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Progress on the Evaluation of the Thermal Scattering Law for Heavy Paraffinic Molecular Materials

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Integrated University Program

U.S. Department of Energy

Objective

- Use a classical molecular dynamics approach to calculate the thermal scattering law and generate the thermal neutron scattering cross section libraries of a representative heavy paraffinic oil material
- Work on this material is motivated by a request from NR to support criticality safety applications

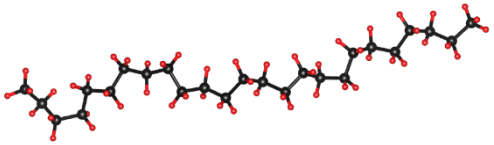
Outline

- Introduction
- Thermal Neutron Scattering in Matter
- Molecular Dynamics Model of heavy paraffinic oil
- Thermal Neutron Scattering Cross Sections of heavy paraffinic oil
- Summary

Introduction

<u>Heavy paraffinic oil</u> :

- Material classification: liquid lubricant (more specifically known as a solvent-dewaxed heavy paraffinic oil)
  - Common uses:
    - Circulating oil systems
    - Compressors
    - Gear casing
  - Characteristics:
    - High viscosity index
    - High film strength
    - Excellent stability
    - Long lubricant life



- Pale appearance with a petroleum oil odor
- Paraffin hydrocarbon $\longrightarrow$ Alkane $\longrightarrow$ general formula: C_nH_{2n+2}

Thermal Neutron Scattering in Matter

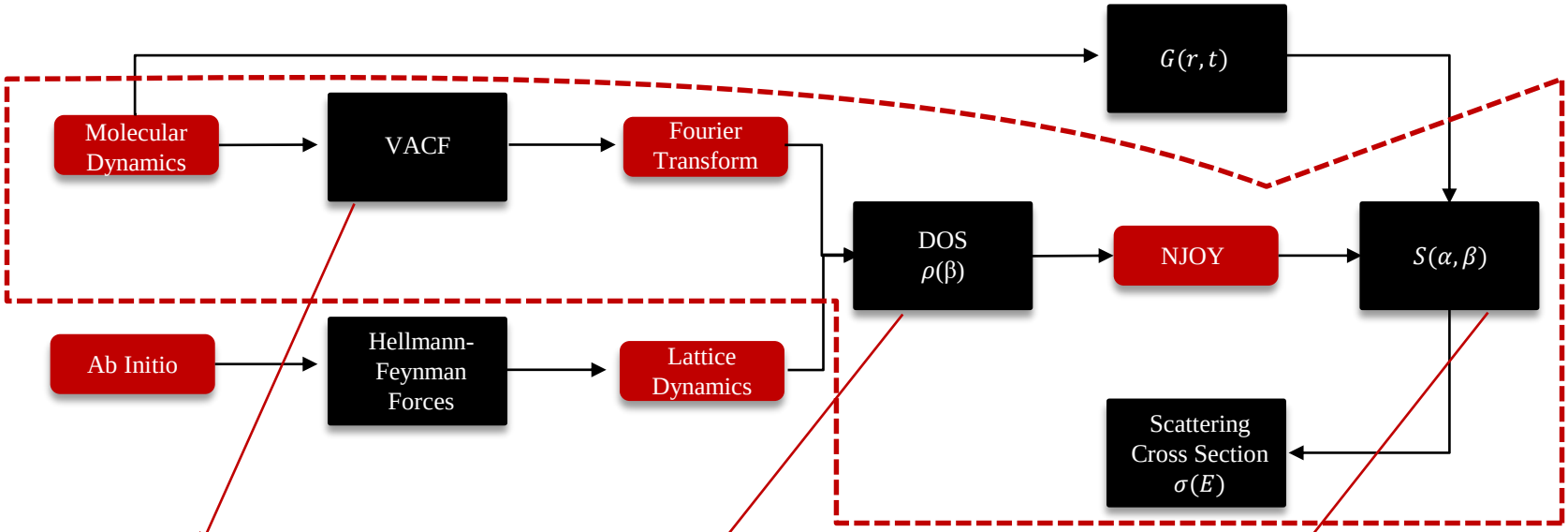
- Thermal neutrons are characterized by energies and de Broglie wave length that are on the order of excitation energy and separation distance in the medium in which they interact

- The scattering behavior of thermal neutrons are quantified by the double differential cross section using the TSL

