Using LAMMPS for reverse-nonequilibrium MD simulations

Craig M. Tenney
Edward J. Maginn

University of Notre Dame

LAMMPS Users' Workshop
February 2010

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motivation

- want to predict viscosity and thermal conductivity for arbitrary fluids...
  - accurately
  - precisely
  - efficiently
  - reliably
- numerous molecular simulation methods exist
  - “best” is rarely obvious *a priori*

content

- calculation of shear viscosity
  - background
  - non-linearity issues
  - avoiding pitfalls
  - comparison with other methods
- calculation of thermal conductivity
- summary

background

- shear viscosity:

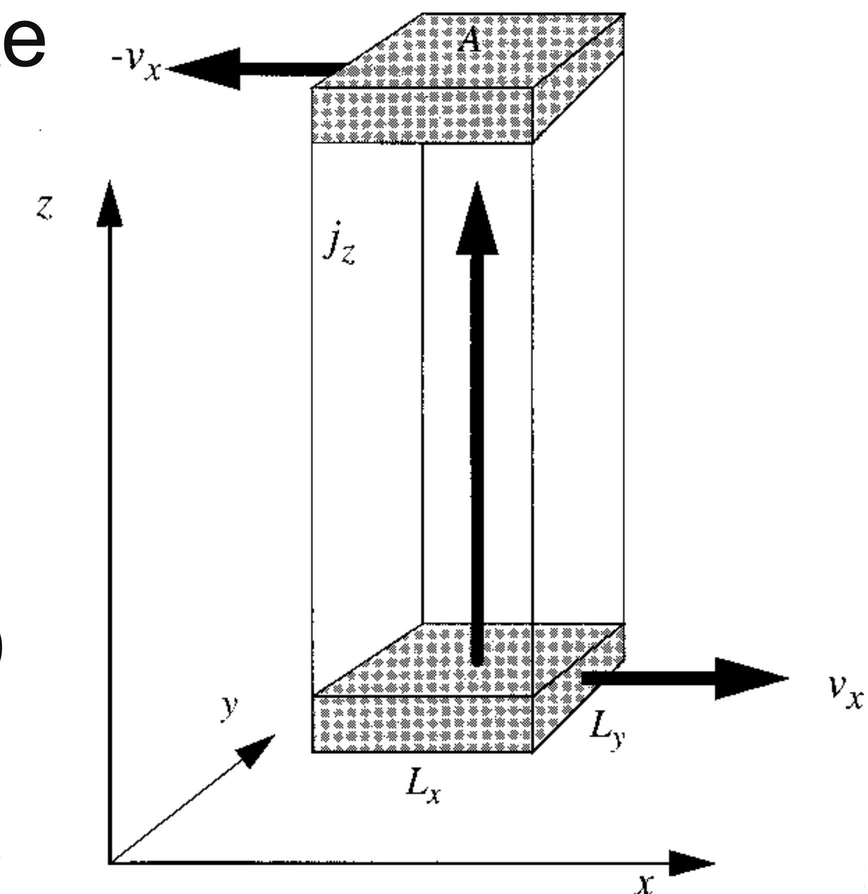
  flux of transverse linear momentum =

  shear viscosity * shear rate

$$j_z = -\eta(\gamma) \cdot \gamma$$

$$\gamma = \frac{\delta v_x}{\delta z}$$

$$Newtonian: \ \eta(\gamma) \rightarrow \eta_0 \ \ as \ \ \gamma \rightarrow 0$$



Muller-Plathe, Phys. Rev. E 59, 1999

MD methods for viscosity calculation

- transient
  - growth or decay of velocity perturbation
- steady-state
  - equilibrium
    - auto-correlation of fluctuations in flux or shear
    - e.g. Einstein or Green-Kubo relations
  - non-equilibrium
    - e.g. SLLOD
      - set shear rate and measure momentum flux
    - reverse-NEMD (RNEMD)
      - set momentum flux and measure shear rate

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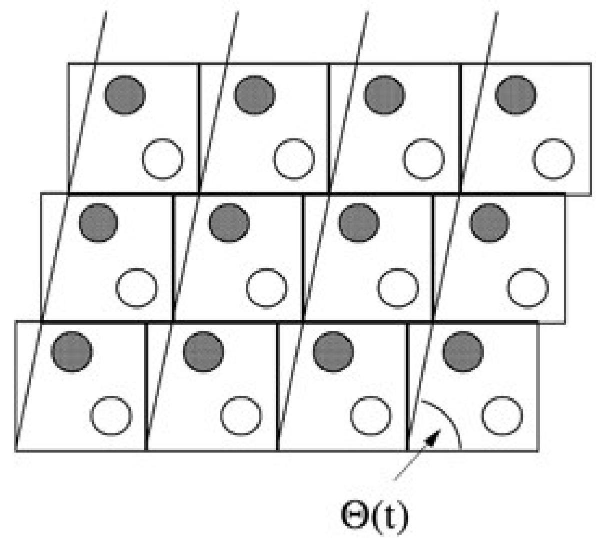
SLLOD (NEMD) algorithm (fix nvt/sllod)

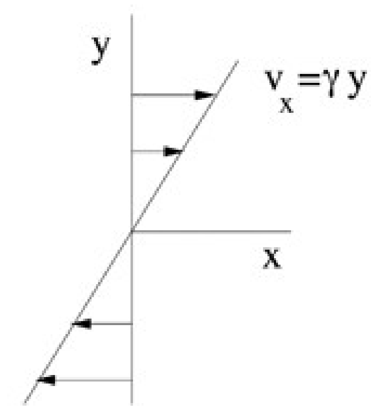
1) set shear rate γ via …

- Lees-Edwards sliding-brick BCs or ...
- deforming simulation box

2) measure resulting momentum flux j = $\langle P_{xy} \rangle$

(thermostat must account for velocity profile)





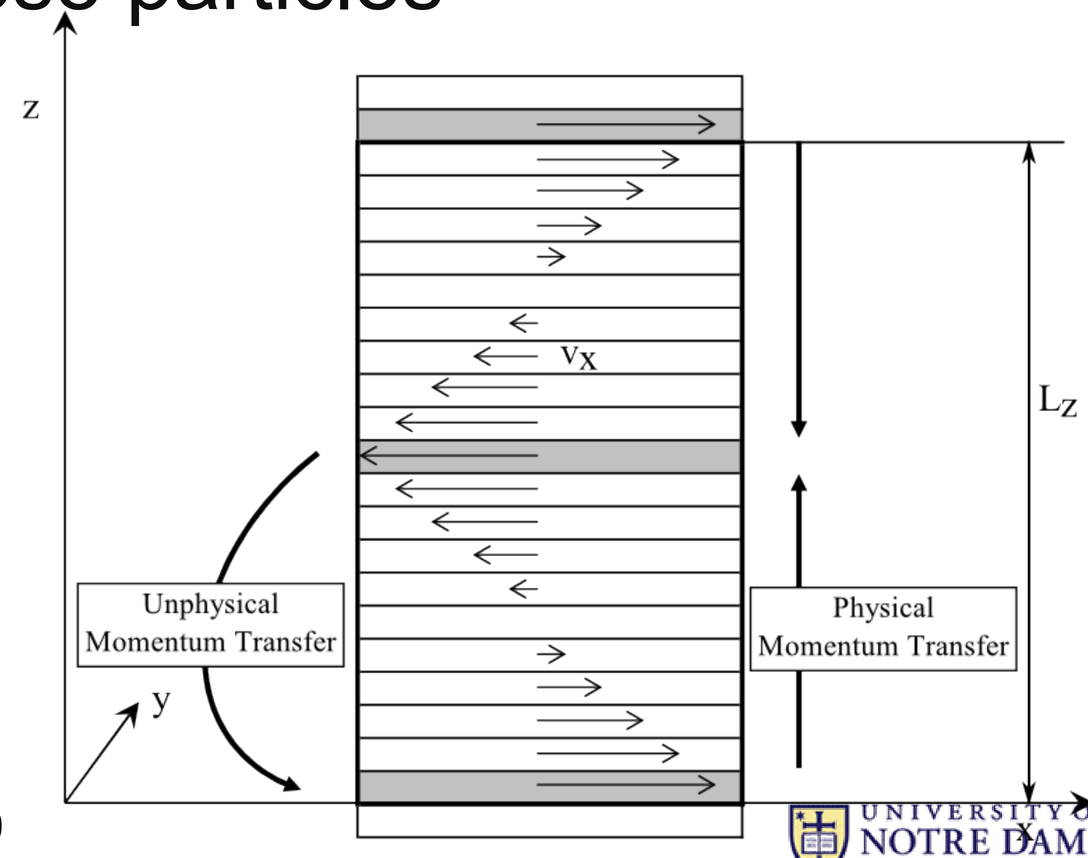
Evans and Morriss, Statistical Mechanics of Non-equilibrium Liquids (1990)

RNEMD algorithm (fix viscosity)

1) from bottom and middle bins, find two particles with "slow" v_x (relative to mean bin v_x)

2) swap v_x between these particles

3) measure resulting velocity profile



(conserves energy)

