Path sampling with stochastic dynamics: Some new algorithms

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The Brownian tube – a new proposal function

Description of the path ensemble

- System of N particles, mass matrix $M = \mathrm{Diag}(m_1, \dots, m_N)$, configuration variable $q = (q_1, \dots, q_N)$, momentum variable $p = (p_1, \dots, p_N)$, stochastic dynamics
$$dX_t = b(X_t)\, dt + \Sigma dW_t,$$
X_t = configurational part q_t, or full phase space variable (q_t, p_t)
- Trajectory length $T = L\Delta t$, discrete trajectory $x = (x_0, \dots, x_L)$
- Weight of an unconstrained path
$$\pi(x) = Z_L^{-1} \rho(x_0) \prod_{i=0}^{L-1} \mathrm{p}(x_i, x_{i+1})$$
- Weight of a reactive path between the sets A and B
$$\pi_{AB}(x) = Z_{AB}^{-1} \mathbf{1}_{\mathrm{A}}(x_0) \rho(x_0) \prod_{i=0}^{L-1} \mathrm{p}(x_i, x_{i+1}) \mathbf{1}_{\mathrm{B}}(x_L)$$

The path ensemble for some discretization of the Langevin dynamics

- Scheme based on splitting

$$\begin{cases} p_{i+1/2} = p_i - \dfrac{\Delta t}{2} \nabla V(q_i), \\ q_{i+1} \;\; = q_i + c_1 \, p_{i+1/2} + U_{1,i}, \\ p_{i+1} \;\; = c_0 \, p_{i+1/2} - \dfrac{\Delta t}{2} \nabla V(q_{i+1}) + U_{2,i}, \end{cases}$$

- The conditional probability $\mathrm{p}((q_{i+1}, p_{i+1}), (q_i, p_i))$ to be in the state $x_{i+1} = (q_{i+1}, p_{i+1})$ starting from $x_i = (q_i, p_i)$ reads

$$\mathrm{p}(x_{i+1}, x_i) = Z^{-1} \exp \left[- \frac{1}{2(1 - c_{12}^2)} \left(\left(\frac{\mathrm{d}_1}{\sigma_1} \right)^2 + \left(\frac{\mathrm{d}_2}{\sigma_2} \right)^2 - 2 c_{12} \left(\frac{\mathrm{d}_1}{\sigma_1} \right) \left(\frac{\mathrm{d}_2}{\sigma_2} \right) \right) \right.$$

where the normalization constant is $Z = \left(2\pi \sigma_1 \sigma_2 \sqrt{1 - c_{12}^2} \right)^{-d}$.

The Metropolis-Hastings scheme for path sampling

- Markov chain kernel ($\mathcal{P}$ is the so-called proposal function)

$$P(x, dy) = r(x,y)\mathcal{P}(x,y)\;dy + \left(1 - \int r(x,y')\mathcal{P}(x,y')\;dy'\right)\delta_x, \qquad (1)$$

  where the density $r(x,\cdot)$ is given by $r(x,y) = \min\left(1, \frac{\pi(y)\mathcal{P}(y,x)}{\pi(x)\mathcal{P}(x,y)}\right)$.

- Brownian tube proposal = new random noises correlated to the previous ones (generalization of usual shooting and 'noise history')

- Denoting by G^x (resp. $\bar{G}^x$) the standard gaussian random numbers used for forward (resp. backward) integration of the path x (shooting index k),

$$\mathcal{P}(x,y) = \prod_{0\le i\le k-1} \mathrm{p}_{\alpha_i}(\bar{G}_i^x, \bar{G}_i^y) \prod_{k\le i\le L-1} \mathrm{p}_{\alpha_i}(G_i^x, G_i^y),$$

  with $\mathrm{p}_\alpha(G,\tilde{G}) = \left(\frac{1}{\sqrt{2\pi(1-\alpha^2)}}\right)^d \exp\left(-\frac{(\tilde{G}-\alpha G)^T(\tilde{G}-\alpha G)}{2(1-\alpha^2)}\right)$.

