materials design

Validation of Thermal Conductivity and Viscosity Calculations Using LAMMPS

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Outline

Statement of Goals

Classes of Materials of Interest

Calculation Methods

Thermal Conductivities by NEMD and EMD Methods

Viscosities Calculated by NEMD and EMD Methods

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Goals

Maximize the opportunities for accurate materials property prediction possible through a combination of advances in computer hardware architectures and associated software-related development, using:

- Parallelized simulation codes (e.g. LAMMPS)
- High accuracy force fields
- Automated setup and analysis tools
- Database and inter/intranet technologies for organization and communication

Initial LAMMPS studies have focused on the area of transport properties, some of which continue to present significant challenges, specifically:

- Thermal conductivity
- Shear viscosity

Materials of Interest

Need to develop and/or fine tune transport property prediction methods for a **wide range of materials** encountered in advanced materials development, for example:

- Simple gases and liquids under extreme conditions (noble gases, N_2, O_2, CO_2, CS_2, SO_2, etc.)
- Organic materials (simple->complex; small molecule->polymer)
- Inorganic materials (crystalline and molten salts, zeolites,...)
- Semiconductor materials (compounds of Si, Ge, Al, Sb, Ga, In, ...)

Transport Property Methods

Two standard classes of method exist for calculation of transport properties from simulations:

- Green-Kubo methods using equilibrium molecular dynamics (EMD), in which the transport coefficient is related to the time integral of a correlation function.

- Various linear-response-based non-equilibrium molecular dynamics (NEMD) approaches, measuring the relationship between an imposed gradient or driving force E, and a resulting flux J

$$J = \lambda E$$

with λ being the transport coefficient.

Variations of NEMD include the so-called "Reverse" NEMD in which the flux is imposed and the resulting steady-state gradient measured - e.g. as studied by Muller-Plathe et al. (see, for example, Comput. Theor. Polymer Sci. **9**, 203 (1999))

Thermal Conductivity

The Green-Kubo relation for thermal conductivity λ is as follows:

$$\lambda = \frac{V}{3\mathrm{kT}^2} \int_0^\infty \langle \boldsymbol{J}(0) \cdot \boldsymbol{J}(t) \rangle dt$$

where $\boldsymbol{J}$ denotes the heat current, defined as:

$$\boldsymbol{J} = \sum_i e_i \boldsymbol{v}_i + \frac{1}{2} \sum_{i<j} \left(\boldsymbol{f}_{ij} (\boldsymbol{v}_i + \boldsymbol{v}_j) \right) \boldsymbol{x}_{ij}$$

Shear Viscosity

The corresponding Green-Kubo relation for shear viscosity θ is as follows:

$$\eta = \frac{V}{kT} \int_0^\infty \langle P_{xy}(0) P_{xy}(t) \rangle \, dt$$

Where $P_{\alpha\beta}$ are off-diagonal components of the pressure tensor.

Transport Property Methodologies

Typical thermal conductivity or viscosity calculation methodologies consist of the following steps:

1. Run NPT dynamics at temperature of interest to determine density and adjust to calculated average (alternatively, use experimental density directly)
2. Perform 50-100ps NVT dynamics to equilibrate at temperature of interest.
3. Perform production run under NVE conditions to generate raw data for computing property of interest. Run durations depend on method (EMD or NEMD) and state of material
    - For EMD, typically need run durations 1000-10000x the decay time of the relevant autocorrelation function
    - For NEMD, require duration sufficient to achieve steady velocity or temperature profiles. Also sample profiles (using fix ave/spatial) frequently to permit estimation of error bars for each point.

