Stochastic Molecular Dynamics Derived from the Time-independent Schrödinger Equation

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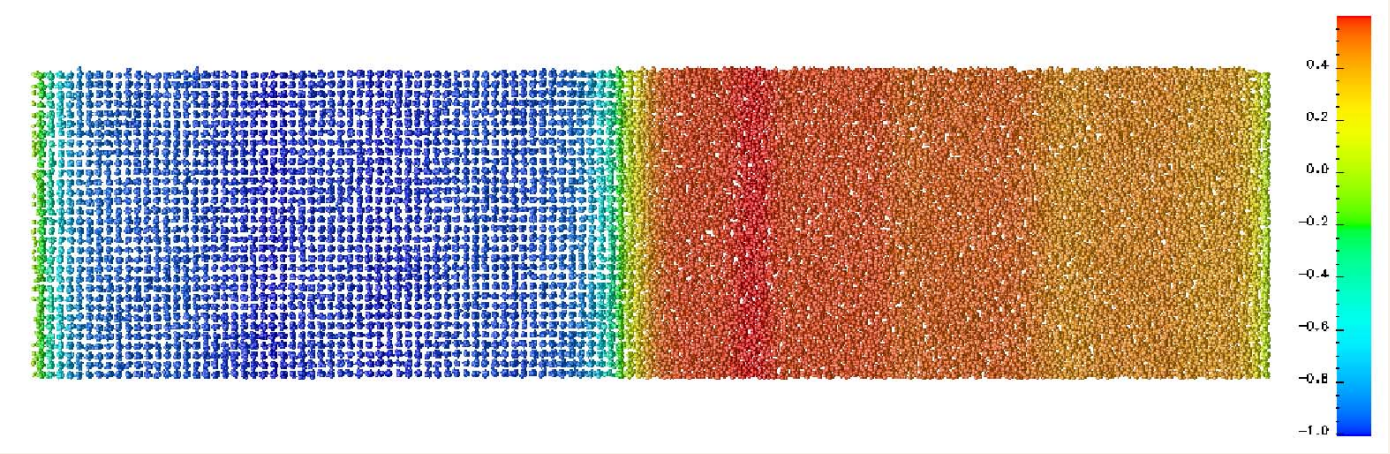
Schrödinger observables approximated by:

- Ehrenfest dynamics $\mathcal{O}(M^{-1})$
- Born-Oppenheimer dynamics $\mathcal{O}(M^{-1/2})$
- Langevin and Smoluchowski dynamics $\mathcal{O}(M^{-1} + \text{gap}^{-1})$

Which Molecular Dynamics?



$$M\ddot{X} = -V'(X) + \,?$$

- What is V?
- Are there fluctuations? How model temperature T?
- Is there dissipation?

The Usual Derivation and the New

Usual start from $time\text{-}dependent$ Schrödinger equation:

- self consistent field equation: wave function is product of nuclei and electron function
- Ehrenfest dynamics: nuclei wave function becomes point measure
- Born-Oppenheimer approximation: electron wave function is the ground state.

The Usual Derivation and the New

Usual start from *time-dependent* Schrödinger equation:

- self consistent field equation: wave function is product of nuclei and electron function
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New start from *time-independent* Schrödinger equation:

- use WKB-Ansatz
- introduce time by momentum from characteristics of Eikonal eq.
- introduce integrating factor from divergence of momentum
- stability from consistency with Schrödinger equation.

Difference Between the Two

+ experimental evidence of time-independent Schrödinger
+ nuclei paths behave classically without separation and small support
+ long time stability
+ stochastic perturbation of ground state leads to Langevin
+ colliding characteristic paths
– only equilibrium situations

Dynamics from the Time-independent Schrödinger

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

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

$$V(x,X) = -\frac{1}{2}\sum_{j=1}^{J}\Delta_{x^j} + \sum_{1\le k<j\le J}\frac{1}{|x^k - x^j|} - \sum_{n=1}^{N}\sum_{j=1}^{J}\frac{Z_n}{|x^j - X^n|} + \sum_{1\le n<m\le N}\frac{Z_n Z_m}{|X^n - X^m|}$$

