

First Principles Molecular Dynamics Simulations of Liquid Water under Pressure

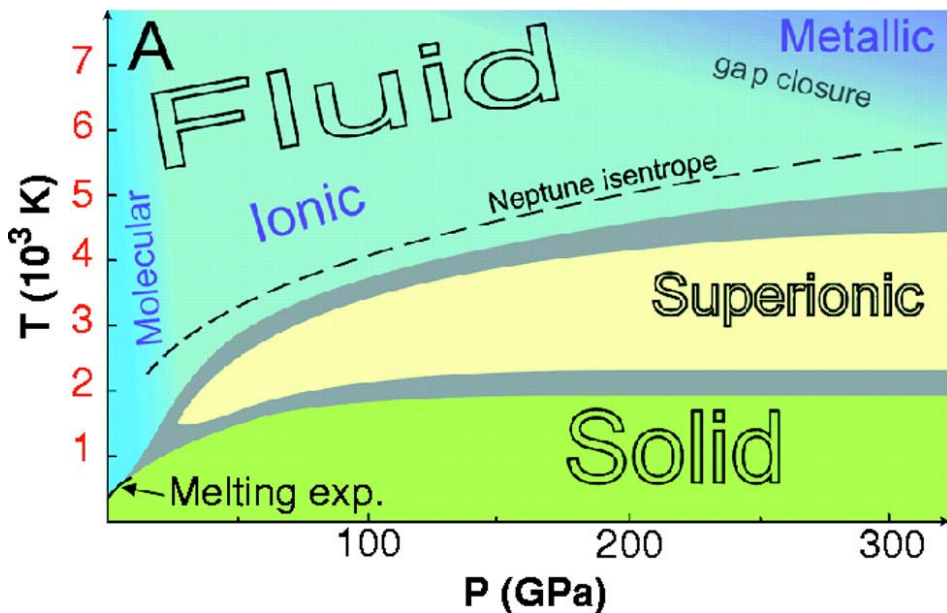
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High pressure structural studies of liquid water

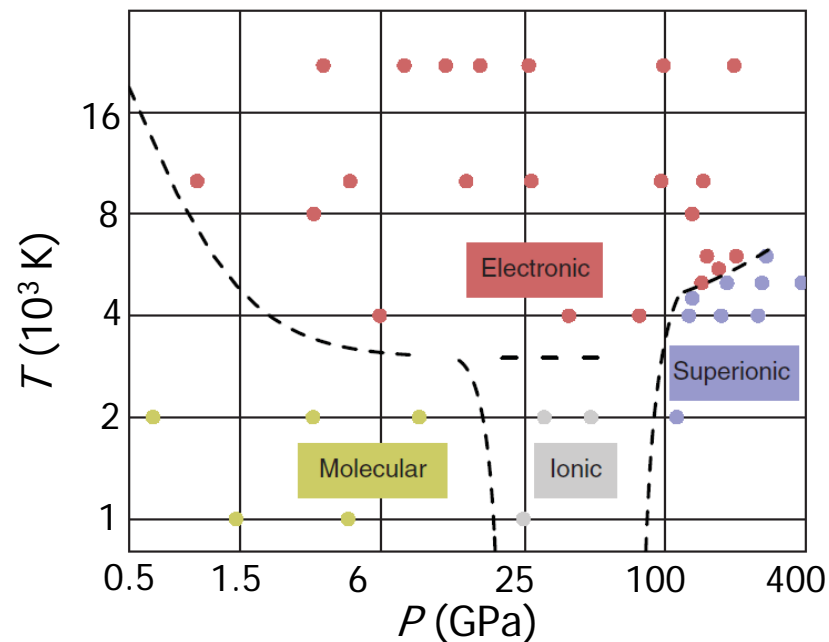
- Simulation

Constant pressure Car-Parrinello MD



C. Cavazzoni *et al.*, Science **283**, 44 (1999).

First principles MD with hot electrons



T. R. Mattsson & M. P. Desjarlais, Phys. Rev. Lett. **97**, 017801 (2006).

The two simulations predicted completely different P - T phase diagram of water.

