# Thermal Scattering in Liquids

## Convolutional Discrete Fourier Transform (CDFT)

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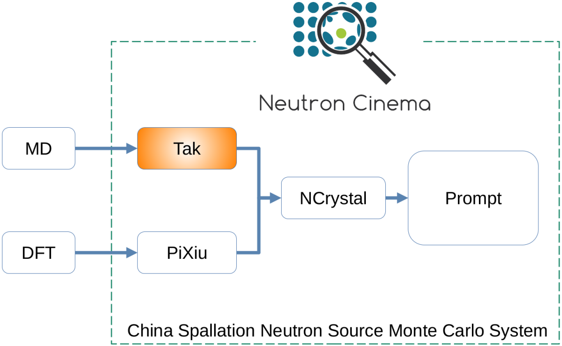
HighNESS International School on Thermal Neutron Scattering Kernel Generation

# Introduction




Tak, Trajectory Analysis Toolkit for molecular dynamics:

- Incoherent inelastic Calculator published in 2022 [1].
- Coherent inelastic calculator is under development.

# Classical approximation

Detailed balance

$$S(\boldsymbol{Q}, -\omega) = \exp(-\hbar\omega/kT)S(\boldsymbol{Q}, \omega)$$

The scattering functions can be evaluated classically by treating the thermal averaging operator as classical ensemble averaging and the position operators as real space vectors.

$$C(\boldsymbol{Q}, \omega) = \lim_{\hbar \to 0} S(\boldsymbol{Q}, \omega)$$

So for classical scattering functions

$$C(\boldsymbol{Q}, -\omega) = C(\boldsymbol{Q}, \omega)$$

# Classical structure factor

$$C(\boldsymbol{Q}) = \frac{1}{N}\left\langle \sum_{j,j'=1}^{N} b_{\mathrm{coh},j} b_{\mathrm{coh},j'} \exp\left[-i\boldsymbol{Q}\boldsymbol{r}_j(0)\right] \exp\left[i\boldsymbol{Q}\boldsymbol{r}_{j'}(0)\right] \right\rangle_c$$

$$= \frac{1}{NM}\sum_{i=1}^{M}\sum_{j,j'=1}^{N} b_{\mathrm{coh},j} b_{\mathrm{coh},j'} \exp\left[-i\boldsymbol{Q}\boldsymbol{r}_j(t_i)\right] \exp\left[i\boldsymbol{Q}\boldsymbol{r}_{j'}(t_i)\right]$$

$$= \frac{1}{NM}\sum_{i=1}^{M}\left(\sum_{j=1}^{N} b_{\mathrm{coh},j} \cos[\boldsymbol{Q}\boldsymbol{r}_j(t_i)]\right)^2 + \frac{1}{NM}\sum_{i=1}^{M}\left(\sum_{j=1}^{N} b_{\mathrm{coh},j} \sin[\boldsymbol{Q}\boldsymbol{r}_j(t_i)]\right)^2$$

Where $N$ is the number of atoms, $M$ is the number of time steps.

# Classical incoherent inelastic

$$
\begin{aligned}
C_{inc}(\boldsymbol{Q},\omega) &= \frac{1}{N}\sum_j b^2_{\text{inc},j}\,\mathcal{F}(\exp[-i\boldsymbol{Q}\boldsymbol{r}^i_j(t)])\,\mathcal{F}(\exp[i\boldsymbol{Q}\boldsymbol{r}^i_j(t)]) \\
&= \frac{1}{N}\sum_j b^2_{\text{inc},j}\,A_j(\boldsymbol{Q},\omega)\,A^*_j(\boldsymbol{Q},\omega)
\end{aligned}
$$

# Classical coherent inelastic scattering

$$
\begin{aligned}
C_{coh}(\boldsymbol{Q},\omega) &= \frac{1}{N}\sum_{jj'=1}^{N} b_{\mathrm{coh},j}\, b_{\mathrm{coh},j'}\, C_{jj'}(\boldsymbol{Q},\omega) \\
&= \frac{1}{N}\sum_{jj'=1}^{N} b_{\mathrm{coh},j}\, b_{\mathrm{coh},j'}\, A_j(\boldsymbol{Q},\omega)\, A^*_{j'}(\boldsymbol{Q},\omega) \\
&= \frac{1}{N}\left(\sum_{j=1}^{N} b_{\mathrm{coh},j}\,\mathrm{Re}[A_j(\boldsymbol{Q},\omega)]\right)^2 + \frac{1}{N}\left(\sum_{j=1}^{N} b_{\mathrm{coh},j}\,\mathrm{Im}[A_j(\boldsymbol{Q},\omega)]\right)^2
\end{aligned}
$$

# There are two possible methods for $S_{coh}(Q,\omega)$.

1. Calculate $C_{coh}(Q,\omega)$, then find a way to perform quantum correction.
   - This method considers anharmonic effects, which is not included in Gaussian approximation. BUT, we need to find the way.
2. Calculate $S_{inco}(Q,\omega)$ and $C(Q)$, and perform Skold approximation as $S_{coh}(Q,\omega) = C(Q)\ S_{inco}\left(Q/\sqrt{S(Q)},\omega\right)$.
   - It works nicely with reactor simulations. BUT, how good is it for total scattering experiments?

