to regrow in a position highly similar to the chain just removed, since that position gave order to the local counterion density. Therefore, a specialized Rosenbluth/distance-bias move that regrows both the chain and its associated counterions was developed in the expectation that it might be more effective at exploring configuration space. The proof of detailed balance is provided here, and also an analysis of the move's effectiveness.

1.1 Proof of Detailed Balance

A complete polyelectrolyte chain regrowth step consists of two distinct steps, each with subparts. The first step is the deletion of one entire chain, completed one monomer at a time, with the deletion of any required counterions at each monomer deletion step. The second step is the reverse process: the addition of one entire chain, completed one monomer at a time, with the addition of any required counterions at each monomer addition step. The only requirement is that the entire move be electroneutral.

Consider two configurations A and B, each containing N_g grafted chains of N monomers. Each chain requires N_{ion} counterions for electroneutrality. The statistical mechanics of a move from a state A to a state B, where A and B differ in the configuration of one chain and its counterions is presented here.

The polymer to be deleted is selected at random, so the probability of deletion is given by,

$$P_{rand}^{mer-} = \frac{1}{N_g} \quad (1)$$

The j^{th} counterion to be deleted is selected from a set of $N_{ion}N_g + 1 - j$ remaining counterions with a probability given by,

$$P_{bias}^{ion-}(j) = \frac{\exp[-\beta Q_b u_j^{Aj}]}{\sum_{i=1}^{N_{ion}N_g+1-j} \exp[-\beta Q_b u_i^{Aj}]} \quad (2)$$

where u_j^{Aj} is the electrostatic energy of the j^{th} counterion selected for removal with the j^{th} unit of charge on the removed chain, which is in configuration A. u_i^{Aj} is the electrostatic energy of the i^{th} counterion in the system with the j^{th} unit of charge on the removed chain. The strength of the bias is modulated using Q_b , a factor used to multiply the electrostatic energy, which is computed as the interaction of two monovalent particles. For example, if a charged chain of length $N = 5$ has the charge sequence $[1 \ 2 \ 0 \ 0 \ 0]$, then, when removing the 3^{rd} counterion the interaction energy with the 2^{nd} bead is used. If the counterion were instead to be selected for deletion at random, the probability would be given by,

$$P_{rand}^{ion-}(j) = \frac{1}{N_{ion}N_g + 1 - j} \quad (3)$$

The position selected using Eq. 2 selects counterions for removal with respect to a single monomer. If N_{trial} hypothetical positions for removed counterions

are nominated using Eq. 2, then the probability of selecting one favorable position from among them is given by

$$P_{bias}^{trial-}(j) = \frac{\exp[-\beta u_j^{Aj}]}{\sum_{m=1}^{N_{trial}} \exp[-\beta u_m^{Aj}]} \quad (4)$$

where u_j^{Aj} is the electrostatic energy of the j^{th} removed counterion with the monomers and associated counterions of chain A not yet removed. u_m^{Aj} is the electrostatic energy of the m^{th} hypothetical trial counterion with the monomers and associated counterions of chain A not yet removed. If one of the hypothetical trials were selected at random, the probability would be given by,

$$P_{rand}^{trial-} = \frac{1}{N_{trial}} \quad (5)$$

These hypothetical counterion removal trials are the required analogues to real counterion placement trials that will be attempted during chain regrowth. They improve chain regrowth because the energetics with the entire electroneutral subsystem of a chain and its counterions can be taken into account.

The second step is chain regrowth. The first bead is always placed at the designated tethering location. The probability of selecting a direction for the j^{th} new monomer is given by,

$$P_{bias}^{mer+}(j) = \frac{\exp[-\beta u_j^{Bj}]}{\sum_{k=1}^Z \exp[-\beta u_k^{Bj}]} \quad (6)$$

where u_j^{Bj} is the electrostatic energy of the j^{th} monomer with monomers and their associated counterions inserted thus far. u_k^{Bj} is the electrostatic energy of a monomer in the k^{th} possible position with the monomers and their associated counterions inserted thus far. If the direction of growth were selected at random,

$$P_{rand}^{mer+} = \frac{1}{Z} \quad (7)$$

The position for the j^{th} added counterion is nominated from a set of V positions with a probability given by,

$$P_{bias}^{ion+}(j) = \frac{\exp[-\beta Q_b u_j^{Bj}]}{\sum_{i=1}^V \exp[-\beta Q_b u_i^{Bj}]} \quad (8)$$

where u_j^{Bj} is the electrostatic energy of the j^{th} unit of charge on chain B with the selected j^{th} counterion. u_i^{Bj} is the electrostatic energy of the j^{th} unit of charge on chain B with a counterion in the i^{th} position.