The WKB-Ansatz

$$\Phi(x, X) = \psi(x, X) e^{iM^{1/2}\theta(X)}$$

implies

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

$$V_n := \frac{\psi \cdot V\psi}{\psi \cdot \psi}, \quad v \cdot w := \int_{\mathbb{R}^{3J}} v^*(x, X, t) w(x, X, t)\, dx$$

The Time-dependence

The Time-dependence[1]

$$\psi' \circ \theta' = \psi' \circ \underbrace{\frac{dX_t}{dt}}_{=:p} = \frac{d\psi(x, X_t)}{dt}$$

[1] Mott 1931; Briggs and Rost 2001

The Time-dependence[2]

$$\psi' \circ \theta' = \psi' \circ \underbrace{\frac{dX_t}{dt}}_{=:p} = \frac{d\psi(x, X_t)}{dt}$$

$$\theta'' = \mathsf{div}\, p = \frac{d}{dt} \log |p|$$

yields the Eikonal and transport equation for $\varphi := |p|^{1/2}\psi$

$$\begin{aligned} 0 &= (H - E)\Phi \\ &= \Big(\underbrace{(\frac{|\theta'|^2}{2} + V_n - E)}_{=0} \psi \\ &+ \underbrace{\big(- \frac{i}{M^{1/2}}\dot{\varphi} + (V - V_n)\varphi - \frac{1}{2M}|p|^{1/2}\Delta_X(\varphi|p|^{-1/2})\big)|p|^{-1/2}}_{=0} \Big) e^{iM^{1/2}\theta}. \end{aligned}$$

[2] Mott 1931; Briggs and Rost 2001

Characteristics of the Schrödinger Equation

$$-\frac{i}{M^{1/2}}\dot{\varphi} + \big(V(X_t) - V_n\big)\varphi = \frac{1}{2M}|p|^{1/2}\Delta_X(\varphi|p|^{-1/2})$$

Characteristics of Eikonal equation:

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

$$V_n = \frac{\varphi \cdot V\varphi}{\varphi \cdot \varphi}$$

The Ehrenfest Approximation

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

is Hamiltonian system for HJ

$$H_E := |p|^2/2 + \phi \cdot V(X)\phi = E$$

with characteristics $(X, \varphi_r; p, \varphi_i)$ and $\varphi := 2^{1/2}M^{-1/4}\phi$;

and $\hat{\psi}_t := \phi_t e^{iM^{1/2}\int_0^t \phi_s \cdot V(X_s)\phi_s ds}$ implies

$$\frac{i}{M^{1/2}}\dot{\hat{\psi}}_t = (V - V_n)\hat{\psi}_t$$

Ehrenfest Accuracy

$$\hat{\Phi} := \hat{\rho}^{1/2}\hat{\psi}e^{iM^{1/2}\hat{\theta}}$$

implies

$$\begin{aligned}(H-E)\hat{\Phi} &= \frac{1}{2M}\Delta_X(\hat{\rho}^{1/2}\hat{\psi}) \\ &= \mathcal{O}(M^{-1})\end{aligned}$$

so that

$$\int g(X)\big(\hat{\rho}-\rho\big)dX = \int g(X)\big(\hat{\Phi}\cdot\hat{\Phi}-\Phi\cdot\Phi\big)dX = \mathcal{O}(M^{-1})$$

Motivation for Stable Eigenstate Perturbation

Orthonormal eigenpairs $\{\lambda_n, \Phi_n\}$, satisfying $H\Phi_n = \lambda_n \Phi_n$,

$$\hat{\Phi} =: \sum_n \alpha_n \Phi_n$$

yields

$$\sum_n (\lambda_n - E)\alpha_n \Phi_n = -\frac{1}{2M} v,$$

which establishes

$$(\lambda_n - E)\alpha_n = -\frac{1}{2M} \underbrace{\int_{\mathbb{T}^{3N}} \Phi_n \cdot v \, dX}_{=:\, \hat{v}_n}.$$

We have $\hat{v}_n = 0$, when $\lambda_n = E$, and let

$$|\hat{v}_n'(E)| := \limsup_{\delta \to 0+} \frac{|\hat{v}_n(E+\delta)|}{\delta},$$

which implies

$$\sum_n \frac{|\hat{v}_n(\lambda_n)|^2}{|\lambda_n - E|^2} \leq \sum_{\{n:|\lambda_n - E|<1\}} |\hat{v}_n'(E)|^2 + \sum_n |\hat{v}_n|^2.$$

