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

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thanks to: M. Kröger, H.C. Öttinger

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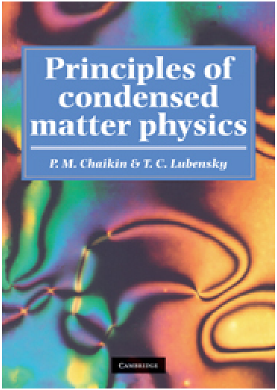
Tutorial Example

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



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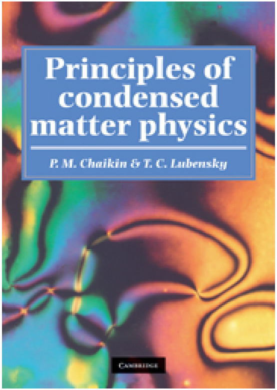
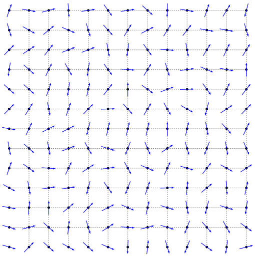


Tutorial Example: XY model

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

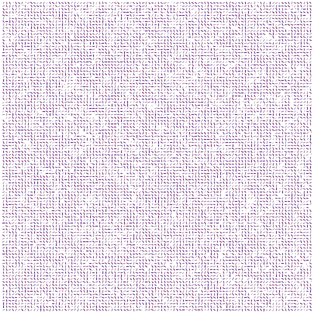
$$\mathcal{H}(z) = \sum_{j=1}^{N} \frac{l_j^2}{2I} - \frac{J}{2} \sum_{<i,j>} \cos(\theta_i - \theta_j)$$



Tutorial Example: XY model dynamics

Hamilton's equations of motion:

$$\begin{aligned}\dot{\theta}_j &= \frac{\partial \mathcal{H}}{\partial l_j} = l_j / I \\ \dot{l}_j &= -\frac{\partial \mathcal{H}}{\partial \theta_j} = -J \sum_{k(\mathrm{nn}j)} \sin(\theta_j - \theta_k)\end{aligned}$$



equivalent formulation

$$\frac{\mathrm{d}}{\mathrm{d}t} A(z) = i\mathcal{L}A = \{A, \mathcal{H}\}$$

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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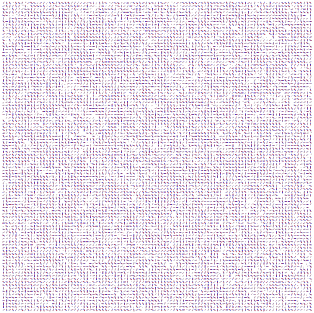

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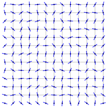
Tutorial Example: Poisson bracket



Properties of *Poisson bracket*

- anti-symmetry

$$\{A, B\} = -\{B, A\}$$

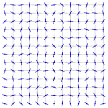
- Leibniz rule

$$\{AB, C\} = A\{B, C\} + \{A, C\}B$$

- Jacobi-identity

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$$

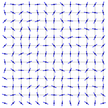
Tutorial Example: conservation laws



Fixed lattice ⇒ only 2 conserved quantities

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

Tutorial Example: choice of collective variables



On macroscopic scales, most disturbances decay rapidly to equilibrium.

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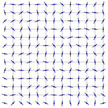

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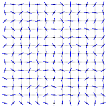

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- broken-symmetry variables

That's all for our tutorial example.

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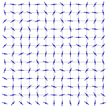

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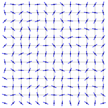

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Tutorial Example: densities of conserved quantities

define macroscopic fields

$$\varepsilon(\mathbf{r},t) = \langle \Pi_\varepsilon(\mathbf{r},t)\rangle, \quad \ell(\mathbf{r},t) = \langle \Pi_\ell(\mathbf{r},t)\rangle$$

with mappings $\Pi_k : z \mapsto \Pi_k$

$$\Pi_\varepsilon(\mathbf{r},t) = \sum_{j=1}^{N} \left(\frac{l_j^2}{2I} - \frac{J}{2} \sum_{i\,(\mathrm{nn}j)} \cos(\theta_{ij}) \right) \chi(\mathbf{r}-\mathbf{r}_j) = \sum_{j=1}^{N} \varepsilon_j \chi(\mathbf{r}-\mathbf{r}_j)$$

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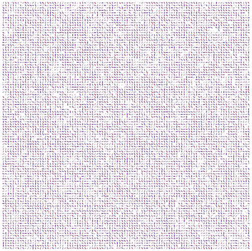

