On the Convergence of the OSRW method

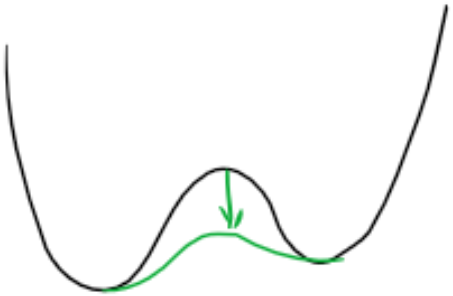
Zhifeng Jing

2016.1.29

The Sampling Problem

- Kinetic barrier

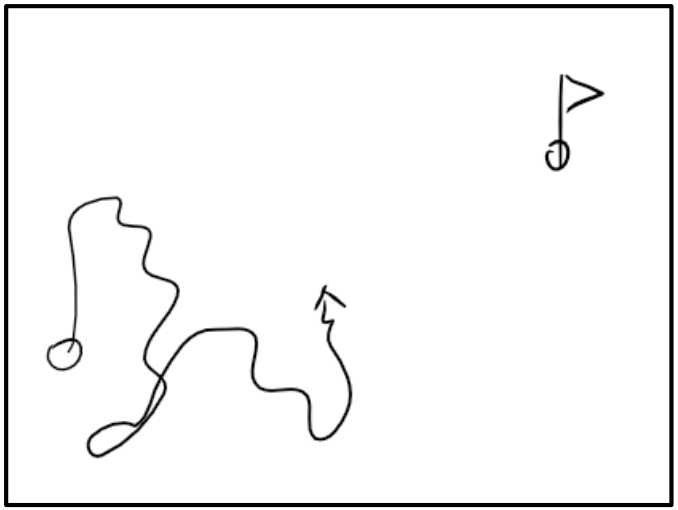
$$k \propto \exp\left(-\Delta G / k_B T\right)$$



- Diffusive barrier

$$t \propto x^2$$

  - Non-equilibrium simulation
  - Fragmentation

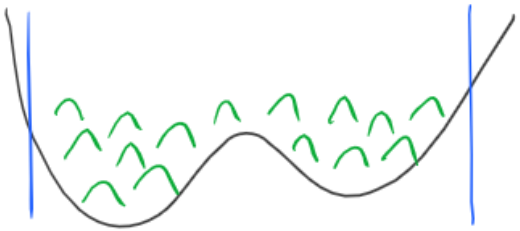


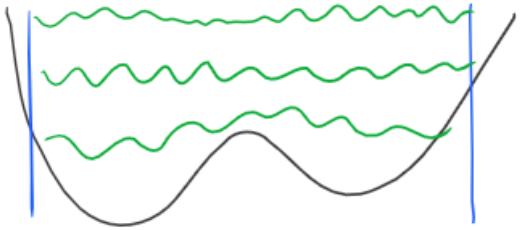
Metadynamics and Well-tempered Metadynamics

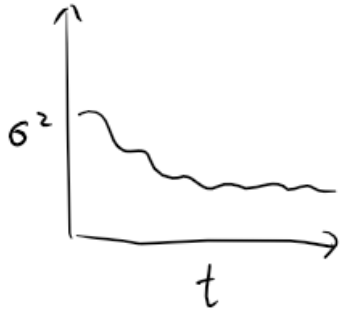
- Metadynamics
  - Fast exploration of the free energy landscape
  - Require boundary condition
  - Finite error of ~*h* at the long time limit

$$F(s,t) = F_0(s) + g(s,t) \rightarrow C(t) \pm h$$

$$g(t) = \sum_{i=1}^{n} h \, \mathrm{e}^{-\frac{\left[s - s(t_i)\right]^2}{2\omega^2}}$$



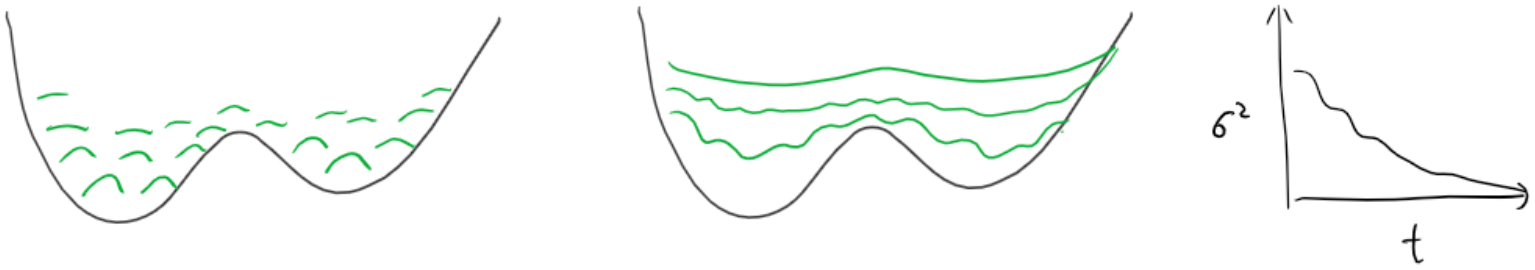




Metadynamics and Well-tempered Metadynamics

- Well-tempered metadynamics
  - Converge asymptotically

$$F(s,t) = F_0(s) + g(s,t) \rightarrow F_0(s)\frac{T}{T+\Delta T} + C$$



A. Barducci *et al.* PRL **100**, 020603 (2008)
J. F. Dama *et al.* PRL **112**, 240602 (2014)

OSRW

- Equation of motion

$$U_m = U_0(\lambda) + g_m(\lambda, F_\lambda) + f_m(\lambda)$$

$$g_m(t_n) = \sum_{i=1}^{n} h\, \mathrm{e}^{-\frac{\left[\lambda - \lambda(t_i)\right]^2}{2\omega_1^2}}\, \mathrm{e}^{-\frac{\left[F_\lambda - F_\lambda(t_i)\right]^2}{2\omega_2^2}}$$