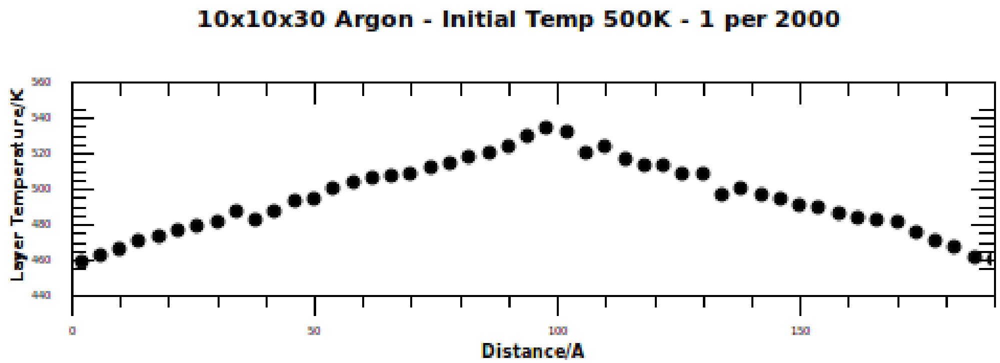
Thermal Conductivity – Systems Studied

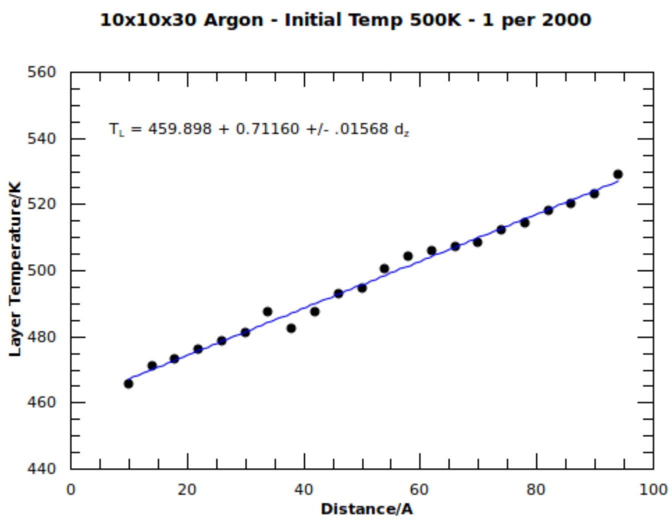
Classes of system studied using either or both of the Muller-Plathe NEMD and Green Kubo approaches, together with the force field(s) used are summarized below:

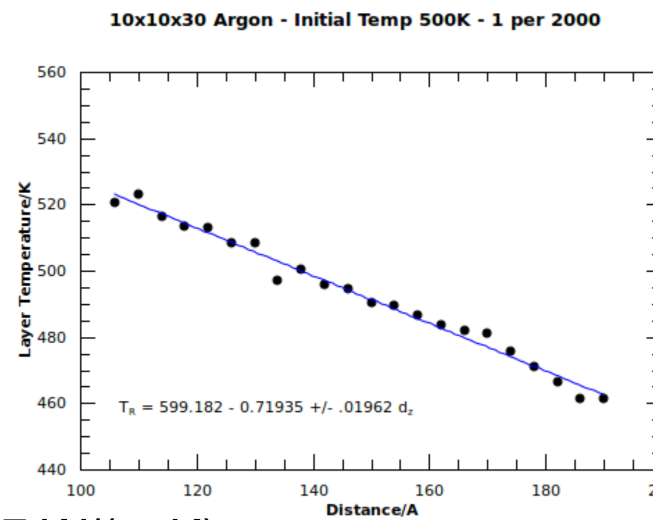
Material	Force Field
Ar, Ne, He and selected mixtures	Various
Cyclohexane	COMPASS
CO_2	COMPASS
Molten NaCl	CFF93
Crystalline NaCl	CFF93
Silicon	COMPASS, Stillinger-Weber, Tersoff

Thermal Conductivity – NEMD Results

State point: $\rho = 0.2652 gcm^{-3}$, P = 30MPa, T = 500K







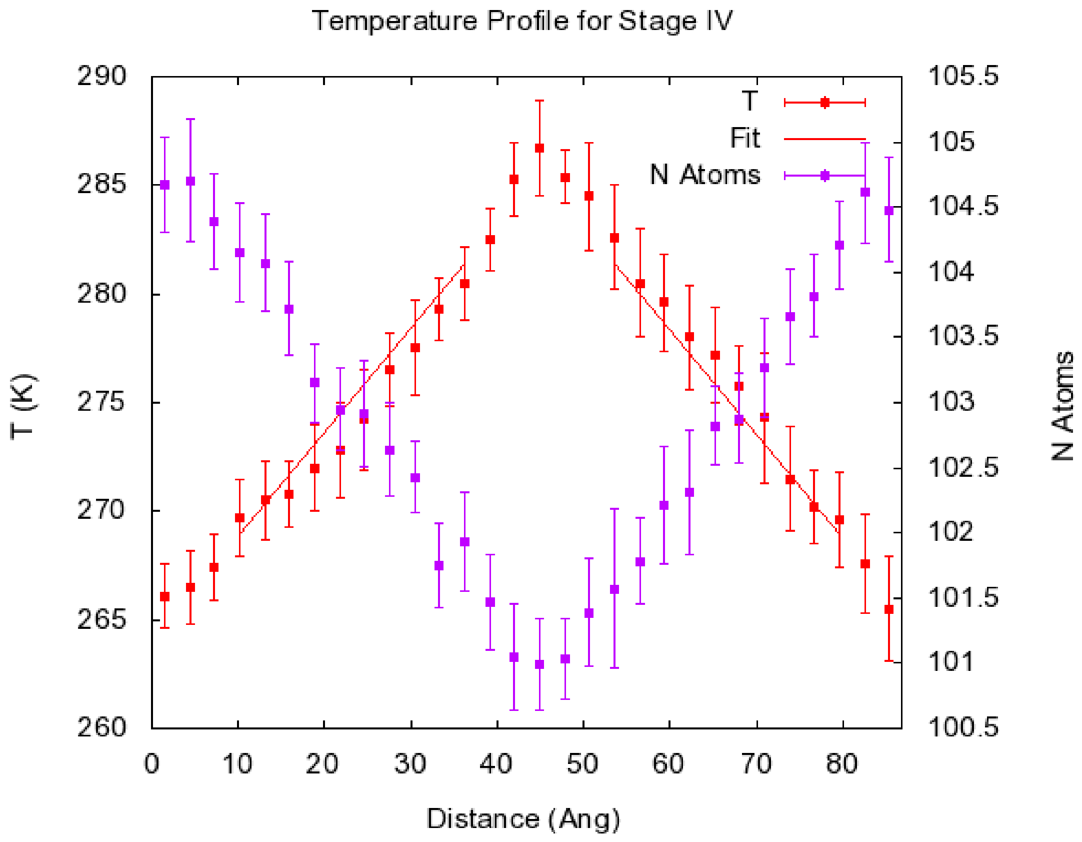
Gives λ = .03247 W/(m.K)

