Flexible Control of the Ensemble

Ben Leimkuhler
University of Edinburgh

IMA workshop on molecular simulation 2009

Molecular Parameters

extensive	bulk
Number of atoms **N**	Chemical potential ***μ***
Volume **V**	Pressure **P**
Energy **E**	Temperature **T**

A system comprised of two independent copies of another system has double N, V, E but same P, T, μ

ensemble: defined by what is constrained

e.g. NVE: 'microcanonical' ensemble

Ensemble Equilibrium Distribution

maximize entropy subject to constraints

NVE	$\rho \propto \delta[H - E]$
NVT	$\rho_\beta \propto e^{-\beta H}$
NPT	$\rho_{\beta,p} \propto e^{-\beta(H+pV)}$

Sampling

$$\mathcal{A}[g] = \int_{\Omega} g(z)\rho(z)\mathrm{d}z$$

Ergodicity: the dynamics generates space-filling curves that map out energy surfaces in the long time limit.

Such dynamics can be used to compute NVE **statistics** according to Birkhoff's theorem:

$$\mathcal{A}[g] = \lim_{T\to\infty} T^{-1} \int_0^T g(z(t))\mathrm{d}t$$

Problems for Sampling

1 Adjust the ensemble

e.g. compute NVT or NPT (or other) statistics from trajectories ***(with quantified error)***

2 Restore Ergodicity

3 Quantify perturbation of dynamics

...gentle stochastic thermostats...

Thermostats

Principles for Thermostats

- The canonical measure should be invariant for the dynamics

- The dynamics should be ergodic

For a weak thermostat

- Dynamics (autocorrelation functions) should be approximated in the thermodynamic limit.

$$N \to \infty, \qquad V \to \infty, \qquad N/V \sim \text{constant}$$

Thermostats

Define:

$$A = \int a(z)\rho_\beta(z)\mathrm{d}z$$

stationary average

$$C(\tau) = \int \underset{\substack{\uparrow \\ \text{flow map}}}{\Phi_\tau(z)} \cdot Bz\rho_\beta(z)\mathrm{d}z$$

autocorrelation function

A **thermostat** generates trajectories *z(t)* such that (a.s.)

$$\hat{A} := \lim_{t\to\infty} t^{-1}\int_0^t a(z(s))\mathrm{d}s = A$$

$$\hat{C}(\tau) := \lim_{t\to\infty} t^{-1}\int_0^t z(s+\tau)\cdot Bz(s)\mathrm{d}s \sim C(\tau) \quad \text{(T.L.)}$$

Dynamic Thermostats

$$\begin{aligned}\dot{z} &= u(z,\xi)\\ \dot{\xi} &= v(z,\xi)\end{aligned}$$

invariant measure:

$$\tilde{\rho} = \tilde{\rho}(z,\xi)$$

$$\int_{\mathcal{R}} \varphi(T(z,\xi))\tilde{\rho}(z,\xi)\mathrm{d}\xi_1\mathrm{d}\xi_2\ldots\mathrm{d}\xi_k = \varphi(z)\rho_\beta(z)$$

Bulgac-Kusnezov

$$\begin{aligned} \dot{z} &= u(z,\xi) \\ \dot{\xi} &= v(z) \end{aligned}$$

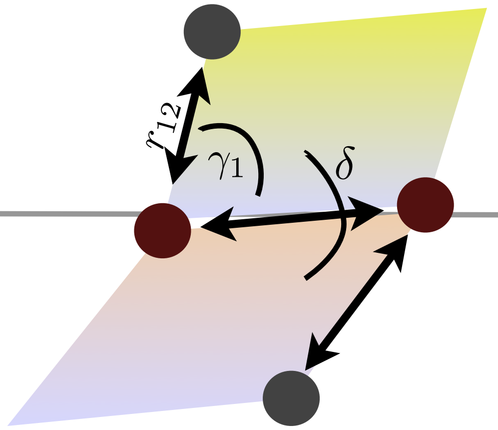
$$\tilde{\rho}(z,\xi) = \rho_\beta(z) e^{-\frac{\beta\xi^2}{2\mu}}$$

e.g. Nosé Hoover

$$H = \frac{p^2}{2} + U(q)$$

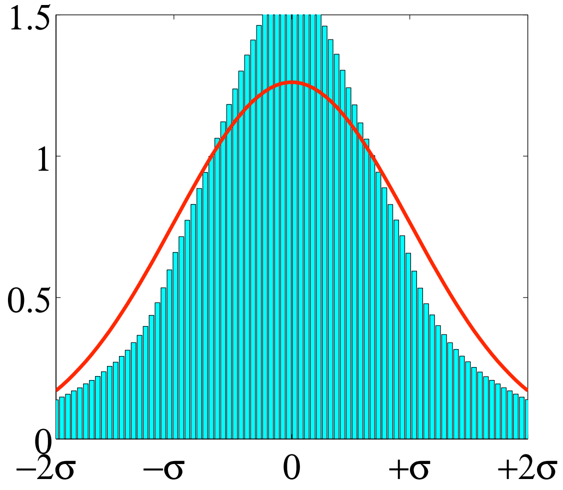
$$\begin{aligned} \dot{q} &= p \\ \dot{p} &= -U'(q) - \xi p \\ \mu\dot{\xi} &= p^2 - \beta^{-1} \end{aligned}$$

Ex: Butane



Error due to discretization
+ lack of ergodicity

lack of ergodicity



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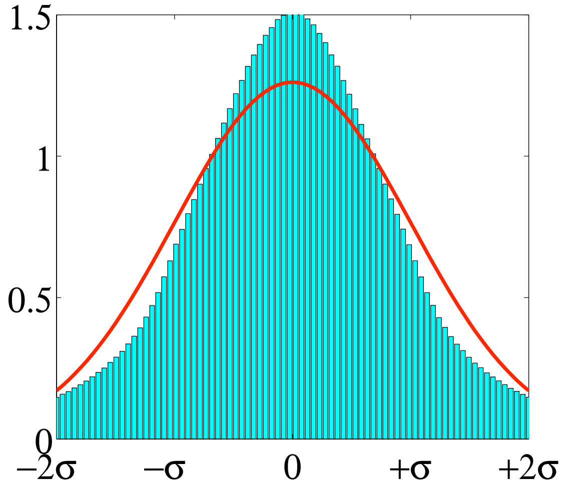

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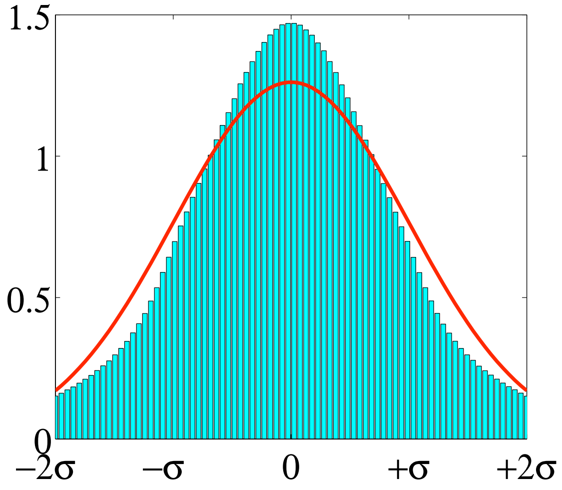

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Legoll, Luskin and Moeckel 2006, 2009:
Nonergodicity of NH for integrable model and (weak coupling)

Nose dynamics **does not restore ergodicity** but it also **does not destroy it**.