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\sigma_b}{4\pi k_b T}\sqrt{\frac{E'}{E}}S_s(\alpha,\beta)$$

- The TSL, $S(\alpha,\beta)$, describes the time-dependent particle correlations in a given material

Generation of Inelastic Thermal Neutron Scattering Cross-sections



$$C(t) = \frac{1}{N}\sum_{i=1}^{N} \frac{\langle v_i(t)\cdot v_i(0)\rangle}{\langle v_i(0)\cdot v_i(0)\rangle}$$

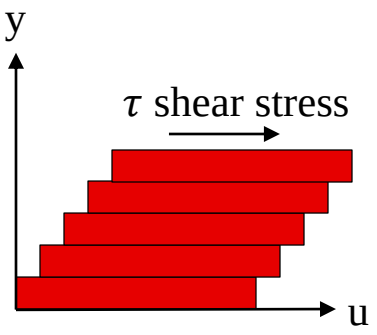
$$\rho(\omega) = \int_{-\infty}^{\infty} dt\, C(t) e^{i\omega t}$$

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

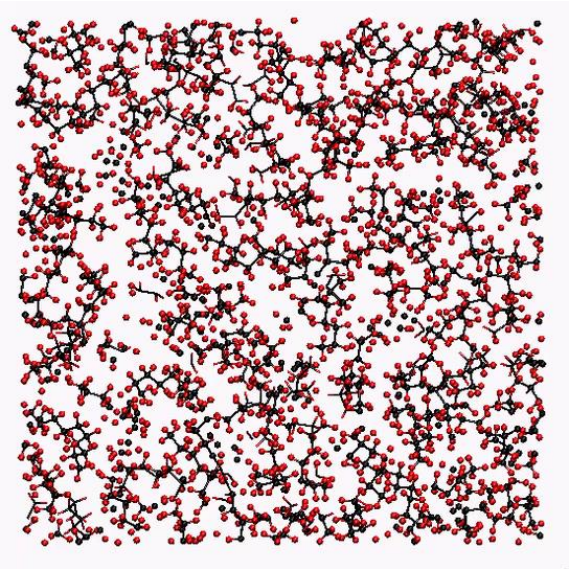
$$\gamma(t) = \frac{\alpha}{2}\int_{-\infty}^{\infty} \frac{\rho(\beta)}{\beta \sinh(\beta/2)}\left[1 - e^{-i\beta t}\right] e^{\beta/2} d\beta$$

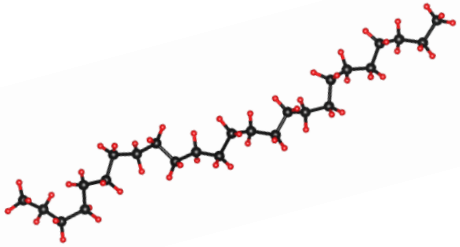
Molecular Dynamics

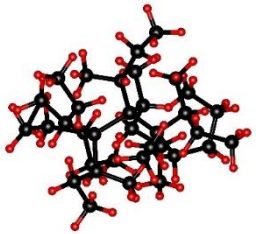
- LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)
  - Equilibrium Molecular Dynamics (EMD)
  - Non-equilibrium Molecular Dynamics (NEMD): imposed control element (e.g. shear stress) that allows for the calculation of various fluid transport properties (e.g. viscosity)
- MD uses semi-empirical forcefields to capture interatomic interactions
- PCFF+ potential
  - Used to model organic systems comprised of C, H, and O



