Viscosity Calculation of Toluene System via MD Simulations:

Step-by-Step Approach

Definition of Viscosity for a Continuous System

Unlike **self-diffusivity**, which is a **single-particle property**, viscosity is a **collective property** and cannot be improved by averaging over all particles in the system.

Viscosity (η) is a measure of a fluid's **internal resistance to flow** under an applied **shear stress**. It quantifies the **extent to which a fluid resists deformation** due to relative motion between its layers.

Mathematically, viscosity is defined as:

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

Where:

- η = Dynamic viscosity (Pa·s or N·s/m^2)

- τ = Shear stress (force per unit area, N/m^2 or Pa)

- $\dot{\gamma}$ = Shear rate (rate of deformation, s^{-1})

Green-Kubo relation

There have been a number of different atomistic simulation methods developed for computing the shear viscosity of liquids. Due to its simplicity, the Green–Kubo relation based on equilibrium molecular dynamics (MD) simulations is perhaps the most widely used method.1 In the Green–Kubo approach, the shear viscosity is calculated from the integral over time of the pressure tensor autocorrelation

$$\eta = \frac{V}{k_{\mathrm{B}}T} \int_0^{\infty} \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle \; dt$$

where V is the system volume, kB is the Boltzmann constant, T is temperature, Pαβ denotes the element αβ of the pressure tensor, and the angle bracket indicates the ensemble average. Theoretically, the pressure tensor autocorrelation function decays to zero in the long-time limit and the integral in above equation will reach a constant value, which corresponds to the calculated shear viscosity.

So, for calculating viscosity we are requiring pressure tensor or stress tensor, here we are using Molecular Dynamics Simulation for calculating shear stress.

Molecular Dynamics Simulation of a Toluene System for Shear Stress Calculation in Material Studio

To perform a molecular dynamics simulation and extract stress tensor data, we first need to construct a well-defined toluene system. This involves several critical steps to ensure accuracy and reliability in our results.

Step 1: Creating a Single Toluene Molecule

The process begins with generating a single toluene molecule within **Material Studio**. This step is crucial, as the accuracy of the molecular structure directly affects the simulation outcomes.
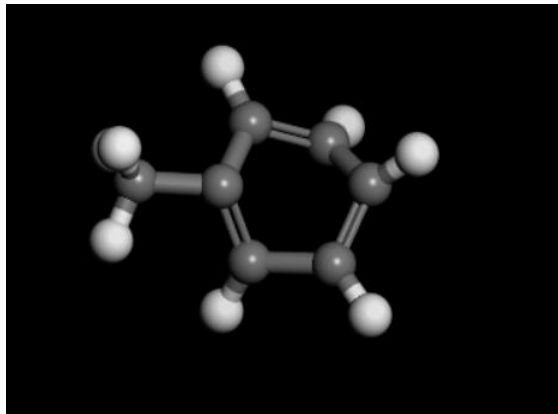

Fig.: After molecule formation

- **Molecular Structure:** The toluene molecule consists of a benzene ring with a methyl (-CH_3) group attached. Ensuring correct bond lengths, angles, and torsions is essential for a realistic representation.

- **Energy Minimization:** Before proceeding further, the molecule should be **energy minimized** using a suitable force field (e.g., COMPASS or Universal). This eliminates steric clashes and ensures a stable conformation for subsequent simulations.

  Once the single molecule is optimized, it serves as the fundamental unit for constructing a larger system, which will be used to analyze shear stress components under simulated conditions.

Step 2: Geometrical Optimization of the Toluene Structure

After creating a single toluene molecule in **Material Studio**, the next crucial step is **geometrical optimization**. This ensures that the molecular structure is stable and represents a realistic configuration before proceeding to system construction and molecular dynamics simulation.
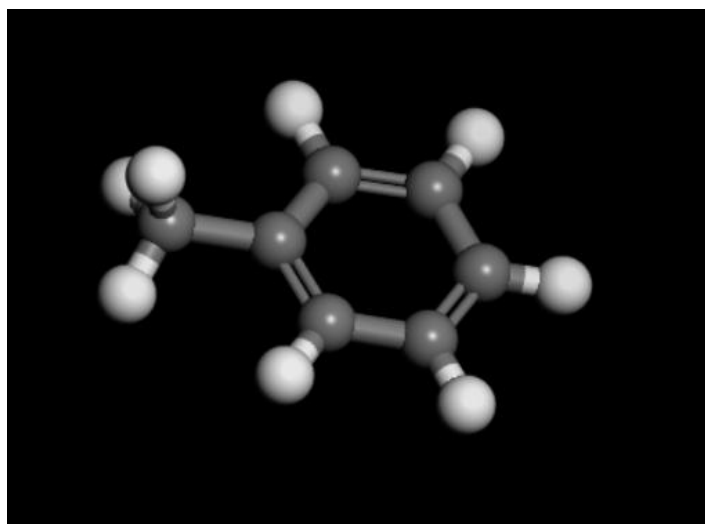
Fig.: Result after Geometric optimization