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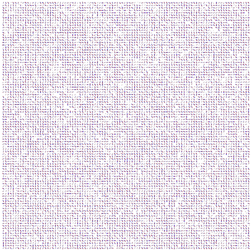

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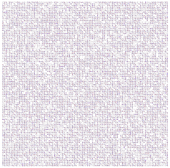

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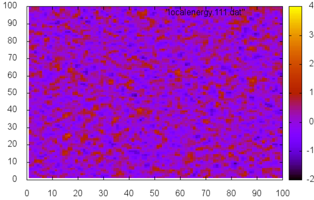
$\Pi \ \Downarrow$

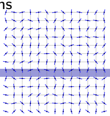


Tutorial Example: time evolution of mapping

direct calculation:

$$\begin{aligned}
\dot{\Pi}_\ell(\mathbf{r},t) &= \{\Pi_\ell(\mathbf{r},t),\mathcal{H}\} \\
&= -\sum_j \frac{\partial \mathcal{H}}{\partial \theta_j}\chi(\mathbf{r}-\mathbf{r}_j) = -J\sum_{<i,j>}\sin(\theta_i-\theta_j)\chi(\mathbf{r}-\mathbf{r}_j) \\
&= -\frac{J}{2}\sum_{<i,j>}\sin(\theta_i-\theta_j)\left(\chi(\mathbf{r}-\mathbf{r}_j)-\chi(\mathbf{r}-\mathbf{r}_i)\right)
\end{aligned}$$

Use identity $\chi(\mathbf{r}-\mathbf{r}_j)-\chi(\mathbf{r}-\mathbf{r}_i) = -\frac{\partial}{\partial \mathbf{r}}\cdot\int_0^1 \mathrm{d}s\, \mathbf{r}_{ij}\chi(\mathbf{r}-\mathbf{r}_i+s\mathbf{r}_{ij})$



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⇒ find form of (instantaneous) local conservation law

$$\begin{aligned}
\dot{\Pi}_\ell(\mathbf{r},t) &= -\frac{\partial}{\partial\mathbf{r}}\cdot\hat{\tau}(\mathbf{r},t) \\
\hat{\tau}(\mathbf{r},t) &= \frac{J}{2}\sum_{<i,j>}\mathbf{r}_{ij}\sin(\theta_{ij})\int_0^1 \mathrm{d}s\,\chi(\mathbf{r}-\mathbf{r}_i+s\mathbf{r}_{ij})
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$\Rightarrow$ find form of (instantaneous) local conservation law

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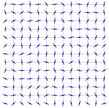

Similar calculation for the energy density gives

$$
\begin{aligned}
\dot{\Pi}_\varepsilon(\mathbf{r},t) &= -\frac{\partial}{\partial \mathbf{r}} \cdot \hat{\jmath}(\mathbf{r},t) \\
\hat{\jmath}(\mathbf{r},t) &= \frac{J}{2I} \sum_{<i,j>} (I_i + I_j)\mathbf{r}_{ij} \sin(\theta_{ij}) \int_0^1 \mathrm{d}s\, \chi(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij})
\end{aligned}
$$

Tutorial Example: closed-form equations?

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, $> 1\mu$s] impossible without multiscale modeling."
- "... progress is coming more through refined simulations than from increased computational power."

Statistical Mechanics: bridge to macro

- 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.

Microscopic dynamics

- microstate $z \in \Gamma \subset IR^n$
- probability density $\rho(z;t)$
  with $\rho(z;t) \geq 0$, $\int_\Gamma \mathrm{d}z\, \rho(z;t) = 1$.
- microscopic dynamics (e.g. Liouville, Fokker-Planck)

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

- averages: $\langle A \rangle(t) = \int_\Gamma \mathrm{d}z\, A(z)\rho(z;t)$

Collective variables and closure problem

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

$$x_k(t) = \int_\Gamma \mathrm{d}z\, \Pi_k(z)\rho(z;t), \quad k = 1, \ldots, n$$

- but no closed-form equations for moments

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}x_k &= \int_\Gamma \mathrm{d}z\, \Pi_k(z)(-i\mathcal{L})\rho(z;t) \\ &= G_k(x_1, \ldots, x_n, x_{n+1}, \ldots)\end{aligned}$$

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.

