Nonlinear-response theory for generalized homogeneous flow in steady state

Remco M. Hartkamp
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Sydney, Australia
Billy Todd

Planar Mixed Flow Response Theory TTCF Yamada and Kawasaki approach

Conclusions
Outline

1. Introduction
2. Planar Mixed Flow
3. Response Theory
4. TTCF
5. Yamada and Kawasaki approach
6. Conclusions
Bulk transport coefficients

Transport coefficients can be obtained from EMD simulation using Green-Kubo relations:

\[
D = \frac{1}{3} \int_0^\infty dr \langle v_i(t) \cdot v_i(0) \rangle
\]

\[
\lambda = \frac{V}{3k_B T^2} \int_0^\infty dr \langle J_Q(t) \cdot J_Q(0) \rangle
\]

\[
\eta = \frac{V}{k_B T} \int_0^\infty dr \langle \sigma_{xz}(t) \cdot \sigma_{xz}(0) \rangle
\]

\[
\eta_V = \frac{1}{V k_B T} \int_0^\infty dr \langle (p(t)V(t) - \langle pV \rangle) (p(0)V(0) - \langle pV \rangle) \rangle
\]

This is very inefficient! Alternatively: use direct NEMD simulations to study transport.
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### Definition

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**Nonequilibrium Molecular dynamics (NEMD)**

**Definition**

A fluid which is driven away from equilibrium by a thermal or mechanical external field or by the boundaries.

- As opposed to equilibrium, the phase space distribution function changes in time out of equilibrium (if the equations of motion are non-Hamiltonian).
- NEMD allows us to study the microscopic physical mechanisms which are important to the transport process.
- It also allows us to study the response far from equilibrium.
Atomic boundary simulation (1)

Density: $\rho = 0.8442$
Temperature: $T = 0.722$
Shear rate: $\dot{\gamma} = 0.5$
Argon atoms
WCA potential
Leapfrog integration
Ordinary PBC’s
Atomic boundary simulation (2)

Boundaries-driven approach comes with disadvantages:

- **Inhomogeneity**
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- Time-dependent properties

'synthetic' indicates that the equations of motion contain a mechanical perturbation which does not appear in nature.
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- **Response theory**
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Adiabatic SLLOD equations of motion

\[\dot{r}_i = \frac{p_i}{m_i} + r_i \cdot \nabla u\]
\[\dot{p}_i = F_i^\phi - p_i \cdot \nabla u\]

- \(r_i\) position of atom \(i\)
- \(p_i\) peculiar momentum of atom \(i\)
- \(F_i^\phi\) Internal force on atom \(i\)
- \(\nabla u\) Velocity gradient (with \(u\) the streaming velocity)

SLLOD is correct arbitrarily far from equilibrium
Note that the work done by the external field causes the fluid to heat up, a thermostat is required to reach a steady state.
Applications

We can use the SLLOD framework to simulate different types of homogeneous flow:

**Planar Couette Flow**

\[ \nabla \mathbf{u} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]

**Planar Elongational Flow**

\[ \nabla \mathbf{u} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{bmatrix} \]
PMF Equations of motion

Linear combination of shear and elongation

$$\nabla \mathbf{u} = \begin{bmatrix}
\dot{\varepsilon} & 0 & 0 \\
\dot{\gamma} & -\dot{\varepsilon} & 0 \\
0 & 0 & 0
\end{bmatrix}$$

Substituting the velocity gradient into the SLLOD algorithm gives:

$$\dot{r}_i = p_i m_i + \dot{\varepsilon} (x_i e_x - y_i e_y) + \dot{\gamma} y_i e_x$$

$$\dot{p}_i = F_\phi i - \dot{\varepsilon} (p_{xi} e_x - p_{yi} e_y) - \dot{\gamma} p_{yi} e_x$$

Need also suitable boundary conditions!!
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Substituting the velocity gradient into the SLLOD algorithm gives:

\[ \dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \dot{\epsilon}(x_i \mathbf{e}_x - y_i \mathbf{e}_y) + \dot{\gamma} y_i \mathbf{e}_x \]
\[ \dot{\mathbf{p}}_i = \mathbf{F}_i^\phi - \dot{\epsilon}(p_{xi} \mathbf{e}_x - p_{yi} \mathbf{e}_y) - \dot{\gamma} p_{yi} \mathbf{e}_x \]

Need also suitable boundary conditions!!
Periodic boundary conditions

Derivable with lattice theory\textsuperscript{1}.

