Using Galilean-Invariance to Resum Green-Kubo Relations in Stochastic Rotation Dynamics

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Motivation

Hydrodynamics of complex liquids
- dynamics of polymers, colloids, emulsions in flow
- wide range of length and time scales
- importance of thermal fluctuations
- physico-chemical effects, phase transitions

→ Mesoscale particle-based methods promising:
solvent modeled by "fluid-particles" with efficient dynamics
- very robust, no instabilities
- easy to implement
- intrinsic thermal fluctuations
Stochastic Rotation Dynamics  
(Malevanets-Kapral method)

- Fluid particles with continuous velocities $v_j$ and positions $r_j$
- "Artificial" many-body interaction: rotation of particle velocities relative to mean velocity $u$ by angle $\pm \alpha$.

\[
\vec{r}'_j = \vec{r}_j + \vec{v}_j \Delta t
\]
\[
\vec{v}'_j = \vec{u} + \Omega(\vec{v}_j - \vec{u})
\]
\[
\Omega = \begin{pmatrix} \cos \alpha & \sin \alpha \\ -\sin \alpha & \cos \alpha \end{pmatrix}
\]
\[
\vec{u} = \frac{1}{M} \sum_{j=1}^{M} \vec{v}_j
\]

**Molecular chaos**

### Important Limits

- Mean free path: \( \lambda = \Delta t \sqrt{k_B T} \)
- Lattice constant: \( a \)

\( \lambda \gg a \):
- Strong mixing of particles from different cells
- **no** correlation before collision \( \rightarrow \) Molecular chaos

\( \lambda \ll a \):
- Isolated communities, collision partners stay the same
- Correlations before collisions \( \rightarrow \) **no** Molecular chaos
Analysing and improving SRD

Why is Galilean invariance broken at $\lambda \ll a$?
Let’s impose a homogenous flow $\vec{V}$:
→ particles are swept quickly to other cells
→ faster exchange of collision partners, correlations decrease
→ transport coefficients depend on $\vec{V}$

Galilean invariance can be exactly restored!

Trick: Mimicking the effect of a homogenous flow
Grid is shifted before every rotation step with random vector $\vec{b}$:
$b_x, b_y \in [0,a]$

Why exact procedure?
Probability to find a particle at certain distance to a cell border:
• is constant now
• does not depend on history of particle anymore
Deriving Green-Kubo relations I

Microscopic operators for conserved quantities

\[ A_\alpha(\xi) = \sum_{j=1}^{N} a_{\alpha,j} \ f(\xi, r_j) \]

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Operator</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>( a_{1,j} = 1 )</td>
<td></td>
</tr>
<tr>
<td>x-velocity</td>
<td>( a_{2,j} = v_{x,j} )</td>
<td></td>
</tr>
<tr>
<td>y-velocity</td>
<td>( a_{3,j} = v_{y,j} )</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>( a_{4,j} = v_{j}^2 / 2 )</td>
<td></td>
</tr>
</tbody>
</table>

Weight function: \( f(\xi, r_j) \)

\[ f(\xi, r_j) = \theta(a/2 - |\xi_x - r_{x,j}|) \ \theta(a/2 - |\xi_y - r_{y,j}|) \]

- reflects shape of the cell
- \( f(\xi, r_j) = 1 \), if particle \( j \) is in cell \( \xi \)
Fourier transformation of operators

\[ A_\alpha(k) = \sum_{j=1}^{N} a_{\alpha,j} e^{ik\xi_j} \]

\( \xi_j \) is index of cell which contains particle \( j \)

Goal:

- Derive macroscopic equations for the discrete dynamics in the limit of large length and time scales
- Find microscopic expressions for transport coefficients
- Evaluate these expressions analytically and numerically
Alternative way: equations for correlation functions

Matrix $G: \quad G_{\alpha\beta}(k,t) = V^{-1} \langle \delta A^*(0) \delta A_\beta(t) \rangle$

