Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

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thanks to: M. Kröger, H.C. Öttinger
Table of contents

Tutorial Example: XY model
Statistical Mechanics
Maximum-Entropy Closures
Mori-Zwanzig approach
Macroscopic Poisson Bracket
Thermodynamic Integration
Friction Matrix
Open questions
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Tutorial Example: XY model

**Tutorial Example**

Chaikin, Lubensky: macroscopic dynamics of real physical systems is either quite complicated ... or confusing because of possibly unfamiliar time evolution.

Thus, study simple model system:
- no known physical realization
- but illustrate essential features
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Thus, study simple model system:
- no known physical realization
- but illustrate essential features
Study simple model system and learn essential features of thermodynamically consistent coarse graining.

Consider a system of $N$ identical, two-dimensional spins $\mathbf{u}_j = (\sin \theta_j, \cos \theta_j)$. The $2N$ microscopic degrees of freedom are $z = (\theta_1, \ldots, \theta_N, l_1, \ldots, l_N)$. Hamiltonian

$$\mathcal{H}(z) = \sum_{j=1}^{N} \frac{l_j^2}{2I} - \frac{J}{2} \sum_{<i,j>} \cos(\theta_i - \theta_j)$$
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Tutorial Example: XY model

Hamilton’s equations of motion:

\[
\begin{align*}
\dot{\theta}_j &= \frac{\partial H}{\partial l_j} = l_j/l \\
\dot{l}_j &= -\frac{\partial H}{\partial \theta_j} = -J \sum_{k(\text{nnj})} \sin(\theta_j - \theta_k)
\end{align*}
\]

equivalent formulation

\[
\frac{d}{dt} A(z) = i\mathcal{L}A = \{A, H\}
\]

with microscopic Poisson bracket

\[
\{A, B\} = \sum_{j=1}^{N} \left( \frac{\partial A}{\partial \theta_j} \frac{\partial B}{\partial l_j} - \frac{\partial A}{\partial l_j} \frac{\partial B}{\partial \theta_j} \right)
\]
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**Tutorial Example: XY model dynamics**

Hamilton’s equations of motion:

\[
\dot{\theta}_j = \frac{\partial \mathcal{H}}{\partial l_j} = \frac{l_j}{l}
\]

\[
\dot{l}_j = -\frac{\partial \mathcal{H}}{\partial \theta_j} = -J \sum_{k(nnj)} \sin(\theta_j - \theta_k)
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with microscopic *Poisson bracket*

\[
\{A, B\} = \sum_{j=1}^{N} \left( \frac{\partial A}{\partial \theta_j} \frac{\partial B}{\partial l_j} - \frac{\partial A}{\partial l_j} \frac{\partial B}{\partial \theta_j} \right)
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Tutorial Example: Poisson bracket

Properties of Poisson bracket

- anti-symmetry
  \[ \{ A, B \} = -\{ B, A \} \]

- Leibniz rule
  \[ \{ AB, C \} = A\{ B, C \} + \{ A, C \}B \]

- Jacobi-identity
  \[ \{ A, \{ B, C \} \} + \{ B, \{ C, A \} \} + \{ C, \{ A, B \} \} = 0 \]
Tutorial Example: conservation laws

Fixed lattice $\Rightarrow$ only 2 conserved quantities

1. total energy $E = \mathcal{H}$
2. total angular momentum $L = \sum_{j=1}^{N} l_j$
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Tutorial Example: XY model

Tutorial Example: choice of collective variables

On macroscopic scales, most disturbances decay rapidly to equilibrium.
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Want to choose collective variables that are slowly evolving.
On macroscopic scales, most disturbances decay rapidly to equilibrium. Want to choose collective variables that are \textit{slowly} evolving. Certainly need:

- densities of conserved quantities
- broken-symmetry variables

That’s all for our tutorial example.
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Tutorial Example: XY model

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Tutorial Example: XY model

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**Tutorial Example: XY model**

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**Tutorial Example: densities of conserved quantities**

define macroscopic fields

\[ \varepsilon(r, t) = \langle \Pi \varepsilon(r, t) \rangle, \quad \ell(r, t) = \langle \Pi \ell(r, t) \rangle \]

with mappings \( \Pi_k : z \mapsto \Pi_k \)

\[
\Pi \varepsilon(r, t) = \sum_{j=1}^{N} \left( \frac{l_j^2}{2I} - \frac{J}{2} \sum_{i\text{(nnj)}} \cos(\theta_{ij}) \right) \chi(r - r_j) \\
= \sum_{j=1}^{N} \varepsilon_j \chi(r - r_j) \\

\Pi \ell(r, t) = \sum_{j=1}^{N} l_j \chi(r - r_j)
\]
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**Tutorial Example: XX model**