Assume that

$$\sum_{\{n:|\lambda_n - E|<1\}} |\hat{v}_n'(E)|^2 + \sum_n |\hat{v}_n|^2 = \mathcal{O}(1). \tag{1}$$

Motivation for bounded $|\hat{v}'|$*:*

Large number of nuclei $N \gg M$

δ perturbation of

$$\lambda_n = |p|^2/2 + V_n$$

yields $\mathcal{O}(\delta N^{-1})$ perturbation of paths

$$(X, p, \psi)$$

and also θ change negligible (with appropriate time) so eigenstate change small

$$\Phi = \psi e^{iM^{1/2}\theta}$$

The Born-Oppenheimer Approximation

An electron eigenstate: $\hat{\psi} = \Psi_n \quad V(X)\Psi_n = \lambda_n(X)\Psi_n$

implies

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

$$(H - E)\hat{\Phi} = \mathcal{O}(M^{-1/2})$$

and

$$\int g(X)\big(\hat{\rho} - \rho\big)dX = \int g(X)\big(\hat{\Phi}\cdot\hat{\Phi} - \Phi\cdot\Phi\big)dX = \mathcal{O}(M^{-1/2})$$

Stochastic Molecular Dynamics Approximation

Improve Born-Oppenheimer

Ehrenfest solution $\hat{\psi}_n = \Psi_n + \psi_n^\perp$

$$\psi_n^\perp(t) = S_{t,0}\psi_n^\perp(0) - iM^{-1/2}\int_0^t S_{t,s}\dot{\Psi}_n(s)ds$$

so perturbation of ground state Ψ_0 yields

- fluctuation from stochastic initial data $\hat{\psi}_n,\ n > 0$
- dissipation from residual $\dot{\Psi}_0(s) = \Psi_0' \circ \dot{X}$

Which Initial Data for $\hat{\psi}_n$?

Liouville eq. for Ehrenfest

$$\partial_t f + \partial_{p_E} H_E \partial_{r_E} f - \partial_{r_E} H_E \partial_{p_E} f = 0$$

has many time-independent solutions $f = h(H_E)$

Which Initial Data for $\hat{\psi}_n$?

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Idea: Nuclei act as heat bath for electrons

independent $\dot{X}_n$ imply $h(H_E) = e^{-H_E/T}$

(nuclei has this (unique) invariant SDE probability density)

so

$$\text{Prob(electron configuration } \hat{\psi}) \sim e^{-\hat{\psi}\cdot(V-\lambda_0)\hat{\psi}/T} d\hat{\psi}^r d\hat{\psi}^i.$$

Stochastic Ehrenfest Dynamics

Let

$$r(X) := \prod_{j\geq 0} \int_{|\gamma_j|^2<C} e^{-\bar{\lambda}_j|\gamma_j|^2/(T\sum_{j\geq 0}|\gamma_j|^2)} d\gamma_j^r \, d\gamma_j^i \sim \prod_{j\geq 0} (\frac{T}{\bar{\lambda}_j})^{1/2},$$

then observable in the Ehrenfest dynamics is

$$\frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} r(X) dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} r(X) dX} = \frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} \, \frac{r(X)}{r(0)} dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} \, \frac{r(X)}{r(0)} dX}.$$

The Spectral Gap Condition

A large spectral gap $\alpha := \sum_{j>0} \bar{\lambda}_j^{-1} \ll 1$ yields

$$\frac{r(X)}{r(0)} = 1 + \mathcal{O}(\alpha),$$

which implies

$$\frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} r(X) dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} r(X) dX} = \frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} dX} + \mathcal{O}(\alpha).$$

Langevin and Smoluchowski Dynamics

The stochastic *Langevin dynamics*

$$dX_t = p_t dt$$
$$dp_t = -\partial_X \lambda_0(X_t)dt - K p_t dt + \sqrt{2TK}\, dW_t$$

and the *Smoluchowski dynamics*

$$dX_s = -\partial_X \lambda_0(X_s)ds + \sqrt{2T}\, dW_s$$

has the unique invariant probability density

$$\frac{e^{-(p\circ p/2+\lambda_0(X))/T} dp\, dX}{\int_{\mathbb{R}^{6N}} e^{-(p\circ p/2+\lambda_0(X))/T} dp\, dX}$$

respectively

$$\frac{e^{-\lambda_0(X)/T} dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} dX}$$

Stochastic Approximation Theorem

Langevin and Smoluchowski dynamics approximate Schrödinger observables with error

$$\mathcal{O}(M^{-1} + \alpha)$$

provided the assumption in Ehrenfest approximation holds together with the spectral gap condition $\alpha = \sum_{j>0} \bar{\lambda}_j^{-1} \ll 1$.

