Electronic Supplementary Material (ESI) for Green Chemistry.

Liquid structure of the choline chloride-urea deep eutectic solvent (reline) from neutron diffraction and atomistic modelling

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A) Theory

Neutron diffraction experiments rely on the often wide difference in coherent neutron scattering lengths between atomic isotopes (b_{coherent}), for example hydrogen (b_{hydrogen} = -3.74 fm) and deuterium ($b_{\text{deuterium}}$ = 6.67 fm). Each sample that is measured with different H/D isotopic substitutions therefore yields a different set of structural information corresponding with the same overall structure, assuming that the substitution does not affect it. For each sample, the differential scattering cross-section is measured, which is then calibrated and background-corrected before subtracting the multiple and inelastic scattering. The product of each contrast is a total structure factor $F_i(Q)$:

$$F_i(Q) = \sum_{\alpha,\beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_\alpha b_\alpha c_\beta b_\beta (S_{\alpha\beta}(Q) - 1) \qquad (1)$$

where Q is defined as the total momentum transfer vector magnitude ($Q = (4\pi/\lambda)\sin\vartheta$), c_α are the concentrations of the atomic constituents of a sample and b_α the scattering lengths of these, and $S_{\alpha\beta}(Q)$ are the partial structure factors, which are a measure of the structural correlations between atoms of type α and β in Q-space, and is obtained from the Fourier transform of the partial pair distribution functions $G_{\alpha\beta}(r)$ by the relation:

$$S_{\alpha\beta}(Q) = 1 + \frac{4\pi\rho_0}{Q} \int_0^\infty r G_{\alpha\beta}(r) \sin(Qr) \, .dr \qquad (2)$$

where ρ_0 is the atomic number density, and the partial radial distribution functions $g_{\alpha\beta}(r)$ are defined as $g_{\alpha\beta}(r) = G_{\alpha\beta}(r) + 1$. As each isotopic contrast gives a different $F_i(Q)$, full determination of all $S_{\alpha\beta}(Q)$ functions is theoretically possible, and subsequently $g_{\alpha\beta}(r)$. In reality total isotopic contrast is unfeasible for most systems more complex than H_2O, and the system is underdetermined. In this instance, a structural model is refined to experimental

data using the known physicochemical properties of the system as constraints such as density, charge and molecular structure. This enables the extraction of the structural information of the system with an atomistic level of detail.[1]

B) Empirical Potential Structure Refinement

Empirical potential structure refinement (EPSR) is a 3D structural modelling technique that evolved from the reverse Monte Carlo (RMC) method.[2,3] The purpose of EPSR is to simulate a 3D configuration that is the most objectively consistent with experimental diffraction data for a system.[4] To achieve a consistent fit to data, RMC uses hard sphere potentials and either accepts or rejects a move depending on whether the fit has improved. Conversely, EPSR employs a Lennard-Jones potential where $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by typical Lorentz-Berthelot mixing rules, using atom-centric point charges and periodic boundary conditions to generate a simulated reference potential (RP) for a disordered system.[5] The residuals between the RP and the experimental data are used to calculate an empirical potential (EP) that is introduced to the RP as a series of Poisson functions to suppress Fourier transform artefacts.[6]

EPSR uses a number of techniques to maximize the objectivity of the fit. Firstly, the properties of a system, including its density, molecular structure, and composition, are used as severe physicochemical constraints on configurations and their overlap. Secondly, EPSR deviates from classical simulation by allowing a degree of intramolecular disorder that is obtained by sampling harmonic potentials for each molecule, allowing for a better fit to experimental data.[7] To fit the diffraction data, the model is iteratively improved by adjusting the EP to bias the model towards experimentally determined molecular configurations, with MC moves accepted or rejected based around the Boltzmann factor:

$$exp\left[-\left\{\Delta U_{intra}+\frac{1}{k_B T}\left(\Delta U_{RP}+\Delta U_{EP}\right)\right\}\right] \quad (3)$$

where $\Delta U_{intra,RP,EP}$ are the energy differences between the new and old model configurations, respectively due to the intramolecular, reference, and empirical potentials.

C) Simulation method

A set of molecules are first constructed to impose the mean intramolecular geometry by using interatomic distance constraints, shown in the main text. These molecules are then parameterized by assigning Lennard-Jones, charge, and atomic mass values to each distinct atom type, which can be seen in Table 1. Parameters for urea were derived from those used by Soper *et al.* in previous diffraction experiments on the aqueous structure of urea at very high concentrations,[8] and parameters for choline and chloride are derived from the OPLS All-Atom force field potential.[9] 200 choline, 200 chloride and 400 urea molecules are introduced to a simulation box which is randomized to generate a disordered starting configuration. The density is initially set to 1/20 of the experimental value to minimize the probability of molecular overlap.

The simulation is allowed to equilibrate in energy by running for a number of MC cycles, where one cycle comprises an attempt to move every atom, rotate every rotational group, and rotate and translate every molecule one time each. The box is compressed by approximately 10% and the process repeated until the experimental density of 0.106 atoms $Å^{-3}$ is obtained. Using the reference potential only, the simulation continues to run until the energy of the system reaches a plateau. By this point, the simulation has equilibrated as a cubic box of diameter 41.6 Å, allowing reliable determination of structures up to $d/2$ = 20.8 Å

in size. The empirical potential is then introduced to begin the refinement against the neutron data, with one refinement cycle comprising five MC cycles and the recalculation of the EP. Following equilibration of the model, the simulation is begun by accumulating statistics over thousands of refinement cycles on the EP and all of the structural information within the model, such as RDFs, SDFs, and coordination numbers. Molecular centre radial distribution functions and spatial density functions that describe the configurations of cations, anions and urea molecules around one another are determined using the spherical harmonics (SHARM) routine of EPSR, and liquid 'hole' sites are determined using the VOIDS routine.

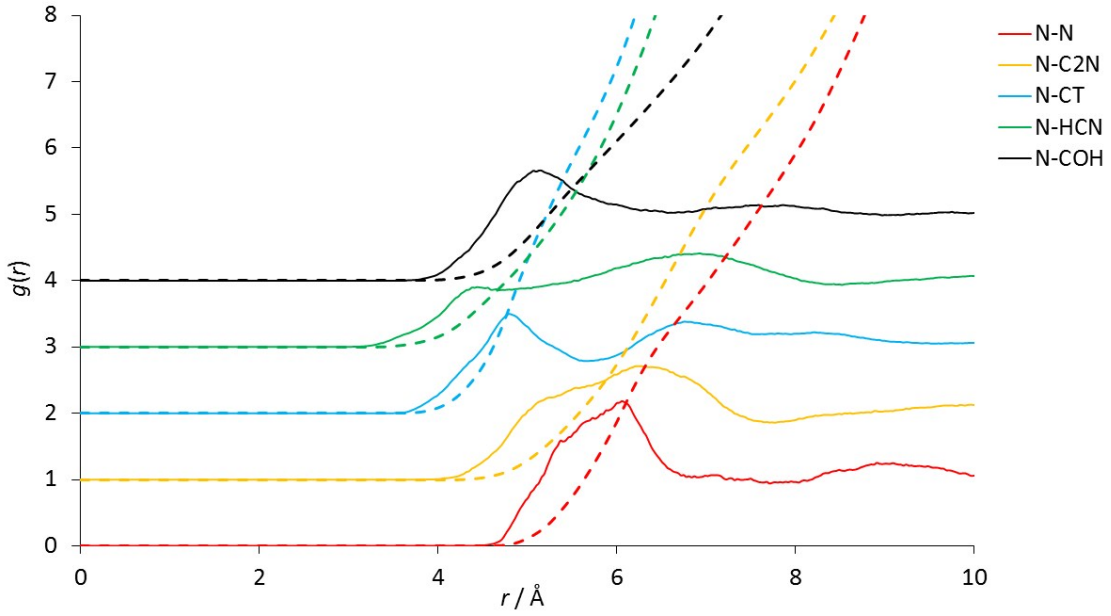
D) Lennard-Jones parameters used in EPSR modelling