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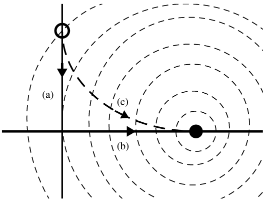
- choose “relevant” density $\rho^* = \rho^*_x$ to capture coarse-grained state
- manifold $\{\rho^*_x\}$ hopefully “slow”



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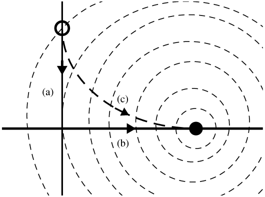

maximum entropy distribution

- entropy functional $S[\rho] = -\int_\Gamma \mathrm{d}z\, \rho \ln(\rho/\rho_0)$
- maximum entropy principle

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

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- solution: quasi-equilibrium (generalized canonical) distribution

$$\begin{aligned}\rho^*(z) &= \rho_0(z)\exp\left[-\lambda_k \Pi_k(z) + \beta G(\lambda)\right] \\ x_k^* &= \int_\Gamma \mathrm{d}z\,\Pi_k(z)\rho^*(z)\end{aligned}$$

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[Gibbs; Jaynes; Grad, etc.]

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Generating function

normalization of probability density:

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

macro variables from derivative

$$\frac{\partial(\beta G)}{\partial \lambda_k} = \int \mathrm{d}z \rho^*(z) \Pi_k(z) = x_k$$

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Quasi-equilibrium entropy

define

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

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insert definition:

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

with $S_0 = \mathrm{const.}$ for $\rho_0 = \mathrm{const.}$
and $S_0 = \beta(F_0 - E)$ if ρ_0 canonical.

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Thus, S is Legendre transform of G and

- Lagrange multipliers as dual variables

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Tutorial Example: statistical mechanics

relevant ensemble: generalized canonical distribution

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

β, λ: Lagrange multipliers conjugate to the collective variables,

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

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

$$S[\varepsilon, \ell] = k_{\mathrm{B}} \ln \Xi + k_{\mathrm{B}} \int \mathrm{d}^d r \, \beta(\mathbf{r})\varepsilon(\mathbf{r}) + k_{\mathrm{B}} \int \mathrm{d}^d r \, \lambda(\mathbf{r})\ell(\mathbf{r})$$

with

$$\left(\frac{\delta S}{\delta \varepsilon(\mathbf{r})}\right)_{\ell} = \frac{1}{T(\mathbf{r})}, \quad \left(\frac{\delta S}{\delta l(\mathbf{r})}\right)_{\varepsilon} = k_{\mathrm{B}} \lambda(\mathbf{r})$$

maximum entropy closures

- closed equations !

$$\frac{\mathrm{d}}{\mathrm{d}t} x_k^* = \int_\Gamma \mathrm{d}z \, \Pi_k(z)(-i\mathcal{L})\rho^*$$

- are we done?

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- maximum entropy closure conserves type of dynamics

$$\frac{\mathrm{d}}{\mathrm{d}t}S^* = \frac{\mathrm{d}}{\mathrm{d}t}S[\rho]\Big|_{\rho^*}$$

[Gorban, Karlin, 1992]

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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?

Mori-Zwanzig approach

- $z = \{\mathbf{p}, \mathbf{r}\} \in \Gamma$
- phase space density $\rho(z; t)$
- Liouville equation $\partial_t \rho = -i\mathcal{L}\rho$
- Liouville operator
  $i\mathcal{L}A = \{A, H\} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial H}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial H}{\partial \mathbf{r}_i} \right)$

Heisenberg picture of classical mechanics

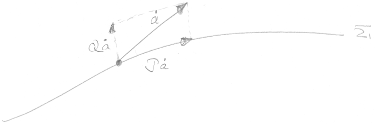
- formal solution ($\mathcal{L}$ not explicitly time-dependent)
  $\rho(z;t) = e^{-i\mathcal{L}t}\rho(z;0)$
- averages: time-dependent observables

$$
\begin{aligned}
\langle A\rangle(t) &= \int_\Gamma \mathrm{d}z\, A(z)\rho(z;t) \\
&= \int_\Gamma \mathrm{d}z\, A(z)e^{-i\mathcal{L}t}\rho(z;0) \\
&= \int_\Gamma \mathrm{d}z\, \rho(z;0)e^{i\mathcal{L}t}A(z) \\
\Rightarrow A(z;t) &= e^{i\mathcal{L}t}A(z)
\end{aligned}
$$

decomposing the dynamics

$$
\begin{aligned}
a(t) = \langle A\rangle(t) \Rightarrow \dot{a}(t) &= \frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle(t) \\
&= \int_\Gamma \mathrm{d}z\,\rho(z;0)\,i\mathcal{L}e^{i\mathcal{L}t}A(z)
\end{aligned}
$$

define projectors $\mathcal{P}, \mathcal{Q} = I - \mathcal{P}$
(with $\mathcal{P}^2 = \mathcal{P}, \mathcal{Q}^2 = \mathcal{Q}, \mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$)



