MedeA Viscosity: Reliable Momentum Transport Properties from Classical Simulations

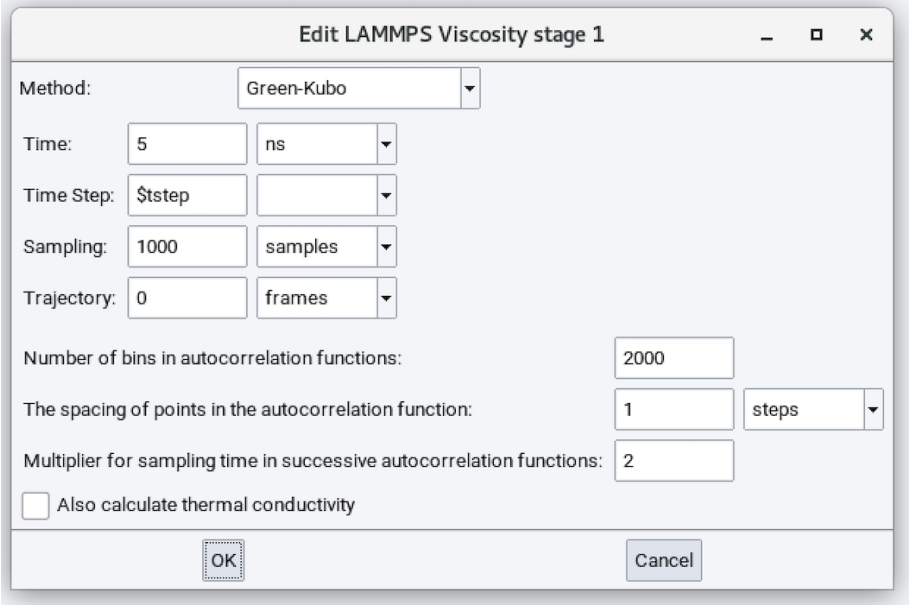
Contents

Key Benefits of *MedeA Viscosity*

- Automatic analysis including the fitting of results
- Quick and easy validation based on graphs, reported fitting errors, and access to all intermediate results through the convenient web interface
- Integrated with *MedeA Forcefields* for advanced forcefield handling and assignment

1 Equilibrium Molecular Dynamics (EMD)

The viscosity of a material can be determined using the equilibrium molecular dynamics method, also known as the Green–Kubo Method, which calculates integrates the autocorrelation function of the shear (off-diagonal) components of the stress tensor. The method is only applicable for homogeneous configurations, i.e., no defects, interfaces, multiple phases, etc. The required length of the simulation depends on the viscosity: higher viscosities require longer simulation times. Good approximations can be obtained for many organic systems, such as hydrocarbons, alcohols, ethers, esters, etc. A significant advantage is that only moderate system sizes are required.



- *Method*: Green–Kubo.
- *Time*: Duration of the simulation run.

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- *Time Step*: Time step size employed in solving the equations of motion.
- *Sampling:* Number of samples employed in performing averaging. This parameter does not affect dynamics.
- *Trajectory:* Number of trajectory frames saved during the molecular dynamics calculation. This parameter does not affect dynamics.
- *Number of bins in autocorrelation functions*: The default is `2000`.
- *The spacing of points in the autocorrelation function*: The default is `1` steps .
- *Multiplier for sampling time in successive autocorrelation functions*: The default is `2`.
- ☐ *Also calculate thermal conductivity*: An option to also compute the autocorrelation function of the heat flux and estimate thermal conductivity from the same trajectory.

Note: This option is only visible if you also have the *MedeA Thermal Conductivity* license.

Hint: This option reduces computational expense when you would like to calculate both the viscosity and thermal conductivity in a single stage!

After completing a simulation, results are written to *Job.out*. For example:

```
Stage 6.4: Viscosity using Green-Kubo, NVE integration for 4 ns with a timestep of 1 fs
        The autocorrelation of the pressure tensor uses 2000 bins, starting with sampling every step,
        then every 2 steps, then every 4, etc.
              Property         Value   +/- Uncertainty    Units      After Steps   % Run
        ------------------  ----------     ----------- ------------- ------------ -------
                         t:  4000000.0                  fs
                         T:     295.61 +/- 0.58         K                       0     0.0%
                         P:       2925 +/- 11           atm                     0     0.0%
                         V:    25163.9 +/- 0            Ang^3                   0     0.0%
                       rho:     1.3497 +/- 0            g/mL                    0     0.0%
                    Etotal:    -324.54 +/- 0.031        kJ/mol                  0     0.0%
                      Epot:    -2208.5 +/- 3.7          kJ/mol                  0     0.0%
                      Ekin:     1883.9 +/- 3.7          kJ/mol                  0     0.0%
                      Evdw:    -2208.5 +/- 3.7          kJ/mol                  0     0.0%
                     Ecoul:           0 +/- 0           kJ/mol                  0     0.0%


     Property     Direct Integral       Fit        RMS        Units   Direct Time    %       Fit Time     %
---------------- -------------------- ---------- ---------- ---------- ---------- ---------- ---------- ---------
          eta x  0.18833 +/- 0.00064    0.17312    0.00062      mPa*s       4700       0.1%        593       0.0%
          eta y  0.16618 +/- 0.00029    0.16403    0.00077      mPa*s       1449       0.0%        498       0.0%
          eta z   0.1804 +/- 0.0065      0.1589       0.001     mPa*s      48512       1.2%        467       0.0%
    eta average   0.1796 +/- 0.0087      0.1635      0.0009     mPa*s      39200       1.0%        493       0.0%
```

