Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

On the Not So Anomalous Water-induced Structural Transformation of Choline Chloride-Urea (Reline) Deep Eutectic System

SUPPORTING INFORMATION

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Table S1 – Urea parameters in the OPLS-DA and OPLS-DA/Urea (in brackets) force fields.

Atom	ε (kJmol^{-1})	σ (nm)	q (e)
C	0.65898 (0.43932)	0.375 (0.375)	+0.124 (+0.142)
O	1.31796 (0.87864)	0.296 (0.296)	-0.322 (-0.390)
N	1.06692 (0.71128)	0.355 (0.325)	-0.453 (-0.542)
H	-	-	+0.276 (+0.333)

Table S2 – MD GAFF0.8-PPC diffusion and shear viscosity coefficients of ChCl:U:W(1:2:ζ) at 298 K and 0.1 MPa.

ζ	D_{Chol} (10^{-8} cm^{2}s^{-1})	D_{Cl} (10^{-8} cm^{2}s^{-1})	D_{Urea} (10^{-8} cm^{2}s^{-1})	D_{Water}[a] (10^{-8} cm^{2}s^{-1})	η[b] (mPa·s)
1	0.011	0.018	0.019	0.076	99.3 ± 0.9
2	0.034	0.062	0.053	0.166	28.6 ± 0.3
5	0.135(5)	0.245	0.193	0.511	7.16 ± 0.02
10	0.320	0.564	0.422	0.938	2.89 ± 0.004
15	0.431	0.808	0.617	1.233	2.02 ± 0.009
20	0.542	0.995	0.737		1.62 ± 0.02
30	0.679	1.210	0.928	1.738	1.22 ± 0.01
40	0.767	1.397	1.047	1.930	1.07 ± 0.002

[a] The diffusion coefficient of TIP4P/2005 water is[1] 2.1×10^{-8} cm^{2}s^{-1} ±0.01 $\times10^{-8}$ cm^{2}s^{-1}; the experimental[2] self-diffusion coefficient of water at 298 K and 0.1 MPa is 2.3×10^{-5} cm^{2}s^{-1}.

[b] The viscosity of TIP4P/2005 water is[1] 0.88±0.05 mPa·s; the experimental viscosity of water at 298 K and 0.1 MPa is[78] 0.89 mPa·s.

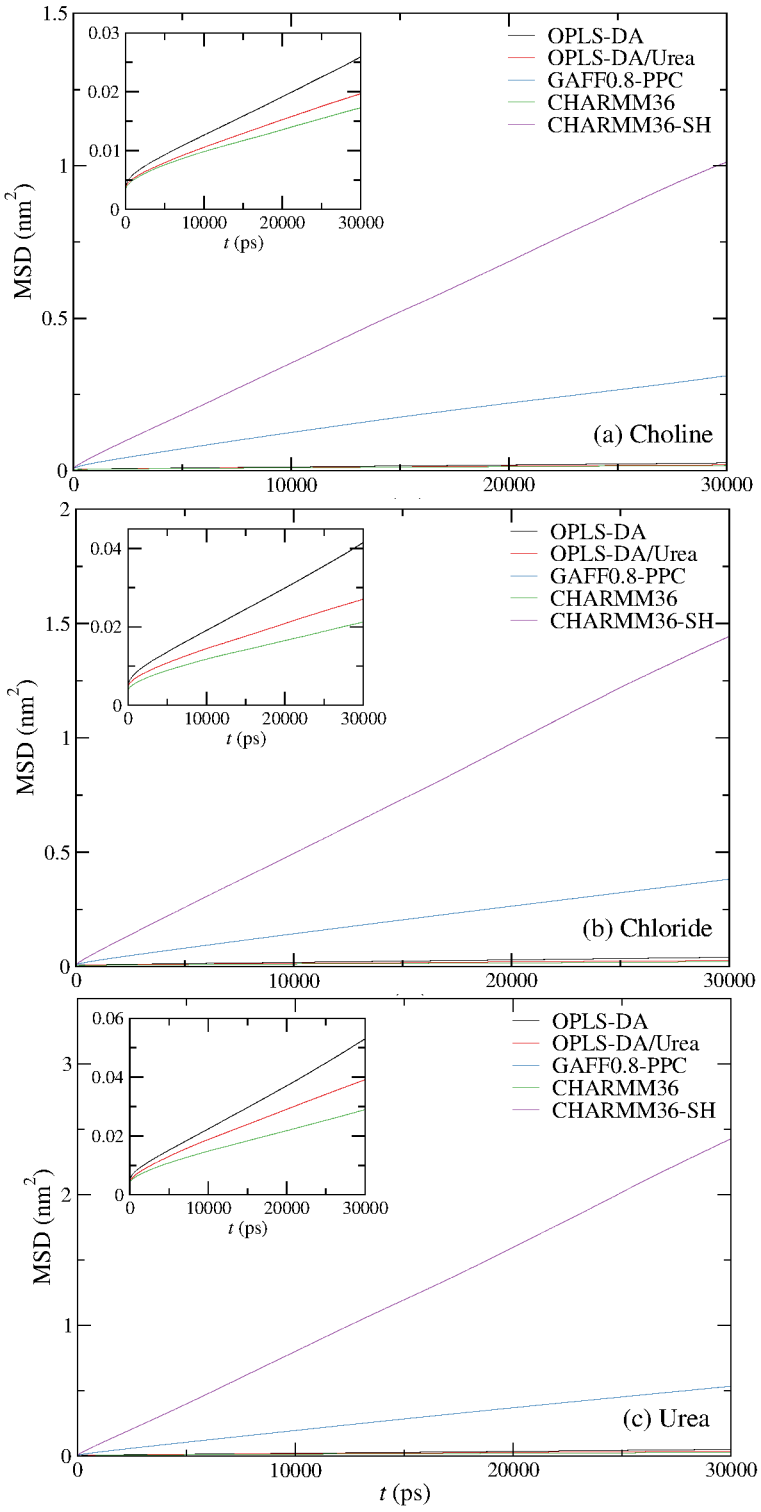

Figure S1 – Mean square displacement for the DES components calculated for the different force fields.