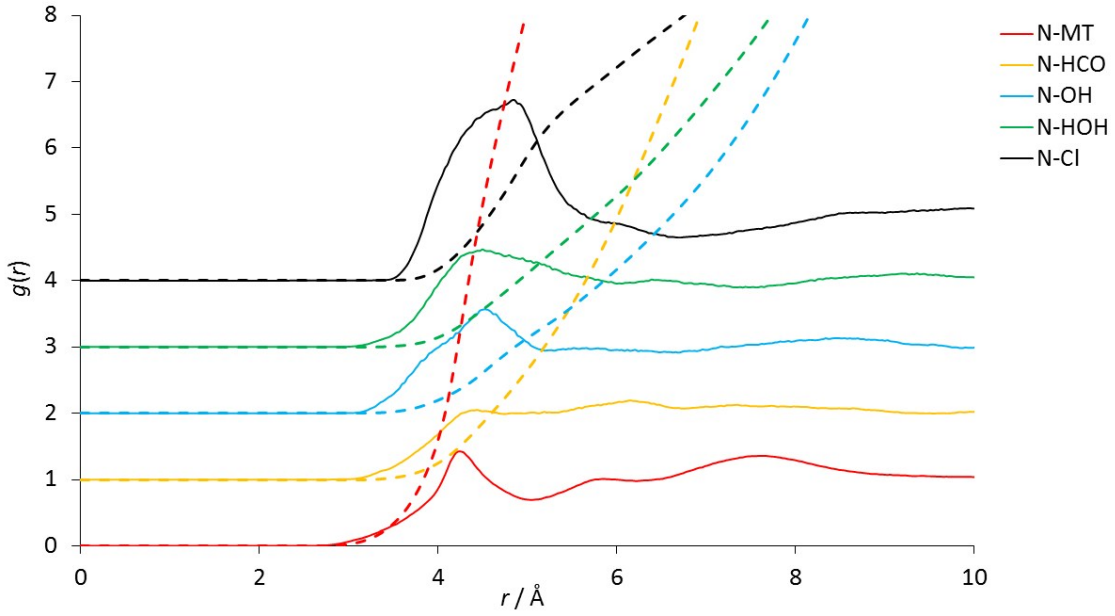
Table 1. Lennard-Jones parameters, including the charges and masses used in the reference potential for simulations of reline.

atom type	ε / kJ mol^{-1}	σ / Å	mass / amu	q / e
N	0.700	3.200	14.0	1.000
C2N	0.800	3.700	12.0	-0.120
CT	0.800	3.700	12.0	-0.180
HCN	0.200	2.580	2.0	0.060
COH	0.800	3.700	12.0	0.145
MT	0.200	2.580	2.0	0.060
HCO	0.200	2.580	2.0	0.060
OH	0.650	3.100	16.0	-0.683
HOH	0.000	0.000	2.0	0.418
Cl	0.566	4.191	36.0	-1.000
CU	0.439	3.750	12.0	0.142
OU	0.878	2.960	16.0	-0.390
NU	0.711	3.250	14.0	-0.542
HU2	0.000	0.000	2.0	0.330
HU1	0.000	0.000	2.0	0.330

E) Complete set of partial (site-site) radial distribution functions for reline

Figures 1-24: The 120 partial radial distribution functions for reline, plotted in blocks of 5 to facilitate viewing. The solid lines show the partial RDF, and the dashed lines plotted in the same colour and at the same origin show the running integral of this peak, and hence the mean coordination number at a certain radius. Sharp peaks denote more intense structural correlations between species at a given radius; note the high relative intensity and short radius of strong hydrogen bonding interaction RDFs, particularly the HOH-Cl correlation.

