

# Validation of the Thermal Neutron Scattering Cross Sections for Heavy Water based on Molecular Dynamics Simulation

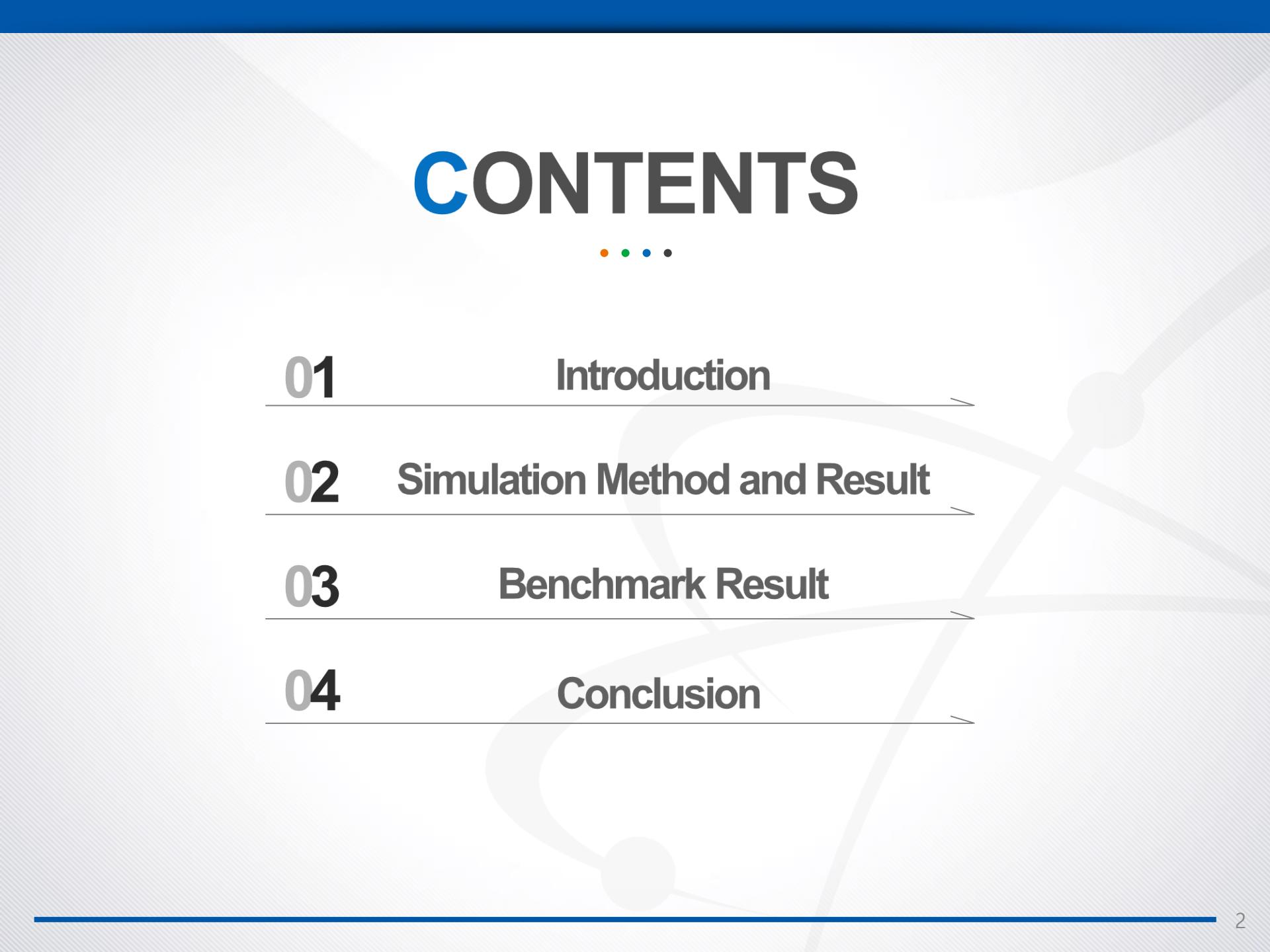


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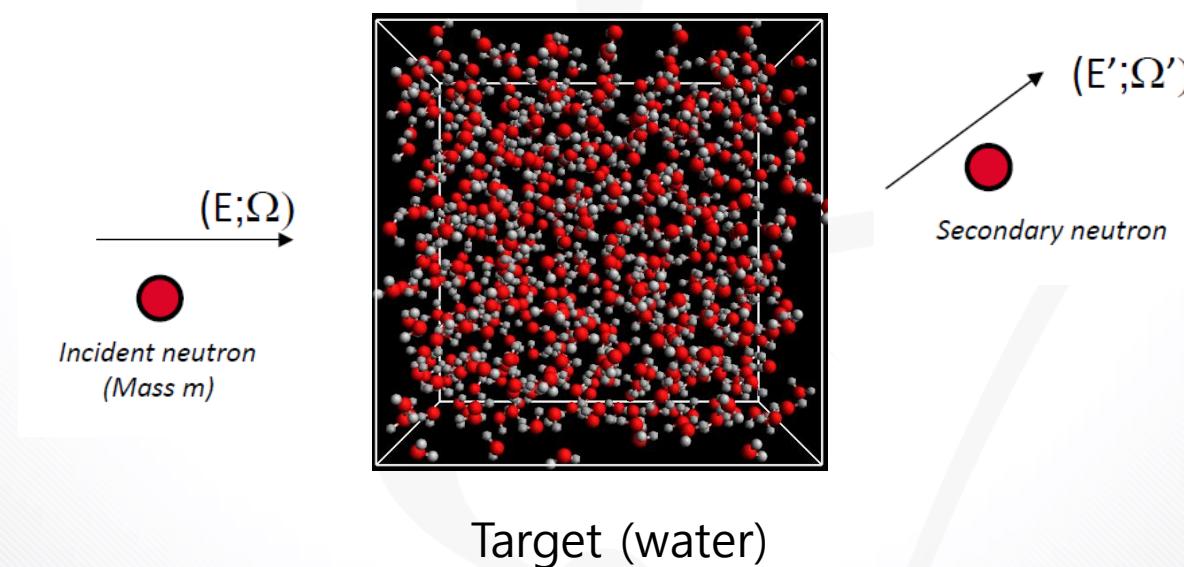
# 01

# Introduction

# 01 Introduction

## » Thermal neutron scattering library

- At thermal energy range (below 5 eV), neutron scattering is affected by the chemical binding state (gas, liquid, solid) of the target system.



# » New light and heavy water data

Table I: Difference between the existing and new library

	Water model	Applied library
Existing	GA model (1969)	ENDF/B-VI.8 / JENDL4.0
	IKE model (2004)	ENDF/B-VII / JEFF3.1
New	*CAB model (2014)	ENDF/B-VIII.0 / JEFF3.3

\* Centro Atomico Bariloche, Argentina

- Recently, the thermal scattering cross section of light and heavy water has been released based on the new model (CAB model) proposed by Damian from Centro Atomico Bariloche, Argentina and it used MD simulation with GROMACS code.

# » Improvement of CAB model applied library

Table II: Coherent and Incoherent Scattering Cross Sections (Unit: barn)

	$\sigma_{coh}$	$\sigma_{inc}$	$\sigma_{scatt}$
1-H-1	1.7583	80.27	82.03
1-H-2	5.592	2.05	7.64
8-O-16	4.232	0	4.232

## 1) Incoherent approximation ( $\sigma_{scatt} = \sigma_{coh} + \sigma_{inc} \cong \sigma_{inc}$ )

- For H:  $\sigma_{coh} / \sigma_{scatt} = 2.14\%$  -> Incoherent approximation can be applied
- For D:  $\sigma_{coh} / \sigma_{scatt} = 73.2\%$  -> Incoherent approximation can **not** be applied
- For heavy water, the incoherent approximation is **not** applied.

