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Soft Matter

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Influence of Charge Sequence on the Adsorption of Polyelectrolytes to Oppositely-Charged Polyelectrolyte Brushes: Supplementary Information

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S1 Average Minimum Distance between the graft monomers

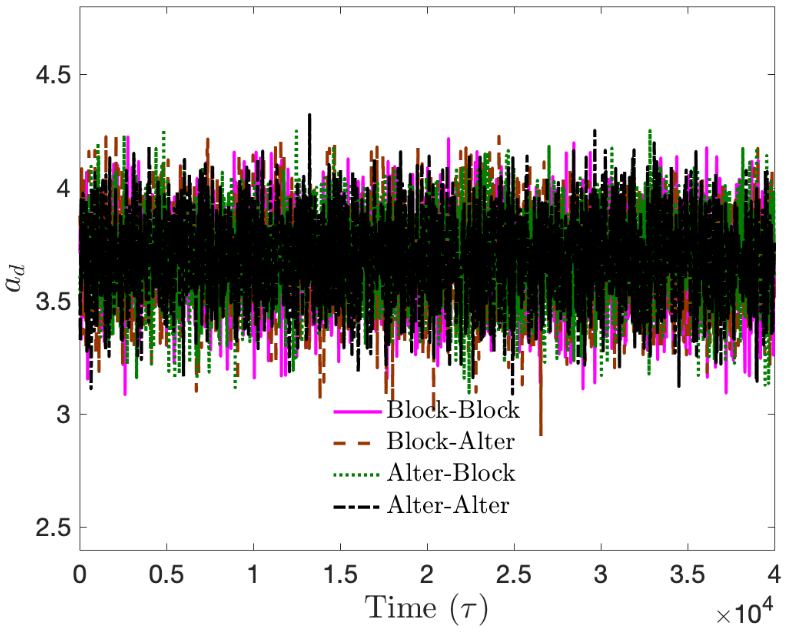

Fig. S1 Time evolution of the average minimum distance between the grafted monomersa_d for N_{pa} = 64.

Fig. S1 displays the average minimum distance between the grafted monomers a_d as a function of time. To compute a_d we visit each grafted monomer at each time instant and then compute the distance between it and all the other monomers. We then compute a_d as the ensemble average of the minimum for such distances at each time instant. It can be seen that $\langle a_d \rangle$ is close to 3.7 σ irrespective of the polyelectrolyte architecture. This distance is more than the Debye length, suggesting that there is no clumping of monomers.

S2 Radial Distribution Function

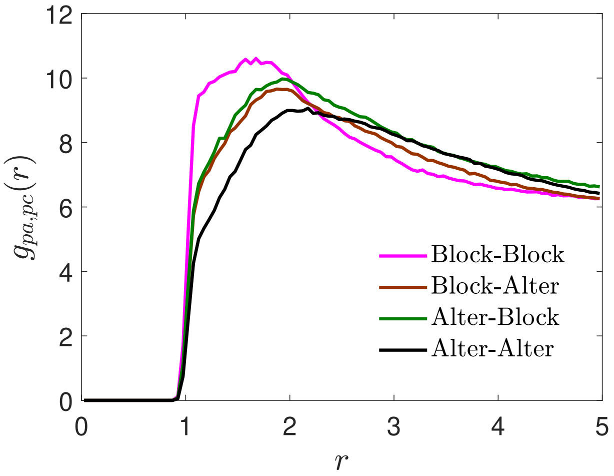

Fig. S2 Radial distribution function ($g_{pa,pc}(r)$) for between polycations and polyanions for different brush/free macromolecule architecture at N_{pa} = 64.