Step 3: Constructing the Toluene System – Amorphous Cell Creation

With the geometrically optimized **single toluene molecule** ready, the next step is to build a **bulk molecular system** that serves as the foundation for molecular dynamics simulations. This is done by generating an **Amorphous Cell** containing a sufficient number of toluene molecules.
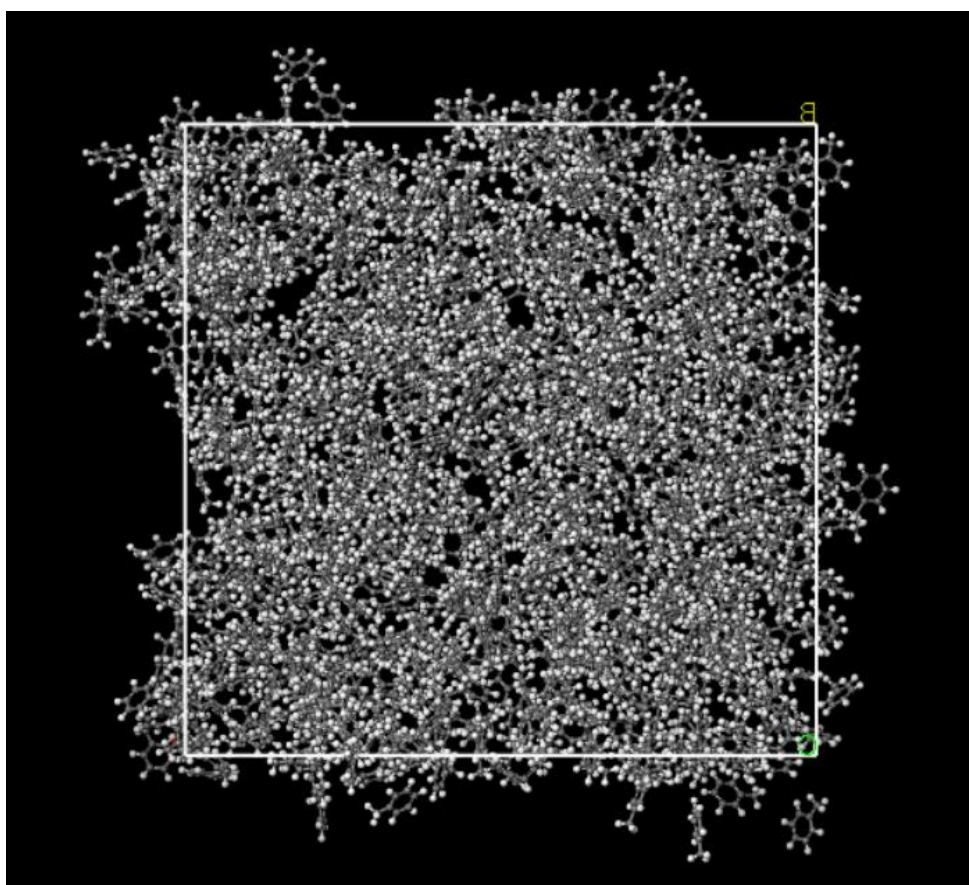

Fig.: Results after Cell Construction

```
Forcite
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Task            : Geometry Optimization
Version         : 2020
Build date      : Oct 18 2019
Host            : fedora1
Threads         : Parallel 4
Operating system : linux
Task started    : Mon Dec  9 16:18:14 2024

---- Geometry optimization parameters ----

Algorithm                    : Smart
Convergence tolerance:
   Energy                    : 0.001 kcal/mol
   Force                     : 0.5 kcal/mol/A
Maximum number of iterations : 500
Motion groups rigid          : NO

---- Energy parameters ----

Forcefield                   : COMPASSII (Version 1.2)
Charges                      : Forcefield assigned
Electrostatic terms:
   Summation method          : Atom based
   Truncation method         : Cubic spline
   Cutoff distance           : 12.5 A
   Spline width              : 1 A
   Buffer width              : 0.5 A

van der Waals terms:
   Summation method          : Atom based
   Truncation method         : Cubic spline
   Cutoff distance           : 12.5 A
   Spline width              : 1 A
   Buffer width              : 0.5 A
```