NIST .03527; Younglove and Hanley(1986) .0352

Thermal Conductivity – NEMD Results

Typical Temperature and Density Profiles

Cyclohexane



Thermal Conductivity – NEMD Results

Cyclohexane – Temp = 293.2K, Pressure = 1 bar, Density = 0.779 gcm^{-3}

4x4x12 molecule cells

Swapping 1 pair of carbon momenta per 500fs, 1-2ns simulation

2 types of simulation
- All bonds flexible
- Fixed C-H bonds (2 runs)

Calculated Thermal Conductivity
- Flexible: λ = 0.095 +/- .007 W/m.K
- Fixed C-H: λ = 0.125 +/- .018 W/m.K and 0.116 +/- .015 W/m.K

Experiment 0.120 W/m.K

Thermal Conductivity – NEMD Results

CO_2 – Temp = 298.2K, Pressure = 500 bar, Density = 1.0341 gcm^{-3}

Simulation cell 28.9 x 28.9 x 86.8 Angstroms (7x7x21 molecules)

Swapping 1 pair of **oxygen** momenta per 2000 fs; 5ns simulation

Calculated Thermal Conductivity - λ = 0.141 +/- .017 W/m.K

Experiment 0.1385 W/m.K

Thermal Conductivity – NEMD Results

NaCl melt – Temp = 1400K, Pressure = 1 bar, Density = 1.3793 gcm^{-3}

Simulation cell 4x4x12 and 4x4x48 $Na^{+}Cl^{-}$ pairs

Swapping 1 pair of **chlorine** momenta per 200fs or 1 per 1000fs; 1ns simulation

Calculated Thermal Conductivity

- Smaller cell: λ = 0.615 +/- .099 W/m.K
- Larger cell: λ = 0.576 +/- .076 W/m.K

Experiment ~0.45 - 0.5 W/m.K

(note that the origin of the cff force field parameters used is uncertain)

Thermal Conductivity – NEMD Results

NaCl crystal – Temp = 298.2K, Density = 2.1635 gcm^{-3}

Various cells 4x4x12, 4x4x28, 4x4x56 and 4x4x112 Na^+Cl^- pairs

Various swapping rates beginning at 1 chlorine pair per 50 steps; 1ns or 2ns simulations

Calculated Thermal Conductivity

- 4x4x12: λ = 2.42 +/- 0.33 W/m.K
- 4x4x28: λ = 4.15 +/- 0.26 W/m.K
- 4X4x56: λ = 6.87 +/- 0.81 W/m.K
- 4X4x112: λ = 11.1 +/- 1.5 W/m.K

Experiment ~6-7 W/m.K

Study of NEMD cell length is warranted, preferably using a system with previously validated force field!

