Continuum of Methods

- Path Integral Monte Carlo
- Ab initio Molecular Dynamics
- Semi-empirical Molecular Dynamics
- Langevin Equation
- Brownian Dynamics or DPD
- Metropolis Monte Carlo
- Kinetic Monte Carlo

The general procedure is to:
- get rid of unimportant variables
- average out fast degrees of freedom.

Monte Carlo Dynamics

- MC was introduced as a way of sampling configuration space so that MC dynamics is purely fictitious.

- However for some types of MC, dynamics is “realistic”: Brownian dynamics, reptation, kinetic MC.

- If we satisfy certain conservation laws in the dynamics (e.g. locality of moves) then the dynamics is a possible model with "local thermodynamic equilibrium".

- For Ising model we speak of Kawasaki Dynamics - this respects the locality of spin.

- MC dynamics is useful because it is so much faster than MD.
Smart Monte Carlo

Same idea but sample from a \textit{displaced Gaussian pdf}.

\[ T(r \rightarrow r') \propto \exp \left( -\frac{\left( r' - r - \tau \beta F(r) \right)^2}{2\tau} \right) \]

with trial displ.: \( \Delta r = \tau \beta F(r) + \delta \) \quad \text{with} \quad \delta < 0 \quad \text{and} \quad \delta^2 = 2\tau

\begin{itemize}
  \item Also moves in the direction of increased probability
  \item Acceptance rate \( A \) will be:
\end{itemize}

\[ \exp \left( -\beta(V(r') - V(r)) - \frac{\beta}{2} \left[ F(r) + F(r') \right] \right) \left[ \left( 2(r' - r) + \tau \beta (F(r') - F(r)) \right) \right] \]

\begin{itemize}
  \item There is a nice way of deriving this -- related to Brownian dynamics and quantum Monte Carlo.
\end{itemize}

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Brownian Dynamics

Let’s explore the connection between Brownian motion and Metropolis Monte Carlo. \textit{Why}?

\begin{itemize}
  \item Connection with \textit{smart MC}
  \item Introduce the idea of \textit{kinetic Monte Carlo}
  \item Get rid of solvent degrees of freedom and have much longer time steps.
\end{itemize}
Local Markov process

Let us make a course approximation to a molecular dynamics of a large molecule in the presence of a solvent that we want to eliminate.

- Particle will follow a continuous trajectory $R(t)$.
- Let us assume that the movement is Markovian and local.
- Describe in terms of the Green’s function $\rho(r,r',t)$, a probability density of a particle at $(r,t)$ starting at $(r',0)$.
- The master equation describes its time evolution:

\[
\frac{d \rho}{dt} = \hat{O}(r,r';t)
\]

Initial condition:

\[
\rho(r,r';0) = \delta(r-r')
\]

General Form of Evolution

- What could we have for $O$?
- Not hard to prove that $O$ must be a sum of first and second derivative operators. The most general form is:

\[
\frac{\partial \rho(R,R';t)}{\partial t} = \nabla \tilde{D}(R) \left( \nabla \rho(R,R';t) - \beta \tilde{F}(R) \rho(R,R';t) \right)
\]

- Probability is conserved. \[ \int dR \rho(R,R';t) = 1 \]
- Steady state solution is:

\[
\frac{d \rho(R,R';t)}{dt} = 0 \Rightarrow \nabla \rho(R,R';t) = \beta \tilde{F}(R) \rho(R,R';t)
\]

Implies that \[ \lim_{\beta \to \infty} \rho(R,R';t) = \frac{e^{-\beta \tilde{F}(R)}}{Z} \]
• How do we prove dynamics is unique?
  – If it is a continuous walk, it has to be made of little random steps.

• Central limit theorem says that the only things that survive adding together many little steps are:
  – Mean value: this is the drift term
  – The variance: this is the diffusion term.

• Hence the “smart MC” Gaussian is the most general Markovian form, if we allow a general diffusion matrix.