High pressure structural studies of liquid water (2)

- Experiment

Fluid cell + X-ray or Neutron diffraction

$P < 1$ GPa

G. W. Neilson *et al.*, J. Phys. D. **12**, 901 (1979). (ND, 1 kbar)

A. Y. Wu *et al.*, Mol. Phys. **47**, 603 (1982). (ND, 15.6 kbar)

G. A. Gaballa & G. W. Neilson, Mol. Phys. **50**, 97 (1983). (ND, 6 kbar)

A. V. Okhulkov *et al.*, J. Chem. Phys. **100**, 1578 (1994). (XD, 7.7 kbar)

M.-C. Bellisent-Funel & L. Bosio, J. Chem. Phys. **102**, 3727 (1995). (ND, 6 kbar)

A. K. Soper & M. A. Ricci., Phys. Rev. Lett. **84**, 2881 (2000). (ND, 400 MPa)

Diamond anvil cell + X-ray diffraction

relatively low S/N ratio

J. Eggert *et al.*, J. Phys.: Condens. Matter **14**, 11385 (2002). (up to 1.1 GPa)

Large volume press + Neutron diffraction

up to 6.5 GPa

Y. Le Godec *et al.*, High Pressure Res. **24**, 205 (2004). (6.5 GPa, only S(Q))

Th. Strässle *et al.*, Phys. Rev. Lett. **96**, 067801 (2006). (EPSR method)

Large volume press + X-ray diffraction

up to 17.1 GPa

Y. Katayama *et al.*, PSJ 2005 Autumn Meeting (19pXG-11)

Y. Katayama *et al.*, PSJ 2006 Spring Meeting (29pTH-2)

Y. Katayama *et al.*, Phys. Rev. B **81**, 014109 (2010).

Structure of liquid water under high pressure up to 17 GPa

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The structure of liquid water was studied along the melting curve up to 17.1 GPa and 850 K by *in situ* x-ray diffraction. Because an oxygen atom has a much larger x-ray scattering power than that of a hydrogen atom, pressure dependence of local molecular arrangements was revealed straightforwardly. At low pressures, the local structure changed toward a simple liquidlike structure through an increase in the coordination number of water molecules. Once densely packed structure was achieved around 4 GPa, the volume was reduced through the decrease in the intermolecular distance on further compression. Classical molecular-dynamics simulations well reproduced the experimental results although the degree of agreement depended on pressure. Limitations of the pair-potential model were discussed.

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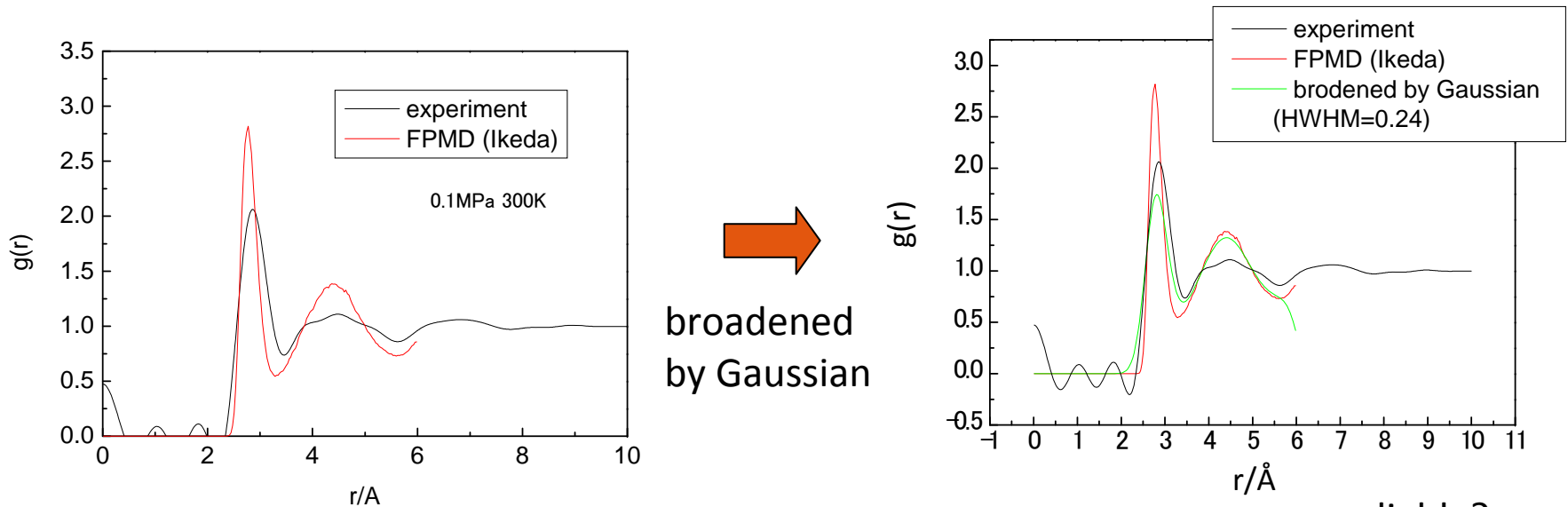
PACS number(s): 64.70.Ja, 61.25.Em, 62.50.-p