**Tutorial Example: densities of conserved quantities**

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\varepsilon(r, t) = \langle \Pi\varepsilon(r, t) \rangle, \quad \ell(r, t) = \langle \Pi\ell(r, t) \rangle
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\Pi\varepsilon(r, t) = \sum_{j=1}^{N} \left( \frac{l_j^2}{2l} - \frac{J}{2} \sum_{i(nnj)} \cos(\theta_{ij}) \right) \chi(r - r_j)
\]

\[
= \sum_{j=1}^{N} \varepsilon_j \chi(r - r_j)
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\Pi\ell(r, t) = \sum_{j=1}^{N} l_j \chi(r - r_j)
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Tutorial Example: XY model

direct calculation:

\[ \dot{\Pi}_\ell(r, t) = \left\{ \Pi_\ell(r, t), \mathcal{H} \right\} \]

\[ = - \sum_j \frac{\partial \mathcal{H}}{\partial \theta_j} \chi(r - r_j) = -J \sum_{\langle i,j \rangle} \sin(\theta_i - \theta_j) \chi(r - r_j) \]

\[ = -\frac{J}{2} \sum_{\langle i,j \rangle} \sin(\theta_i - \theta_j) (\chi(r - r_j) - \chi(r - r_i)) \]

Use identity \( \chi(r - r_j) - \chi(r - r_i) = -\frac{\partial}{\partial r} \cdot \int_0^1 ds r_ij \chi(r - r_i + sr_{ij}) \)
Tutorial Example: time evolution of mapping

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\( \Rightarrow \) find form of (instantaneous) local conservation law

\[ \dot{\Pi}_\ell(r, t) = -\frac{\partial}{\partial r} \cdot \hat{\tau}(r, t) \]

\[ \hat{\tau}(r, t) = \frac{J}{2} \sum_{<i,j>} r_{ij} \sin(\theta_{ij}) \int_0^1 ds \chi(r - r_i + sr_{ij}) \]
Tutorial Example: time evolution of mapping

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Tutorial Example: XY model

**Tutorial Example: time evolution of mapping**

Similar calculation for the energy density gives

\[
\dot{\Pi}_\varepsilon(r, t) = -\frac{\partial}{\partial r} \cdot \hat{j}(r, t)
\]

\[
\hat{j}(r, t) = \frac{J}{2l} \sum_{<i,j>} (l_i + l_j) r_{ij} \sin(\theta_{ij}) \int_0^1 ds \chi(r - r_i + sr_{ij})
\]
balance equations for mappings

- fields are smeared out in space
- but rapidly varying in time
- microscopic expressions can be evaluated in MD
- but are not in closed-form for coarse-grained description,

\[
\dot{\Pi}_k \neq G_k(\Pi_{\varepsilon}, \Pi_\ell), \quad k = (\varepsilon, \ell)
\]

- how to obtain closed-form equations for macroscopic variables

\[
x_k = \langle \Pi_k \rangle?
\]
scale bridging!

- brute force approach is computationally very expensive or even unfeasible
- “... molecular modeling has become standard ... severe time and length scale limitations. Simulations on scales [>100nm, > 1µs] impossible without multiscale modeling.”
- “... progress is coming more through refined simulations than from increased computational power.”
it is neither feasible nor desirable to specify initial conditions for \( z \) for a macroscopic system. 

rather specify probability density of initial conditions \( \rho(z; 0) \). 

aim is then to find \( \rho(z; t) \) for some later time \( t \). 

\( \rho(z; t) \) still too detailed, really only interested in a few macroscopic quantities \( x \).
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Statistical Mechanics

Microscopic dynamics

- microstate \( z \in \Gamma \subset IR^n \)

- probability density \( \rho(z; t) \)
  with \( \rho(z; t) \geq 0, \int_{\Gamma} dz \rho(z; t) = 1. \)

- microscopic dynamics (e.g. Liouville, Fokker-Planck)

\[
\frac{\partial}{\partial t} \rho = -i \mathcal{L} \rho
\]

- averages: \( \langle A \rangle(t) = \int_{\Gamma} dz A(z) \rho(z; t) \)
Collective variables and closure problem

- coarse-grained state specified by a few macroscopic (collective) variables only, $x = \{x_1, \ldots, x_n\}$,

\[ x_k(t) = \int_{\Gamma} dz \, \Pi_k(z) \rho(z; t), \quad k = 1, \ldots, n \]

- but no closed-form equations for moments

\[
\frac{d}{dt} x_k = \int_{\Gamma} dz \, \Pi_k(z)(-i\mathcal{L})\rho(z; t) \\
= G_k(x_1, \ldots, x_n, x_{n+1}, \ldots)
\]
Example of “closure problems”

- BBGKY hierarchy
- rare events
- polymers and soft matter
- subgrid turbulence modeling
- reaction kinetics
- ...
slow manifolds

how to close moment system?
simply truncating is dangerous, often leads to thermodynamically inadmissible, ill-behaved equations.

choose \( \rho^* \) to capture coarse-grained manifold \( \{ \rho^* \} \) hopefully "slow"
slow manifolds

how to close moment system?
simply truncating is dangerous, often leads to thermodynamically inadmissible, ill-behaved equations.

