ASSOCIATED CONTENT

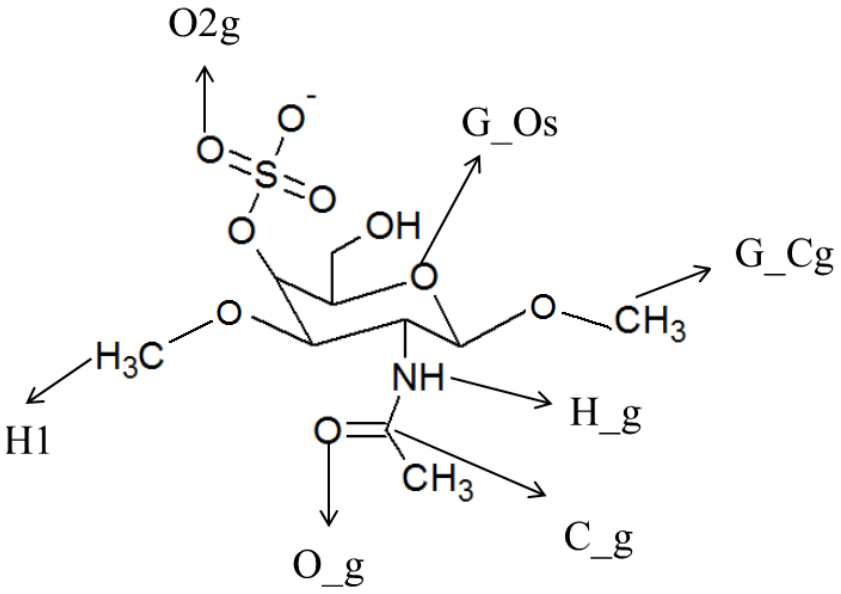
Supporting Information. Potential parameters used in this work. Adsorption positions of GlcA and GalNAc-4s on to the dry surfaces. Average structures of the monomers in water. RDF graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

Table S1 Parameters for HAP and water.

Species		**Charge (e)**		**Spring constant (ev Å^{-2})**
		core	shell	
Ca		+2.000	-	-
P		+1.180	-	-
Phosphate O (O2)		+0.587	-1.632	507.4000
Hydroxyl O (O1)		+0.90	-2.300	74.92038
H		+0.400	-	-
HW		+0.417		
OW		-0.8340		
Buckingham Potential		**A (ev)**	**ρ (Å)**	**C (ev Å^6)**
Ca—$O2_{shell}$		1550.00	0.29700	0.0
Ca—$O1_{shell}$		1250.00	0.3437	0.0
$O2_{shell}$—$O2_{shell}$		16372.00	0.2130	3.47
$O1_{shell}$—$O1_{shell}$		22764.00	0.1490	6.97
$O2_{shell}$—$O1_{shell}$		22764.00	0.1490	4.92
H—$O2_{shell}$		312.000	0.2500	0.0
H—$O1_{shell}$		312.000	0.2500	0.0
Ca—OW		1237.00	0.29700	0.0
H—OW		413.10	0.2500	0.0
$O1_{shell}$—OW		21836.50	0.1490	17.14
$O2_{shell}$—OW		12022.600	0.2130	12.09
$O1_{shell}$—HW		325.300	0.2500	0.0
$O2_{shell}$—HW		413.100	0.2300	0.0
Three-Body Potential		**k (ev rad-2)**		**Θ_0**
$O2_{core}$— P — $O2_{core}$		1.322626		109.47
HW— OW — HW		8.672821		104.52
Morse potential	**D (ev)**	**α(Å^{-1})**		**r_0 (Å)**
P—$O2_{core}$	3.4700	2.030		1.600
H—$O1_{core}$	7.0525	3.1749		0.9485
Harmonic Potential		**k (ev Å^{-2})**		**r_0 (Å)**
OW—HW		47.960699		0.957