Muller-Plathe, Phys. Rev. E 59, 1999

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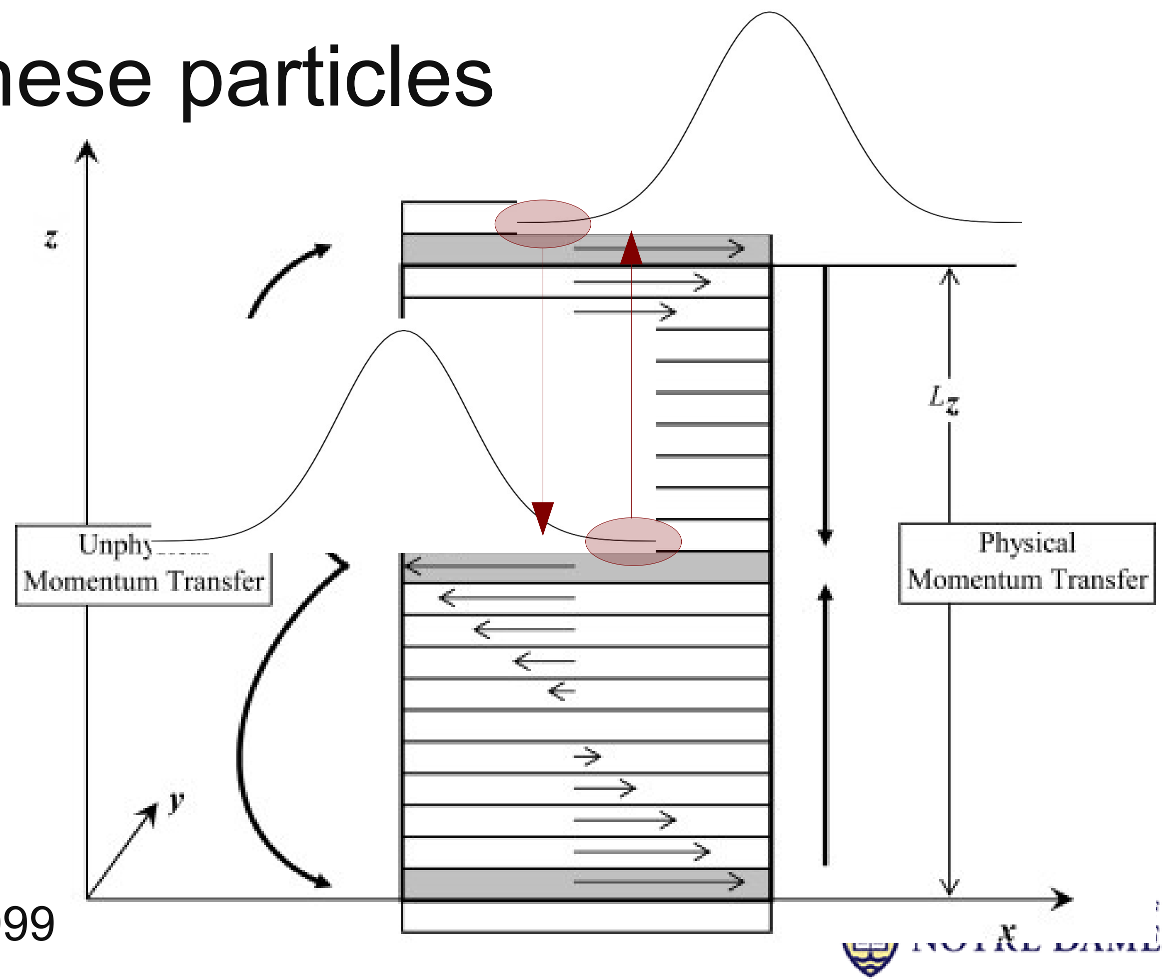


(conserves energy)

Muller-Plathe, Phys. Rev. E 59, 1999

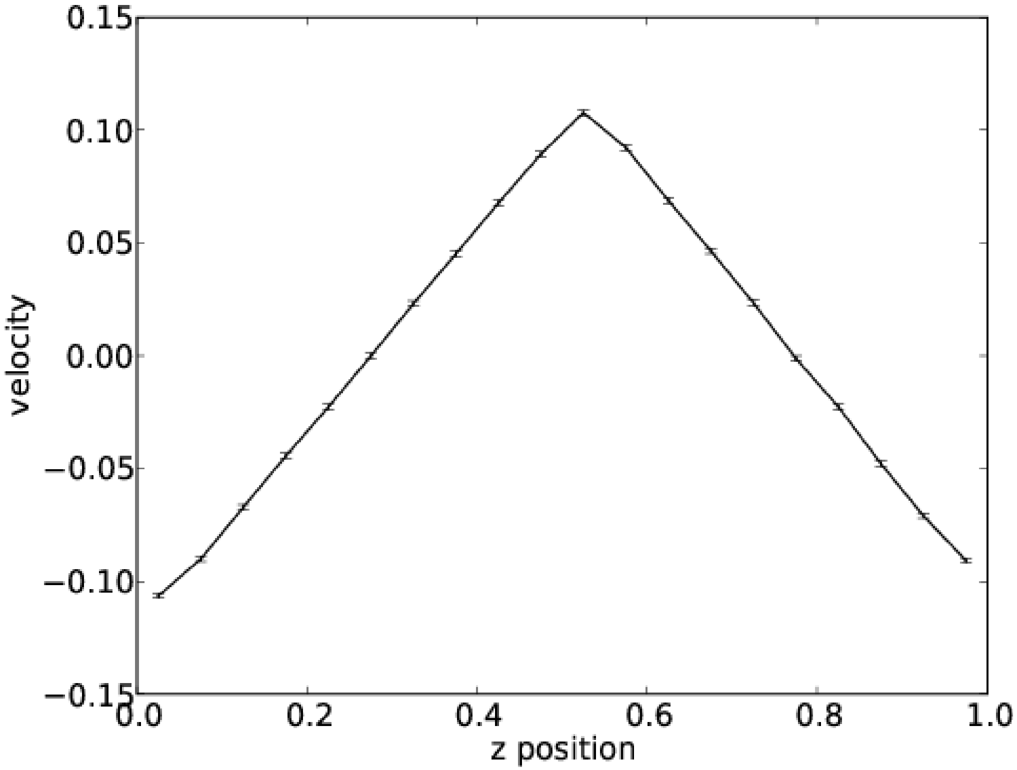
simulation details

(similar to original Muller-Plathe (MP) paper)

- Lennard-Jones fluid
  - reduced density = 0.849
  - reduced temperature = 0.722
- RNEMD
  - 3000 particles
  - 10.56 x 10.56 x 31.68 σ   (aka “10x10x30”)
  - 20 bins
  - 500k steps
  - reduced timestep = 0.005

RNEMD viscosity example

- "base case"
  - swap target v_x every 1 step
  - momentum flux = 0.0466 (equivalent to swapping "slowest" v_x every 60 steps)
  - L_z ~ "30" σ



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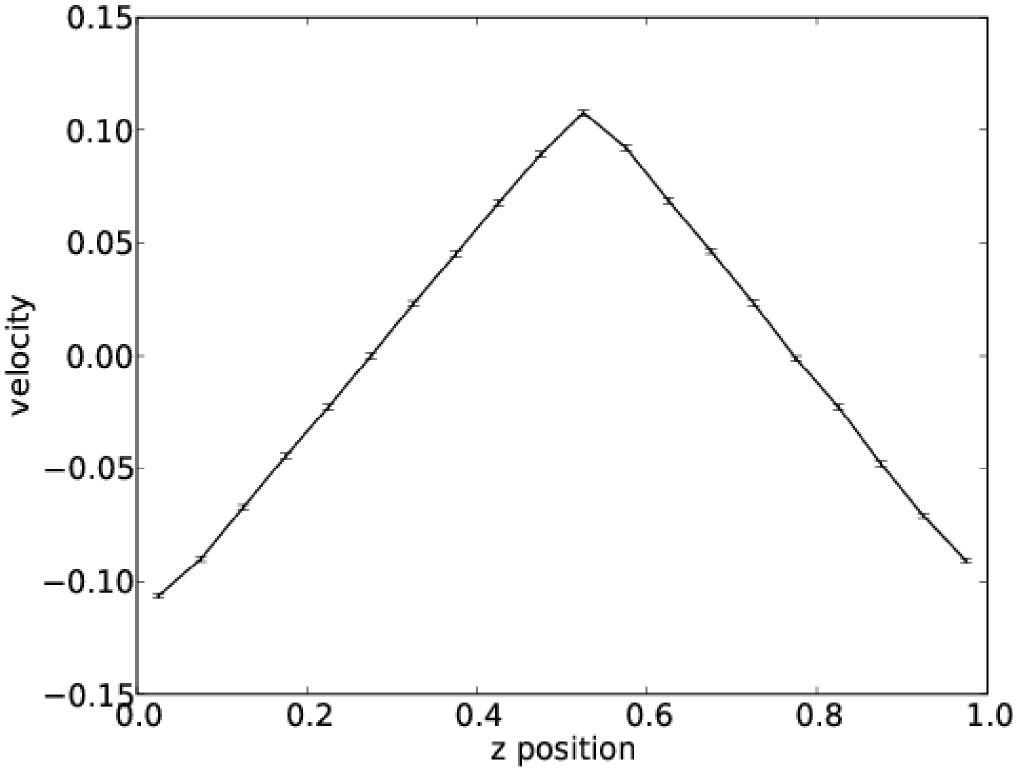
  - L_z ~ "30" σ
- dv_x/dz = 0.0142

→ η = 3.28 (+/- 0.05)

500k steps, 3000 particles



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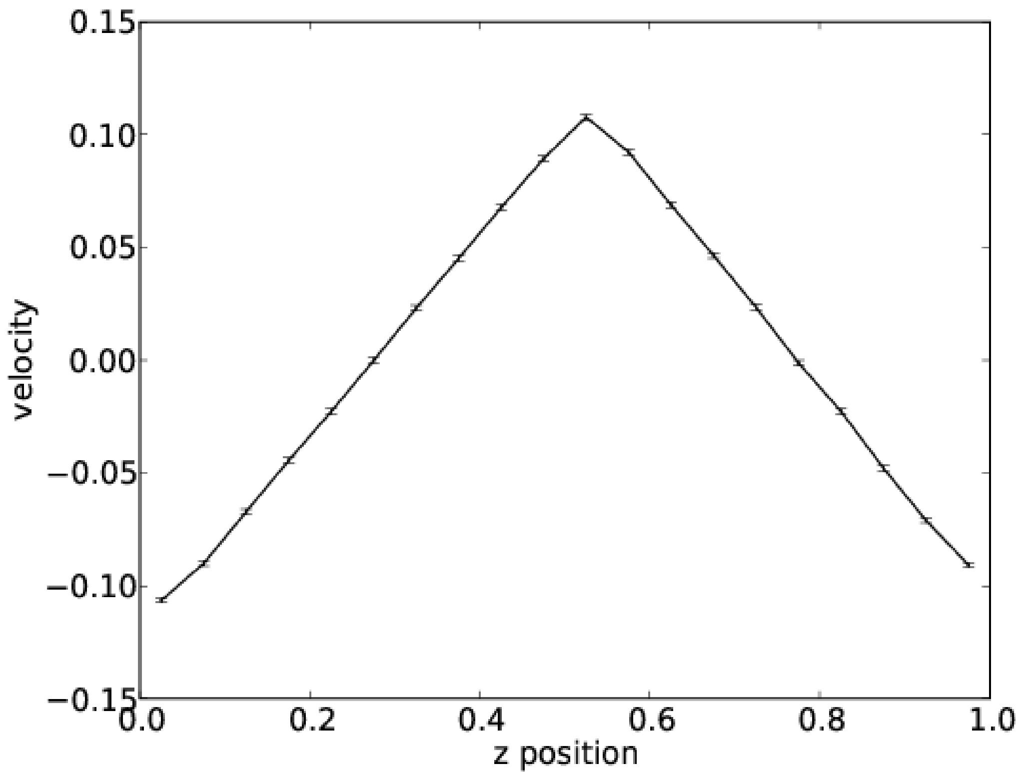
  - L_z ~ "30" σ
- $dv_x/dz = 0.0142$