I. INTRODUCTION

The structure of water and its pressure variations have been widely studied because they are crucial for understanding the unusual properties of water.¹⁻¹⁷ In ordinary ice (ice Ih), each water molecule forms hydrogen bonds with four nearest-neighbor molecules in the tetrahedral position. This relatively open network structure shows a remarkably rich response to pressure and temperature: there are at least 13

It is not, however, trivial to obtain an O-O partial structure from neutron scattering because the contribution of O-O pairs to the total scattering is less than 9%. The O-O partial structure reported in the aforementioned study²⁰ was obtained with a help of a Monte Carlo simulation based on a classical water model (empirical potential structural refinement method) (Refs. 9-11): an initial structural model was constructed by a simulation using the extended simple point

How to compare FPMD and experimental results?



broadened
by Gaussian

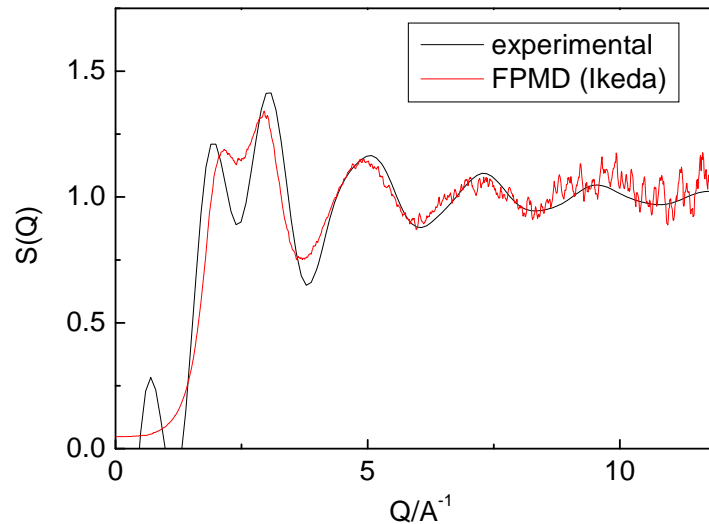
reliable?

r range is too narrow...



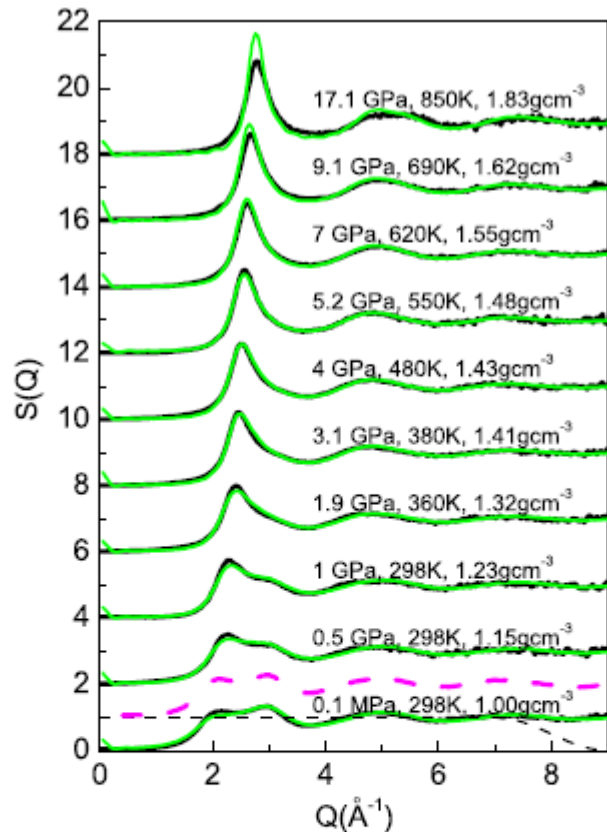
$$S(K) = 1 + \int_0^\infty 4\pi r^2 \{\rho(r) - \rho_0\} \frac{\sin Kr}{Kr} dr$$

$$\rho(r) = \rho_0 g(r)$$



reliable?

