Stochastic molecular dynamics

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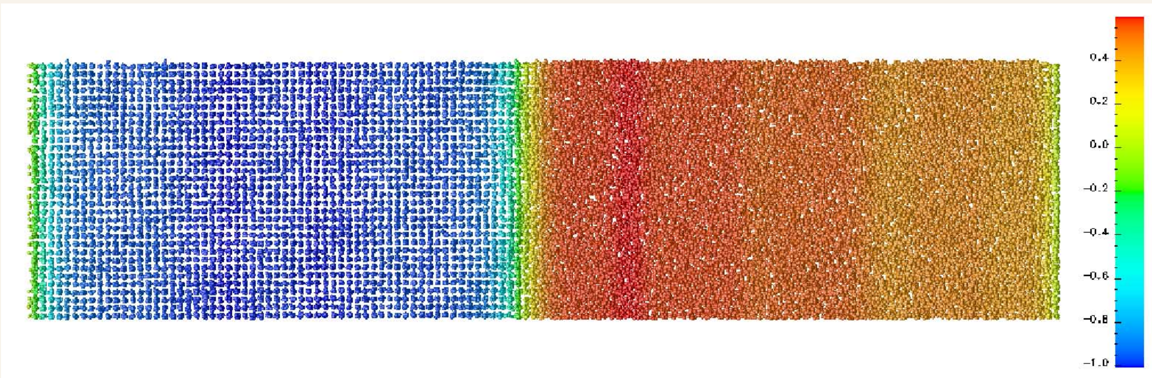


Which MD ?

Which MD?

MD (NVE):

$$\ddot{X}_t = -\lambda'(X_t)$$

What is λ?

NVT:

Langevin:

$$\ddot{X}_t = -\lambda'(X_t) - K\dot{X}_t + (2KT)^{1/2}\dot{W}_t$$

$$\lambda = ?$$

$$K = ?$$

Stochastics in Schrödinger?

Usually: coupling to external heat bath

Here:

- time-independent Schrödinger as Hamiltonian system
- Gibbs measure for Schrödinger Hamiltonian system

Results:

- initial Gibbs electrons derived
- spectral gaps and low temperature
  $\Longrightarrow$ Langevin, with certain K, approximates nuclei

Plan:

- Time-independent Schrödinger as Hamiltonian system
- Born-Oppenheimer and Ehrenfest molecular dynamics
- Zwanzig's model almost Ehrenfest
- Derivation of Gibbs measure
- Two theorems: Langevin approximates Ehrenfest

1.Time-independent Schrödinger as Hamiltonian system

Schrödinger: $H(x,X)\Phi(x,X) = E\Phi(x,X)$

$$H(x,X) = V(x,X) - \frac{1}{2M}\sum_{n=1}^{N}\Delta_{X^n}, \quad M \gg 1$$

The WKB-Ansatz

$\Phi(x,X) = \psi(x,X)e^{iM^{1/2}\theta(X)}$ (no caustic: Fourier integral for caustics) implies

$$
\begin{aligned}
&(H-E)\psi e^{iM^{1/2}\theta(X)} \\
&= \Big((\frac{|\theta'|^2}{2} + V - E)\psi \\
&\quad - \frac{i}{M^{1/2}}(\psi' \circ \theta' + \frac{1}{2}\psi\theta'') - \frac{1}{2M}\psi'' \Big) e^{iM^{1/2}\theta},
\end{aligned}
$$

HJ:

$$
0 = \frac{|\theta'(X)|^2}{2} + \frac{\psi \cdot V(X)\psi}{\psi \cdot \psi} - E + \text{h.o.t.}
$$

$$
v \cdot w := \int_{\mathbb{R}^{3J}} v^*(x, X) w(x, X)\, dx
$$

Molecular dynamics Hamiltonian systems

Born-Oppenheimer dynamics $\psi =$ eigenfunction $= \Psi$:

$H_{BO} = \frac{|p|^2}{2} + \lambda(X) - E = 0, \quad$ eigenvalueproblem $\; V\Psi = \lambda\Psi$

$$\dot{X}_t = p_t$$
$$\dot{p}_t = -\lambda'(X_t).$$

Born-Oppenheimer dynamics:

$H_{BO} = \frac{|p|^2}{2} + \lambda(X) - E = 0$, eigenvalueproblem $V\Psi = \lambda\Psi$

$$\begin{aligned}\dot{X}_t &= p_t\\ \dot{p}_t &= -\lambda'(X_t).\end{aligned}$$

Ehrenfest dynamics:

$H_E = \frac{|p|^2}{2} + \frac{\phi\cdot V\phi}{\phi\cdot\phi} - E = 0$,

$$\begin{aligned}\dot{X}_t &= p_t\\ \dot{p}_t &= -\frac{\phi_t \cdot V'(X_t)\phi_t}{\phi_t\cdot\phi_t}\\ i\dot{\phi}_t &= M^{1/2}V\phi_t,\end{aligned}$$