Duhamel-Dyson identity

$$\frac{\mathrm{d}}{\mathrm{d}t}A = e^{i\mathcal{L}t} i\mathcal{L}A = e^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}A + O_A$$

projected dynamics: hopefully slow

orthogonal dynamics: $O_A = e^{i\mathcal{L}t}\mathcal{Q}i\mathcal{L}A$

rewrite O_A using Duhamel-Dyson relation

$$e^{i\mathcal{L}t} = e^{\mathcal{Q}i\mathcal{L}t} + \int_0^t \mathrm{d}s\, e^{i\mathcal{L}(t-s)}\mathcal{P}i\mathcal{L}e^{\mathcal{Q}i\mathcal{L}s}$$

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equation of motion: exact

projection operator approach uses operator identity

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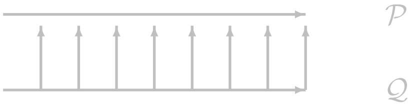
choose $A = \Pi_k$

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\Pi_k &= e^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}\Pi_k + \int_0^t \mathrm{d}s\, e^{i\mathcal{L}(t-s)}\mathcal{P}i\mathcal{L}F_k(s) + F_k(t) \\ F_k(t) &= e^{\mathcal{Q}i\mathcal{L}t}\mathcal{Q}i\mathcal{L}\Pi_k \end{aligned}$$



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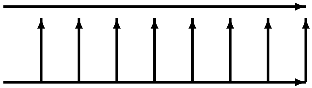

$\mathcal{P}$

$\mathcal{Q}$

choice of projector

here: [H. Grabert, 1982]

$$
\begin{aligned}
\mathcal{P}A &= \int_\Gamma \mathrm{d}z\, \rho^*(z)A(z) + (x_j - \Pi_j) \int_\Gamma \mathrm{d}z\, \frac{\partial \rho^*}{\partial x_j} A(z) \\
e^{i\mathcal{L}t}\mathcal{P}A &= \int_\Gamma \mathrm{d}z\, \rho^*_{x(t)}(z)A(z) + (x_j - \Pi_j) \int_\Gamma \mathrm{d}z\, \frac{\partial \rho^*}{\partial x_j(t)} A(z)
\end{aligned}
$$

note: other choices (Robertson, etc.) lead to same equations for averages

exact, non-Markovian time evolution

use generalized canonical ensemble for ρ^*

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} x_k &= v_k + \int_0^t \mathrm{d}s\, K_{kj}(t,s)\lambda_j(t-s) \\
v_k &= \langle\{\Pi_k, H\}\rangle_{x(t)} \quad \text{deterministic drift} \\
K_{kj}(t,s) &= \langle F_k(0)F_j(s)\rangle_{x(t-s)} \quad \text{memory kernel} \\
F_k(t) &= e^{\mathcal{Q}i\mathcal{L}t}\mathcal{Q}i\mathcal{L}\Pi_k \quad \text{“random force”} \\
\lambda_j &= \frac{\partial S^*}{\partial x_j}
\end{aligned}
$$

[H. Mori 1965, R. Zwanzig 1961]

Markovian approximation

crucial assumption: separation of time scales.
collective variables: slowly evolving ($\gg \tau_\mathrm{s}$)
fast fluctuations ($\ll \tau_\mathrm{s}$) $\Rightarrow$ short memory $\Rightarrow$ Markovian approximation

$$
\begin{aligned}
\int_0^t \mathrm{d}s\, K_{kj}(t,s)\, \frac{\partial S^*}{\partial x_j}\bigg|_{x(t-s)} &\approx M_{kj}(x(t))\, \frac{\partial S^*}{\partial x_j}\bigg|_{x(t)} \\
M_{kj}(x) &= \int_0^{\tau_\mathrm{s}} \mathrm{d}s\, \langle F_k(0) F_j(s) \rangle
\end{aligned}
$$

$$
\boxed{\frac{\mathrm{d}}{\mathrm{d}t} x_k = \langle \{ \Pi_k, H \} \rangle + M_{kj} \frac{\partial S^*}{\partial x_j}}
$$