How to compare FPMD and experimental results? (2)



FT with window

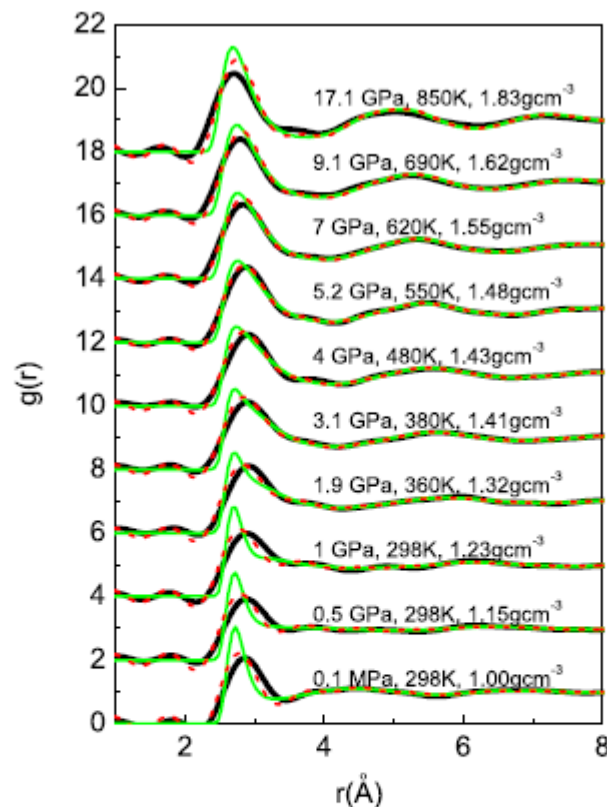


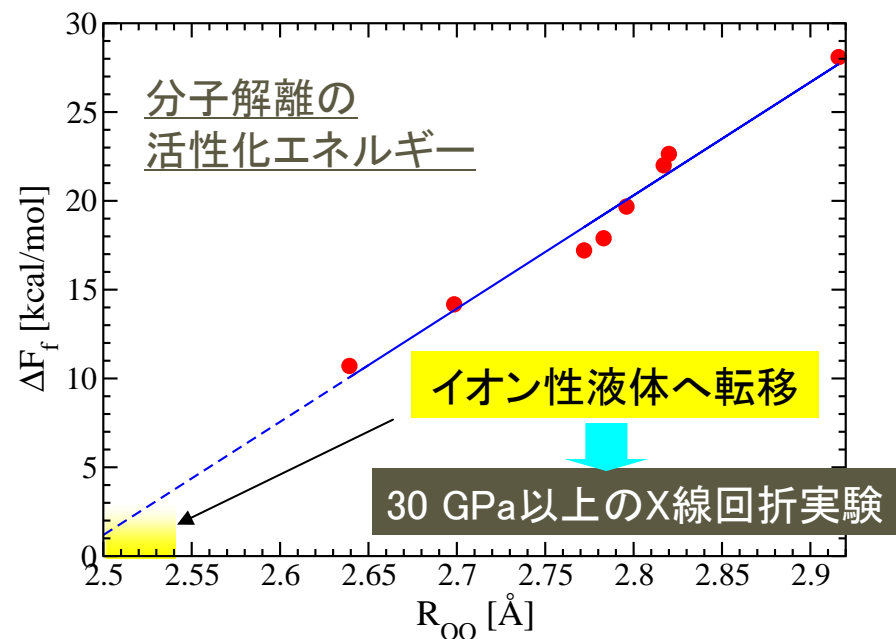
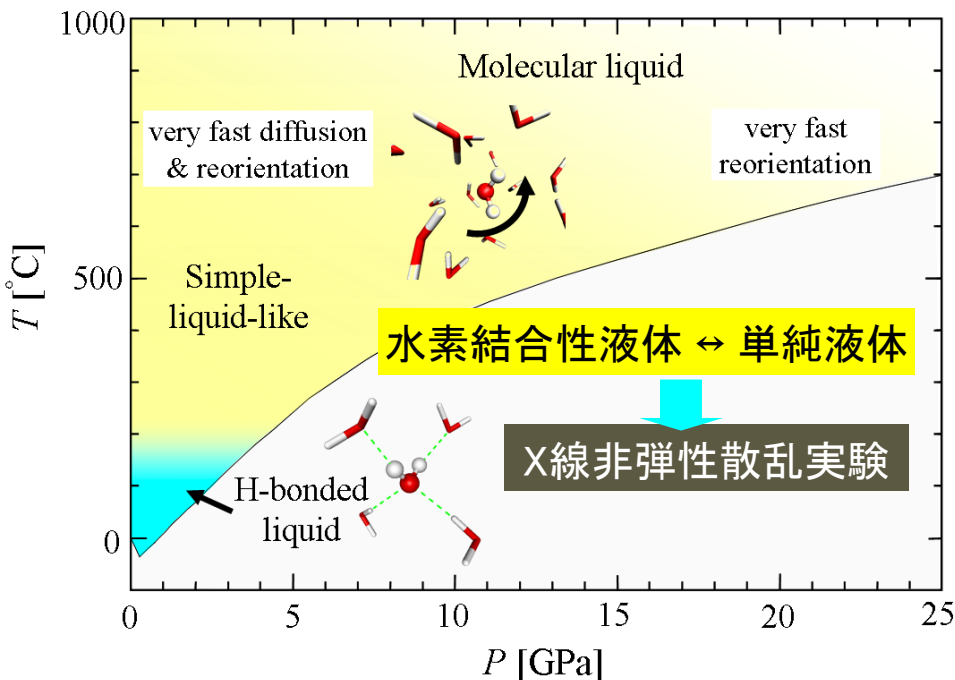
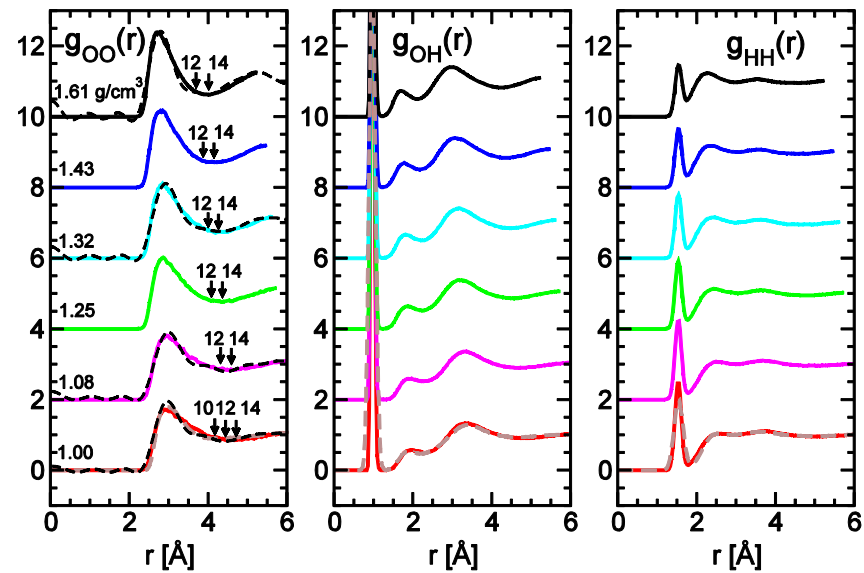
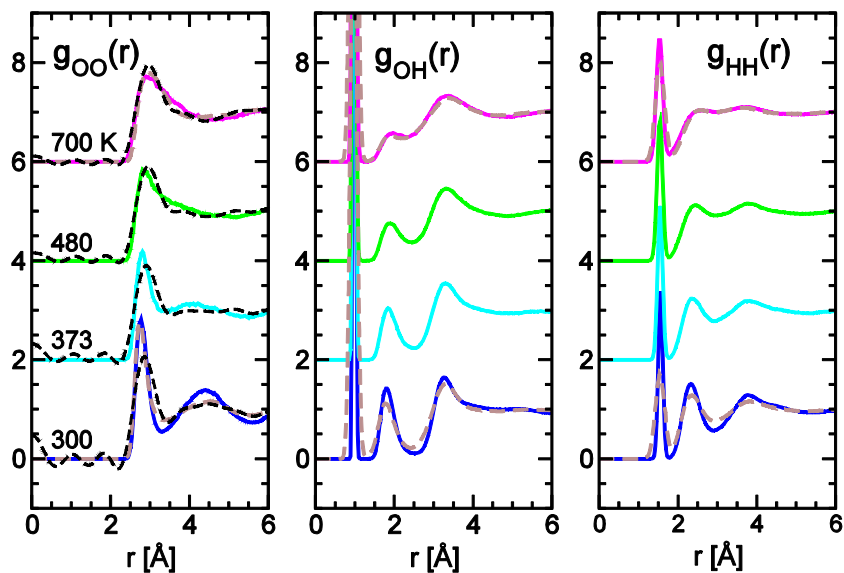
FIG. 2. (Color online) Molecular structure factor, $S(Q)$, at various pressures and temperatures. Thick solid lines (black) indicate $S(Q)$ obtained by the present x-ray diffraction experiments. Dashed (violet) line indicates $S(Q)$ at ambient conditions reported in the literature (Ref. 8). Solid gray (green) lines indicate results of classical MD simulations, obtained by Fourier transformation of the simulated O-O pair-correlation function. Dotted (black) line indicates window function used for the Fourier transformation of $S(Q)$ to obtain pair-correlation function.