Ehrenfest is Hamiltonian system for $H_E(X, \phi^r; p, \phi^i)$ using

$$\frac{M^{1/2}}{2} = \frac{1}{\phi \cdot \phi}$$

$$\phi = \phi^r + i\phi^i$$

$$p = \partial_X \theta(X, \phi^r)$$

$$\phi^i = \partial_{\phi^r} \theta(X, \phi^r)$$

Modify Hamiltonian to include h.o.t. !

$$
\begin{aligned}
H_S &:= \frac{|\theta'_X(X,\phi_r)|^2}{2} + V_S - E = 0 \\
V_S &:= \frac{M^{1/2}}{2}\left(\phi \cdot V\phi + \frac{G}{2M}\Delta\frac{\phi\cdot\phi}{G}\right) \\
\theta'_X \bullet \partial_X \log G &= \frac{1}{2}\theta'' \\
\phi &= G\psi
\end{aligned}
$$

$$
\begin{aligned}
&(H-E)\psi e^{iM^{1/2}\int \theta'_X(X,\phi_r)dX} \\
&= \Big((\frac{|\theta'_X|^2}{2} + V_S - E)\psi \\
&\quad - \frac{i}{M^{1/2}}(\psi'_X \circ \theta'_X + \frac{1}{2}\psi\theta'') + (V - V_S)\psi - \frac{1}{2M}\psi'' \Big) e^{iM^{1/2}\int \theta'_X(X,\phi_r)dX} \\
&= 0,
\end{aligned}
$$

$$
\begin{aligned}
\dot{X} &= \partial_p H_S = p \\
\dot{p} &= -\partial_X H_S = \frac{M^{1/2}}{2}\big(\phi \cdot V'\phi + \partial_X \frac{G}{2M}\Delta \frac{\phi \cdot \phi}{G}\big) \\
i\dot{\phi} &= M^{1/2}\check{V}\phi
\end{aligned}
$$

$$\check{V}\phi := V\phi - \frac{G}{2M}\Delta_X\frac{\phi}{G}$$

$$\frac{M^{1/2}}{2} = \frac{\int G^{-2}dX}{\int \phi\cdot\phi G^{-2}dX}$$

$$\hat{\psi} = \phi e^{iM^{1/2}\int V_S ds}$$

$$iM^{-1/2}\dot{\hat{\psi}} = (\check{V} - V_S)\hat{\psi}$$

2. Gibbs measure for Schrödinger Hamiltonian system

Zwanzig's model[1]

Idea: Hamiltonian with light (harmonic) and heavy particles

- light particles initially Gibbs
- implies generalized Langevin for heavy particles
- certain weak coupling and Debye frequency gives pure Langevin
- invariant Langevin is Gibbs, averaged over light particles

[1] Ford, Kac, Mazur JMP 1965; Zwanzig JSP 1973

Langevin eq. from heat bath: Zwanzig's model

Hamiltonian

$$H_Z := \frac{|\dot{X}|^2}{2} + \lambda(X) + \frac{m}{2}(x - \hat{\Psi}(X)) \cdot \hat{V}(x - \hat{\Psi}(X)) + \frac{q \cdot \hat{V} q}{2m}$$

dynamics for $\psi := x - \hat{\Psi}(X) + i m^{-1} q$

$$\begin{aligned} \ddot{X}_t =& - \lambda'(X_t) + \Re(m \hat{V} \psi_t \cdot \hat{\Psi}') \\ i\dot{\psi}_t =& \hat{V} \psi_t - i \hat{\Psi}' \dot{X}_t, \end{aligned}$$

$\psi(0)$ from $e^{-H_Z/T} dx dq \implies$ independent normal

Gibbs initial data

$\{\Psi_j\}$ diagonalize $\hat{V}$ with eigenvalues $\{\tilde{\lambda}_j\}$

$$\psi(0) = \sum_j \gamma_j \Psi_j$$

γ_j independent, real and imaginary parts, $N\big(0, T/(m\tilde{\lambda}_j)\big)$, $j > 0$.

Compare Ehrenfest and Zwanzig dynamics

$$\begin{aligned}
\ddot{X}_t &= -\lambda'(X_t) + 2\Re(\tilde{V}\tilde{\psi}_t \cdot \Psi_0') - \tilde{\psi}_t \cdot \tilde{V}'\tilde{\psi}_t && \text{slow nuclei dynamics} \\
i\dot{\tilde{\psi}}_t &= M^{1/2}\tilde{V}\tilde{\psi}_t - i\Psi_0'\dot{X}_t && \text{fast electron dynamics}
\end{aligned}$$

$$\begin{aligned}
\ddot{X}_t &= -\lambda'(X_t) + \Re(m\hat{V}\,\psi_t \cdot \hat{\Psi}') && \text{heavy Zwanzig} \\
i\dot{\psi}_t &= \hat{V}\psi_t - i\hat{\Psi}'\dot{X}_t && \text{light Zwanzig}
\end{aligned}$$

$$H_E = \frac{|p|^2}{2} + \lambda(X) + \frac{\phi\cdot\tilde{V}\phi}{\phi\cdot\phi} - E = 0 \quad \text{Hamiltonian}$$

$$\begin{aligned}
V &= \tilde{V} + \lambda && \text{splitting} \\
V\Psi_0 &= \lambda\Psi_0 && \text{eigenvalue} \\
\psi &= \frac{\phi}{\sqrt{\phi\cdot\phi}} && \text{normalize} \\
\psi &= \Psi_0 + \tilde{\psi} && \text{splitting}
\end{aligned}$$