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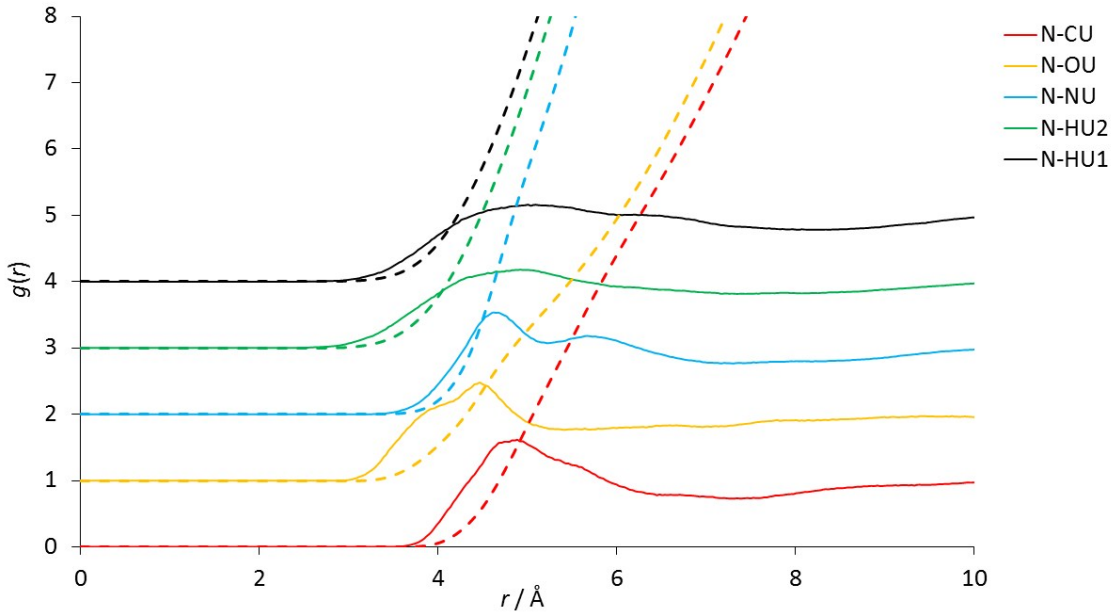
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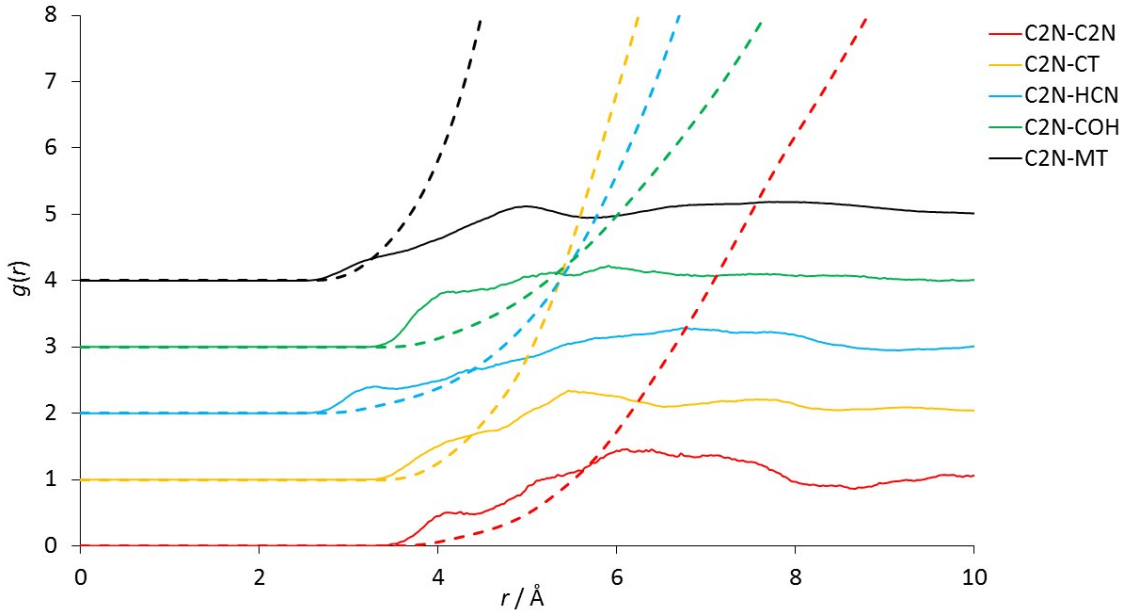
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C2N-COH
C2N-MT
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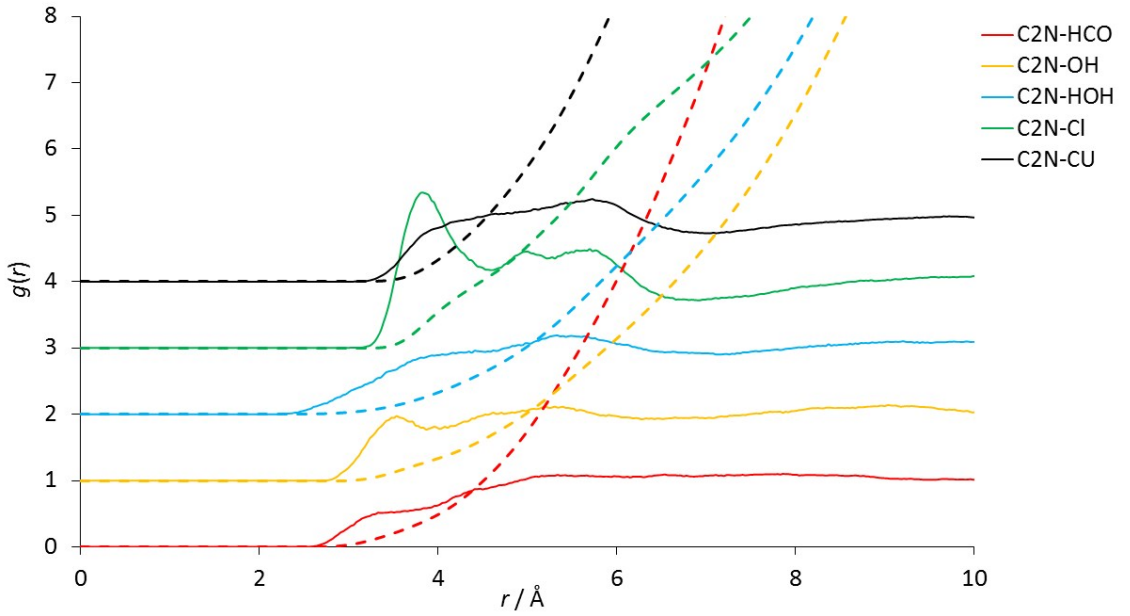