FIG. 3. (Color online) Pair-correlation function, $g(r)$, at various pressures and temperatures. Thick solid lines (black) indicate experimental results. Solid gray (green) lines indicate O-O pair-correlation functions obtained by classical MD simulations. Dotted (red) lines indicate theoretical O-O pair-correlation functions after broadening by the experimental resolution function. See text for details.

高温高压水の研究(1)

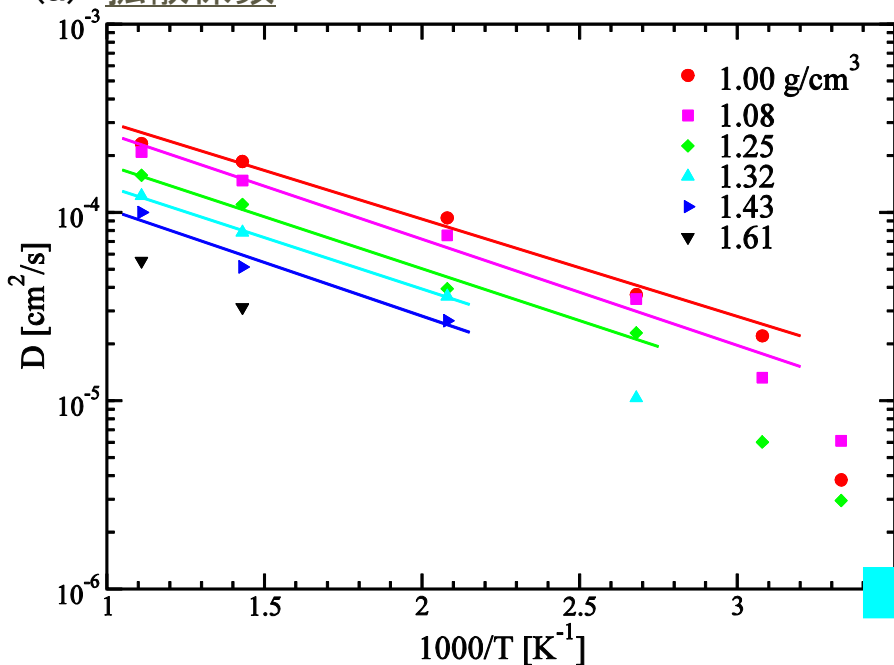
(a) 等密度条件 (1.00 g/cm^3)

(b) 等温条件 (700 K)

