

On the existence of a scattering pre-peak in the mono-ols and diols

M. Požar^{1,2}, A. Perera¹

¹ Laboratoire de Physique Théorique de la Matière Condensée (UMR CNRS 7600), Université Pierre et Marie Curie, 4 Place Jussieu, F75252 Paris cedex 05, France

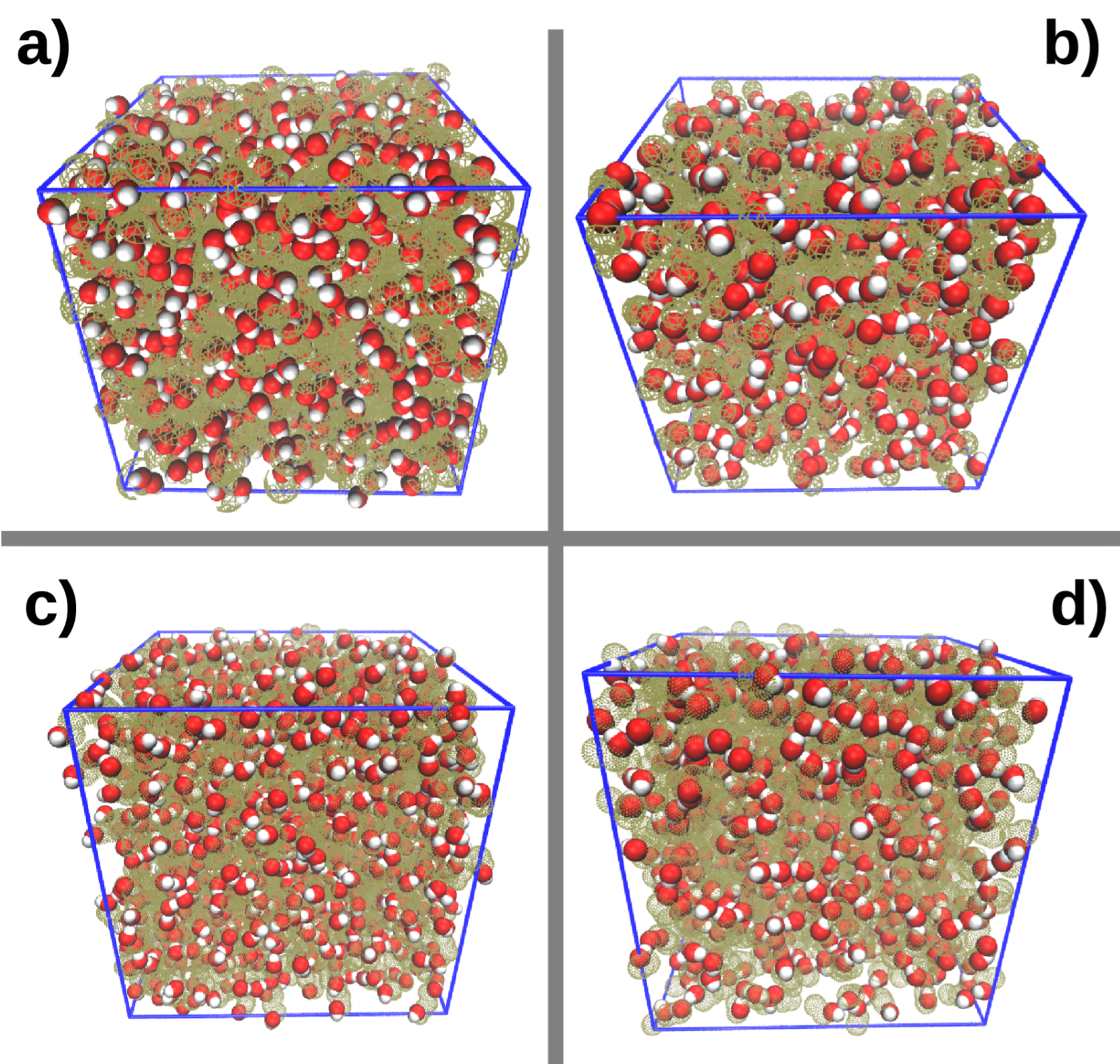
² Department of Physics, Faculty of Sciences, University of Split, Rudera Boškovića 33, 21000 Split, Croatia



Associating liquids, such as water and alcohols, exhibit a wealth of structural organization at the microscopic level. The existence of specific structuring in neat mono-ols [1] has been pointed out by the results of scattering experiments on those alcohols, which have revealed a pre-peak in scattering intensity [2]. With the increase of alkyl chain length, the pre-peak in scattering intensity becomes more prominent [2], showing the increase of chain-like clusters. But what happens in alcohols which have two hydroxyl groups bound by an alkyl chain?