Ehrenfest & Zwanzig agree

$$\begin{aligned}\hat{\Psi}(X) &= \Psi_0(X),\\ \hat{V} &= M^{1/2}\tilde{V},\\ m &= 2M^{-1/2},\\ \lambda &= \lambda_0,\end{aligned}$$

$\tilde{V}$ constant $\Longrightarrow$ Ehrenfest=Zwanzig

Extension $\hat{V}(X)$ $\Longrightarrow$ Zwanzig=Ehrenfest

Zwanzig's solution

$$\psi(t) = -\int_0^t e^{i(t-s)\hat{V}}\hat{\Psi}'\dot{X}_s ds + \underbrace{e^{it\hat{V}}\psi(0)}_{z_t}$$

$$\ddot{X}_t = -\lambda'(X_t) - \int_0^t m\hat{V}\cos\left((t-s)\hat{V}\right)\hat{\Psi}'\dot{X}_s \cdot \hat{\Psi}' ds + \underbrace{\Re m\hat{V} z \cdot \hat{\Psi}'}_{\zeta^t}$$

covariance

$$E[\zeta_s^* \otimes \zeta_t] = Tm\hat{V}\cos\left((t-s)\hat{V}\right)\hat{\Psi}' \cdot \hat{\Psi}'$$

Debye Distribution

Write $\hat{\Psi}' =: \sum_{j=1}^{J} \hat{\Psi}'_j \Psi_j$ to obtain

$$\hat{V}\cos\Big((t-s)\hat{V}\Big)\hat{\Psi}'\cdot\hat{\Psi}' = \sum_{j=1} \lambda_j \cos\Big((t-s)\lambda_j\Big)\hat{\Psi}'_j\hat{\Psi}'_j.$$

assume

$$J^{-1}\sum_{j=1}^{J} h(\lambda_j) \to \int_0^{\lambda_d} h(\lambda)\frac{3\lambda^2}{\lambda_d^3}d\lambda$$

and $3\lambda_j^3\hat{\Psi}'_j\hat{\Psi}'_j = \kappa J^{-1}$ imply

$$\text{covariance} = \frac{3\kappa}{\lambda_d^3}\frac{\sin\lambda_d(t-s)}{t-s}$$

and

$$dX_t = v_t dt,$$
$$dv_t = \Big(-\lambda'(X_t) - Kv_t\Big)dt + \sqrt{2TK}dW_t$$

as $\lambda_d \to \infty$ and $\frac{m\pi\kappa}{2\lambda_d^3} \to K$.

Why the Gibbs measure?

- Start with any equilibrium measure, J light $\ll N$ heavy
- $H_l \ll H_h \implies$ Gibbs for light
- Zwanzig heavy dynamics $\implies$ time-asymptotic Gibbs for heavy
- consistency

Derivation of the Gibbs measure

Equilibrium measure $f\Big(H(X, x, \dot{X}, \dot{x})\Big) dX d\dot{X} dx d\dot{x}$:

Assume

$$H(X, x, \dot{X}, \dot{x}) = H_h(X, \dot{X}) + H_l(X, x, \dot{x})$$

$$H_l/H_h = \mathcal{O}(J/N) \ll 1,$$

$$g := -\log f$$

$$\overline{\lim}_{H\to\infty} |H \frac{g'(H)}{g(H)}| \leq C, \qquad \overline{\lim}_{H\to\infty} |H \frac{g''(H)}{g'(H)}| \leq C.$$

Then

$$-\log f(H_h + H_l) =: g(H_h + H_l) \simeq g(H_h) + g'(H_h)H_l$$

$\implies$ Light particle distribution: $e^{-H_l/T} dx d\dot{x}, \quad T := 1/g'(H_h)$

$\implies$ Ehrenfest splitting $H_l/H_h = \mathcal{O}(TJ/N) \ll 1$

$\implies$ heavy particle asymptotic distribution $e^{-H_h/T} dX d\dot{X}$

Consistency: $f(H) = e^{-H/T}$

Schrödinger $\longrightarrow$ stochastic MD ideas:

1. time-independent Schrödinger eq. as Hamiltonian system
2. Gibbs measure for Schrödinger Hamiltonian system
3. Modify Zwanzig's model with fast electrons as light particles

Result:

- Invariant measure, yields λ and friction matrix$=$diffusion matrix
- bounded time correlation, yields K

Langevin from Ehrenfest dynamics

Idea:

Apply Zwanzig's model to Ehrenfest dynamics

Issues:

- Fast linear ψ-equation; instead of explicit solution
- Nonlinear coupling; by low temperature
- Error representation by residual of Langevin Kolmogorov eq. evaluated along Ehrenfest dynamics
- A long time result uses exponential decay in time of the first variation of the observable with respect to perturbations in the momentum.