$= \langle A_\alpha(0)|A_\beta(t) \rangle$

Find linearized hydrodynamics

$$\frac{\partial}{\partial t} G + (ik\Omega + k^2 \Lambda)G = 0$$

$\Omega = $ Frequency matrix, contains Euler terms

$\Lambda = $ Matrix of transport coefficients
Deriving Green-Kubo relations IV

Discrete evolution of $A_\alpha(k, t)$

\[
\Delta_t A_\alpha = A_\alpha(t+1) - A_\alpha(t) = \sum_{j=1}^{N} \left\{ a_{\alpha,j}(t+1) e^{ik\xi_j(t+1)} - a_{\alpha,j}(t) e^{ik\xi_j(t)} \right\}
\]

This leads to formal definition of the flux $D_\alpha$:

\[
\Delta_t A_\alpha + ik D_\alpha = 0,
\]

multiplying by $A_\alpha(0)$ and averaging gives

\[
\Delta_t \langle A_\alpha(0)|A_\beta(t)\rangle + ik \langle A_\alpha(0)|D_\beta(t)\rangle = 0
\]
Outline

- manipulate expression for $\Delta t G_{\alpha\beta}$ using stationarity:
  $$\langle A(t)|A(t')\rangle = \langle A(t+\tau)|A(t'+\tau)\rangle,$$
  and conservation laws

- collect contributions in lowest order in $k$

- perform Laplace transform; go to the limit of $k, \omega \to 0$

Microscopic expression of conservation laws

$$\sum_{j=1}^{N} e^{ik\xi_j^S(t+1)} \{a_{\alpha,j}(t+1) - a_{\alpha,j}(t)\} = 0$$

It means:
Collisions (stochastic rotations) do not change cell densities
Expression for flux at small $k$

$$D_{\alpha}|_{k=0} = -\sum_{j=1}^{N} \left\{ \Delta \xi_{j} a_{\alpha,j} + \Delta a_{\alpha,j} \Delta \xi_{j}^{S} \right\} e^{ik\xi_{j}}$$

$$\Delta \xi_{j} = \xi_{j}(t+1) - \xi_{j}(t), \quad \Delta \xi_{j}^{S} = \xi_{j}(t+1) - \xi_{j}^{S}(t+1)$$

$$\Delta a_{\alpha,j} = a_{\alpha,j}(t+1) - a_{\alpha,j}(t),$$

Laplace transform

$$\tilde{A}_{\alpha}(k, \omega) = \sum_{t=0}^{\infty} A_{\alpha}(k, t+1) e^{-\omega t}$$

$$\tilde{D}_{\alpha}(k, \omega) = \sum_{t=0}^{\infty} D_{\alpha}(k, t) e^{-\omega t}$$

Stationarity: $\langle A|D(t)\rangle = \langle D|A(t+1)\rangle \rightarrow \langle A|\tilde{D}(\omega)\rangle = \langle D|\tilde{A}(\omega)\rangle$
Looking at the poles of the equation for $\tilde{G}_{\alpha\beta}$ at small $\omega$ and $k$ gives matrix of transport coefficients:

$$\Lambda = V^{-1} \left\{ \frac{1}{2} \langle I|I(0)\rangle + \sum_{t=1}^{\infty} \langle I|I(t)\rangle \right\} X^{-1}$$

$X=$Susceptibility matrix, $X_{\alpha\beta} = \langle A_\alpha(0)|A_\beta(0)\rangle$,

$I_\alpha(t)$: Reduced flux

$$I_\alpha(t) = \hat{k} \left\{ D_\alpha - \langle D_\alpha|A_\gamma\rangle X^{-1}_{\gamma\beta} A_\beta(t) \right\}$$

$I_\alpha(t)$ is component of the flux $\hat{k}D_\alpha$ that is orthogonal to the hydrodynamic variables $A$. 
Shear viscosity

\[ \nu = \frac{1}{N k_B T} \left\{ \frac{1}{2} \langle \sigma_{xy}^2(0) \rangle + \sum_{t=1}^{\infty} \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \right\} \]