In this work, we are looking into four neat 1,n-diols (1,2-ethanediol to 1,5-pentanediol), which were studied by means of molecular dynamics simulations. Radial distribution functions, site-site structure factors, cluster size distribution probabilities and calculated X-ray intensities are reported and compared with corresponding mono-ols [3]. It's found that in diols, just like in monools, the increase in carbon chain length leads to an increase in the hydroxyl group associations. However, our calculated X-ray intensities show that the pre-peak tends to diminish to a shoulder, which is in variance with monools. We attribute this contrasting finding to the fact that the alkyl chain is constrained between the two hydroxyl groups in linear diols, while they are free in linear mono-ols.

Snapshots



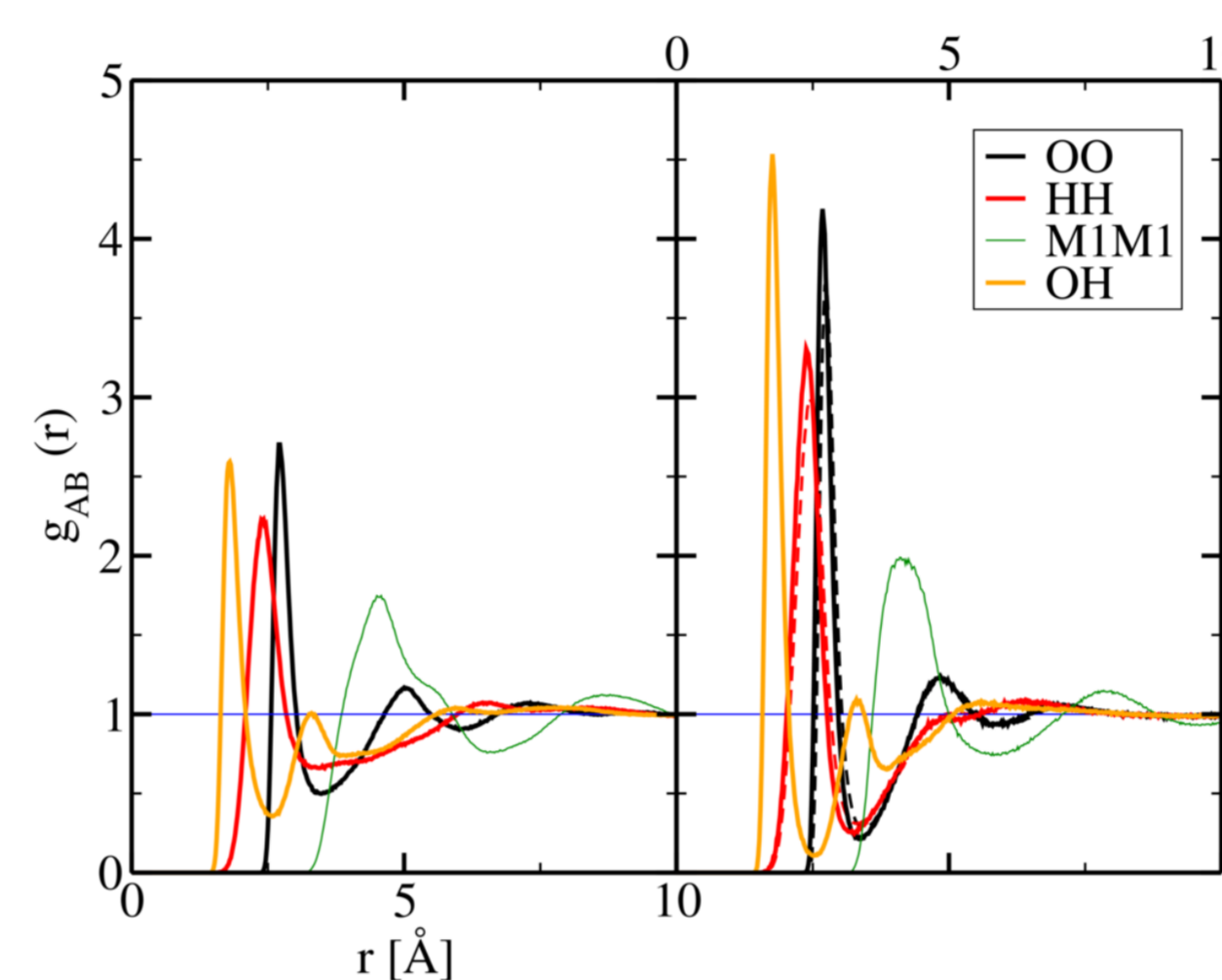
a) ETHANEDIOL and b) METHANOL;
c) 1,4-BUTANEDIOL and d) ETHANOL