Conditions for Colliding Characteristics Paths (Caustics)

At a point X of two colliding characteristic paths, (X, p^-, z^-) and (X, p^+, z^+), we need:

- the phase θ is *continuous*, i.e. $z^- = z^+$,
- a *stable* φ,

$$\frac{i}{M^{1/2}}\dot{\varphi} = (V - V_n)\varphi - \frac{|p|^{1/2}}{2M}\sum_j \Delta_{X^j}(|p|^{-1/2}\varphi),$$

so take

$$|p^+| = |p^-|,$$

- θ is max-norm *stable* towards perturbations of the initial data,

which implies the *irreversible viscosity solution* θ.

SPDE from Smoluchowski MD with Erik von Schwerin

Energy conservation:

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

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

$$k_0 \partial_t \phi = \mathsf{div}(k_1 \nabla \phi) - V'(\phi) + k_2 T + \mathsf{noise}$$

Why noise?

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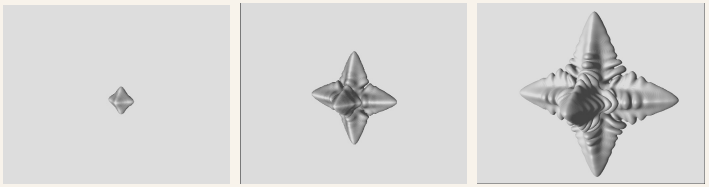
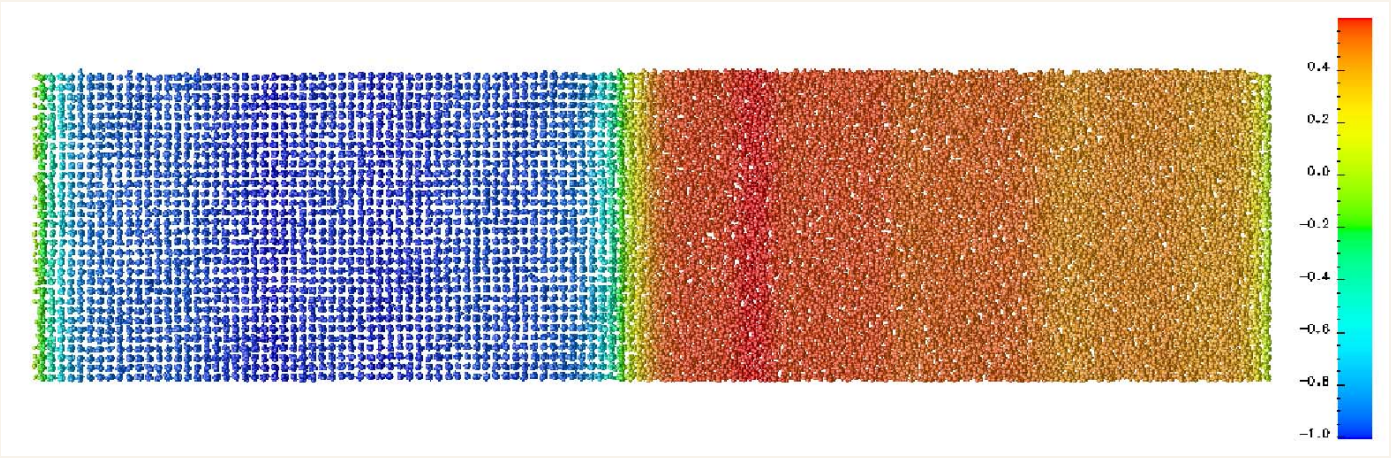


Which Noise and Phase Field Equation?