  → η = 3.28 (+/- 0.05)

  500k steps, 3000 particles
- SLLOD: η = 3.40 (+/- 0.12)

  500k steps, 1000 particles
- EMD: η_0 = 3.35 (+/- 0.25)

  1M steps, 1000 particles



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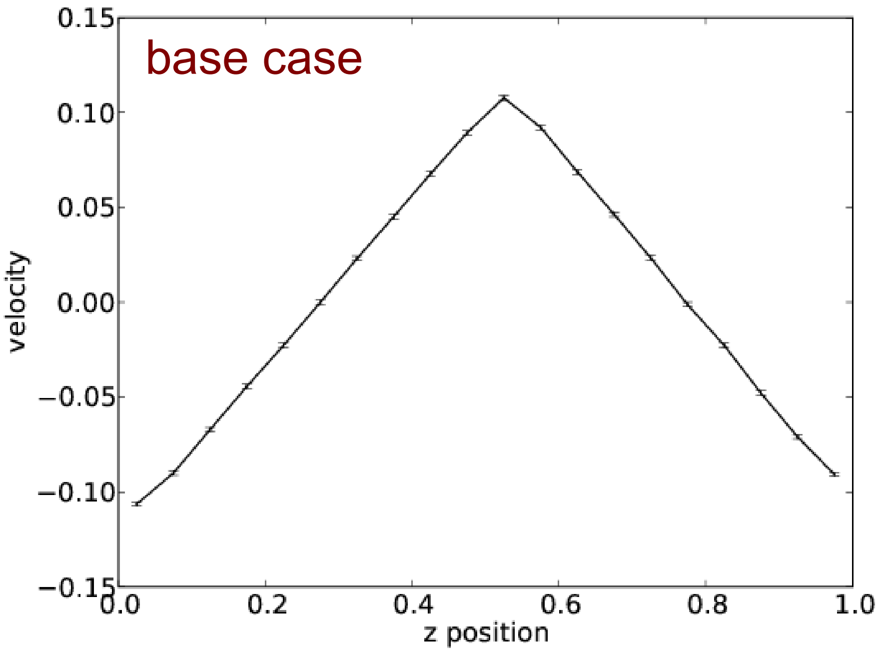
RNEMD at high momentum flux



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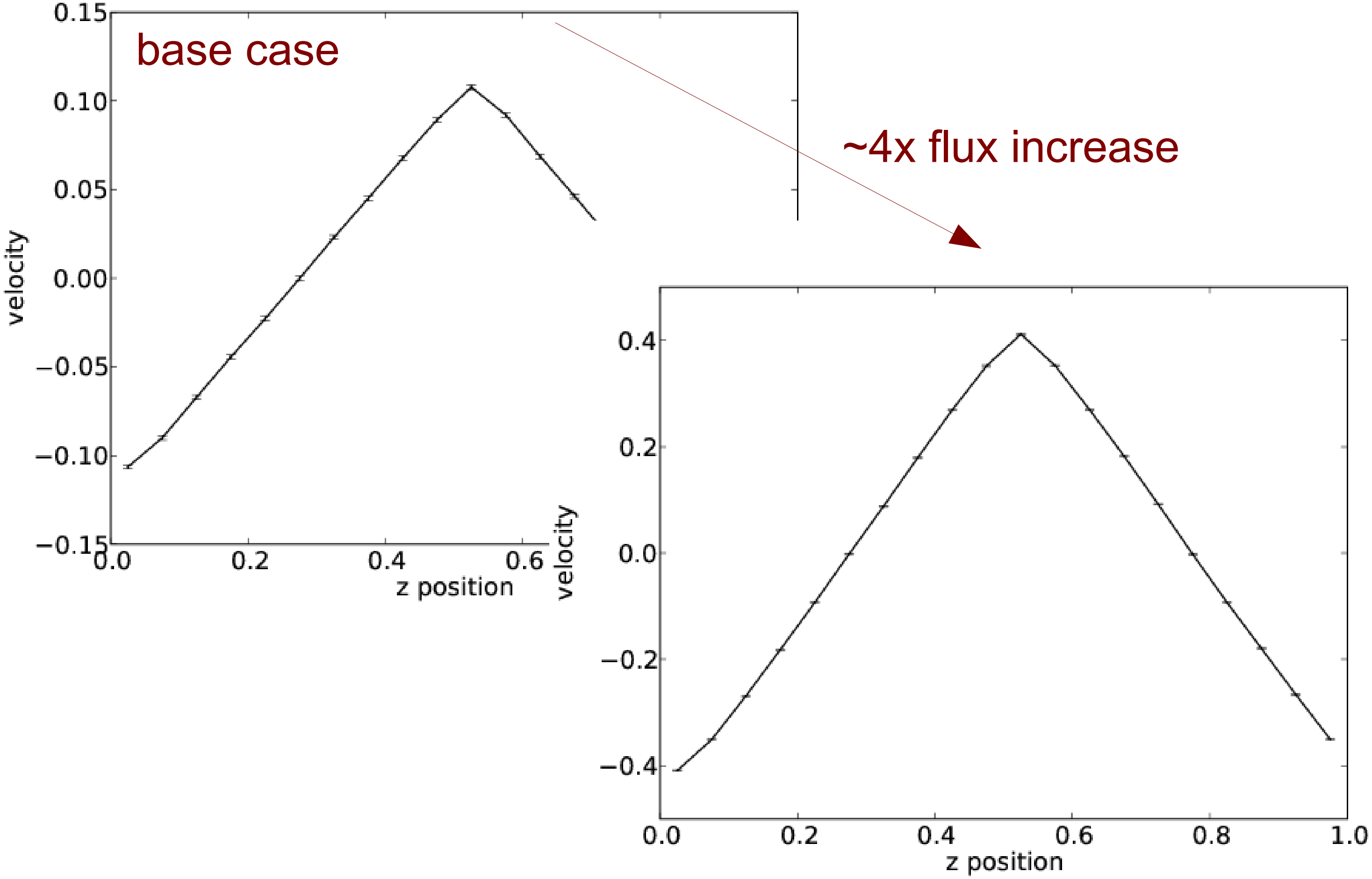

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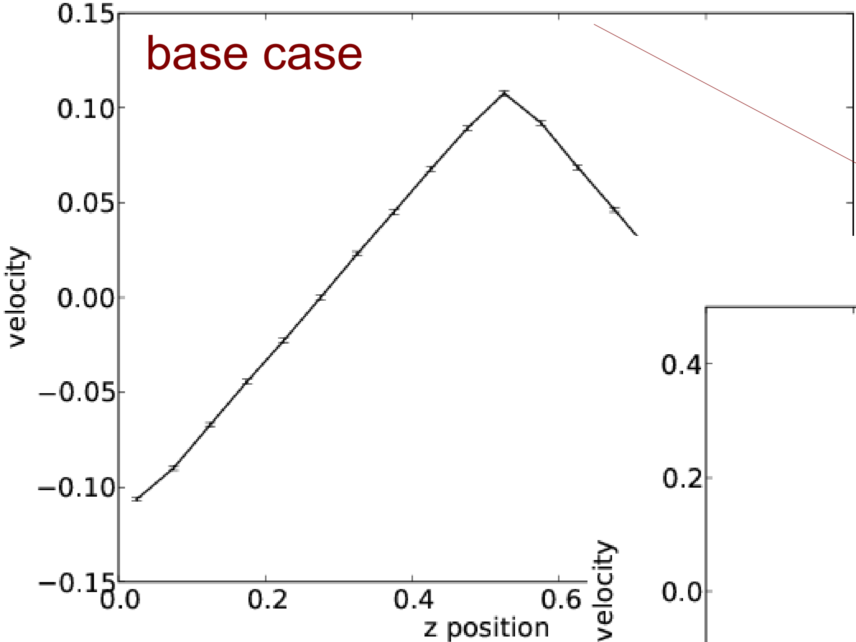
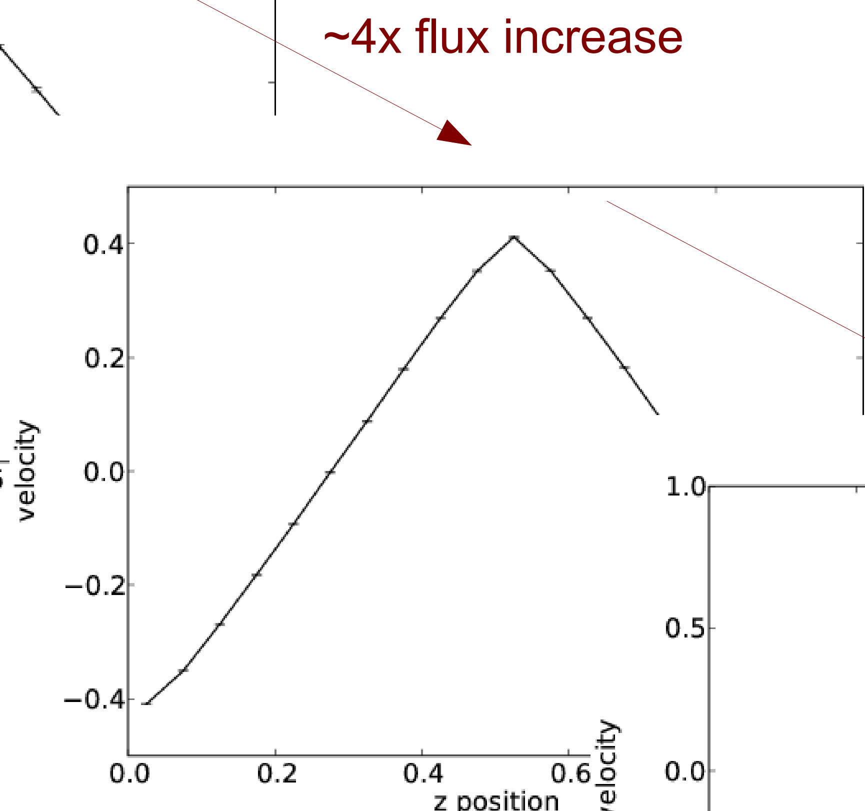
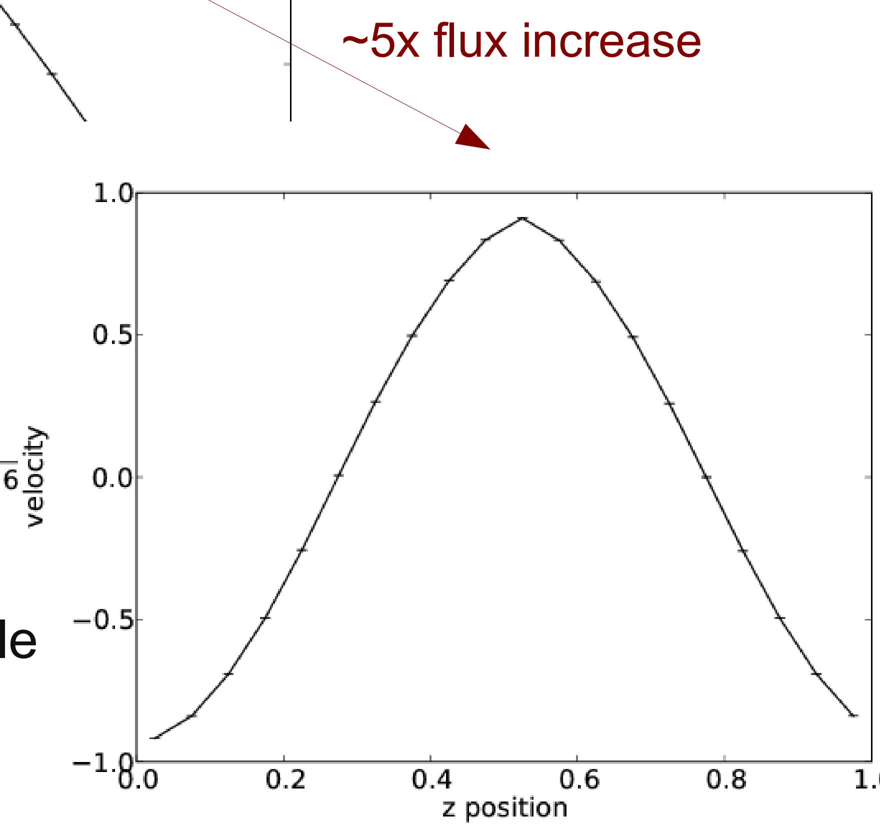