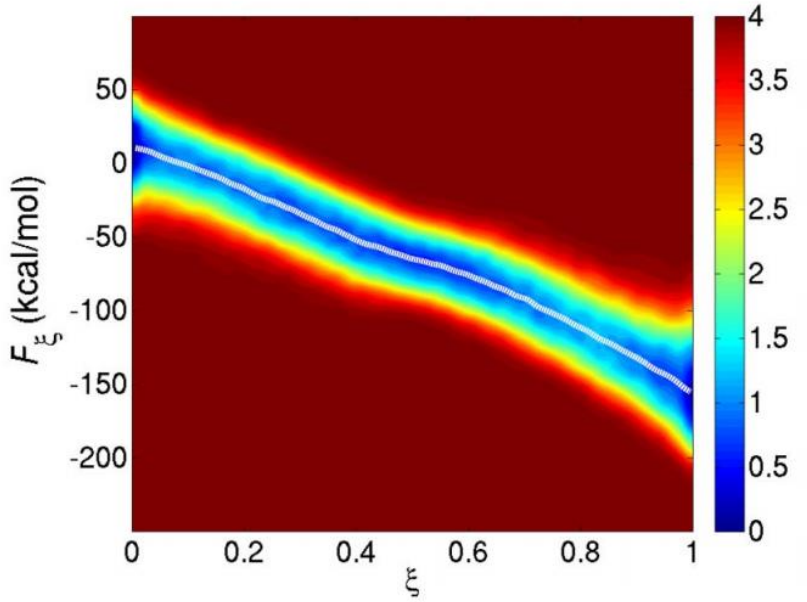
Standard metadynamics recursion

No boundary for F_λ

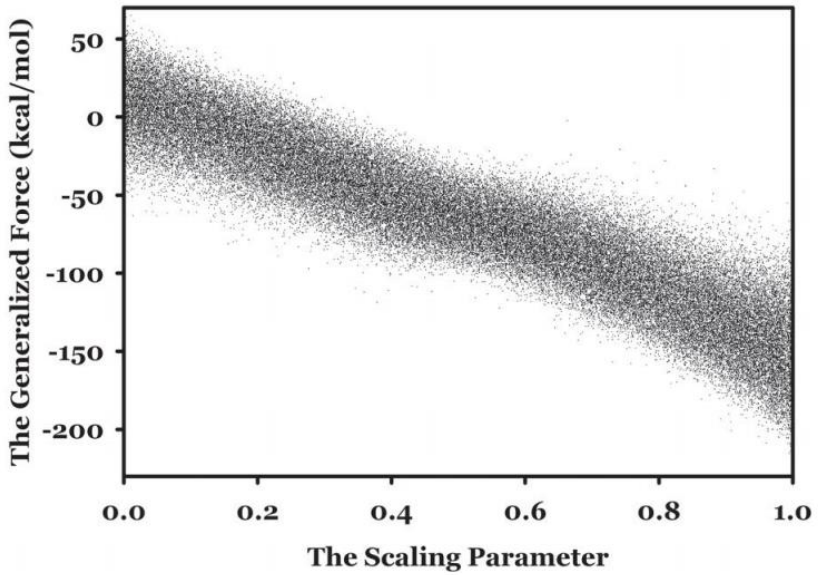
$$f_m(t_n) = -G_0(\lambda, t_n)$$