Step 4: Density Optimization of the Toluene System

With the **800-molecule amorphous cell** created, the next critical step is **density optimization** to ensure that the system accurately represents experimental conditions. The initially assigned density was an approximation, so adjustments are required to bring it closer to the **experimental density of toluene (~0.866 g/cm³ at 25°C)**.
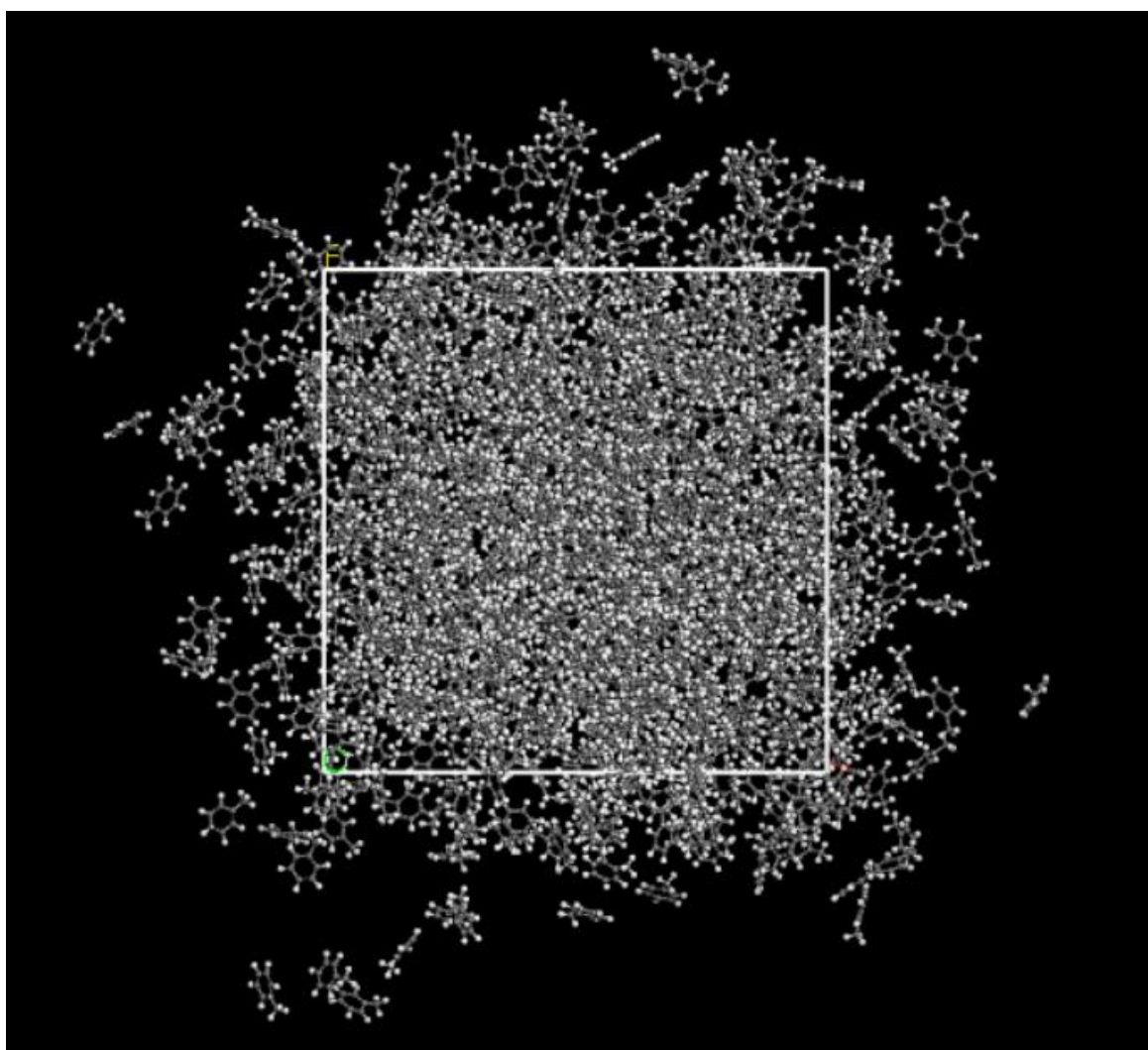
Fig.: Results After Density Optimization

```
Dynamics status

Step      : 50000
CPU time  : 0:51:51
Time      : 13:05:31

Total enthalpy              : 9025.470 kcal/mol
Total energy                : 9054.563 kcal/mol
Temperature                 :  299.248 K
Pressure                    :   -0.001 GPa
Volume                      : 141930.761 A^3
Density                     :    0.862 g/cm^3

Contributions to total energy (kcal/mol):|
  Valence energy (diag. terms)  : 7377.523
    Bond                        : 2838.723
    Angle                       : 3782.231
    Torsion                     :  379.460
    Inversion                   :  377.109
  Valence energy (cross terms)  : -1149.867
    Stretch-Stretch             :  116.338
    Stretch-Bond-Stretch        : -259.600
    Stretch-Torsion-Stretch     : -121.633
    Separated-Stretch-Stretch   :  101.853
    Torsion-Stretch             : -3062.287
    Bend-Bend                   :  -22.149
    Torsion-Bend-Bend           :   61.375
    Bend-Torsion-Bend           : 2036.236
  Non-bond energy               : -5973.264
    Hydrogen bond               :    0.000
    van der Waals               : -2747.691
    Electrostatic               : -2955.541
    3-Body                      :    0.000
  Restraint energy              :    0.000

Cell parameters:      a:   52.16 A       b:   52.16 A       c:   52.16 A
                  alpha:   90.00 deg  beta:   90.00 deg  gamma:   90.00 deg
```