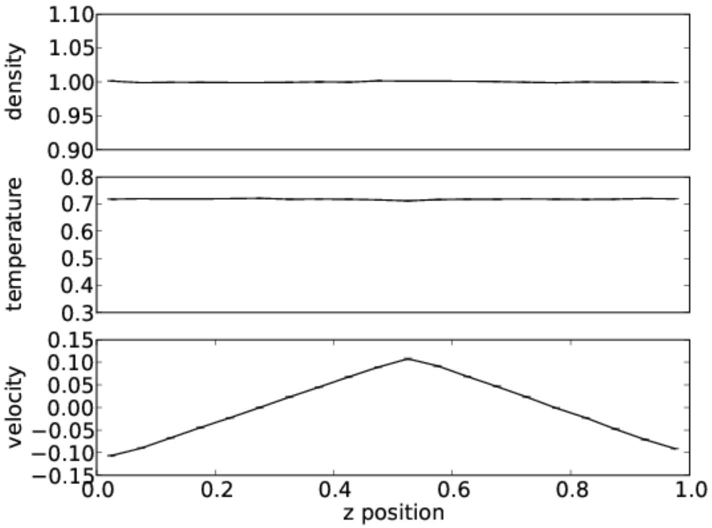




high momentum flux → non-linear velocity profile

RNEMD non-linearity

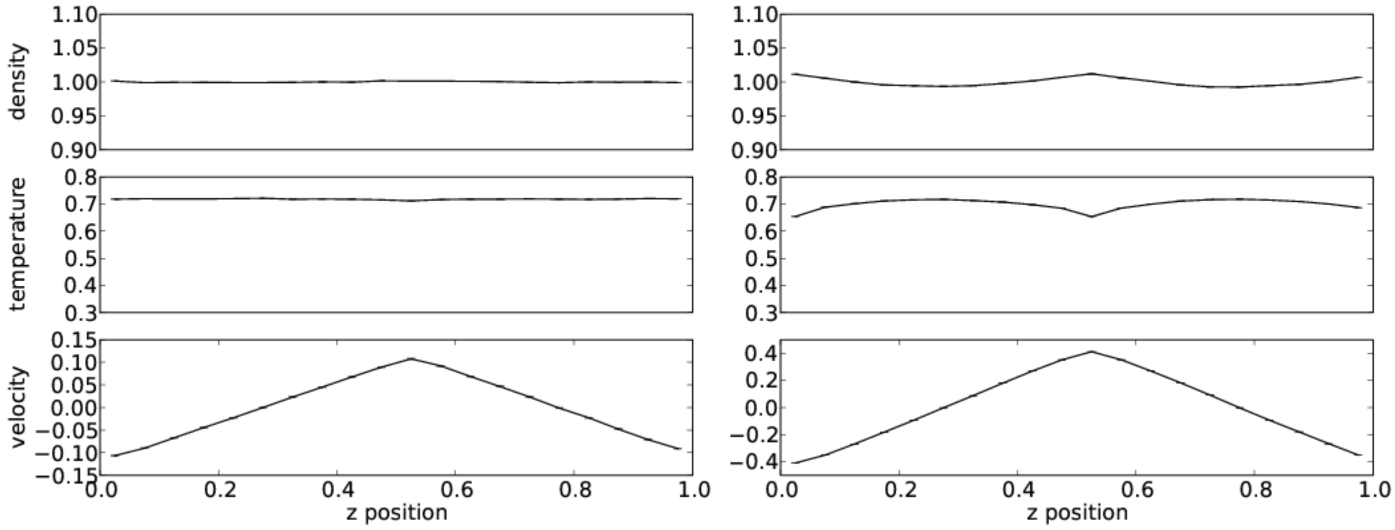
base case



RNEMD non-linearity

base case

~4x flux increase



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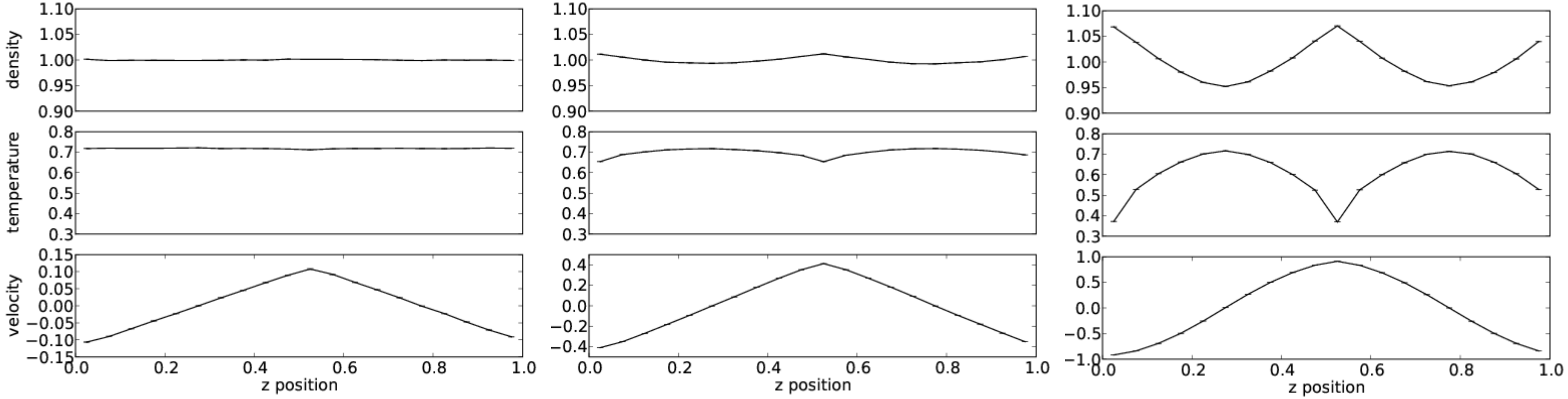
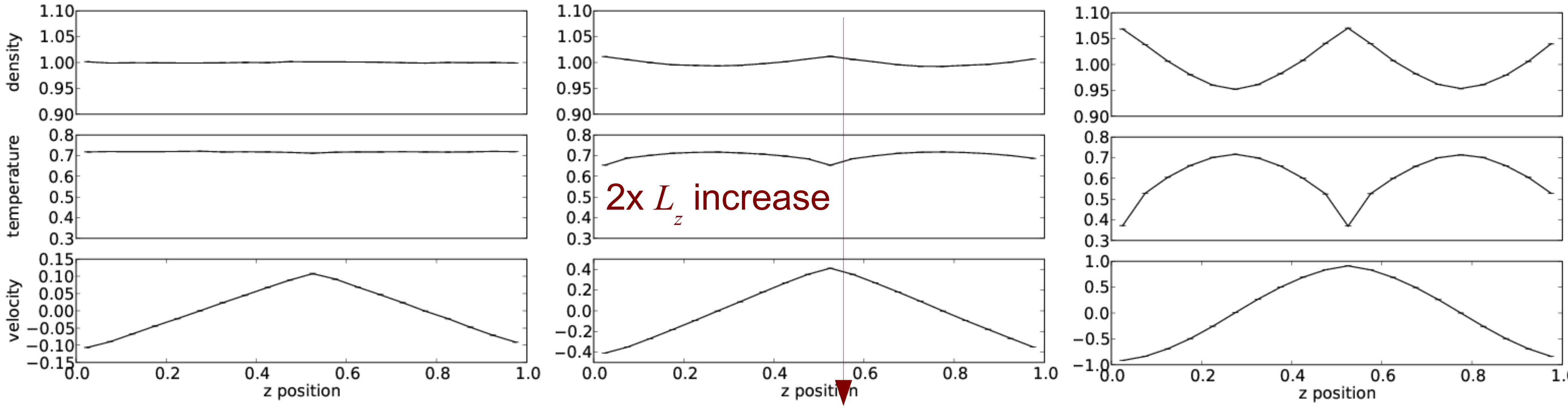
RNEMD non-linearity