Thermal Conductivity – NEMD Results

<u>Cell length study</u> using **500K Silicon** and both Stillinger-Weber and Tersoff potentials – compare with Schelling et al. Phys. Rev. B **65**, 144306 (2002)

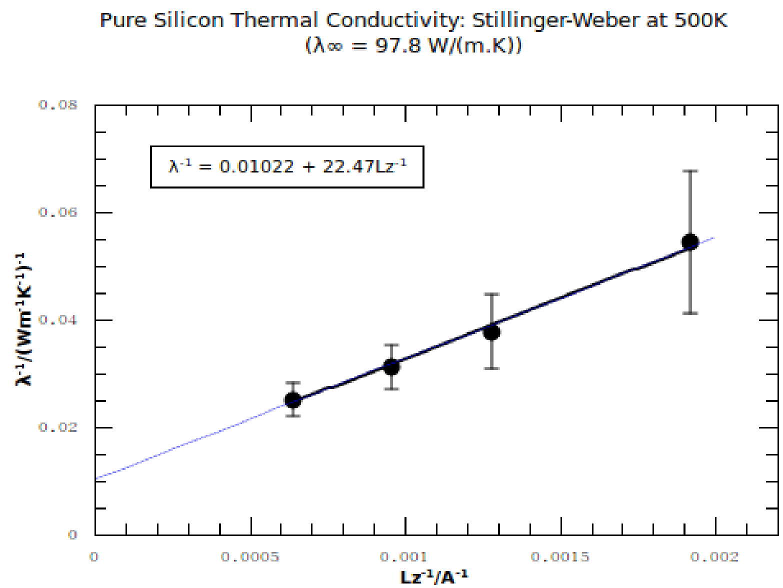
System	Length (A)	S-W λ (W/m.K)	Tersoff λ (W/m.K)
4x4x96	521.3	19.5 +/- 4.7	16.5 +/- 2.9
4x4x144	781.9	27.4 +/- 5.0	-
4x4x192	1042.6	32.6 +/- 4.2	28.9 +/- 6.0
4x4x288	1563.8	40.6 +/- 5.0	41.5 +/- 5.1

Schelling (digitized data)

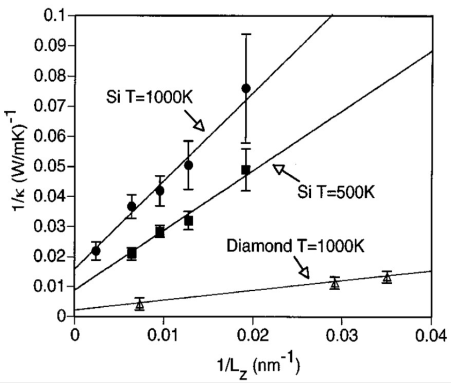
System	Length (A)	S-W λ (W/m.K)
4x4x96	521.5	20.5
4x4x144	782.2	31.2
4x4x192	1042.1	35.3
4x4x288	1560.5	48.0

Thermal Conductivity – NEMD Results

Cell length study using **500K** Silicon – Extrapolation to infinite length



Schelling (At **500K**: extrapolated λ = 119 +/- 40 W/m.K; expt ~80 W/m.K)



Thermal Conductivity – EMD Results

Isotope Effects in Si and Ge

300K thermal conductivities for isotopically pure and 'natural' isotopic mixtures of pure Si and Ge calculated using the Green-Kubo approach (units: W/m.K)

	Isotopically Pure	Isotopic Mixture	Expt(*)
Si (4x4x4)	272	128	130
Ge (4x4x4)	98	37	58

* http://www.ioffe.rssi.ru/SVA/NSM/Semicond/SiGe/thermal.html#Thermal conductivity

Shear Viscosity – Systems Studied

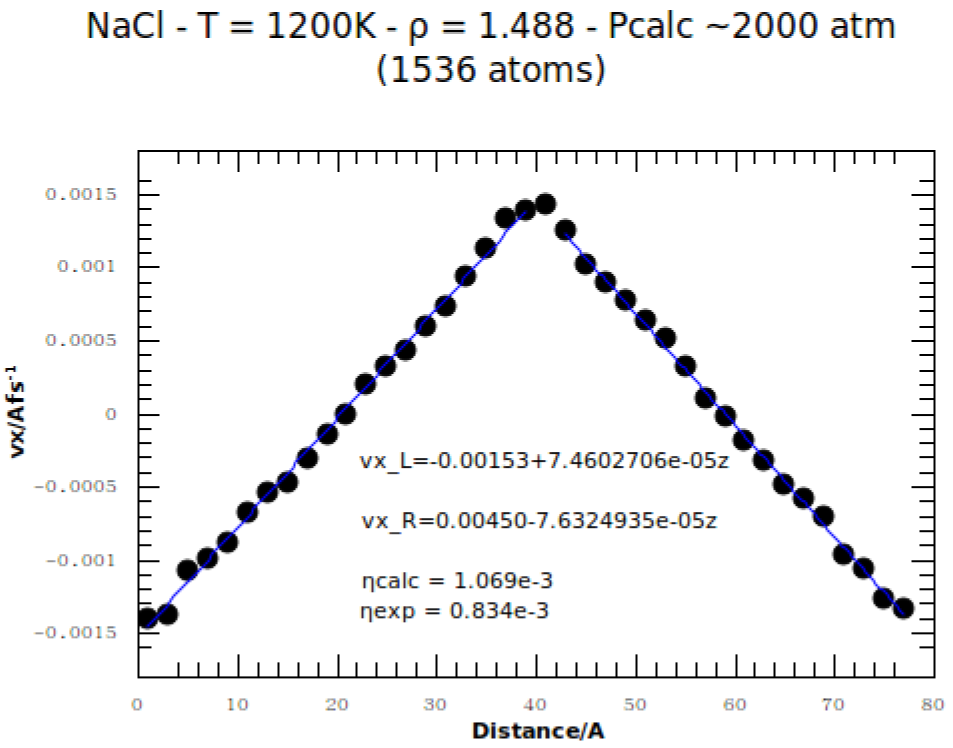
A variety of systems has been studied using different force fields and mostly the Green Kubo approach, with isolated cases also studied by NEMD.