S3 Internal Energy

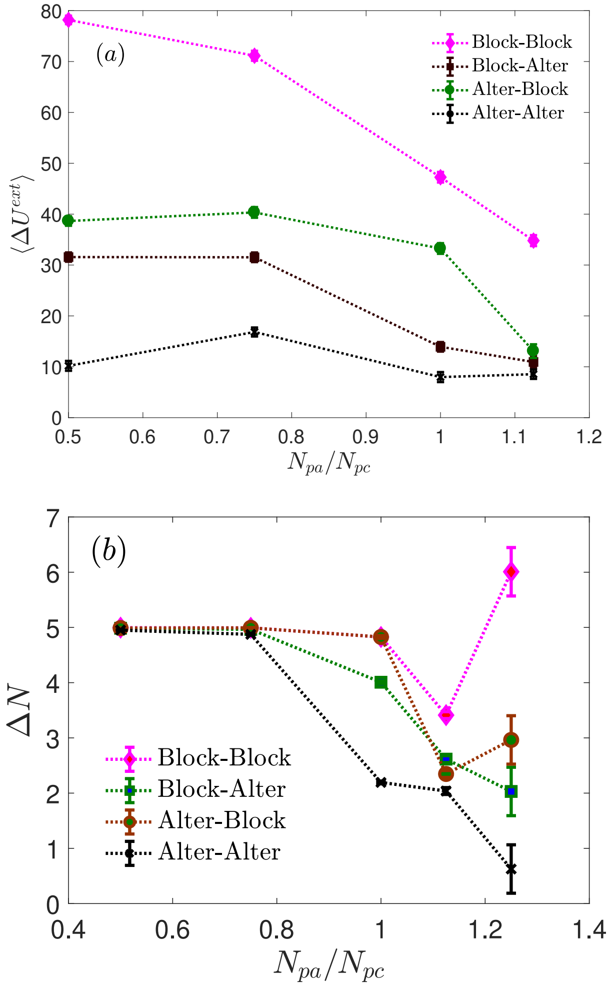

Fig. S3 (a) Change in total internal energy (sum of potential and kinetic energies) of the system; (b) Difference in number of chains at equilibrium between biased and unbiased simulations.