The position selected using Eq. 2 may be occupied or be placed in a position energetically unfavorable to the inserted chain as a whole. If instead N_{trial} positions are nominated using Eq. 2 but one unoccupied position among those nominated positions is selected, then the probability of selecting one unoccupied position is given by

$$P_{bias}^{trial+}(j) = \frac{\exp[-\beta u_j^{Bj}]}{\sum_{m=1}^{N_{trial}} \exp[-\beta u_m^{Bj}]} \quad (9)$$

where u_j^{Bj} is the electrostatic energy of the j^{th} trial counterion with all previously successfully inserted monomers and counterions for chain B. u_m^{Bj} is the electrostatic energy of the m^{th} trial counterion with all previously successfully inserted monomers and counterions for chain B. If instead one of the trials is selected at random, the probability is given by,

$$P_{rand}^{trial+} = \frac{1}{N_{trial}} \quad (10)$$

If the counterions are added without distance bias and without avoidance of occupied sites, but truly at random, the probability is given by,

$$P_{rand}^{ion+} = \frac{1}{V} \quad (11)$$

Because the probability of regrowing the entire polyelectrolyte is the product of all the individual event probabilities, the probability of going from configuration A to B is given by,

$$\alpha(A \rightarrow B) = \prod_{j=1}^{N_{ion}} \frac{P_{bias}^{ion-}(j)}{P_{rand}^{ion-}(j)} \prod_{j=1}^{N_{ion}} \frac{P_{bias}^{trial-}(j)}{P_{rand}^{trial-}(j)} \prod_{j=2}^N \frac{P_{bias}^{mer+}(j)}{P_{rand}^{mer+}(j)} \prod_{j=1}^{N_{ion}} \frac{P_{bias}^{ion+}(j)}{P_{rand}^{ion+}(j)} \prod_{j=1}^{N_{ion}} \frac{P_{bias}^{trial+}(j)}{P_{rand}^{trial+}(j)} \quad (12)$$

All five terms are ratios of the odds of an event to the odds of that same event if it all events of its kind were equally probable. The events are 1) counterion selection for removal among all counterions with 2) adjustment for respect to entire removed system 3) direction selection for growth of new chain 4) counterion position nomination for addition and 5) selection among those positions with respect to added system.

The condition of detailed balance is given by,

$$N(A)\alpha(A \rightarrow B)acc(A \rightarrow B) = N(B)\alpha(B \rightarrow A)acc(B \rightarrow A) \quad (13)$$

where $N(A)$ is the probability of being in state A, α is the probability of a transition between states, and acc is the probability of accepting a trial move to a new state. Rearrangement gives,

$$\frac{acc(A \rightarrow B)}{acc(B \rightarrow A)} = \frac{N(B)\alpha(B \rightarrow A)}{N(A)\alpha(A \rightarrow B)} \quad (14)$$

Recognizing that $\alpha(B \rightarrow A)$ is derived similarly as Eq. 12, substituting values of $N(state)$ and α , and then performing some cancellation of terms, it can be written,

$$\begin{aligned} \frac{acc(A \rightarrow B)}{acc(B \rightarrow A)} &= \exp[-\beta(U_B - U_A)] \prod_{j=2}^N \frac{\sum_{k=1}^Z \exp[-\beta u_k^{Bj}]}{\sum_{k=1}^Z \exp[-\beta u_k^{Aj}]} \\ &\times \prod_{j=1}^{N_{ion}} \frac{\sum_{i=1}^V \exp(-\beta Q_b u_i^{Bj}) \sum_{i=1}^{N_{ion} N_g + 1 - j} \exp(-\beta Q_b u_i^{Aj})}{\sum_{i=1}^V \exp(-\beta Q_b u_i^{Aj}) \sum_{i=1}^{N_{ion} N_g + 1 - j} \exp(-\beta Q_b u_i^{Bj})} \\ &\times \prod_{j=1}^{N_{ion}} \frac{\sum_{m=1}^{N_{trial}} \exp(-\beta u_m^{Bj})}{\sum_{m=1}^{N_{trial}} \exp(-\beta u_m^{Aj})} \end{aligned} \quad (15)$$