## 2) The effect of scattering by oxygen in $H_2O$ / $D_2O$

- For  $H_2O$ :  $\sigma_{scatt}^0 / \sigma_{scatt}^H = 4.232 / 82.03 = 5.15\%$  -> H in  $H_2O$
- For  $D_2O$ :  $\sigma_{scatt}^0 / \sigma_{scatt}^D = 4.232 / 7.64 = 55.4\%$  -> D in  $D_2O$  / O in  $D_2O$

	$H_2O$	$D_2O$
Existing library	H in $H_2O$	D in $D_2O$
New library	H in $H_2O$	<b>D in <math>D_2O</math></b> <b>O in <math>D_2O</math></b>

# » LEARP input for generating thermal scattering XS

## Leapr [Sköld correction factor]

500 0.05 / NKA DKA

7.2442e-02 7.5553e-02 8.1080e-02 8.7803e-02 9.7503e-02  
1.0796e-01 1.1891e-01 1.2993e-01 1.3989e-01 1.4932e-01  
1.5769e-01 1.6546e-01 1.7322e-01 1.8105e-01 1.8993e-01  
1.9995e-01 2.1158e-01 2.2520e-01 2.4073e-01 2.5879e-01  
2.7950e-01 3.0353e-01 3.3185e-01 3.6536e-01 4.0574e-01  
4.5431e-01 5.1268e-01 5.8230e-01 6.6381e-01 7.5775e-01  
.  
.  
.  
.  
9.9910e-01 9.9666e-01 9.9426e-01 9.9189e-01 9.8958e-01  
9.8734e-01 9.8519e-01 9.8314e-01 9.8119e-01 9.7935e-01  
9.7761e-01 9.7597e-01 9.7442e-01 9.7296e-01 9.7159e-01  
9.7030e-01 9.6910e-01 9.6800e-01 9.6700e-01 9.6614e-01  
9.6541e-01 9.6482e-01 9.6438e-01 9.6409e-01 9.6395e-01  
9.6394e-01 9.6404e-01 9.6425e-01 9.6455e-01 9.6494e-01  
9.6540e-01 9.6593e-01 9.6654e-01 9.6722e-01 9.6799e-01  
9.6884e-01 9.6978e-01 9.7080e-01 9.7190e-01 9.7305e-01  
9.7426e-01 9.7551e-01 9.7678e-01 9.7807e-01 9.7937e-01 /  
0.73194 / CFRAC

## Leapr [Frequency spectrum]

1.2650e-03 95 / frequency distribution: DELTA NI  
0.0000e+00 7.9077e-01 2.2091e+00 3.2990e+00 3.7676e+00  
3.7629e+00 3.3613e+00 2.8299e+00 2.5036e+00 2.4096e+00  
2.4494e+00 2.5727e+00 2.7441e+00 2.9355e+00 3.1776e+00  
3.4579e+00 3.7056e+00 3.9656e+00 4.3015e+00 4.6395e+00  
4.9321e+00 5.2439e+00 5.5530e+00 5.7806e+00 5.9544e+00  
6.1321e+00 6.3277e+00 6.6194e+00 7.0419e+00 7.5440e+00  
8.1049e+00 8.7798e+00 9.5107e+00 1.0145e+01 1.0633e+01  
1.1017e+01 1.1243e+01 1.1279e+01 1.1188e+01 1.0995e+01  
1.0745e+01 1.0501e+01 1.0269e+01 9.9852e+00 9.6259e+00  
9.2590e+00 8.9436e+00 8.6511e+00 8.3231e+00 7.9476e+00  
7.5850e+00 7.2711e+00 6.9404e+00 6.5533e+00 6.1831e+00  
5.8692e+00 5.5635e+00 5.2451e+00 4.9560e+00 4.7119e+00  
4.4934e+00 4.2604e+00 3.9995e+00 3.7440e+00 3.5199e+00  
3.2839e+00 2.9836e+00 2.6348e+00 2.2994e+00 1.9978e+00  
1.7372e+00 1.5136e+00 1.3243e+00 1.1687e+00 1.0570e+00  
9.6916e-01 8.8894e-01 8.3066e-01 7.8859e-01 7.4386e-01  
7.0477e-01 6.8276e-01 6.5989e-01 6.3120e-01 6.1411e-01  
6.0199e-01 5.8391e-01 5.6944e-01 5.5868e-01 5.4148e-01  
5.2748e-01 5.2270e-01 5.1311e-01 5.0467e-01 5.0914e-01  
1.6293e-02 3.1934e+00 5.4490e-01 / weights: TWT C TBETA