The friction matrix

$$\lim_{M\to\infty} 2M^{1/2}\int_0^\tau \Re\cos(\sigma M^{1/2}\tilde{V})\frac{d}{d\tau}\Psi_0(X^{\tau-\sigma})\cdot\tilde{V}\partial_X\Psi_0(X^\tau)d\sigma$$

$$= \lim_{M\to\infty} 2\int_0^{M^{1/2}\tau} \Re\cos(\hat{\sigma}\tilde{V})\frac{d}{d\tau}\Psi_0(X^{\tau-M^{-1/2}\hat{\sigma}})\cdot\tilde{V}\partial_X\Psi_0(X^\tau)d\hat{\sigma}$$

$$= 2\int_0^\infty \lim_{M\to\infty} \Re\underbrace{1_{\hat{\sigma}\le M^{1/2}\tau}\tilde{V}\cos(\hat{\sigma}\tilde{V})\frac{d}{d\tau}\Psi_0(X^{\tau-M^{-1/2}\hat{\sigma}})}_{=:\Gamma_M(\hat{\sigma})}\cdot\partial_X\Psi_0(X^\tau)\,d\hat{\sigma}$$

$$= 2\int_0^\infty \tilde{V}_\infty\cos(\hat{\sigma}\tilde{V}_\infty)\partial_X\Psi_0(X^\tau)\cdot\partial_X\Psi_0(X^\tau)d\hat{\sigma}\,\dot{X}^\tau$$

$$=: K(X^\tau)\dot{X}^\tau$$

Theorem 1: bounded time

Assume

$$K_{mn}(X^\tau) := \mathbb{E}_\gamma\Big[2 \lim_{M,J\to\infty} \int_0^{\tau M^{1/2}}$$

$$\Re\big(\tilde S_{\hat\tau,\hat\tau-\hat\sigma}\partial_{X_n}\Psi_0(X^{\tau-\hat\sigma M^{-1/2}})\cdot \tilde V(X^\tau)\partial_{X_m}\Psi_0(X^\tau)\big)d\hat\sigma \mid X^\tau\Big],$$

spectral gaps and low temperature $T\sum_{j=1}^J \tilde\lambda_j^{-1} = o(1)$, then

$$\Big|\mathbb{E}_\gamma\big[g(X^E_{\mathcal{T}}, p^E_{\mathcal{T}})) \mid X_0, p_0)\big] - \mathbb{E}_W\big[g(X^L_{\mathcal{T}}, \dot X^L_{\mathcal{T}}) \mid X_0, p_0)\big]\Big| = o(M^{-1/2}), \tag{1}$$

for any g provided

$$u(X,p,\sigma) := \mathbb{E}_W[g(X^L_{\mathcal{T}}, \dot X^L_{\mathcal{T}}) \mid X^L_\sigma = X,\ \dot X^L_\sigma = p]$$

satisfies

$$\int_0^{\mathcal{T}} \sup_{(X,p)} |Du(X,p,\sigma)|_{\ell^1}\, d\sigma = \mathcal{O}(1), \quad D = \partial_p, \partial_{pp}, \partial_{pX}.$$

Observable examples

Expected potential energy: $g(X) = \lambda_0(X)$.

Expected diffusion coefficient

$$D = \mathbb{E}_W[\underbrace{(6N\mathcal{T})^{-1}|X_L^{\mathcal{T}} - X_L^0|^2}_{=g(X_L^{\mathcal{T}},\dot{X}_L^{\mathcal{T}};X_L^0,p_L^0)} \mid X^0].$$

Conditions

$$
\begin{aligned}
&T \sup_X \textstyle\sum_{j=1}^{J} \frac{|\partial_X \tilde{\lambda}_j(X)|_{\ell^1(\mathbb{R}^{3N})}}{\tilde{\lambda}_j(X)} = o(M^{-1/2}), \\
&\sup_X \| |\tilde{V} \partial_X \Psi_0(X)|_{\ell^1(\mathbb{R}^{3N})} \|_{L^1(dx)} = \mathcal{O}(1), \\
&\sup_X |\partial_{X_k} \tilde{V}(X)| + \sup_X |\partial_{X_j X_k} \tilde{V}(X)| = \mathcal{O}(1), \\
&\sigma \mapsto \tilde{V}(X^\sigma) \text{ is real analytic on } (0,\infty), \\
&|\tilde{\lambda}_n - \tilde{\lambda}_m| > c \text{ for } n \neq m \text{ and } c \gtrsim M^{-1/5},
\end{aligned}
\tag{2}
$$