1. Stochastic Smoluchowski molecular dynamics
2. Quantitative atomistic definition of phase field
3. Numerical computation of coarse-grained model functions



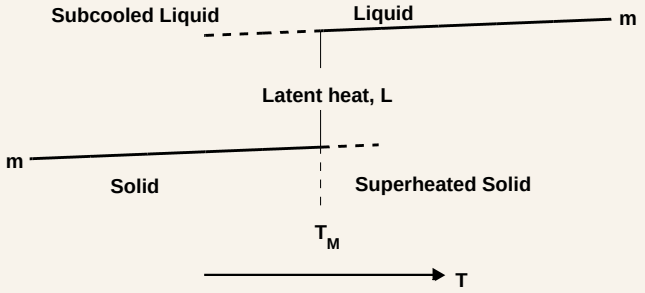
1. Stochastic Molecular Dynamics

Energy: $\underbrace{\sum_i \frac{|v_i|^2}{2}}_{c_v T} + \underbrace{V(X_1, \ldots, X_N)}_{m}$

Smoluchowski dynamics in diffusion time scale ($\gamma = k_B T$):

$$dX^t = -\partial V(X^t)dt + \sqrt{2\gamma}\, dW^t$$

2. Molecular Potential Energy



Pair interactions

$$V(X) = \frac{1}{2} \sum_i \sum_{j \neq i} \tilde{V}(X_i - X_j)$$

Localized average (as SPH)

$$m(X, x) := \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} \tilde{V}(X_i - X_j) \eta(x - X_i)}_{\text{observable}}$$

3. Coarse-Grained Stochastic MD

Want coarse-grained approximation $\bar{m}$

$$d\bar{m}^t = a(\bar{m}^t)dt + \sum_k b_k(\bar{m}^t)d\bar{W}_k^t$$

such that

$$\min_{a,b} \mathbb{E}\big[g\big(m(X^T,\cdot)\big) - g(\bar{m}^T)\big].$$

1. Ito implies

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

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

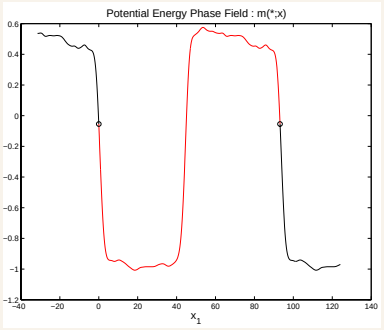
$$\begin{aligned}
&\mathbb{E}\big[g\big(m(X^T, \cdot)\big) - g(\bar{m}^T)\big] \\
&= \mathbb{E}[\int_0^T \langle \bar{u}', \alpha - a\rangle + \langle \bar{u}'', \sum_j \beta_j \otimes \beta_j - \sum_k b_k \otimes b_k\rangle \; dt]
\end{aligned}$$

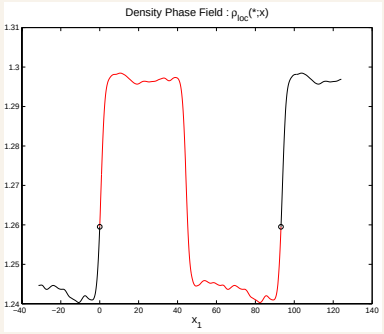
3. Expansion in $\alpha - a$

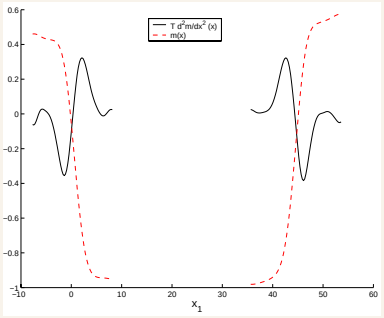
$$a = \frac{1}{\mathcal{T}}\mathbb{E}\big[\int_0^{\mathcal{T}} \alpha \, dt\big],$$