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

4 tasks for coarse grainers

Coarse-graining program has to meet four tasks

1. choice of collective variables x, mapping Π
2. deterministic drift v_k
3. entropy $S^*(x)$
4. friction matrix M

Macroscopic Poisson bracket

deterministic drift:

$$v_k = \langle \{\Pi_k, H\} \rangle_{x(t)}$$

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

$$\begin{aligned} \langle \{\Pi_k, H\} \rangle &= L_{kj} \frac{\partial E}{\partial x_j} \\ L_{kj} &= \langle \{\Pi_k, \Pi_j\} \rangle \quad \text{anti-symmetric} \end{aligned}$$

and the powerful GENERIC structure emerges

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t} x_k = L_{kj} \frac{\partial E}{\partial x_j} + M_{kj} \frac{\partial S^*}{\partial x_j}}$$

[M. Grmela, H.C. Öttinger (1997)]

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

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

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Back to our tutorial example

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

Thus,

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

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insert:

$$v_\varepsilon(\mathbf{r}, t) = -\frac{\partial}{\partial \mathbf{r}} \cdot \langle \hat{\boldsymbol{\jmath}}(\mathbf{r}, t) \rangle_x, \quad v_\ell(\mathbf{r}, t) = -\frac{\partial}{\partial \mathbf{r}} \cdot \langle \hat{\boldsymbol{\tau}}(\mathbf{r}, t) \rangle_x$$

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Include Magnetization

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

$$\Pi_{\mathbf{m}}(\mathbf{r},t) = \sum_{j=1}^{N} \mathbf{u}_j \chi(\mathbf{r}-\mathbf{r}_j) = \sum_{j=1}^{N} \begin{pmatrix} \sin\theta_j \\ \cos\theta_j \end{pmatrix} \chi(\mathbf{r}-\mathbf{r}_j)$$

with $\mathbf{m} = \langle \Pi_{\mathbf{m}} \rangle$ the macroscopic magnetization.

Note: $\mathbf{m}$ is NOT a conserved quantity.

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Need to find the deterministic drift for the magnetization

$$v_{\mathbf{m}}(\mathbf{r}) = \int \mathrm{d}r' \, L_{\mathbf{m},\varepsilon}(\mathbf{r},\mathbf{r}')$$

$$\begin{aligned} L_{\mathbf{m},\varepsilon}(\mathbf{r},\mathbf{r}') &= \langle\{\Pi_{\mathbf{m}}(\mathbf{r}),\Pi_{\varepsilon}(\mathbf{r}')\}\rangle \\ &= \langle\sum_j \begin{pmatrix} \cos\theta_j \\ \sin\theta_j \end{pmatrix} \frac{I_j}{I}\chi(\mathbf{r}-\mathbf{r}_j)\chi(\mathbf{r}'-\mathbf{r}_j)\rangle \end{aligned}$$

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Averages over angular momenta can be done analytically:

$$L_{\mathbf{m},\varepsilon}(\mathbf{r}, \mathbf{r}') = \boldsymbol{\Omega}(\mathbf{r}) \times \mathbf{m}(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r})$$

with $\boldsymbol{\Omega}(\mathbf{r}) = (0, 0, \omega(\mathbf{r}))$ and $\omega(\mathbf{r}) = I^{-1}\ell(\mathbf{r}) = \lambda(\mathbf{r})/\beta(\mathbf{r})$.

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Tutorial example

generating function

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

ideal orientational contribution

$$e^{-\beta G_{\mathrm{id}}(\lambda)} = e^{-\beta G_0} \int \mathrm{d}\mathbf{u}\, e^{-\boldsymbol{\lambda}\cdot\mathbf{u}} = e^{-\beta G_0} I_0(\lambda)$$

magnetization

$$m = \frac{\partial(\beta G)}{\partial \lambda} = \frac{I_1(\lambda)}{I_0(\lambda)}$$

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Tutorial example: ideal contribution to entropy

entropy

$$S(m) = S_0 + \beta G - k_{\mathrm{B}} \boldsymbol{\lambda} \cdot \mathbf{m}$$

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

$$\Rightarrow S_{\mathrm{id}}(m) \approx S_0 - m^2 - m^4/4 - 5m^6/36 + \ldots$$

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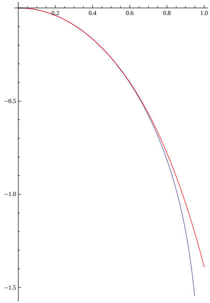