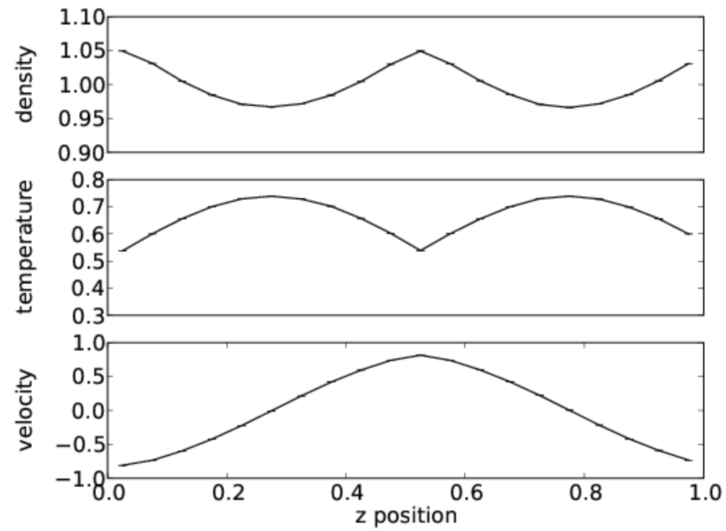
base case → ~4x flux increase → ~5x flux increase



RNEMD non-linearity

base case ~4x flux increase ~5x flux increase





in theory …

$$\Delta T = \frac{L_z^2 j_z^2}{32 \lambda \eta} \frac{(N-2)(N-4)}{N^2}$$

but it looks like …

$$\Delta T \sim L_z^2 \ j_z$$

Tenney and Maginn, J. Chem. Phys 132, 2010

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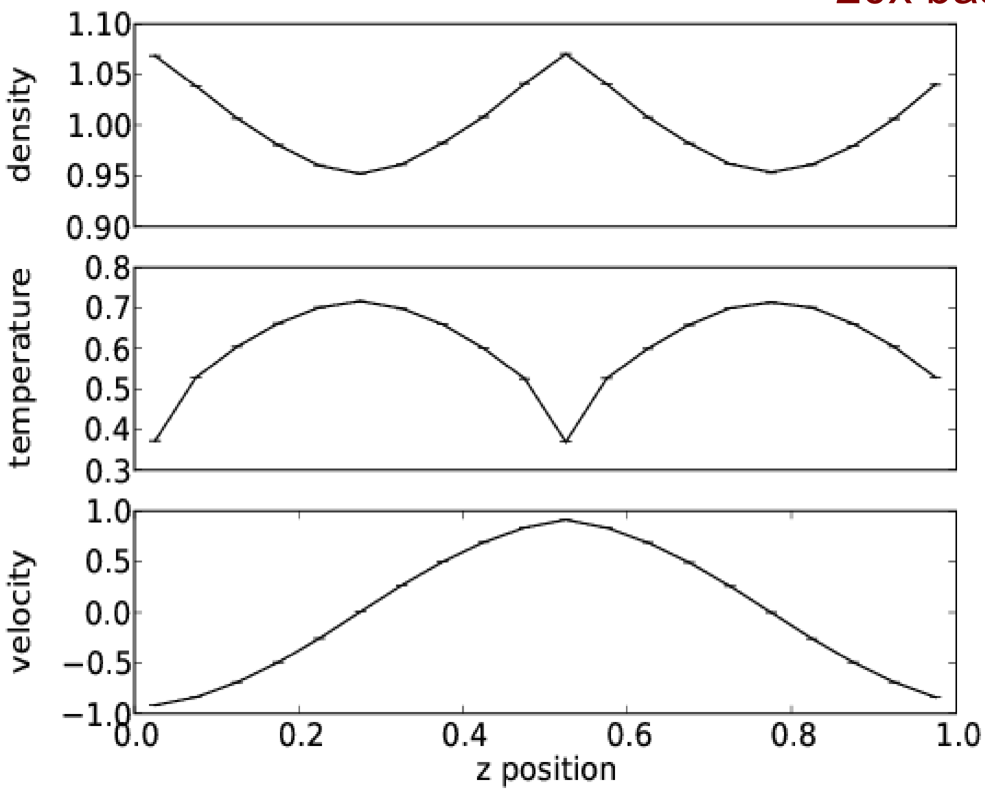
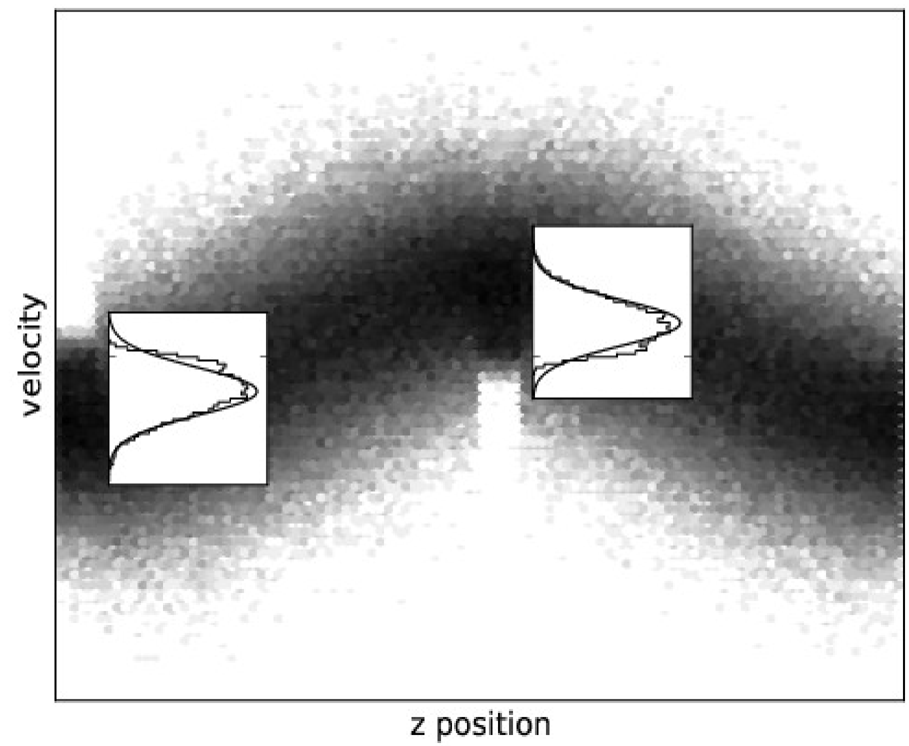
RNEMD non-linearity