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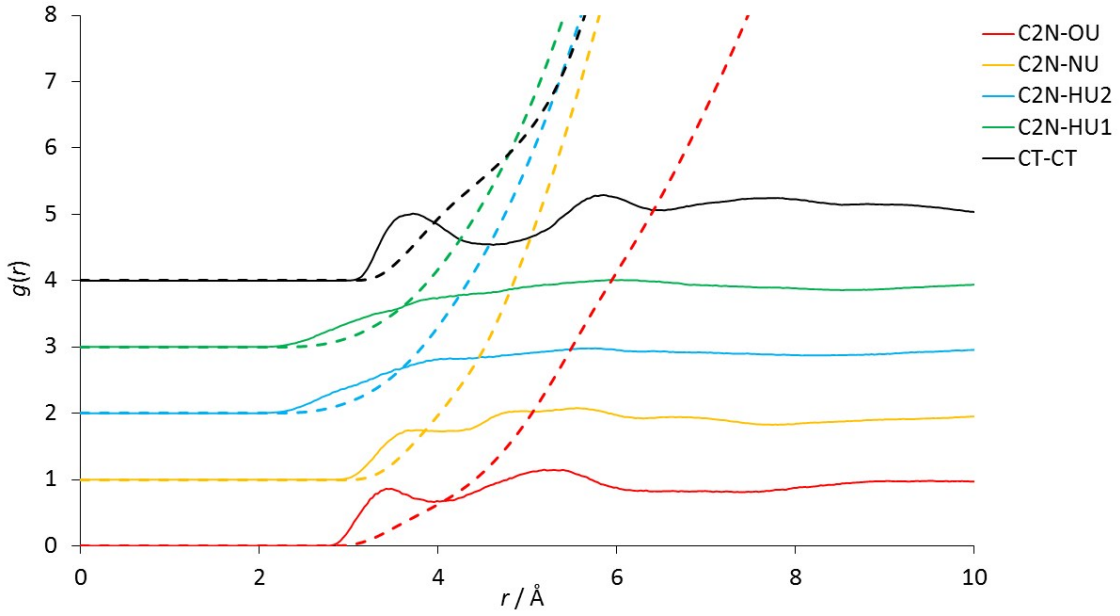
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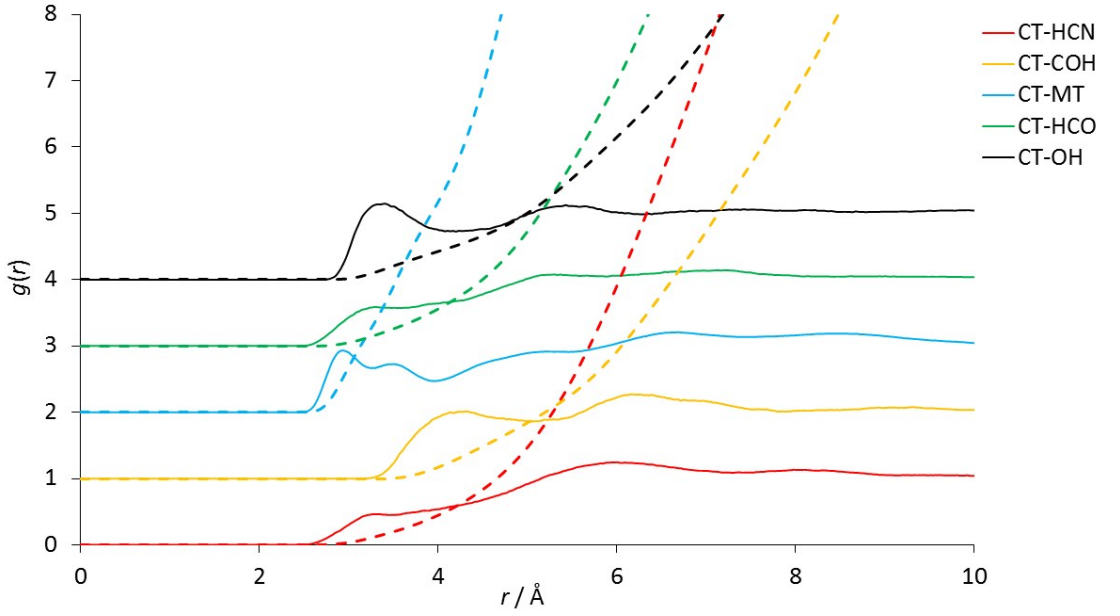
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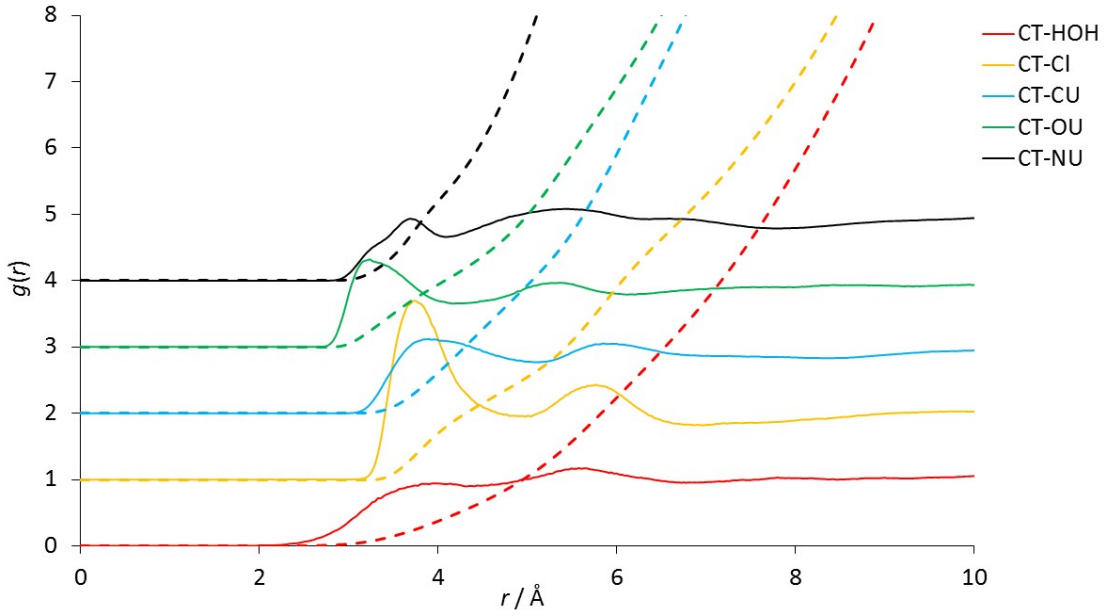
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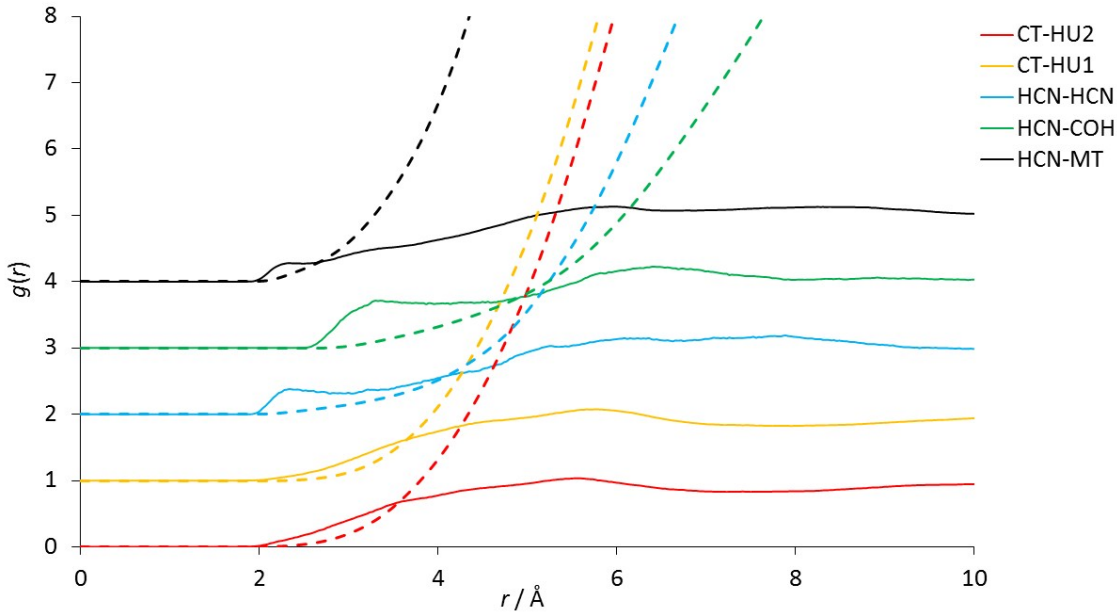