Step 5: Simulated Annealing for System Stabilization

After optimizing the **density of the toluene system**, the next step is **simulated annealing** to ensure the system reaches its most stable energy state. This process helps in refining molecular arrangements, reducing residual stress, and improving the accuracy of shear stress calculations.

Procedure for Simulated Annealing:

1. **Heating Phase**

   o   Gradually **increase** the system temperature from **298 K to ~800–1000 K** over a period of **100–200 ps** using an **NVT ensemble** (constant **Number of molecules, Volume, and Temperature**).

   o   Use a **Nosé–Hoover thermostat** to maintain temperature control.

2. **High-Temperature Equilibration**

   o   Maintain the system at **high temperature (~1000 K) for 100–200 ps** to allow molecular rearrangement and escape from local energy wells.

3. **Controlled Cooling Phase**

   o   Gradually **cool down** the system from **1000 K back to 298 K** over **200–500 ps** using an **NPT ensemble** (constant **Number of molecules, Pressure, and Temperature**).

- A slow cooling rate ensures that molecules settle into a **low-energy configuration** rather than trapping in unstable states.

4. **Final Energy Minimization**

- Perform a final **energy minimization step** to remove any remaining steric clashes.

- Verify that the **potential energy of the system is at its lowest stable value**.

Step 6: Generating Independent Trajectories for Enhanced Accuracy

With the **annealed and stabilized toluene system** ready, the next crucial step is to **generate multiple independent trajectories**. This ensures that the system is sampled thoroughly, reducing statistical errors and improving the accuracy of **shear stress component calculations**.

Why Generate Independent Trajectories?

- **Reduces Correlation Effects:** If molecules have the same initial velocities, results may be biased toward specific configurations.

- **Improves Statistical Accuracy:** Multiple independent trajectories help capture a wider range of molecular interactions.

- **Enhances Convergence of Shear Stress Calculations:** A larger dataset ensures more reliable and reproducible stress tensor values.

Calculation of Viscosity from above generated trajectories:

First, we need to extract stress tensor values from the trajectory files generated by material studio:

For each trajectory we need to run the following Perl script to do so,

```perl
d# Perl script to extract and save the stress tensor for the first 5 frames of TOL.xtd to a CSV file

use strict;
use Getopt::Long;
use MaterialsScript qw(:all);
use warnings;

# Open the trajectory document
my $trajectoryDoc = $Documents{"NVT1 NoMatter.xtd"};
my $trajectory = $trajectoryDoc->Trajectory;
my $symmetrysystem = $trajectoryDoc->SymmetrySystem;

# Define the output file path
```

```perl
my $outputFilePath =
"D:/Users/Jayati/WinterProject/Priyanshu/TOL_Viscosity_Files/Documents/Production/NVT1/stress_tens
or.csv";

# Open a CSV file for writing
open(my $csv_fh, '>', $outputFilePath) or die "Cannot open $outputFilePath: $!";

# Write CSV header
print $csv_fh "Frame,StressXX,StressYY,StressZZ,StressXY,StressXZ,StressYZ\n";

# Loop through the first 5 frames
for (my $frame = 1; $frame <= 5; ++$frame) {
  $trajectory->CurrentFrame = $frame;
  my $stressTensor = $symmetrysystem->Stress;

  # Extract stress tensor components
  my $stressXX = $stressTensor->Eij(1, 1);
  my $stressYY = $stressTensor->Eij(2, 2);
  my $stressZZ = $stressTensor->Eij(3, 3);
  my $stressXY = $stressTensor->Eij(1, 2);
  my $stressXZ = $stressTensor->Eij(1, 3);
  my $stressYZ = $stressTensor->Eij(2, 3);

  # Write stress tensor to CSV file
  print $csv_fh "$frame,$stressXX,$stressYY,$stressZZ,$stressXY,$stressXZ,$stressYZ\n";
}

close($csv_fh);
print "Stress tensor extraction complete. Results saved to $outputFilePath.\n";
```

Above Script will generate CSV file storing Stress tensor data following below formatting:

Frame	StressXX	StressYY	StressZZ	StressXY	StressXZ	StressYZ
1	-0.06665	-0.13673	-0.10209	0.014428	-0.01319	0.046994
2	-0.03544	-0.07522	-0.05382	0.018979	-0.02007	0.036212
3	0.011986	0.035665	0.012144	0.020924	-0.01581	0.023884
4	0.0184	0.108809	0.039716	0.018956	-0.00278	0.013983
5	-0.03312	0.098713	0.013485	0.011868	0.01538	0.009206
6	-0.09582	0.041265	-0.02546	-0.00103	0.033512	0.010921
7	-0.0922	0.021224	-0.00892	-0.01889	0.046392	0.017838

. . . .

Now for calculating Viscosity from the above trajectories we need to use a python Script below link of GitHub repository of doing it is given,

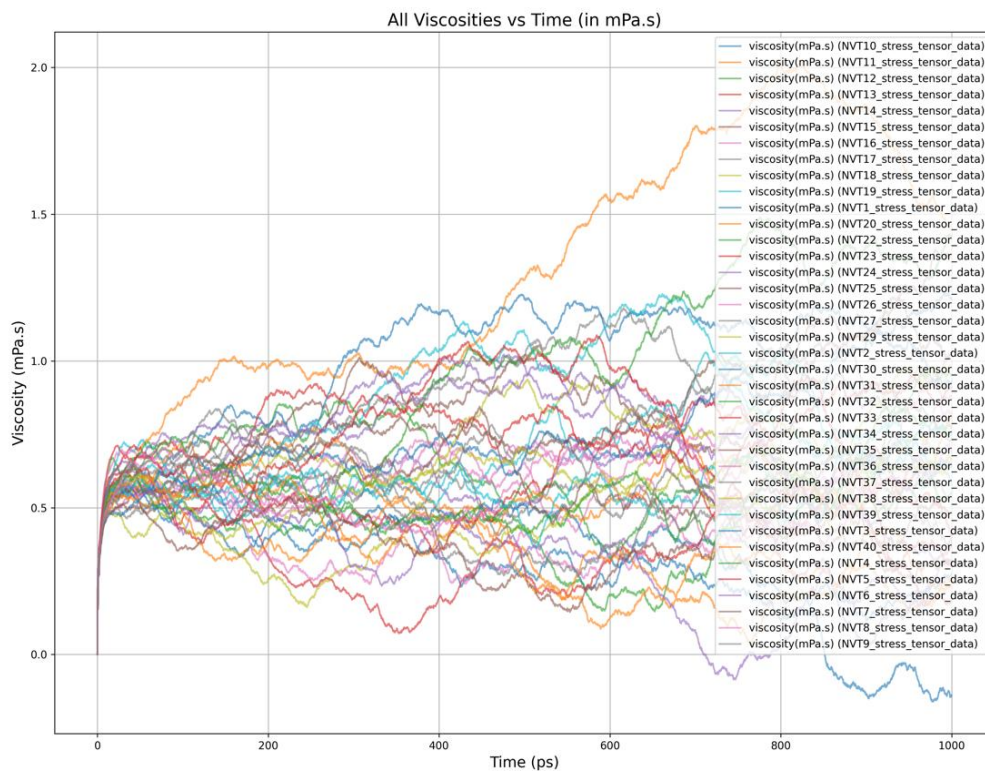The results obtained after analysis of 40 trajectories the calculated viscosity from above script:

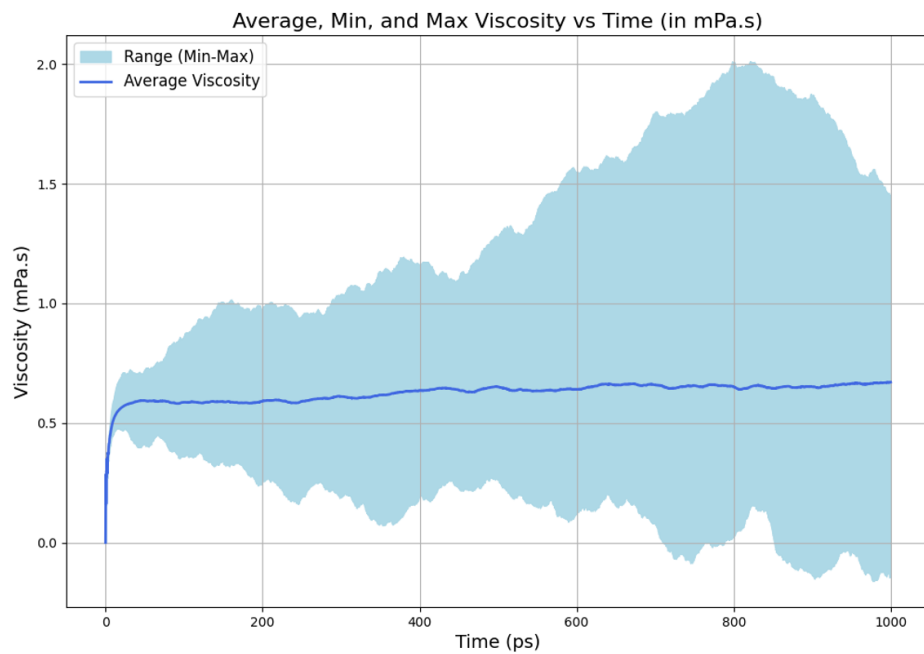

Fig.: viscosity vs Time of 40 NVT Trajectories

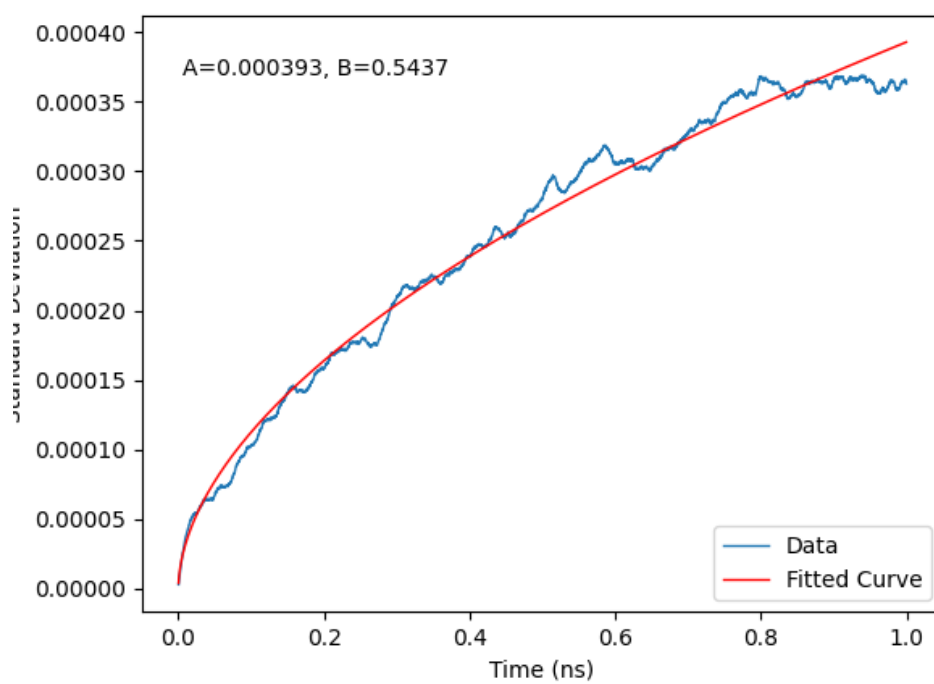Fig. : avg, max and min Viscosity vs time of 40 trajectories