Simulation details

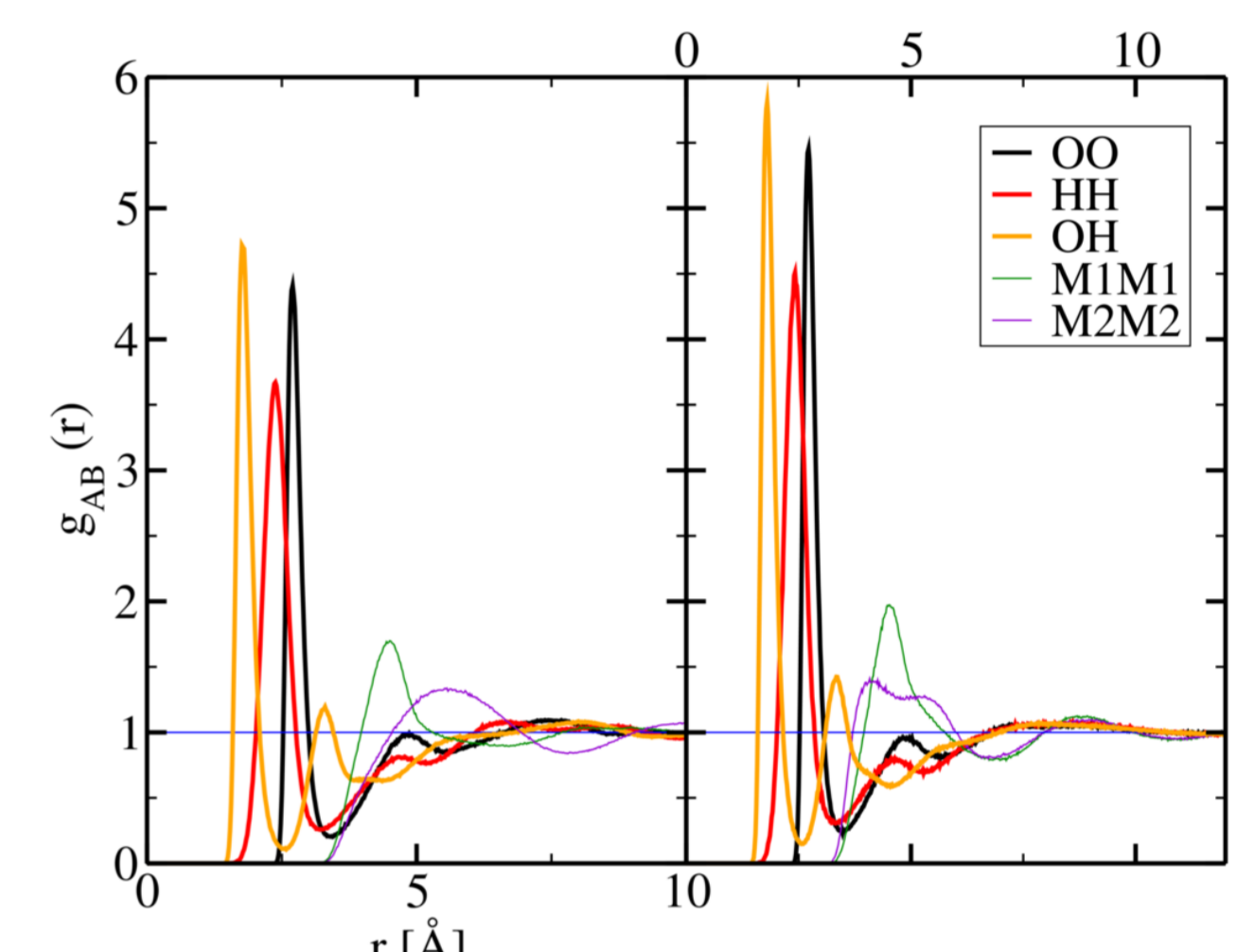
All the simulations were performed in Gromacs 4.6 [4]. The systems were ~1000 particles. Packmol [5] was used for obtaining the initial configurations, which were then equilibrated for at least 2 ns. The production runs lasted for 2 ns and 1500 configurations were sampled for the static properties. The simulations were done at atmospheric pressures and room temperature.