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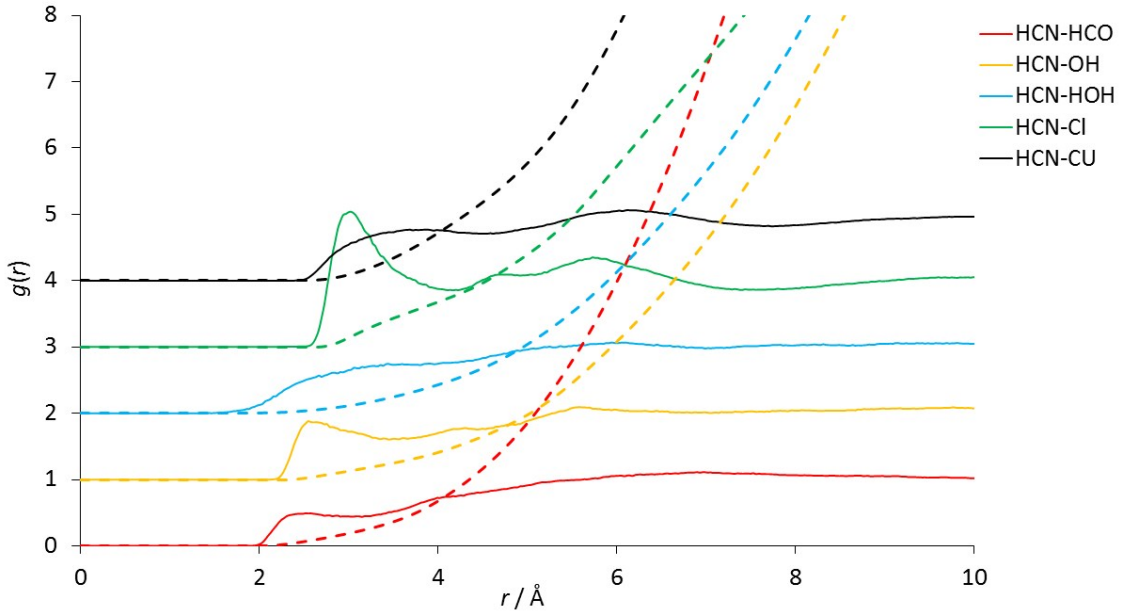
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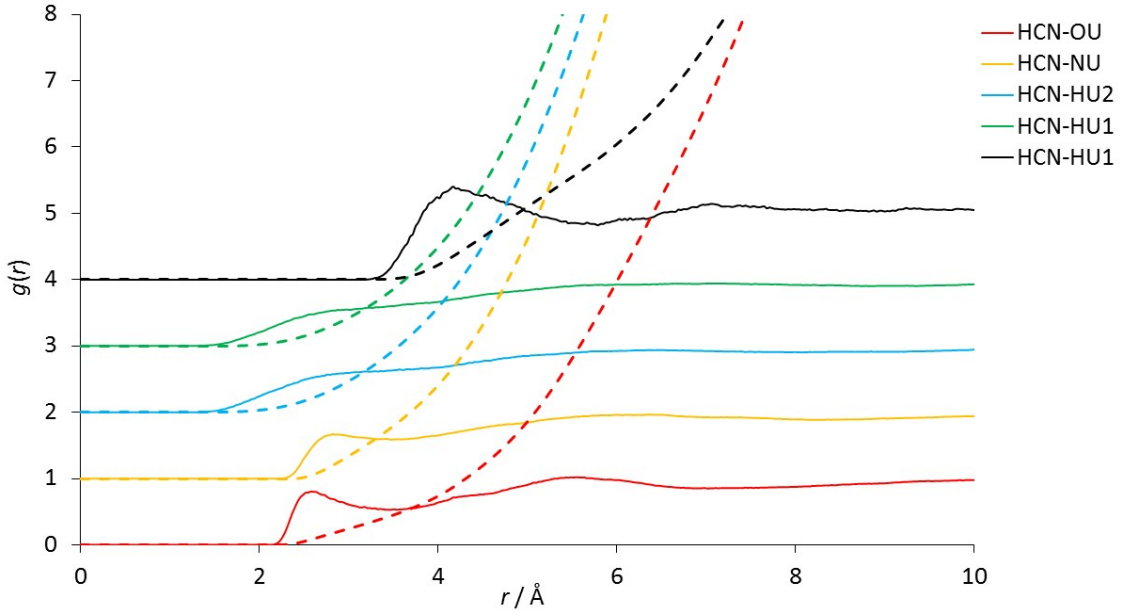
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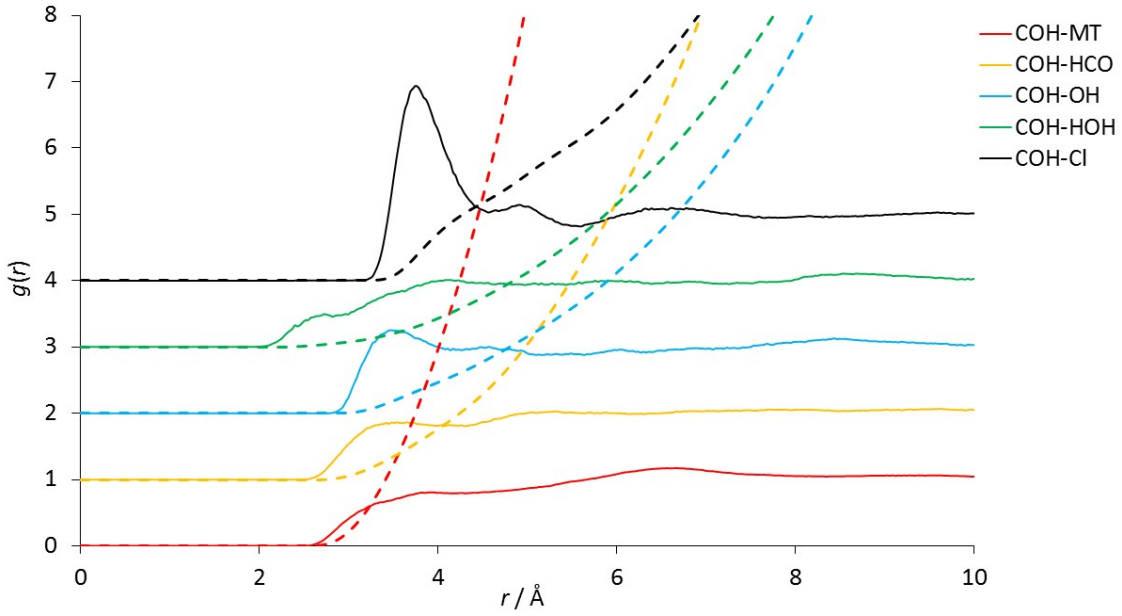
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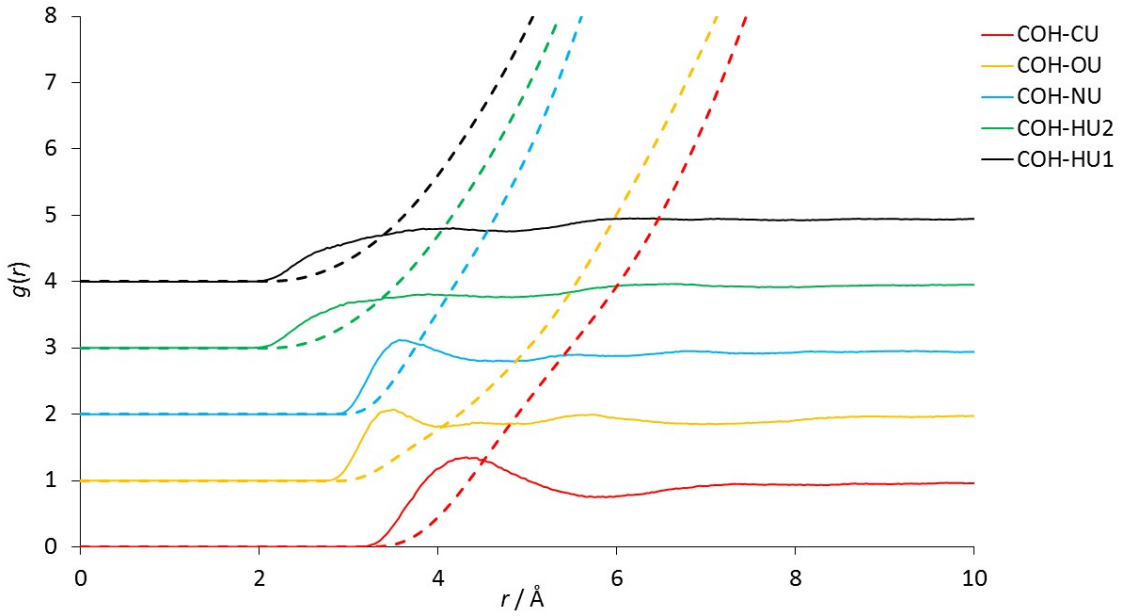