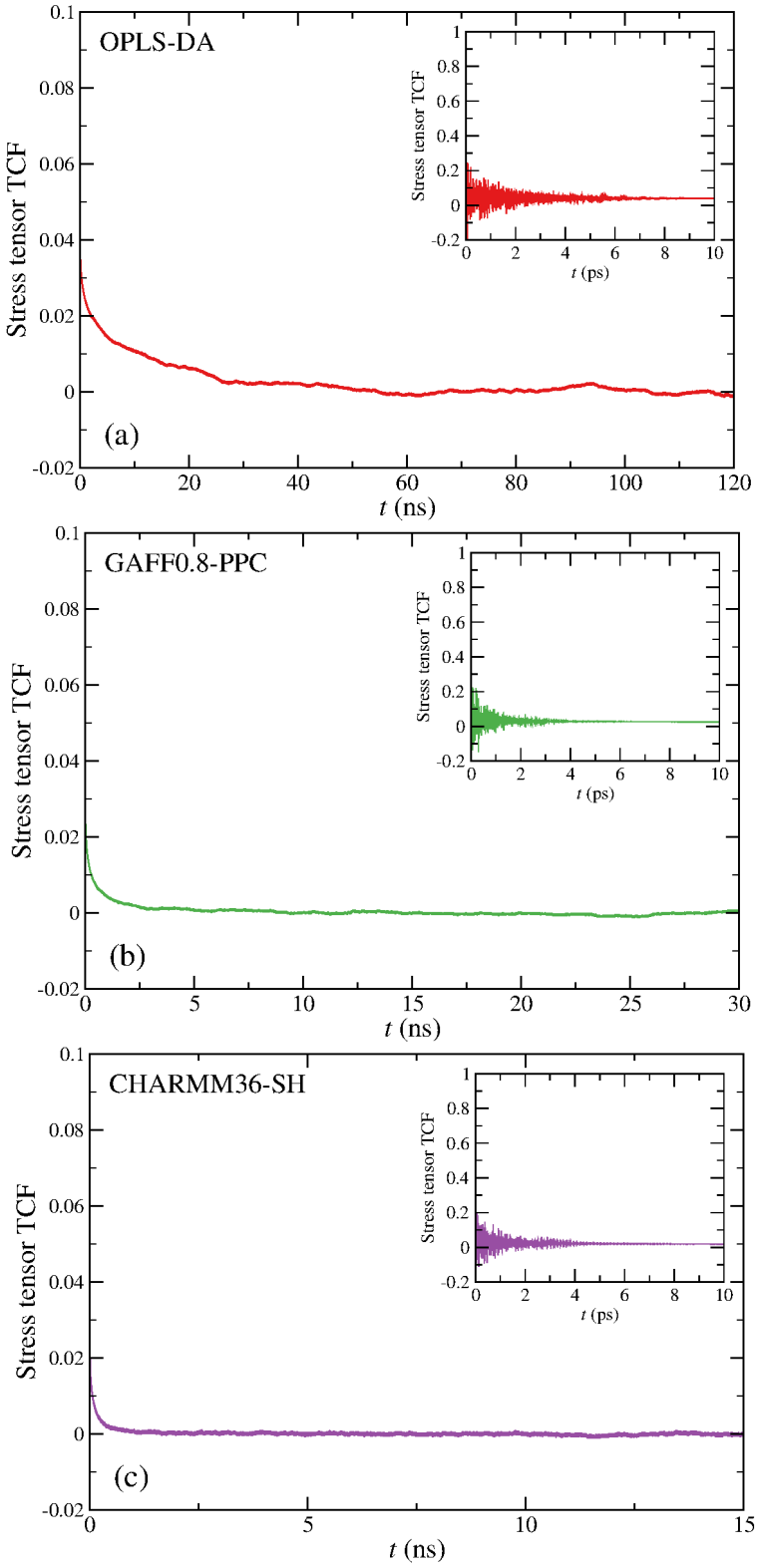

Figure S2 – Normalized stress tensor tcfs for the (a) OPLS-DA, (b) GAFF0.8-PPC, and (c) CHARMM36-SH force fields. The *y*-scale of the main plots is truncated at 0.1 ps. The inset plots show the fluctuations observed during the first 10 ps.

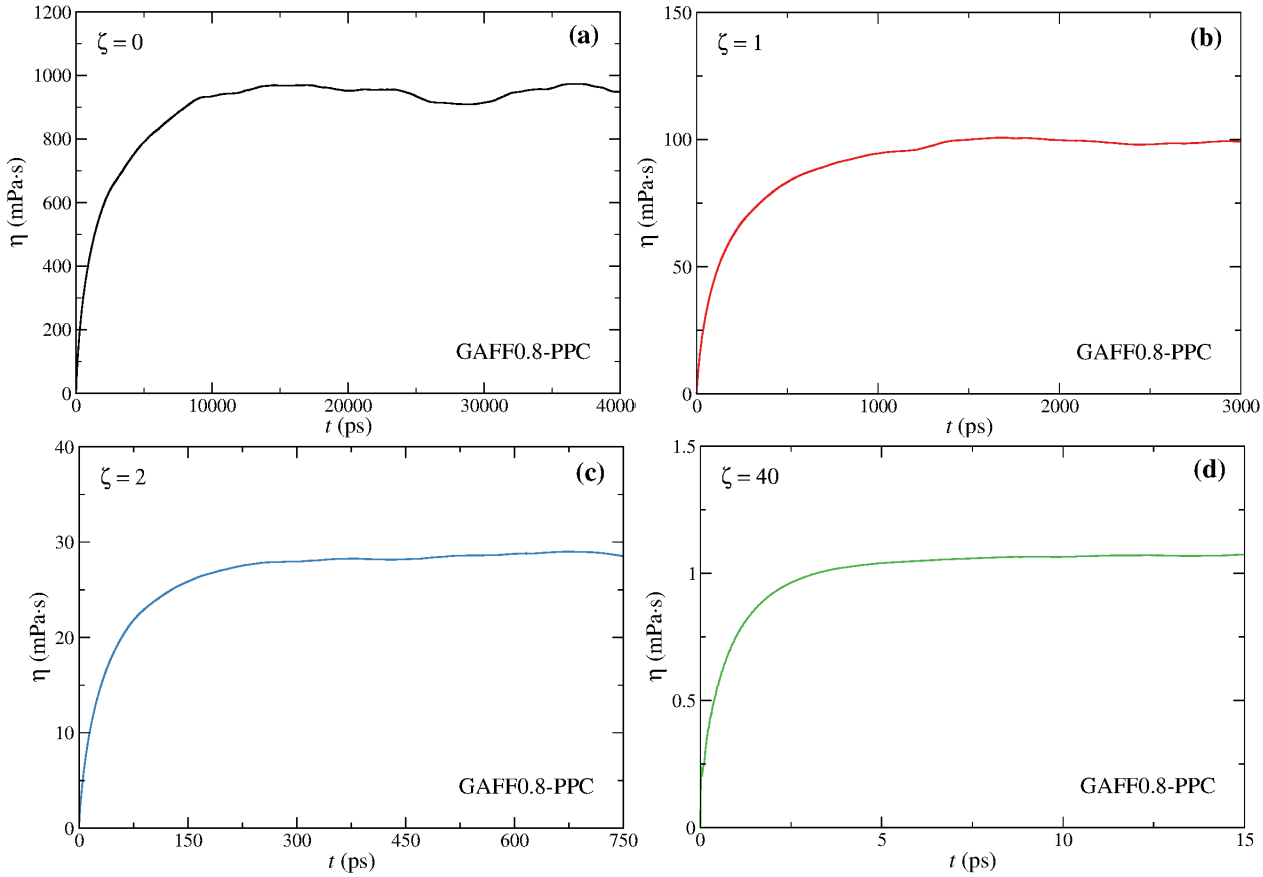

Figure S3 – Cumulative viscosity of GAFF0.8-PPC reline as obtained from eq. (2), at different water ratios, ζ.