• If we choose it to be isotropic and independent of position then $D(R)$ is a constant.
  – it could vary in some media both in position and direction
  – also it could couple particles far apart, hydrodynamic effects.

\[
\frac{\partial \rho(R,R';t)}{\partial t} = \nabla \cdot \vec{D}(R) \left( \nabla \rho(R,R';t) - \beta \vec{F}(R) \rho(R,R';t) \right)
\]

\[
\left\langle \frac{dR}{dt} \right\rangle = \int dR \int dR' \frac{\rho(R,R';t)}{dt}
\]

\[
= \int dR R \nabla \cdot \vec{D}(R) \left( \nabla \rho(R,R';t) - \beta \vec{F}(R) \rho(R,R';t) \right)
\]

\[
= -\int dR \vec{D}(R) \left( \nabla \rho(R,R';t) - \beta \vec{F}(R) \rho(R,R';t) \right)
\]

\[
= -\int dR \left( -\nabla \vec{D}(R) - \vec{D}(R) \beta \vec{F}(R) \right) \rho(R,R';t)
\]

\[
\left\langle \frac{dR}{dt} \right\rangle \bigg|_{t=0} = \nabla \vec{D}(R') + \beta \vec{D}(R) \vec{F}(R')
\]

For the variance:
\[
\frac{d}{dt} \left( \left\langle (R-R')(R-R') \right\rangle \right) \bigg|_{t=0} = 2\vec{D}(R')
\]
Trotter’s formula

- How do we find the solution of:  
\[ \frac{d\hat{\rho}}{dt} = (A + B)\hat{\rho} \]
- The operator solution is:
\[ \hat{\rho} = e^{(A+B)t} \]
- Trotter’s formula (1959):
\[ \hat{\rho} = \lim_{n \to \infty} \left[ e^{tA} e^{tB} \right]^n \]
- Assumes that A, B and A+B are reasonable operators.

\[ \left\langle R_n \left[ e^{\frac{t}{n}A} e^{\frac{t}{n}B} \right]^n \right\rangle = \left\langle R_n \left| e^{z_1} \right| R_1 \right\rangle \left\langle R_1 \left| e^{z_2} \right| R_2 \right\rangle \cdots \left\langle R_{n-1} \left| e^{z_i} \right| R_i \right\rangle \left\langle R_i \left| e^{z_{i+1}} \right| R_{i+1} \right\rangle \cdots \left\langle R_{n-1} \left| e^{z_n} \right| R_n \right\rangle \]

- This means we just have to figure out what each operator does independently and then alternate their effect. This is rigorous in the limit as \( n \to \infty \).
- For Brownian dynamics, A is diffusion operator, B is a drift operator.
- Like “molecular dynamics”, at small \( t \) we evaluate each operator separately.

Generalized Trotter Formula

- True of any number of operators, as long as they are each bounded below.
\[ \hat{\rho} = e^{-\beta(\hat{A} + \hat{B} + \hat{C})} \]
\[ \hat{\rho} = \lim_{n \to \infty} \left[ e^{-\frac{\tau}{n}\hat{A}} e^{-\frac{\tau}{n}\hat{B}} e^{-\frac{\tau}{n}\hat{C}} \right]^n \quad \tau = \beta / n \]
- Interpret \( \rho \) as a probability; evolution equation is:
\[ -\frac{\partial \hat{\rho}}{\partial \beta} = (\hat{A} + \hat{B} + \hat{C})\hat{\rho} \quad \text{initial value:} \hat{\rho}\big|_{\beta=0} = \hat{I} \]
- Discrete-time version:
\[ \hat{\rho}(\beta + \tau) \approx e^{-\tau\hat{A}} e^{-\tau\hat{B}} e^{-\tau\hat{C}} \hat{\rho}(\beta) \]
- We can use the effects of operators separately as long as we take small enough time steps.
Evaluation of diffusion term

\[ \langle r | e^{-i \hat{T}} | r' \rangle = \sum_{\alpha} \phi_{\alpha}^*(r) \phi_{\alpha}(r') e^{-i T_{\alpha}} \quad T = -D \nabla^2 \]

In PBC eigenfunctions of \( \hat{T} = \frac{1}{\sqrt{\Omega}} e^{-i \hat{\rho}} \)

and eigenvalues are \( D k^2 \)

\[ \langle r | e^{-i \hat{T}} | r' \rangle = \sum_{k} \frac{1}{\Omega} e^{-i \hat{\rho}} e^{i \hat{\rho}'} e^{-i \tau D k^2} \]

convert to an integral

\[ \langle r | e^{-i \hat{T}} | r' \rangle = \frac{1}{(2\pi)^2} \int dke^{i(\hat{\rho} - \hat{\rho}') - i \tau D k^2} = (4\pi D \tau)^{-3/2} e^{-(r-r')^2 / 4D \tau} \]

Danger: makes assumption about boundaries.
This is a diffusion process.

Green’s function for a gradient

What is Green’s function for the operator?

\[ \hat{F} \hat{\nabla} \quad (\text{variables separate to 1D problems}) \]

Evolution equation for Green’s function:

\[ \frac{\partial \rho(x,t)}{\partial t} = -F \frac{\partial \rho(x,t)}{\partial x} \quad \text{solution} \quad \rho(x,t) = h(x - Ft) \]

This operator just causes probability distribution to drift in the direction of \( F \).