The OPLS [6] and TraPpe [7] models were used for methanol, while ethanol and the 1,n-diols were modelled with only with the TraPpe [7, 8] forcefield.

Pair correlation functions



Comparison of: ETHANEDIOL (LEFT) and METHANOL (RIGHT) g(r)

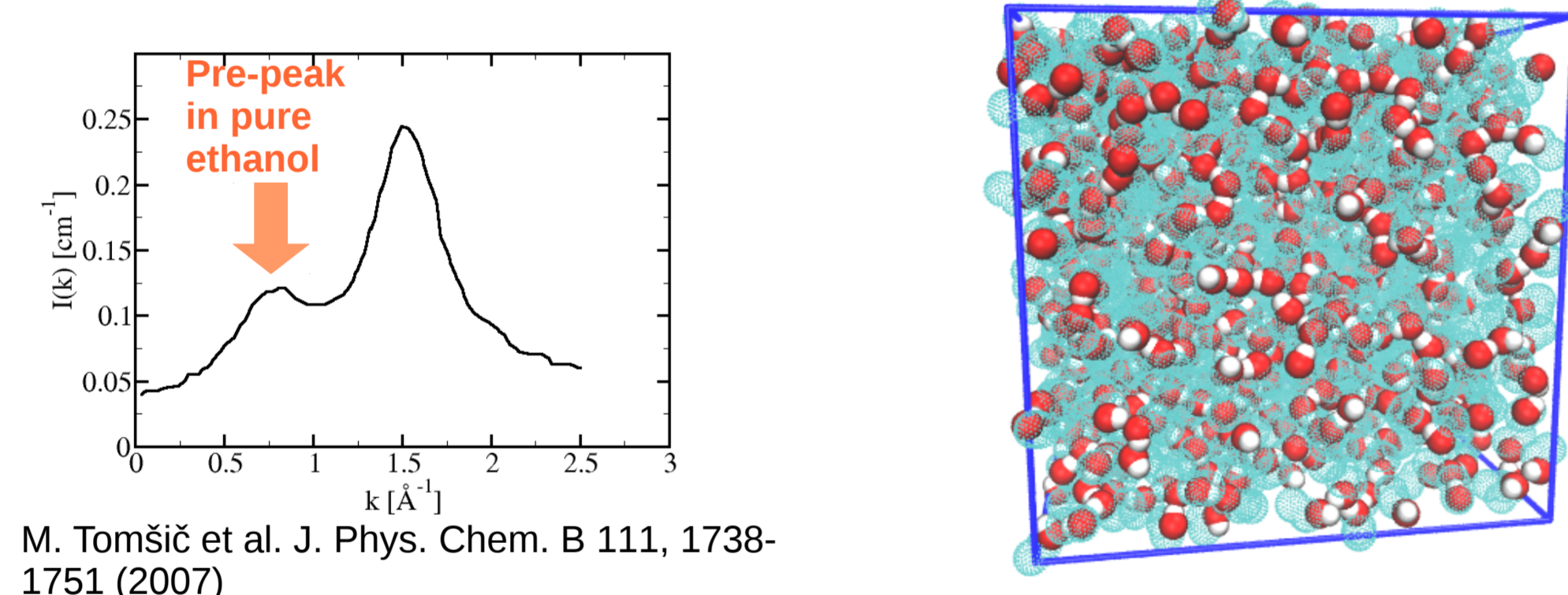


Comparison of: 1,4-BUTANEDIOL (LEFT) and ETHANOL (RIGHT) g(r)

Scattering experiments in neat mono-ol alcohols

Scattering experiments yield scattering intensity $I(k)$.