- choose “relevant” density $\rho^* = \rho^*_x$ to capture coarse-grained state
- manifold $\{\rho^*_x\}$ hopefully “slow”
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Maximum-Entropy Closures

**slow manifolds**

how to close moment system?
simply truncating is dangerous, often leads to thermodynamically inadmissible, ill-behaved equations.

- choose “relevant” density $\rho^* = \rho_x^*$ to capture coarse-grained state
- manifold $\{\rho_x^*\}$ hopefully “slow”
maximum entropy distribution

- entropy functional \( S[\rho] = - \int_{\Gamma} dz \rho \ln(\rho/\rho_0) \)
- maximum entropy principle

\[
S[\rho] \rightarrow \text{max, } x_k[\rho] \text{ fixed}
\]
maximum entropy distribution

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- maximum entropy principle

$$S[\rho] \rightarrow \text{max}, \quad x_k[\rho] \text{ fixed}$$

- solution: quasi-equilibrium (generalized canonical) distribution

$$\rho^*(z) = \rho_0(z) \exp \left[ -\lambda_k \Pi_k(z) + \beta G(\lambda) \right]$$

$$x_k^* = \int_{\Gamma} dz \Pi_k(z) \rho^*(z)$$
Maximum-Entropy Closures

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- with Lagrange multiplier \( \lambda_k = \lambda_k(x) \)

[Gibbs; Jaynes; Grad, etc.]
maximum entropy distribution

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[Gibbs; Jaynes; Grad, etc.]
Generating function

normalization of probability density:

\[ e^{-\beta G(\lambda)} = \int dz \rho_0(z) e^{-\lambda_k \Pi_k(z)} \]

macro variables from derivative

\[ \frac{\partial (\beta G)}{\partial \lambda_k} = \int dz \rho^*(z) \Pi_k(z) = x_k \]
Generating function

normalization of probability density:

$$e^{-\beta G(\lambda)} = \int \text{d}z \, \rho_0(z) e^{-\lambda_k \Pi_k(z)}$$

macro variables from derivative

$$\frac{\partial (\beta G)}{\partial \lambda_k} = \int \text{d}z \, \rho^*(z) \Pi_k(z) = x_k$$
Quasi-equilibrium entropy

define

\[ S^*(x) = S[\rho^*] \]
Quasi-equilibrium entropy

define

\[ S^*(x) = S[\rho^*] \]

insert definition:

\[ S^*(x) = -\beta G + \lambda_k x_k + S_0 \]

with \( S_0 = \text{const. for } \rho_0 = \text{const.} \)
and \( S_0 = \beta(F_0 - E) \) if \( \rho_0 \) canonical.
**Quasi-equilibrium entropy**

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Thus, \( S \) is Legendre transform of \( G \) and

- Lagrange multipliers as dual variables

\[ \frac{\partial S^*}{\partial x_k} = \lambda_k \]
Quasi-equilibrium entropy

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Maximum-Entropy Closures

Tutorial Example: statistical mechanics

relevant ensemble: generalized canonical distribution

\[ \rho(z) = \frac{1}{\Xi} \exp \left[ -\int d^d r \beta(r) \Pi_\varepsilon(z;r) - \int d^d r \lambda(r) \Pi_\ell(z;r) \right] \]

\[ \Xi(T,\lambda) = \int d^N \theta d^N l \exp \left[ -\int d^d r \beta(r) \Pi_\varepsilon(z;r) - \int d^d r \lambda(r) \Pi_\ell(z;r) \right] \]

\( \beta, \lambda \): Lagrange multipliers conjugate to the collective variables,

\[ -\frac{\delta \ln \Xi}{\delta \beta(r)} = \langle \Pi_\varepsilon \rangle = \varepsilon(r), \quad -\frac{\delta \ln \Xi}{\delta \lambda(r)} = \langle \Pi_\ell \rangle = \ell(r) \]
Tutorial Example: statistical mechanics

relevant ensemble: generalized canonical distribution

\[
\rho(z) = \frac{1}{\Xi} \exp \left[ - \int d^d r \beta(r) \Pi_\varepsilon(z; r) - \int d^d r \lambda(r) \Pi_\ell(z; r) \right]
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\[
\Xi(T, \lambda) = \int d^N \theta d^N l \ exp \left[ - \int d^d r \beta(r) \Pi_\varepsilon(z; r) - \int d^d r \lambda(r) \Pi_\ell(z; r) \right]
\]

