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Status of clathrate Monte Carlo simulation tools

Work Package 2

S. Xu, S. Laporte, D. Di Julio, J. I. Marquez Damian, T. Kittelmann,

M. Bernasconi, D. Campi, G. Gorini and V. Santoro

PRESENTED BY S. XU

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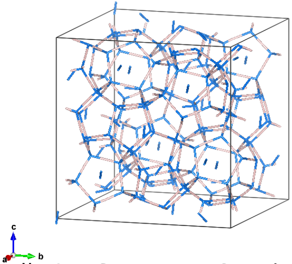
Motivations

Clathrate hydrates are ice-like compounds having a cage structure. Small molecules such as methane can be enclathrated in the cage, stabilising the structure.

- Tetrahydrofuran (THF/TDF)-containing clathrate hydrates: low energy modes
- Oxygen-containing clathrate hydrates: neutron inelastic magnetic scattering

- large Bragg cutoff wavelength (2 nm)
- small absorption of deuterium



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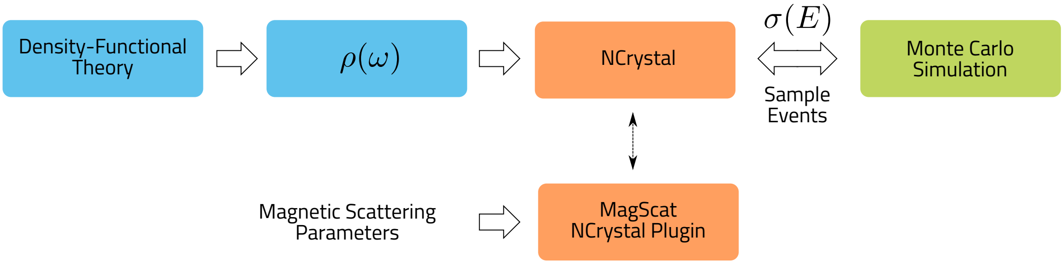
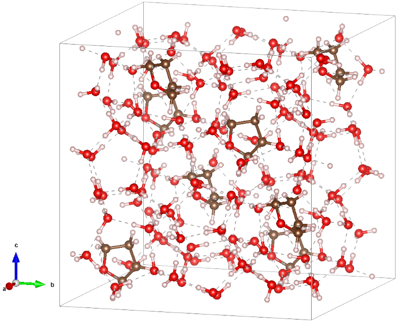
Data flow

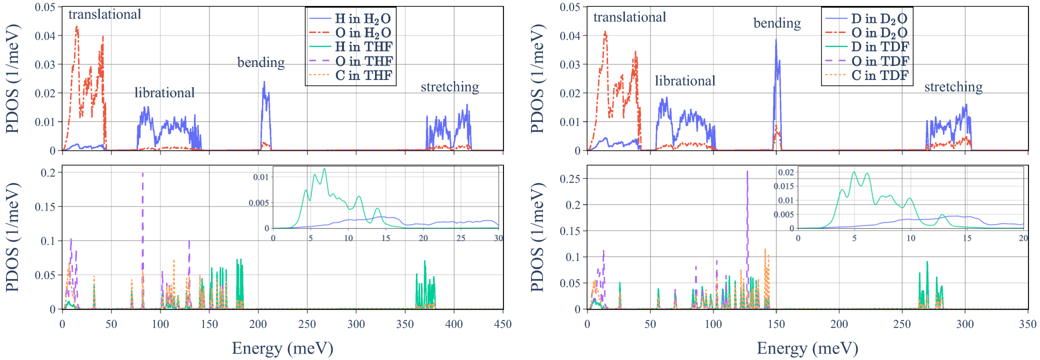

Density-Functional Theory
$\rho(\omega)$
NCrystal
$\sigma(E)$
Sample Events
Monte Carlo Simulation
Magnetic Scattering Parameters
MagScat NCrystal Plugin

