Supporting Information

Structure retrieval in liquid-phase electron scattering

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Contents

1.   Simulating *CPDF* contributions under IAM

CPDF contains contribution from intraatomic, interatomic and inelastic components. For interatomic part, it is interesting to further separate it into nucleus-nucleus, nucleus-electron and electron-electron pairs, as shown in Fig. 3 and 5. This section introduces how each component is simulated.

In general, we first simulate the scattering pattern of each term, the *CPDF* is then calculated using Eq. (19) in the main text. Under IAM, the form factor for elastic X-ray scattering $F^X(Q)$ and inelastic X-ray scattering $S^X(Q)$ is tabulated in ref.[1]. The form factor for elastic and inelastic electron scattering, $F^E(Q)$ and $S^E(Q)$, can be written as[2,3]

$$F^E(Q) = \frac{Z - F^X(Q)}{Q^2} \tag{S1}$$

$$S^E(Q) = \frac{S^X(Q)}{Q^4} \tag{S2}$$

The superscript *E* and *X* represents electron and X-ray scattering, respectively. *Z* is the nuclear charge of the atom. In Eq. (S1), *Z* represents the elastic scattering from the nucleus, $F^X(Q)$ represents the elastic scattering from the electrons, and the denominator Q^2 comes from the r^{-1} Coulomb potential.[2]

The inelastic scattering pattern is simply the sum of inelastic scattering cross section of individual atoms

$$I_{ine}^E(Q) = \sum_{m=1}^{N} S_m^E(Q) \tag{S3}$$

where the subscript m is summed over all atoms in the target system, and N is the total number of atoms. The elastic scattering pattern can be calculated using the following formula[2]

$$I_{elastic}^{E}(Q) = I_{intra}^{E}(Q) + I_{inter}^{E}(Q) = \sum_{m=1}^{N} |F_m^E(Q)|^2 + \sum_{m=1}^{N} \sum_{n=1,n\neq m}^{N} |F_m^E(Q)||F_n^E(Q)|\frac{\sin(Qr_{mn})}{Qr_{mn}} \tag{S4}$$

where r_{mn} is the distance between the mth and the nth atom. Here the first term is intraatomic component and the second term is interatomic component. Re-writing Eq. (S1) as:

$$F^E(Q) = F^{nuc}(Q) + F^{ele}(Q) \tag{S5}$$

where

$$F^{nuc}(Q) = \frac{Z}{Q^2}, F^{ele}(Q) = -\frac{F^X(Q)}{Q^2} \tag{S6}$$

The intermolecular component can then be written as:

$$I_{inter}^{E}(Q) = \sum_{m=1}^{N} \sum_{n=1,n\neq m}^{N} [F_m^{nuc}(Q) + F_m^{ele}(Q)][F_n^{nuc}(Q) + F_n^{ele}(Q)]\frac{\sin(Qr_{mn})}{Qr_{mn}}$$
$$= \sum_{m=1}^{N} \sum_{n=1,n\neq m}^{N} [F_m^{nuc}(Q)F_n^{nuc}(Q) + F_m^{ele}(Q)F_n^{ele}(Q) + F_m^{nuc}(Q)F_n^{ele}(Q) + F_n^{nuc}(Q)F_m^{ele}(Q)]\frac{\sin(Qr_{mn})}{Qr_{mn}} \tag{S7}$$

where the first term $F_m^{nuc}(Q)F_n^{nuc}(Q)$ represents nuclear-nuclear pairs, the second term $F_m^{ele}(Q)F_n^{ele}(Q)$ represents electron-electron pairs, and the other two terms $F_m^{nuc}(Q)F_n^{ele}(Q) + F_n^{nuc}(Q)F_m^{ele}(Q)$ represent nuclear-electron pairs. Substituting Eq. (S6) into Eq. (S7) one can calculate each component separately.

For liquid phase samples, it is usually more efficient to directly simulate scattering patterns from $g_{mn}(r)$, the radial distribution function of atom pair mn. We use the method proposed by Dohn et al. [4]

$$I_{elastic}^{E} = \sum_{m=1}^{N} F_m^E(Q)^2 + \sum_{m,n} F_m^E(Q)F_n^E(Q)\frac{N_m(N_n - \delta_{m,n})}{V}\int_0^R \frac{\sin(Qr)}{Qr}4\pi r^2[g_{mn}(r)-1]dr \tag{S8}$$

where $\delta_{m,n}$ is the kronecker delta function, V is the volume of the box in simulation, and R is the largest distance in $g_{mn}(r)$.