Table S2. Charges of the GAGs

GalNac-4S	
Specie	**Charge (e)**
H1	0.000
G_Cg	0.264
H1	0.000
H1	0.000
G_Os	-0.458
G_Cg	0.305
H2	0.000
G_Os	-0.408
G_Cg	0.136
H1	0.000
G_Cg	0.353
H1	0.000
H1	0.000
G_Oh	-0.714
G_Ho	0.427
G_Cg	0.253
H1	0.000
G_Os	-0.632
S	1.577
O2g	-0.732
O2g	-0.732
O2g	-0.732
G_Os	0.152
H1	0.000
G_Os	-0.484
G_Cg	0.234
H1	0.000
H1	0.000
H1	0.000
G_Cg	0.544
H1	0.000
G_Ng	-0.686
H_g	0.254
C_g	0.586
O_g	-0.564
G_Cg	0.056
H1	0.000
H1	0.000
H1	0.000



GlcA	
Specie	**Charge (e)**
H1	0.000
G_Cg	0.264
H1	0.000
H1	0.000
G_Os	-0.458
G_Cg	0.251
H2	0.000
G_Os	-0.413
G_Cg	0.075
H1	0.000
C_g	0.893
O2g	-0.818
O2g	-0.818
G_Cg	0.267
H1	0.000
G_Os	-0.552
G_Cg	0.248
H1	0.000
H1	0.000
H1	0.000
G_Cg	0.266
H1	0.000
G_Oh	-0.701
G_Ho	0.403
G_Cg	0.411
H1	0.000
G_Oh	-0.740
G_Ho	0.422

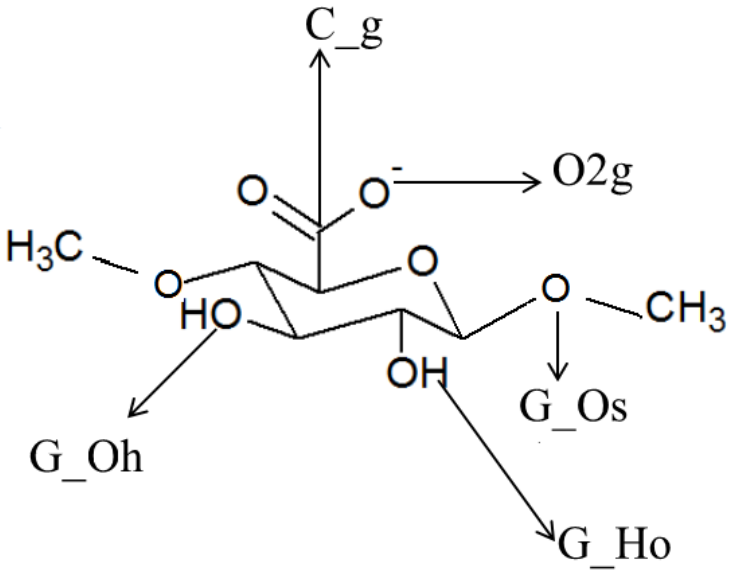


Table S3. Additional non-bonded parameters

Van der Waals Parameters		
Specie	**r_i (Å)**	**ε_i (eV/23.0451mol)**
Ca	1.7131	0.4598
P	2.1000	0.2000
O2	1.6612	0.2100
O1	1.7210	0.2104
H	0.0000	0.0000

For the interactions between HAP surfaces and the GAGs we also have used a Lennard-Jones. The Lennard-Jones can be expressed as:

$$U = \varepsilon_{ij}\left[\left(\frac{R_{ij}}{r}\right)^{12} - \left(\frac{R_{ij}}{r}\right)^{6}\right]$$

where $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $R_{ij} = r_i + r_j$

Table S4 Hydroxyapatite lattice parameters and bulk modulus (Hill)

Parameter	**de Leeuw et al**	**$\%\Delta_{DFT}$**	**$\%\ \Delta_{exp}$**
a=b (Å)	9.42	1.69	-0.02
c (Å)	6.88	0.72	-0.07
α=β (°)	90.0	0.0	0.0
γ (°)	120.0	0.0	0.0
V (Å^3)	528.61	4.27	-0.09
B_H	89.75	-14.88	-7.97

Table S4 shows a comparison of the cell parameters and Bulk modulus of HAP obtained with this model and more computationally expensive DFT method (Bhat et al., 2014), and experimental data (Katz and Ukraincik, 1971)

Bhat, S. S., Waghmare, U. V. & Ramamurty, U. *Crystal Growth & Design,* 2014, 14**,** 3131-3141.
Katz, J. L. & Ukraincik, K.. Journal of Biomechanics, 1971, 4, 221-227.