For \textit{Smoluchowski equation for Brownian motion} it was the effect of gravitational field on the motion of colloids.
In practice, we \underline{limit} the gradient so the walk is not pushed too far.
• Using a symmetrized operator:
\[ \rho(R \rightarrow R') = e^{-\beta(V(R') - V(R))} \left( \langle R | e^{-\beta H} | R' \rangle \right) \]
• Exact property of Green’s function (detailed balance)
\[ e^{-\beta V(R)} \rho(R \rightarrow R') = e^{-\beta V(R')} \rho(R' \rightarrow R) \]
• We enforce detailed balance to decrease time step errors.
\[ A(R \rightarrow R') = \min \left[ 1, \frac{\rho(R' \rightarrow R)}{\rho(R \rightarrow R')} e^{-\beta(V(R') - V(R))} \right] \]
• Typically we choose time step with 99% acceptance ratio.
• Method gives exact result if time step is small or sampling is exact and always the right static properties

Summary of Brownian Dynamics

The Smoluchowski equation is:
\[
\frac{\partial \rho(R,t)}{\partial t} = D \nabla^2 \rho(R,t) - \beta D \nabla [ F(R) \rho(R,t) ]
\]
\[ R(t + \tau) = R(t) + \tau \beta D F(R(t)) + \eta(t) \]
\[ \langle \eta(t) \rangle = 0 \quad \langle \eta(t)^2 \rangle = 2 \tau D \]

Enforce detailed balance by rejections! (hybrid method)
This makes sure that we get correct s.s. state.
\[
T(R \rightarrow R') = c \exp \left( \frac{(R' - R - \beta D \tau F(R))^2}{2D\tau} \right)
\]
BUT, we need acceptance ratio close to 1 to get dynamics correct!
Hydrodynamical effects

- Brownian dynamics neglects long-time correlations which can arise from hydrodynamical effects.
- One can treat this within Brownian dynamics by using the Oseen tensor. \( D(R) \) is calculated in perturbation theory. Then the noise on 2 particles becomes correlated.

\[
\bar{D}(R)_{ij} = \frac{kT}{8\pi \eta v_i} \left( 1 + \frac{r_i r_j}{r_r^2} \right)
\]

- We sample the noise by Choleski decomposition as described in the lecture on sampling.
- This is only a linear approximation to the hydrodynamics.

Langevin Equation

- If we want to be more realistic we have to keep the momentum of the heavy particle.

\[
\frac{dr}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = F + p_{\text{solv}}(t) - \zeta p
\]

- Where we have added a random force and a friction.
- To get detailed balance we must have:

\[
\left\langle p_{\text{solv}}(t) p_{\text{solv}}(t') \right\rangle = 2m kT \zeta \delta(t - t')
\]

- As friction goes to zero. MD is recovered
- As friction goes to infinity: Smoluchowski Eq is found.
- We can have more general memory also

\[
\left\langle p_{\text{solv}}(t) p_{\text{solv}}(t') \right\rangle = C(t - t')
\]
Dissipative Particle Dynamics (DPD)
FS 465, Hoogerbrugge, Koelman 93

- DPD can treat hydrodynamics more realistically without including explicit solvent atoms.

\[
F_i = \sum_{j \neq i} f(r_{ij}) + \zeta \hat{r}_{ij}
\]

\[
\langle \zeta \rangle = -\omega (r_{ij})^2 (\nabla \cdot \hat{r}_{ij})
\]

\[
\langle \zeta^2 \rangle = 2k_B T \omega^2 (r_{ij})
\]

- Conserves momentum because equal and opposite random forces are applied to each pair.
- Implies NS hydrodynamics by conservation laws.
- Steady state distribution is canonical (prove that it is the unique stationary state)
- \(\omega(r) = (1-r/r_c)^2\) is a randomized force cut off at \(r_c\)
How to do the DPD

- Verlet algorithm
  
  \[ v(t + \Delta t / 2) = v(t - \Delta t / 2) + \Delta t f(t) / m \]
  
  \[ r(t + \Delta t) = r(t) + \Delta t v(t + \Delta t / 2) \]

- But \( f(t) \) depends on velocity at time \( t \), \( f(v(t)) \) requiring future velocity:
  
  \[ v(t) = \frac{1}{2} [v(t + \Delta t / 2) + v(t - \Delta t / 2)] \]

- Solve equation for \( v \) self-consistently by iterating.
- Now it is time-reversible and thus will satisfy detailed balance.