# » Thermal scattering law $S(\alpha, \beta)$

## Double differential scattering cross section for thermal neutrons:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = \frac{\sigma_b}{4\pi kT} \sqrt{\frac{E'}{E}} S(\alpha, \beta)$$

$\sigma_b$ : characteristic bound cross section

$E$  and  $E'$ : incident and secondary neutron energy

$k$ : Boltzmann constant

$T$ : temperature

## Thermal scattering law

$$S(\alpha, \beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\beta\hat{t}} e^{-\gamma(\hat{t})} d\hat{t}$$

$$\alpha = \frac{E' + E - 2\sqrt{EE'} \cos \theta}{AkT}; \text{ momentum transfer}$$

$$\beta = \frac{E' - E}{kT}; \text{ energy transfer}$$

- TSL contains the dynamical and structure information of the target system
- TSL determines the energy and angular distribution of the secondary neutron

# » Thermal scattering law $S(\alpha, \beta)$

## Thermal scattering law

$$S(\alpha, \beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\beta\hat{t}} e^{-\gamma(\hat{t})} d\hat{t}$$

The intermediate scattering function  $\gamma(\hat{t})$  is given by

$$\gamma(\hat{t}) = \alpha \int_{-\infty}^{\infty} P(\beta) [1 - e^{-i\beta\hat{t}}] e^{-\beta/2} d\beta$$

$$P(\beta) = \frac{\rho(\beta)}{2\beta \sinh(\beta/2)}$$

$\rho(\beta)$ : the frequency spectrum of material (**NJOY input**)

$\rho(\beta)$ : information about the excitation states of the scattering material obtained through experimental measures or molecular dynamics simulations

# » Thermal scattering law $S(\alpha, \beta)$



## Sköld approximation

$$S(\alpha, \beta) = S_{inc}(\alpha, \beta) + S_{coh}(\alpha, \beta)$$

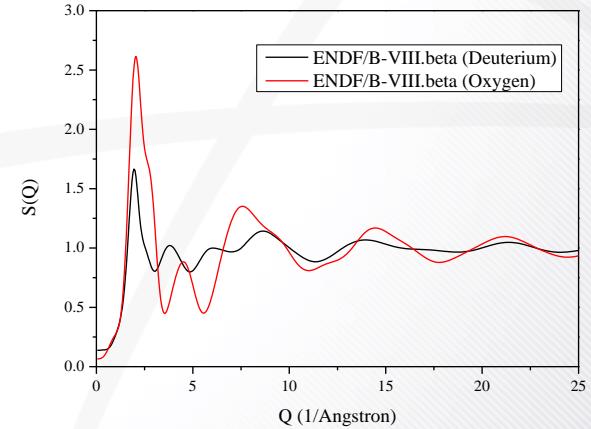
$$S^D \text{ in } D_2O(\alpha, \beta) = (1 - {}^*f) S_{inc}^D(\alpha, \beta) + {}^*f S_{inc}^D \left( \frac{\alpha}{\tilde{S}^D}, \beta \right) \tilde{S}^D(Q) = S(\alpha, \beta)_coh^D$$
$$S^O \text{ in } D_2O(\alpha, \beta) = S_{inc}^O \left( \frac{\alpha}{\tilde{S}^O}, \beta \right) \tilde{S}^O(Q)$$

${}^*f \cdot \sigma_{coh} / \sigma_{scatt} = \sim 0.732$

where  $\tilde{S}^D$  and  $\tilde{S}^O$  are the Sköld correction factors for deuterium and oxygen, respectively. (NJOY input)

$$\tilde{S}^D(Q) = 1 + \frac{2}{3} [S_{DD}(Q) - 1] + \frac{1}{3} \frac{\sigma_{coh}^o}{\sigma_{coh}^D} [S_{DO}(Q) - 1]$$

$$\tilde{S}^O(Q) = 1 + \frac{1}{3} [S_{OO}(Q) - 1] + \frac{2}{3} \frac{\sigma_{coh}^D}{\sigma_{coh}^o} [S_{DO}(Q) - 1]$$