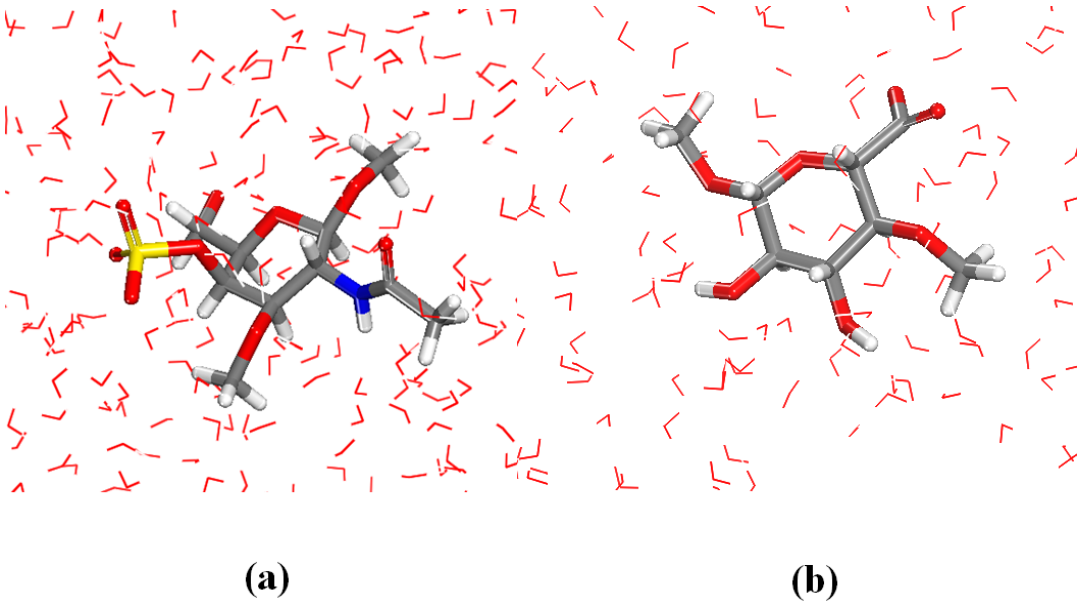


Figure S4. Monomers of Ch4S in water. **(a)** GalNAc-4S **(b)** GlcA. Oxygen in red, Hydrogen in white, Sulfur in yellow, Nitrogen in blue, Carbon in gray.

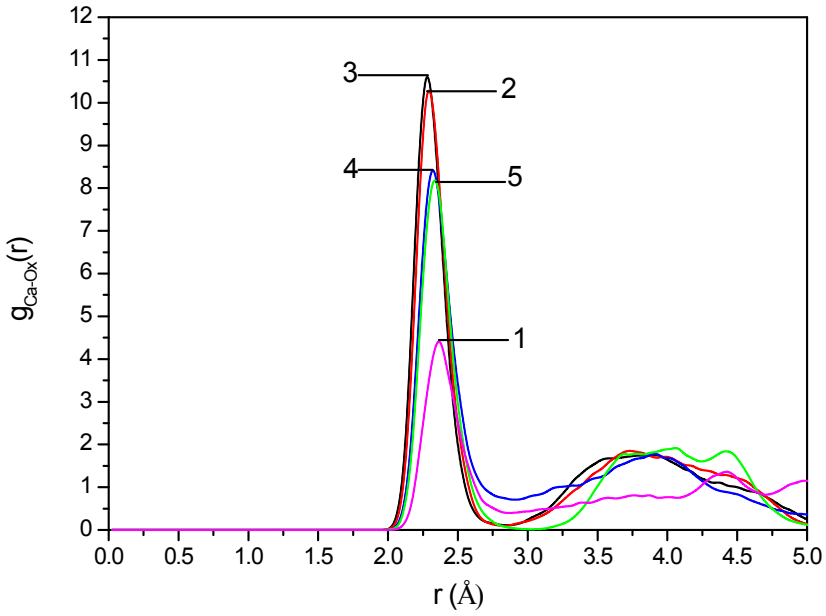


Figure S7. RDF Ca^{2+}—$O_{carboxylate}$ for GlcA on the flat (01Error!0) surface. All studied configurations showed intense interactions of carboxylate oxygen atoms with calcium, where configuration 2 shows the strongest binding to the surface.