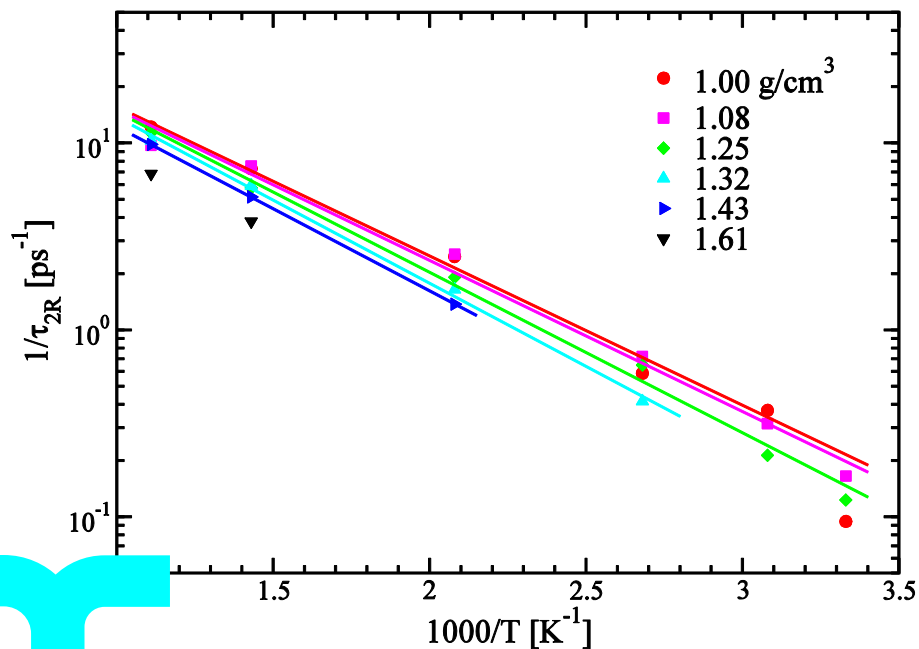


高温高压水の研究(2)

(a) 拡散係数



(b) 回転相関時間



水分子の回転運動と
拡散運動が分離

T. Ikeda *et al.*, appear in J.
Chem. Phys.

仮説

500 K, 10 GPa付近に
が存在

NMR, 中性子回折等を用いた検証実験

Fundamental issues

● A series of first principles MD simulations has already been performed and successfully predicted various interesting physical and chemical features of water at high temperatures and high pressures. However, ...

Some fundamental issues including

➤ **quality of the present density functional for liquid water**

- long-range dispersion interaction

I.-C. Lin *et al.*, J. Phys. Chem. B **113**, 1127 (2009).

- self-interaction ← $\rho \leftrightarrow \bar{V}$

T. Todorova *et al.*, J. Phys. Chem. B **110**, 3685 (2006).

➤ **system size dependence**

T. D. Kühne *et al.*, J. Chem. Theory Comput. **5**, 235 (2009).

$$D_{\text{PBC}}(L) = D_{\infty} - \frac{k_B T \zeta}{6\pi\eta L} \quad \leftarrow \text{hydrodynamic consideration}$$

B. Dünweg & K. Kremer, J. Chem. Phys. **99**, 6983 (1993).

➤ **quantum effects of protons**

J. A. Morrone & R. Car, Phys. Rev. Lett. **101**, 017801 (2008).

should be investigated in order to validate the results.

高温高压水の研究(3)

計算手法の改良

- **Born-Oppenheimer molecular dynamics** (BOMD) based on density functional theory (DFT) within Becke-Lee-Yang-Parr (**BLYP**) generalized gradient approximation (GGA) combined with Grimme's dispersion corrections (**BLYP-D**):