Hamiltonian Extension

Nosé-Poincaré

$$\tilde{\rho} = \delta\left[s\left(H(q,p/s) + \frac{\pi^2}{2\mu s^2} + \beta^{-1}\ln s - \tilde{E}\right)\right]$$

pseudo-microcanonical dynamics

$$\begin{aligned}\dot{q} &= p \\ \dot{p} &= -U'(q) - \xi p \\ \mu\dot{\xi} &= p^2 - \beta^{-1}\end{aligned}$$

Nosé-Hoover

$$\begin{aligned}\dot{q} &= p \\ \dot{p} &= -U'(q) - \xi p \\ \mu\dot{\xi} &= p^2 - \beta^{-1} - \Delta H_N \\ \dot{s} &= s\xi\end{aligned}$$

→ *symplectic methods*

Generalized Distributions

B. Laird, BL and E. Barth, JCP, 2003

Arbitrary $\rho(z)$ *or (better)* $\rho = f(H)$

$$\begin{aligned} \dot{q} &= p \\ \dot{p} &= -U'(q) - \phi(\eta,\xi)\xi p \\ \dot{\eta} &= \phi(\eta,\xi)\xi \\ \dot{\xi} &= \mu^{-1}[p^2 - \phi(\eta,\xi)\beta^{-1}] \end{aligned}$$

semi-implicit
reversible scheme

(or symplectic
alternative)

$$\phi(\eta,\xi) = \frac{1}{f'(f^{-1}(\tilde{E} - \frac{\mu\xi^2}{2} - \eta\beta^{-1}))}$$

Why Symplectic Methods?

- **Stability**

E. Hairer et al
energy drift for a **time-reversible** method

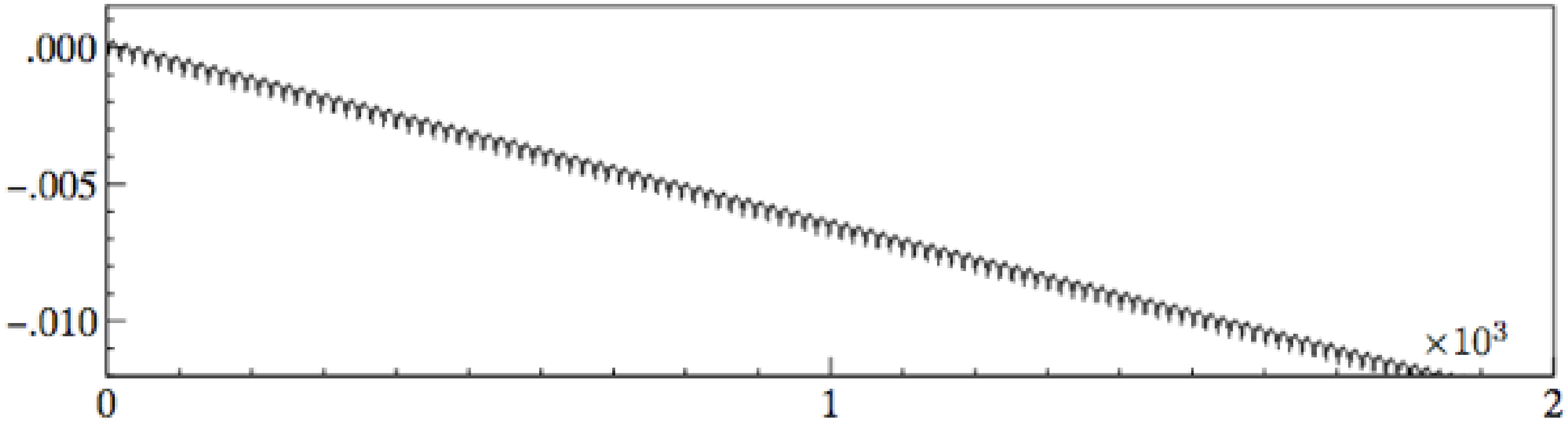
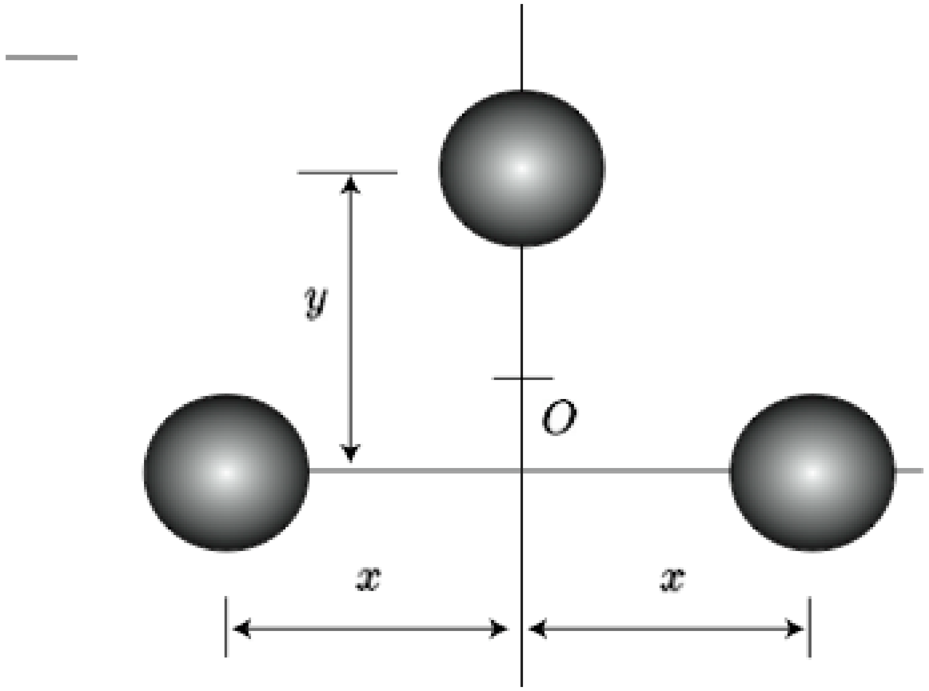
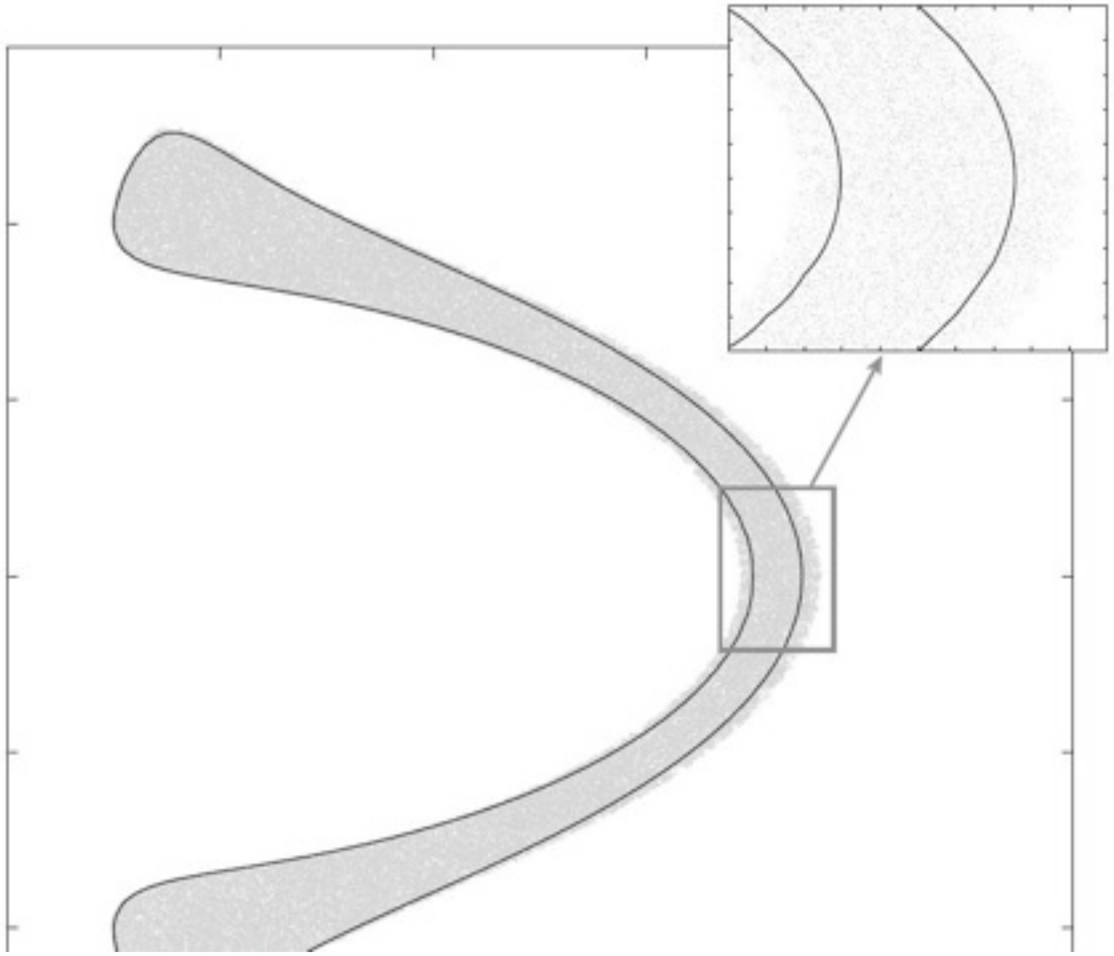