The product over monomers is Rosenbluth biasing [1]. The product over the counterions with the sums over the volume is a distance bias. The product over the counterions with the sums over the number of trials is, in practice, incorporated into the Rosenbluth bias term as the chain is grown. The acceptance criteria that fulfills the requirements of detailed balance is:

$$acc(A \rightarrow B) = \min(1, \text{R.H.S. of Eq. 15}) \quad (16)$$

Two complications are inherent in the ready calculation of Eq. 15, both due to the finiteness of the geometry. One complication is that the calculation of the electrostatic energy in a system periodic in two dimensions and finite in a third is cumbersome. The second is that the sums over V cannot be removed from the product as they would in a fully periodic geometry. In a fully periodic geometry, regardless of a monomer's coordinate, the sum of its interactions over every lattice site within V is unchanging. In a geometry

finite in z the value of the sum is dependant on which layer the monomer (around which ions are inserted) is located. Nonetheless, the precomputation of these sums is possible because the precomputation of the energy is possible when a lattice is used. Just as a lookup table is used to store all possible $\exp[-\beta Q_b u(r_{ij})]$, one is also used to store the $L_z - 1$ possible sums over V .

1.2 Analysis

The computer code for this study was developed in such a way that the regrowth move could be carried out in the following ways:

1. Chain alone without Rosenbluth
 2. Chain alone with Rosenbluth
 3. Chain with Rosenbluth together with counterions with no distance biasing
 4. Chain with Rosenbluth together with counterions with distance biasing
- Method 4 is the one just presented with all terms and $Q_b \neq 0$. In method 3, $Q_b = 0$. In method 2, the 2^{nd} product in Eq. 15 disappears. In method 1, all the products of Eq. 15 disappear and only simple unbiased NVT MC remains. The methods are listed in order from lowest acceptance rate to highest acceptance rate. Though acceptance rates improve as more complex methods are employed, trial moves take longer. It was found that method 2 was the fastest overall for the systems studied. Though acceptance rates improved with method 4, the additional complexity and computer time required for the distance-biasing repositioning of the counterions during a chain regrowth offset the gain. However, at a few high charge strength, high-density conditions, for example, $\xi = 2.86$, $\sigma_g = 0.04$, method 4 had a slight edge. Method 1 was used to check the results of the other methods. In this work, method 2 was used primarily.

2 Implementation and Testing

During each step of MC algorithm development comparisons to existing literature results were made to demonstrate correct function. Comparison of our MC algorithm's results to Chakabarti and Toral's MC results [2] for an uncharged chain of length $N = 49$ and $\sigma_g = 0.04$ (Fig. 1a of Ref. [5]) showed agreement.

To test the functionality and correctness of our implementation of the 2D Ewald algorithm of Heyes *et al.* [3] (HBC), the electrostatic energy of two

charge arrangements corresponding exactly to those examined by Widmann and Adolf [4] were calculated, and the results were compared. The first test arrangement consists of a checkerboard pattern of 25 charges in the same plane and a 26th particle raised $z = 0.2L_z$ above the central particle (of opposite sign). The second test arrangement consists of 100 particles arranged in a checkerboard, where 99 lie in the same plane and one has been elevated to $z = 0.5L_z$. Widmann reports that the electrostatic energies of these two systems are $U_{Coulomb} = -86.56586$ and $U_{Coulomb} = -792.5880$, respectively. Our calculations agree with these results to all decimal places.

Several tests were then carried out to demonstrate the correct functioning of the Ewald sum lookup table creation scheme. At the beginning of each simulation the electrostatic energy of the initial geometry is computed using the HBC method. A precomputed lookup table of the electrostatic energy is then created. The energy of the same initial particle configuration is then found using the lookup tables and compared to the whole-system results. If the results are not the same, the simulation is terminated.

Random grafting was used to create the initial geometries used in the MC calculations. For each grafting density, typically five different random sets of tethering locations were used. The average density profile observed during production runs from each configuration are averaged together to calculate the density profile of a “random” tethering. The estimated error of the density in a layer is the standard deviation of the density in that same layer as found using different starting tethering locations.

3 Tabulated Results

Table 1: Grafted layer heights found using Monte Carlo simulation for charged wall systems of $\sigma_{\pm} = +.2, +.1, -.1, -.2, -.4$, and -0.8 .