\(\beta, \lambda\): Lagrange multipliers conjugate to the collective variables,

\[
- \frac{\delta \ln \Xi}{\delta \beta(r)} = \langle \Pi_\varepsilon \rangle = \varepsilon(r), \quad - \frac{\delta \ln \Xi}{\delta \lambda(r)} = \langle \Pi_\ell \rangle = \ell(r)
\]
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Maximum-Entropy Closures

Tutorial Example: Entropy

Physically, entropy emerges since we have eliminated degrees of freedom. Legendre transform

\[ S[\varepsilon, \ell] = k_B \ln \Xi + k_B \int d^d r \beta(r) \varepsilon(r) + k_B \int d^d r \lambda(r) \ell(r) \]

with

\[ \left( \frac{\delta S}{\delta \varepsilon(r)} \right)_\ell = \frac{1}{T(r)}, \quad \left( \frac{\delta S}{\delta \ell(r)} \right)_\varepsilon = k_B \lambda(r) \]
maximum entropy closures

▶ closed equations!

\[
\frac{d}{dt} x_k^* = \int_\Gamma dz \Pi_k(z)(-i\mathcal{L})\rho^*
\]

▶ are we done?
maximum entropy closures

- closed equations!

\[
\frac{d}{dt} x_k^* = \int_{\Gamma} dz \Pi_k(z)(-i\mathcal{L})\rho^*
\]

- are we done?

- maximum entropy closure conserves type of dynamics

\[
\frac{d}{dt} S^* = \frac{d}{dt} S[\rho] \bigg|_{\rho^*}
\]

[Gorban, Karlin, 1992]
maximum entropy closures

- closed equations!

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\frac{d}{dt} x_k^* = \int_{\Gamma} dz \, \Pi_k(z)(-i\mathcal{L})\rho^*
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- are we done?

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\]

[Gorban, Karlin, 1992]
example applications

- polymer solutions
- magnetic fluids
- liquid crystals
- chemical reactions
- etc.
limitations and improvements

- improvement of maximum entropy closures: 
  *method of invariant manifolds*  
  (A.N. Gorban, I.V. Karlin)

- but how to derive irreversible equations?
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Mori-Zwanzig approach

- \( z = \{p, r\} \in \Gamma \)
- Phase space density \( \rho(z; t) \)
- Liouville equation \( \partial_t \rho = -i \mathcal{L} \rho \)
- Liouville operator

\[
i \mathcal{L} A = \{A, H\} = \sum_{i=1}^{N} \left( \frac{\partial A}{\partial r_i} \cdot \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \cdot \frac{\partial H}{\partial r_i} \right)
\]

Mori-Zwanzig approach
Heisenberg picture of classical mechanics

- formal solution ($\mathcal{L}$ not explicitly time-dependent)
  \[ \rho(z; t) = e^{-i\mathcal{L}t} \rho(z; 0) \]
- averages: time-dependent observables

\[
\langle A \rangle(t) = \int_{\Gamma} dz \ A(z) \rho(z; t) \\
= \int_{\Gamma} dz \ A(z) e^{-i\mathcal{L}t} \rho(z; 0) \\
= \int_{\Gamma} dz \ \rho(z; 0) e^{i\mathcal{L}t} A(z)
\]

\[ \Rightarrow A(z; t) = e^{i\mathcal{L}t} A(z) \]
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Mori-Zwanzig approach

decomposing the dynamics

\[ a(t) = \langle A \rangle(t) \Rightarrow \dot{a}(t) = \frac{d}{dt} \langle A \rangle(t) \]

\[ = \int_{\Gamma} dz \, \rho(z; 0) i \mathcal{L} e^{i \mathcal{L} t} A(z) \]

define projectors \( \mathcal{P}, \mathcal{Q} = I - \mathcal{P} \)
(with \( \mathcal{P}^2 = \mathcal{P}, \mathcal{Q}^2 = \mathcal{Q}, \mathcal{PQ} = \mathcal{QP} = 0 \))
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**Mori-Zwanzig approach**

\[ \frac{d}{dt} A = e^{i\mathcal{L}t}i\mathcal{L}A = e^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}A + O_A \]

**Duhamel-Dyson identity**

Projected dynamics: hopefully slow

Orthogonal dynamics: \( O_A = e^{i\mathcal{L}t}Q_i\mathcal{L}A \)

Rewrite \( O_A \) using Duhamel-Dyson relation

\[ e^{i\mathcal{L}t} = e^{Q_i\mathcal{L}t} + \int_0^t ds \, e^{i\mathcal{L}(t-s)}\mathcal{P}i\mathcal{L}e^{Q_i\mathcal{L}s} \]
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Mori-Zwanzig approach