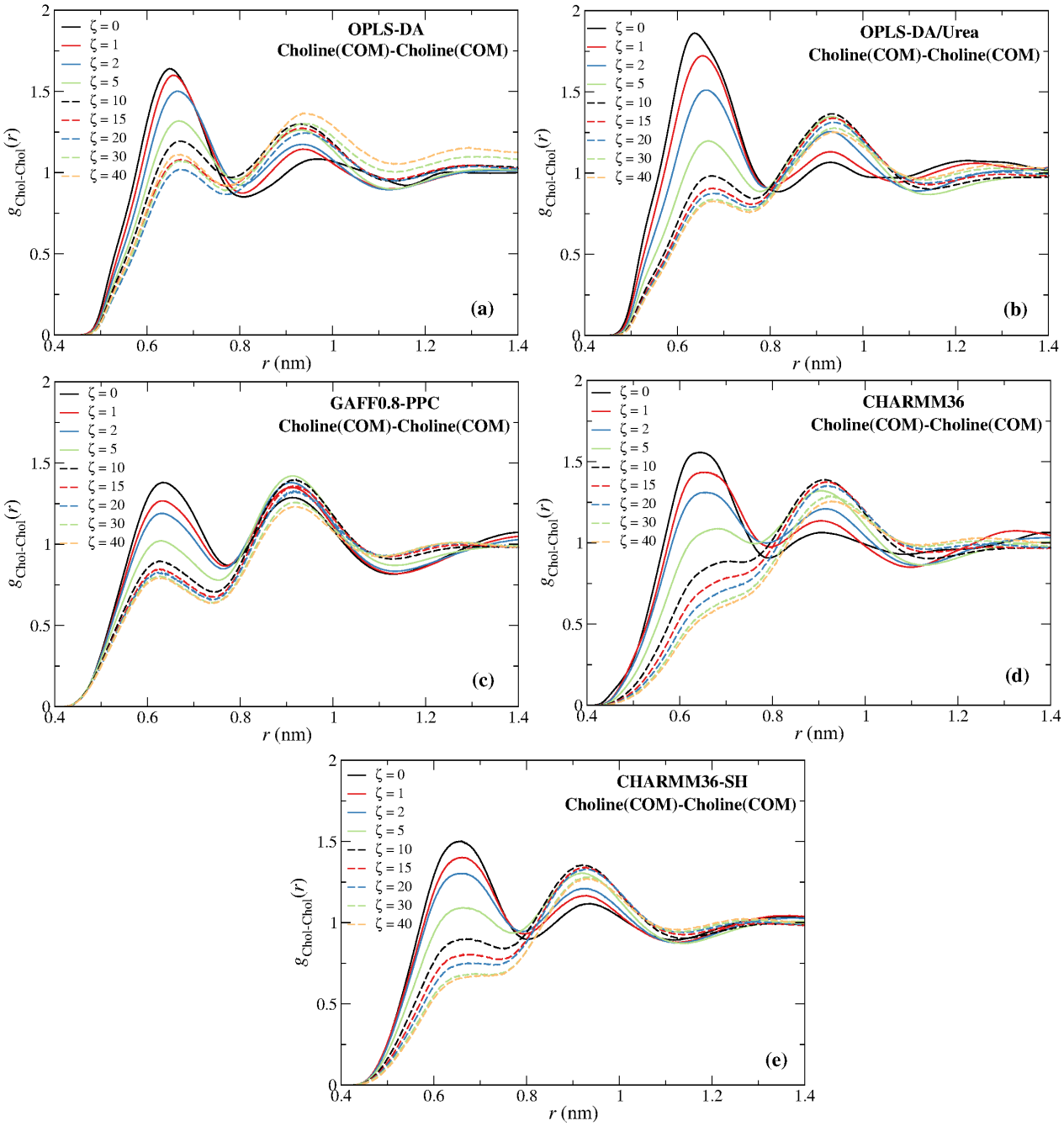

Figure S4 – Choline-Choline rdfs for the different force fields and water contents. The COM of choline was used to calculate the rdfs.

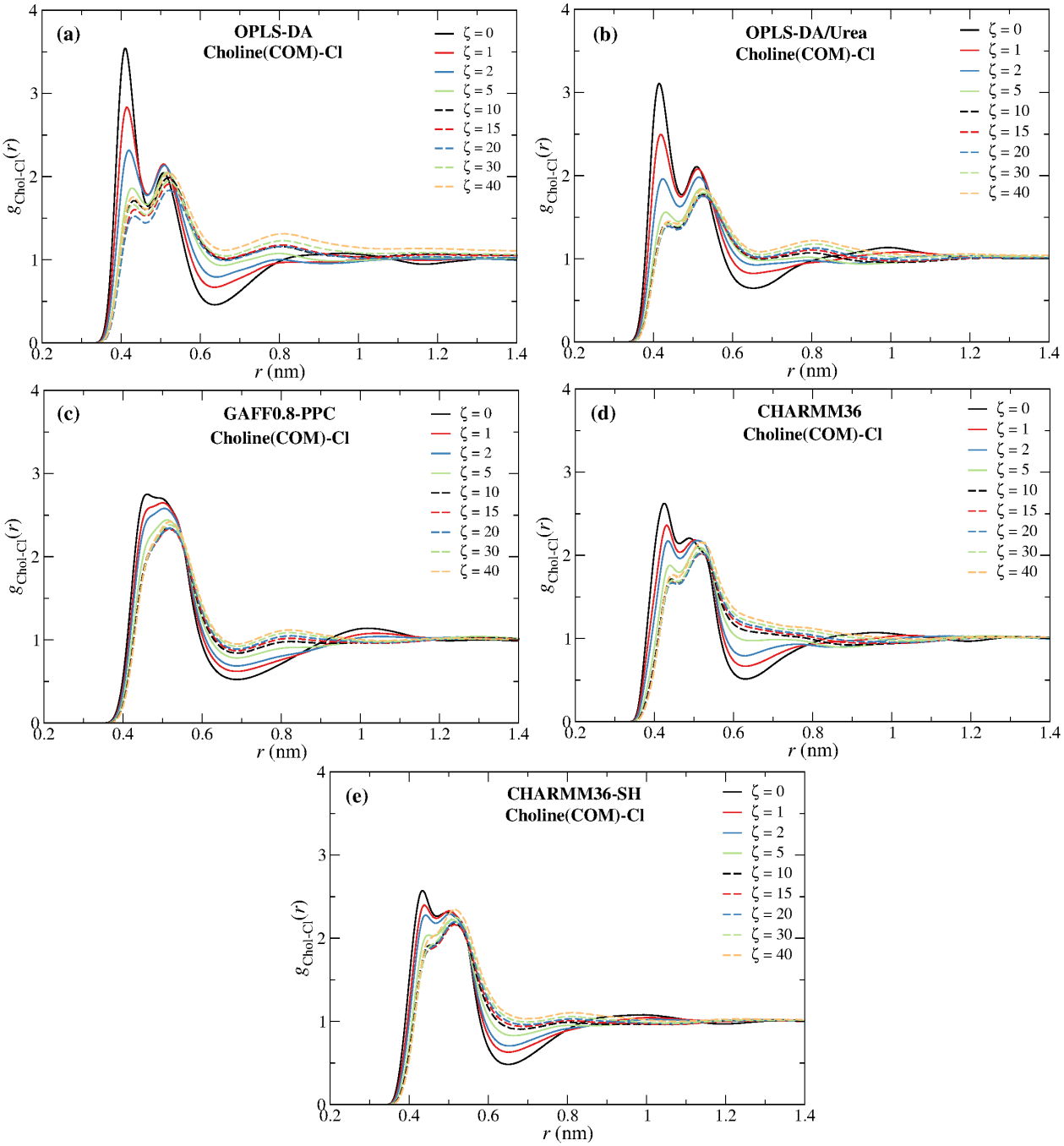

Figure S5 – Choline-Chloride rdfs for the different force fields and water contents. The COM of choline was used to calculate the rdfs.