FIGURE 2. Unsymmetric pendulum: error in the shifted modified energy $H(p_n, q_n)+h^2 H_3(p, q)$ along the numerical solution of the simplified Takahashi–Imada method (6).

- Implies phase space **volume preservation** (needed, e.g. in Hybrid Monte Carlo)
- Allows straightforward **error analysis** for observables based on backward error analysis (BL. and Bond '07)
- Good foundation for designing **stochastic** dynamics methods with small noise





backward error analysis for Verlet

$$\bar{H}_r\left(q,p\right) = H\left(q,p\right) + h^2 H_{[2]}\left(q,p\right) + \cdots + h^r H_{[r]}\left(q,p\right).$$

$$H_{[2]} = \frac{1}{12} p^T M^{-1} V'' M^{-1} p - \frac{1}{24} \nabla V^T M^{-1} \nabla V$$

Nosé-Poincaré Distribution

2nd order BEA for discretized Nosé Poincaré

$$\bar{\rho}\left(q,p\right) = \rho_c\left(q,p\right)\omega\left(q,p\right) + \mathcal{O}\left[h^4\right],$$

$$\omega \propto \exp\left\{-\frac{h^2}{24k_BT}\left[\sum_j\sum_k \frac{2p_jp_kV_{q_jq_k}}{m_jm_k} - \sum_j \frac{V_{q_j}^2}{m_j} - \frac{1}{\mu}\left(\sum_j \frac{p_j^2}{m_j} - gk_BT\right)^2\right]\right\}.$$

- **remove stepsize error** (as long as reweighting works)
- Corrections computable by **finite differences**
- Extends to **NVE** (S. Bond)

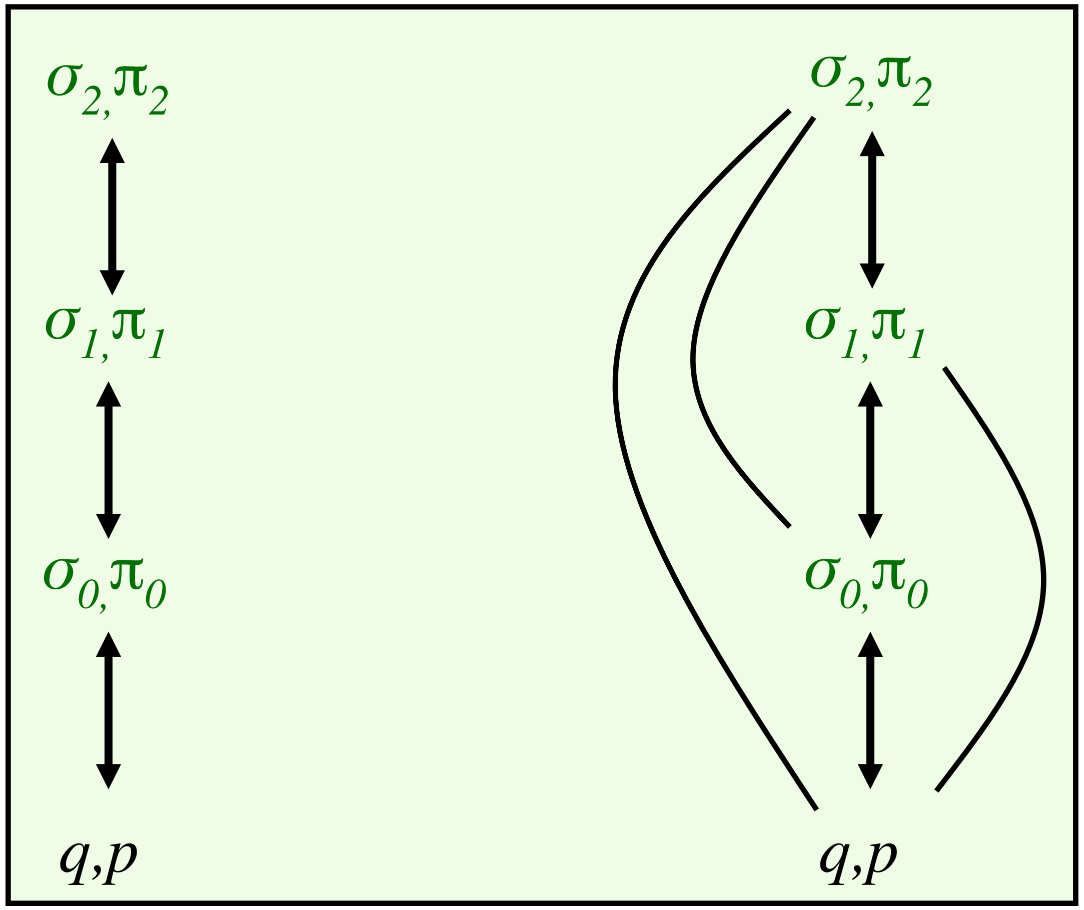
Restoring Ergodicity

More complicated thermostats

Hamiltonian thermostat chains (BL + Laird, Sweet)

$$H_{\mathrm{GN}} = H(q, p/\Pi\sigma_\alpha) + H_{\mathrm{G}}(\sigma_1, \sigma_2, \ldots, \sigma_m, \pi_1, \pi_2, \ldots, \pi_m)$$

various
coupling
structures



$\sigma_{2,}\pi_2$ $\sigma_{2,}\pi_2$

$\sigma_{1,}\pi_1$ $\sigma_{1,}\pi_1$

$\sigma_{0,}\pi_0$ $\sigma_{0,}\pi_0$

q,p q,p

BK Thermostats

$$\tilde{\rho}(z,\xi) = e^{-\beta H} e^{-\beta w(\xi)}$$

$$\begin{aligned} \dot{z} &= J\nabla H(z) + \Phi(z,\xi) \\ \dot{\xi} &= g(z) \end{aligned}$$