Material	**Force Field**
Ar, Ne, He and selected mixtures	Various
CO_2	COMPASS
Molten NaCl	Born-Mayer-Huggins-Tosi-Fumi
Alkanes	COMPASS, OPLSAA
Alcohols, diols and glycerol	COMPASS, OPLSAA

Shear Viscosity – NEMD Results

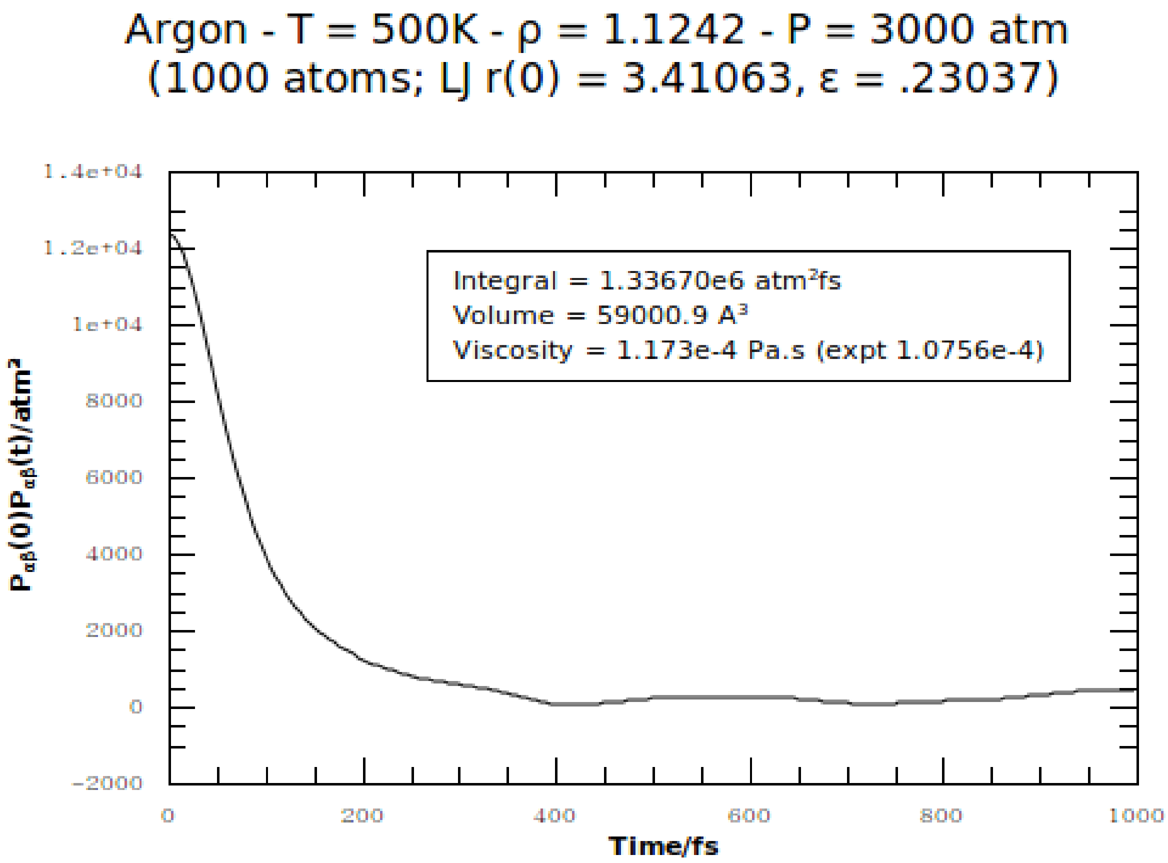
<u>Sodium Chloride</u>

Molten NaCl at 1200K has been modeled using the Born-Mayer-Huggins-Tosi-Fumi potential. Steady state velocity profiles and resulting viscosities are illustrated below:



Shear Viscosity – EMD Results

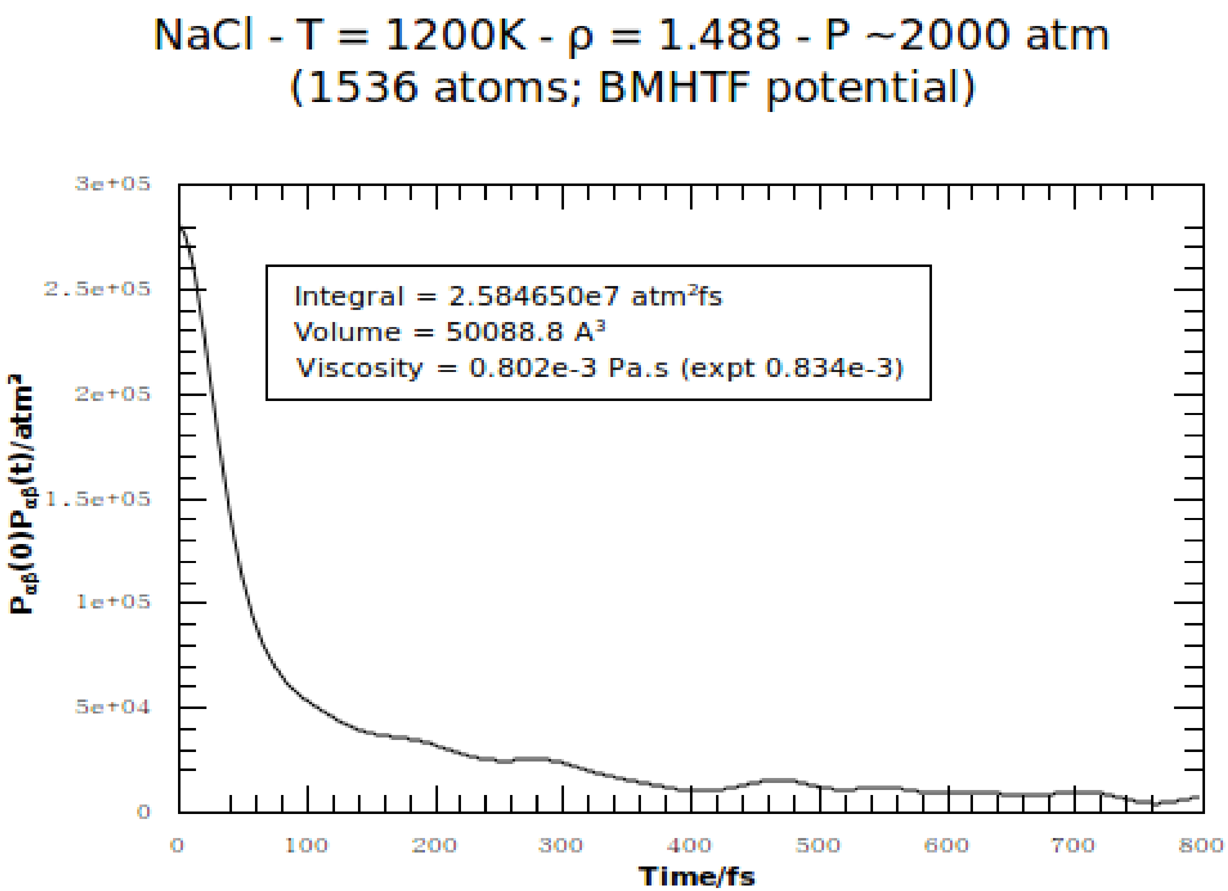
Argon Green-Kubo shear viscosity at P=3000atm, T=500K state point