Current estimate of free energy

OSRW



Free energy surface

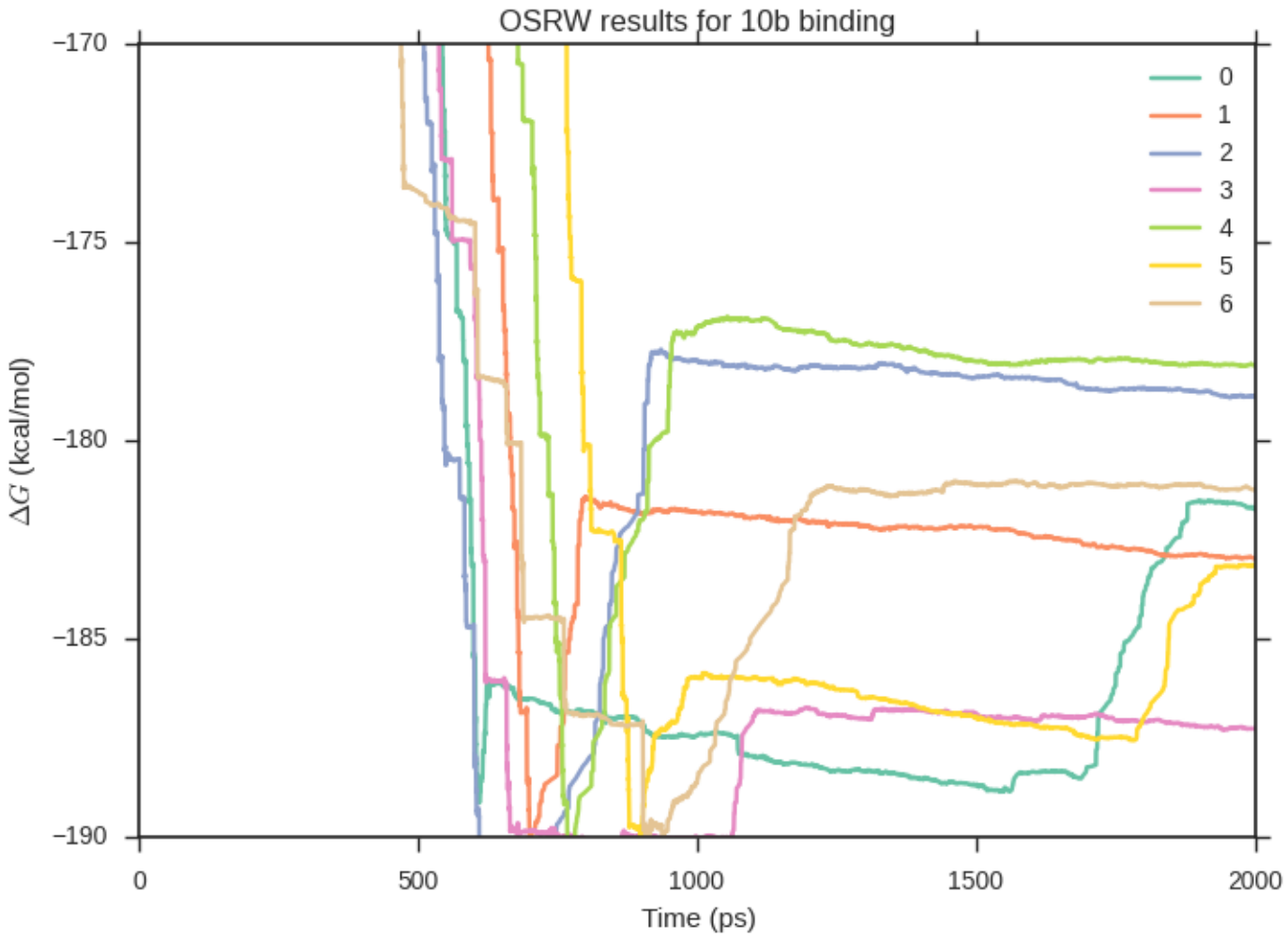


Distribution of samples

L. Zheng *et al.* PNAS **105** (51), 20227 (2008)