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

Coarse-Grained Variables

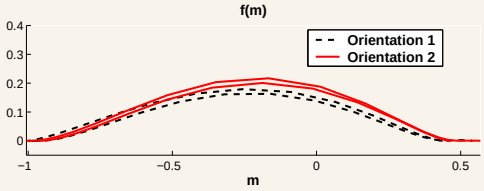


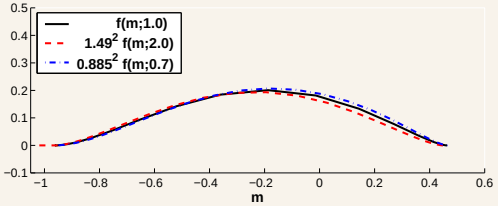




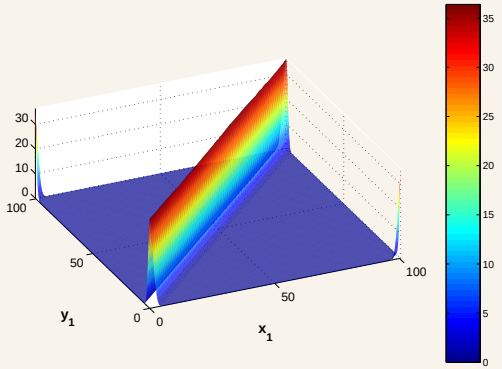
1. $\alpha = \gamma \partial_{xx} m + \partial_x A_1 + A_0$
2. $a = \int_0^{\mathcal{T}} \alpha dt / \mathcal{T} \to 0.$

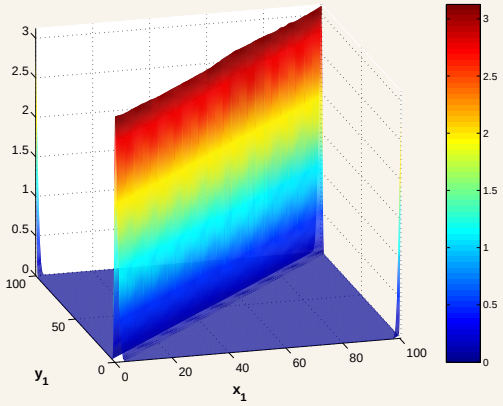
Drift


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


30
20
10
0
100
50
0
y1
0
50
100
x1
35
30
25
20
15
10
5
0


3
2.5
2
1.5
1
0.5
0
100
50
0
y1
0
20
40
60
80
100
x1
3
2.5
2
1.5
1
0.5
0

Orientation dependence

Let

$$q_i := \overline{A_0(O_i)}/\overline{A_0(O_1)}$$
$$r_i := \tau(O_i)/\tau(O_1)$$

Then

$$d\bar{m}_i = r_i q_i \big(\gamma q_i^{-1} \bar{m}_i'' + \overline{A_0}(\bar{m}_i; O_1)\big) dt + r_i^{1/2} \bar{b}(\bar{m}_i; O_i) dW^t$$

becomes

$$(r_i q_i)^{-1} d\bar{m} = \big(\gamma q_i^{-1} \bar{m}'' + \overline{A_0}(\bar{m}; O_1)\big) dt + r_i^{-1/2} q_i^{-1} \bar{b}(\bar{m}; O_i) dW^t$$

Extensions

- more directions
- constant pressure
- undercooled melt
- real material
- hybrid simulations

3. Expansion in $\alpha - a$

$$m(X^t, x) \approx \bar{m}(x)$$

leads to

$$\mathbb{E}\Big[\int_0^{\mathcal{T}} \big\langle \bar{u}'\big(m(X^t, x), t\big), \alpha(x) - a\big(\bar{m}(x)\big)\big\rangle dt\Big] \approx$$

$$\big\langle \bar{u}'\big(\bar{m}(x), \mathcal{T}\big), \mathbb{E}\Big[\int_0^{\mathcal{T}} \alpha(x) - a\big(\bar{m}(x)\big) dt\Big]\big\rangle$$

2. Derivation of the Error

$$\mathbb{E}\big[g\big(m(X^{\mathcal{T}},\cdot)\big) - g(\bar{m}^{\mathcal{T}})\big]$$

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$$\mathbb{E}\big[g\big(m(X^{\mathcal{T}},\cdot)\big) - g(\bar{m}^{\mathcal{T}})\big]$$
$$= \mathbb{E}[\bar{u}(m^{\mathcal{T}},\mathcal{T}) - \bar{u}(m^{0},0)]$$