Planar Mixed Flow simulation (1)
Planar Mixed Flow simulation

Density: \( \rho = 0.8442 \)
Temperature: \( T = 0.722 \)
Shear rate: \( \dot{\gamma} = 0.2 \)
Elongational rate: \( \dot{\epsilon} = 0.1 \)
WCA potential (Argon atoms)
Gear predictor corrector integration
Response theory (1)

We want to compare the phase space average of an observable $B$ from response theory to one obtained directly from simulations.
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Solve the Liouville equation:

$$\frac{\partial f(t)}{\partial t} = -i\mathcal{L}f(t),$$

Formal solution:

$$f(t) = e^{-i\mathcal{L}t}f(0),$$

where $i\mathcal{L}$ is the $f$-Liouvillian, which depends on the equations of motion.

$$i\mathcal{L} = \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma}\right), \quad \Gamma = (r_1, r_2, \ldots, r_N, p_1, p_2, \ldots, p_N)^T$$
Response theory (2)

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Now imagine a $6N$-dimensional hypersurface.

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Response theory (3)

Substitute the solution for $f(t)$ into:

$$\langle B(t) \rangle = \int d\Gamma B(\Gamma, t) f(t), \quad (1 = \int d\Gamma f(t) \quad \forall t),$$

where $B$ is an arbitrary phase variable and the brackets a phase space average.
Nonlinear response theory

From here, the Transient Time-Correlation Function (TTCF) formulation for nonlinear response can be derived:

\[
\langle B(t) \rangle = \langle B(0) \rangle - \beta V \int ds \langle B(s)(P(0) : \nabla u) \rangle
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$$\langle B(t) \rangle = \langle B(0) \rangle - \beta V \int ds \langle B(s)(P(0) : \nabla u) \rangle$$

- The calculation of the phase space distribution function is not required.
- Note that the energy dissipation ($P(0) : \nabla u$) follows from the equations of motion.
Stress response for PMF

\[ \langle P(t) \rangle = \langle P(0) \rangle - \beta V \int ds \, \langle P(s)(\dot{e}(P_{xx}(0) - P_{yy}(0)) + \dot{\gamma}P_{xy}(0)) \rangle \]

Again, a linear combination of shear flow and elongational flow can be identified in the response.
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Again, a linear combination of shear flow and elongational flow can be identified in the response.
The phase space average of the stress response can be calculated and compared to direct NEMD result for stress.
Why are we interested in TTCF? (1)

Factor 10 between driving forces $f$

Both data sets are averaged over 2000 frames after equilibration
Why are we interested in TTCF? (2)
When to use which method?

We have seen 3 methods now
Yamada and Kawasaki (1)

Consider a linear velocity profile superimposed on fluid in equilibrium, but the fluid is not relaxed to steady state yet.
Yamada and Kawasaki (1)

Consider a linear velocity profile superimposed on fluid in equilibrium, but the fluid is not relaxed to steady state yet. For shear flow:

- $t=0^-$: Global eq.
- $t=0^+$: Local eq.

Thermal velocity distribution

\[ u(y) \]
Yamada and Kawasaki (2)

Introduce an operator $U$ which has the property of superimposing the streaming velocity on the system in (canonical) equilibrium\(^3\). The local equilibrium distribution function is given by:

$$f_l = U^{-1} f_0 = \frac{e^{-\beta U^{-1} H_0}}{\int d\Gamma e^{-\beta U^{-1} H_0}}$$

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Propagate the local equilibrium backwards in time with the phase variable propagator derived from Newton’s equations of motion.

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The same distribution function should be obtained with SLLOD.

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Yamada and Kawasaki (3)

From the local equilibrium, the system is evolved with Newton’s equations of motion.

\[ F_i = m_i \dot{\epsilon}_r \]

For PCF:
\[ F_E = 0. \]

For PEF:
\[ F_E = m_i \dot{\epsilon}_r \]

The total energy also contains a potential energy contribution due to the driving force.

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...which, in general, includes an external force to drive the fluid!\(^4\)

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\]

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For PEF: \(F^E = m_i \dot{\epsilon}^2 \dot{r}_i\).

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\(^4\)Peter J. Daivis and B.D. Todd, JCP, 124, 194103 (2006)
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For PEF: \( F^E = m_i \dot{\epsilon}^2 \mathbf{r}_i \).

The total energy \( H_0 \) also contains a potential energy contribution due to the driving force!

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Conclusions and outlook

- Response theory can be used to demonstrate the correctness of the SLLOD equations of motion.
- Response theory is sometimes preferable over direct simulations to obtain properties.
- An external force is required to drive elongational flow.

- TTCF results will be compared to PMF simulation results.
- The correctness of the SLLOD equations of motion will be demonstrated with the Yamada and Kawasaki approach.
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