Measure of efficiency

- Decorrelation of transition times
- Intrinsic decorrelation: related to the existence of some distance or norm on path space. Given a distance function $\mathrm{d}(x,y)$, and $p \geq 1$,

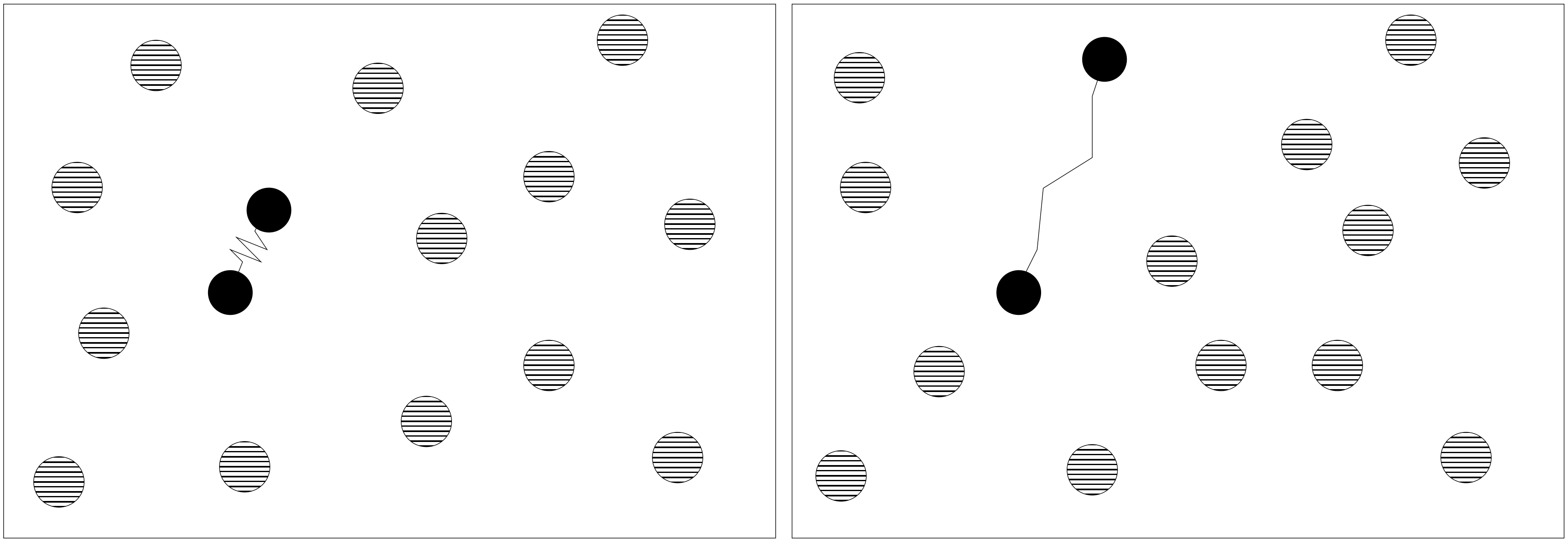
$$D_p(n) = \left(\int\int [\mathrm{d}(y,x)]^p \;\; P^n(x,dy)\, d\pi(x) \right)^{1/p}$$

- In practice, assuming ergodicity, $D_p(n) = \lim_{N \to +\infty} \left[\frac{1}{N} \sum_{k=1}^{N} \mathrm{d}^p(x^{k+n}, x^k) \right]^{1/p}$.
- Choices for the distance d
  - (weighted) norm $||\cdot||$ on the whole underlying phase-space
  - projection of the configurations onto level sets of a given order parameter
  - align the paths projected onto some submanifold around a given value of the reaction coordinate ξ

Application to a model system of conformational changes

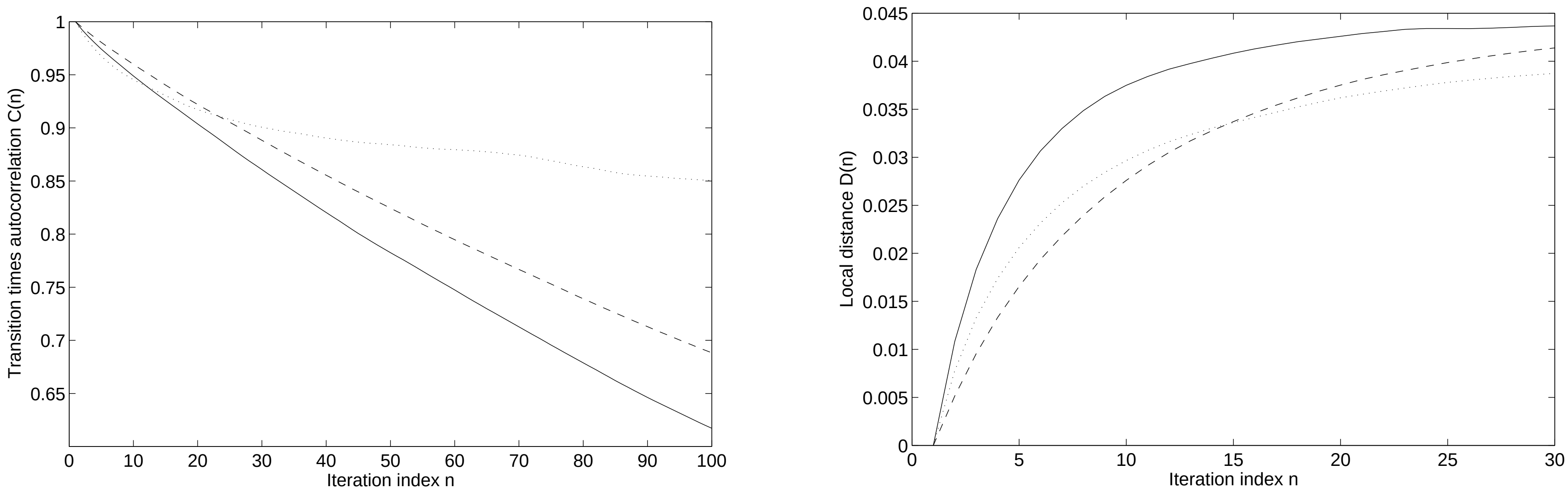
Dimer in a WCA solute (WCA potential = truncated LJ, dimer = double well)