<u>Examples</u>

$$\Phi = \xi G(z), \quad \eta = \xi^2/2$$

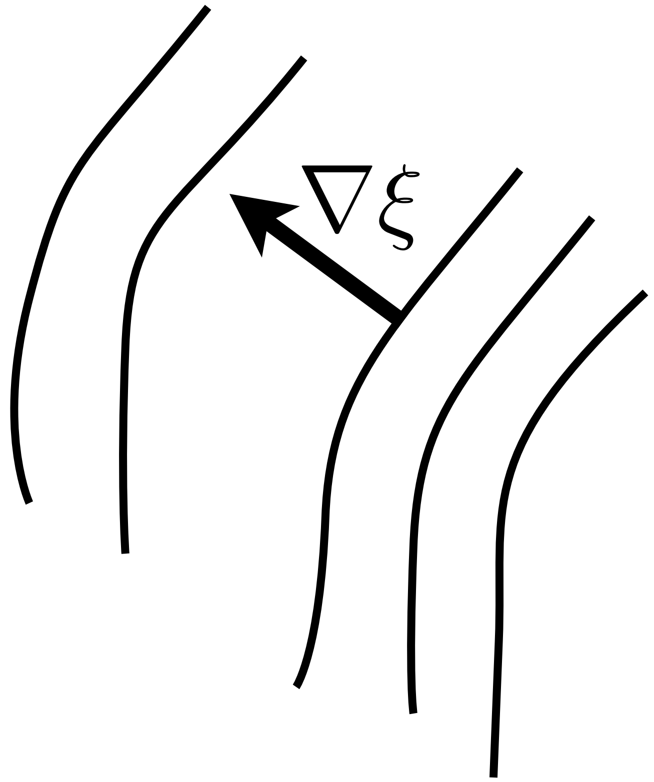
$$\Phi = (\xi I + S(\xi))\nabla H, \eta = \xi^2/2 \; S = -S^T$$

$$\Phi = Q(\xi + S(\xi))Q\nabla H, \quad \eta = \xi^2/2$$

$$S = -S^T \qquad Q = Q^T = Q^2$$

Projective Thermostatting

Separate thermostats in "reaction coordinate", transverse directions



$$\hat{\mathcal{R}}(q) = I - \frac{\nabla\xi\nabla\xi^T}{|\nabla\xi|^2}$$

$$\begin{aligned} \dot{q} &= p, \\ \dot{p} &= -\nabla U(q) - \xi\mathcal{R}p - \xi_\perp\hat{\mathcal{R}}p \\ \dot{\xi} &= p^T\mathcal{R}p - \theta, \\ \dot{\xi}_\perp &= p^T\hat{\mathcal{R}}p - \theta(m-1), \end{aligned}$$

$$\theta = \beta^{-1}$$

Also configurational thermostats...

Generalized BK Thermostat

$$\begin{aligned} \dot{z} &= u(z,\xi) \\ \dot{\xi} &= v(z,\xi) \end{aligned}$$

$$\tilde{\rho}(z,\xi) = \rho_\beta(z) e^{-\beta w(\xi)}$$

Condition for augmented canonical distribution:

$$u \cdot \nabla_z H - \beta^{-1} \nabla_z \cdot u + \nabla_\xi w \cdot v - \beta^{-1} \nabla_\xi \cdot v \equiv 0.$$

Many new possible candidates for thermostats...

Building Thermostats

Given two additive perturbations *A,B* of Hamiltonian dynamics preserving an augmented canonical distribution

the perturbation *A+B* also preserves an augmented canonical distribution

Extreme Thermostatting

This preserves an augmented canonical measure for some choice of a,b:

$$\begin{aligned} \dot{q} &= p \\ \dot{p} &= +\lambda p \\ \dot{\lambda} &= p^2 - \theta + e^{\lambda^2/2}\left[a + b\,\mathrm{erf}(\lambda/\sqrt{2})p \cdot \nabla V\right] \end{aligned}$$

But is this in any sense molecular dynamics?? And is it ergodic??

D. Smith: *erf*-based thermostat for self-guided MD

Stochastic-Dynamics

$$\begin{aligned}\dot{z} &= u(z,\xi) + \text{noise} + \text{dissipation} \\ \dot{\xi} &= v(z,\xi) + \text{noise} + \text{dissipation}\end{aligned}$$

- Additivity properties still apply to verify augmented canonical measure

- Stochastic terms stabilize dynamical thermostats by adding diffusive terms (distribution evolves according to Fokker-Planck equation)

A "Barrier Thermostat"

$$\begin{aligned}\dot q &= p \\ \dot p &= -\bar U'(q) + \beta\xi^2 F(q) \\ \dot \xi &= \beta\xi p \cdot F - \gamma\xi + \sqrt{2\gamma\beta^{-1}}\dot W\end{aligned}$$

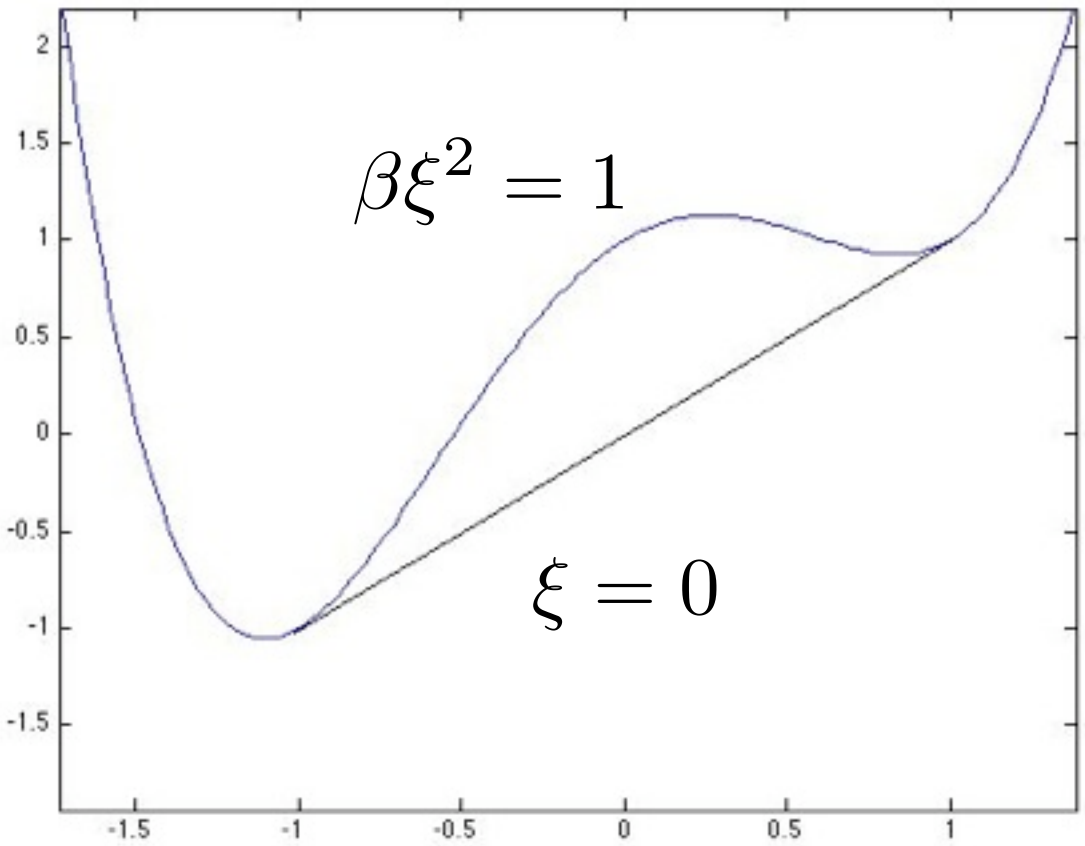
$$\langle \beta\xi^2\rangle = 1$$

- Part of force field is activated by the auxiliary variable

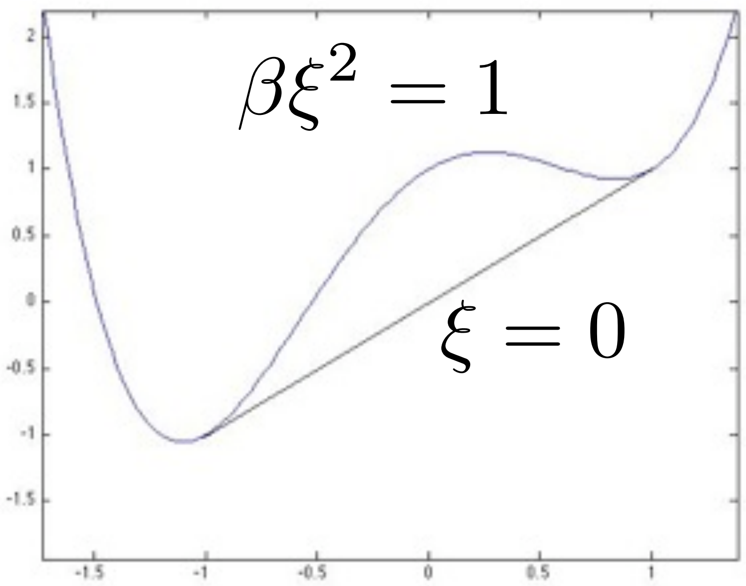
- Inertial part: reversible (non-Hamiltonian) dynamics