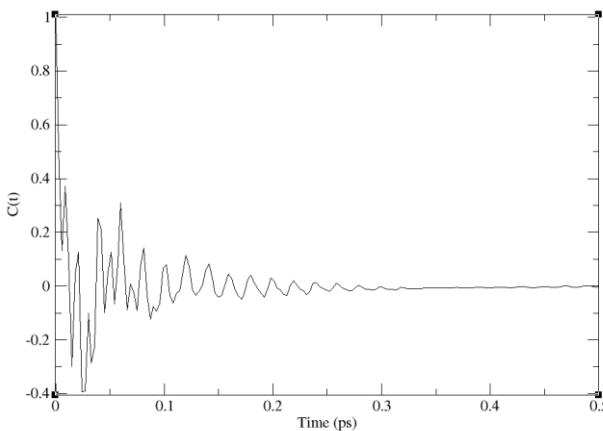
$S_{DD}(Q)$ ,  $S_{DO}(Q)$  and  $S_{OO}(Q)$  : static structure factors-> MD simulation

# » Thermal scattering law $S(\alpha, \beta)$

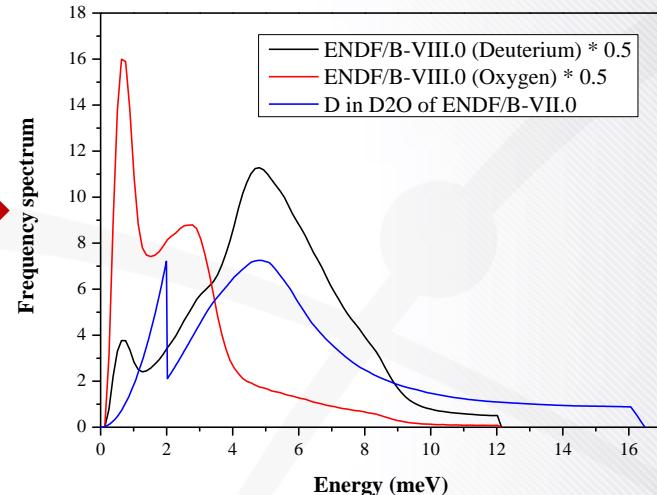


## Frequency spectrum

Velocity Autocorrelation Function



$$\rho(\varepsilon) = \frac{M}{3\pi kT} \frac{1}{2\pi} \int_{-\infty}^{\infty} VACF(\tau) \cos(\omega\tau) d\tau$$



**Velocity Autocorrelation Function (VACF)  
(calculated by MD simulation)**

**Frequency spectrum**



- First peak: bending motion due to the hydrogen bond
- Second peak: stretching motion due to the hydrogen bond
- Third peak: librational band

# 02

## Simulation Method and Result

# 02 Simulation Method and Result

## » GROMACS simulation

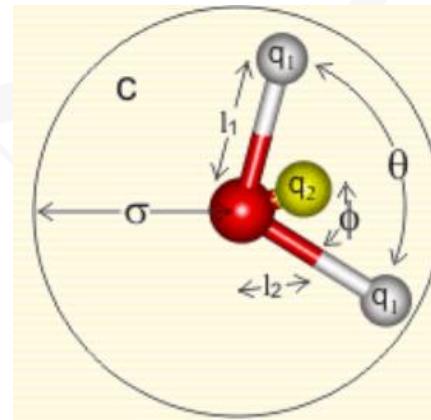
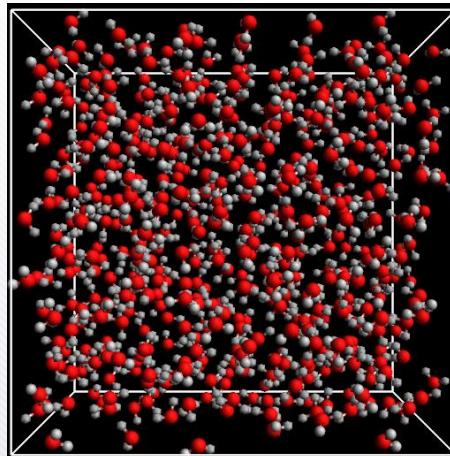
### GROMACS

GROMACS is an engine to perform molecular dynamics simulations by solving Newtonian equations of motion for a system of N interacting atoms.

$$m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = \mathbf{F}_i, \quad i = 1, 2, \dots, N.$$