DFT Simulations - crystalline structure



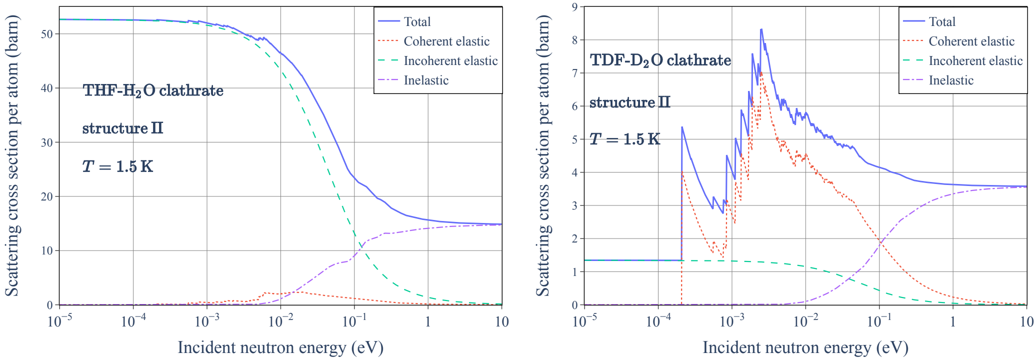
- Crystalline structure of THF-containing clathrate hydrate (structure II) optimised with DFT calculations
- Unit cell having 136 water molecules and 8 THF molecules inserted in large cages
- Phonon DOS computed using CP2K and phonopy

DFT Simulations - phonon density of states



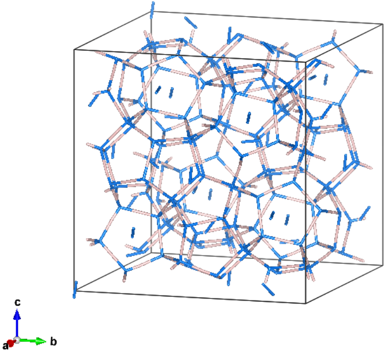
Low energy modes of the guest molecules make the TDF-clathrates a promising cold moderator candidate.

NCrystal Calculations - neutron scattering cross sections



The theoretical neutron scattering cross sections serve to compare against existing or future experimental data.

DFT Simulations - crystalline structure



- Crystalline structure obtained from DFT calculations
- Unit cell composed of 136 D_2O and 24 O_2 enclathrated in both large and small cages

Neutron slowdown by paramagnetic oxygen

Based on Zimmer's paper [1], the neutron magnetic scattering kernels or dynamic structure factors $S_{\mathrm{mag}}(Q, \omega)$ are derived:

$$\frac{\mathrm{d}^2\sigma_{\mathrm{mag}}}{\mathrm{d}\Omega\,\mathrm{d}E'} = b_{\mathrm{m}}^2 \left(\sqrt{\frac{E'}{E}} S_{\mathrm{mag},\pm}(Q, \omega) + S_{\mathrm{mag},0}(Q, \omega) \right), \tag{1}$$

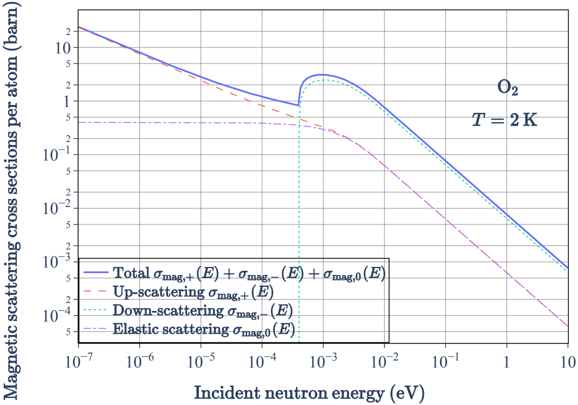
where

$$S_{\mathrm{mag},\pm}(Q, \omega) = \exp\left(-(\langle u^2 \rangle + \frac{\ln(2)}{\Gamma_{\mathrm{mag}}^2}) Q_{\pm}^2 \right) g_{\pm}(T) \delta(\hbar\omega \pm D), \tag{2}$$