Duhamel-Dyson identity

\[
\frac{d}{dt} A = e^{i\mathcal{L}t} i\mathcal{L}A = e^{i\mathcal{L}t} \mathcal{P} i\mathcal{L}A + O_A
\]

projected dynamics: hopefully slow
orthogonal dynamics: \( O_A = e^{i\mathcal{L}t} Q i\mathcal{L}A \)
rewrite \( O_A \) using Duhamel-Dyson relation

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e^{i\mathcal{L}t} = e^{Q i\mathcal{L}t} + \int_0^t ds \ e^{i\mathcal{L}(t-s)} \mathcal{P} i\mathcal{L}e^{Q i\mathcal{L}s}
\]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Mori-Zwanzig approach

**equation of motion: exact**

projection operator approach uses operator identity

\[
e^{i\mathcal{L}t} = e^{i\mathcal{L}_t} \mathcal{P} + \int_0^t ds \ e^{i\mathcal{L}_s} \mathcal{P} i\mathcal{L} Q e^{i\mathcal{L}_Q(t-s)} + Q e^{i\mathcal{L}_Q(t)}
\]

choose \( A = \Pi_k \)

\[
\frac{d}{dt} \Pi_k = e^{i\mathcal{L}_t} \mathcal{P} i\mathcal{L} \Pi_k + \int_0^t ds \ e^{i\mathcal{L}_t} \mathcal{P} i\mathcal{L} F_k(s) + F_k(t)
\]

\[
F_k(t) = e^{Q i\mathcal{L}_t} Q i\mathcal{L} \Pi_k
\]
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Mori-Zwanzig approach

**equation of motion: exact**

projection operator approach uses operator identity

\[ e^{i\mathcal{L}t} = e^{i\mathcal{L}_t} \mathcal{P} + \int_0^t ds e^{i\mathcal{L}_s} \mathcal{P} i\mathcal{L} Q e^{i\mathcal{L}_Q(t-s)} + Q e^{i\mathcal{L}_Q t} \]

choose \( A = \Pi_k \)

\[ \frac{d}{dt} \Pi_k = e^{i\mathcal{L}_t} \mathcal{P} i\mathcal{L} \Pi_k + \int_0^t ds e^{i\mathcal{L}_s(t-s)} \mathcal{P} i\mathcal{L} F_k(s) + F_k(t) \]

\[ F_k(t) = e^{Q_i\mathcal{L}_t} Q i\mathcal{L} \Pi_k \]
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Mori-Zwanzig approach

choice of projector

here: [H. Grabert, 1982]

\[
\mathcal{P}A = \int_{\Gamma} dz \rho^*(z)A(z) + (x_j - \Pi_j) \int_{\Gamma} dz \frac{\partial \rho^*}{\partial x_j} A(z)
\]

\[
e^{i\mathcal{L}t}\mathcal{P}A = \int_{\Gamma} dz \rho_{x(t)}^*(z)A(z) + (x_j - \Pi_j) \int_{\Gamma} dz \frac{\partial \rho^*}{\partial x_j(t)} A(z)
\]

note: other choices (Robertson, etc.) lead to same equations for averages
exact, non-Markovian time evolution

use generalized canonical ensemble for $\rho^*$

$$\frac{d}{dt} x_k = v_k + \int_0^t ds \ K_{kj}(t, s) \lambda_j(t - s)$$

$$v_k = \left\langle \{ \Pi_k, H \} \right\rangle_{x(t)} \text{ deterministic drift}$$

$$K_{kj}(t, s) = \left\langle F_k(0) F_j(s) \right\rangle_{x(t-s)} \text{ memory kernel}$$

$$F_k(t) = e^{QL_t} Q_i \mathcal{L} \Pi_k \text{ "random force"}$$

$$\lambda_j = \frac{\partial S^*}{\partial x_j}$$

[H. Mori 1965, R. Zwanzig 1961]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Mori-Zwanzig approach

Markovian approximation

**crucial assumption**: separation of time scales.

**collective variables**: slowly evolving \((\gg \tau_s)\)

fast fluctuations \((\ll \tau_s) \Rightarrow \text{short memory} \Rightarrow \text{Markovian approximation}\)

\[
\int_0^t ds \ K_{kj}(t, s) \frac{\partial S^*}{\partial x_j} \bigg|_{x(t-s)} \approx M_{kj}(x(t)) \frac{\partial S^*}{\partial x_j} \bigg|_{x(t)}
\]

\[
M_{kj}(x) = \int_0^{\tau_s} ds \langle F_k(0) F_j(s) \rangle
\]

\[
\frac{d}{dt} x_k = \langle \{ \Pi_k, H \} \rangle + M_{kj} \frac{\partial S^*}{\partial x_j}
\]
choice of collective variables

Statistical mechanics does not tell us what the relevant variables are. This is our choice. If we choose well, the results may be useful; if we choose badly, the results will probably be useless.