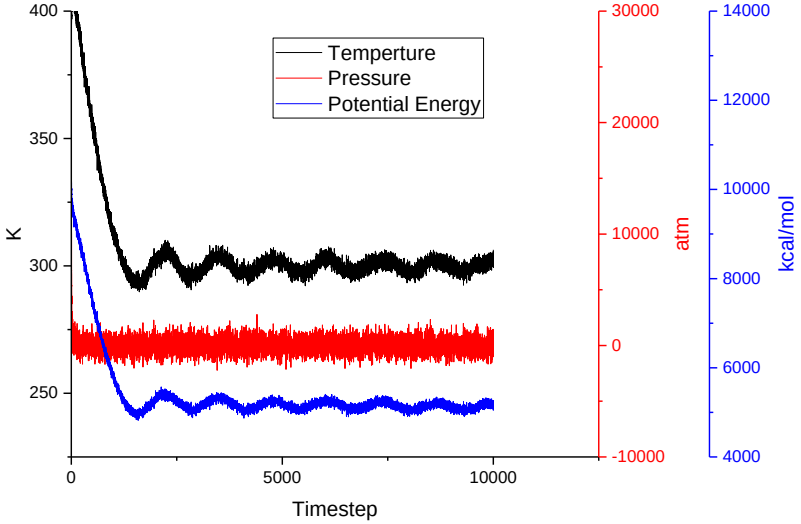
Heavy-Paraffinic Oil Model







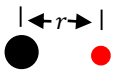
- 10775 atoms
- 100 molecules
- 46x46x46 $Å^3$ supercell
- Equilibration:



PCFF+ Potential

$$\epsilon\left[2\left(\frac{\sigma}{r}\right)^9 - 3\left(\frac{\sigma}{r}\right)^6\right] + \frac{Cq_iq_j}{\epsilon r}$$

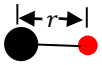
<u>Pair term</u> (intermolecular) with
Lenard Jones and Coulombic components

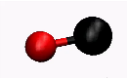


$$K_2(r-r_0)^2 + K_3(r-r_0)^3 + K_4(r-r_0)^4$$

<u>Bond term</u> (intramolecular)

- Symmetric/asymmetric stretching

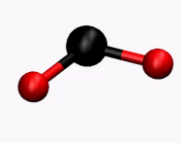




$$K_2(\theta-\theta_0)^2 + K_3(\theta-\theta_0)^3 + K_4(\theta-\theta_0)^4 + N_1(r_{ij}-r_1)(\theta-\theta_0) + N_2(r_{jk}-r_2)(\theta-\theta_0) + M(r_{ij}-r_1)(r_{jk}-r_2)$$

<u>Angle term</u> (intramolecular)

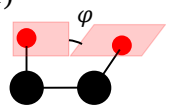
- Twist (out of plane)
- Scissor (in plane)

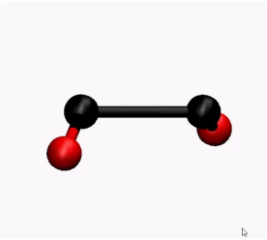


$$\sum_{n=1}^{3} K_n[1-\cos(n\emptyset-\emptyset_n)]$$
$$+ (r_{jk}-r_2)[A_1\cos(\emptyset) + A_2\cos(2\emptyset) + A_3\cos(3\emptyset)]$$
$$+ (r_{ij}-r_1)[B_1\cos(\emptyset) + B_2\cos(2\emptyset) + B_3\cos(3\emptyset)]$$
$$+ (r_{kl}-r_3)[C_1\cos(\emptyset) + C_2\cos(2\emptyset) + C_3\cos(3\emptyset)]$$
$$+ (\theta_{ijk}-\theta_1)[D_1\cos(\emptyset) + D_2\cos(2\emptyset) + D_3\cos(3\emptyset)]$$
$$+ (\theta_{jkl}-\theta_2)[E_1\cos(\emptyset) + E_2\cos(2\emptyset) + E_3\cos(3\emptyset)]$$
$$+ M(\theta_{ijk}-\theta_1)(\theta_{jkl}-\theta_2)\cos(\emptyset) + N(r_{ij}-r_1)(r_{kl}-r_3)$$

<u>Dihedral term</u> (intramolecular)

- Rock (in plane)
- Wag (out of plane)
- Twist
- Scissor

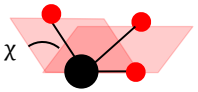


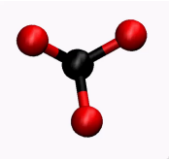


$$K\left[\frac{\chi_{ijkl}-\chi_{kjli}-\chi_{ljik}}{3} - \chi_0\right]^2 + M_1(\theta_{ijk}-\theta_1)(\theta_{kjl}-\theta_3) + M_2(\theta_{ijk}-\theta_1)(\theta_{ijl}-\theta_2) + M_1(\theta_{ijl}-\theta_2)(\theta_{kjl}-\theta_3)$$

<u>Improper term</u> (intramolecular)

