Supplementary Information:
All-atom Molecular Dynamics Simulations Showing the Absorption of Small Organic Molecules in Water-Solvated Polyelectrolyte Brush Layers

Leon A. Smook[&][*], Raashiq Ishraaq[#], Tanmay Sarkar Akash[#],
and Sissi de Beer[&], and Siddhartha Das[#]

February 2024

[&]Department of Molecules & Materials, MESA+ Institute, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands,
[#]Department of Mechanical Engineering, University of Maryland, College Park, MD 20742, USA

Contents

[*]Email: l.a.smook@utwente.nl

S1 OPLS-AA Force field parameters

In our Molecular Dynamics simulations, we use the OPLS-AA force field for the lactone (Table S1) and poly(acrylic acid) molecules (Table S2). We use SPC/E water as a solvent. The counterion is sodium.

Table S1: OPLS-AA Parameters: Lactone

Atoms

Number	Element	Type	Charge
1	C	C	0.44
2	C	Ct	-0.25
3	C	Ct	-0.23
4	C	Ct	0.00
5	O	Os	-0.34
6	O	O	-0.39
7	H	Hc	0.15
8	H	Hc	0.15
9	H	Hc	0.12
10	H	Hc	0.12
11	H	Hc	0.12
12	H	Hc	0.12

Atom types

Type	Epsilon	Sigma	Mass
C	0.11	3.75	12.01
Ct	0.07	3.50	12.01
Os	0.14	2.90	16.00
O	0.21	2.96	16.00
Hc	0.03	2.50	1.01

Bonds

Type1	Type2	K	r0
C	Ct	317.00	1.52
C	O	570.00	1.23
C	Os	214.00	1.33
Ct	Ct	268.00	1.53
Ct	Hc	340.00	1.09
Ct	Os	320.00	1.41

Potentials

$U_{\text{bond}} = K(r - r_0)$

$U_{\text{angle}} = K(\theta - \theta_0)$

$U_{\text{dihedral}} = \sum_{1-5} A_n \sin^{n-1}(\psi)$

$U_{\text{pair}} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$

10*

Dihedrals

Type1	Type2	Type3	Type4	A1	A2	A3	A4	A5
c	ct	ct	ct	-1.01	-1.73	0.46	1.17	0.00
c	ct	ct	hc	-0.04	0.11	0.00	-0.15	0.00
c	os	ct	ct	-0.53	-1.24	0.13	0.84	0.00
c	os	ct	hc	0.10	-0.30	0.00	0.40	0.00
ct	c	os	ct	7.46	2.33	-5.12	0.00	0.00
ct	ct	c	o	0.00	0.00	0.00	0.00	0.00
ct	ct	c	os	-0.28	0.83	0.00	-1.11	0.00
ct	ct	ct	hc	0.15	-0.45	0.00	0.60	0.00
ct	ct	ct	os	0.69	-0.14	0.50	1.33	0.00
ct	os	c	o	5.12	0.00	-5.12	0.00	0.00
hc	ct	c	o	0.00	0.00	0.00	0.00	0.00
hc	ct	c	os	0.07	-0.20	0.00	0.26	0.00
hc	ct	ct	hc	0.15	-0.45	0.00	0.60	0.00
hc	ct	ct	os	0.23	-0.70	0.00	0.94	0

Angles

Type1	Type2	Type3	K	Theta0
C	Ct	Ct	63.00	111.10
C	Ct	Hc	35.00	109.50
C	Os	Ct	83.00	116.90
Ct	C	O	80.00	120.40
Ct	C	Os	81.00	11.40
Ct	Ct	Ct	58.35	180.00
Ct	Ct	Hc	37.50	110.70
Ct	Ct	Os	50.00	109.50
Hc	Ct	Hc	33.00	107.80
Hc	Ct	Os	35.00	109.50
O	C	Os	83.00	123.40

Table S2: OPLS-AA Parameters: Poly(acrylic acid)

Atoms

Atom	Element	Type	Charge
1	C	C1	-0.12
2	C	C2	-0.16
3	C	C	0.7
4	C	Ce	-0.18
5	O	O	-0.8
6	O	O	-0.8
7	H	H	0.06
8	H	H	0.06
9	H	H	0.06
10	Na	Na	1
11	H	H	0.06
12	H	H	0.06
13	H	H	0.06