Theorem 2: unbounded time

Assume that condition (1) in Theorem 1 is replaced by

$$\lim_{\tau\to\infty}\int_0^\tau |\mathcal{D}u(X^\sigma,p^\sigma,\sigma;\tau)|_{\ell^1}\,d\sigma=\mathcal{O}(M^{1/2}),\quad \mathcal{D}:=\partial_p,\partial_{pp},\partial_{pX},$$

then Langevin dynamics approximates long time observables of Ehrenfest dynamics

$$\lim_{\mathcal{T}\to\infty}\mathcal{T}^{-1}\Big|\int_0^{\mathcal{T}}\mathbb{E}_\gamma\big[g(X^\tau,p^\tau)\big]-\mathbb{E}_W\big[g(X_L^\tau,\dot X_L^\tau)\big]\,d\tau\Big|=o(1)\text{ as }M\to\infty.$$

Error representation

$$
\begin{aligned}
&\mathbb{E}_\gamma[g(X^{\mathcal{T}}, p^{\mathcal{T}}) \mid X^0 = X, p^0 = p] - \mathbb{E}_W[g(X_L^{\mathcal{T}}, p_L^{\mathcal{T}}) \mid X_L^0 = X, p_L^0 = p] \\
&= \mathbb{E}_\gamma[u(X^{\mathcal{T}}, p^{\mathcal{T}}, \mathcal{T}) - u(X^0, p^0, 0) \mid X^0, p^0] \\
&= \int_0^{\mathcal{T}} \mathbb{E}[\, du(X^\tau, p^\tau, \tau) \mid X^0, p^0] \\
&= \int_0^{\mathcal{T}} \mathbb{E}[\partial_\tau u + \dot{X}^\tau \cdot \partial_X u + \dot{p}^\tau \cdot \partial_p u \mid X^0, p^0] \, d\tau \\
&= \int_0^{\mathcal{T}} \mathbb{E}\Big[\underbrace{(\dot{X}^\tau - p^\tau)}_{=0} \cdot \partial_X u \\
&\qquad + \big(\dot{p}^\tau + \lambda_0'(X^\tau) + M^{-1/2} K(X^\tau) p^\tau\big) \cdot \partial_p u \\
&\qquad - T M^{-1/2} K(X^\tau) \partial_{pp} u \mid X^0, p^0 \Big] \, d\tau \\
&= \int_0^{\mathcal{T}} \mathbb{E}\Big[\big(2\Re\langle \tilde{\psi}, \tilde{V} \Psi_0' \rangle - \langle \tilde{\psi}, \tilde{V}' \tilde{\psi} \rangle + M^{-1/2} K(X^\tau) p^\tau\big) \cdot \partial_p u \\
&\qquad - T M^{1/2} K(X^\tau) \partial_{pp} u \mid X^0, p^0 \Big] \, d\tau.
\end{aligned}
$$

Main lemma

There holds

$$\lim_{M\to\infty} -M^{1/2}\mathbb{E}\big[2\Re\langle \int_0^\tau S_{\tau,\sigma}\dot{\Psi}_0^\sigma d\sigma, \tilde{V}\Psi_0'^\tau\rangle \mid X^\tau, p^\tau\big] = K(X^\tau)p^\tau,$$

$$\lim_{M\to\infty} M^{1/2}\mathbb{E}\big[2\Re\langle \sum_{n=1}^J \tilde{\gamma}_n\tilde{\psi}_n^\tau, \tilde{V}\Psi_0'^\tau\rangle \cdot \partial_p u^\tau \mid X^\tau, p^\tau\big] = TK^\tau\partial_{pp}u^\tau,$$

$$\lim_{M\to\infty} M^{1/2}\mathbb{E}\big[\langle \tilde{\psi}^\tau, \tilde{V}'\tilde{\psi}^\tau\rangle \cdot \partial_p u^\tau \mid X^\tau, p^\tau\big] = 0.$$

$$\partial_{\tilde{\gamma}_n}(X,p,\psi) =: (X,p,\psi)'_n$$

Equation for first variations in $\tilde{\gamma}_k$

$$\begin{aligned}
&\dot{X}' = p', \\
&\dot{p}'_k = -X'_k \cdot \partial_{XX}\lambda_0 - 2\Re\langle\tilde{\psi}_k, \partial_X \tilde{V}\psi\rangle - \langle\psi, X'_k \cdot \partial_{XX}\tilde{V}\psi\rangle \\
&\qquad -2\Re\langle \textstyle\sum_n \tilde{\gamma}_n \partial_{\tilde{\gamma}_k}\tilde{\psi}_n, \partial_X \tilde{V}\psi\rangle, \\
&i\dot{\tilde{\psi}}'_m = M^{1/2}\tilde{V}\tilde{\psi}'_m + M^{1/2}X' \cdot \partial_X \tilde{V}\tilde{\psi}_m, \\
&(X,p,\psi)'(0) = 0,
\end{aligned}$$