\( \sigma_{xy} \): off-diagonal element of stress tensor

\[ \sigma_{xy} = \sigma_{Kin} + \sigma_{Rot} \]

\[ \sigma_{Kin} = \sum_{j=1}^{N} v_{y,j} \Delta \xi_{x,j} \]

\[ \sigma_{Rot} = \sum_{j=1}^{N} \Delta v_{y,j} \Delta \xi_{x,j}^{S} \]

Leads to: \( \nu = \nu_{Kin} + \nu_{Mix} + \nu_{Rot} \)

\( \rightarrow \) measurements in equilibrium; long time tails
First terms in series for viscosity

\[ \nu = \frac{1}{N k_B T} \left( \frac{1}{2} C_0 + C_1 + C_2 + \ldots \right) \]

\[ C_0 = \sum_{i,j} \langle \Delta \xi_{x,i}(0) v_{y,i}(0) \Delta \xi_{x,j}(0) v_{y,j}(0) \rangle \]

\[ C_1 = \sum_{i,j} \langle \Delta \xi_{x,i}(0) v_{y,i}(0) \Delta \xi_{x,j}(1) v_{y,j}(1) \rangle \]

Analytical expressions; effect of the cell shape

\[ \langle \Delta \xi_{x,j}^2 \rangle = a^2 \left\{ \frac{1}{6} + \left( \frac{\lambda}{a} \right)^2 - \sum_{n=1}^{\infty} \frac{1}{\pi^2 n^2} \exp(-2\pi^2 n^2 (\lambda/a)^2) \right\} \]

\[ \lambda = \Delta t \sqrt{k_B T} : \text{mean free path, } \ a : \text{lattice constant} \]
Limits

\[ \langle \Delta \xi^2_{x,j} \rangle = \frac{1}{6} a^2 + \lambda^2, \quad \lambda \gg a \]

\[ = a\lambda \sqrt{2/\pi}, \quad \lambda \ll a \]

Expressions for next term

(rotation angle 90° and large particle density)

\[ \langle \Delta \xi_{x,j}(0) v_{y,j}(0) \Delta \xi_{x,j}(1) v_{y,j}(1) \rangle = \]

\[ -\frac{k_B T a\lambda}{2\sqrt{\pi}} \sum_{n=-\infty}^{\infty} \exp \left( -(an/2\lambda)^2 \right) \]

Similar treatment of other terms and at different rotation angles
Resummation

- occurrence of $\Delta \xi$ in stress correlations
- $\Delta \xi$ depends on velocity and position $\rightarrow$ complicated correlations
- only the first terms in sum could be obtained analytically

Symmetrized expression:

$$
\nu = \frac{1}{2N k_B T} \langle \sigma_{xy}(0) \sum_{t=-\infty}^{\infty} \sigma_{xy}(t) \rangle
$$

Successive cancellation of terms:

- $\{\xi(2) - \xi(1)\} \nu(1) + \{\nu(2) - \nu(1)\}\{\xi(2) - \xi^S(1)\}$
- $+ \{\xi(3) - \xi(2)\} \nu(2) + \{\nu(3) - \nu(2)\}\{\xi(3) - \xi^S(2)\}$
- $+ \{\xi(4) - \xi(3)\} \nu(3) + \{\nu(4) - \nu(3)\}\{\xi(4) - \xi^S(3)\}$
New Green-Kubo relations

using stationarity to further simplify expression:

→ new stress tensor in Green-Kubo relation:

\[ \tilde{\sigma}_{Kin} = \sum_{j=1}^{N} v_{j,y} v_{j,x} \]

\[ \tilde{\sigma}_{Rot} = \sum_{j=1}^{N} v_{j,y} B_{j,x} \]

\[ B_{j,x}(t) = \xi_{j,x}^S(t + 1) - \xi_{j,x}^S(t) - \Delta t v_{j,x}(t) \]

New random variables \( B_{j,x} \) are uncorrelated to velocities:

\[ \langle B_{j,\alpha} \rangle = 0 \]

\[ \langle B_{j,\alpha} v_{i,\beta} \rangle = 0 \]