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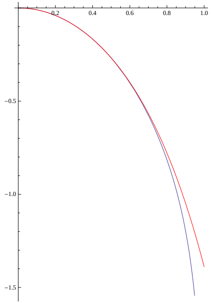


Tutorial example: ideal contribution to entropy

entropy

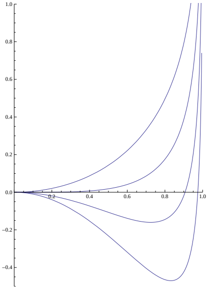
$$S(m) = S_0 + \beta G - k_{\mathrm{B}} \boldsymbol{\lambda} \cdot \mathbf{m}$$

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

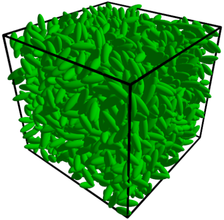
$$\Rightarrow S_{\mathrm{id}}(m) \approx S_0 - m^2 - m^4/4 - 5m^6/36 + \ldots$$

$\Rightarrow S_{\mathrm{id}}(m)$ is NOT quadratic, diverges near perfectly ordered state!

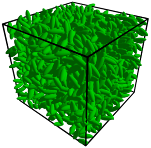
$\Rightarrow$ recover $S = S_{\mathrm{id}} + S_{\mathrm{exc}}$ numerically from thermodynamic integration
(or mean-field calculation).



example: Landau-de Gennes free energy for Liquid Crystals

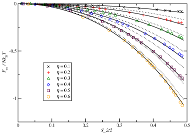


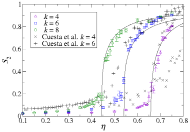
example: Landau-de Gennes free energy for Liquid Crystals



- 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:
  $\mathcal{F} = F_0 - \int \lambda \mathrm{d} S_2$
- reconstructed free energy

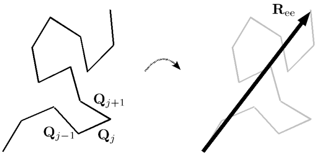
$$\mathcal{F} = \mathcal{F}^{\mathrm{id}} - aS_2 - bS_2^2$$





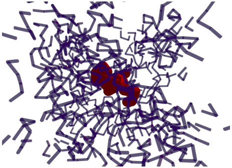
[A. Luo, L. Sagis, PI, JCP 2014]

example: random walk

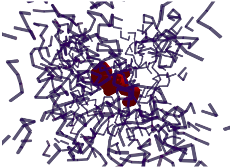


- 3d random walk of N steps $\mathbf{Q}_1, \ldots, \mathbf{Q}_N$, each of size b
- end-to-end vector $\mathbf{R} = \sum_{i=1}^{N} \mathbf{Q}_i$.
- collective variable $\mathbf{x} = \{M_1, \ldots, M_6\} = \langle \mathbf{R}\mathbf{R} \rangle$
- $\rho(\mathbf{Q}) = \rho_0 \exp\left[-\mathbf{R} \cdot \mathbf{\Lambda} \cdot \mathbf{R} - \lambda_0\right]$
- identify $\mathbf{\Lambda} = -\frac{3}{2Nb^2}\mathbf{1} + \frac{1}{2}\mathbf{x}^{-1}$
- QE entropy: $S^*(\mathbf{x}) = \frac{1}{2}\ln\det\mathbf{x} - \frac{1}{2Nb^2}\mathrm{tr}(\mathbf{x})$
  "entropy spring" potential

example: entropic spring for unentangled polymers



example: entropic spring for unentangled polymers



- bead-spring model of polymer melt
- Monte-Carlo simulations in generalized canonical ensemble
- $\rho(\mathbf{Q}) = \rho_0 \exp\left[-\mathbf{R}\cdot\boldsymbol{\Lambda}\cdot\mathbf{R} - \lambda_0\right]$
- thermodynamic integration: $S^*(\mathbf{x}) = S_{\mathrm{eq}} + \int_{x_{\mathrm{eq}}}^{\mathbf{x}} \boldsymbol{\Lambda} \colon \mathrm{d}\mathbf{x}$

example: entropic spring for unentangled polymers

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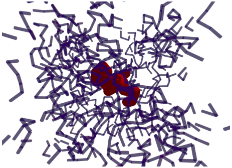
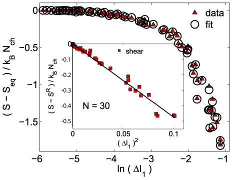