R. Zwanzig
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

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Mori-Zwanzig approach

4 tasks for coarse grainers

Coarse-graining program has to meet four tasks

1. choice of collective variables $x$, mapping $\Pi$
2. deterministic drift $v_k$
3. entropy $S^*(x)$
4. friction matrix $M$
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Mori-Zwanzig approach

Macroscopic Poisson bracket

deterministic drift:

\[ \nu_k = \langle \{ \Pi_k, H \} \rangle_x(t) \]

require: energy accessible on coarse-grained level \( \mathcal{H}(z) = E(\Pi(z)) \).

Then,

\[ \langle \{ \Pi_k, H \} \rangle = L_{kj} \frac{\partial E}{\partial x_j} \]

\[ L_{kj} = \langle \{ \Pi_k, \Pi_j \} \rangle \text{ anti-symmetric} \]

and the powerful GENERIC structure emerges

\[
\frac{dx_k}{dt} = L_{kj} \frac{\partial E}{\partial x_j} + M_{kj} \frac{\partial S^*}{\partial x_j}
\]

[M. Grmela, H.C. Öttinger (1997)]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations
— Mori-Zwanzig approach

4 tasks for coarse grainers

Coarse-graining program has to meet four tasks

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   - macroscopic energy $E(x)$.
   - macroscopic Poisson bracket

   $$L_{kj} = \langle \{ \Pi_k, \Pi_j \} \rangle$$

3. entropy $S^*(x)$
4. friction matrix $M(x)$
Back to our tutorial example

Macroscopic energy: \( E = \int \! \! d\mathbf{r} \; \varepsilon(\mathbf{r}) \) and \( \frac{\delta E}{\delta \varepsilon(\mathbf{r})} = 1. \)

Thus,

\[
v_k(\mathbf{r}) = L_{kj} \frac{\partial E}{\partial x_j} = \int d^d r' \langle \{ \Pi_k(\mathbf{r}), \Pi_\varepsilon(\mathbf{r}') \} \rangle
\]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Macroscopic Poisson Bracket

Back to our tutorial example

macroscopic energy: $E = \int \! \! d r \, \varepsilon(r)$ and $\frac{\delta E}{\delta \varepsilon(r)} = 1$.

Thus,

$$v_k(r) = L_{kj} \frac{\partial E}{\partial x_j} = \int \! \! d^d r' \langle \{ \Pi_k(r), \Pi_\varepsilon(r') \} \rangle$$

insert:

$$v_\varepsilon(r, t) = - \frac{\partial}{\partial r} \cdot \langle \hat{j}(r, t) \rangle_x, \quad v_\ell(r, t) = - \frac{\partial}{\partial r} \cdot \langle \hat{\tau}(r, t) \rangle_x$$
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

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In the absence of external perturbations there are no reversible fluxes and therefore

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Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

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\]
Include Magnetization

want to describe also anisotropic phase, include additional collective variable:

$$\Pi_m(r, t) = \sum_{j=1}^{N} u_j \chi(r - r_j) = \sum_{j=1}^{N} \left( \begin{array}{c} \sin \theta_j \\ \cos \theta_j \end{array} \right) \chi(r - r_j)$$

with $m = \langle \Pi_m \rangle$ the macroscopic magnetization.

Note: $m$ is NOT a conserved quantity.
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additional Poisson bracket

Need to find the deterministic drift for the magnetization

\[ v_m(r) = \int \, dr' \, L_{m,\varepsilon}(r, r') \]

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\[ = \langle \sum_j \left( \begin{array}{c} \cos \theta_j \\ \sin \theta_j \end{array} \right) \frac{l_j}{l} \chi(r - r_j) \chi(r' - r_j) \rangle \]
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Averages over angular momenta can be done analytically:

\[ L_{m,\varepsilon}(r, r') = \Omega(r) \times m(r) \delta(r' - r) \]

with \( \Omega(r) = (0, 0, \omega(r)) \) and \( \omega(r) = l^{-1} \ell(r) = \lambda(r)/\beta(r) \).
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Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

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Quasi-equilibrium entropy

Want to determine macroscopic entropy $S^*(x)$. Remember dual nature of Lagrange multipliers:

- Lagrange multipliers as dual variables

$$\frac{\partial S^*}{\partial x_k} = \lambda_k$$
Quasi-equilibrium entropy

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- recover entropy via thermodynamic integration
  \[ S^*(x) - S_0^* = \int_0^x \lambda_k \, dx_k \]
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near equilibrium

- quasi-equilibrium \( \neq \) near equilibrium
- near equilibrium: linear relation \( x_k = x_{k,eq} - C_{kj} \lambda_j \) with
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Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

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- therefore quadratic entropy:
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Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

**Thermodynamic Integration**

**near equilibrium**

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  \]
- starting point for Einstein’s fluctuation theory
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Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