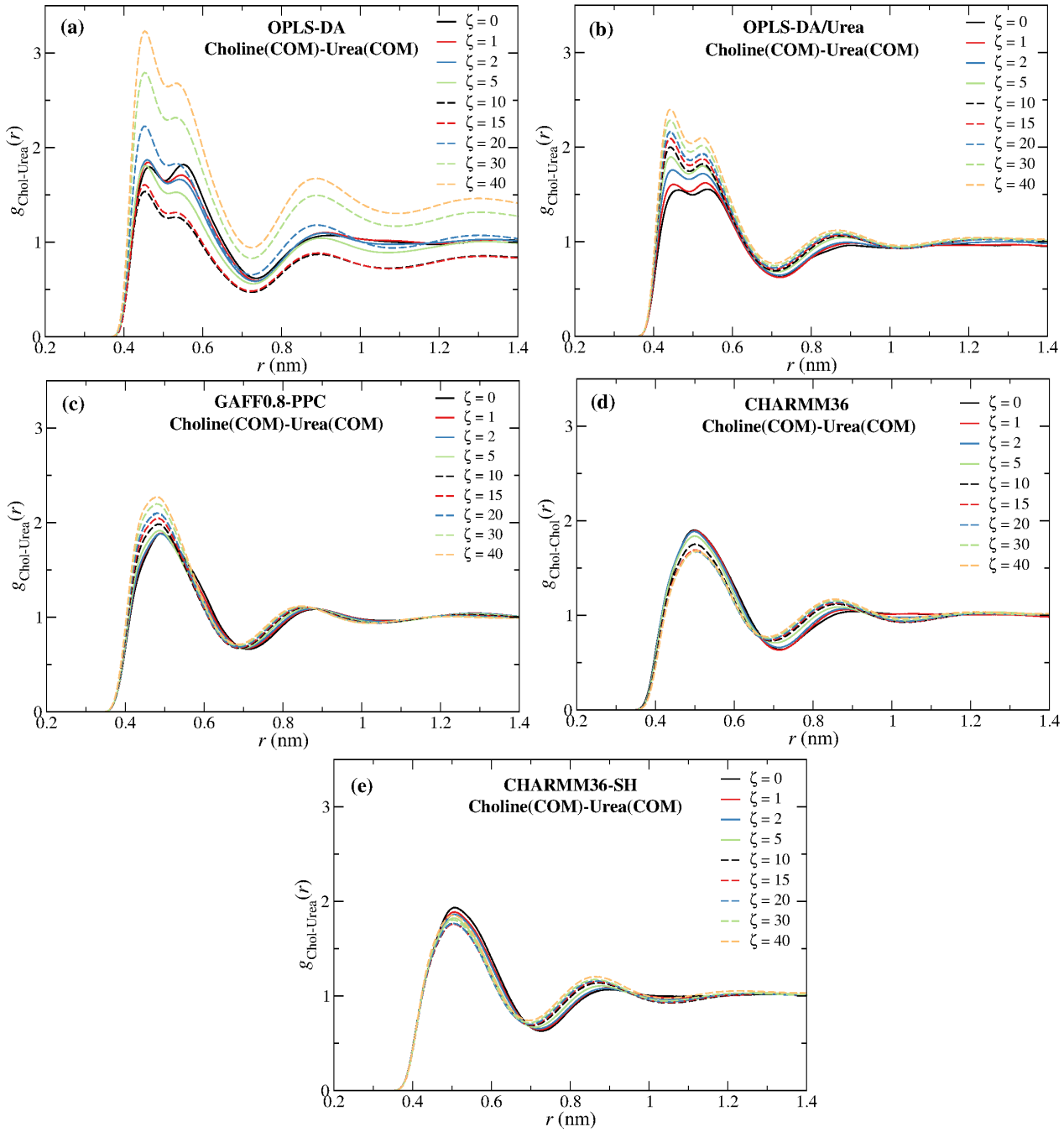

Figure S6 – Choline-Urea rdfs for the different force fields and water contents. The COM of choline and urea were used to calculate the rdfs.

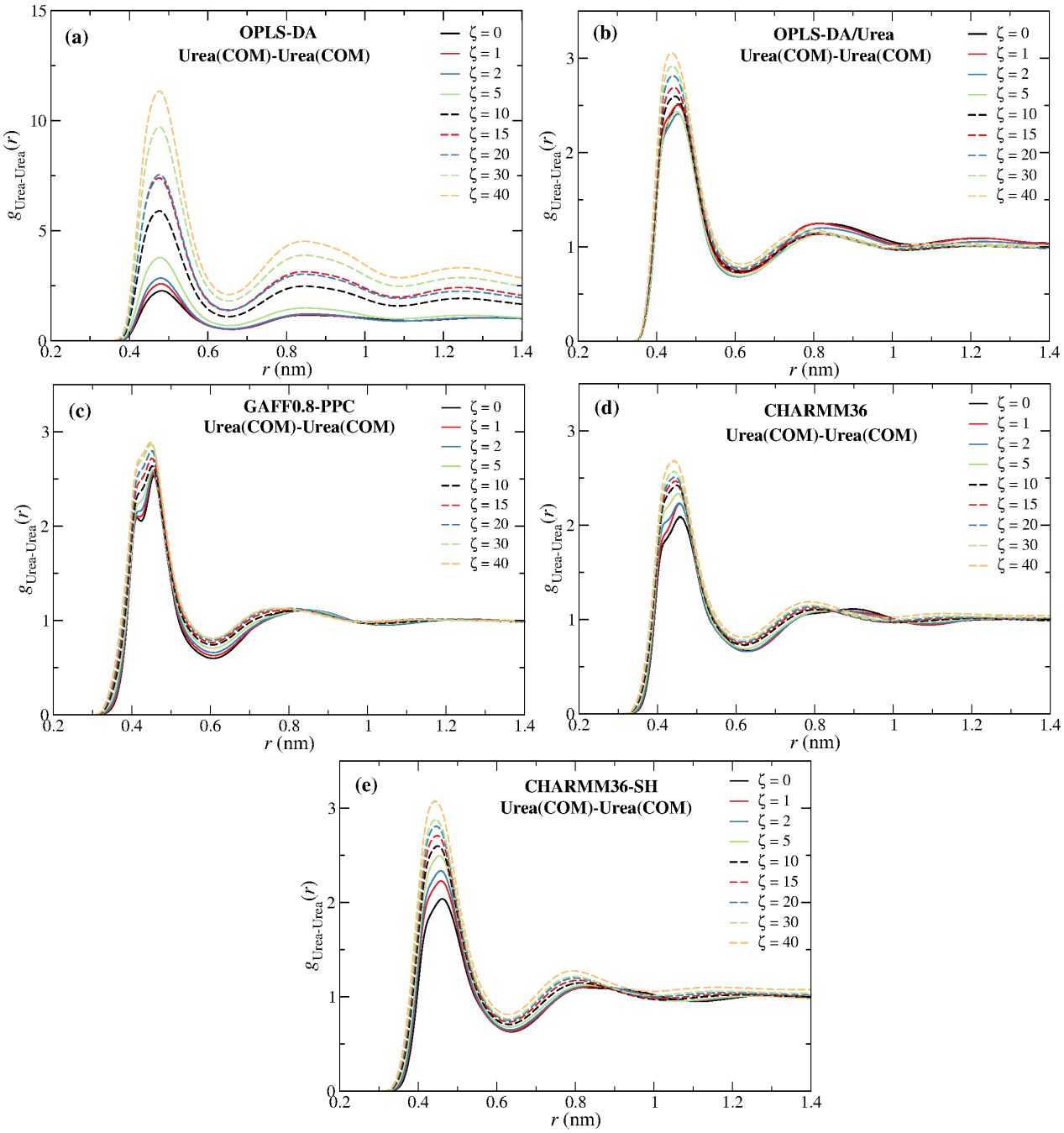

Figure S7 – Urea-Urea rdfs for the different force fields and water contents. The COM of urea was used to calculate the rdfs. Notice the different scale of the rdf for the OPLS-DA force field. This is associated with the aggregation of urea observed with this force field.