$$V_{\mathrm{WCA}}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon & \text{if } r \le r_0, \\ 0 & \text{if } r > r_0, \end{cases} \quad , V_{\mathrm{DW}}(r) = h\left[1 - \frac{(r - r_0 - w)^2}{w^2}\right]$$



Compact state (Left), stretched state (Right).

Balanced acceptance/rejection rate (can theoretically be set to an arbitrary value).



Comparison of efficiencies for different Metropolis-Hastings proposal moves ($h = 10$). Left: Plot of $D(n)$ (local sampling efficiency) for the Brownian tube proposal with $\alpha \equiv 0.8$ (solid line), usual shooting dynamics (dashed line), and noise history (dotted line). Right: Same study for the correlation of the transition times $C(n)$ (related to some global sampling efficiency).

(Non)equilibrium sampling of paths

- Switching dynamics (Jarzynski) using a family of functions h_λ such that $h_0 = \mathbf{1}$, $h_1 = \mathbf{1}_B$: family of measures

$$\pi_\lambda(x) = Z_{L,\lambda}^{-1} \mathbf{1}_{\mathrm{A}}(x_0)\rho(x_0) \prod_{i=0}^{L-1} \mathrm{p}(x_i, x_{i+1}) h_\lambda(x_L) \tag{2}$$

- Energy $\mathcal{E}_\lambda(x)$ associated with a path x as $\pi_\lambda(x) = Z_{L,\lambda}^{-1} \mathrm{e}^{-\mathcal{E}_\lambda(x)}$.
- **Algorithm 0.1** *Starting from $W^0 = 0$ and $m = 0$,*
  - *Replace λ^m by λ^{m+1};*
  - *Update the work as $W^{m+1} = W^m + \mathcal{E}_{\lambda^{m+1}}(x^m) - \mathcal{E}_{\lambda^m}(x^m)$;*
  - *Do a Monte Carlo path sampling move using a Metropolis-Hastings scheme with the measure $\pi^{\lambda^{m+1}}$, so that the current path x^m is transformed into the new path x^{m+1}.*
- Estimated ratio of partition functions $C_M(L\Delta t) = -\ln\left(\frac{1}{M}\sum_{k=1}^{M} \mathrm{e}^{-W^{k,n}}\right)$.

Equilibrium sampling of the path ensemble

- **Algorithm 0.2** *Initial distribution* $(x^{1,0}, \ldots, x^{M,0}) \sim \pi_0$.
  - *Replace* λ^m *by* λ^{m+1}*;*
  - *Update* $W^{k,m+1} = W^{k,m} + \Delta\mathcal{E}^{k,m} = W^{k,m}\mathcal{E}_{\lambda^{m+1}}(x^{k,m}) - \mathcal{E}_{\lambda^m}(x^{k,m})$*, and compute the mean work update* $\overline{\Delta\mathcal{E}}^m = M^{-1}\sum_{1\le k\le M}\Delta\mathcal{E}^{k,m}$*;*
  - *(Diffusion step) Monte Carlo path sampling for* $\pi_{\lambda^{m+1}}$ *to obtain* $x^{k,m+1}$ *from* $x^{k,m}$*;*
  - *(Birth/death process) Update times* $\Sigma^{k,b}$ *and* $\Sigma^{k,d}$ *as*

$$\Sigma^{k,b} = \Sigma^{k,b} + \beta(\overline{\Delta\mathcal{E}}^m - \Delta\mathcal{E}^{k,m})^-, \quad \Sigma^{k,d} = \Sigma^{k,b} + \beta(\overline{\Delta\mathcal{E}}^m - \Delta\mathcal{E}^{k,m})^+.$$