Green's function representation

$$\begin{aligned}
(X,p,\psi)'_n(\tau) &= -2\int_0^\tau G_{\cdot p}(\tau,\sigma)\Re\langle\tilde{\psi}_n, \partial_X \tilde{V}(X)\psi\rangle(\sigma)d\sigma \\
&\simeq -2\int_0^\tau G_{\cdot p}(\tau,\sigma)\Re\langle\tilde{\psi}^\sigma_n, \tilde{V}\partial_X \Psi^\sigma_0\rangle d\sigma
\end{aligned} \tag{3}$$

Fluctuation-Dissipation: $\tilde\psi = \sum_n \gamma_n \tilde\psi_n$

$$\mathbb{E}[\sum_{n=1}^{\bar J}\sum_{m=1}^{\bar J}\langle S_{\tau,\sigma}\gamma_n\tilde\psi_n^\sigma, \tilde V \Psi_0'^\tau\rangle\langle \tilde V \Psi_0'^\sigma, \gamma_m\tilde\psi_m^\sigma\rangle \mid X]$$

$$\simeq \sum_{n=1}^{\bar J}\sum_{m=1}^{\bar J}\cdots \quad \underbrace{\mathbb{E}[\gamma_n^*\gamma_m]}_{=2T(\tilde\lambda_n^0)^{-1}\delta_{nm}}$$

$$\simeq 2T\sum_{n=0}^{\infty}\langle\tilde\psi_n^\sigma, (S_{\tau,\sigma})^*\tilde V \Psi_0'^\tau\rangle\langle\Psi_0'^\sigma, \tilde\psi_n^\sigma\rangle$$

$$= 2T\langle\Psi_0'^\sigma, (S_{\tau,\sigma})^*\tilde V^\tau\Psi_0'^\tau\rangle$$

$$= 2T\langle S_{\tau,\sigma}\Psi_0'^\sigma, \tilde V^\tau\Psi_0'^\tau\rangle$$

as for friction

Motivation of $\lim_{\tau\to\infty}\int_0^\tau \partial_p u(X^\sigma, p^\sigma, \sigma; \tau)d\sigma = \mathcal{O}(M^{1/2})$

$$
\begin{aligned}
&\partial_p u(X, p, \sigma; \tau) = \partial_p \mathbb{E}[g(X_L^\tau, p_L^\tau) \mid X_L^\sigma = X, p_L^\sigma = p] \\
&= \mathbb{E}[\partial_{p_L^\sigma} g(X_L^\tau, p_L^\tau) \mid X_L^\sigma = X, p_L^\sigma = p] \\
&= \mathbb{E}[\partial_X g(X_L^\tau, p_L^\tau)\frac{\partial X_L^\tau}{\partial p_L^\sigma} + \partial_p g(X_L^\tau, p_L^\tau)\frac{\partial p_L^\tau}{\partial p_L^\sigma} \mid X_L^\sigma = X, p_L^\sigma = p]
\end{aligned}
$$

Stochastic flow

$$
\begin{aligned}
\frac{d}{d\varsigma}X_L'(\varsigma;\sigma) &= p_L'(\varsigma;\sigma) \\
\frac{d}{d\varsigma}p_L'(\varsigma;\sigma) &= -\partial_{XX}\lambda_0(X_L^\varsigma)X_L'(\varsigma;\sigma) - \bar{K}p_L'(\varsigma;\sigma)
\end{aligned}
$$

for $\bar{K} := M^{-1/2}K = M^{-1/2}k\,I$, with $k > 0$.

Definition

$$
\hat{A}(\varsigma) := \begin{bmatrix} 0 & I \\ -\lambda_0''(X_L^\varsigma) & -\bar{K} \end{bmatrix}
$$

gives the representation

$$\begin{bmatrix} X_L'(\varsigma;\sigma) \\ p_L'(\varsigma;\sigma) \end{bmatrix} \simeq \Big(\prod_{n=1}^{\hat N} e^{\Delta t \hat A(\varsigma_n)}\Big) \begin{bmatrix} 0 \\ I \end{bmatrix} := e^{\Delta t \hat A(\varsigma_N)} \dots e^{\Delta t \hat A(\varsigma_1)} \begin{bmatrix} 0 \\ I \end{bmatrix}.$$

Diagonalize with real part of eigenvalues

$$\Re a_\pm \le -k/2 + (k^2/4 - \bar\lambda''(\varsigma_n))_+^{1/2} := -k/2 + \sqrt{\max_m(0, k^2/4 - \bar\lambda_m''(\varsigma_n))},$$

implies

$$\begin{aligned} \|\prod_{n=1}^{\hat N} e^{\Delta t \hat A(\varsigma_n)}\| &\le \prod_{n=1}^{\hat N} \exp\Big(\Delta t\big(-k/2 + (k^2/4 - \bar\lambda''(\varsigma_n))_+^{1/2}\big)\Big) \\ &= \exp\Big(\sum_{n=1}^{\hat N} \Delta t\big(-k/2 + (k^2/4 - \bar\lambda''(\varsigma_n))_+^{1/2}\big)\Big) \\ &\simeq \exp\Big(\int_\sigma^\tau \big(-k/2 + (k^2/4 - \bar\lambda''(\varsigma))_+^{1/2}\big) d\varsigma\Big). \end{aligned}$$

For $T \ll 1$, paths X_L^ς spend long time around stable equilibria, where $\bar{\lambda}_m > 0$, and at rare events make short time $\tau_e \sim 1$ excursions between such equilibria.