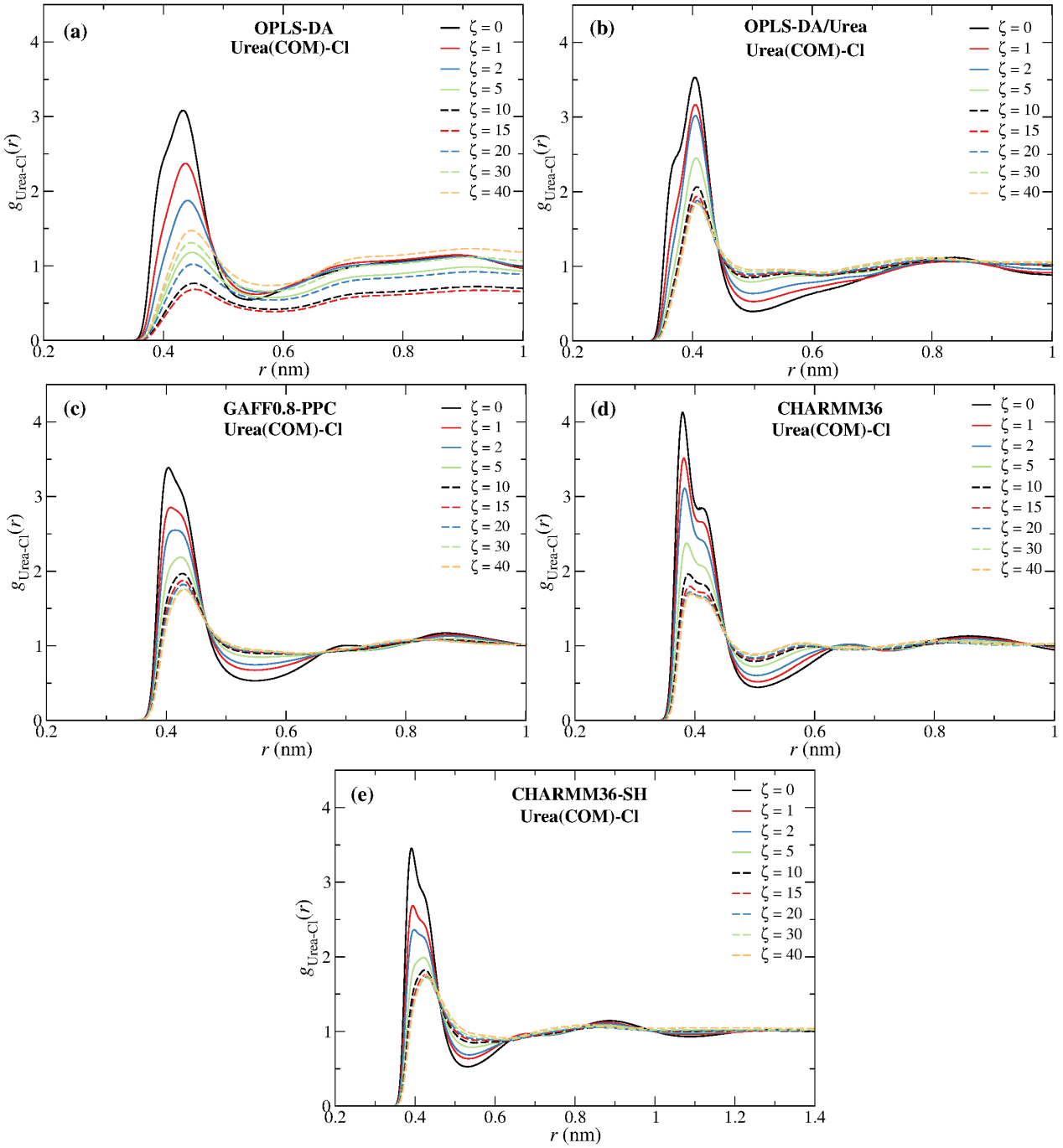

Figure S8 – Urea-Chloride rdfs for the different force fields and water contents. The COM of urea was used to calculate the rdfs.