$S^* = S^{\mathrm{R}}(I_1, I_3) + \Delta S(I_1)$

[PI, M. Kröger, JOR 2011]

4 tasks for coarse grainers

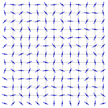
Coarse-graining program has to meet four tasks

1. choice of collective variables, mapping
2. deterministic drift:
   - ✓ macroscopic energy $E(x)$.
   - ✓ macroscopic Poisson bracket

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

3. entropy $S^*(x)$
   - ✓ thermodynamic integration $S^*(x) - S^*_0 = \int \lambda_k \mathrm{d}x_k$
4. friction matrix $M(x)$

Fluctuations

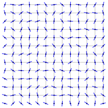


approximate $\dot{\Pi}^{\mathrm{f}}_{\ell}(t) = -\frac{\partial}{\partial r_\alpha} e^{i\mathcal{Q}\mathcal{L}t}\hat{\tau}_\alpha \approx -\frac{\partial}{\partial r_\alpha}\hat{\tau}_\alpha(t)$ and $\dot{\Pi}^{\mathrm{f}}_{\varepsilon}(t) \approx -\frac{\partial}{\partial r_\alpha}\hat{\jmath}^{\mathrm{f}}_\alpha(t)$ with $\hat{\jmath}^{\mathrm{f}}_\alpha(t) = \frac{1}{2I}\sum_{<i,j>}(\tilde{l}_i + \tilde{l}_j)\mathbf{r}_{ij}F_{ij}\int_0^1 \mathrm{d}s\,\chi(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij})$

$$M_{\ell\ell}(\mathbf{r},\mathbf{r}') = \frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r'_\beta}\frac{1}{k_{\mathrm{B}}}\int_0^{\tau_{\mathrm{s}}} \mathrm{d}t\,\langle\hat{\tau}_\alpha(\mathbf{r},t)\hat{\tau}_\beta(\mathbf{r}',0)\rangle_x$$

$$M_{\varepsilon\varepsilon}(\mathbf{r},\mathbf{r}') = \frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r'_\beta}\frac{1}{k_{\mathrm{B}}}\int_0^{\tau_{\mathrm{s}}} \mathrm{d}t\,\langle\hat{\jmath}^{\mathrm{f}}_\alpha(\mathbf{r},t)\hat{\jmath}^{\mathrm{f}}_\beta(\mathbf{r}',0)\rangle_x$$

Fluctuations



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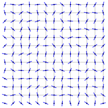
Macroscopic balance equations



On macro scales: correlations are short-range in space ⇒ locality

$$
\begin{aligned}
\frac{\partial}{\partial t}\varepsilon &= \frac{\partial^2}{\partial \mathbf{r}^2}\kappa\frac{1}{T} \\
\frac{\partial}{\partial t}\ell &= \frac{\partial^2}{\partial \mathbf{r}^2}\Gamma\lambda
\end{aligned}
$$

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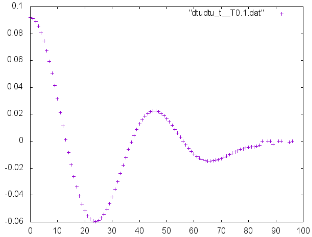
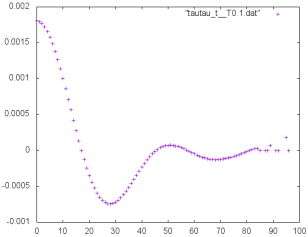
Correlated fluctuations

$$M_{\mathbf{mm}}(\mathbf{r},\mathbf{r}') = \frac{1}{k_{\mathrm{B}}}\mathbf{D}(\mathbf{r})\delta(\mathbf{r}'-\mathbf{r})$$

$$\mathbf{D}(\mathbf{r}) = \sum_i \mathbf{D}(\mathbf{r}_i)\chi(\mathbf{r}-\mathbf{r}_i), \quad \mathbf{D}(\mathbf{r}_i) = \int_0^{\tau_{\mathrm{s}}} \mathrm{d}t\, \langle \dot{\mathbf{u}}_i(t)\dot{\mathbf{u}}_i(0)\rangle$$

$$M_{m_\alpha\varepsilon}(\mathbf{r},\mathbf{r}') = -\frac{\partial}{\partial r'_\mu}\int_0^{\tau_{\mathrm{s}}} \mathrm{d}t\, \langle \sum_i \dot{u}_{i,\alpha}(t)\hat{\jmath}^{\mathrm{f}}_\mu(\mathbf{r}',0)\rangle$$