- Twist
- Wag

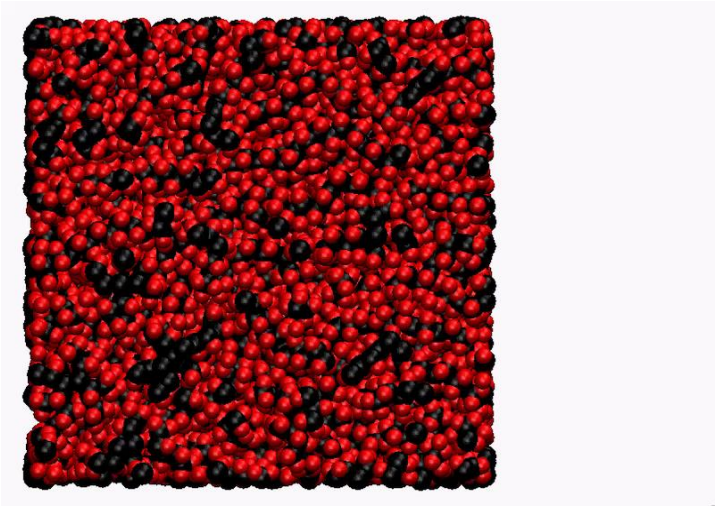




Density and Viscosity

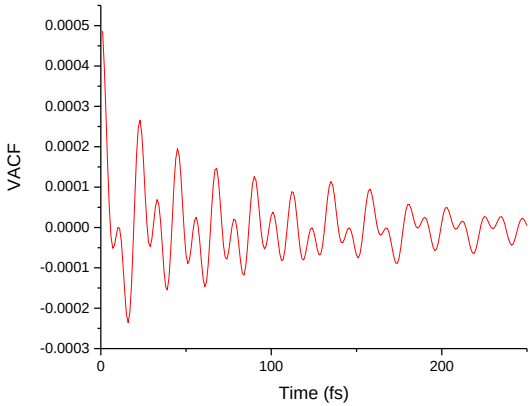
Property	Target Value	Current Simulation Results
Density (300K) [g/cc]	0.86	0.8602 +/- 0.0014
Viscosity (373K) [cSt]	4	3 *work in progress

Shearing Simulation:

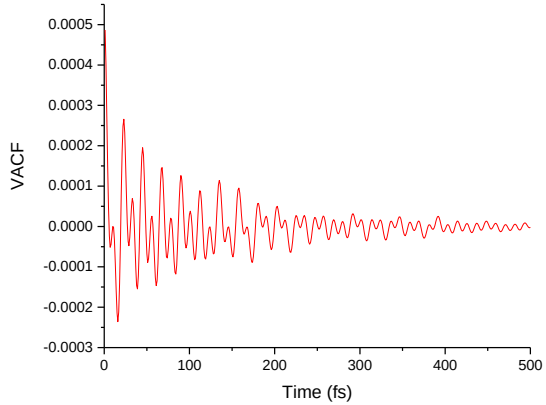


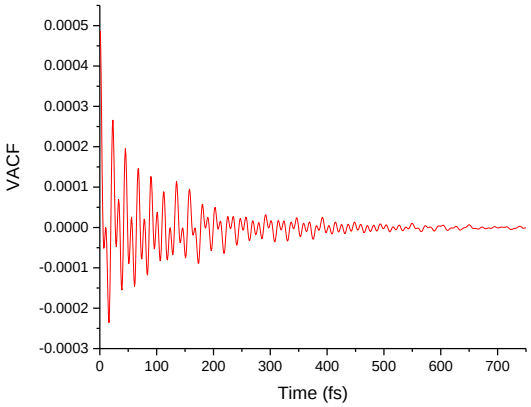
$$\eta = \frac{-\tau}{\dot{\gamma}}$$

Velocity Auto-correlation function (VACF)