The scattering intensity of pure monool alcohols has a pre-peak (at small k values) → Signature of **clusters** (loops and chains)



M. Tomšič et al. J. Phys. Chem. B 111, 1738-1751 (2007)

Scattering calculations

To calculate the scattering intensity, we use the Pings-Waser expression [9], which conveniently allows to express this quantity in terms of the individual structure factors:

$$I(k) = \sum_i f_i(k)^2 + \rho \sum_{ij} f_i(k) f_j(k) \tilde{h}_{ij}(k)$$

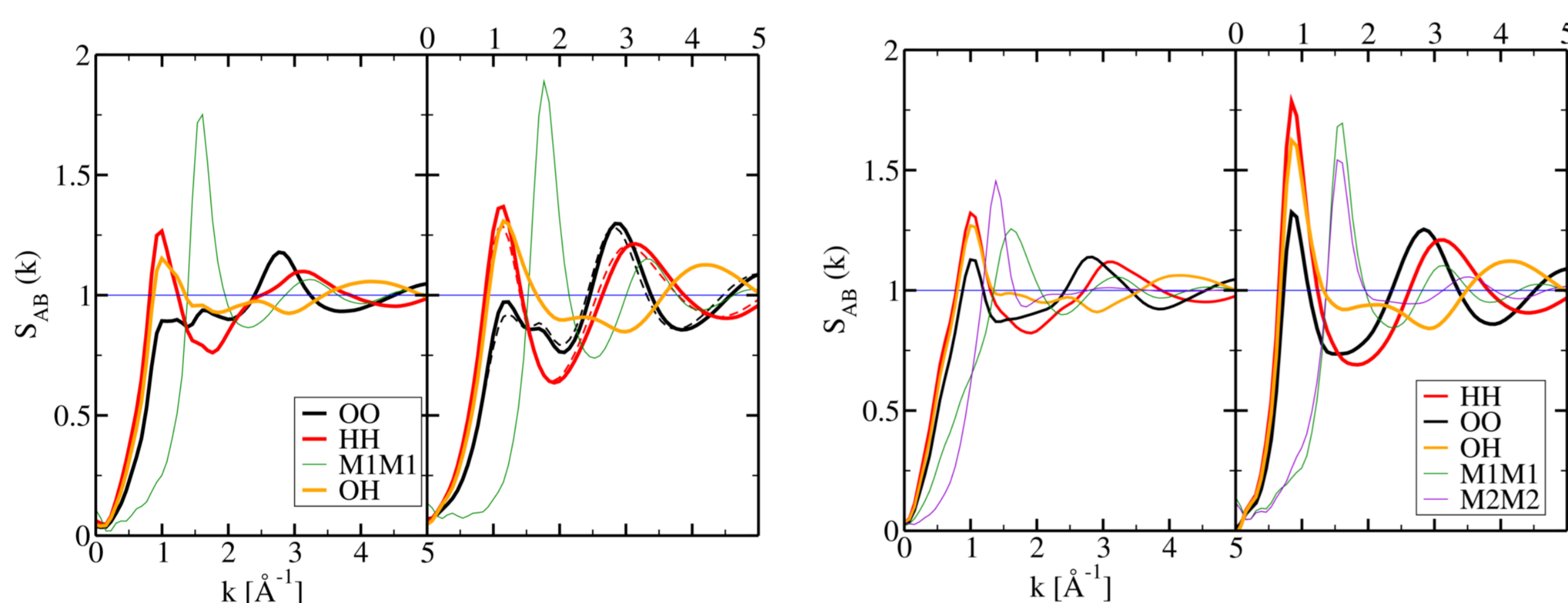
where the first term is the ideal contribution: $I_{ideal}(k) = \sum_i f_i(k)^2$

while the second is the sum runs over all type of atoms. The f -functions are the atomic form factors, ρ is the number of particles N per volume V , and the h functions are the Fourier transforms of the pair correlation functions. Thanks to the definition of the structure factor, one can rewrite the second contribution as:

$$I(k) = \sum_{ij} f_i(k) f_j(k) S_{ij}(k)$$

Since the forcefields used in this work feature united atoms for methyl and methylene groups, we used the following approximation for describing the form-factor of the united atom groups: $f_M(k) = f_C(k) + n f_H(k)$

Structure factors



Comparison of: ETHANEDIOL (LEFT) and METHANOL (RIGHT) S(k)

Comparison of: 1,4-BUTANEDIOL (LEFT) and ETHANOL (RIGHT) g(r)