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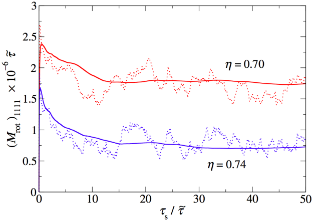
\Rightarrow \partial_t \mathbf{m} &= \boldsymbol{\Omega}\times\mathbf{m} + \mathbf{D}\cdot\boldsymbol{\lambda} - \nabla\cdot\mathbf{A}\frac{1}{T}
\end{aligned}
$$

example: rigid ellipsoids in 2d

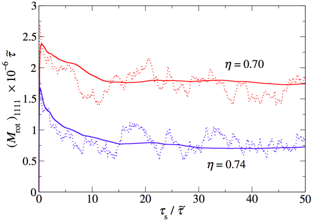


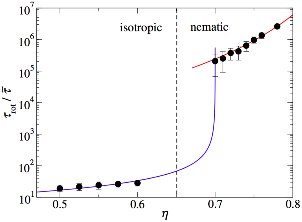
[A. Luo, L.M.C. Sagis, H.C.Öttinger, C. De Michele, PI, 2015]

example: rigid ellipsoids in 2d

theoretical expectation:

$$(M_{\mathrm{rot}})_{ijkl} = \frac{1}{k_{\mathrm{B}} n_{\mathrm{p}} \tau_{\mathrm{rot}}} (C_{ik}\delta_{jl} + C_{il}\delta_{jk} + C_{jl}\delta_{ik} + C_{jk}\delta_{il} - 4C^{(4)}_{ijkl})$$

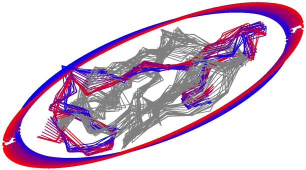




[A. Luo, L.M.C. Sagis, H.C.Öttinger, C. De Michele, PI, 2015]

example: polymer melts

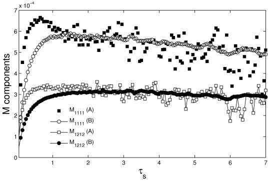
perform nonequilibrium MD simulations
choose gyration tensor as collective variable $\mathbf{x} = \langle \mathbf{\Pi} \rangle$



analyze fluctuations of Π:

$$F_k(t) = e^{\mathcal{Q}i\mathcal{L}t}\mathcal{Q}i\mathcal{L}\Pi_k \approx \dot{\Pi}_k(t) - \dot{x}_k(t), \quad t \leq \tau_{\rm s}$$

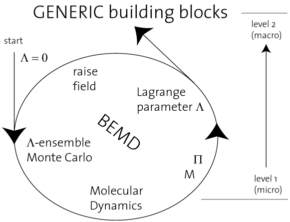
$$M_{kj}(x) = \int_0^{\tau_{\rm s}} \mathrm{d}s \, \langle F_k(0) F_j(s) \rangle_x$$



[PI, M. Kröger, H.C.Öttinger, 2009]

hybrid simulations

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



known analytically

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

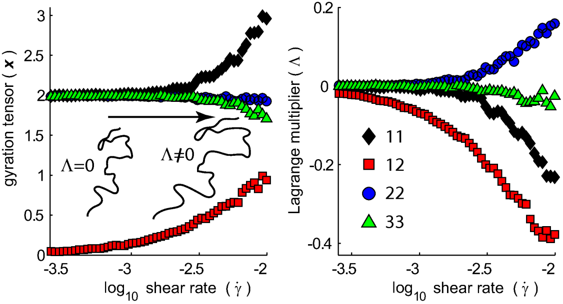
determine λ consistently!

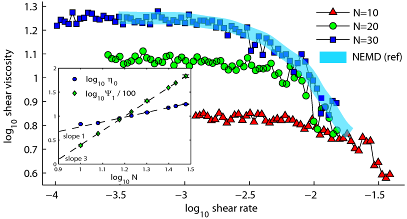
non-equilibrium molecular dynamics

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

[PI, M. Kröger, H.C. Öttinger, 2009]

results


gyration tensor (x)
Λ=0
Λ≠0
log10 shear rate (γ̇)
Lagrange multiplier (Λ)
11
12
22
33
log10 shear rate (γ̇)


log10 shear viscosity
N=10
N=20
N=30
NEMD (ref)
log10 η0
log10 Ψ1 / 100
slope 1
slope 3
log10 N
log10 shear rate

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??