B’s are uncorrelated for time lags larger than one time step

\[ \langle B_{j,\alpha}(n) B_{i,\beta}(m) \rangle = \frac{a^2}{12} \delta_{\alpha\beta} (1 + \delta_{ij}) \{ 2\delta_{nm} - \delta_{n,m+1} - \delta_{n,m-1} \} \]
Results

- transport coefficients contain only two terms, no mixed contributions:

\[
\nu = \nu_{Rot} + \nu_{Kin}
\]

\[
\nu_{Rot} = \frac{a^2}{6d \Delta t} \left( \frac{M - 1 + e^{-M}}{M} \right) \{1 - \cos \alpha\}
\]

\[
D_T = D_{Rot} + D_{Kin}
\]

\[
D_{Rot} = \frac{a^2}{3(d + 2) \Delta t} \frac{1}{M} \left( 1 - e^{-M} \left\{ \int_0^M \frac{e^x - 1}{x} \, dx \right\} \right) (1 - \cos \alpha)
\]

- Fluctuation of particle number per box included (Poisson-distribution assumed)

- \(M\): average number of particles per cell,
  
- \(d\): dimension, \(\alpha\): rotation angle
Numerical simulations

Measuring the viscosity in 2D

\[ \nu = \frac{a^2}{12 \Delta t} \left( 1 - \frac{1}{M} \right) \left( 1 - \cos \alpha \right) + \frac{k_B T \Delta t}{2} \left( \frac{1}{(1 - 1/M) \sin^2 \alpha} - 1 \right) \]

\( \alpha \): rotation angle

\( M \): average particle number per cell (here \( M \gg 1 \))
• measuring density correlations $\langle \rho_k(t)\rho_{-k}(0) \rangle$ and the structure factor $S(k,\omega)$

• comparison with theoretical values for bulk viscosity, heat diffusivity, and speed of sound

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Structure Function
L=32 $\lambda/a=1.00$ M=10 $\alpha=120$

- Simulation
- Theory $\zeta=0$
- Theory $\zeta=0.5k_B T$
Density correlations II

- fitting bulk viscosity and heat diffusivity
- shear viscosity and speed of sound set to theoretical values

L=32.64 λ/a=1.00 M=10 α=120
Beyond Molecular Chaos

- so far assumption of molecular chaos
- deviations due to correlated collisions start at time=2
- similar to ring collisions, but here multi-particle collisions and non-local interaction

Example: stress correlations: \[ \langle v_{i,x}(0) v_{i,y}(0) v_{j,x}(2) v_{j,y}(2) \rangle \]

- analytic expression in limit \( \lambda \to 0 \)
Measuring stress correlations: \( \langle v_{i,x}(0) v_{i,y}(0) v_{j,x}(t) v_{j,y}(t) \rangle \)

\[
\lambda/a = 0.01
\]

Relative deviation

\[
\alpha = 90
\]

\[
\alpha = 120
\]

\[
\text{Relative correction to } \langle \sigma_{xy}^{\text{kin}}(0) \sigma_{xy}^{\text{kin}}(2\tau) \rangle
\]
Summary

• restoring Galilean-invariance at small mean free path by random shift

• derivation of Green-Kubo relations by means of projector-operator technique

• resumming Green-Kubo relations by using properties of random shift

• formulae for transport coefficients assuming molecular chaos

• measuring bulk viscosity and heat diffusivity via structure factor

• corrections beyond molecular chaos
Long time tails

Back flow effect

Velocity auto-correlation: \( \langle v_{j,x}(0) v_{j,x}(t) \rangle \sim \frac{A}{t^{d-1}} \)

Stress correlation: \( \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \sim \frac{B}{t^{d-1}} \)

Logarithmic divergence in 2 D: \( \nu(t) = C + B \ln t \)

In 2D we have for example:

\[
A = \frac{k_B T}{8\pi \rho (\nu + D)}
\]

\( D \): bare self-diffusion constant
\( \rho \): Mass density