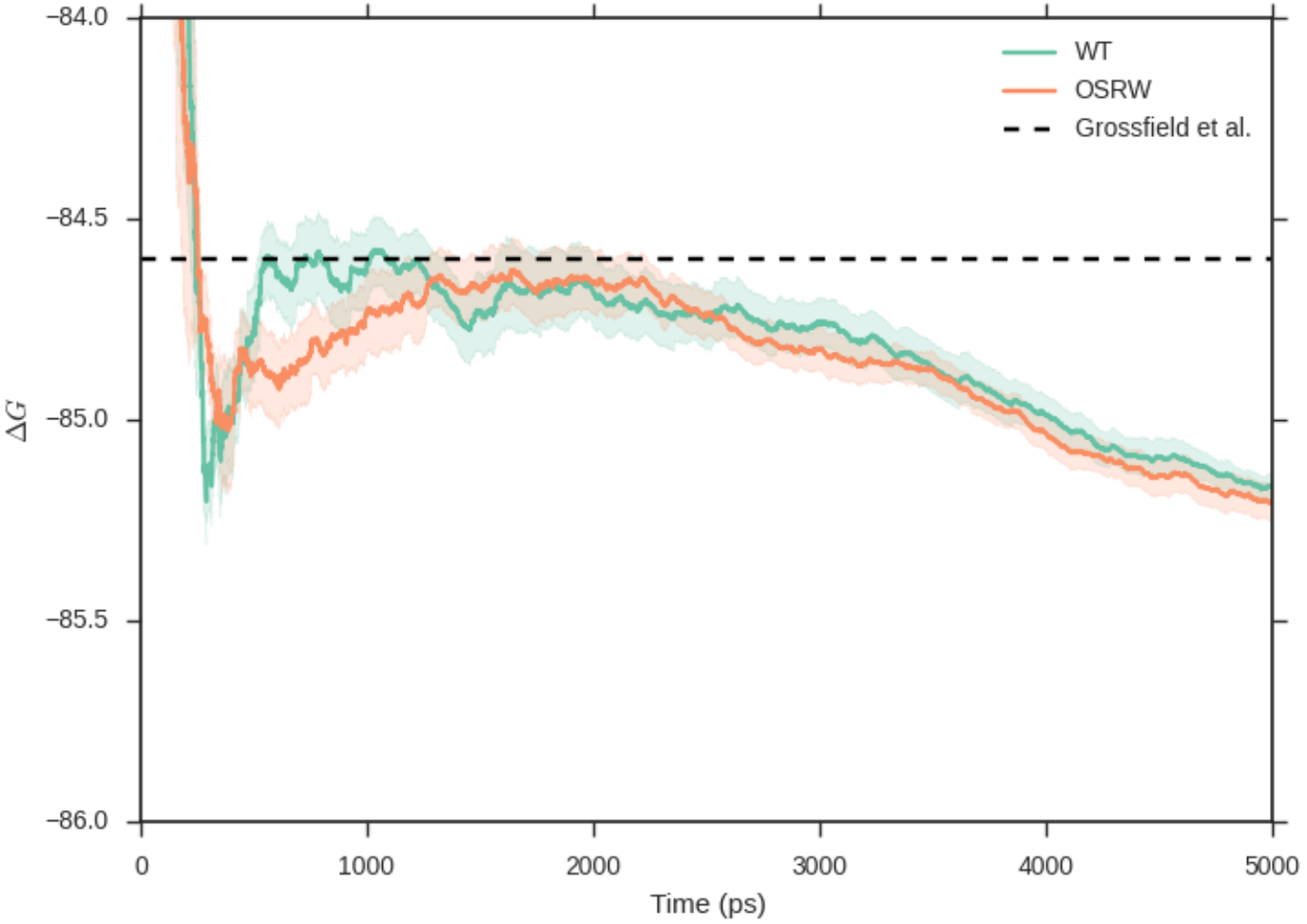
Convergence of OSRW

- Test on SAMPL4



OSRW and Well-tempered OSRW

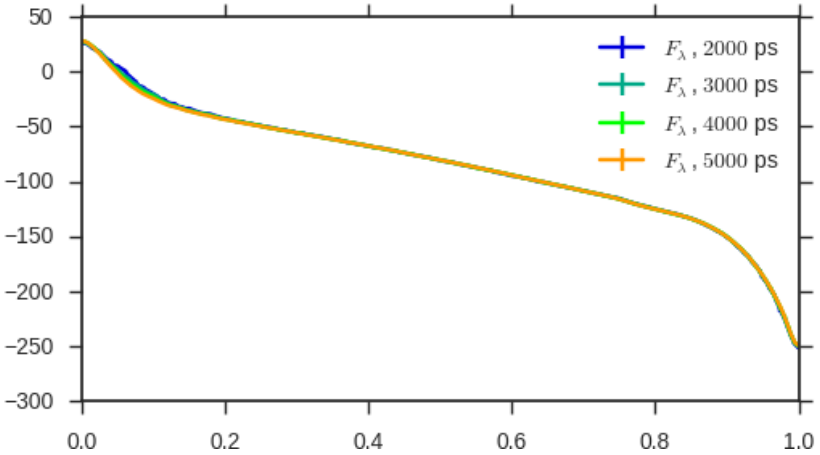
- Cl^- solvation

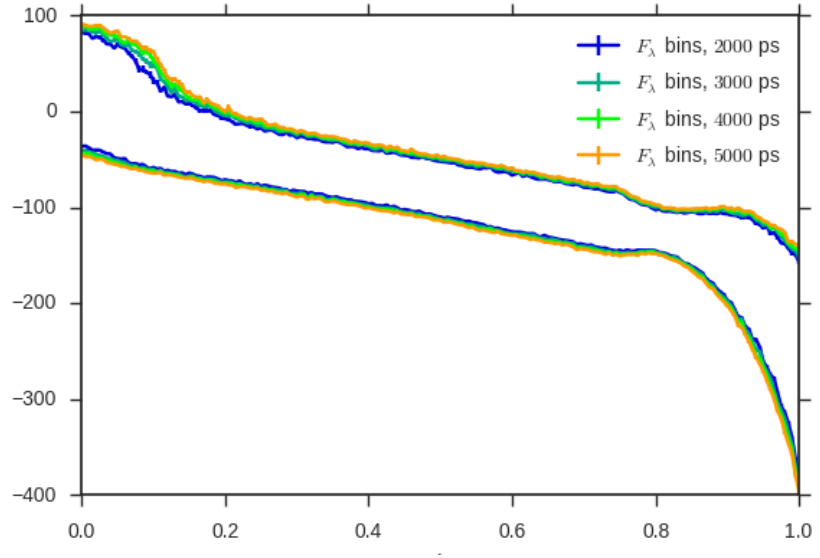