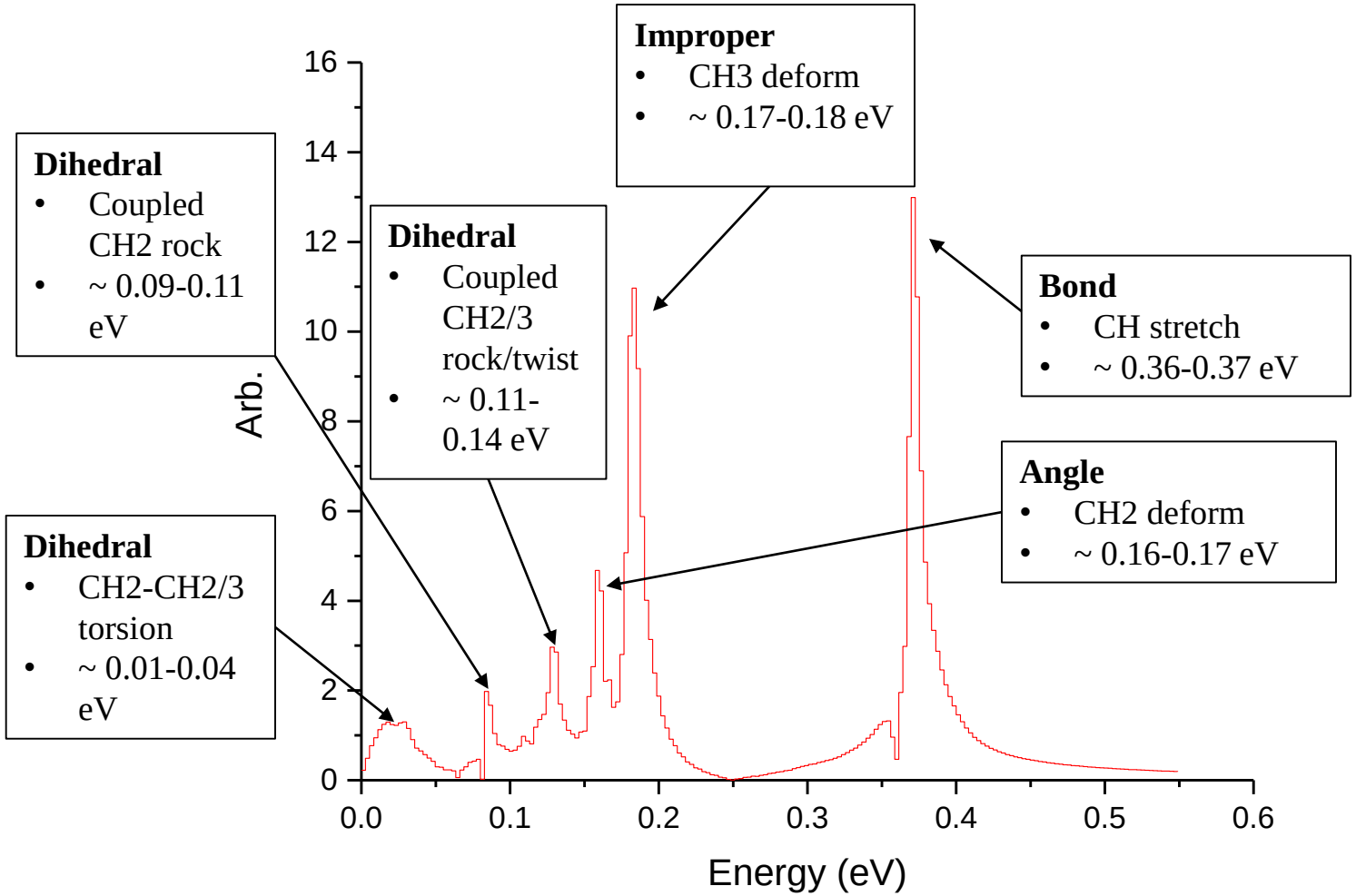


- Correlative relaxation time: ~ 750 fs