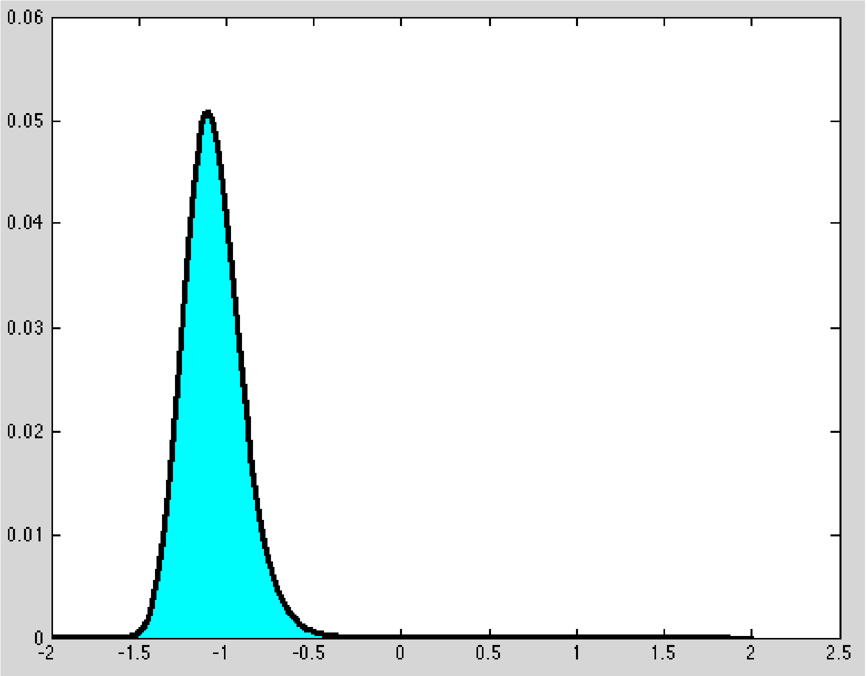
A “Barrier Thermostat”

$$\begin{aligned}\dot{q} &= p \\ \dot{p} &= -\bar{U}'(q) + \beta\xi^2 F(q) \\ \dot{\xi} &= \beta\xi p \cdot F - \gamma\xi + \sqrt{2\gamma\beta^{-1}}\dot{W}\end{aligned}$$



A “Barrier Thermostat”





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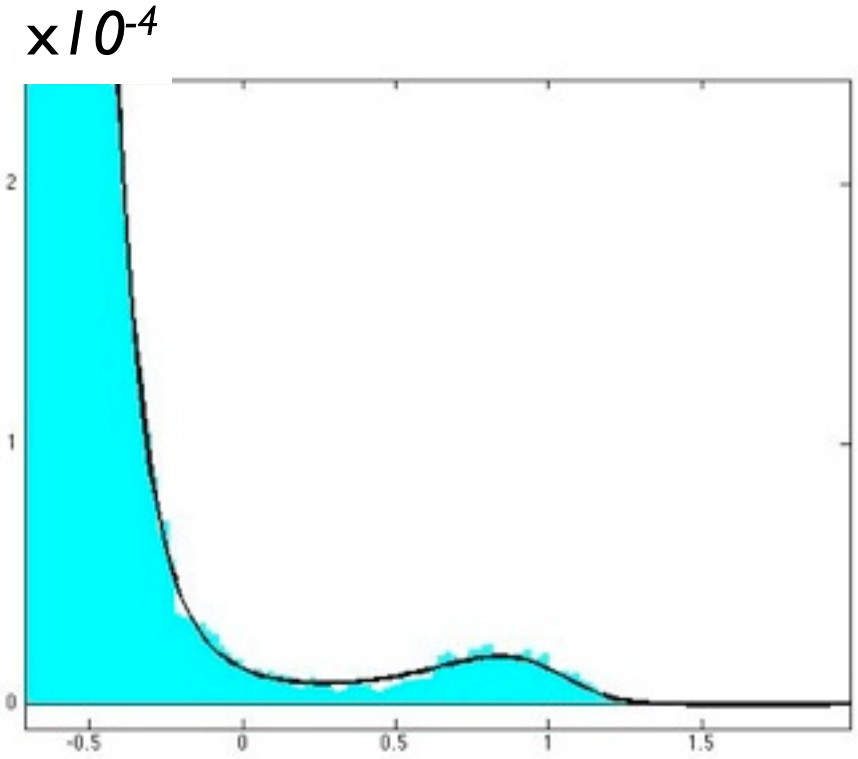


Langevin dynamics: does well on this also if low friction is used.

Gentle Stochastic Thermostats

Hoover-Langevin

BL., Noorizadeh, and Theil, J. Stat. Phys. to appear

$$\begin{aligned}\dot{q} &= M^{-1}p \\ \dot{p} &= -U'(q) - \epsilon\xi p \\ d\xi &= [p^T M^{-1} p - N\beta^{-1}]dt - \gamma\xi dt + \sigma dW\end{aligned}$$

a method suggested by *Samoletov, Dettmann &Chaplain*

- **Unifies** Nosé-Hoover and Langevin thermostats
- Includes **kinetic energy regulator**
- **Scalar** stochastic process

Degenerate Diffusions

stochastic analysis literature
Mattingley, Stuart, E...

Fokker-Planck Equation

$$\frac{\partial \rho}{\partial t} = \mathcal{L}^* \rho$$

$\mathcal{L}^*$ **Hypoelliptic:**

Elliptic only in some components
Mixing

$\Longrightarrow$ **Stationary solutions are smooth**
Uniqueness of invariant measure

Hörmander condition

If Hoover-Langevin is decomposed into X_0 (no noise) and X_1 (multiplying noise) and these satisfy the Hörmander condition, then $\mathcal{L}^*$ is hypoelliptic

The vector fields $X_0(x), \ldots, X_r(x)$ satisfy a Hörmander condition if

$$Span\{X_0(x), \ldots, X_r(x), [X_i, X_j](x),\ [X_i, [X_j, X_k]](x) \ldots\} = \mathbb{R}^N$$

Difficult to verify globally in general setting, due to high order Lie brackets.

Linear system w/o resonance

$$H = \frac{p^T M^{-1} p}{2} + \frac{q^T B q}{2}$$

$$A = M^{-1} B, \qquad A\varphi_k = \omega_k \varphi_k$$

$$\omega_k \neq \omega_l, \qquad k \neq l$$

Theorem: Hoover-Langevin is ergodic for this problem.

Example: clamped harmonic spring chain.