Atom types

Type	Epsilon	Sigma	Mass
C1	0.066	3.5	12.011
C2	0.066	3.5	12.011
C	0.105	3.75	12.011
Ce	0.066	3.5	12.011
O	0.21	2.96	15.999
H	0.03	2.5	1.008
Na	0.352642	2.1595	22.99

Potentials

$$U_{\text{bond}} = K(r - r_0)$$
$$U_{\text{angle}} = K(\theta - \theta_0)$$
$$U_{\text{dihedral}} = \sum_{1-4} \tfrac{1}{2} K_n \left[1 + (-1)^{n-1} \cos(n\psi)\right]$$
$$U_{\text{pair}} = 4\epsilon \left[\left(\tfrac{\sigma}{r}\right)^{12} - \left(\tfrac{\sigma}{r}\right)^{6}\right]$$

14*

Bonds

Type1	Type2	K	r0
C1	H	340	1.09
C1	C2	268	1.529
C2	H	340	1.09
Ce	H	340	1.09
C2	C	317	1.522
Ce	C1/C2	268	1.529
C	O	656	1.25

Impropers

Type1	Type2	Type3	Type4	K	xi0
C2	O	C	O	21	0

Angles

Type1	Type2	Type3	K	theta0
H	C1	H	33	107.8
H	C1	C2	37.5	110.7
C1	C2	H	37.5	110.7
C1/C2	Ce	H	37.5	110.7
H	Ce	H	33	107.8
H	C2	C	35	109.5
O	C	O	80	126
C1	C2	C	63	111.1
Ce	C2	C	63	111.1
C1	C2	C1	58.35	112.7
C1	C2	Ce	58.35	112.7
C2	C	O	70	117
Ce	C2	H	37.5	110.7
C2	C1	C2	58.35	112.7

Dihedrals

Type1	Type2	Type3	Type4	K1	K2	K3	K4
H	C1	C2	H	0	0	0.300	0
C	C1	C2	C	0	0	-0.100	0
H	C1	C2	C1	0	0	0.300	0
H	C1	C2	Ce	0	0	0.300	0
H	C2	C	O	0	0	0	0
H	C2	Ce	H	0	0	0.300	0
C1	C2	C	O	0	0.820	0	0
C1	C2	C1	C2	1.300	-0.500	0.200	0
H	Ce	C2	C1	0	0	0.300	0
Ce	C2	C	O	0	0.820	0	0
C2	C1	C2	C	-3.185	-0.825	0.493	0
C2	C1	C2	Ce	1.300	-0.050	0.200	0
H	C2	C1	C2	0	0	0.300	0
H	Ce	C2	C	0	0	-0.100	0

S2 Brush height convergence

To check equilibration of the system we monitor the brush height of each system (Figure S1). In each save frame (every 2 ps), we compute the instantaneous brush height by finding the z-coordinate below which 99% of the polymer atoms are residing. We observe that brush heights settle around an equilibrium value after approximately 7 to 8 ns. Hence, the 5 ns trajectories used for analysis at the end of each simulation have equilibrated in terms of brush height.
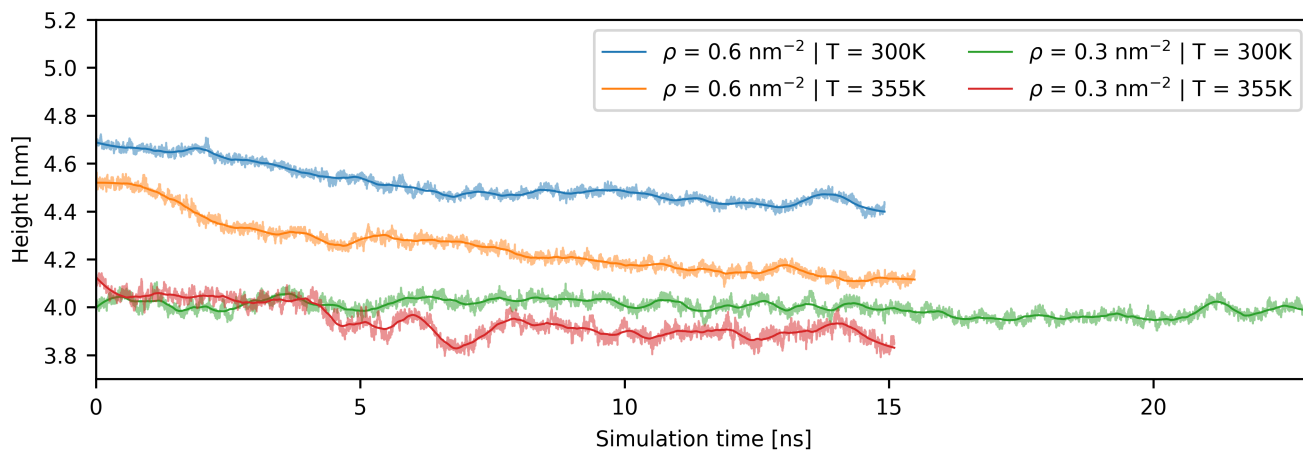