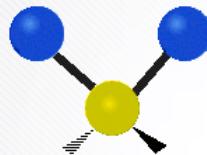
### “TIP4P/2005f” - A flexible model for water based on TIP4P/2005

1084 heavy water molecules  
Cubic box=32.768 nm<sup>3</sup>



# 02 Simulation Method and Result

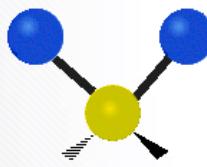
## Parameters of TIP4P/2005f water model



Morse potential for the Intramolecular stretching

$$V_{OH_i} = D_r \{1 - \exp[-\beta(r_{OH_i} - r_{eq})]\}^2$$

$D_r$  = Bond strength     $r_{eq}$  = Bond length at equilibrium  
 $\beta$  = Bond width             $r_{OH_i}$  = Instantaneous distance



Harmonic angle potential for the Intramolecular bending

$$V_{HOH}(\theta) = \frac{1}{2} K_\theta (\theta - \theta_{eq})^2$$

$K_\theta$  = Strength constant  
 $\theta_{eq}$  = Angle at equilibrium

Table III: Potential parameters for simulating TIP4P/2005f water model

Parameter	TIP4P/2005f	Parameter	TIP4P/2005f
$\epsilon$ (kJ × mol <sup>-1</sup> )	0.7749	$r_{eq}$ (Å)	0.9419
$\sigma$ (Å)	3.1644	$\theta_{eq}$ (deg)	107.4
$q_H$ (e)	0.5564	$\beta$ (nm <sup>-1</sup> )	22.87
$q_M$ (e)	-1.1128	$K_\theta$ (kJ/(mol rad <sup>2</sup> ))	367.81
$d_{OM}$	0.13194	$D_r$ (kJ/mol)	432.581

# » GROMACS simulation

## ● Simulation procedure

Energy minimization > Energy equilibration > Production run > Result analysis

## ● Result 1. Radial distribution function -> static structure factor

$$S_{\alpha\beta}(Q) = 1 + 4\pi\rho \int_0^{\infty} dr (g(r) - 1)r^2 \frac{\sin(Qr)}{Qr}$$

$g(r)$  = Radial distribution function (RDF)       $dr$  = Increment of the  $r$        $Q$  = Wave number

$r$  = Distance from the center of the system       $\rho$  = Density of the system

The radial distribution function gives the probability to find the atoms at distance  $r$  from the center of the system.

## ● Result 2. Velocity autocorrelation function

$$VACF_{\alpha} = \langle v_{\alpha}(t) \cdot v_{\alpha}(t + \tau) \rangle$$

$\langle \cdot \rangle$ : ensemble average

$\tau$  = time interval (0.3fs)

# » EPSR simulation

## ● EPSR(Empirical Potential Structure Refinement) code

EPSR is a Monte Carlo code, which attempts to build a structural model of a glass or liquid, and which evolved to evaluate disordered materials structure on the basis of diffraction experiments.

$$U^{tot} = U^{ref}(r) + U^{EP}(r)$$

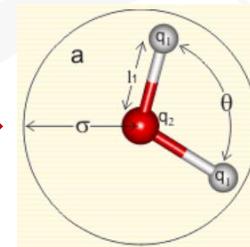
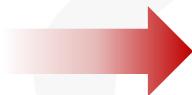
Experimental data