S4 Free Energy

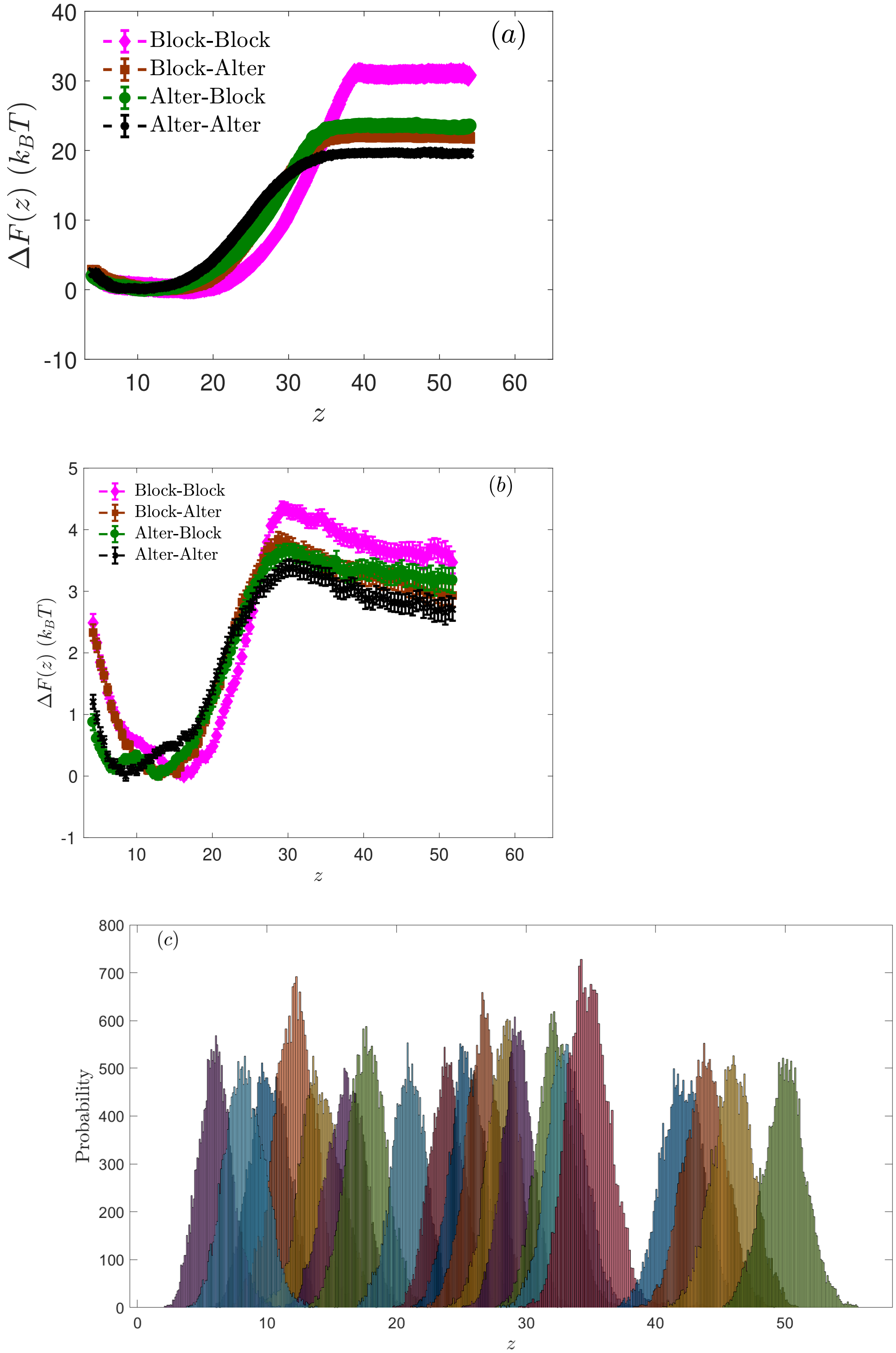

Fig. S4 Free energy computed from WHAM analysis along the reaction coordinate for (a) $N_{pa} = 32$, (b) $N_{pa} = 80$. (c) Histogram for the simulations performed for a block polycation-block polyanion architecture at N_{pa} = 32.

S5 Parameters for Umbrella Sampling and Bootstrapping Methods

We divide the histogram obtained from each umbrella sampling simulation into 100 bins for computing the potential of mean force. Therefore, we will have exactly 100 points for each of the computed potential of mean force. For all the free energy calculations, we use a relative tolerance of 0.001 for the change in the maximum value of each of the free energy in each window of the histogram.

For bootstrapping, we utilize 1000 Monte Carlo trials for each simulation with a correlation time of 20.0τ. Each of these trials will thus generate new set of data points with values of the position of the center of mass of the biased chain chosen at random and are at least 20.0τ apart (correlation time), where where τ is the Lennard-Jones time unit.

