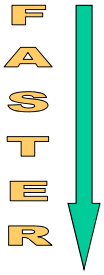
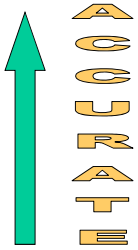
Continuum of Methods



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 ***displaced Gaussian pdf***.

$$T(r \to r') \propto \exp\left(-\frac{\left(r' - r - \tau\beta F(r)\right)^2}{2\tau} \right)$$

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

- Also moves in the direction of increased probability
- Acceptance rate A will be:

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

- There is a nice way of deriving this -- related to Brownian dynamics and quantum Monte Carlo.

Brownian Dynamics

Let's explore the connection between Brownian motion and Metropolis Monte Carlo. Why?

- Connection with smart MC
- Introduce the idea of kinetic Monte Carlo
- Get rid of solvent degrees of freedom and have much longer time steps.

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:

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

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:

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

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

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

Implies that $$\lim_{t\to\infty}\rho(R,R';t) = \frac{e^{-\beta V(R)}}{Z}$$

- 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.

Moment Expansion

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

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

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

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

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

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

For the variance: $$\frac{d\left\langle \overrightarrow{(R-R')}\overrightarrow{(R-R')} \right\rangle}{dt}\Bigg|_{t=0} = 2\overleftrightarrow{D}(R')$$

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): $\hat{\rho} = \lim_{n\to\infty}\left[e^{\frac{t}{n}\hat{A}}e^{\frac{t}{n}\hat{B}}\right]^n$
- Assumes that A, B and A+B are reasonable operators.

$$\left\langle R_0\left|\left[e^{\frac{t}{n}\hat{A}}e^{\frac{t}{n}\hat{B}}\right]^n\right|R_n\right\rangle = \left\langle R_0\left|e^{\frac{t}{n}\hat{A}}\right|R'_1\right\rangle\left\langle R'_1\left|e^{\frac{t}{n}\hat{B}}\right|R_1\right\rangle....\left\langle R_{n-1}\left|e^{\frac{t}{n}\hat{A}}\right|R'_n\right\rangle\left\langle R'_n\left|e^{\frac{t}{n}\hat{B}}\right|R_n\right\rangle$$

• 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→∞.
• 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.

$$\hat{\rho} = e^{-\beta(\hat{A}+\hat{B}+\hat{C})}$$

$$\hat{\rho} = \lim_{n\to\infty}\left[e^{-\tau\hat{A}}e^{-\tau\hat{B}}e^{-\tau\hat{C}}\right]^n \qquad \tau = \beta/n$$

- Interpret ρ 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

$$\left\langle r\left|e^{-\tau\hat{T}}\right|r'\right\rangle=\sum_{\alpha}\phi_{\alpha}^{*}(r)\phi_{\alpha}(r')e^{-\tau T_{\alpha}}\quad T=-D\nabla^{2}$$

In PBC eigenfunctions of $\hat{T}=\frac{1}{\sqrt{\Omega}}e^{-i\vec{k}\vec{r}}$

and eigenvalues are Dk^{2}

$$\left\langle r\left|e^{-\tau\hat{T}}\right|r'\right\rangle=\sum_{k}\frac{1}{\Omega}e^{-i\vec{k}\vec{r}}e^{i\vec{k}\vec{r}'}e^{-\tau Dk^{2}}$$

convert to an integral

$$\left\langle r\left|e^{-\tau\hat{T}}\right|r'\right\rangle=\frac{1}{(2\pi)^{3}}\int dke^{i\vec{k}(\vec{r}'-\vec{r})-\tau Dk^{2}}=(4\pi D\tau)^{-3/2}e^{-(r-r')^{2}/4D\tau}$$

Danger: makes assumption about boundaries.

This is a diffusion process.

Green's function for a gradient

What is Green's function for the operator?

$\vec{F}\vec{\nabla}$ (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 *Smoluchowski equation for Brownian motion* it was the effect of gravitational field on the motion of colloids.

In practice, we limit the gradient so the walk is not pushed too far.