OSRW and WT-OSRW with T^*=6000 K

Convergence of generalized force

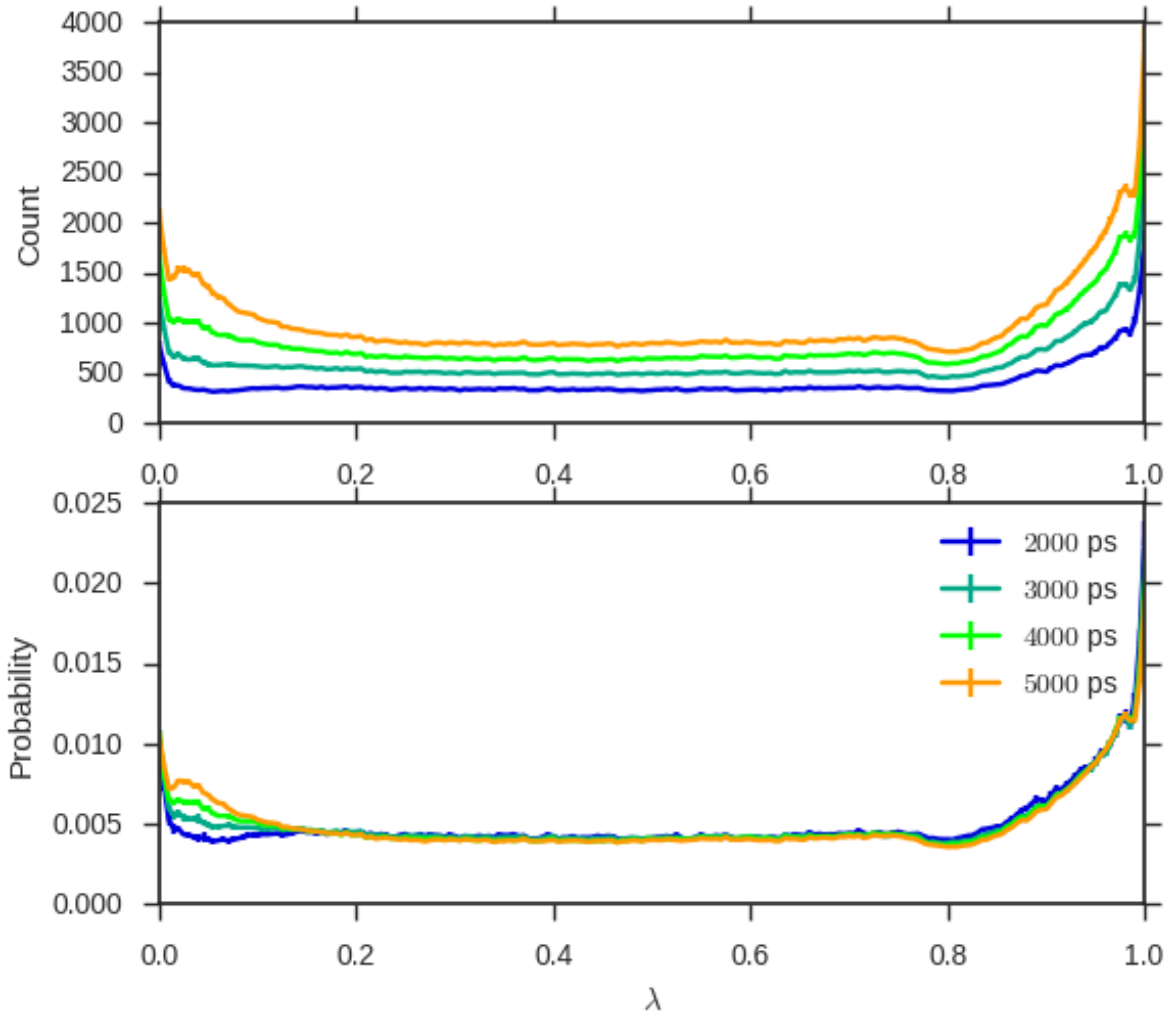
- Evolution of F_λ





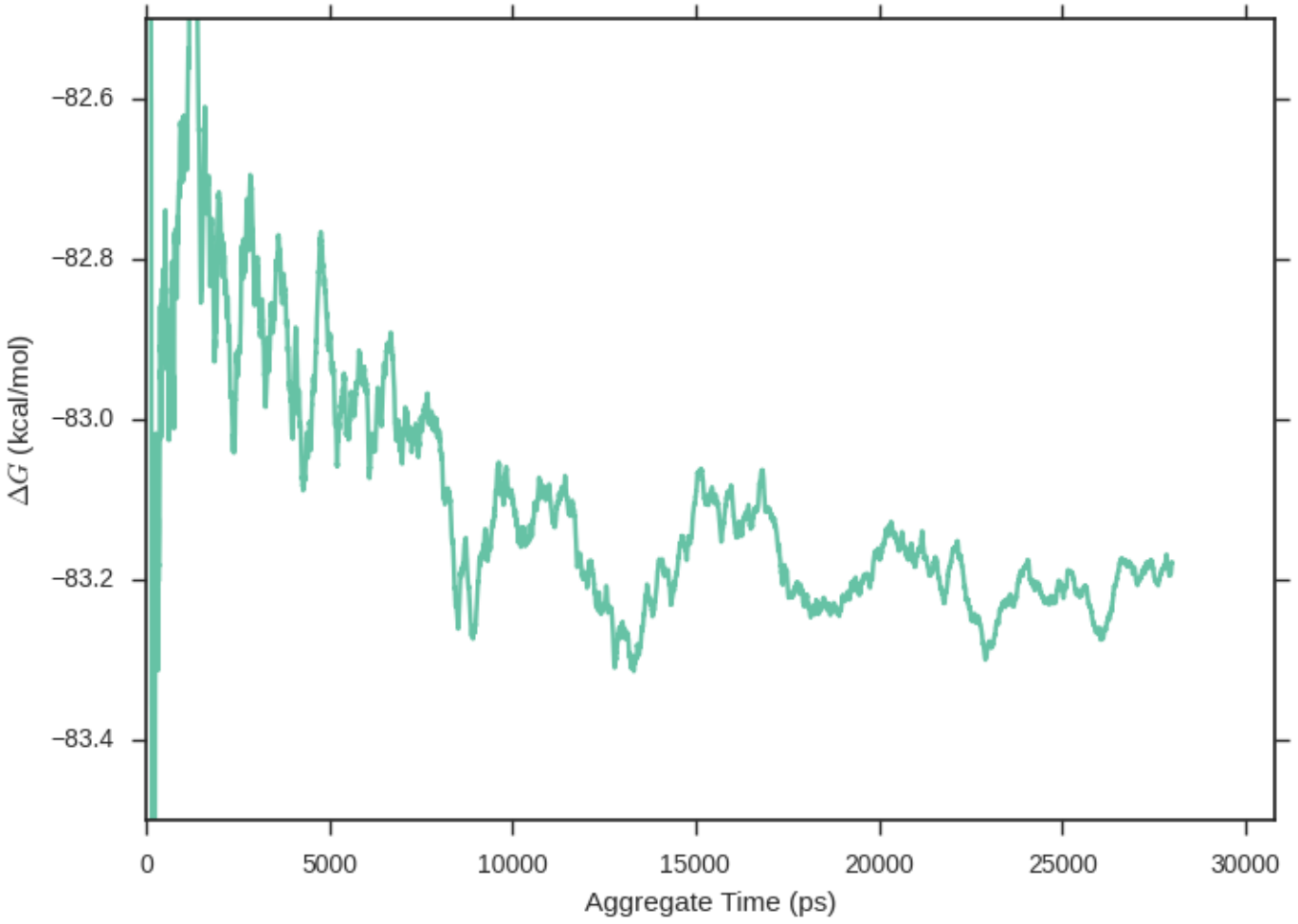