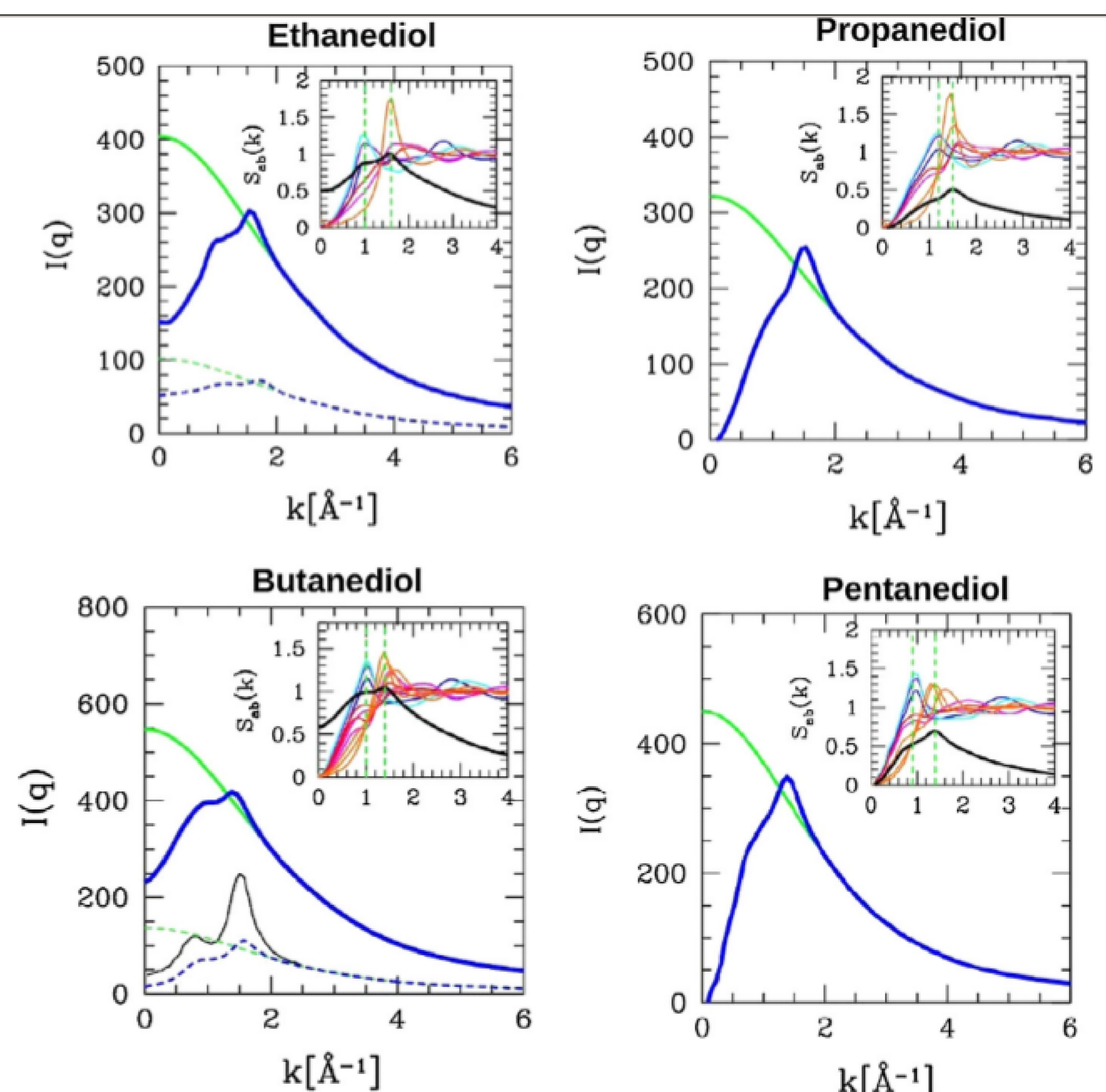
The atom-atom structure factors are defined in relation to the Fourier transforms of the site-site pair correlation functions $g_{ij}(r)$:

$$S_{ij}(k) = \delta_{ij} + \rho \int d\vec{r} [g_{ij}(r) - 1] \exp(i\vec{k} \cdot \vec{r})$$

References

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BLUE: calculated scattering intensities $I(k)$ for diols; GREEN: ideal contribution to the scattering. DASHED BLUE: $I(k)$ for methanol (shown under ethanediol) and ethanol (shown under butanediol). DASHED GREEN: ideal contribution for methanol and ethanol scattering. BLACK: experimental data for ethanol, taken from [2].

INSETS: atom-atom structure factors for each diol, with a scaled $I(k)$ (in thick black line), with vertical lines indicating the position of the pre-peak and main peak.