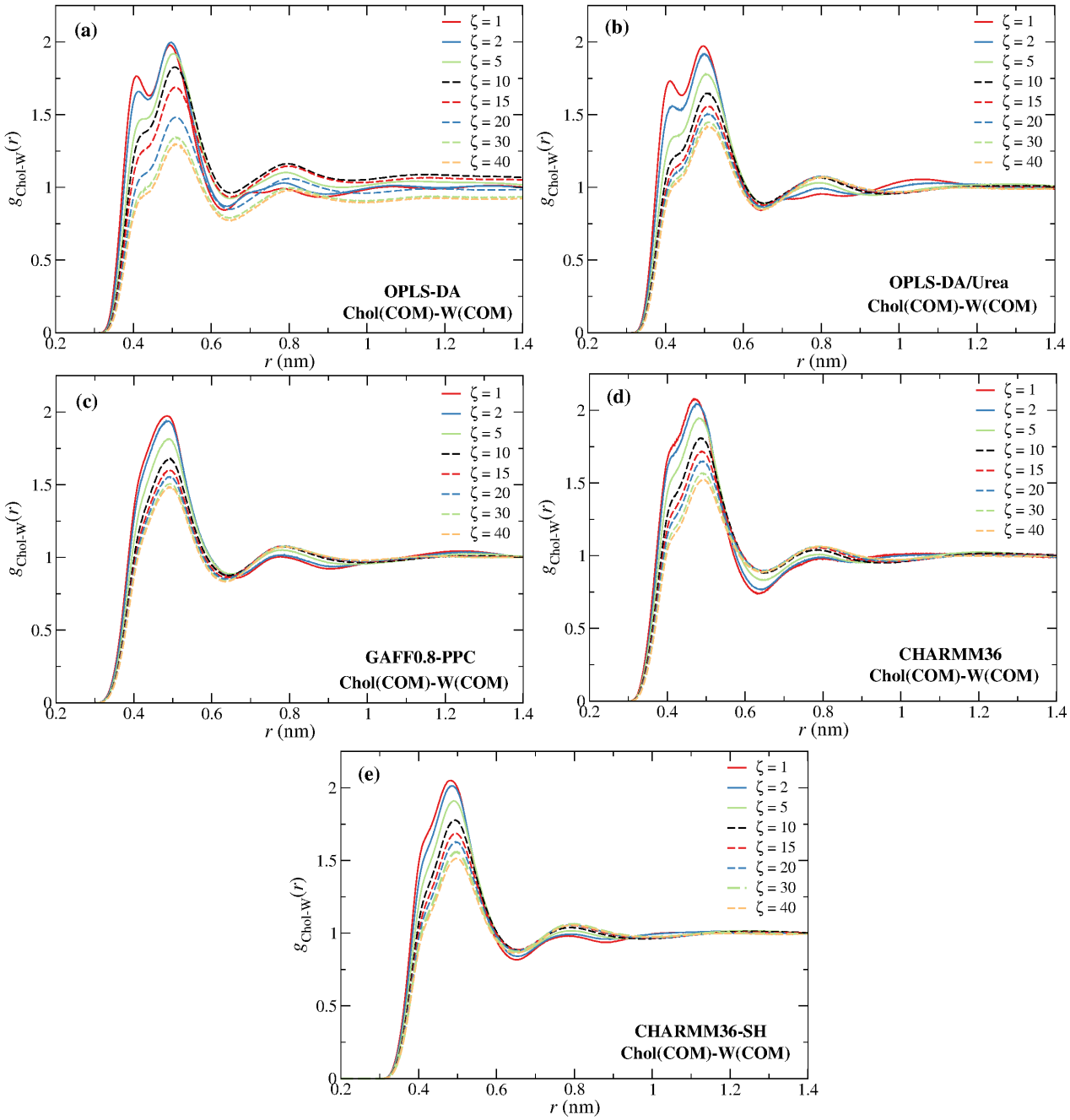

Figure S9 – Choline-Water rdfs for the different force fields and water contents. The COM of choline and water were used to calculate the rdfs.

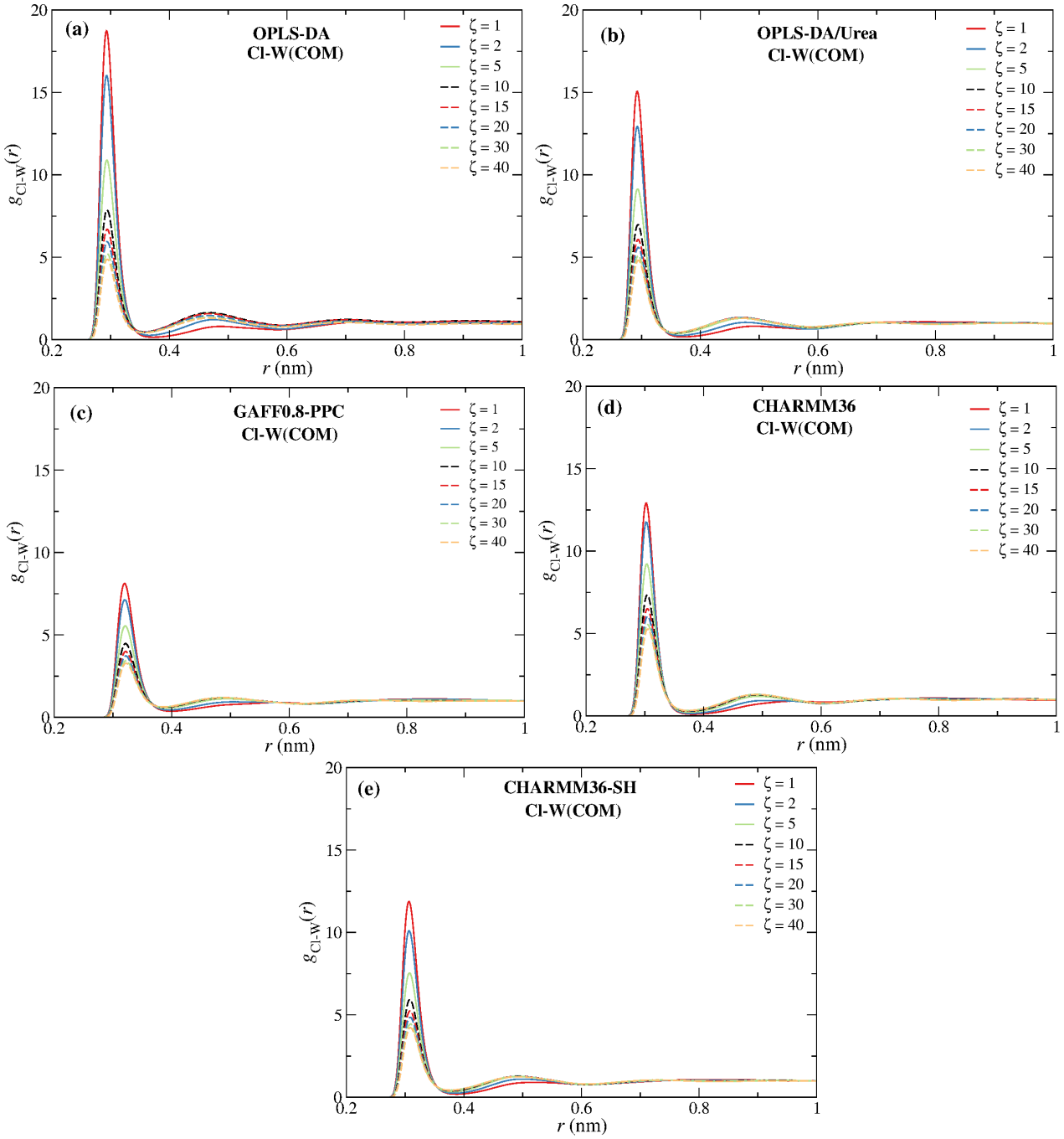

Figure S10 – Chloride-Water rdfs for the different force fields and water contents. The COM of water was used to calculate the rdfs.