Figure S1: Instantaneous brush height of poly(acrylic acid) brushes in a mixture of water and lactone. The dark line is smoothed using a second order Savitsky-Golay filter with a window size of 501.

To ensure sufficient sampling and confirm equilibration, we compute the autocorrelation function of the instantaneous height during the production run (Figure S2). Based on these autocorrelation functions $C(t)$, we can compute an autocorrelation decay time in line with Refs. [2] and previous work [1, 3]. We find that this decay time varies between 0.14 and 0.32 ns, so our 5 ns production run is at least one order of magnitude longer in time, indicating sufficient sampling of the system.
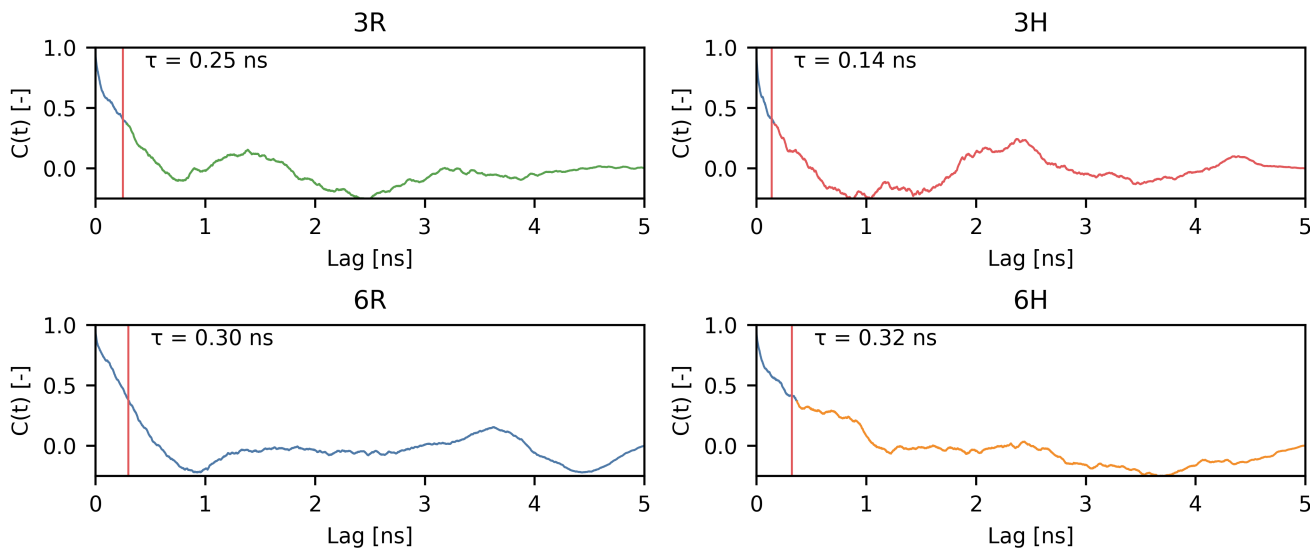

Figure S2: Autocorrelation functions of the production run for the instantaneous height for the four systems.