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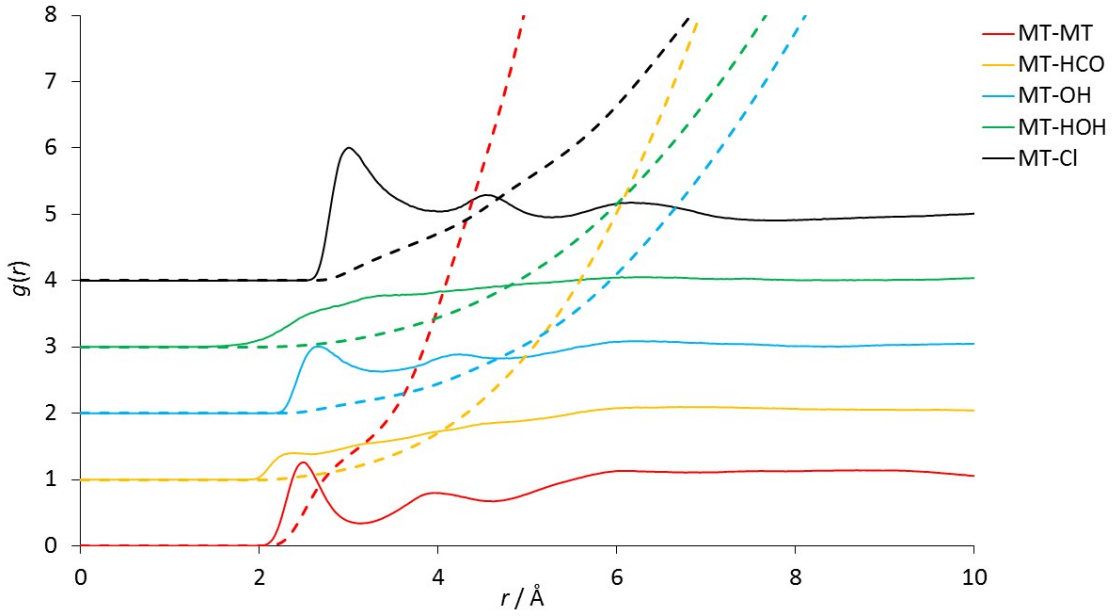
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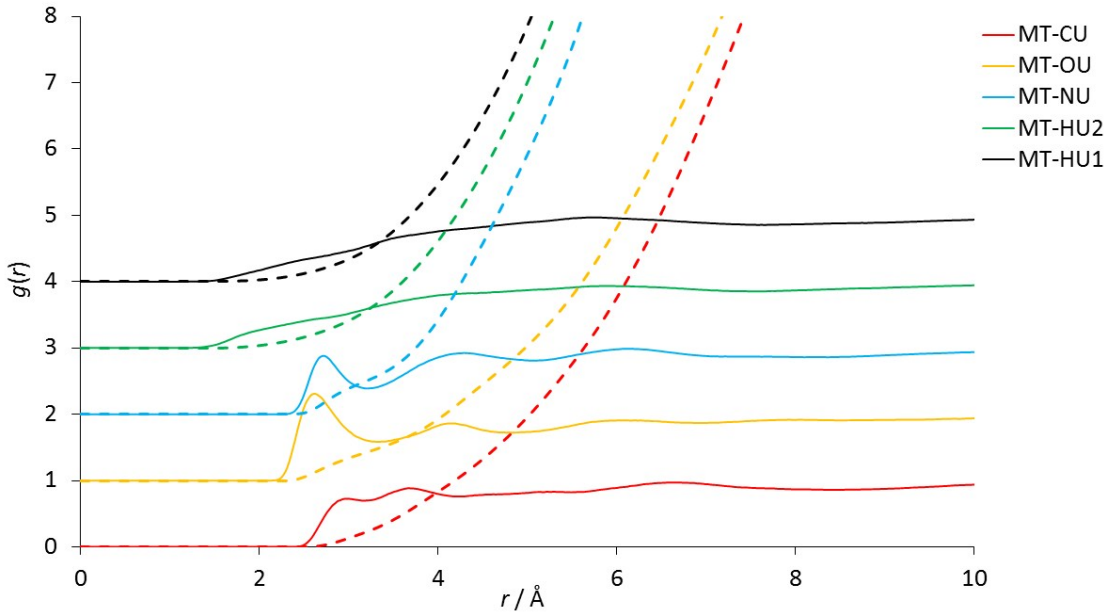
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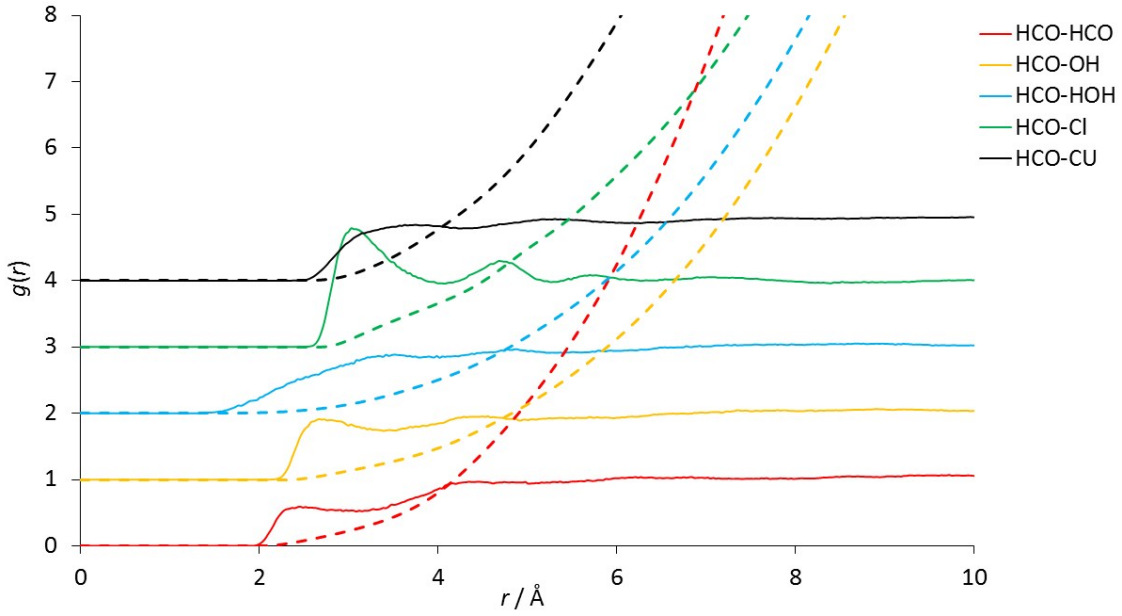
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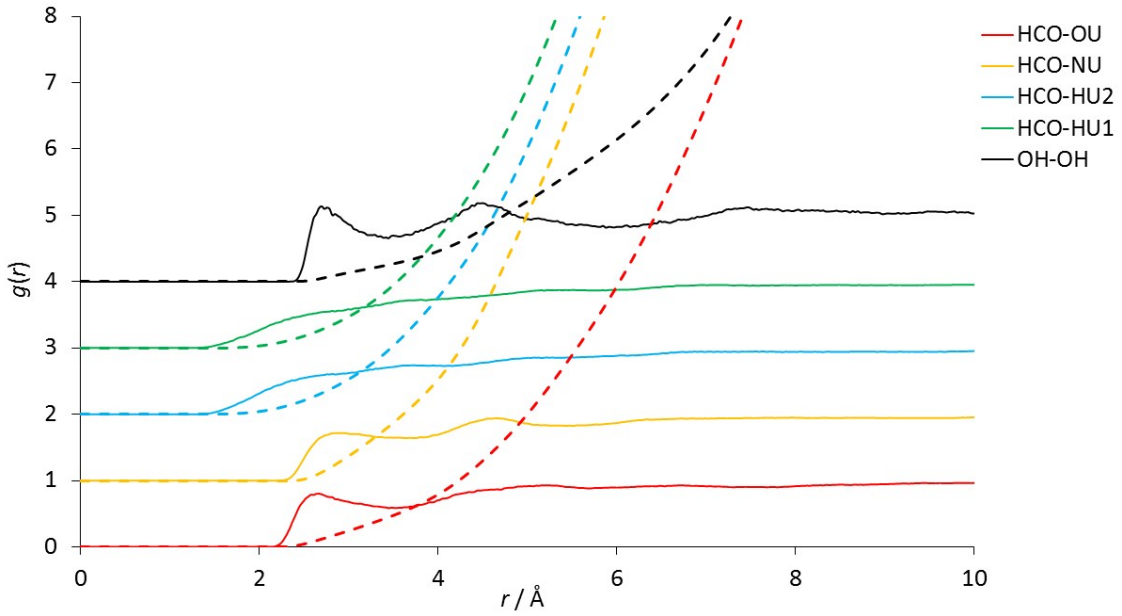