and

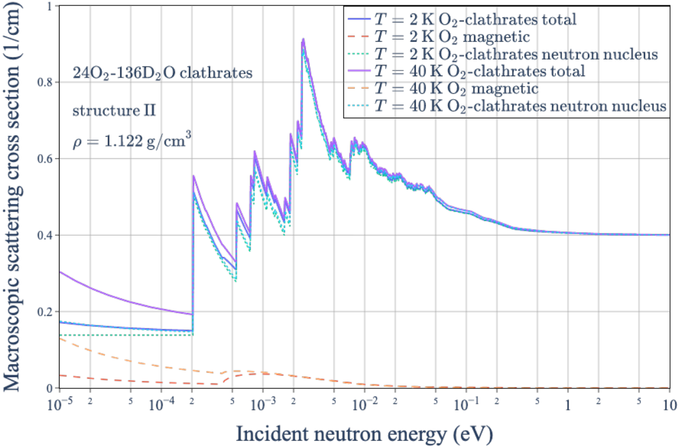
$$S_{\mathrm{mag},0}(Q, \omega) = \exp\left(-(\langle u^2 \rangle + \frac{\ln(2)}{\Gamma_{\mathrm{mag}}^2}) Q_0^2 \right) g_0(T) \delta(\hbar\omega). \tag{3}$$

NCrystal Calculations - Magnetic scattering cross sections



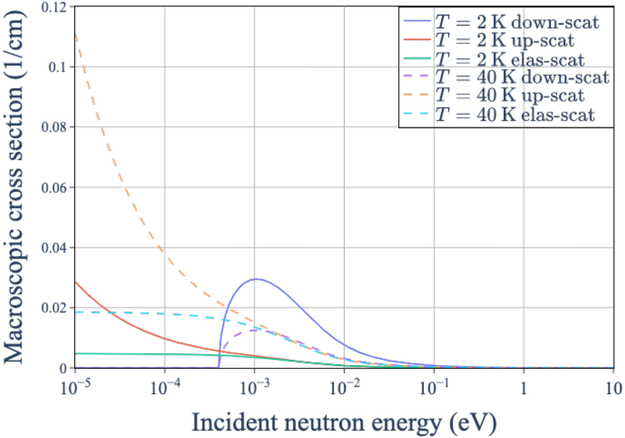
- Magnetic cross sections generated by the developed plugin `ncplugin-MagScat`