Sample distribution

- Distribution of samples along λ



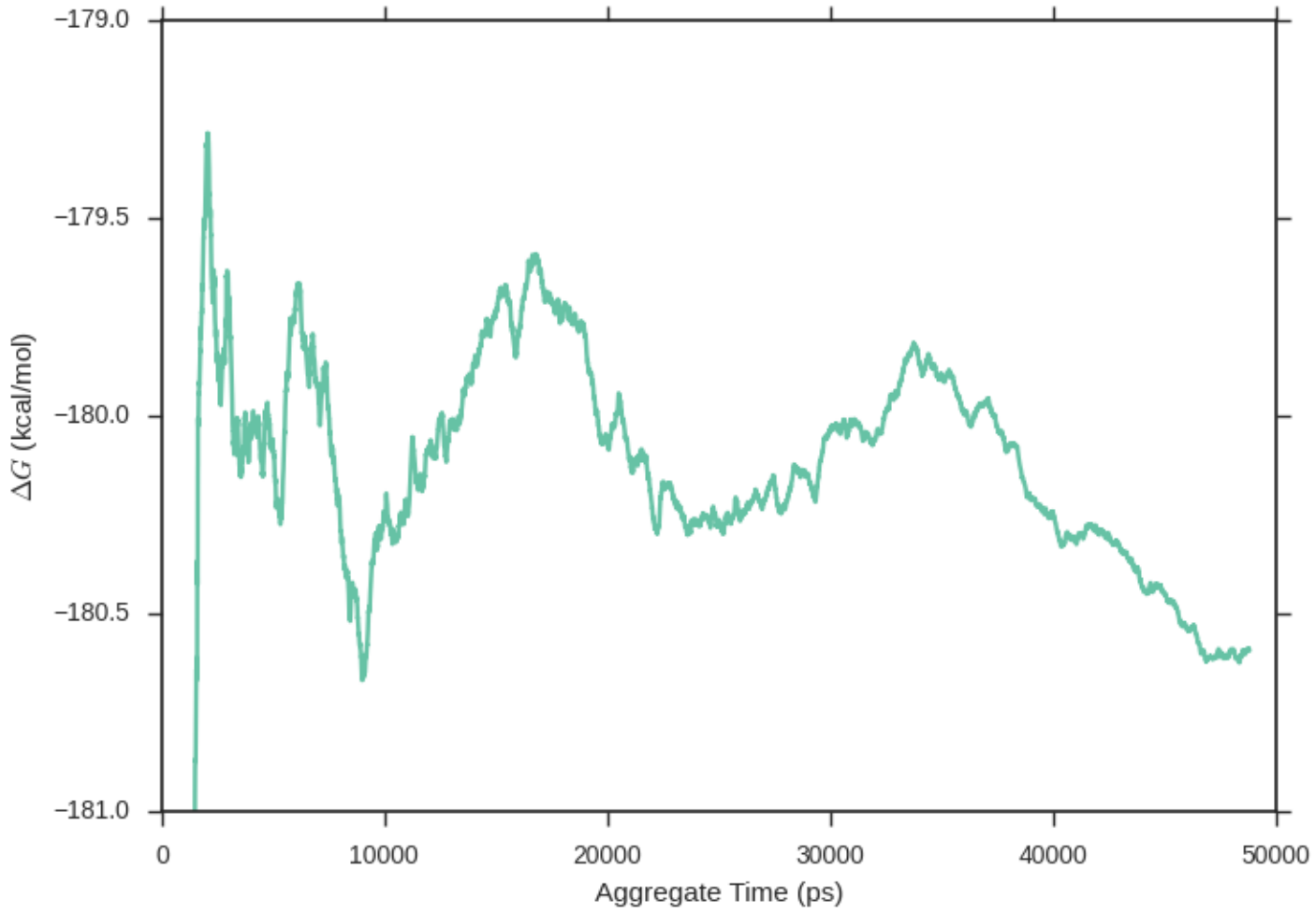
Well-tempered Thermodynamic Integration

- Cl^- solvation, T^* = 1500 K