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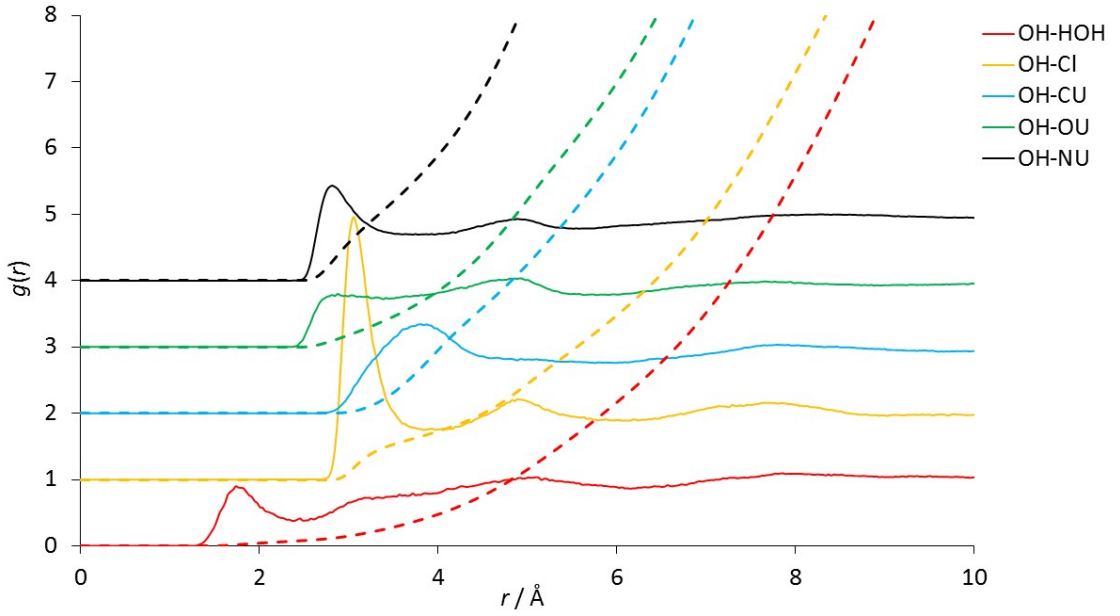
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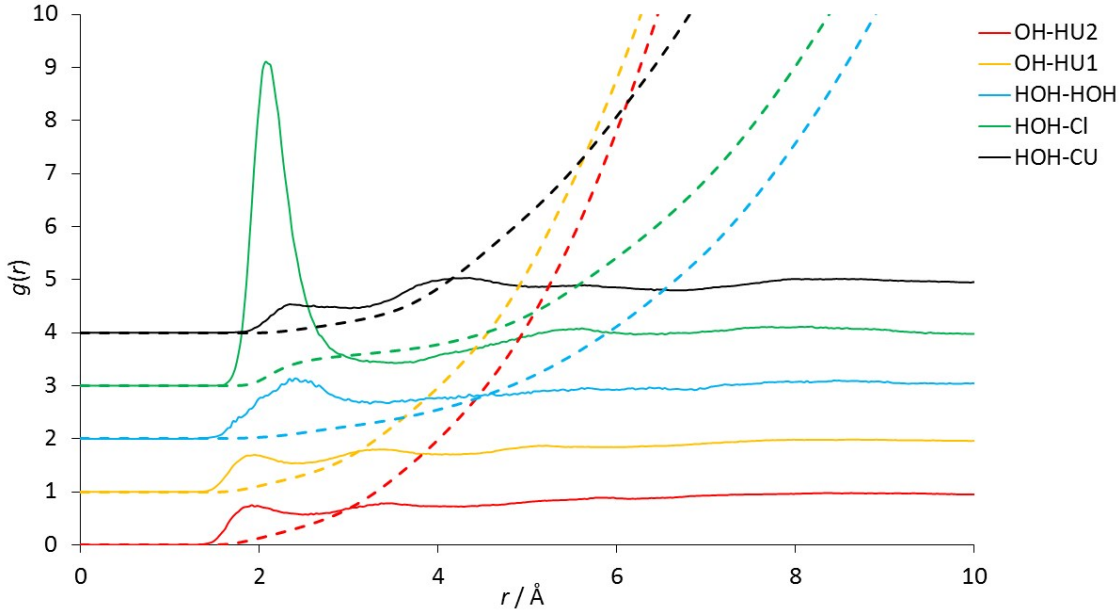
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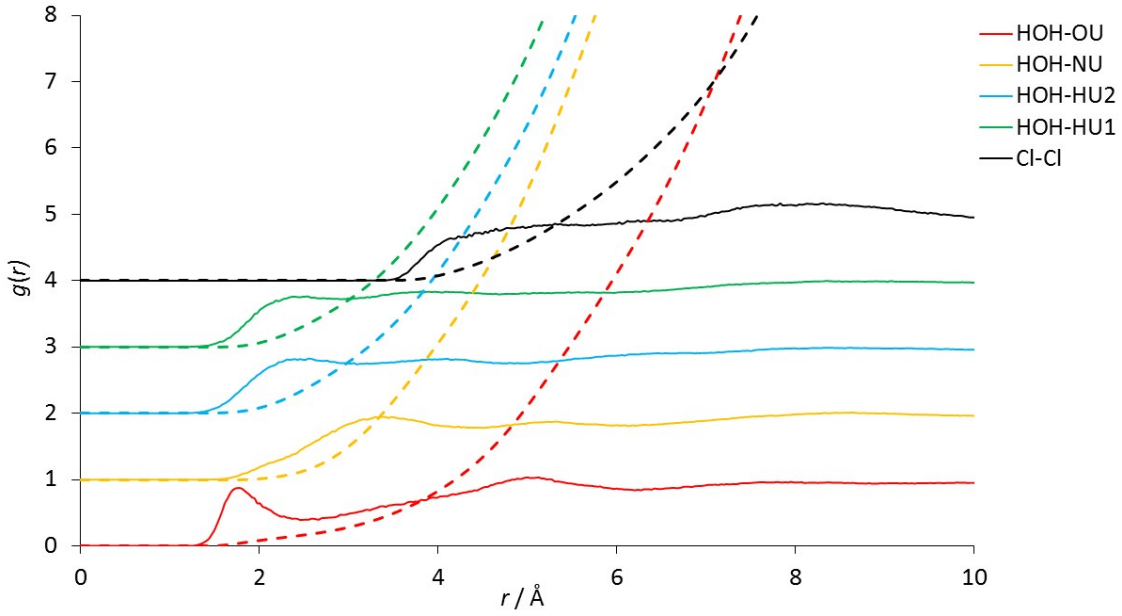
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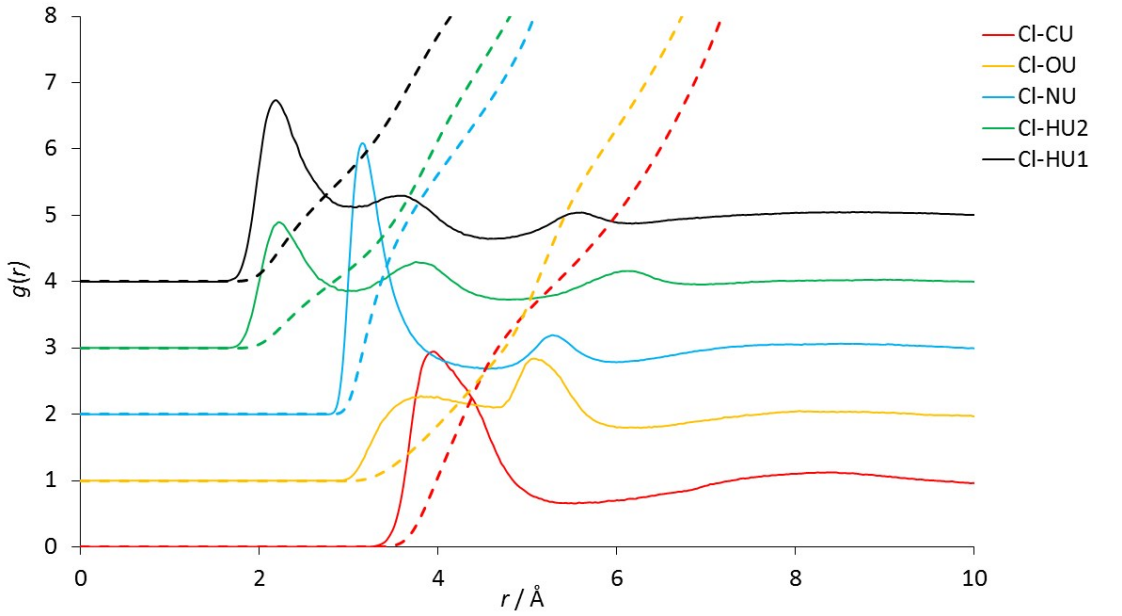