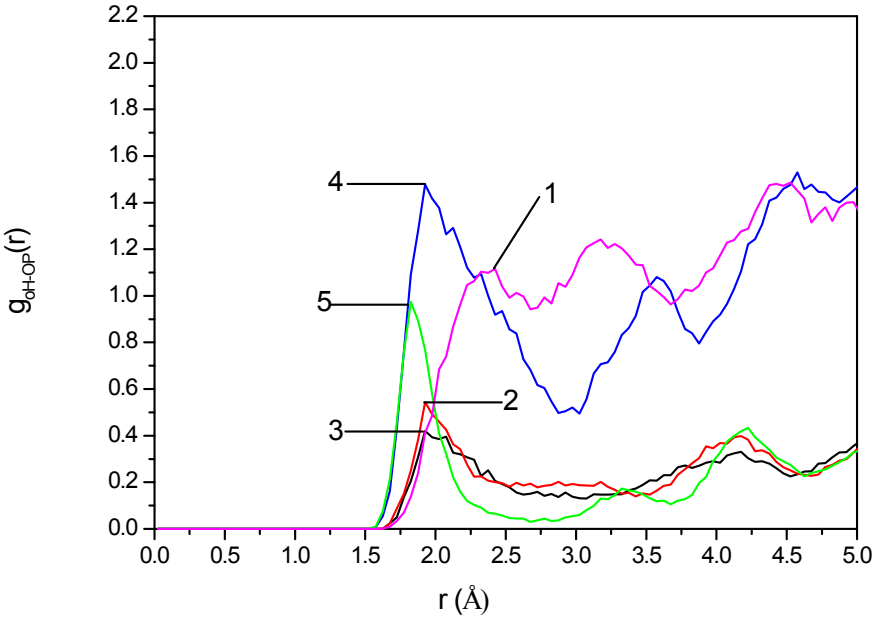


Figure S8. RDF $H_{hydroxy}$—$O_{phospate}$ for GlcA on the flat (01Error!0) surface. All configurations present a peak around 2.0—2.25 Å, indicating hydrogen-bond formation.