2. Influence of maximum Q range on *CPDF*

In our LES experiment, we measure diffraction up to Q_{max}=11.8Å^{-1}, which is much smaller than the state-of-the-art for both neutron and X-ray scattering. Here we use the simulated liquid water scattering to show the impact of Q range to the *CPDF* retrieval.

The interatomic, intraatomic and inelastic *CPDF* for Q_{max}=6, 9, 12, 15, 18, 21 Å^{-1} are shown in Fig. S1. To avoid edge effects in the sine transform, the damping factor α is chosen so that $e^{-\alpha Q_{max}^2}=2.3\times10^{-4}$, matching the case for this experiment (α = 0.06 and Q_{max} =11.8 Å^{-1}). This choice of the damping factor treats the edge effect equally for various Q_{max}, but does introduce different level of peak broadening. For this reason, *CPDF*$_{intra}$ and *CPDF*$_{ine}$ extends to different r range for different Q_{max}, and the hydrogen bond peak at ~1.9 Å is absent in *CPDF*$_{inter}$ for Q_{max}=6 Å^{-1} and Q_{max}=9 Å^{-1}. For Q_{max}=6 Å^{-1} the *CPDF*$_{inter}$ becomes the dominating term at roughly r=2.7 Å, while for Q_{max}=21 Å^{-1} the *CPDF*$_{inter}$ becomes the dominating term at roughly r=1.3 Å. In the current experiment, this separation is at ~2 Å, right above the ~1.9 Å

hydrogen bond peak, and a background removal is needed to reveal this peak. The simulations in Fig. 7 show that an experiment with a higher Q range should be able to resolve the hydrogen bond peak directly without background removal. However, since the high Q signal in the current experiment might be dominated by multi-scattering (Fig. 3B in the main text), this might require a thinner liquid sheet.
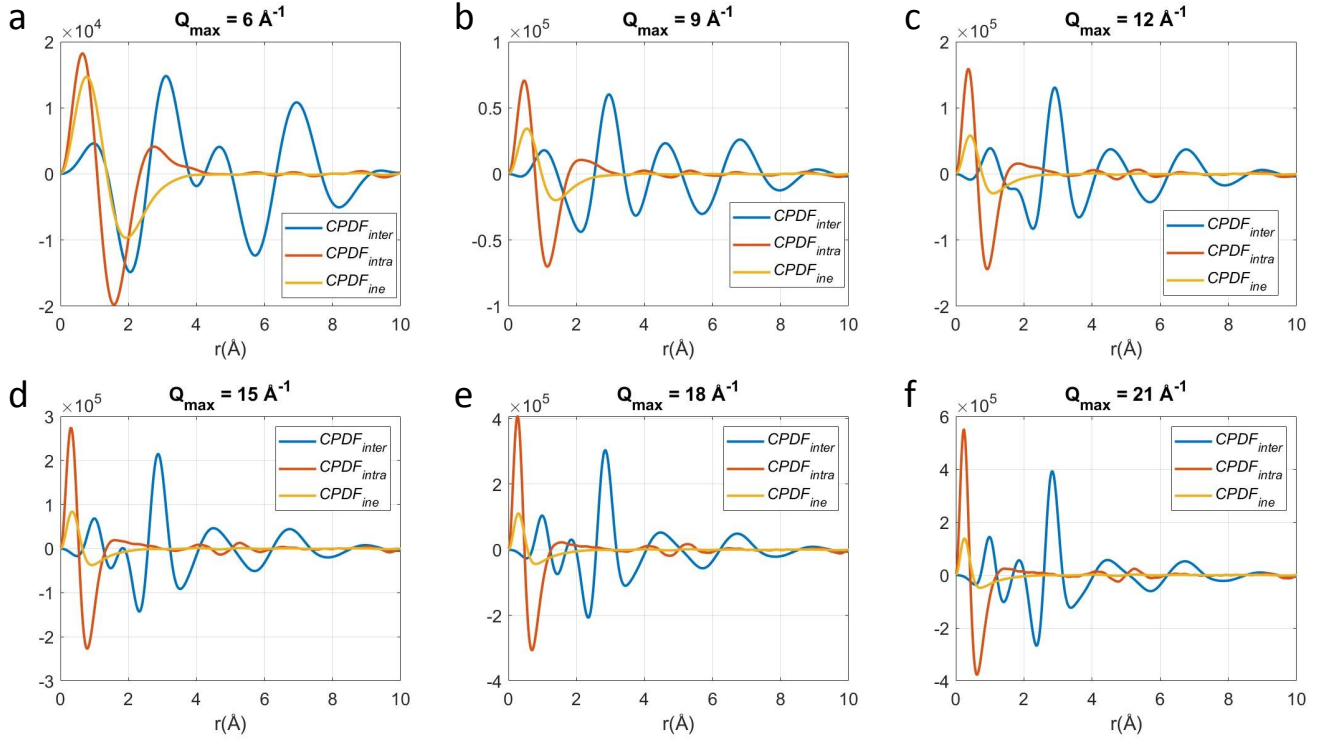