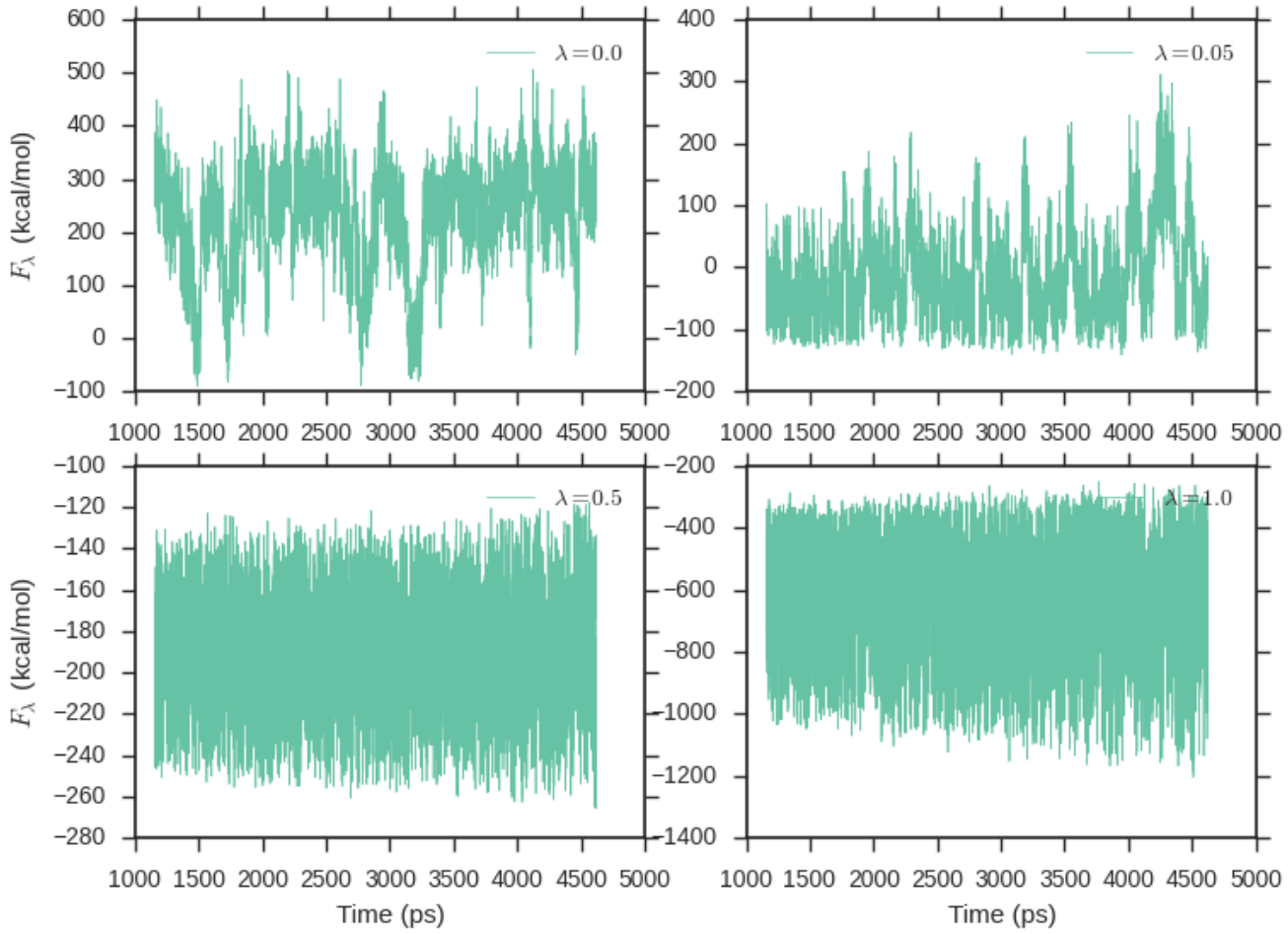
Well-tempered Thermodynamic Integration

- SAMPL4, T^* = 1500 K



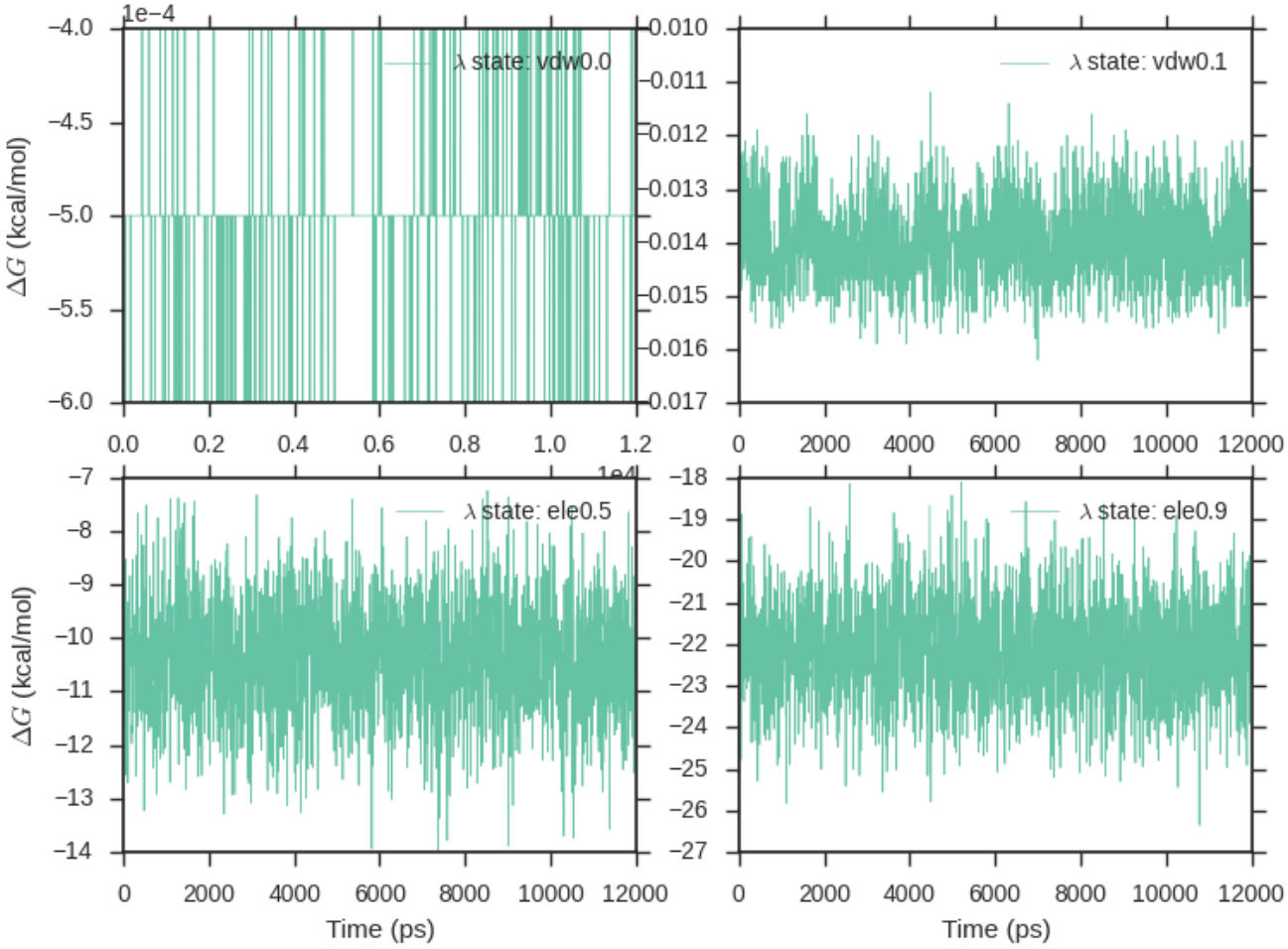
Comparing the dynamics of the generalized force