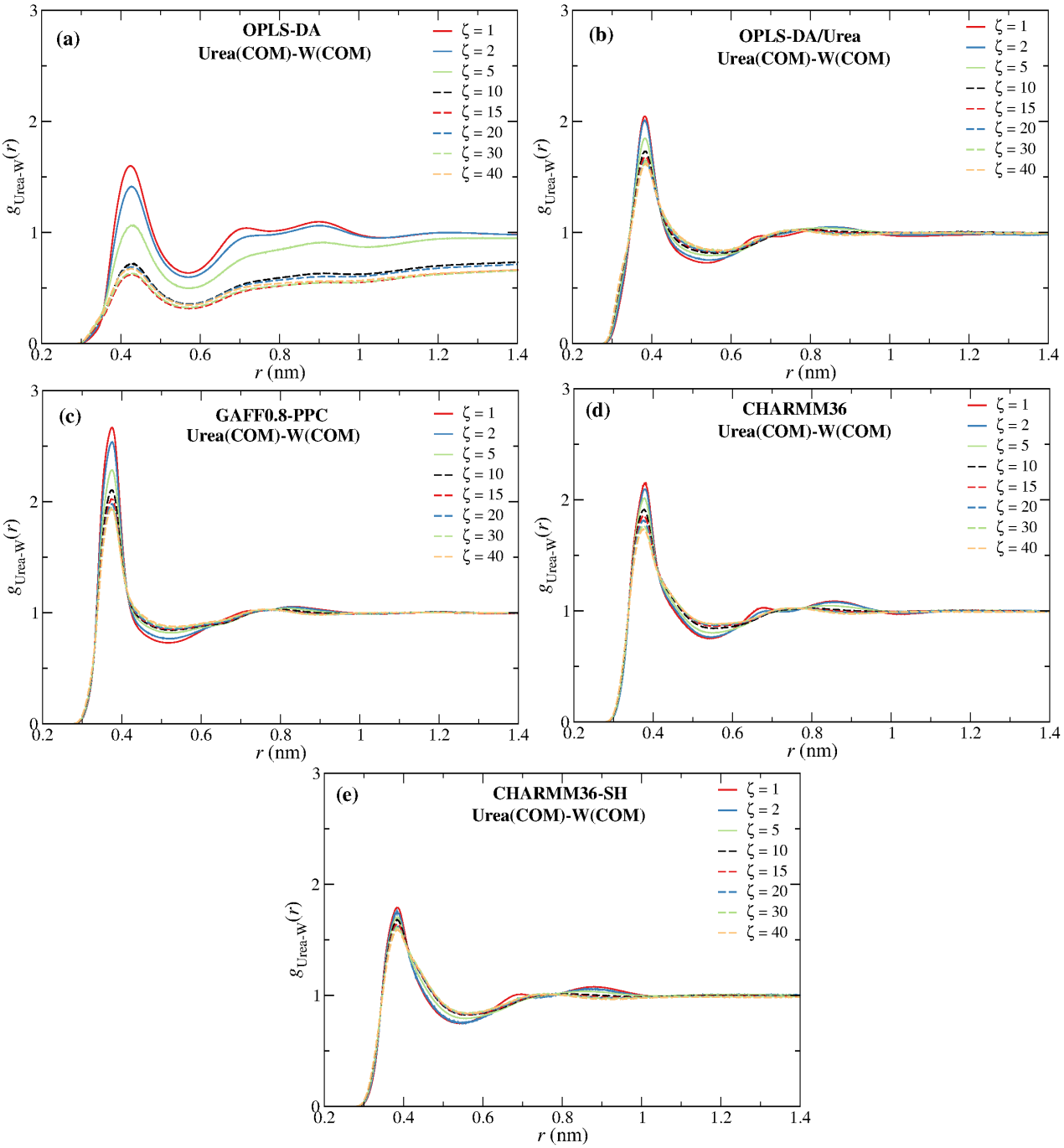

Figure S11 – Urea-Water rdfs for the different force fields and water contents. The COM of urea and water were used to calculate the rdfs.

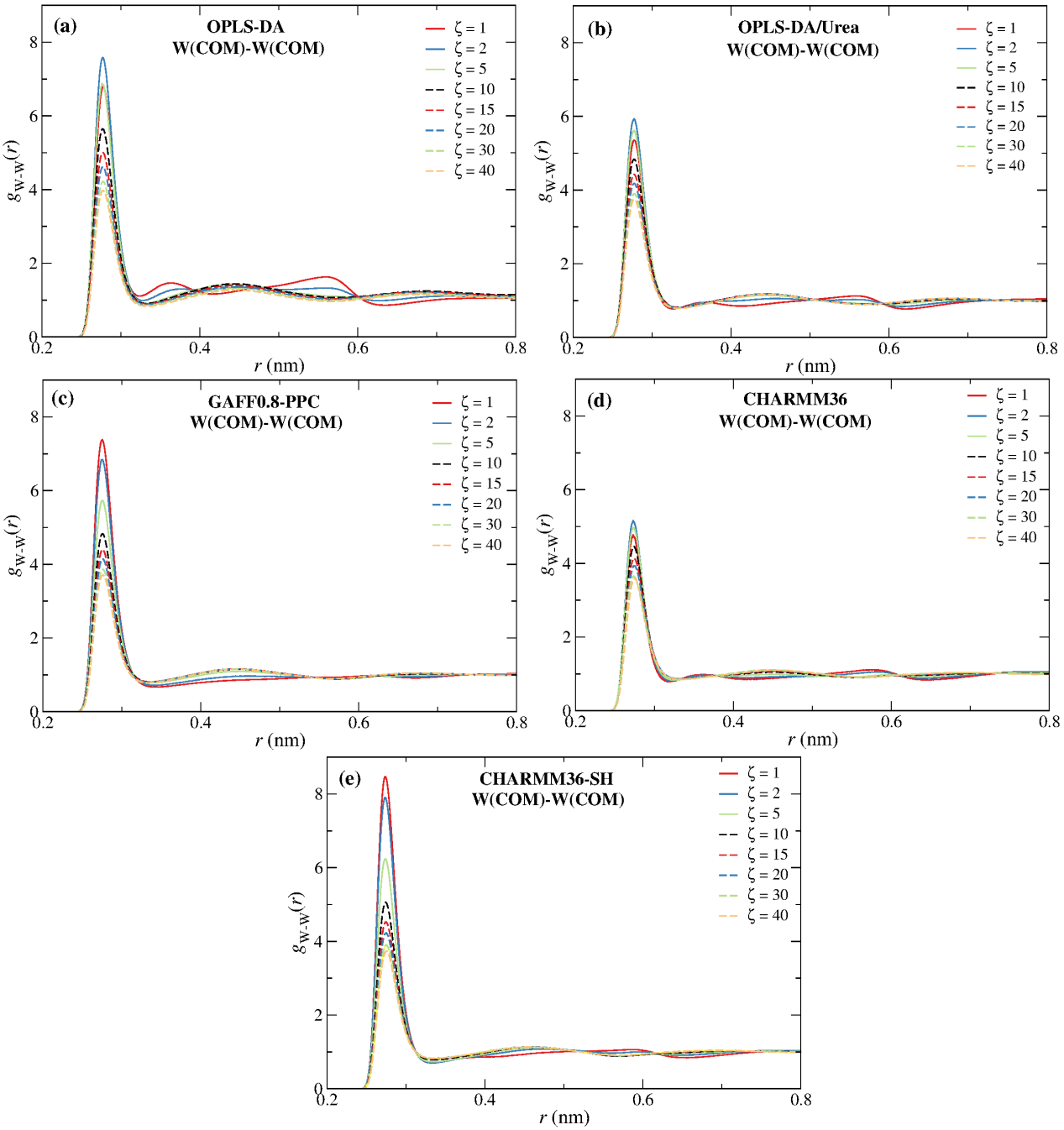

Figure S12 – Water-Water rdfs for the different force fields and water contents. The COM of water was used to calculate the rdfs. These rdfs are nearly indistinguishable from the oxygen-oxygen (OW-OW) rdfs. Notice the resemblances between the GAFF0.8-PPC and CHARMM36-SH rdfs for which a faster dynamics is observed.