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Thermodynamic Integration

**Tutorial example**

generating function

\[ e^{-\beta G(\lambda)} = \int dz \rho_0(z) e^{-\lambda_k \Pi_k(z)} \]

ideal orientational contribution

\[ e^{-\beta G_{id}(\lambda)} = e^{-\beta G_0} \int du e^{-\lambda \cdot u} = e^{-\beta G_0} I_0(\lambda) \]

magnetization

\[ m = \frac{\partial (\beta G)}{\partial \lambda} = \frac{l_1(\lambda)}{l_0(\lambda)} \]
Tutorial example

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Tutorial example: ideal contribution to entropy

entropy

\[ S(m) = S_0 + \beta G - k_B \lambda \cdot m \]

expansion for weak ordering:
\[ \beta (G - G_0) \approx -\lambda^2 / 4 + \lambda^4 / 64 + \ldots \]

\[ \Rightarrow S_{id}(m) \approx S_0 - m^2 - m^4 / 4 - 5m^6 / 36 + \ldots \]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

**Thermodynamic Integration**

**Tutorial example: ideal contribution to entropy**

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Thermodynamic Integration

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Thermodynamic Integration

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Thermodynamic Integration

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Thermodynamic Integration

example: Landau-de Gennes free energy for Liquid Crystals
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

example: Landau-de Gennes free energy for Liquid Crystals

- system of $N$ hard, prolate particles
- orientations $\mathbf{u}_i$
- orientational order parameter
  \[ S_2 = \langle P_2(\mathbf{u}_i \cdot \mathbf{n}) \rangle \]
- Monte-Carlo simulations in generalized canonical ensemble
- thermodynamic integration:
  \[ \mathcal{F} = F_0 - \int \lambda dS_2 \]
- reconstructed free energy
  \[ \mathcal{F} = \mathcal{F}^{id} - aS_2 - bS_2^2 \]

[A. Luo, L. Sagis, PI, JCP 2014]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

example: random walk

- 3d random walk of $N$ steps $Q_1, \ldots, Q_N$, each of size $b$
- end-to-end vector $R = \sum_{i=1}^{N} Q_i$
- collective variable $x = \{M_1, \ldots, M_6\} = \langle RR \rangle$
- $\rho(Q) = \rho_0 \exp \left[-R \cdot \Lambda \cdot R - \lambda_0\right]$
- identify $\Lambda = -\frac{3}{2Nb^2} I + \frac{1}{2} x^{-1}$
- QE entropy: $S^*(x) = \frac{1}{2} \ln \det x - \frac{1}{2Nb^2} tr(x)$
  “entropy spring” potential
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

eexample: entropic spring for unentangled polymers
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

example: entropic spring for unentangled polymers

- bead-spring model of polymer melt
- Monte-Carlo simulations in generalized canonical ensemble
- \( \rho(Q) = \rho_0 \exp \left[ -R \cdot \Lambda \cdot R - \lambda_0 \right] \)
- thermodynamic integration:
  \( S^*(x) = S_{eq} + \int_{x_{eq}}^{x} \Lambda : dx \)
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Thermodynamic Integration

example: entropic spring for unentangled polymers

- bead-spring model of polymer melt
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  \[ S^*(x) = S_{eq} + \int_{x_{eq}}^{x} \mathbf{A} : dx \]

\[ S^* = S^R(l_1, l_3) + \Delta S(l_1) \]

[PI, M. Kröger, JOR 2011]
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   ✓ thermodynamic integration $S^*(x) - S_0^* = \int \lambda_k dx_k$

4. friction matrix $M(x)$
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Fluctuations

\[ \dot{\Pi}_f^\ell(t) = -\frac{\partial}{\partial r_\alpha} e^{iQCL} \hat{\tau}_\alpha \approx -\frac{\partial}{\partial r_\alpha} \hat{\tau}_\alpha(t) \text{ and } \dot{\Pi}_f^\varepsilon(t) \approx -\frac{\partial}{\partial r_\alpha} \hat{\tau}_\alpha(t) \]

\[ \hat{\tau}_\alpha(t) = \frac{1}{2l} \sum_{<i,j>}(\tilde{l}_i + \tilde{l}_j)r_{ij}F_{ij} \int_0^1 ds \chi(r - r_i + sr_{ij}) \]

\[ M_{\ell\ell}(r, r') = \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r'_\beta} \frac{1}{k_B} \int_0^{\tau_s} dt \langle \hat{\tau}_\alpha(r, t) \hat{\tau}_\beta(r', 0) \rangle_x \]