Additionally, visualization of the autocorrelation function and the viscosity integral are available in the file {*stage_id*}_*SSt_decay_average.gif*. For example:

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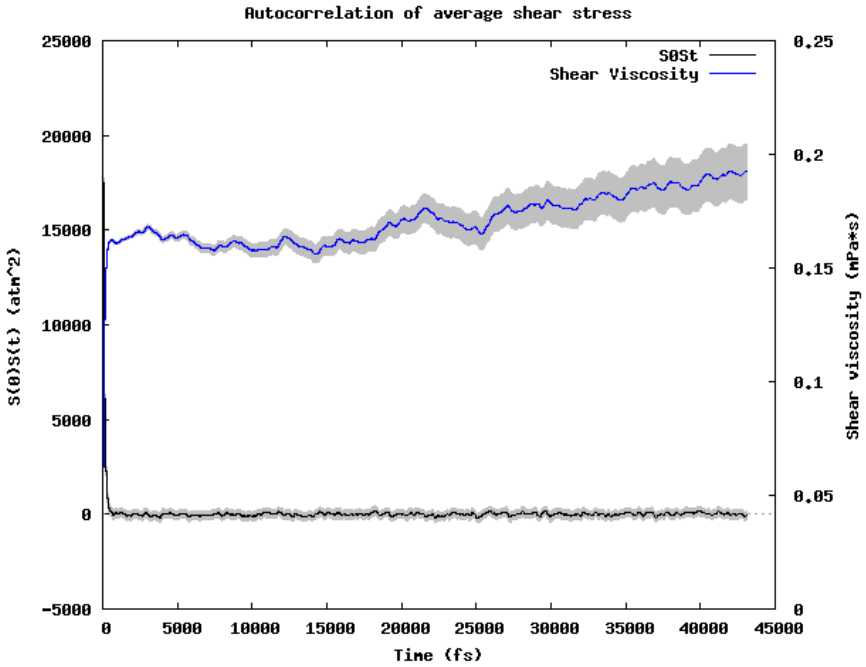

2 Reverse Non-Equilibrium Molecular Dynamics Method (RNEMD)

The reverse non-equilibrium molecular dynamics method, also known as the Müller-Plathe [1] method, induces a flow gradient (shear velocity or momentum flux) by performing momentum swaps between positive and negative shearing atoms and monitoring the resulting velocity profile. Viscosity is then calculated using the slope of the induced shear velocity profile.

This method applies to all systems but requires elongated cells in the direction of flow. Higher viscosities, which arise from stronger interactions, require correspondingly longer cells. The effect of the cell cross-section and length should ideally be examined, and the momentum transfer rate may need to be optimized, requiring some user intervention. Zero shear rate viscosities may be obtained by performing several simulations, followed by extrapolation.

[1] Florian Müller-Plathe and Dirk Reith, "Cause and Effect Reversed in Non-Equilibrium Molecular Dynamics: an Easy Route to Transport Coefficients", *Computational and Theoretical Polymer Science* 9, no. 3 (1999): 203-209.

DOCUMENTATION

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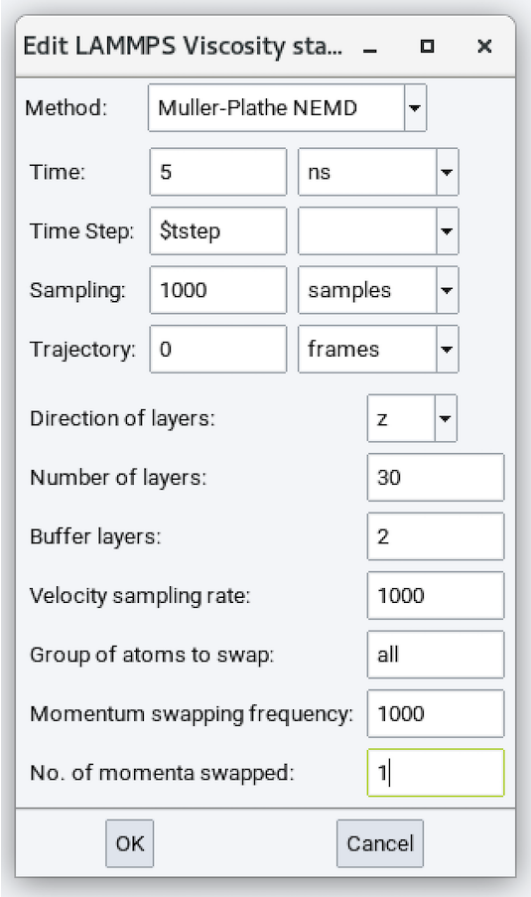