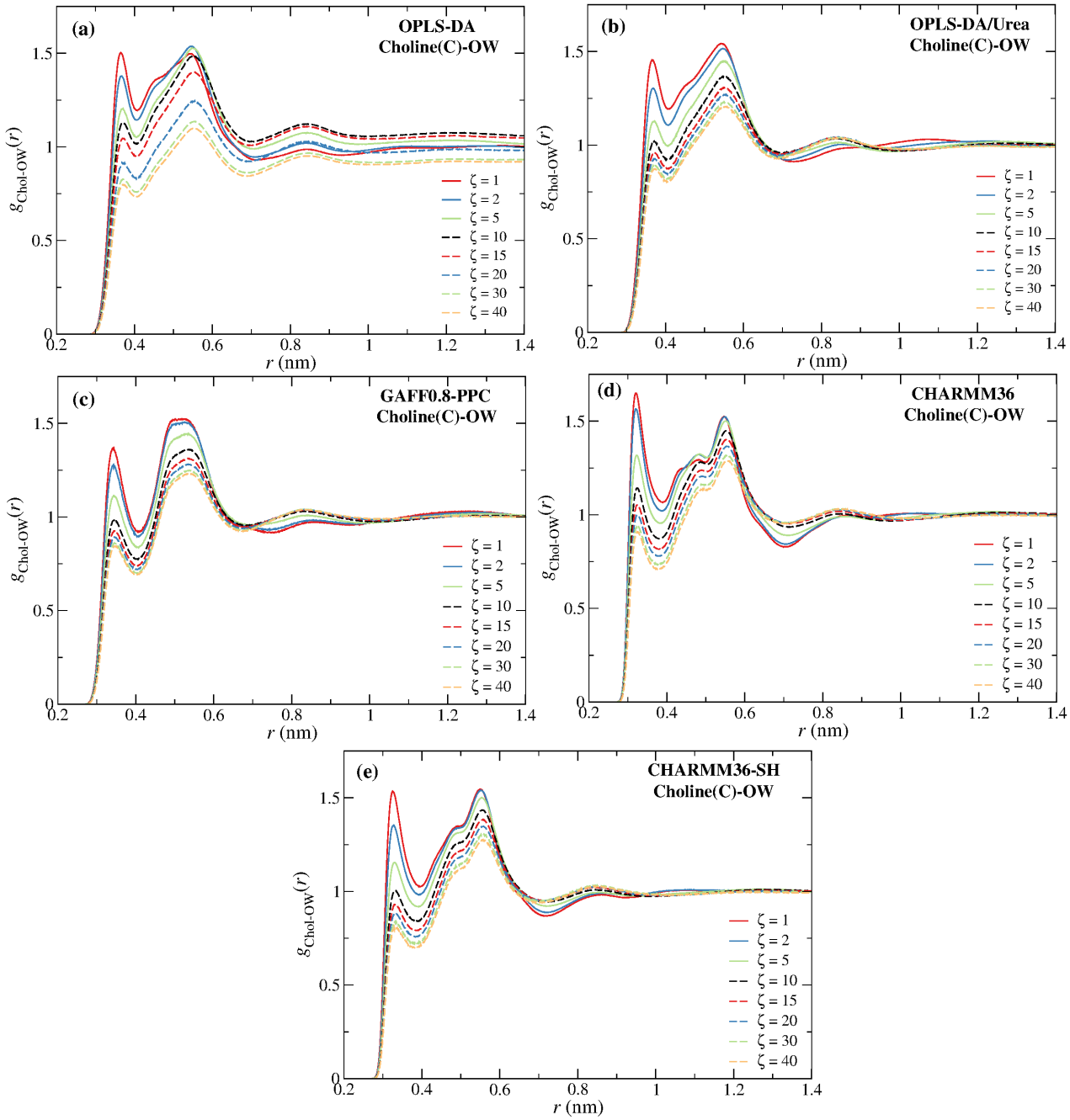

Figure S13 – Choline-Water rdfs calculated for the C atom of choline (see **Fig. 1**) and the oxygen atom of water. The second minimum was used to calculate the coordination numbers. The coordination numbers corresponding to the first minimum are lower than 3 for every ζ exhibiting a monotonic increase with the water content.

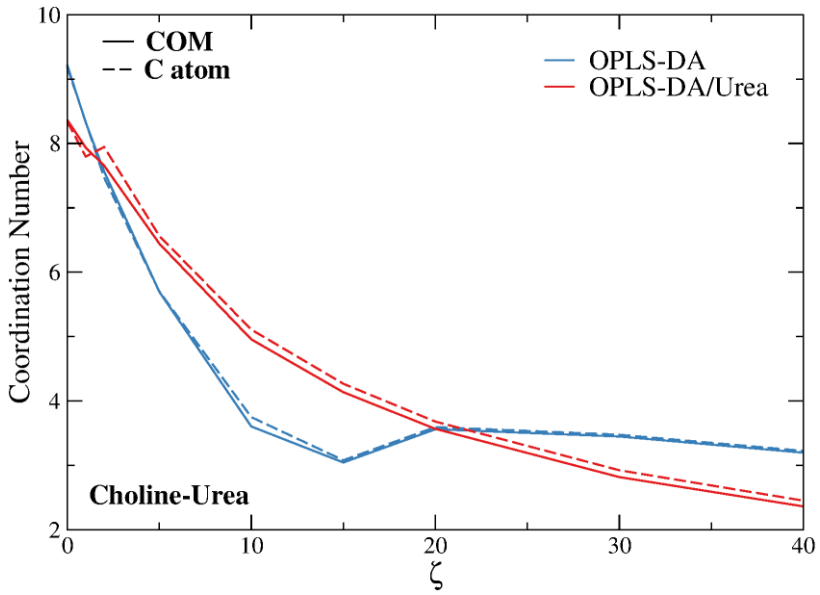

Figure S14 – Choline-urea coordination number for the OPLS-DA and OPLS-DA/Urea force fields calculated for the COM and the C atom of Fig. 1 of the manuscript. The non-monotonic variation for the OPLS-DA force field is related with the water-induced aggregation of urea.

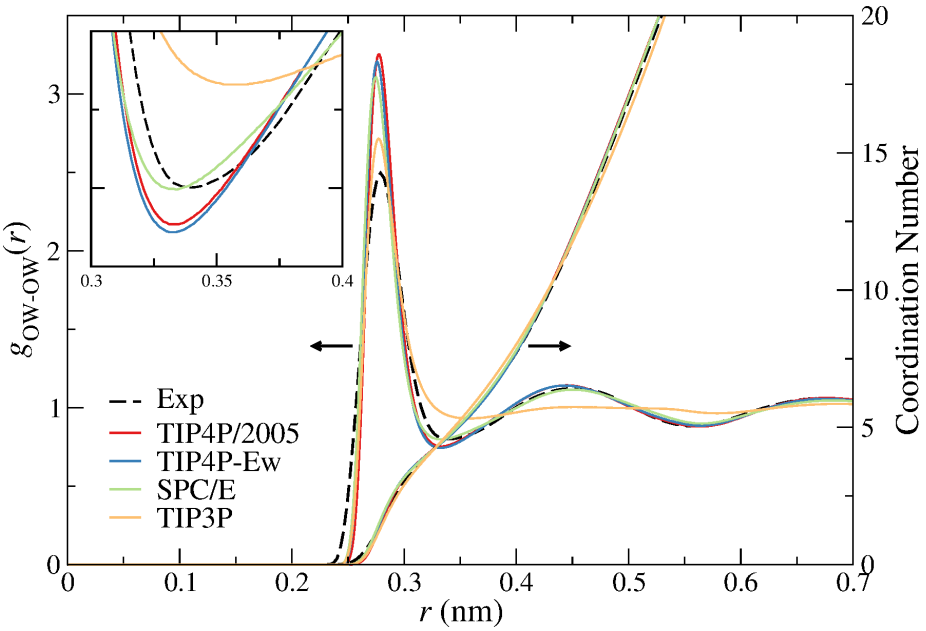

Figure S15 –Experimental and MD oxygen-oxygen (OW-OW) rdf for pure water for the different water models.