2. Derivation of the Error

$$
\begin{aligned}
&\mathbb{E}\big[g\big(m(X^{\mathcal{T}},\cdot)\big) - g(\bar{m}^{\mathcal{T}})\big] \\
&= \mathbb{E}[\bar{u}(m^{\mathcal{T}},\mathcal{T}) - \bar{u}(m^0,0)] \\
&= \mathbb{E}[\textstyle\int_0^{\mathcal{T}} d\bar{u}(m^t,t)]
\end{aligned}
$$

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\begin{aligned}
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&= \mathbb{E}[\textstyle\int_0^{\mathcal{T}} d\bar{u}(m^t,t)] \\
&= \mathbb{E}\Big[\textstyle\int_0^{\mathcal{T}} \langle \bar{u}', \alpha\rangle + \langle \bar{u}'', \sum_j \beta_j \otimes \beta_j\rangle + \partial_t \bar{u}\; dt\Big]
\end{aligned}
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&= \mathbb{E}\Big[\textstyle\int_0^{\mathcal{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\Big]
\end{aligned}
$$

Factorization of the density

The Ehrenfest equation

$$0 = \Big(\frac{|\hat\theta'|^2}{2} + V - E\Big)\check\psi - \frac{i}{M^{1/2}}(\check\psi'\hat\theta' + \frac{1}{2}\check\psi\hat\theta'')$$

yields

$$\begin{aligned} 0 &= \sum_j \int_{\mathbb{T}^{3J}} (\partial_{X^j}\check\psi^*\check\psi + \check\psi^*\partial_{X^j}\check\psi)dx\ \partial_{X^j}\hat\theta + \int_{\mathbb{T}^{3J}} \check\psi^*\check\psi dx\ \partial_{X^jX^j}\hat\theta \\ &= \sum_j \partial_{X^j}(\hat\rho\partial_{X^j}\hat\theta) \end{aligned}$$

and

$$\sum_j \partial_{X^jX^j}\theta = \mathsf{div}\, p = \frac{\partial p_1^1}{\partial X_1^1} = \frac{\frac{\partial p_1^1}{\partial t}}{\frac{\partial X_1^1}{\partial t}} = \frac{\dot p_1^1}{p_1^1} = \frac{\frac{d}{dt}|p|^2}{2|p|^2} = \frac{d}{dt}\log|p|$$

implies

$$\begin{aligned}\dot{\hat{\rho}}(\hat{X}_t) &= \sum_j \partial_{\hat{X}^j}\hat{\rho}(\hat{X}_t)\dot{\hat{X}}^j \\ &= \sum_j \partial_{\hat{X}^j}\hat{\rho}(\hat{X}_t)\partial_{\hat{X}^j}\hat{\theta}_n \\ &= -\hat{\rho}(\hat{X}_t)\sum_j \partial_{\hat{X}^j\hat{X}^j}\hat{\theta}_n \\ &= -\hat{\rho}(\hat{X}_t)\ \mathsf{div}\,\hat{p} \\ &= -\hat{\rho}(\hat{X}_t)\frac{d}{dt}\log|\hat{p}_t|\end{aligned}$$

with the solution

$$\hat{\rho}(\hat{X}_t) = \frac{C}{|\hat{p}_t|},$$

where C is a positive constant for each characteristic. Coordinates $X_1^1 \in \mathbb{R}$ parallel and $X_0 \in \mathbb{R}^{3N-1}$ orthogonal to the characteristic

direction $\dot{X}$ gives

$$\hat{\rho}(X)dX = \hat{\rho}(X_0)\frac{dX_0}{\int_0^{X_1^1(T)} \frac{dX_1^1}{|\hat{p}_1^1|}} \frac{dX_1^1}{|\hat{p}_1^1|} = \hat{\rho}(X_0)dX_0\frac{dt}{T}, \qquad (2)$$

using

$$\frac{d\hat{X}_1^1}{|\hat{p}_1^1|} = \frac{|d\hat{X}_1^1|}{|d\hat{X}_1^1/dt|} = dt,$$

and the observable

$$\int_{\mathbb{T}^{3N}} g(\hat{X}, \hat{\psi}, \hat{\rho})d\hat{X} = \int_0^T \int_I A(X_t)\hat{\rho}(\hat{X}_0)d\hat{X}_0\frac{dt}{T}.$$