σ_g	$\xi^* = 2.86$	2.0	1.0	0.5	0.2	0.1
$\sigma_{\pm} = +.2$						
0.08	3.04(1)	3.255(8)	3.51(1)	3.63(1)	3.67(1)	3.610(2)
$\sigma_{\pm} = +.1$						
0.08	3.60(2)	3.79(2)	3.96(2)	4.02(1)	3.98(1)	3.864(4)
$\sigma_{\pm} = -.1$						
0.01		4.47(1)	4.69(3)	4.59(2)		
0.04		4.27(1)	4.46(2)	4.476(8)	4.33(1)	
0.08	4.11(1)	4.274(9)	4.42(1)	4.46(1)	4.405(7)	4.253(3)
$\sigma_{\pm} = -.2$						
0.01		3.0(1)	4.76(1)	4.74(2)		
0.04		4.535(7)	4.546(3)	4.61(2)	4.493(7)	
0.08	4.147(8)	4.342(6)	4.523(6)	4.579(2)	4.53(1)	4.387(3)
$\sigma_{\pm} = -.4$						
0.04		4.29(2)	4.63(2)	4.73(3)	4.67(1)	
0.08	4.11(1)	4.345(7)	4.58(1)	4.68(1)	4.679(9)	4.575(3)
$\sigma_{\pm} = -.8$						
0.08	4.10(2)	4.37(1)	4.641(9)	4.761(2)	4.803(2)	4.773(2)

Table 2: Grafted layer heights found using the molecular theory for charged wall systems at $\sigma_g = 0.08$. Figures are significant to all decimal places.

σ_{\pm}	$\xi^* = 5.0$	2.0	1.0	0.5	0.2	0.1
+ .2	2.767	3.253	3.502	3.613	3.652	3.635
+ .1	3.167	3.620	3.840	3.920	3.911	3.818
- .1	3.625	4.061	4.267	4.332	4.291	4.162
- .2	3.711	4.155	4.368	4.445	4.416	4.290
- .4	3.844	4.265	4.481	4.575	4.578	4.476
- .8	3.981	4.381	4.596	4.705	4.747	4.690

Table 3: Grafted layer heights found using the molecular theory for uncharged wall systems of $N = 10$ and $N = 20$. Figures are significant to all decimal places.

σ_g	$\xi^* = 5.0$	2.0	1.0	0.5	0.2	0.1
$N = 10$						
0.01	3.077	3.885	3.905	3.738	3.387	3.129
0.04	3.236	3.837	4.039	4.057	3.925	3.718
0.08	3.501	3.899	4.101	4.163	4.125	4.005
$N = 20$						
0.01	5.117	7.175	7.417	7.334	6.921	6.348
0.04	5.542	6.945	7.451	7.586	7.555	7.389
0.08	6.198	7.101	7.570	7.749	7.801	7.745

Table 4: Grafted layer heights found using Monte Carlo simulation for uncharged wall systems of $N = 10$

ξ	$\langle h \rangle$	Std. Dev.
$\sigma_g = 0.01$		
4.00	3.589	0.030
2.86	3.849	0.031
2.00	4.054	0.032
1.00	4.155	0.029
0.50	3.958	0.010
0.20	3.510	0.004
0.10	3.181	0.011
0.05	2.961	0.013
$\sigma_g = 0.04$		
5.00	3.308	0.024
2.86	3.869	0.028
2.00	4.058	0.029
1.00	4.215	0.028
0.50	4.196	0.020
0.20	4.015	0.008
0.10	3.762	0.007
$\sigma_g = 0.08$		
2.86	3.988	0.023
2.00	4.149	0.026
1.00	4.271	0.024
0.50	4.285	0.017
0.20	4.224	0.007
0.10	4.067	0.005
0.05	3.823	0.011

Table 5: Grafted layer heights found using Monte Carlo simulation for uncharged wall systems of $N = 20$

ξ	$\langle h \rangle$	Std. Dev.
$\sigma_g = 0.01$		
1.67	7.591	0.061
1.43	7.737	0.075
1.00	7.922	0.061
0.50	7.827	0.051
0.20	7.266	0.028
0.10	6.582	0.008
0.05	5.724	0.006
$\sigma_g = 0.04$		
1.33	7.668	0.023
1.00	7.786	0.029
0.50	7.889	0.027
0.20	7.807	0.019
0.10	7.590	0.014
0.05	7.172	0.019
$\sigma_g = 0.08$		
1.00	7.844	0.048
0.50	7.935	0.037
0.20	7.909	0.063
0.10	7.850	0.050
0.05	7.676	0.009
0.02	7.188	0.014

References

- [1] M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **23**, 356 (1955).
- [2] A. Chakrabarti and R. Toral, *Macromolecules* **23**, 2016, (1990).
- [3] D. M. Heyes, M. Barber, and J. H. R. Clarke, *J. Chem. Soc. Faraday Trans. II* **73**, 1485 (1977).
- [4] A. H. Widmann and D. B. Adolf, *Computer Phys. Comm.* **107**, 167 (1997).