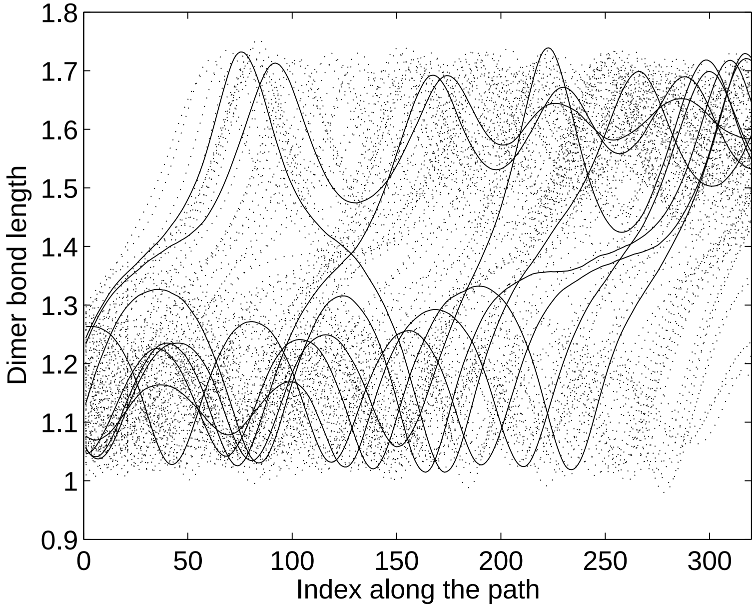
    (Death) If $\Sigma^{k,d} \geq \tau^{k,d}$*, select an index* $m \in \{1, \ldots, M\}$ *at random, and replace the* k*-th path by the* m*-th path. Generate a new time* $\tau^{k,d}$ *from an exponential law of mean* 1*, and set* $\Sigma^{k,d} = 0$*;*
    (Birth) same as death but a particle m *chosen at random is replaced by the* k*-th particle*
- Estimate $C_M(L\Delta t) = \frac{1}{M}\sum_{k=1}^M W^{k,n}$

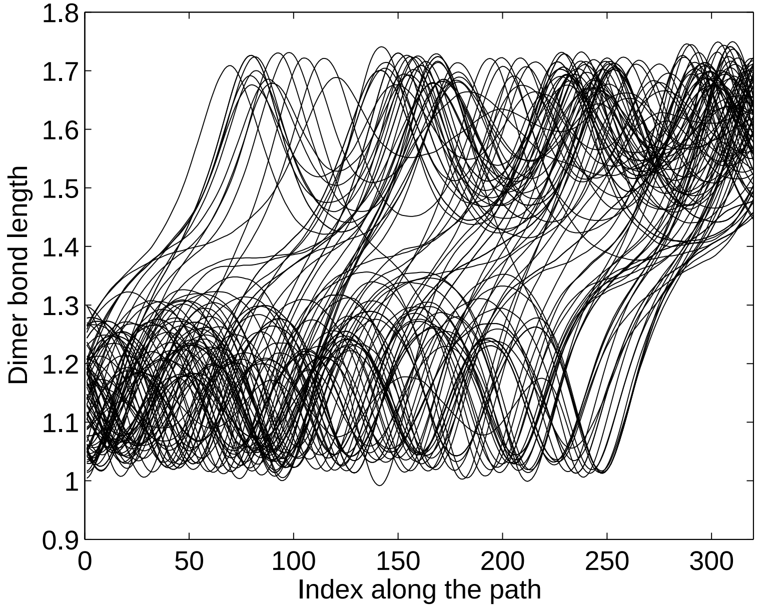
Application to a model system of conformational changes

- Compute of ratio of partition functions: reduction of variance

M	n	Backward	Forward	IPS (forward)
2000	5000	5.34 (5.04-5.58)	5.41 (5.32-5.50)	5.19 (5.16-5.23)
2000	10000	5.45 (5.32-5.58)	5.40 (5.34-5.46)	5.40 (5.36-5.43)
2000	15000	5.42 (5.35-5.49)	5.40 (5.35-5.45)	5.45 (5.42-5.48)

- The final sample of paths is non-degenerate





Some references

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