FIG. S1. Impact of Q_{max} on $CPDF$. The $CPDF_{inter}$, $CPDF_{intra}$ and $CPDF_{ine}$ for 6 different maximum Q ranges for H_2O, using simulated scattering patterns under IAM. The damping factor α is chosen so that $e^{-\alpha Q_{max}^2} = 2.3 \times 10^{-4}$ (see text).

3. Simulated $CPDF_{inter}$ by atom pairs in four liquids

Fig. S2 show the simulated $CPDF_{inter}$ by different atom pairs for all 4 liquids under GROMACS+IAM simulation.
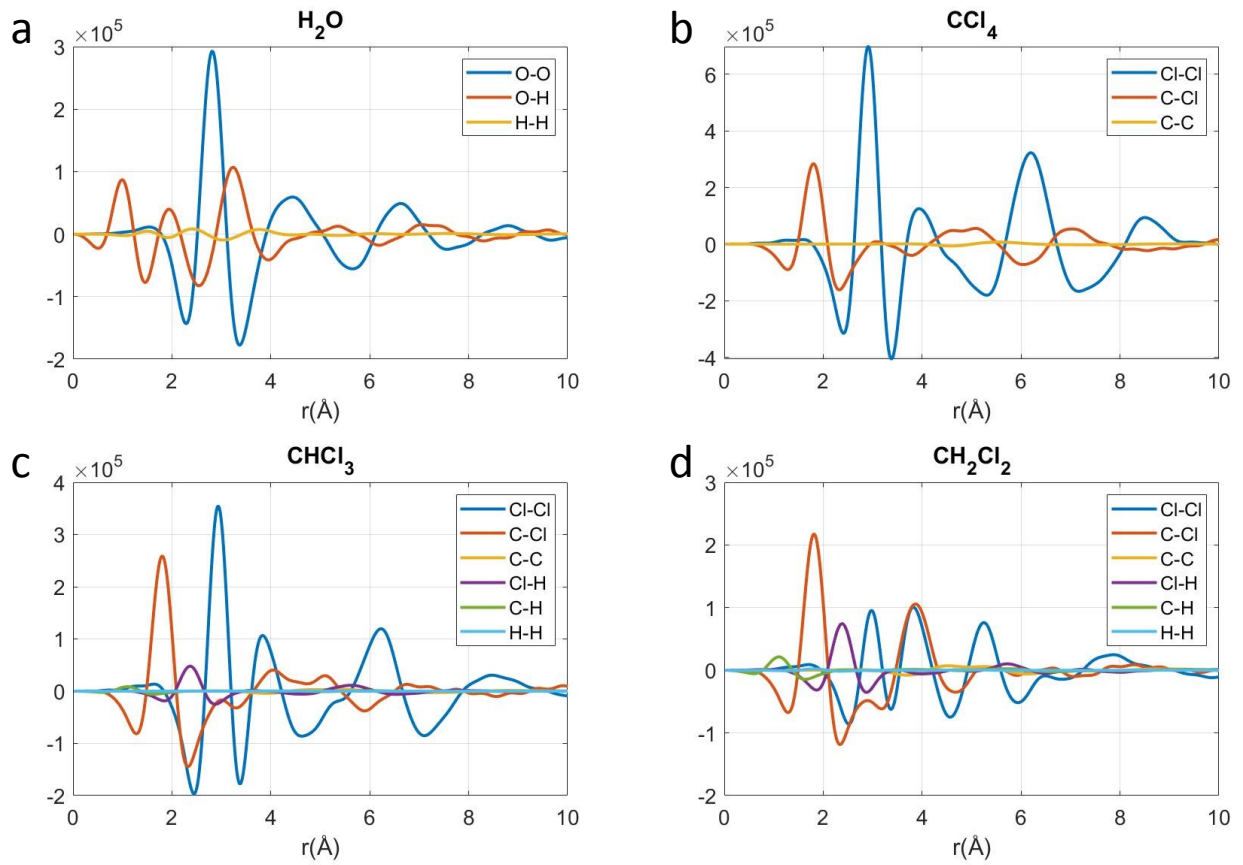
FIG. S2. Simulated $CPDF_{inter}$ by pairs for 4 liquids. Each panel gives the $CPDF_{inter}$ by each types of atom pairs, calculated using Eq. (19) in the main text with damping factor α = 0.03 and Q_{max} =11.8 Å^{-1}.