Linear system w/o resonance

$$X_0 = \begin{bmatrix} p \\ -Bq - \xi p \\ \|p\|^2 - n - \frac{\xi}{2} \end{bmatrix}, \qquad X_1 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

$$Z_k = \frac{1}{2}[Y_k, X_3], \qquad Y_{k+1} = -\frac{1}{2}[Z_k, X_3]$$

$$\overline{X}_0 = X_0 - \left((\|p\|^2 - n) - \tfrac{1}{2}\xi \right) X_1 = (p, -Bq - \xi p, 0),$$

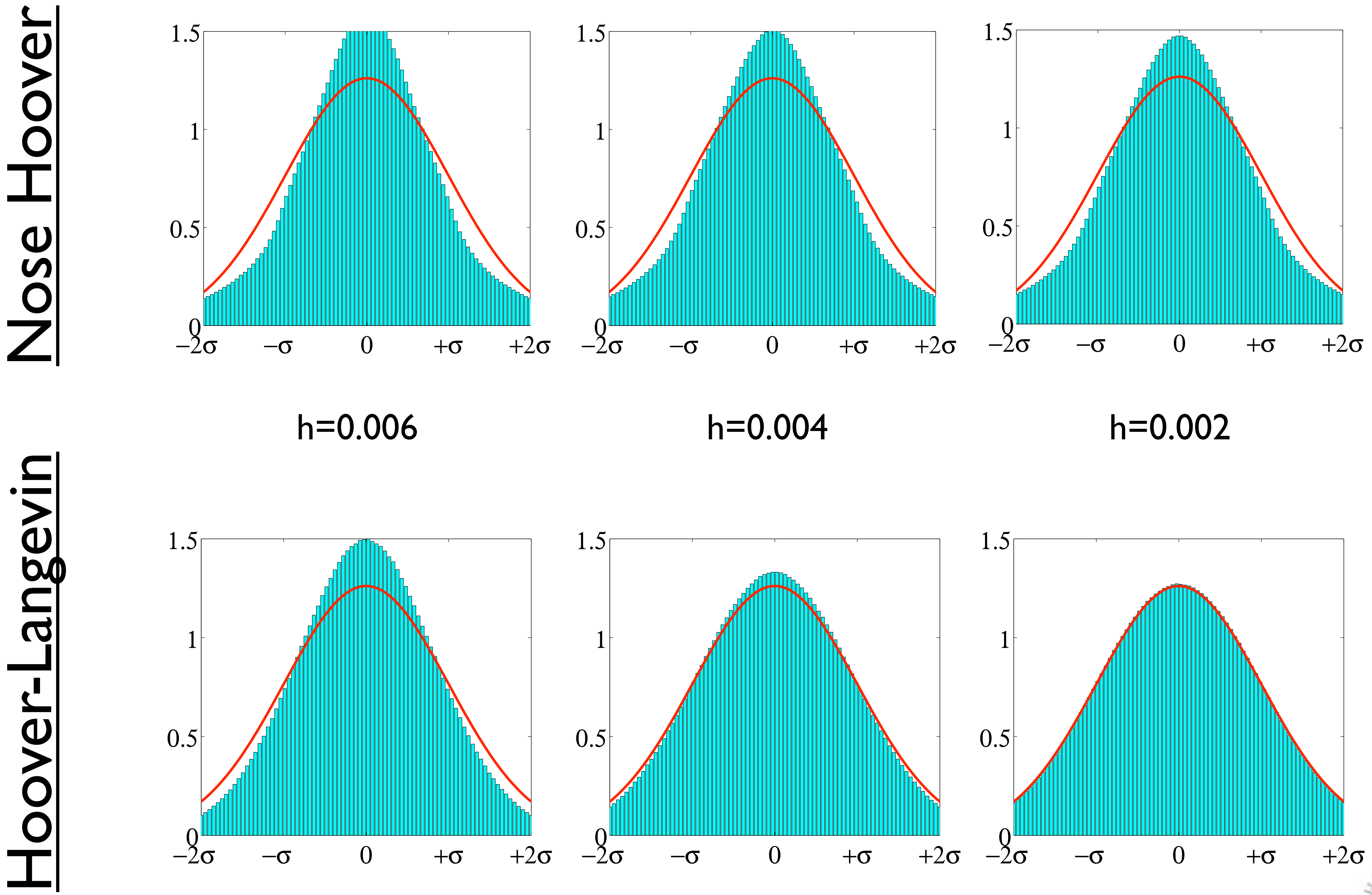
$$X_2 = [\overline{X}_0, X_1] = (0, p, 0),$$

$$X_3 = \overline{X}_0 + \xi X_2 = (p, -Bq, 0),$$

$$Y_1 = [X_2, X_3] = (p, Bq, 0).$$

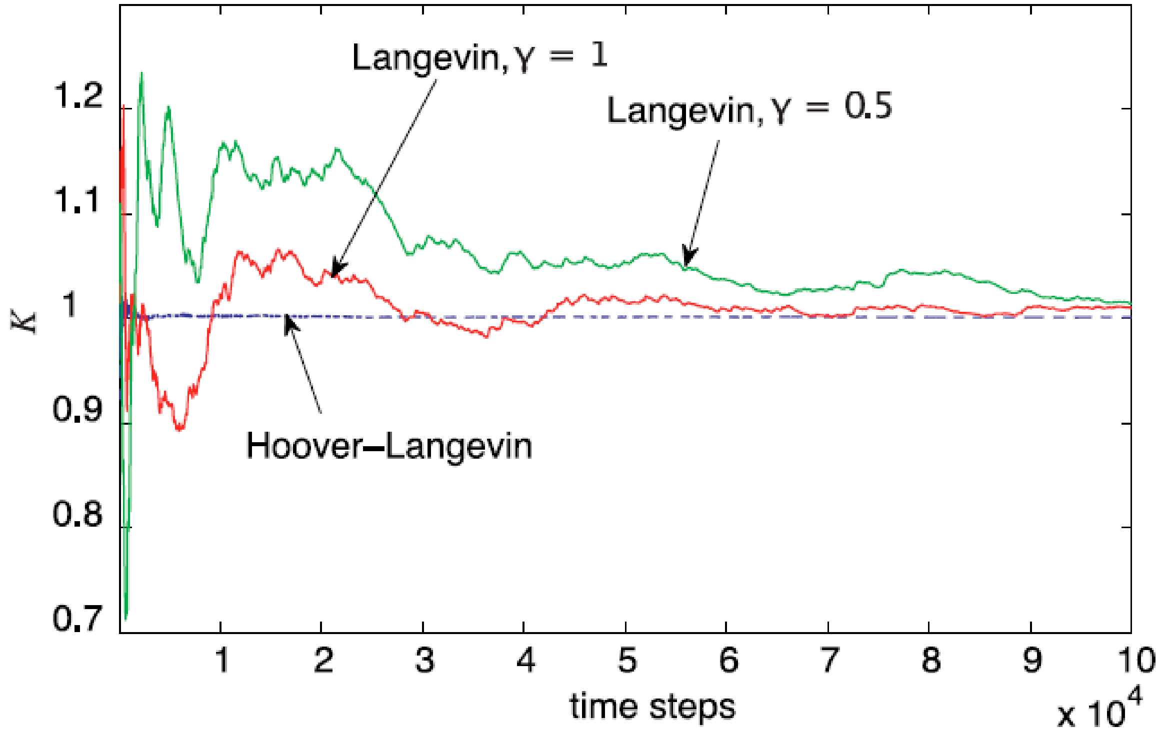
generates a sequence of vectors that span R^{2n}