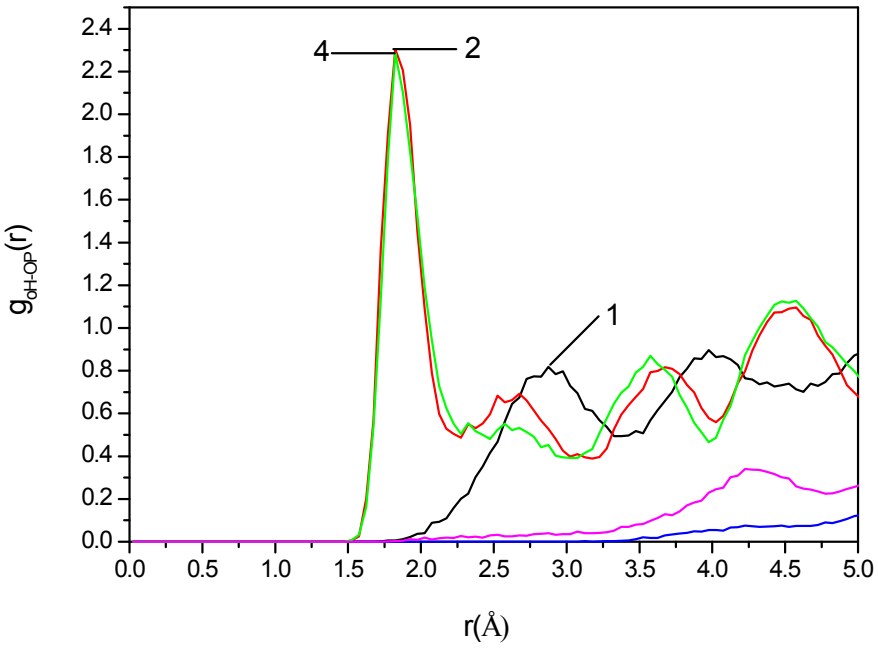


Figure S9. RDF $H_{hydroxy}$─$O_{phospate}$ for GlcA on the crenellated (01**Error!**0) surface. Only three configurations present a peak up to 2.75 Å, indicating hydrogen-bond formation.

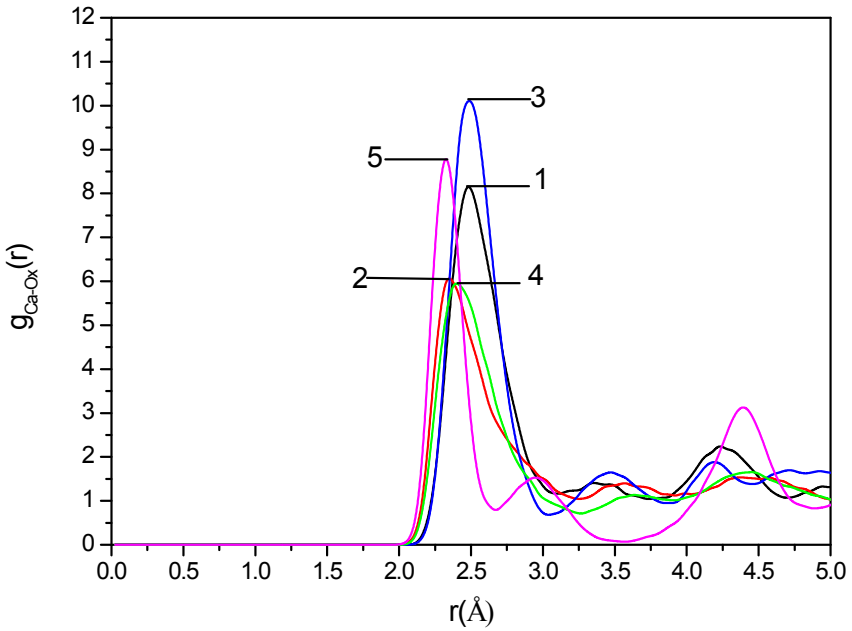


Figure S10. RDF Ca^{2+}─$O_{carboxylate}$ for GlcA on the crenellated (01Error!0) surface. The position of the first peak is shifted beyond 2.5 Å, for configurations 1 and 3 with lowest positive adsorption energies.