## Frame Title

We picked method no.2 and working in two directions

1. Total scattering experiments using our total scattering instrument for light and heavy water. Perform data inelasticity corrections on the raw data.
2. Development of a method for calculating $S_{inco}(Q, \omega)$. The CDFT (convolutional discrete Fourier transform) method.

## The incoherent inelastic scattering in liquids

The scattering function $S(Q,\omega)$ is given by the Fourier transform of the intermediate scattering function $F(Q,t)$, which can be approximated by a Gaussian [2]

$$S(Q,\omega) = \frac{1}{2\pi}\int e^{-i\omega t}\exp\left[-\frac{Q^2}{2}\Gamma(t)\right]\mathrm{d}t$$

With the fluctuation-dissipation theorem, it has been shown that, $\Gamma(t)$ in liquids can be expressed as [2]

$$\Gamma(t) = \frac{\hbar}{m}\int_0^\infty \mathrm{d}\omega\frac{\rho(\omega)}{\omega}\left[\coth\left(\frac{\hbar\omega}{2k_B T}\right)(1-\cos\omega t) - i\sin\omega t\right]$$

# The formulation is identical to that of harmonic crystals

## Theory of Slow Neutron Scattering by Liquids. I*

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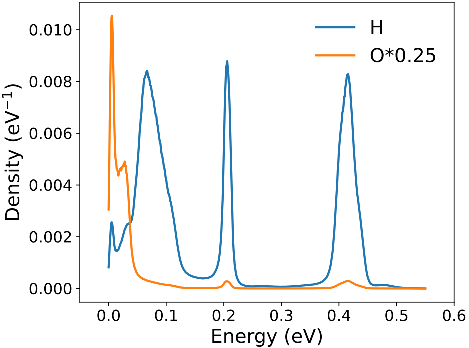
This is exactly the same expression as obtained earlier for a harmonic solid.[30] We thus see that this particular form for $\gamma_1(t)$ is not a consequence of the harmonic nature of the motion but purely a consequence of the fluctuation-dissipation theorem. The system is here characterized by a velocity spectrum $f(\omega)$, which in the case of a harmonic solid is identical with the frequency distributions of the normal modes.

# Why the calculations are not as simple as those for crystals?




The density of states for hydrogen and oxygen in light water for CAB model at $297\,\mathrm{K}$. Additional diffusive motion violates the basic numerical assumption of $\omega^2$ behaviour near zero.

# The CDFT method

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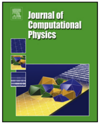


## Convolutional discrete Fourier transform method for calculating thermal neutron cross section in liquids

Check for updates

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# Expansion for a general $\exp[-f(t)]$ function

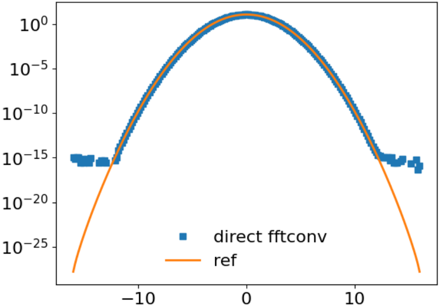
$$F(\omega) = \int e^{-i\omega t} \exp[-f(t)] \mathrm{d}t$$
$$= \sum_{n=0}^{\infty} \frac{1}{n!} \int e^{-i\omega t} [-f(t)]^n \mathrm{d}t$$
$$= e^{-f_{max}} \sum_{0}^{\infty} \frac{(f_{max})^n}{n!} g_n(\omega)$$

With

$$r(t) = f_{max} - f(t)$$

$$g_n(\omega) = \int e^{-i\omega t} \left[\frac{r(t)}{r(0)}\right]^n \mathrm{d}t$$

# Numerical issues with FFT convolution

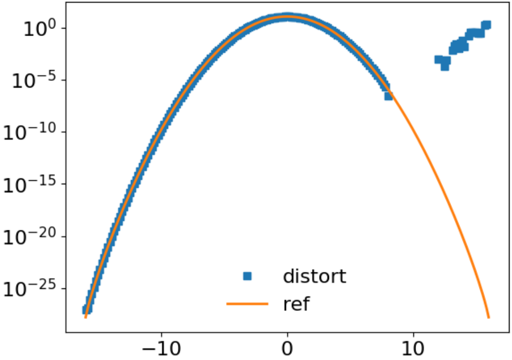



The result of convoluting $\exp(-\frac{x^2}{2}) \otimes \exp(-\frac{x^2}{2})$.