S6 Brush Height and Debye Length

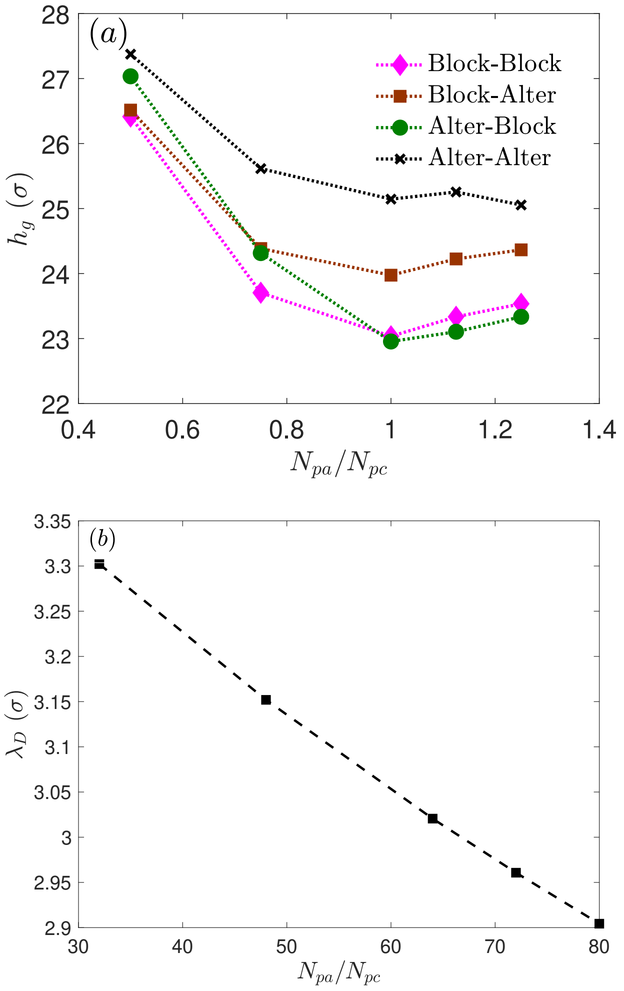

Fig. S5 (a) Brush height as a function of N_{pa}/N_{pc}. (b) Debye length as a function of N_{pa}/N_{pc}.

S7 Error Analysis

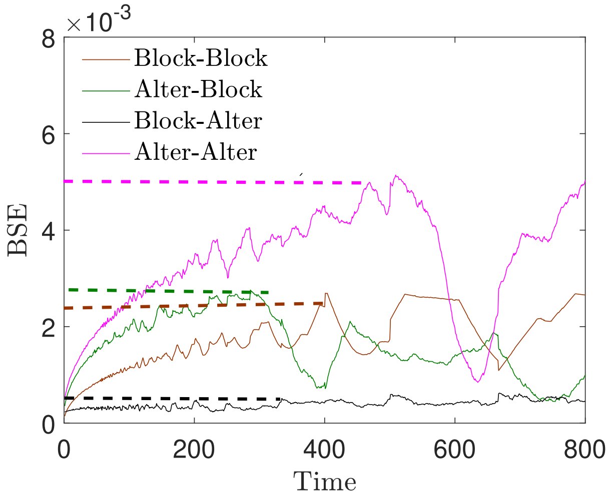

Fig. S6 Block standard error (BSE) for f_{ads} for different charge sequences at $N_{pa}/N_{pc} = 1$. The dashed lines denote the error for each charge sequence. Time is in shown in reduced units.

For all the measured quantities, an ensemble average of the corresponding quantity is reported. To obtain the statistical uncertainty in the data, we use a block averaging error estimation method.[1] The standard error of the mean ($\Sigma_{\bar{x}}$) for a quantity x is computed using

$$\Sigma_{\bar{x}} = \Sigma_n / \sqrt{M}, \tag{1}$$

where M corresponds to the number of statistically uncorrelated segments, and consists of n snapshots in each segment with a sample standard mean of Σ_n. Fig. S6 displays a representative figure of the error analysis of the adsorbed polymer chain fraction at $N_{pa} = 64$. The values utilized for the error bars are indicated in dotted lines.

For free energy calculations using the umbrella sampling method alone, a boot–strapping method is utilized with a correlation time of 20.0 τ, where τ represents the time in Lennard-Jones units. For the free energy analysis, although a Boltzmann weighted free energy was utilized to compute the bias free energy, the propagation of errors is computed using $\sqrt{e^2_{\mathrm{bulk}} + e^2_{\mathrm{min}(\Delta \mathrm{F_c})}}$, where e_{bulk} is the standard deviation of the free energy values of the bulk and $e_{\mathrm{min}(\Delta \mathrm{F_c})}$ is the error bar obtained from WHAM analysis for the point where the bias free energy is the minimum.

The values obtained for the errors in free energy by the method above are subsequently used to compute the errors in change in entropy using $e_s = \sqrt{\left(e^2_f + e^2_u\right)}$, where e_s, e_f and e_u denote the error in change in entropy, change in free energy and change in internal energy respectively for a given system.