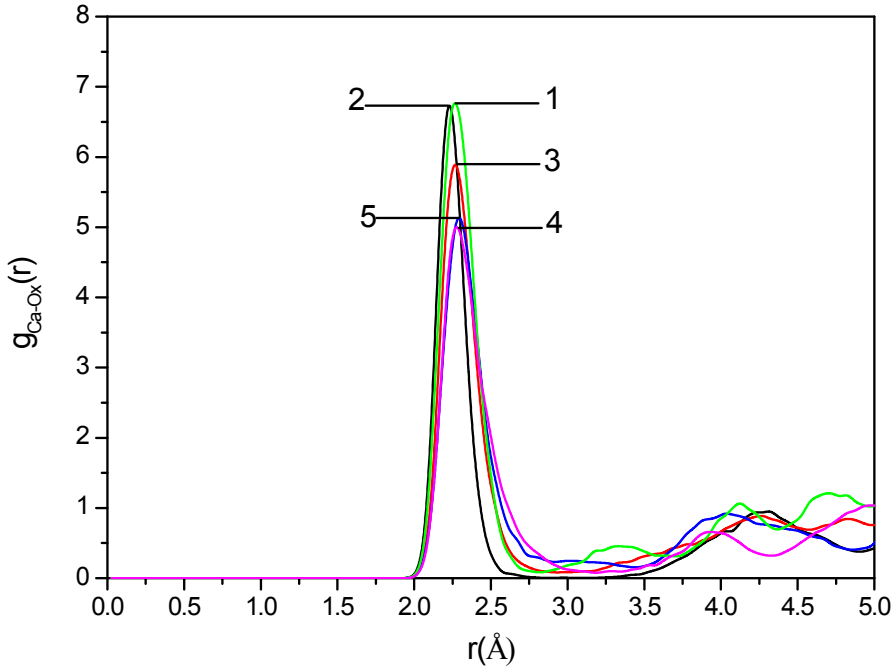


Figure S11. RDF Ca^{2+}─$O_{carboxylate}$ GlcA flat (0001) surface. The numbers indicate the configuration in Table 1.

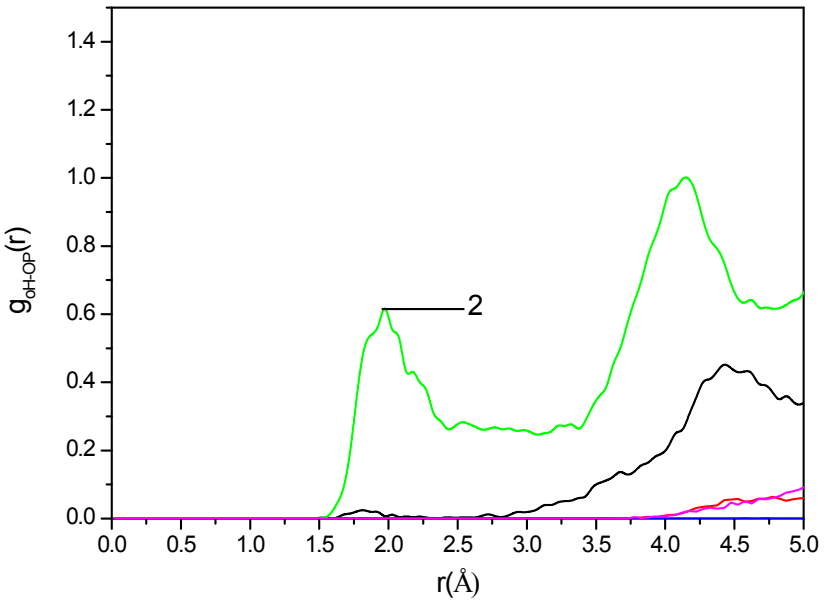


Figure S12. RDF $H_{hydroxy}$─$O_{phospate}$ for GalNAc-4S on the flat (01Error!0) surface. The GalNAc-4S is only forming hydrogen-bonds in configuration 2

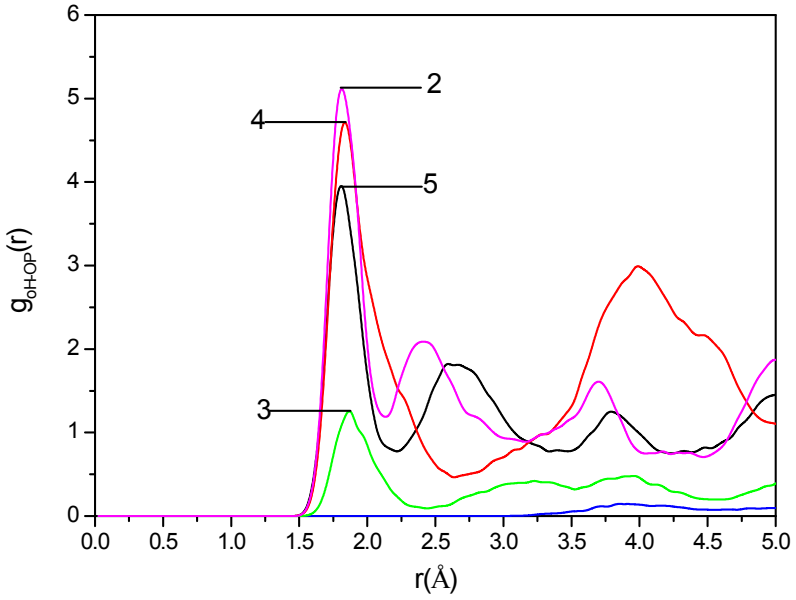


Figure S13. RDF $H_{hydroxy}$─$O_{phospate}$ for GalNAc-4S on the crenellated (01Error!0) surface. The GalNAc-4S is not forming hydrogen-bonds with the surface in configuration 1.