NCrystal Calculations - Neutron scattering cross sections

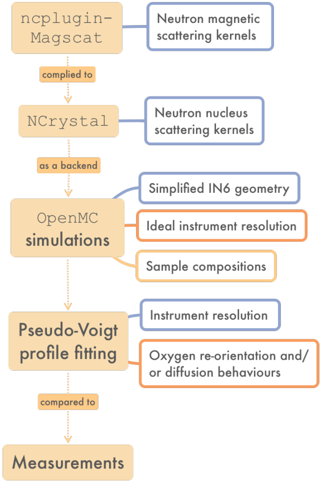


- Cross sections calculated for 136 D_2O + 24 O_2

NCrystal Calculations - Neutron scattering cross sections

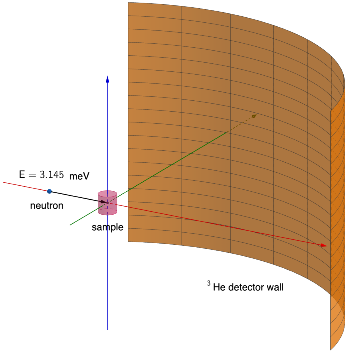


Monte-Carlo simulations of measurements

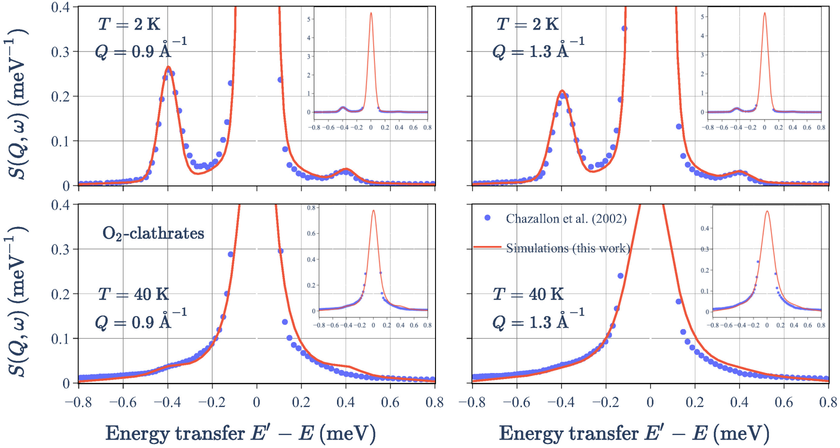


OpenMC [2] Monte-Carlo simulations on experiments performed by Chazallon et al. [3] on O_2-clathrates and Renker et al. [4] on O_2-C_{60}.

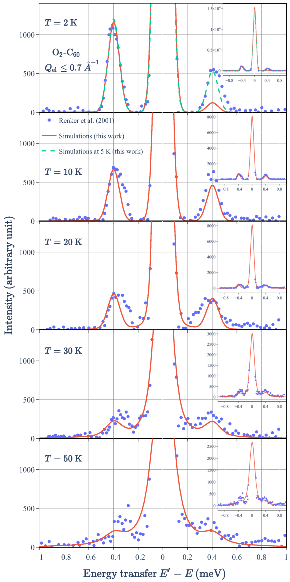
Inelastic neutron scattering measurements on time-of-flight spectrometer IN6 at ILL



Monte-Carlo simulations on O_2-clathrates

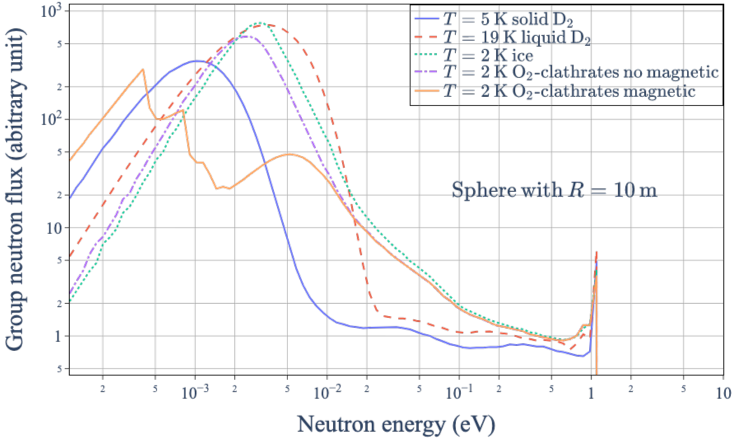


O_2-C_{60}



T = 2 K
O2-C60
Qel ≲ 0.7 Å−1
Renker et al. (2001)
Simulations (this work)
Simulations at 5 K (this work)
T = 10 K
T = 20 K
T = 30 K
T = 50 K
Intensity (arbitrary unit)
Energy transfer E′ − E (meV)

Comparisons of neutron spectra



- Preliminary results
- Further optimisation of configuration by Blahoslav Rataj from WP4 on going

Summary

- The scattering cross sections of THF/TDF-clathrates generated by using the crystalline structure and phonon density of states obtained from DFT calculations serve to compare against existing or future experimental data.
- Based on Ref. [1], we derive the equations for the scattering kernels and implement them in a plugin named `ncplugin-MagScat` which can be complied in `NCrystal` and further used in Monte-Carlo simulations.
- Good agreement is obtained for both measurements on O_2-clathrates [3] and O_2-C_{60} [4] for temperatures from 2 K to dozens of K.
- First preliminary results on oxygen-containing clathrates as cold neutron moderator.

Thanks for your time.
Questions?

References

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  Intercalation of molecular gases into c_{60}.