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

Cole A. Manring, A. I. Hawari

Department of Nuclear Engineering
North Carolina State University
Raleigh, North Carolina, USA
Acknowledgements

- Funding by the NCSP and NR programs
  - Collaboration with David Heinrichs (LLNL), Mike Zerkle and Jesse Holmes (BAPL)

This material is based upon work supported under an Integrated University Program Graduate Fellowship.

Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the Department of Energy Office of Nuclear 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**

**Heavy paraffin oil:**

- **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 $\rightarrow$ Alkane $\rightarrow$ general formula: $C_n H_{2n+2}$
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

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

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

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

\[ S_s(\alpha, \beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\beta t} e^{-\gamma(t)} dt \]
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 Å³ supercell
- Equilibration:
PCFF+ Potential

\[ \epsilon \left[ 2 \left( \frac{\sigma}{r} \right)^9 - 3 \left( \frac{\sigma}{r} \right)^6 \right] + \frac{C_{ij}q_iq_j}{er^2} \]

Pair term (intermolecular) with Lenard Jones and Coulombic components

\[ K_2(r - r_0)^2 + K_3(r - r_0)^3 + K_4(r - r_0)^4 \]

Bond term (intramolecular)
- Symmetric/asymmetric stretching

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

Angle term (intramolecular)
- Twist (out of plane)
- Scissor (in plane)

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

Dihedral term (intramolecular)
- Rock (in plane)
- Wag (out of plane)
- Twist
- Scissor

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

Improper term (intramolecular)
- Twist
- Wag

Pair term (intermolecular) with Lenard Jones and Coulombic components

Bond term (intramolecular)
- Symmetric/asymmetric stretching

Angle term (intramolecular)
- Twist (out of plane)
- Scissor (in plane)

Dihedral term (intramolecular)
- Rock (in plane)
- Wag (out of plane)
- Twist
- Scissor

Improper term (intramolecular)
- Twist
- Wag
# Density and Viscosity

<table>
<thead>
<tr>
<th>Property</th>
<th>Target Value</th>
<th>Current Simulation Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (300K) [g/cc]</td>
<td>0.86</td>
<td>0.8602 +/- 0.0014</td>
</tr>
<tr>
<td>Viscosity (373K) [cSt]</td>
<td>4</td>
<td>3 *work in progress</td>
</tr>
</tbody>
</table>

Shearing Simulation:

\[ \eta = \frac{-\tau}{\dot{\gamma}} \]
Velocity Auto-correlation function (VACF)

- Correlative relaxation time: ~ 750 fs
Density of States (DOS)

**Dihedral**
- Coupled CH2 rock
  - ~ 0.09-0.11 eV

**Improper**
- CH3 deform
  - ~ 0.17-0.18 eV

**Dihedral**
- Coupled CH2/3 rock/twist
  - ~ 0.11-0.14 eV

**Bond**
- CH stretch
  - ~ 0.36-0.37 eV

**Angle**
- CH2 deform
  - ~ 0.16-0.17 eV

**Dihedral**
- CH2-CH2/3 torsion
  - ~ 0.01-0.04 eV
Thermal Scattering Law

- The scattering law plotted against $\beta$ exhibits a maximum in the low energy range.
Differential Scattering Cross Section

- Increased scattering mode availability with higher initial neutron energies

~ 0.18 eV
Integrated Scattering Cross Section

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

![Graph showing cross section vs energy with labels: Inelastic, Incoherent Elastic, Total, and Free atom asymptote]
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