- Using a symmetrized operator:

$$\rho(R \to R') = e^{-\beta\left(V(R')-V(R)\right)}\left\langle R\left|e^{-\tau H}\right|R'\right\rangle$$

- Exact property of Green's function (detailed balance)

$$e^{-\beta V(R)}\rho\left(R \to R'\right) = e^{-\beta V(R')}\rho\left(R' \to R\right)$$

- We enforce detailed balance to decrease time step errors.

$$A\left(R \to R'\right) = \min\left[1, \frac{\rho(R' \to R)}{\rho(R \to R')} e^{-\beta\left(V(R')-V(R)\right)}\right]$$

- 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:

$$\frac{\partial\rho(R,t)}{\partial t} = D\nabla^2\rho(R,t) - \beta D\nabla[F(R)\rho(R,t)]$$
$$R(t+\tau) = R(t) + \tau\beta DF(R(t)) + \eta(t)$$
$$\left\langle\eta(t)\right\rangle = 0 \qquad \left\langle\eta(t)^2\right\rangle = 2\tau D$$

Enforce detailed balance by rejections! (hybrid method)
This makes sure that we get correct s.s. state.

$$T(R \to R') = c\exp\left(-\frac{(R' - R - \beta D\tau F(R))^2}{2D\tau}\right)$$

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.

$$\overleftrightarrow{D}(R)_{ij} = \frac{kT}{8\pi\eta r_{ij}}\left(1+\frac{\overleftrightarrow{r_{ij}\,r_{ij}}}{r_{ij}^{\,2}}\right)$$

- 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.

$$\frac{dr}{dt} = \frac{p}{m} \qquad \frac{dp}{dt} = F + p_{solvent}(t) - \zeta p$$

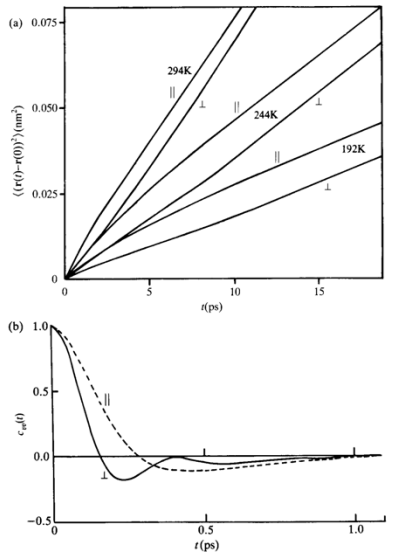
- Where we have added a random force and a friction.
- To get detailed balance we must have:

$$\left\langle p_{solvent}(t)\, p_{solvent}(t')\right\rangle = 2mkT\zeta\delta\left(t-t'\right)$$

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

$$\left\langle p_{solvent}(t)\, p_{solvent}(t')\right\rangle = C(t-t')$$

From A&T Chpt. 6



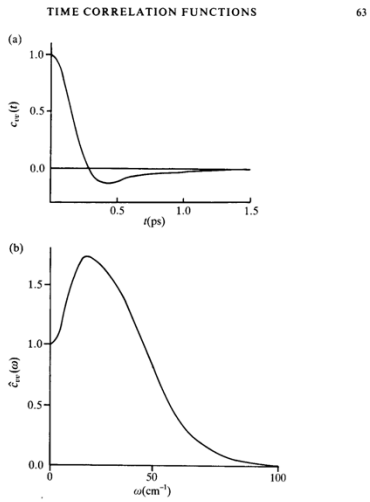


Fig. 6.5 Calculating the diffusion coefficient in CS_2. (a) Mean square displacements at $T = 192$ K, 244 K, 294 K. (b) Velocity autocorrelation functions at $T = 192$ K. In each case we show components parallel and perpendicular to the molecular axis system at $t = 0$ [Tildesley and Madden 1983]

(a) The velocity autocorrelation function and (b) its Fourier transform, for the ones liquid near the triple point ($\rho^* = 0.85$, $T^* = 0.76$).

Dissipative Particle Dynamics (DPD)

FS 465, Hoogerbrugge, Koelman 93

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

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

$$\langle \zeta \rangle = -\omega(r_{ij})^2 (\vec{v}_{ij} \bullet \hat{r}_{ij})$$

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

- 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:

$$v(t) = \frac{1}{2}\left[v(t+\Delta t/2) + v(t-\Delta t/2)\right]$$

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