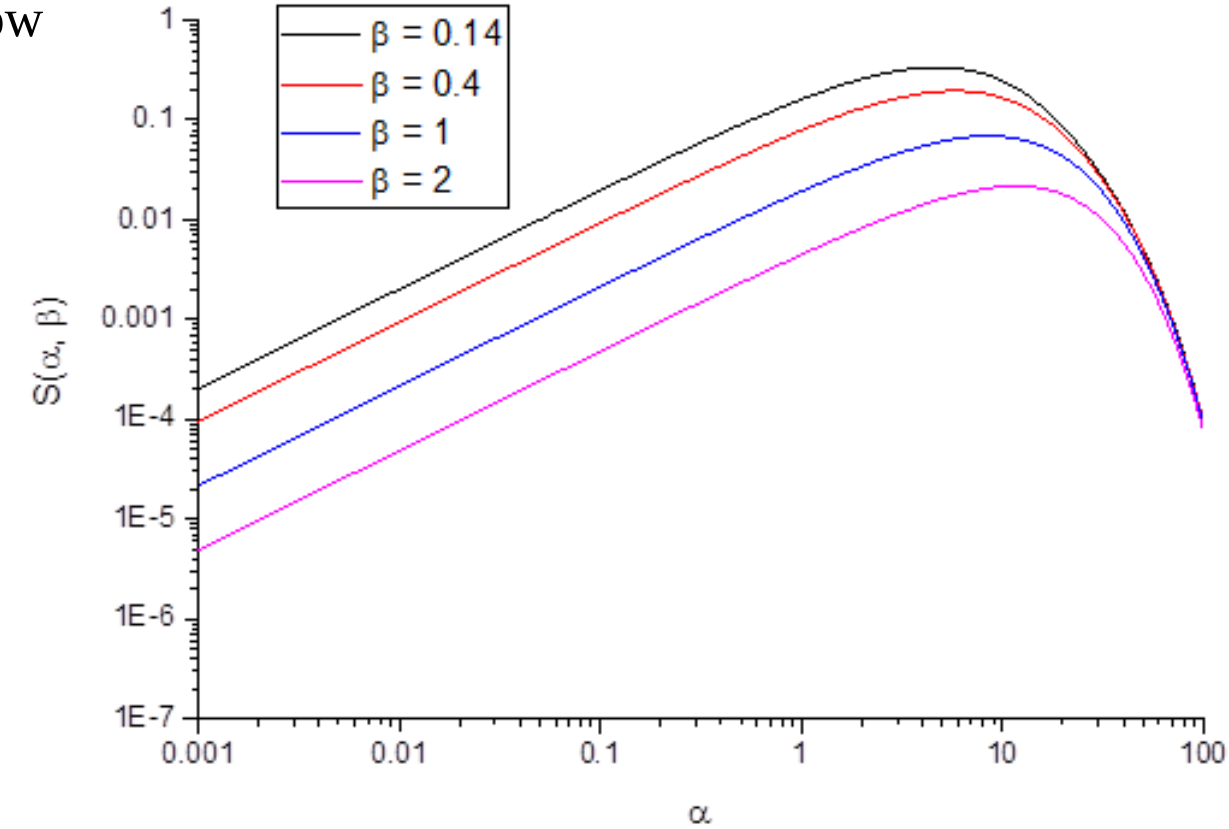


Density of States (DOS)