4. Experimental background-removed *CPDF* in four liquids

Fig. S3 show the experimental background-removed CPDF together with simulated $CPDF_{inter}$ for four liquids studied in this work. The background removal method is based on an empirical polynomial fitting that is described in the main text. In the fitting, part (a) used a third order polynomial and parts (b-d) used a fourth order polynomial.
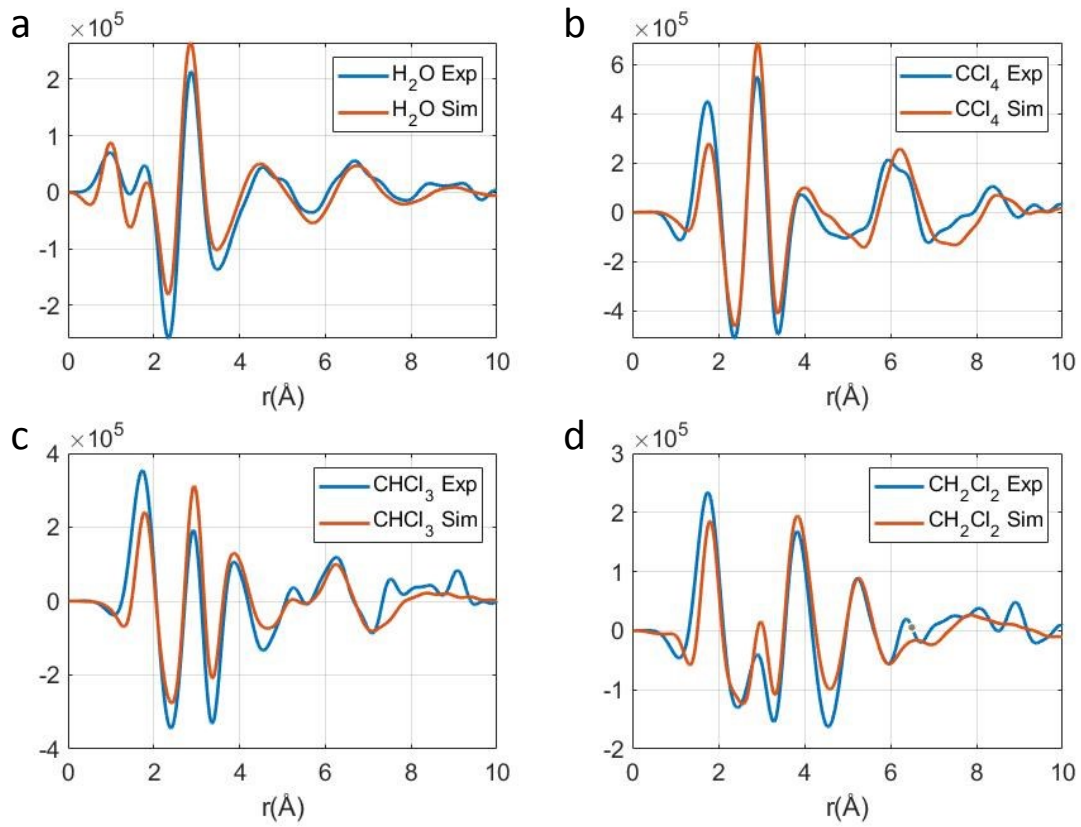
FIG. S3. Experimental background removed CPDF (blue) and simulated $CPDF_{inter}$ (red) for (a) H_2O, (b) CCl_4, (c) $CHCl_3$ and (d) CH_2Cl_2. All curves are calculated using Eq. (19) in the main text with damping factor α = 0.03 and Q_{max} =11.8 Å^{-1}.

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