Monte Carlo computer simulation

Molecular structure parameters

## ● “SPC/E” – Extended Simple Point Charged water model

1000 heavy water molecules  
Cubic box=29.94 nm<sup>3</sup>

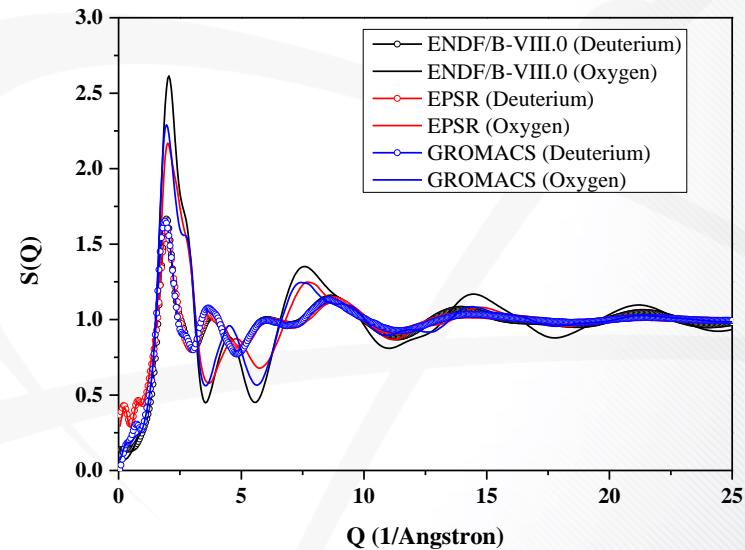
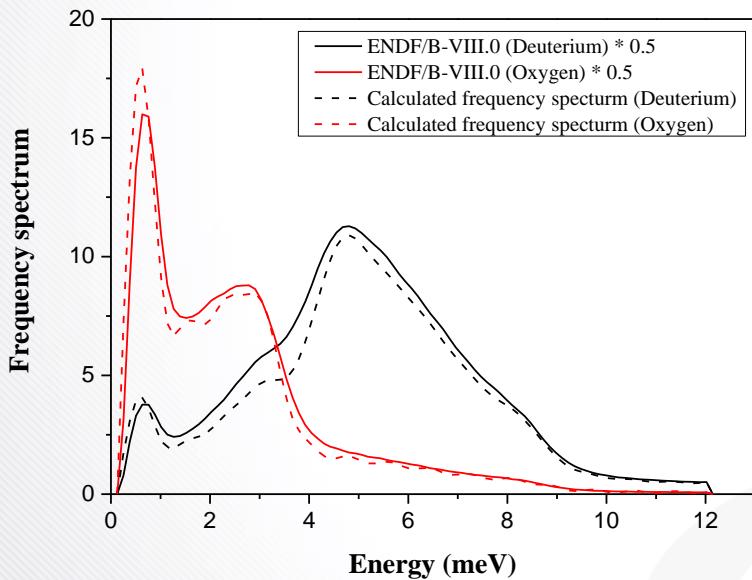


Parameter	SPC/E
$\epsilon$ (kJ × mol <sup>-1</sup> )	0.650
$\sigma$ (Å)	3.166
$q_H$ (e)	0.4238
$q_O$ (e)	-0.8476
$r_{eq}$ (Å)	0.1
$\theta_{eq}$ (deg)	109.47

# » Simulation result

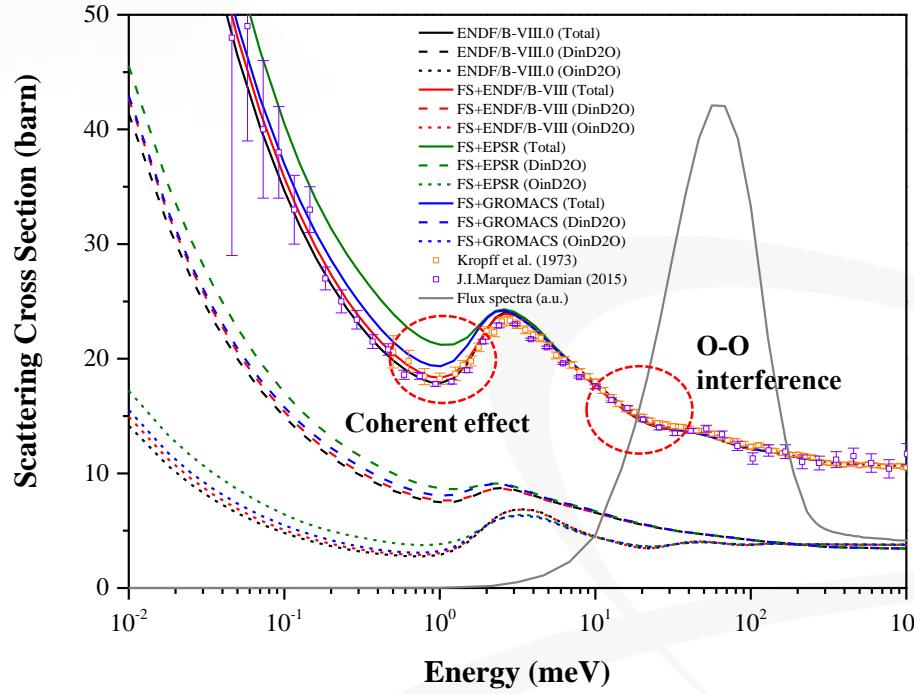
## Heavy water ( $D_2O$ )