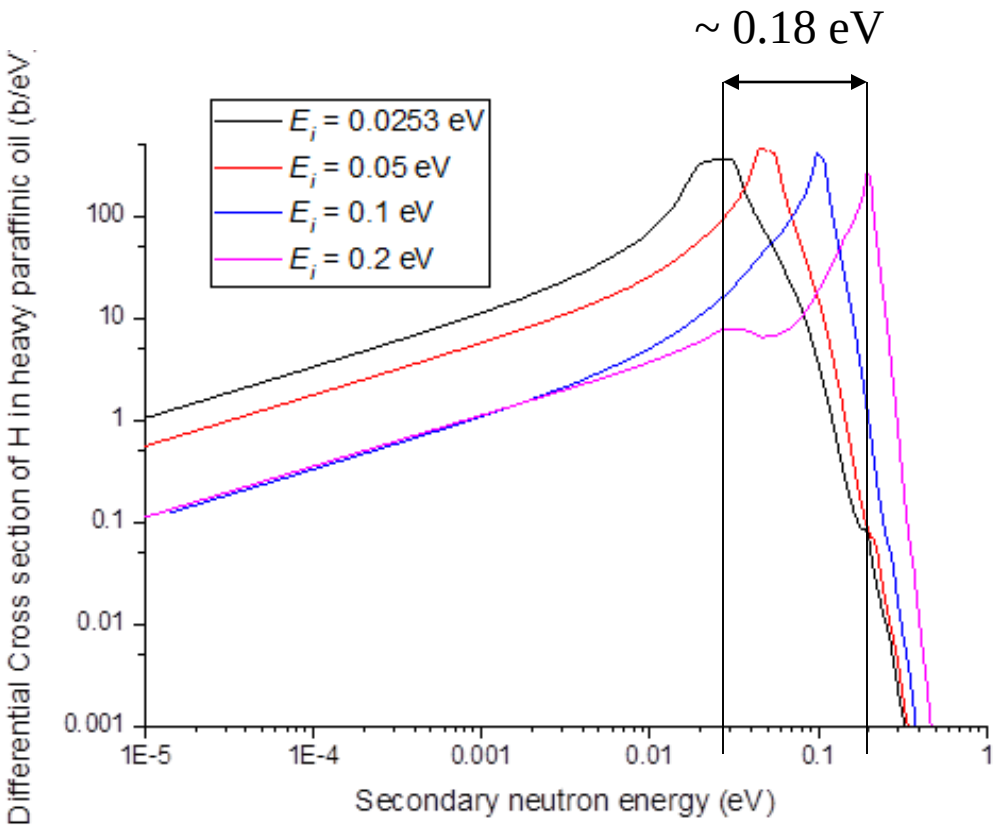
Thermal Scattering Law

- The scattering law plotted against β exhibits a maximum in the low energy range



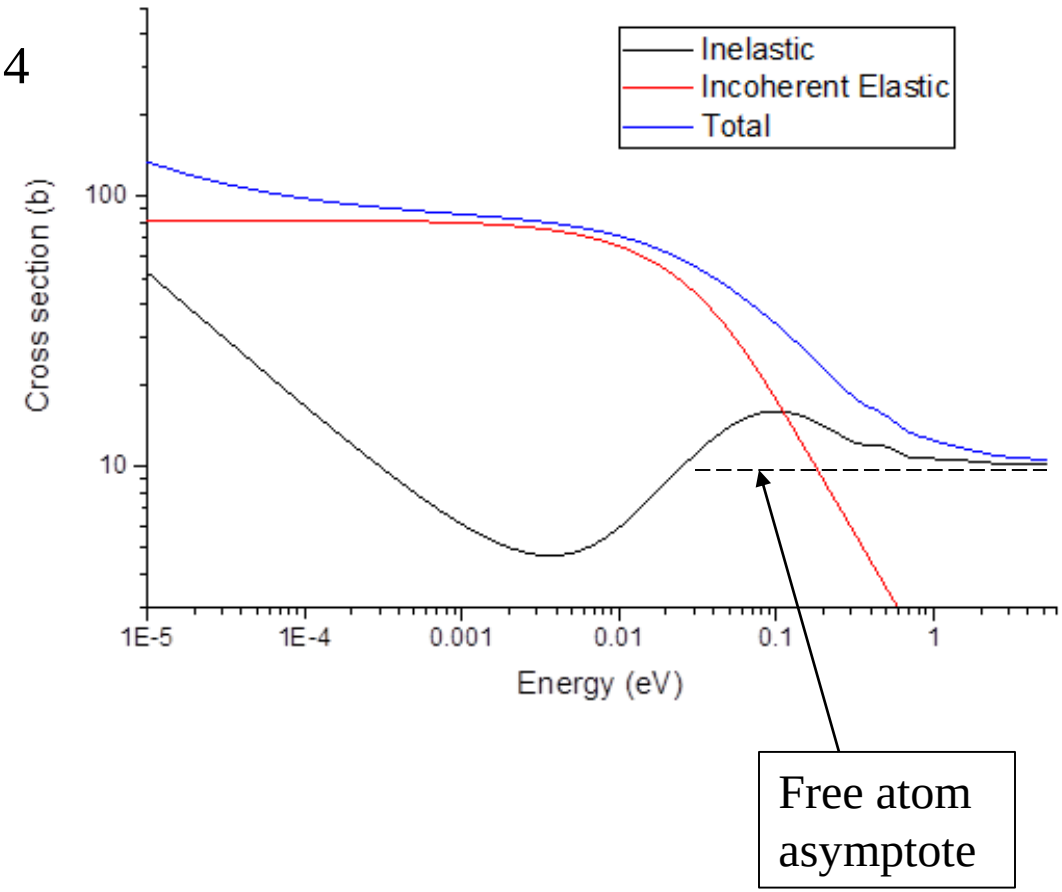
Differential Scattering Cross Section

- Increased scattering mode availability with higher initial neutron energies



Integrated Scattering Cross Section

- Free atom cross section overshoot due to availability of scatter modes between 0.04 to 0.4 eV



Summary

- Heavy paraffinic oil is modeled utilizing the LAMMPS molecular dynamics code
- The calculated density and viscosity are in reasonable agreement with experimental data
- The resulting hydrogen density of states is used to calculate the thermal scattering law
- The thermal neutron scattering cross sections are generated for hydrogen in heavy paraffinic oil