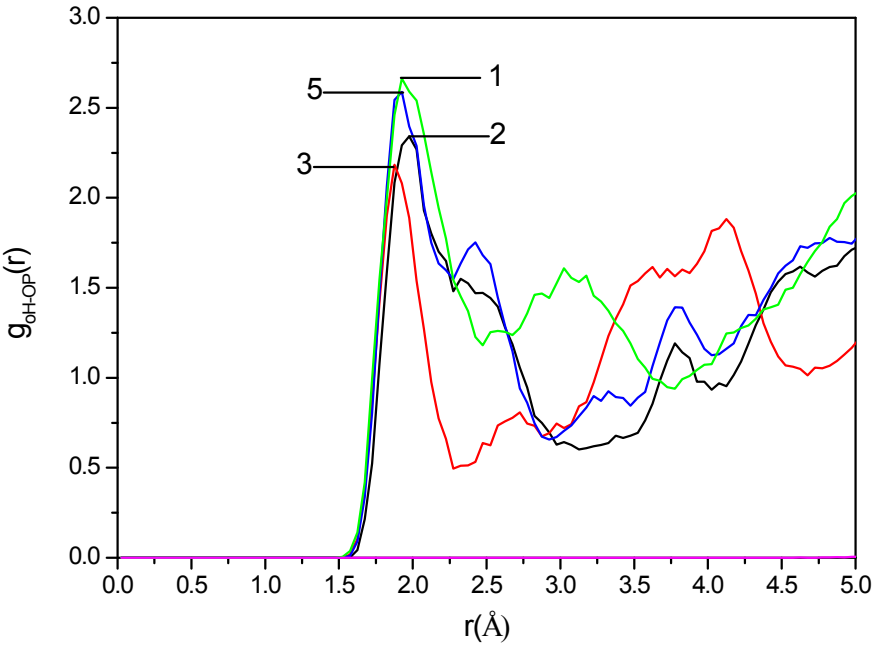


Figure S14 RDF $H_{hydroxy}$—$O_{phospate}$ for GlcA on the (0001) surface. The hydroxy groups of the GAG interact with the surface forming hydrogen bonds

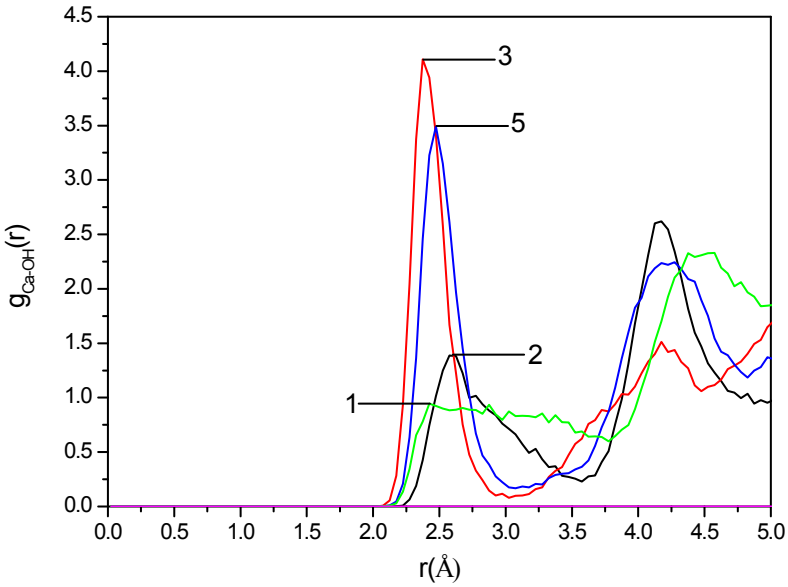


Figure S15 RDF Ca^{2+}—$O_{hydroxy}$ for GlcA on the (0001) surface. The hydroxy goups of the GAG replace the missing Ca^{2+}—Ow interactions.