The number of such rare events in a time interval $[0, \tau - \sigma]$ can be approximately modelled by a Poisson process $m_{\tau-\sigma}$ with the intensity ξ, proportional to $e^{\Delta\lambda_0/T} \sim e^{-1/T}$

Let $\kappa := \max_X \left(k^2/4 - \bar{\lambda}''(X)\right)_+^{1/2}$, and $\beta := t_e\kappa$.

$$\left| \begin{bmatrix} \partial_{p_k} X_L(\varsigma;\sigma) \\ \partial_{p_k} p_L(\varsigma;\sigma) \end{bmatrix} \right| \leq \exp\left(\int_\sigma^\tau \left(- k/2 + (k^2/4 - \bar{\lambda}''(\varsigma))_+^{1/2} \right) d\varsigma \right)$$

so that

$$\lim_{\mathcal{T}\to\infty}\mathcal{T}^{-1}\int_0^{\mathcal{T}}\int_0^{\tau}|\partial_p u(X^\sigma,p^\sigma,\sigma;\tau)|_{\ell^1}d\sigma d\tau$$

$$\leq C\lim_{\mathcal{T}\to\infty}\mathcal{T}^{-1}\int_0^{\mathcal{T}}\int_0^{\tau}e^{\int_\sigma^\tau -k/2+(k^2/4-\bar{\lambda}''(\varsigma))_+^{1/2}d\varsigma}d\sigma d\tau$$

$$= C\lim_{\tau\to\infty}\int_0^{\tau}\mathbb{E}[e^{\int_\sigma^\tau -k/2+(k^2/4-\bar{\lambda}''(\varsigma))_+^{1/2}d\varsigma}]d\sigma$$

$$\mathbb{E}[e^{\int_\sigma^\tau -k/2+(k^2/4-\bar{\lambda}''(\varsigma))_+^{1/2}d\varsigma}]\leq\mathbb{E}[e^{-k(\tau-\sigma)/2+\beta m_{\tau-\sigma}}]$$

$$= e^{-(\xi+k/2)(\tau-\sigma)}\sum_{m=0}^{\infty}e^{\beta m}\frac{\big(\xi(\tau-\sigma)\big)^m}{m!}$$

$$= e^{\big((e^\beta-1)\xi-k/2\big)(\tau-\sigma)}.$$

Since $T\ll\log M$, $\xi\sim e^{-1/T}\ll k\sim M^{-1/2}$,

$$\lim_{\mathcal{T}\to\infty}\mathcal{T}^{-1}\int_0^{\mathcal{T}}\int_0^{\tau}|\partial_p u(X^\sigma,p^\sigma,\sigma;\tau)|_{\ell^1}d\sigma d\tau=\mathcal{O}(M^{1/2}).$$

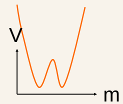
3. SPDE for phase transition

Energy conservation:

$$\partial_t(c_v T + m) = \mathrm{div}(k\nabla T)$$

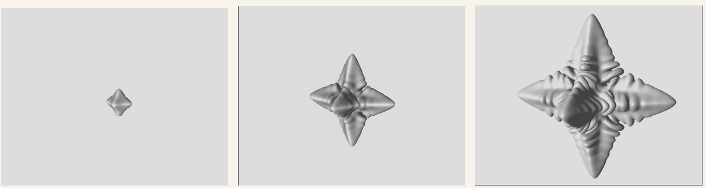
Phase field for $m = g(\phi)$:

$$k_0\partial_t\phi = \mathrm{div}(k_1\nabla\phi) - f'(\phi) + k_2 T + \text{noise}$$



Which f?

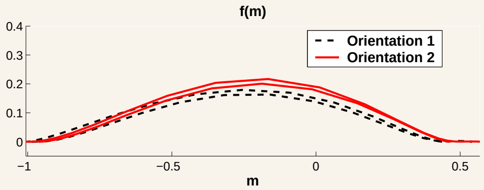
Why noise?