Butane Momentum Distributions

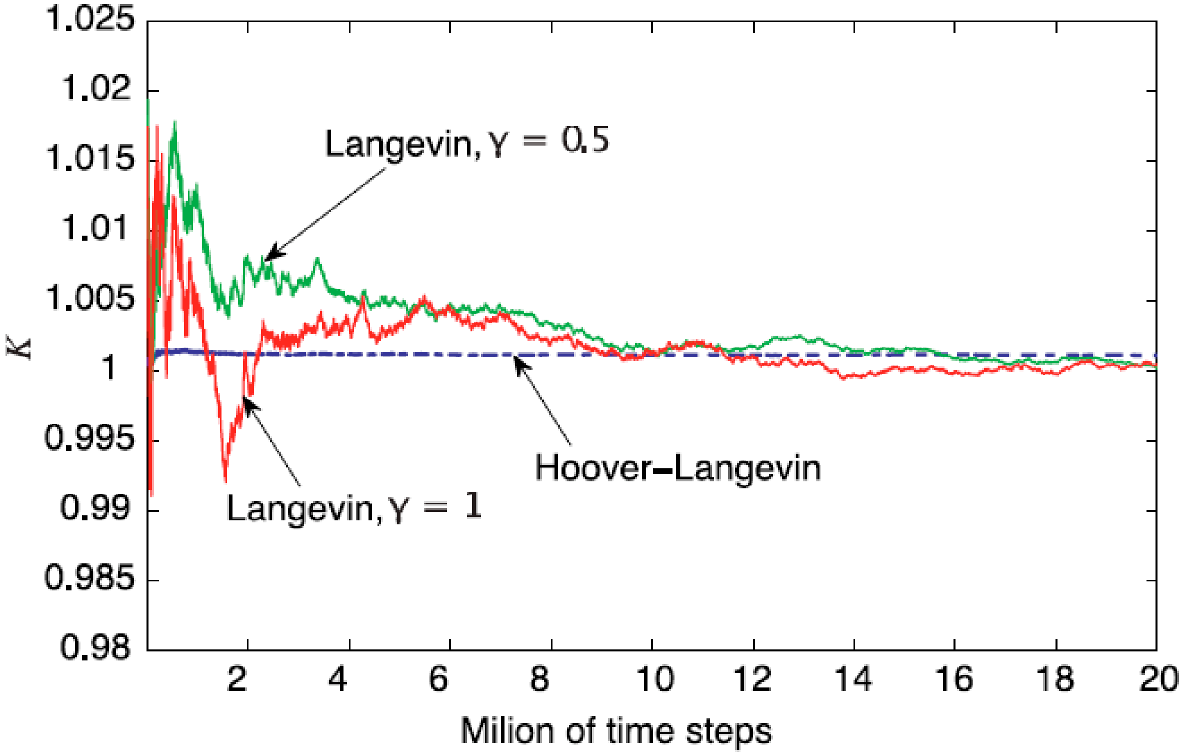


Comparisons

K.E. in 10K steps of simulation



K.E. in 20M steps of simulation



Near equilibrium

With Noorizadeh, Oliver Penrose:

$$\theta = \frac{\mathbf{E}^0 p^2}{N} - \beta^{-1} \qquad \nu = \mathbf{E}^0 \xi$$

near equilibrium: $$\begin{bmatrix} \dot\theta \\ \dot\nu \end{bmatrix} = \begin{bmatrix} 0 & -N\beta^{-1}C_V^{-1} \\ \epsilon N & -\gamma \end{bmatrix} \begin{bmatrix} \theta \\ \nu \end{bmatrix}$$

$$\lambda = \frac{-\gamma \pm \sqrt{\gamma^2 - 4\frac{\epsilon N^2}{\beta C_V}}}{2}$$

two real negative evals or complex pair in negative half plane

Damped Oscillations if strong coupling is used

Comparisons

- For Nosé-Hoover, coupling (inverse to thermal mass) has to be sufficiently large for system to reach equilibrium.

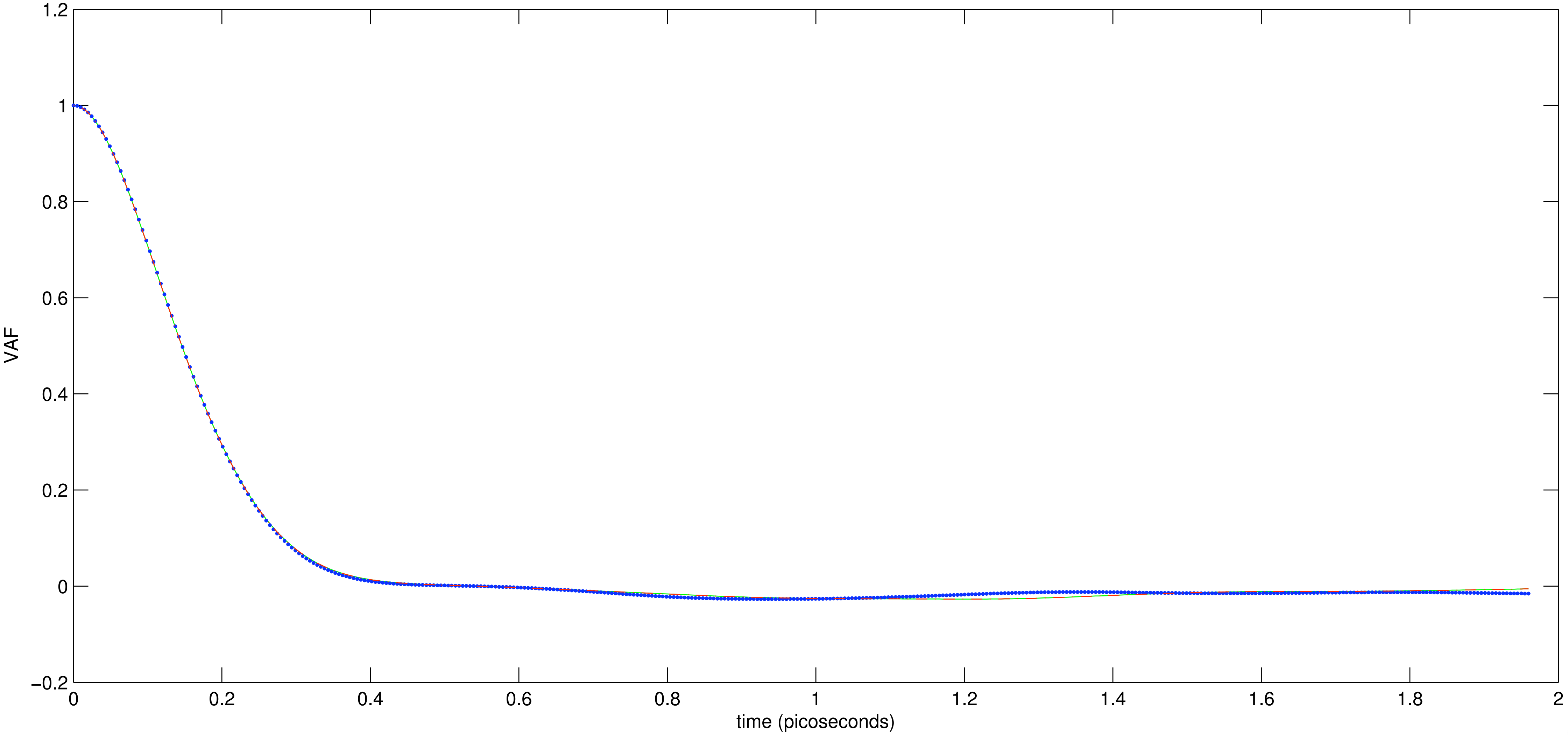
- No restriction for Hoover-Langevin (however, rate of decay of energy depends on coupling strength)

- Compared to Nosé Hoover Chains, Hoover Langevin is more reliable-- it is ergodic for all parameter choices and only one coupling parameter needs to be selected.