- swap moves conserve energy, but …
- they remove heat (entropy) from swap bins

~20x base case flux





Tenney and Maginn, J. Chem. Phys 132, 2010

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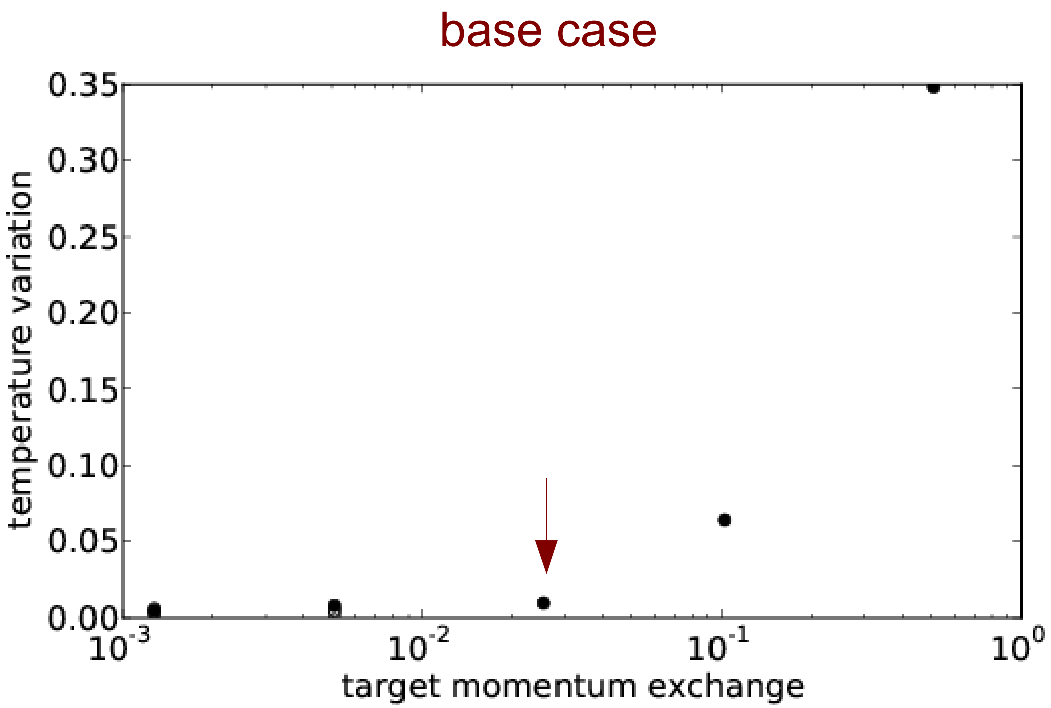
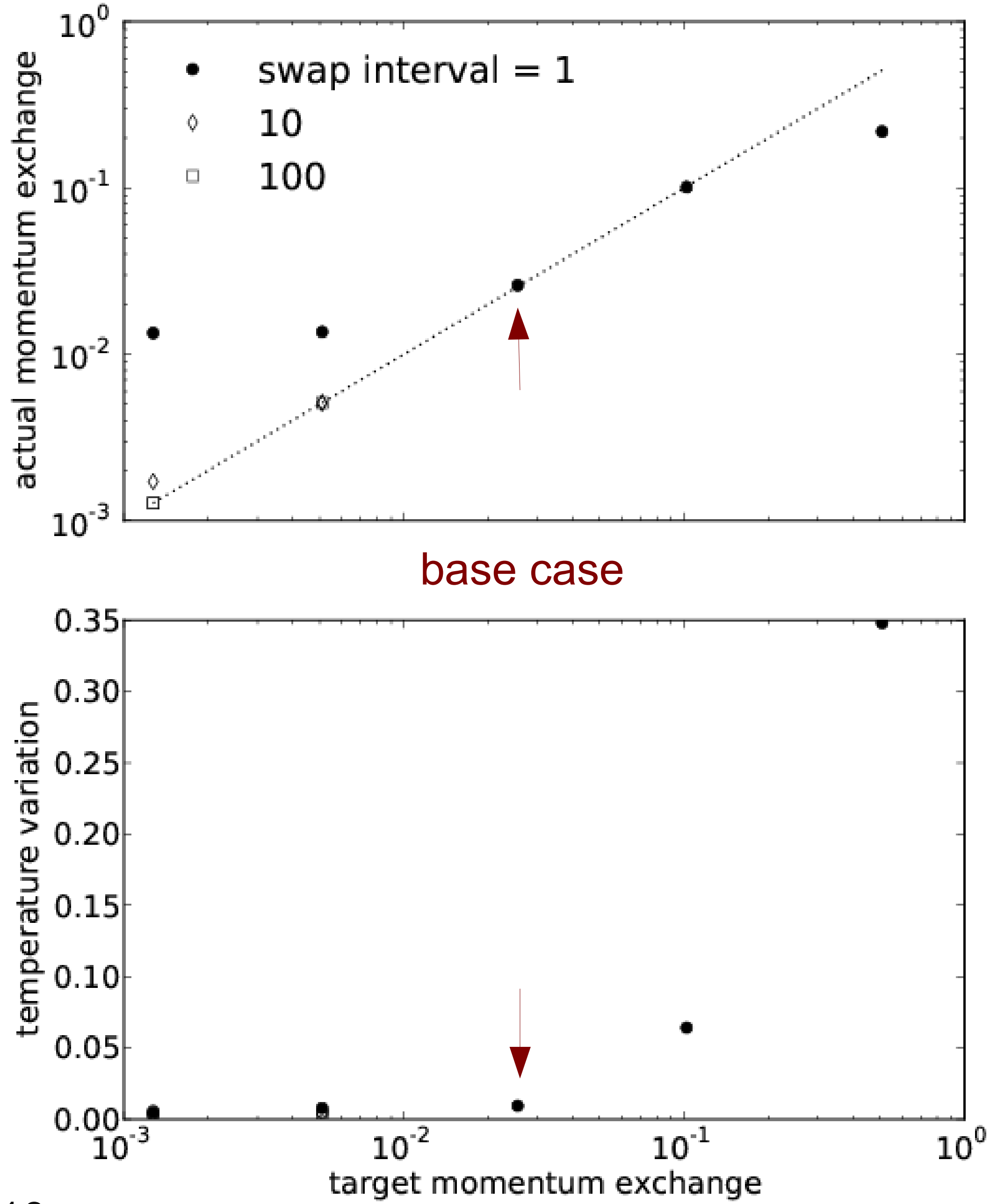
setting RNEMD momentum flux



setting RNEMD momentum flux

target flux	ΔT	actual flux
high	excessive	< target
moderate	reasonable	just right
low	negligible	≥ target

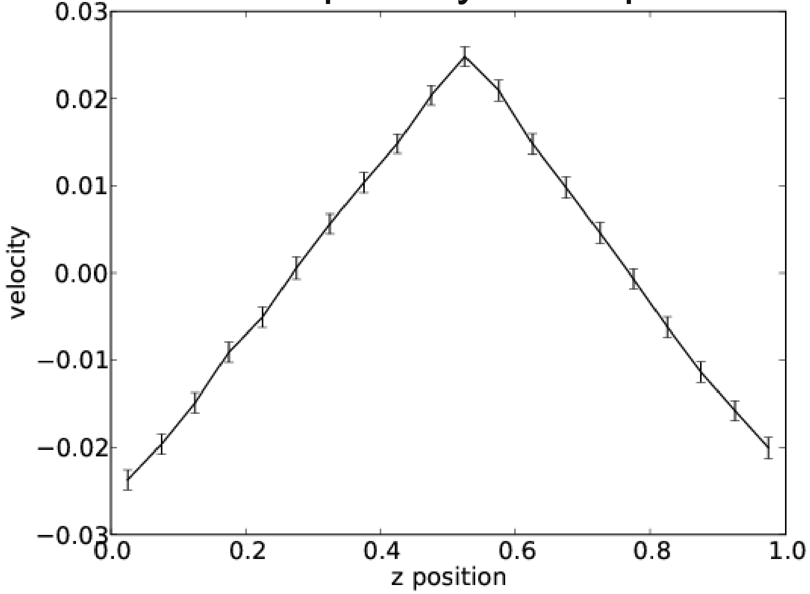


Tenney and Maginn, J. Chem. Phys 132, 2010

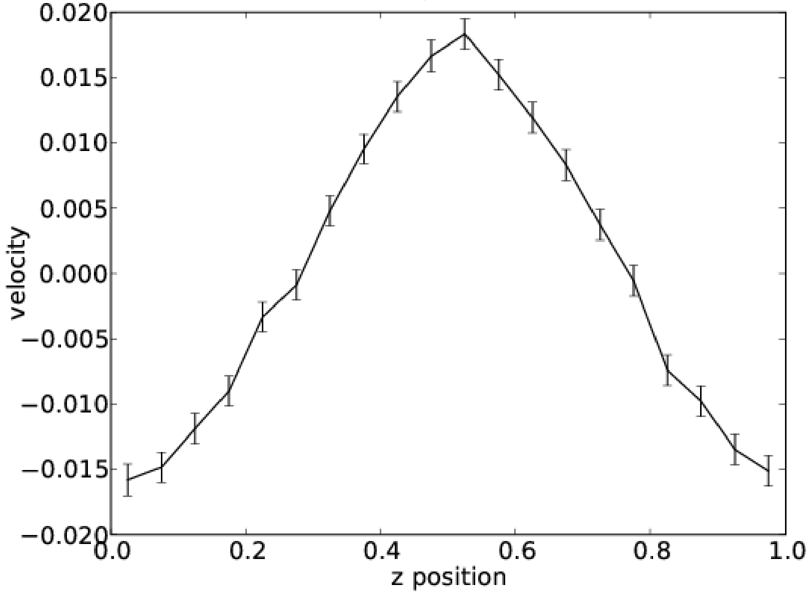
RNEMD at low momentum flux

~20% base case flux

swap every 10 steps



swap every 100 steps



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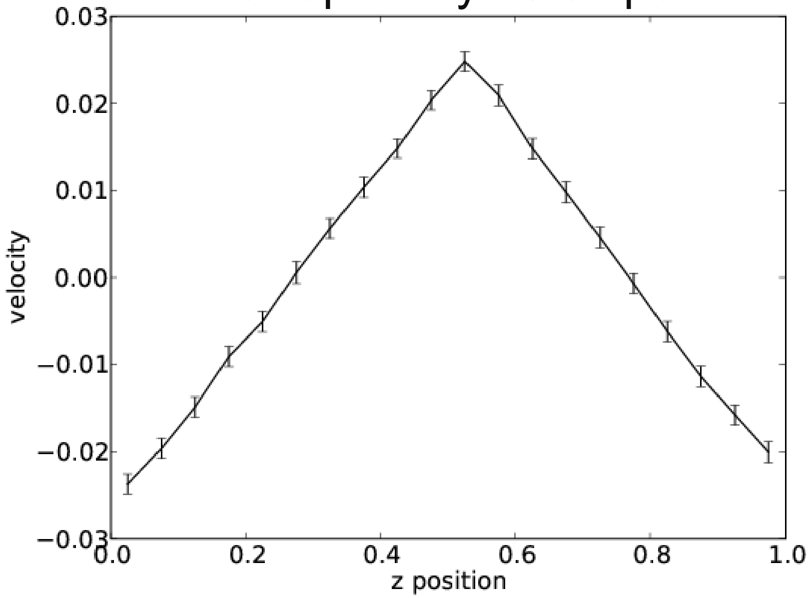
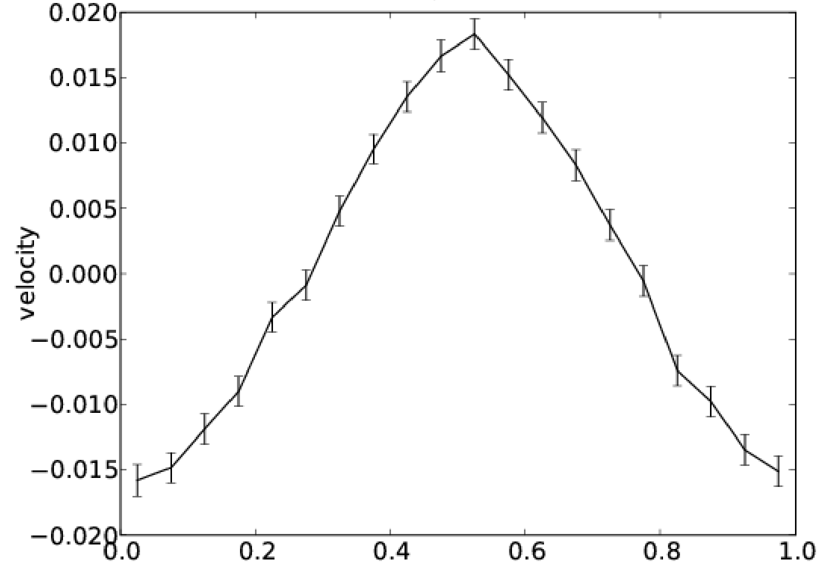
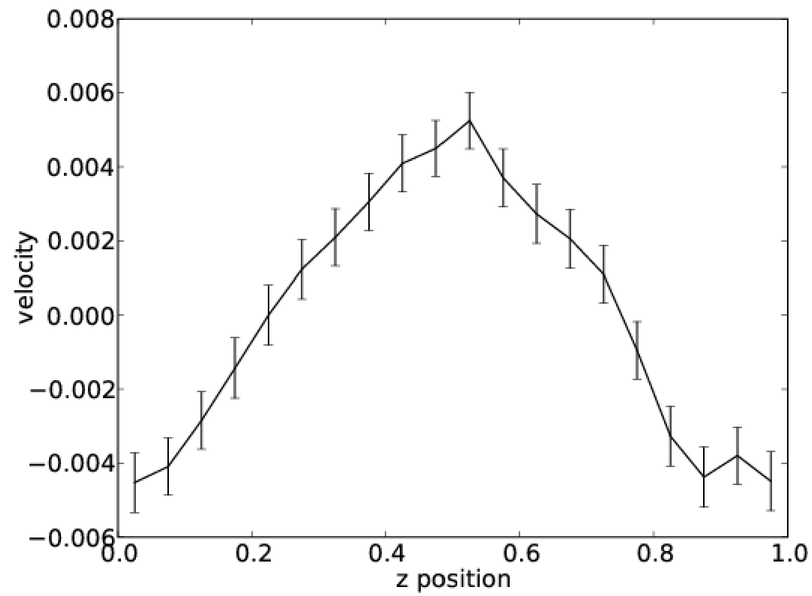