Shear Viscosity – EMD Results

<u>Sodium Chloride</u>

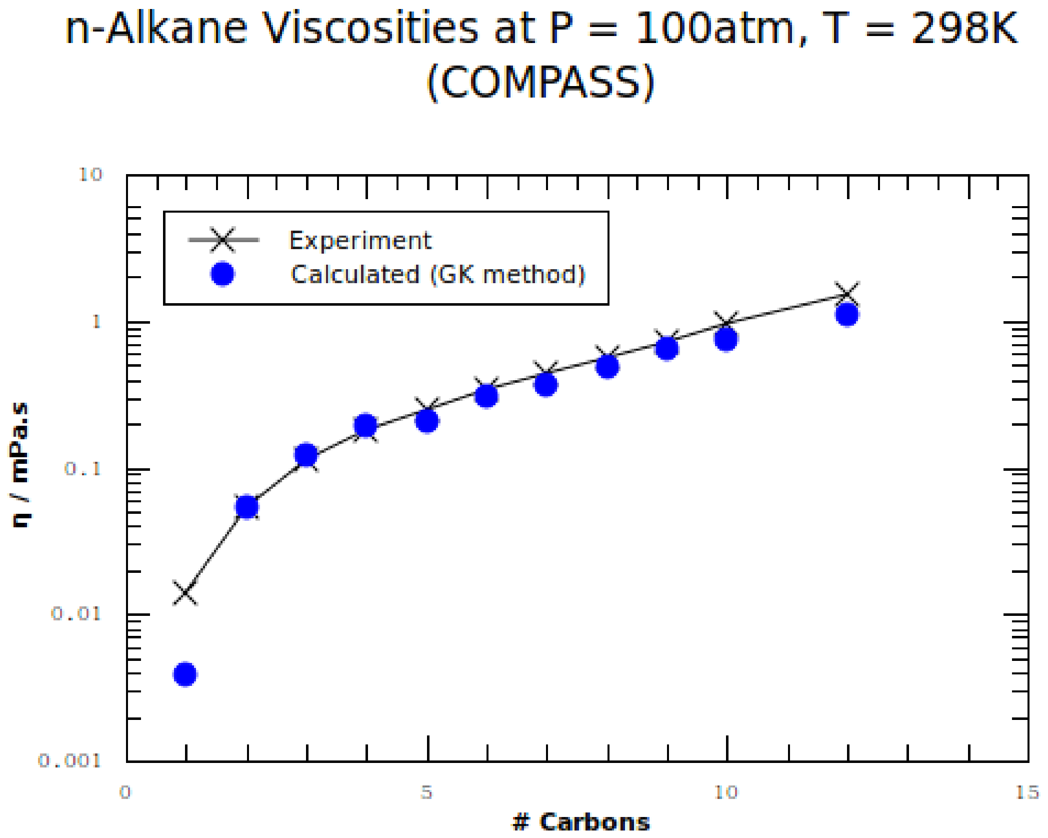
GK shear viscosity, T=1200K – Born-Mayer-Huggins-Tosi-Fumi potential (compare viscosity of 1.069 mPa.s obtained using NEMD)



Shear Viscosity – EMD Results

Alkanes

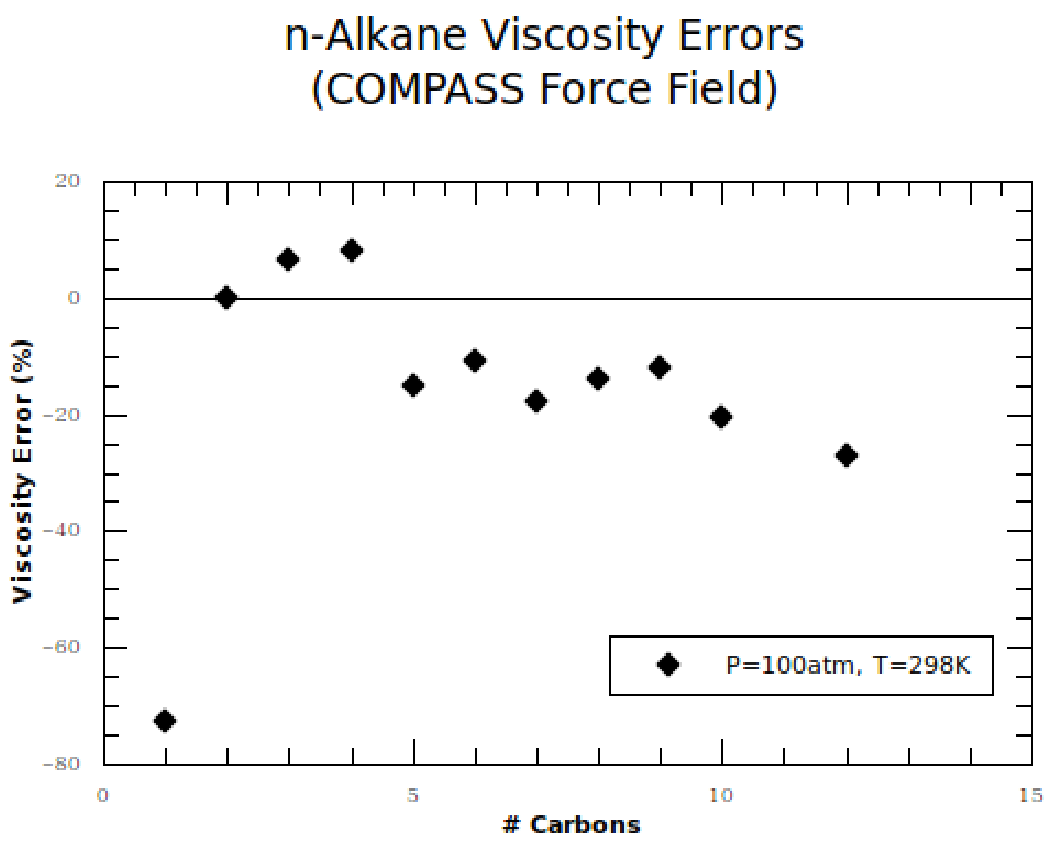
Green-Kubo viscosities using the COMPASS force field- may be underestimated for longer molecules