- SAMPL4, WT-TI



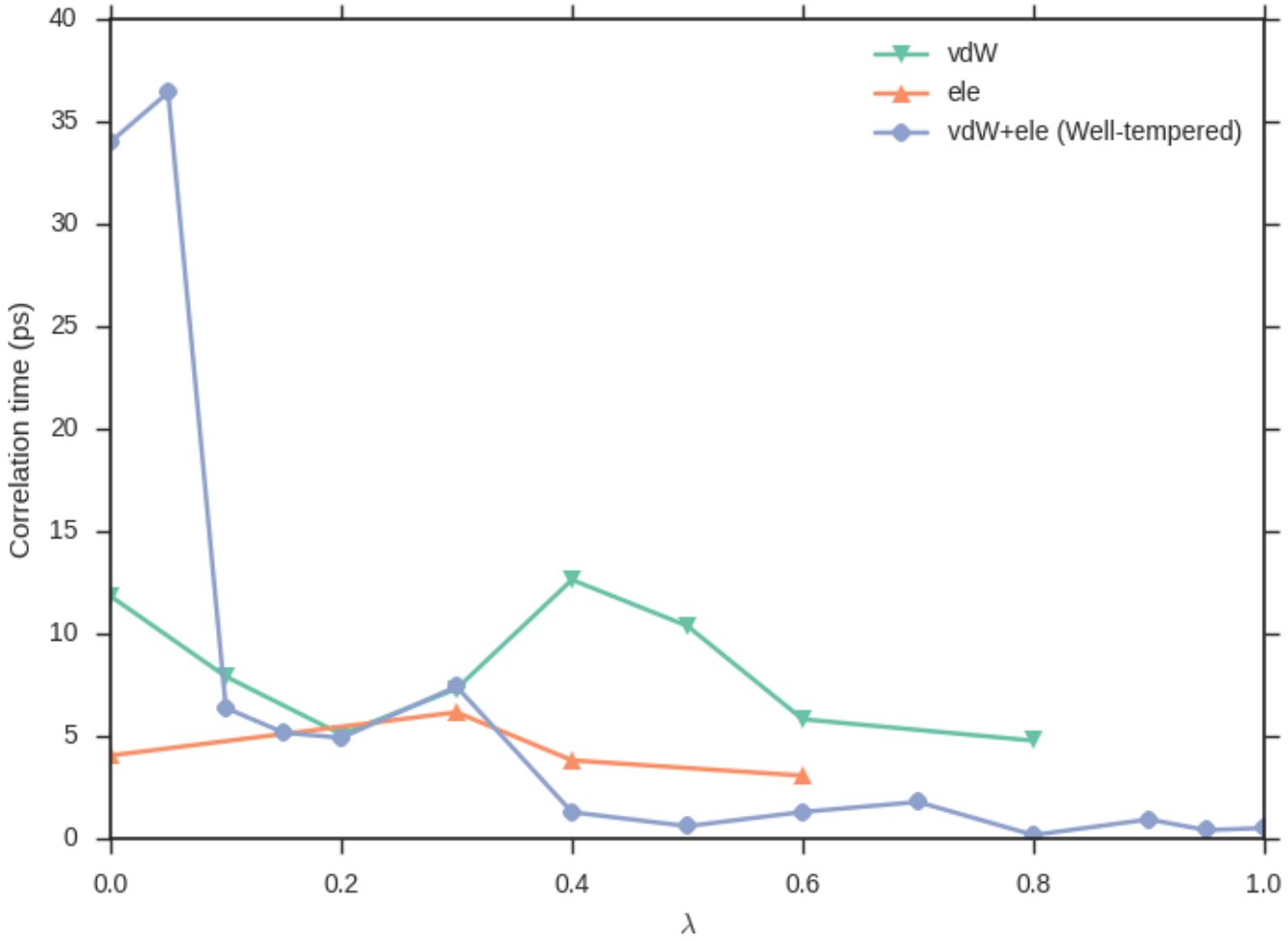
Comparing the dynamics of the generalized force

- SAMPL4, Bennet Acceptance Ratio



Comparing the dynamics of the generalized force

- Correlation of samples



Summary

- OSRW creates a two-dimensional free energy surface that exaggerates the diffusive barrier
- The sampling space along F_λ should be kept small enough
- When electrostatics and vdW are coupled simultaneously, the slow dynamics of F_λ causes large errors