S8 Equilibrium Conformations

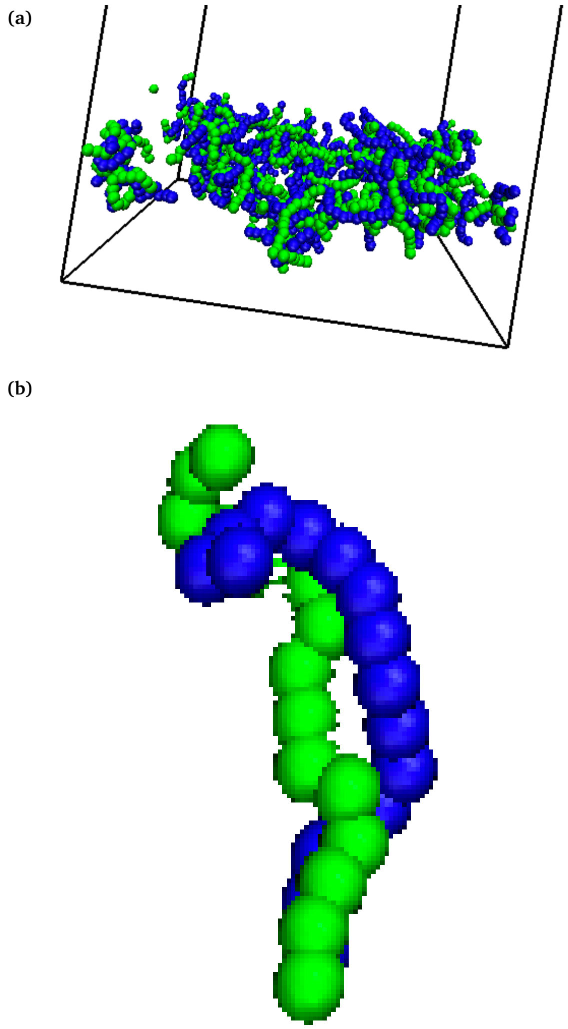

Fig. S7 (a) Snapshot of a block-block system with N_{pa} = 72. Legends: green – charged polycations, blue – charged polyanions. Only the grafted region is shown here. (b) Zoomed version of the snapshot. The density profiles in Figs. 5 and 6 of the main text are averaged over several configurations, the snapshots should be treated only as an anecdotal representation.

S9 Charge Density Profiles at Low Polyanion Concentrations

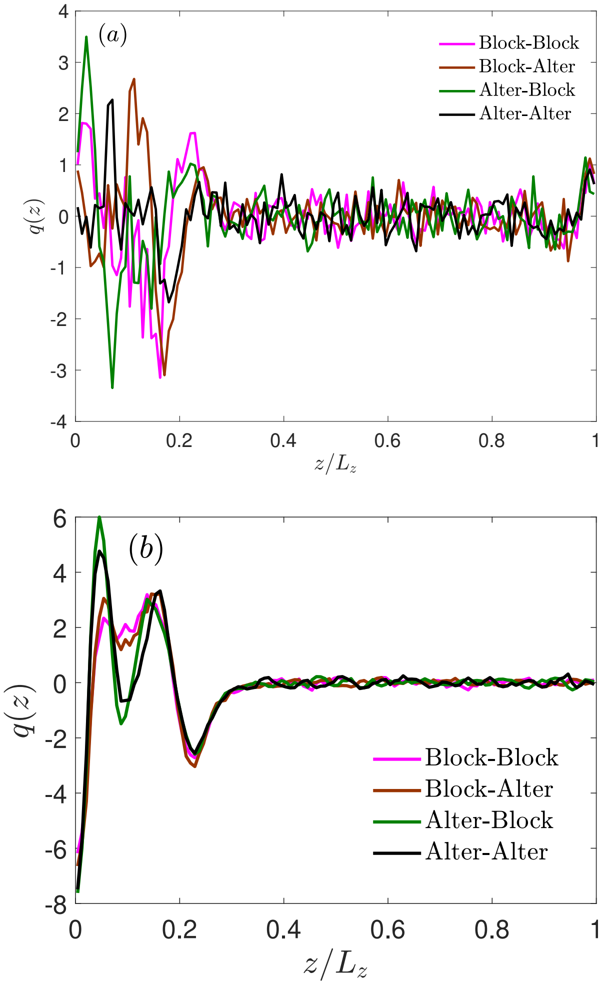

Fig. S8 Original (before smoothing) charge density profile as a function of distance from the interface for $N_{pa} = 100$. (b) Charge density profile (after three point moving average) as a function of distance from the interface for $N_{pa} = 32$.

Notes and references

1 A. Grossfield and D. M. Zuckerman, *Annu. Rep. Comput. Chem.*, 2009, **5**, 23 – 48.