- Compared to Langevin dynamics, Hoover-Langevin has a built in kinetic energy regulator and adds a smoother disturbance of dynamics, with only one stochastic diffusion

It (can be) a gentle thermosat

8 Butane molecules
periodic boundary conditions



A gentler Hybrid Monte Carlo

Metropolis Adjusted Nosé Hoover (MANH)
[L.&Reich M2AN '09]

- Randomly perturbs thermostat variable ξ only

- Uses a volume-preserving reversible formulation for NH *[Klein '98]*

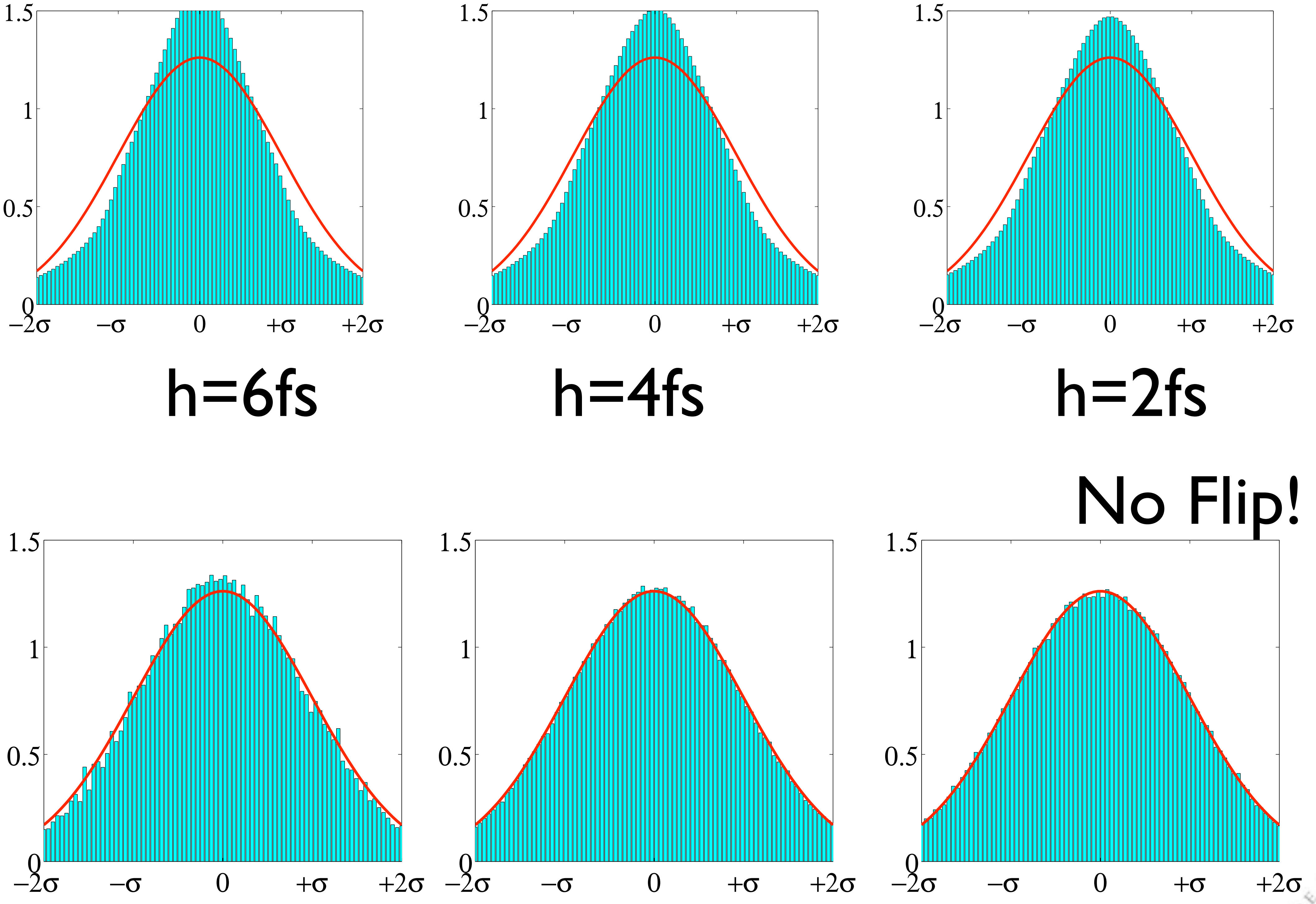
- Metropolis test based on $\exp(-\theta^{-1}\Delta E_{NH})$

$$\Delta E_{NH} = H + \frac{\xi^2}{2\mu} + \theta \ln s$$

Butane Momentum Distributions

NH

Metropolis-
Adjusted NH



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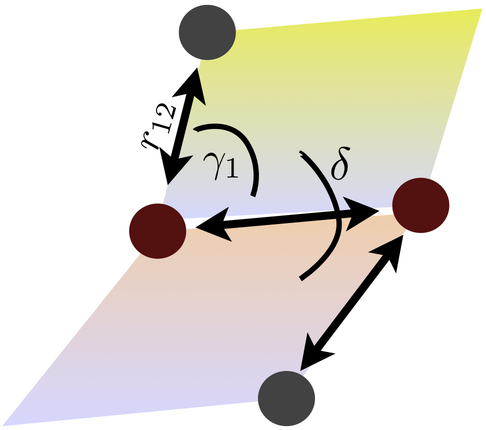
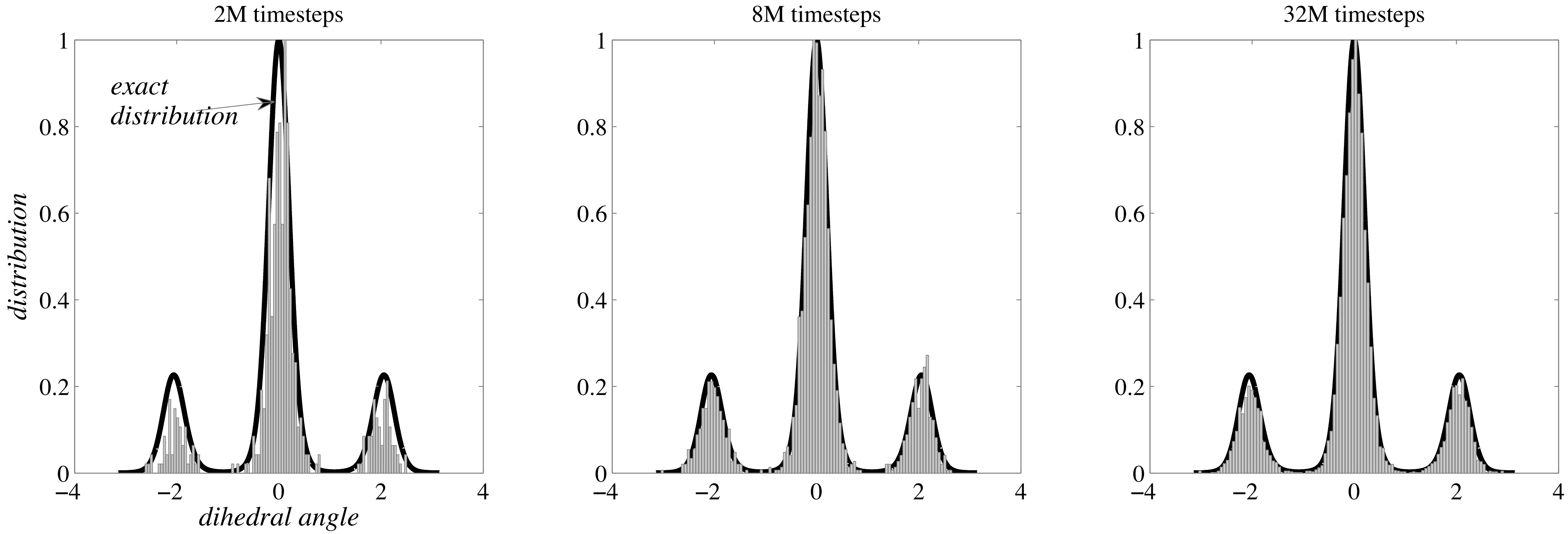
No Flip!

Butane Angle Distribution





Summary

Possible to construct a wide variety of different thermostats within an extension of the Bulgac-Kusnezov framework

One example: “barrier thermostat”

Hoover-Langevin method provides canonical sampling with small perturbations and secondary noise

Gentler HMC methods are also possible based on Nosé-Hoover dynamics