\[ M_{\varepsilon\varepsilon}(r, r') = \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r'_\beta} \frac{1}{k_B} \int_0^{\tau_s} dt \langle \hat{\tau}_\alpha^f(r, t) \hat{\tau}_\beta^f(r', 0) \rangle_x \]
approximate $\dot{\Pi}_f(t) = -\frac{\partial}{\partial r_\alpha} e^{iQ\mathcal{L}t} \hat{\tau}_\alpha \approx -\frac{\partial}{\partial r_\alpha} \hat{\tau}_\alpha(t)$ and $\dot{\Pi}_f(t) \approx -\frac{\partial}{\partial r_\alpha} \hat{j}_\alpha(t)$ with $\hat{j}_\alpha(t) = \frac{1}{2l} \sum_{<i,j>} (\tilde{l}_i + \tilde{l}_j) r_{ij} F_{ij} \int_0^1 ds \chi(r - r_i + sr_{ij})$

\[
\begin{align*}
M_{\ell\ell}(r, r') &= \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r'_\beta} \frac{1}{k_B} \int_0^{\tau_s} dt \langle \hat{\tau}_\alpha(r, t) \hat{\tau}_\beta(r', 0) \rangle_x \\
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\end{align*}
\]
Macroscopic balance equations

On macro scales: correlations are short-range in space $\Rightarrow$ locality

\[
\frac{\partial}{\partial t} \varepsilon = \frac{\partial^2}{\partial r^2} \kappa \frac{1}{T} \\
\frac{\partial}{\partial t} \ell = \frac{\partial^2}{\partial r^2} \Gamma \lambda
\]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Friction Matrix

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Friction Matrix

Correlated fluctuations

\[ M_{mm}(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B} D(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r}) \]

\[ D(\mathbf{r}) = \sum_i D(\mathbf{r}_i) \chi(\mathbf{r} - \mathbf{r}_i), \quad D(\mathbf{r}_i) = \int_0^{\tau_s} dt \left\langle \dot{u}_i(t) \dot{u}_i(0) \right\rangle \]

\[ M_{m\alpha \varepsilon}(\mathbf{r}, \mathbf{r}') = -\frac{\partial}{\partial \mathbf{r}_{\mu}} \int_0^{\tau_s} dt \left\langle \sum_i \dot{u}_i, \alpha(t) J_{\mu}^f (\mathbf{r}', 0) \right\rangle \]
Towards constitutive equations of complex fluids derived from thermodynamically guided molecular simulations

Correlated fluctuations

\[ M_{mm}(r, r') = \frac{1}{k_B} D(r) \delta(r' - r) \]

\[ D(r) = \sum_i D(r_i) \chi(r - r_i), \quad D(r_i) = \int_0^{\tau_s} dt \langle \dot{u}_i(t) \dot{u}_i(0) \rangle \]

\[ M_{m\alpha\varepsilon}(r, r') = -\frac{\partial}{\partial r'_\mu} \int_0^{\tau_s} dt \langle \sum_i \dot{u}_{i,\alpha}(t) \dot{j}_\mu^f(r', 0) \rangle \]

\[ \Rightarrow \partial_t m = \Omega \times m + D \cdot \lambda - \nabla \cdot A \frac{1}{T} \]
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example: rigid ellipsoids in 2d

[A. Luo, L.M.C. Sagis, H.C. Öttinger, C. De Michele, PI, 2015]
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Friction Matrix

equation: rigid ellipsoids in 2d

Theoretical expectation:

\[
(M_{\text{rot}})_{ijkl} = \frac{1}{k_B n_p \tau_{\text{rot}}} \left( C_{ik} \delta_{jl} + C_{il} \delta_{jk} + C_{jl} \delta_{ik} + C_{jk} \delta_{il} - 4 C_{ijkl}^{(4)} \right)
\]

[A. Luo, L.M.C. Sagis, H.C. Öttinger, C. De Michele, PI, 2015]
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example: polymer melts

perform nonequilibrium MD simulations
choose gyration tensor as collective variable $x = \langle \Pi \rangle$

analyze fluctuations of $\Pi$:

$$F_k(t) = e^{QiLt}QiL\Pi_k$$

$$\approx \dot{\Pi}_k(t) - \dot{x}_k(t), \quad t \leq \tau_s$$

$$M_{kj}(x) = \int_0^{\tau_s} ds \langle F_k(0)F_j(s) \rangle_x$$

[PI, M. Kröger, H.C. Ottinger, 2009]
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**Friction Matrix**

**hybrid simulations**

non-equilibrium stationary state:
Monte-Carlo simulations in relevant ensemble $\rho^* = \rho_0 e^{-\lambda_k \Pi_k}$

known analytically

\[ \langle \{ \Pi_k, H \} \rangle = -M_{kj} \lambda_j \]

determine $\lambda$ consistently!

non-equilibrium molecular dynamics

\[ M_{kj}(x) = \int_0^{\tau_s} ds \langle F_k(0)F_j(s) \rangle_x \]

[PI, M. Kröger, H.C. Öttinger, 2009]
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Friction Matrix

results
Open questions

- how successful is this approach for different systems?
- how-to identify collective variables?
- better approximation for friction matrix?
- what to do if time-scale separation does not hold?