J. Antony & S. Grimme, Phys. Chem. Chem. Phys. **8**, 5287 ('06).

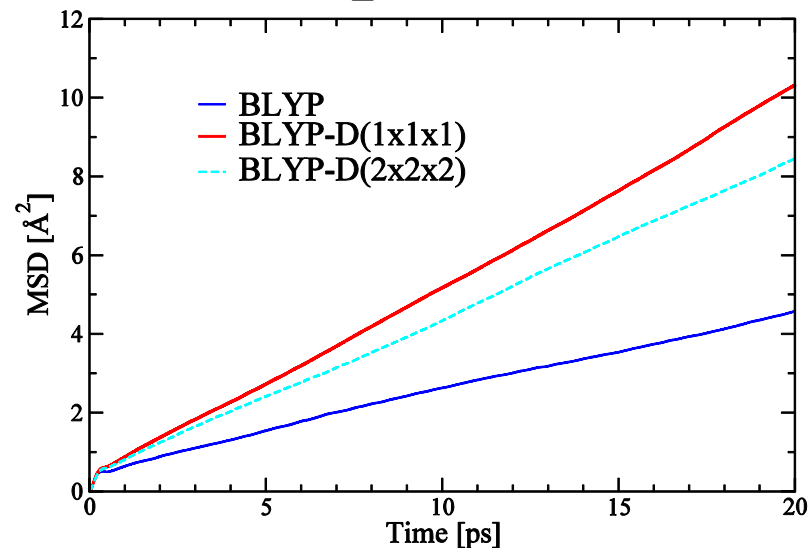
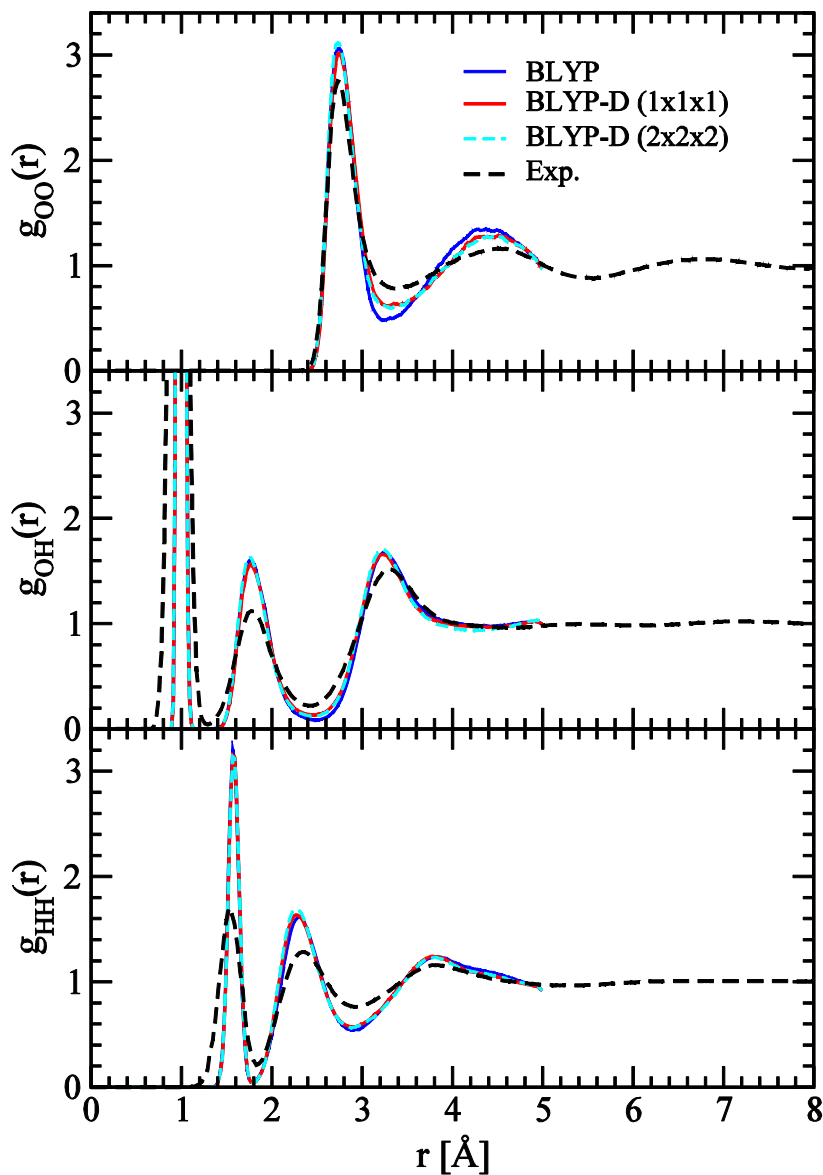
$$E_{\text{DFT-D}} = E_{\text{DFT}} - s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}),$$

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}.$$

- Norm conserving Troullier-Martins **pseudopotentials** (PP) for O and analytical Car-von Barth PP for H
- **Plane wave basis set** with $E_{\text{cut}} = 70 \text{ Ry}$
- **32, 64, and 128 H₂O** in cubic supercell
- **Production runs of ~60 ps**

高温高压水の研究(4)

Effects of dispersion corrections: 32H₂O system



Method	D [$\times 10^{-5}$ cm ² /s]
BLYP	0.30 ± 0.05
BLYP-D (1x1x1)	0.83 ± 0.07
BLYP-D (2x2x2)	0.67 ± 0.06
Exp.	2.2

結論

●分散力補正は必須

より汎用性の高い補正の検討