swap every 100 steps



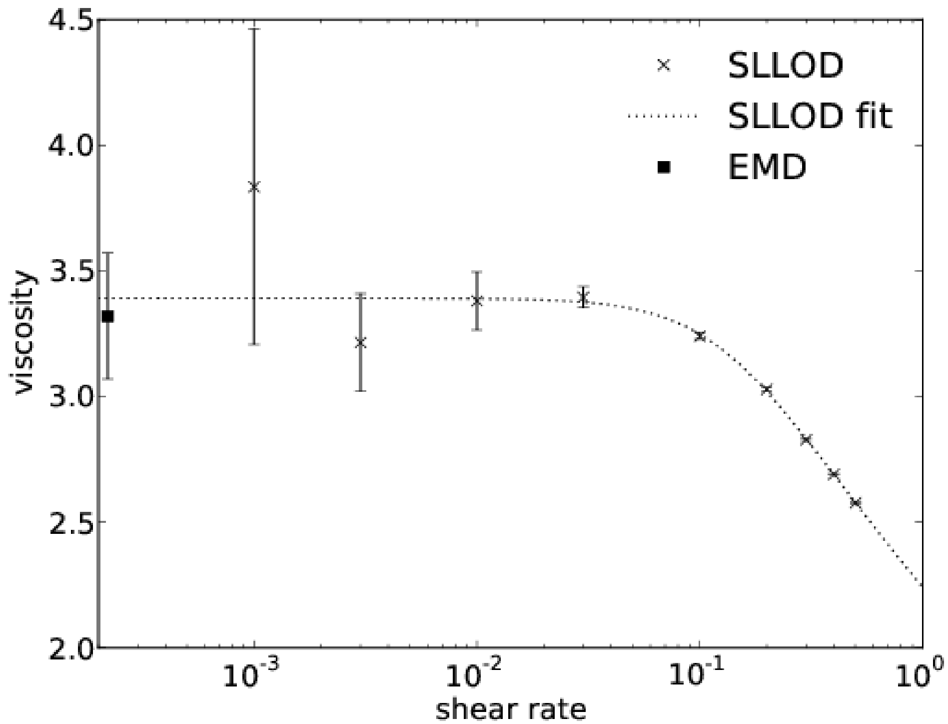
~5% base case flux

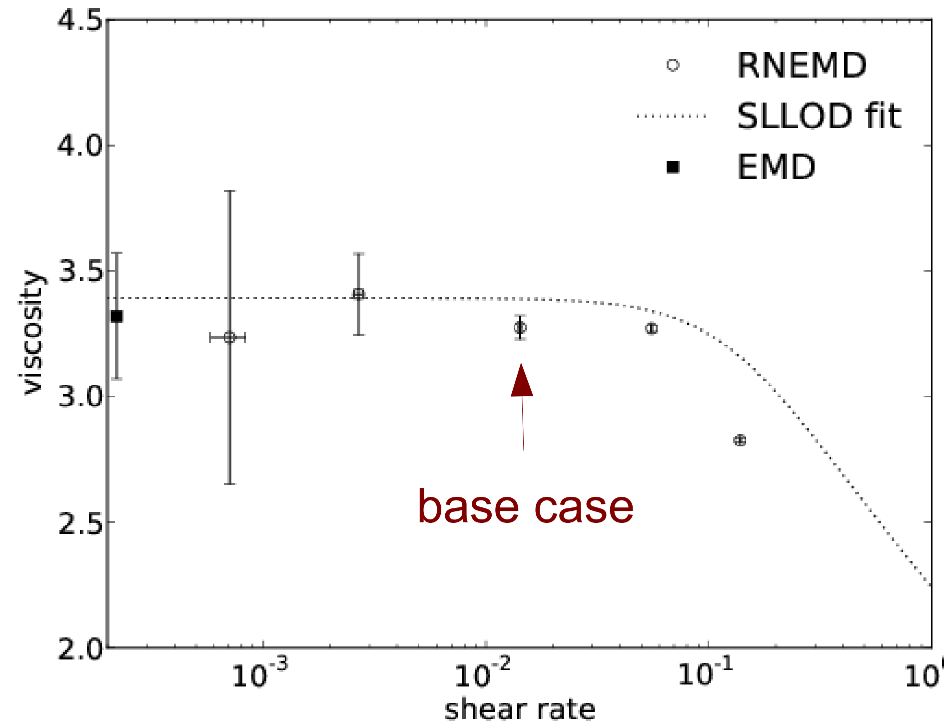
4x longer simulation
(2M steps)



Tenney and Maginn, J. Chem. Phys 132, 2010

RNEMD, SLLOD, and EMD results





- SLLOD results fit to Curreau equation:

$$\eta(\gamma) = \frac{\eta_0}{\left(1+(\lambda\gamma)^2\right)^{\alpha}}, where\ \gamma = shear\ rate$$

Tenney and Maginn, J. Chem. Phys 132, 2010

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RNEMD viscosity summary

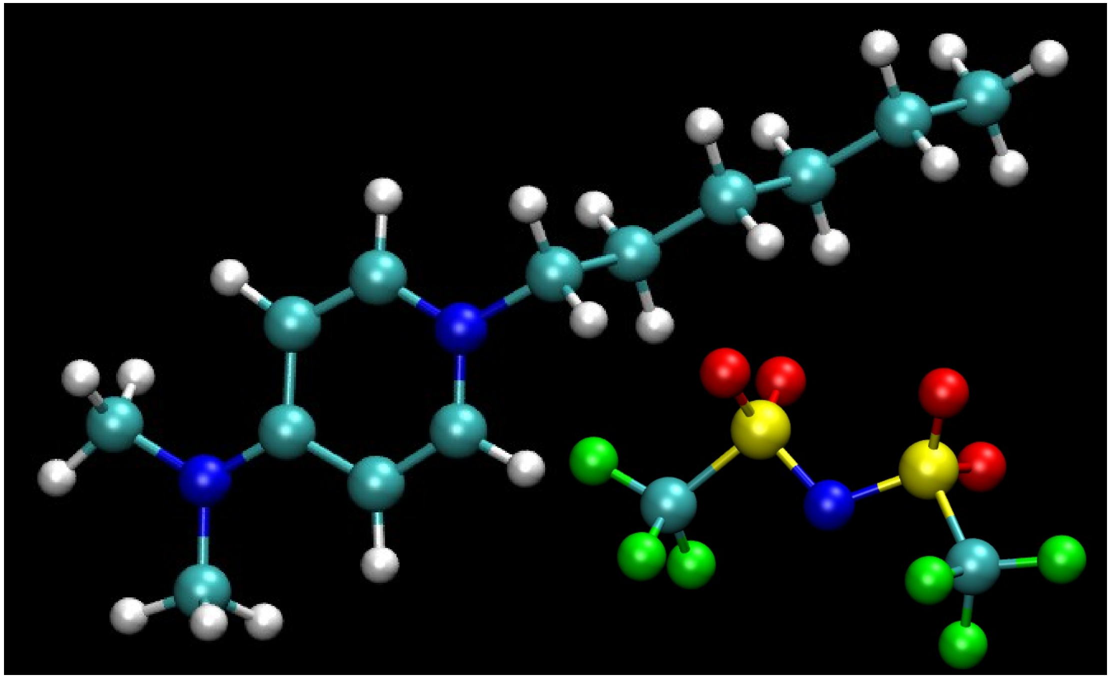
- potential advantages
  - NVE ensemble
  - shear profile is not imposed by deforming space
- disadvantages
  - fails at high momentum flux
  - “pulse” issues at low flux
- ambiguities
  - comparable computational efficiency