# The distortion algorithm

$$
\begin{aligned}
F_1(\omega) \otimes F_2(\omega) &= \int F_1(\mu) \cdot F_2(\omega - \mu) d\mu \\
&= \int e^{a\mu} \hat{F}_1(\mu) \cdot e^{a(\omega-\mu)} \hat{F}_2(\omega - \mu) d\mu \\
&= e^{a\omega} \int \hat{F}_1(\mu) \cdot \hat{F}_2(\omega - \mu) d\mu \\
&= e^{a\omega} \hat{F}_1(\mu) \otimes \hat{F}_2(\omega - \mu)
\end{aligned}
$$

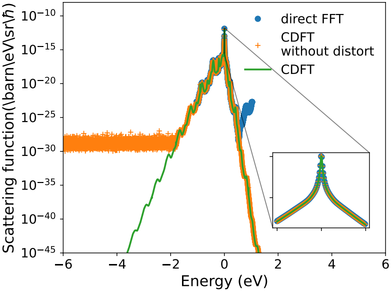
# Resolution can be increased significantly




With $a = 2$

# The CDFT formulated scattering function

$$S(Q,\omega) = \exp\left(-\frac{\Gamma_{max} Q^2}{2} + a\omega\right) \sum_{n=0}^{\infty} \left(\frac{\Gamma_{max} Q^2}{2}\right)^n \frac{1}{n!} \hat{g}_n(\omega)$$




Comparison of scattering function with different scattering orders, $Q = 1$

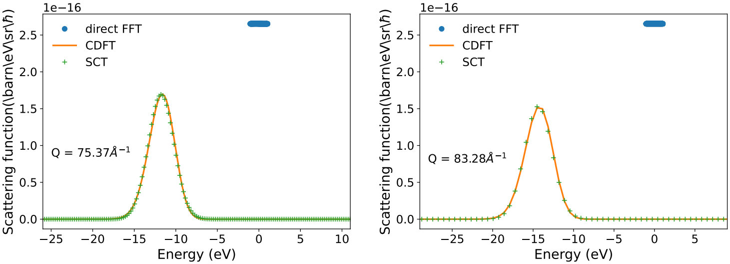
# Numerical problem at large Q

But, at large $Q$, the factor $\exp(\Gamma_{max} Q^2)$ may overflow. To prevent that, we apply the convolutional method again.

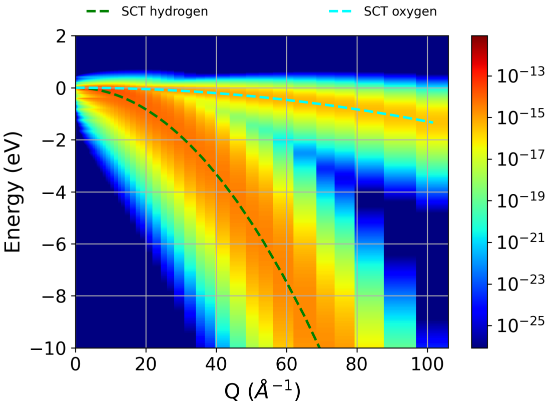
$$S(\sqrt{2^{n-1}}Q, \omega) = \underbrace{S(Q,\omega) \otimes S(Q,\omega) \cdots \otimes S(Q,\omega)}_{n}$$

Skipped direct calculations at large Q!

# Calculated function at large Q

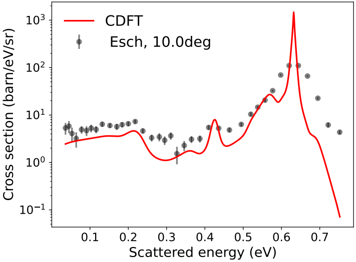


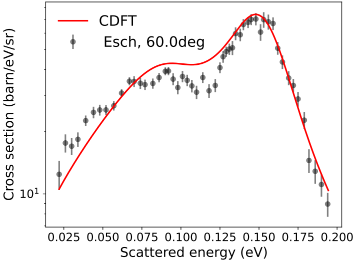
# CDFT results I



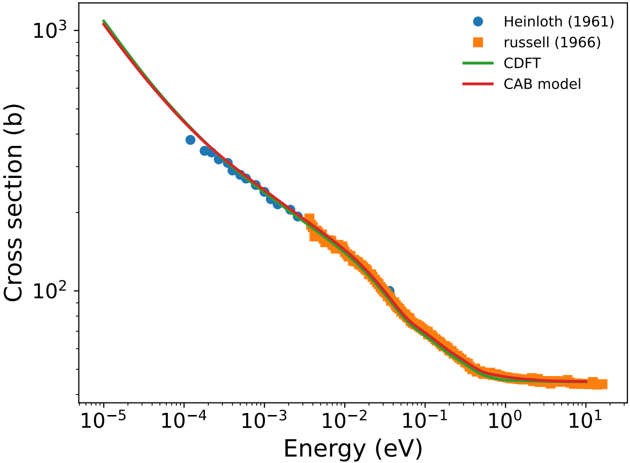

CDFT, a unified approach from DOS to $S_{inco}(Q, \omega)$.

# CDFT results II



# CDFT results III



# Outlook

- It is open source by default. A python prototype is available along side with the reference paper.
- Will be translated into C++ to accelerate the calculation.

[1] R. Du, X.-X. Cai. Convolutional discrete fourier transform method for calculating thermal neutron cross section in liquids[J]. Journal of Computational Physics, 2022, 466: 111382

[2] A. Rahman, K. S. Singwi, A. Sjölander. Theory of slow neutron scattering by liquids. i[J]. Physical Review, 1962, 126: 986-996