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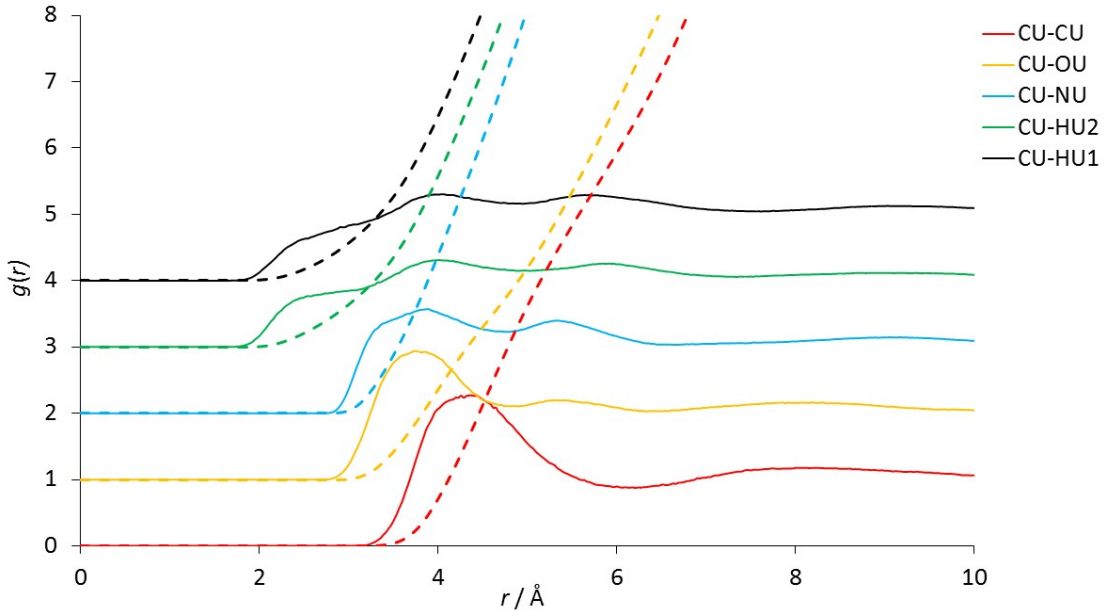
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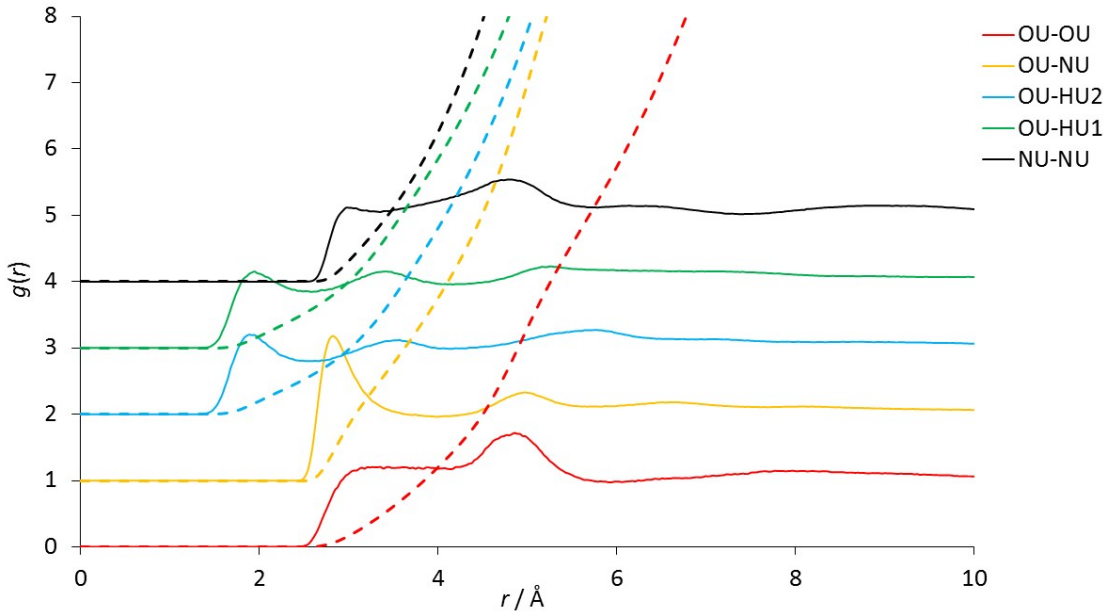
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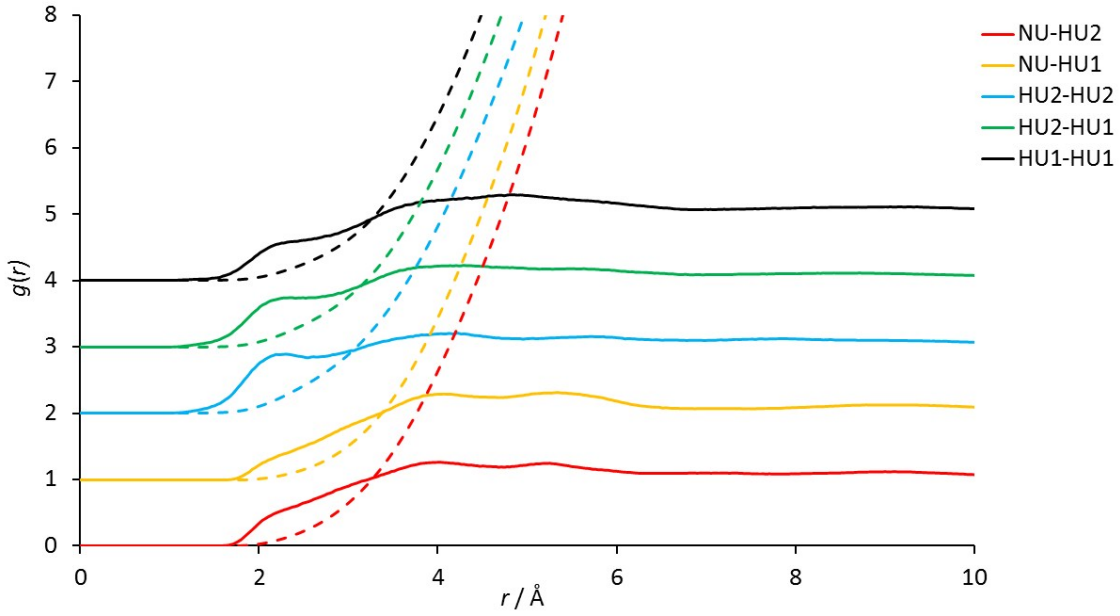

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