S3 Lactone absorption along trajectory

Not only the brush height should equilibrate before the production run, the number of lactone molecule should also reach an equilibrium value. In Figure S3 we present the instantaneous lactone adsorption inside the poly(acrylic acid) brush. This value is computed by counting the number of lactone molecules with a center of mass below the instantaneous brush height and normalizing this value by the area of the brush. We observe that the adsorption starts to fluctuate around an equilibrium value between 6 to 8 ns. Hence, the 5 ns trajectories used for analysis represent equilibrium conditions.
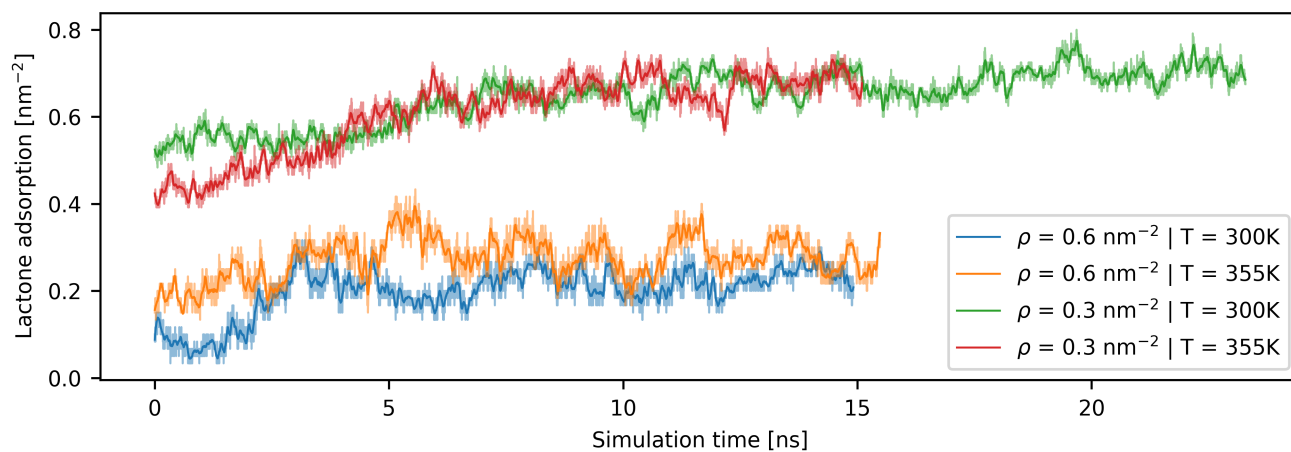
Figure S3: Instantaneous adsorption of lactone molecules in poly(acrylic acid) brushes. The dark line is smoothed using a second order Savitsky-Golay filter with a window size of 501.

S4 Water structure of non-solvating water

We compare the water structure of free and solvating water molecules in our manuscript. We use an internal reference based on water molecules that are at least 4Å removed form any lactone atom. To text the validity of this internal reference, we performed an additional simulation in a lactone-free system. Figure S5 shows that the structure in the lactone-free and lactone-containing simulations are nearly identical.
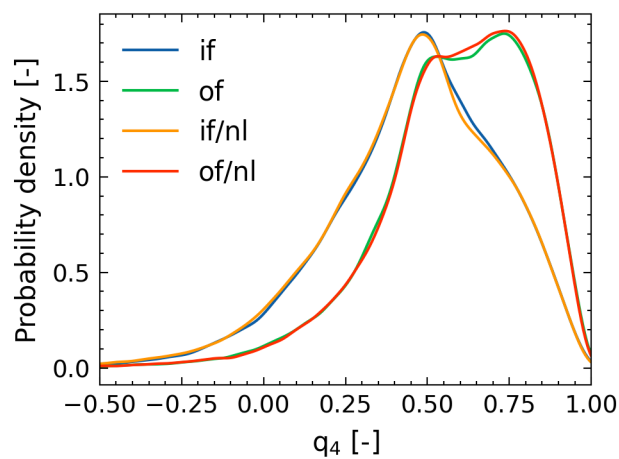

Figure S4: Comparison of the structure of non-solvating water in the poly(sodium acrylate) brushes 0.6 nm^{-2} brush at 300 K for a system with lactones (if–inside the brush, of–outside the brush) and without lactones (if/nl–inside the brush, of/nl–outside the brush).