- Frequency spectrum (from GROMACS)
- Sköld correction factor (from GROMACS and EPSR)



# » Simulation result

## Scattering cross sections for heavy water



- The scattering cross sections show similar values over 3meV.
- However, because the neutron flux in thermal systems is much higher at the energy range of the second dip, the description of the second dip is more important.

# 03

# Benchmark Result

# 03 Benchmark Result

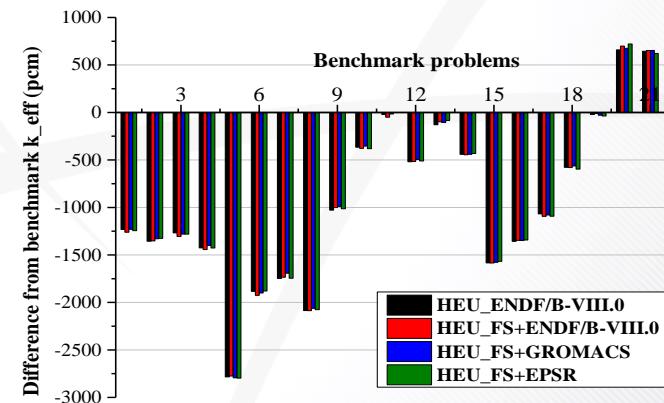
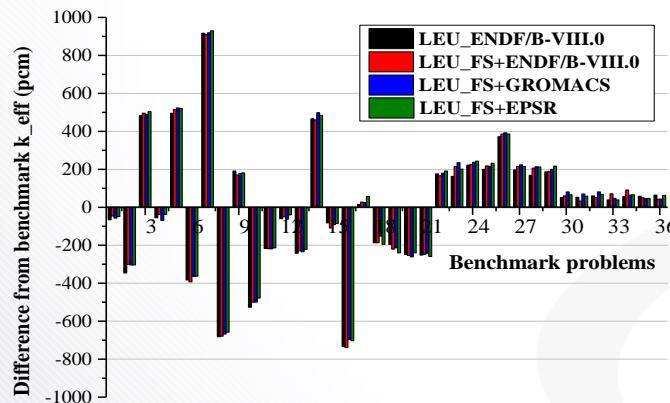
## » Difference from benchmark k\_eff

Category	Number of Benchmark Problems
HEU*	21
IEU*	1
LEU*	36
U233	1
WHOLE	59

\*HEU: Highly Enriched Uranium

IEU: Intermediate Enriched Uranium

LEU: Low Enriched Uranium



# 03 Benchmark Result

## » Comparison of RMS error

Table III: Comparison of RMS error (Unit: %)

Category (# of cases)	ENDF/B-VIII.0	FS+ENDF/B-VIII.0	FS+GROMACS	FS+EPSR
HEU (21)	1.273	1.279	1.265	1.273
IEU (1)	0.139	0.167	0.172	0.178
LEU (36)	0.327	0.328	0.328	0.328
U233 (1)	0.570	0.549	0.558	0.528
TOTAL (39)	0.805	0.808	0.801	0.805



$$\text{RMS}(\%) = \sqrt{\frac{\sum_{i=1}^N (k_{C,i} - k_{B,i})^2}{N}}$$

# 04

# Conclusion

# 04 Conclusion

- In this work, we generated the thermal scattering libraries for heavy water by MD simulation.
  - GROMACS and EPSR are used for generating sköld correction factor.
  - The frequency spectrum is calculated by GROMACS code.
- In comparison with ENDF/B-VIII.0, newly calculated scattering cross sections using MD simulations show differences under 3meV.
- However, because the neutron flux spectrum in thermal system is biased at the energy range of 10~100 meV, that discrepancies did not seriously affect the benchmark performance of the thermal scattering cross section.

# THANK YOU