Dynamics from the time-dependent Schrödinger

$$i\partial_t \Phi(x, X, t) = H(x, X)\Phi(x, X, t)$$

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

$$\begin{aligned} V(x, X) = &-\frac{1}{2}\sum_{j=1}^{J} \Delta_{x^j} + \sum_{1\le k<j\le J} \frac{1}{|x^k - x^j|} \\ &- \sum_{n=1}^{N}\sum_{j=1}^{J} \frac{Z_n}{|x^j - X^n|} + \sum_{1\le n<m\le N} \frac{Z_n Z_m}{|X^n - X^m|} \\ =: &-\frac{1}{2}\sum_{j=1}^{J} \Delta_{x^j} + H_I \end{aligned}$$

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

$$\langle v, w \rangle := \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3J}} v^*(x, X, t) w(x, X, t)\, dx\, dX$$

Usual derivation:

1. self consistent field equation: wave function is product of nuclei and electron function
2. Ehrenfest dynamics: nuclei wave function becomes point measure
3. Born-Oppenheimer approximation: electron wave function is the ground state.

1. Time-dependent self consistent field equations

Approximation Ansatz of separation

$$\Phi(x,X,t) = \Psi_N(X,t)\Psi_E(x,t)\,\exp\Big(i\int_0^t \underbrace{\langle \Psi_N^s\Psi_E^s, H_I\Psi_E^s\Psi_N^s\rangle}_{\bar{H}_I}\,ds\Big)$$

satisfies time dependent *self consistent field equation*[3]

$$i\partial_t\Psi_N = \Big(-(2M)^{-1}\sum_{n=1}^{N}\Delta_{X_n} + \Psi_E\cdot H_I(X)\Psi_E\Big)\Psi_N,$$

$$i\partial_t\Psi_E = \Big(\int_{\mathbb{R}^{3N}}\Psi_N^*(X)V(X)\Psi_N(X)\,dX\Big)\Psi_E.$$

[3]Dirac P.A.M., Proc. Cambridge Phil. Soc. **26** (1930) 376–385.

Φ solves perturbed full Schrödinger

$$i\partial_t\Phi = \Big(-(2M)^{-1}\sum_{n=1}^{N}\Delta_{X_n} - \frac{1}{2}\sum_{j=1}^{J}\Delta_{x_j} + \Psi_E \cdot H_I\Psi_E + \int_{\mathbb{R}^{3N}} \Psi_N^* H_I \Psi_N dX - \bar{H}_I\Big)\Phi,$$

and compactly supported Ψ_N in δ small domain leads[4] to $\mathcal{O}(\delta)$ approximation of full Schrödinger in $L^2(dxdX)$.

[4]Bornemann F.A., Nettesheim P. and Schütte C., J. Chem. Phys, **105** (1996) 1074–1083.

2. Ehrenfest dynamics from WKB

$$\Psi_N = \psi e^{iM^{1/2}\theta}$$

leads to Ehrenfest

$$\ddot{X} = -\Psi_E \cdot \partial_X V(X) \Psi_E$$
$$iM^{-1/2}\dot{\Psi}_E = V\Psi_E$$

(X, Ψ_E) approximates[5] TDSCF with error $\mathcal{O}(\delta^2 + M^{-1/2})$

[5] Bornemann F.A., Nettesheim P. and Schütte C., J. Chem. Phys, **105** (1996) 1074–1083.
Tully J.C., Faraday Discuss., **110** (1998) 407–419.
Marx D. and Hutter J., *Ab initio molecular dynamics: Theory and implementation, Modern Methods and Algorithms of Quantum Chemistry*, J.Grotendorst(Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000

3. Born-Oppenheimer approximation: $\Psi_E =$ ground state

An electron eigenstate: $\Psi_E = \Psi_n$

$$V(X)\Psi_n = \lambda_n(X)\Psi_n$$

implies

$$\ddot{X} = -\Psi_n \cdot \partial_X V(X)\Psi_n = -\partial_X \lambda_n(X)$$

Spectral gap can be used to prove[6] $\mathcal{O}(M^{-1/4})$ approximation of Schrödinger in L^2.

[6] Hagedorn G.A., Commun. Math. Phys., **77** (1980) 1–19.
Panati G., Spohn H. and Teufel S., Math. Mod. Numer. Anal.