S5 Water coordination number

The q-parameter does not take into account the coordination number of water as always the four closest water molecules are used in the analysis. We additionally studied the coordination of water as a function of distance from the central water molecule. This analysis shows that the coordination number of water is slightly lower in the solvating group (is/os) than the non-solvating group (if/of). Nevertheless, the distance to reach a coordination number of 4 increases in the order of < if ∼ is, while the structure increase in the different order of < os < is ∼ if. Hence, this coordination change cannot fully explain changes in the q-parameter.
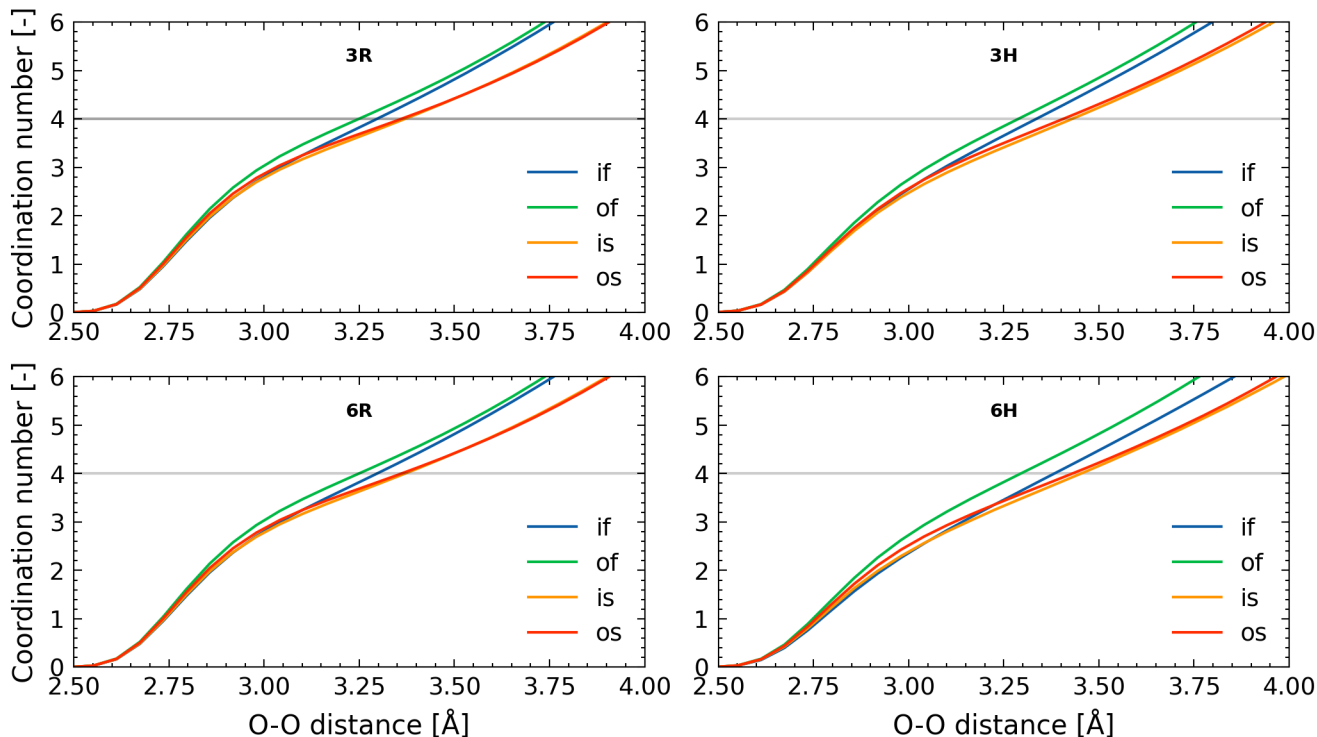

Figure S5: Solvation number as distance from central water oxygen for the four different cases studied.

References

1. Ishraaq, R. & Das, S. All-Atom Molecular Dynamics Simulations of Cationic Polyelectrolyte Brushes in the Presence of Halide Counterions. *Macromolecules* **57,** 3037–3046. ISSN: 0024-9297 (2024).

2. Murat, M. & Grest, G. S. Structure of a grafted polymer brush: a molecular dynamics simulation. *Macromolecules* **22,** 4054–4059. ISSN: 0024-9297 (1989).

3. Sachar, H. S. *et al.* Densely Grafted Polyelectrolyte Brushes Trigger "Water-in-Salt"-like Scenarios and Ultraconfinement Effect. *Matter* **2,** 1509–1521. ISSN: 2590-2385 (2020).