The required parameters are:

- *Method*: Muller-Plathe NEMD.
- *Direction of layers*: Direction in which the shear velocity gradient should be established.
- *Number of layers*: Divides the above direction into this many layers to calculate the shear velocity profile.
- *Buffer layers*: Number of layers on and near the boundary that are not used in the final analysis.
- *Velocity sampling rate*: Sample shear velocity profile every this many steps. The default value of `1000` can usually be accepted.
- *Group of atoms to swap*: Defaults to `all`.
- *Momentum swapping frequency*: Defaults to `1000`.
- *No. of momenta swapped*: Defaults to `1`.

After completing a simulation, results are written to *Job.out*. For example:

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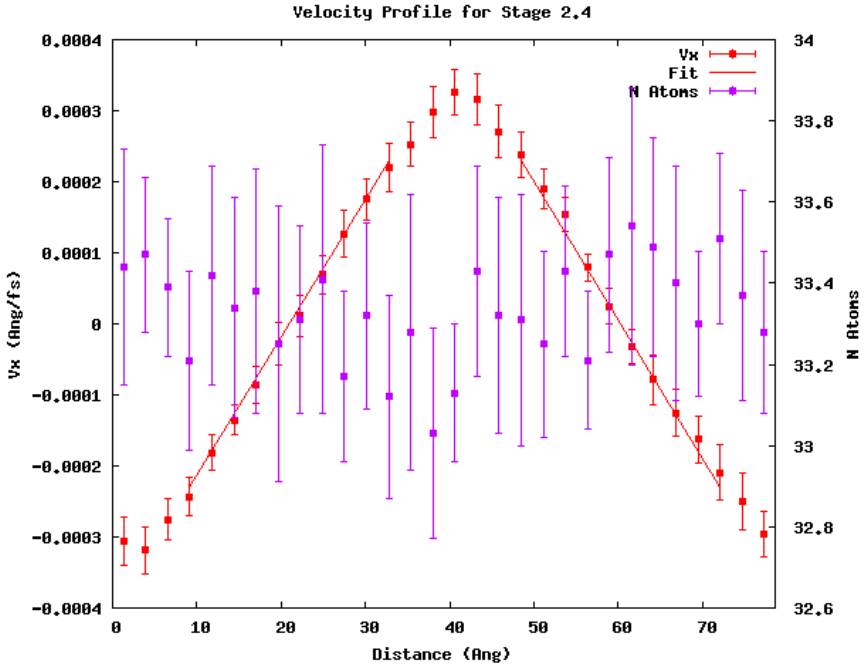
```
Stage 2.6: Viscosity using Muller-Plathe NEMD, NVE integration for 5 ns with a timestep of 1 fs
          10 momenta from group 'all' are interchanged every 1000 timesteps using 30 layers in the z direction
```

Property	Value	+/- Uncertainty	Units	After Steps	% Run
t:	5000000.0		fs		
T:	350.5	+/- 0.24	K	0	0.0%
P:	0	+/- 20	atm	0	0.0%
V:	78706.2	+/- 5.3e-10	Ang^3	0	0.0%
rho:	0.63424	+/- 0	g/mL	0	0.0%
Etotal:	7737.7	+/- 8.2	kcal/mol	1500	30.0%
Epot:	523.3	+/- 6.6	kcal/mol	0	0.0%
Ekin:	7207.9	+/- 4.9	kcal/mol	0	0.0%
Evdw:	-1773.68	+/- 0.94	kcal/mol	0	0.0%
Ecoul:	489.47	+/- 0.3	kcal/mol	0	0.0%
t:	5000000.0		fs		
deltapx:	-3270.9099999999999		Ang/fs*g/mol		
dpx/dt:	-0.00065433	+/- 3.5e-07	Ang/fs*g/mol/fs	500	10.0%
dv/dx(left):	2.65e-05	+/- 1.4e-06	(Ang/fs)/Ang	0	0.0%
v0(left):	-0.000637	+/- 3.8e-05	Ang/fs	0	0.0%
dv/dx(right):	2.61e-05	+/- 1.5e-06	(Ang/fs)/Ang	0	0.0%
v0(right):	-0.000627	+/- 4.4e-05	Ang/fs	0	0.0%
dv/dx:	2.63e-05	+/- 1.1e-06	(Ang/fs)/Ang	0	0.0%
v0:	-0.000632	+/- 2.4e-05	Ang/fs	0	0.0%
eta:	0.2339	+/- 0.0096	mPa*s	500	10.0%

Additionally, visualization of the shear velocity profiles is available as {*stage_id*}_*average_velocity_profile.png*. For example:



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