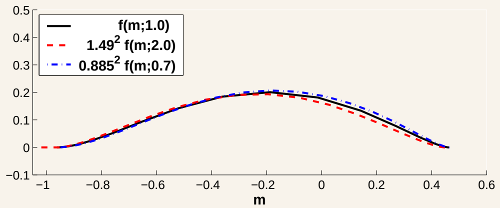
3. Phase-field SPDE from MD

1. $m(x, X)$ equals local potential energy at $x \in \mathbb{R}^3$
2. $dm = \alpha(X)dt + \beta(X)dW$
3. Find SPDE $d\bar{m} = a(\bar{m})dt + b(\bar{m})dW$:
   - computed traveling MD wave m gives a
   - $b \otimes b \simeq$ computed average $\beta \otimes \beta$

Drift

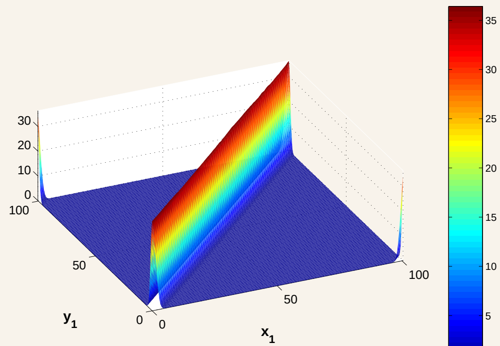


f(m)
Orientation 1
Orientation 2
0.4
0.3
0.2
0.1
0
−1
−0.5
0
0.5
m

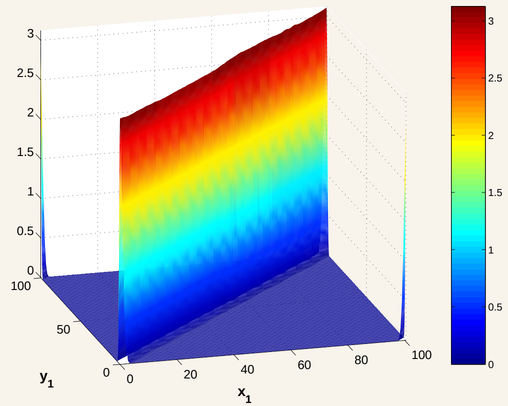


f(m;1.0)
1.49^2 f(m;2.0)
0.885^2 f(m;0.7)
0.5
0.4
0.3
0.2
0.1
0
−0.1
−1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
0.6
m

Diffusion

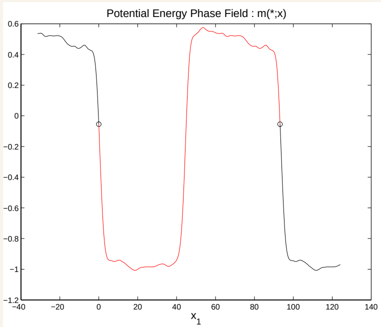


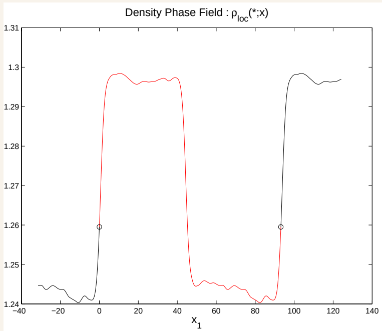
35
30
25
20
15
10
5
0
30
20
10
0
100
50
0
0
50
100
y_1
x_1

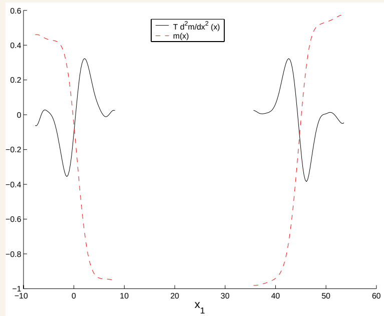


3
2.5
2
1.5
1
0.5
0
3
2.5
2
1.5
1
0.5
0
100
50
0
0
20
40
60
80
100
y_1
x_1

3. Coarse-Grained drift







$$\alpha = \kappa(\gamma\partial_{xx}m + \underbrace{\partial_x A_1}_{=0} + A_0)$$

κ set from equilibrium fluctuations

3. Coarse-grained diffusion

1. Ito implies

$$dm(X^t, \cdot) = \alpha(X^t)dt + \sum_j \beta_j(X^t)dW_j^t.$$

2. Kolmogorov equation for $\bar{u}(n,t) := \mathbb{E}[g(\bar{m}^T) \,|\, \bar{m}^t = n]$

$$\mathbb{E}\big[g\big(m(X^T, \cdot)\big) - g(\bar{m}^T)\big]$$
$$= \mathbb{E}[\int_0^T \langle \bar{u}', \alpha - a\rangle + \langle \bar{u}'', \sum_j \beta_j \otimes \beta_j - \sum_k b_k \otimes b_k\rangle \; dt]$$

3. Expansion in $\alpha - a$

$$a = \frac{1}{\mathcal{T}}\mathbb{E}[\int_0^{\mathcal{T}} \alpha \, dt],$$
$$\sum_k b_k \otimes b_k = \frac{1}{\mathcal{T}}\mathbb{E}[\int_0^{\mathcal{T}} \sum_j \beta_j \otimes \beta_j \, dt].$$