RNEMD thermal conductivity

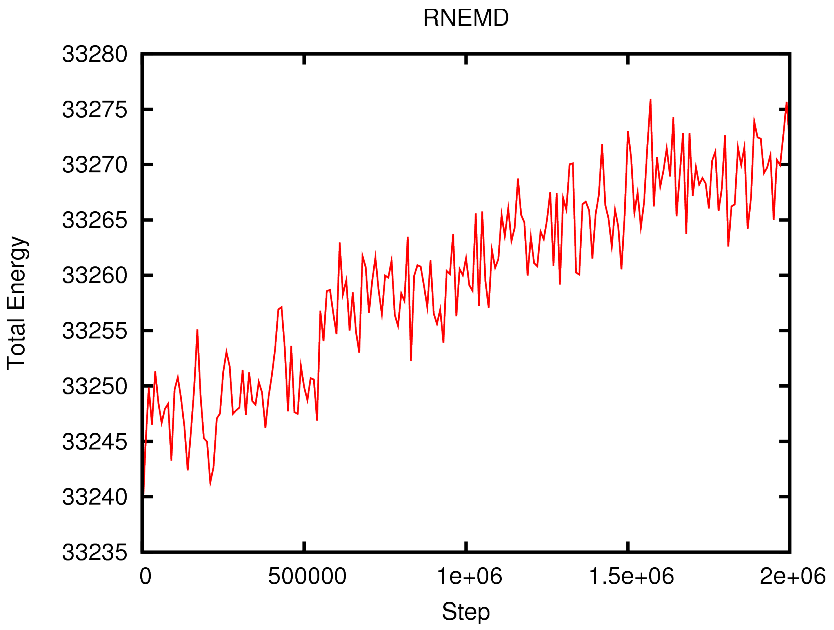
Muller-Plathe, J. Chem. Phys. 106, 1997

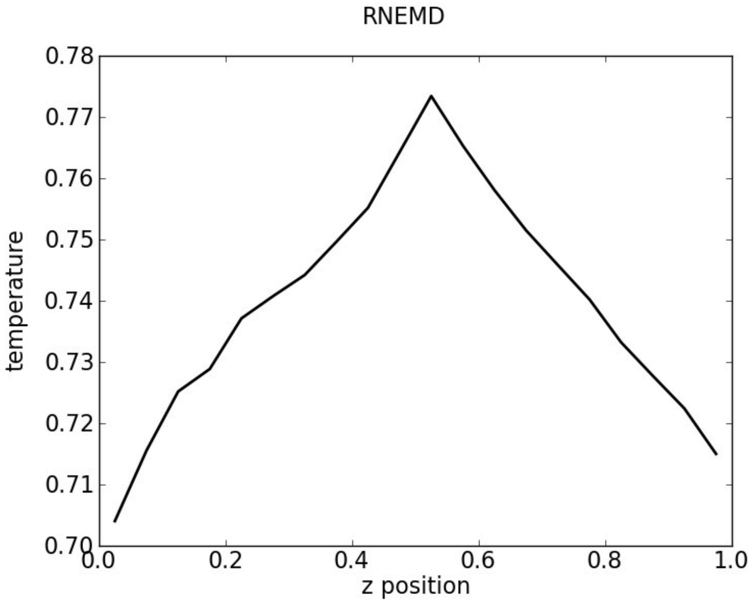
- swap kinetic energy instead of momentum
- fix thermal/conductivity

- example: ionic liquid @ 373K



RNEMD thermal conductivity





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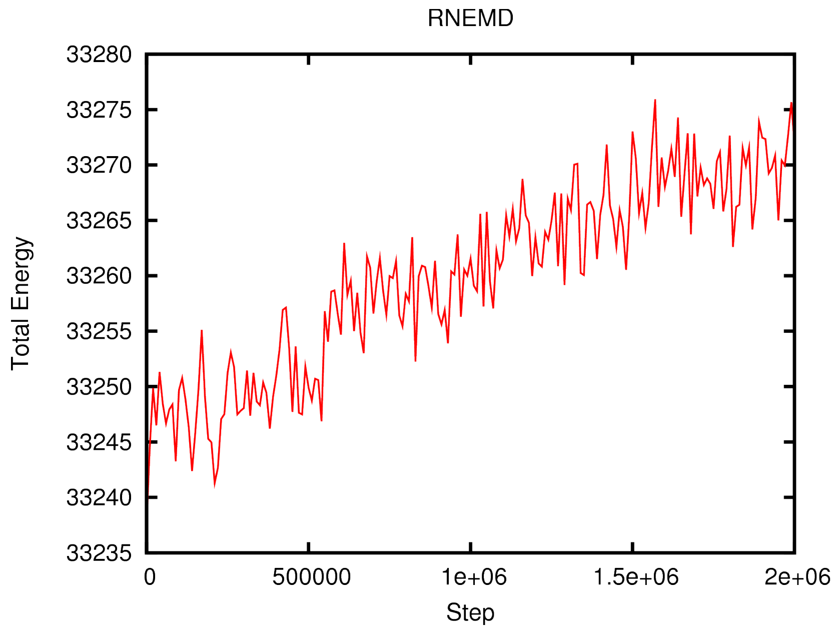

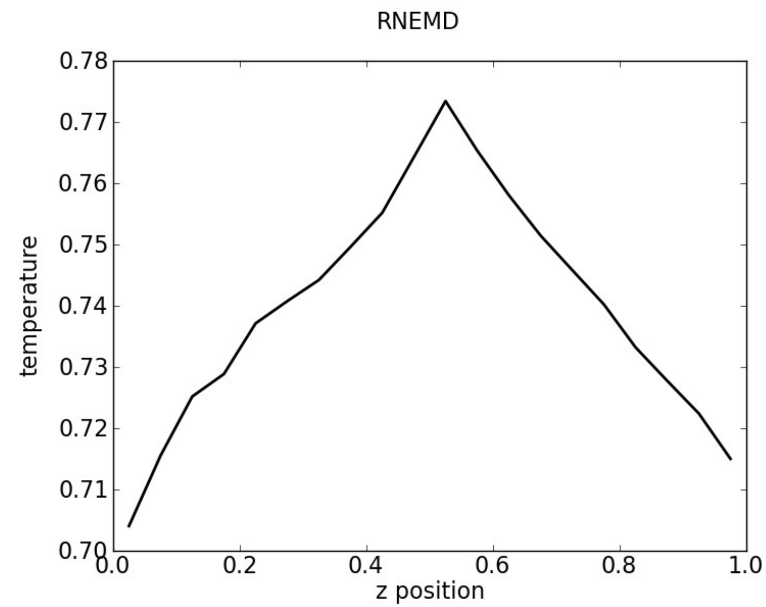

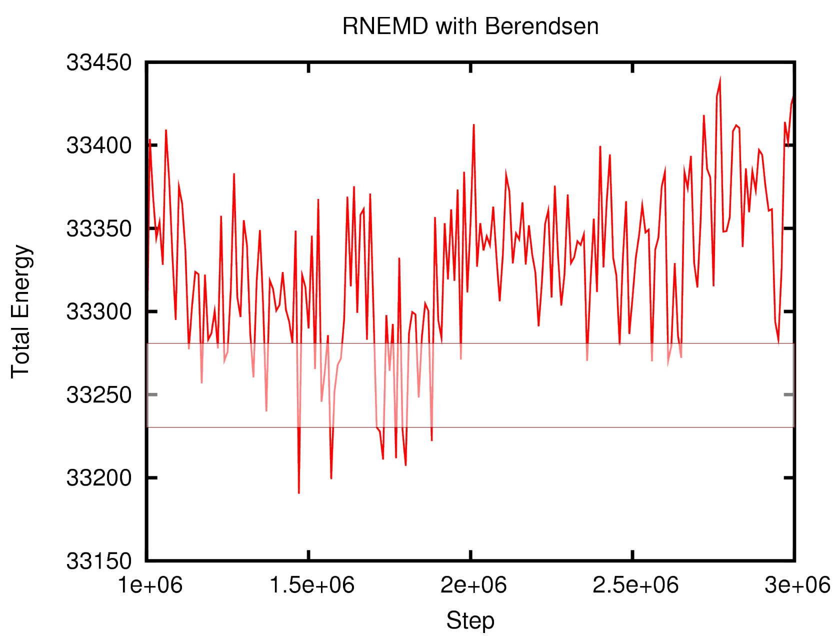

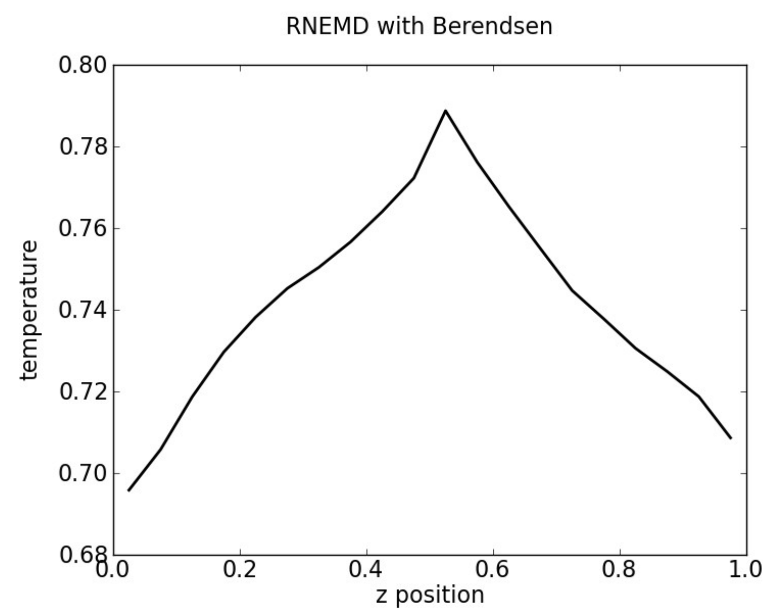

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RNEMD thermal conductivity

- other options
  - swap between atoms of any mass (LAMMPS mod)
    - hypothetical elastic collision
    - available if Steve wants it
  - swap molecular (c.o.m) kinetic energy
    - allows constraints
    - probably more expensive (not implemented in LAMMPS)
    - possibly better energy conservation
  - instead of swapping, thermostat hot and cold bins
    - track steady-state flux
    - compute temp/region, fix langevin

conclusions

- RNEMD can efficiently provide good viscosity results for 'moderate' shear rates
- RNEMD is less robust than SLLOD
- if SLLOD or EMD won't work, consider RNEMD

- RNEMD thermal conductivity calculations are less finicky than viscosity calculations

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acknowledgments

- members of the Maginn group (particularly Sai, for sharing his LAMMPS scripts)
- U.S. Department of Energy
- University of Notre Dame Center for Research Computing

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about RNEMD statistics

- we want the uncertainty of $\eta = -j/\gamma$
- from the mean value theorem, for a reasonable number N of independent calculations of a …

$$a \approx \langle a \rangle \pm \sqrt{\frac{\langle a^2 \rangle - \langle a \rangle^2}{N}}$$

- but at low flux, γ oscillates around 0^+, so η blows up
- consequently, we used a propogation-of-error model:

$$\Delta \eta = \sqrt{(\Delta \gamma)^2 + (\Delta j)^2}$$