Shear Viscosity – EMD Results

Alkanes (cont'd)

Green-Kubo viscosities at 298K and 100atm – COMPASS Force Field



Shear Viscosity – EMD Results

Glycerol Green-Kubo viscosities at various temperatures – COMPASS Force Field

Temp/K	ρ(expt)	η(expt)/cP	η(calc)/cP	ρ(calc)	η(calc_ρx)/cP
373.2	1.209	13	4.5	1.1625	-
423.2	1.154	1.7	1.7	1.1126	1.55
473.2	1.090	0.22	0.56	1.0641	0.79

Results do not show expected variation with temperature (note also that NPT-calculated densities are low by more than the generally expected 0-2%). Investigation of other force fields (e.g. OPLSAA) desirable for these systems...

Shear Viscosity – EMD
Note on Recent Developments

For convenience, a new correlation fix has been written to compute auto or cross-correlation 'on-the-fly', and therefore avoid having to generate large raw data files for subsequent analysis (modeled after `fix ave/time`)

```
/* ----------------------------------------------------------------------

fix correlation command.
Syntax:
    fix ID group-ID correlation Nevery Nbins value1 value2 ... keywords args

  value = c_ID, c_ID[N], f_ID, f_ID[N], v_name

  c_ID = global scalar value calculated by a compute with ID
  c_ID[N] = Nth component of global vector calculated by a compute with ID
  f_ID = global scalar value calculated by a fix with ID
  f_ID[N] = Nth component of global vector calculated by a fix with ID
  v_name = global value calculated by an equal-style variable with name

  Keywords + args:
        file arg = filename
          filename = name of file to output correlation(s) to
   type full | simple : when 2 values are provided, 'simple' means
     to sample only cross correlation, and 'full' (default) implies
     also the computation of autocorrelation.

Author: Benoit Leblanc
                                                                       */
```

Green Kubo – Recent Developments (cont'd)

Example of usage scenario for 'fix correlation':

```
#--------------------------------------------------------------------------------
# Stage II.4: Viscosity from nVE simulation for 10.0 ns with a timestep of 1fs
#           using Green-Kubo method.
#--------------------------------------------------------------------------------

reset_timestep 0
fix            II_4_1 all nve

fix            II_4_2 all correlation 1 10000 v_pxy file autocorrelation_pxy_1_II.4.txt
fix            II_4_3 all correlation 1 10000 v_pxz file autocorrelation_pxz_1_II.4.txt
fix            II_4_4 all correlation 1 10000 v_pyz file autocorrelation_pyz_1_II.4.txt

fix            II_4_5 all ave/time 5000  1 5000  v_myTime c_thermo_temp c_thermo_press
v_sysvol   v_sysdensity v_etotal c_thermo_pe v_evdwl v_coulomb file instantaneous_II.4.txt
fix            II_4_6 all ave/time 1 1000000 1000000 v_myTime c_thermo_temp c_thermo_press
v_sysvol v_sysdensity v_etotal c_thermo_pe v_evdwl v_coulomb file averages_II.4.txt

timestep       1
run            10000000
```

Summary & Ongoing Work

- For many materials, both thermal conductivities and viscosities can be calculated with a reasonable accuracy and precision using either NEMD or EMD methods
- For NEMD, careful selection of control parameters, such as swapping frequencies and run duration, may be necessary to avoid large gradients in temperature or velocity, while keeping error bars (uncertainty in slope) small.
- Thermal conductivity prediction for solids using NEMD generally requires extrapolation to long(infinite) cell lengths when 'bulk' thermal conductivities are sought.
- For EMD, production runs must ensure that a sufficient number of independent samples of the autocorrelation function decay curve are included in the averaging (e.g. 1000-10000x the decay time).
- Ongoing work:
  - Estimation of errors for GK-based methods
  - Critical examination of performance of different force fields (and improvement where necessary)