A=0.000393, B=0.5437
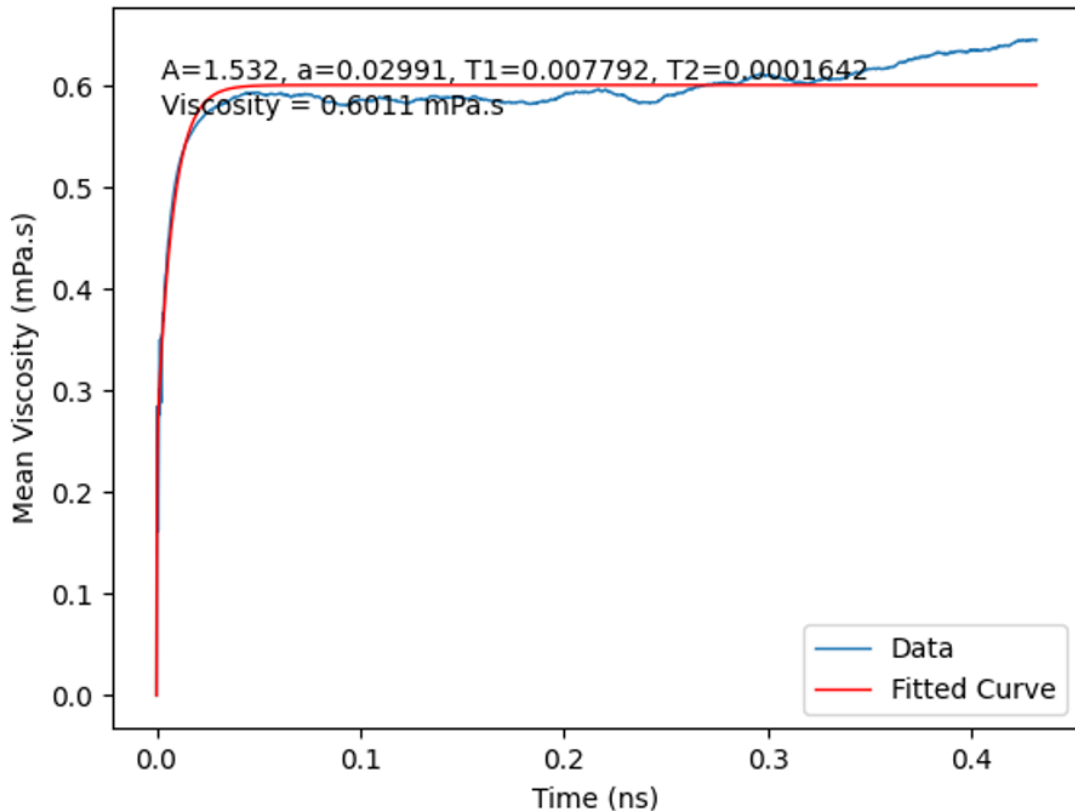
Fig.: Standard Deviation vs Time

Fig.: Double Exponential fitted Viscosity vs Time

Results:

The shear viscosity obtained after fitting the running integral is **0.6011 mPa·s**, which is in close agreement with the experimentally measured value of **0.554 mPa·s**. This small deviation can be attributed to factors such as finite simulation time, system size effects, and statistical uncertainties inherent in molecular dynamics simulations.

To improve the accuracy of the computed viscosity, a larger dataset with an extended trajectory can be utilized. Increasing the number of sampled data points will help reduce fluctuations in the pressure tensor autocorrelation function, leading to a more reliable estimation of viscosity. Additionally, averaging over multiple independent simulations can further minimize statistical errors and improve convergence toward the experimental value.

References:

- Reliable Viscosity Calculation from Equilibrium Molecular Dynamics Simulations: A Time Decomposition Method Yong Zhang, Akihito Otani, and Edward J. Maginn

- Best Practices for Computing Transport Properties. Self-Diffusivity and Viscosity from Equilibrium Molecular Dynamics Edward J. Maginn, Richard A. Messerly, Daniel J. Carlson, Daniel R. Roe, J. Richard Elliott