Flexible Control of the Ensemble

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## Molecular Parameters

<table>
<thead>
<tr>
<th>extensive</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of atoms $N$</td>
<td>Chemical potential $\mu$</td>
</tr>
<tr>
<td>Volume $V$</td>
<td>Pressure $P$</td>
</tr>
<tr>
<td>Energy $E$</td>
<td>Temperature $T$</td>
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</tbody>
</table>

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

**ensemble**: defined by what is constrained

e.g. $NVE$: ‘microcanonical’ ensemble
**Ensemble Equilibrium Distribution**

*maximize entropy subject to constraints*

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Equation</th>
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<tbody>
<tr>
<td>NVE</td>
<td>$\rho \propto \delta[H - E]$</td>
</tr>
<tr>
<td>NVT</td>
<td>$\rho_\beta \propto e^{-\beta H}$</td>
</tr>
<tr>
<td>NPT</td>
<td>$\rho_{\beta,p} \propto e^{-\beta(H+pV)}$</td>
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</table>
Sampling

\[ A[g] = \int_{\Omega} g(z) \rho(z) \, dz \]

**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:

\[ A[g] = \lim_{T \to \infty} T^{-1} \int_{0}^{T} g(z(t)) \, dt \]
Problems for Sampling

1 Adjust the ensemble
e.g. compute NVT or NPT (or other) statistics from trajectories \textit{(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.

\[ N \to \infty, \quad V \to \infty, \quad N/V \sim \text{constant} \]
Thermostats

Define:

\[ A = \int a(z) \rho_\beta(z) dz \]

stationary average

\[ C(\tau) = \int \Phi_\tau(z) \cdot B z \rho_\beta(z) dz \]

autocorrelation function

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

\[ \hat{A} := \lim_{t \to \infty} t^{-1} \int_0^t a(z(s)) ds = A \]

flow map

\[ \hat{C}(\tau) := \lim_{t \to \infty} t^{-1} \int_0^t z(s + \tau) \cdot B z(s) ds \sim C(\tau) \quad (T.L.) \]
Dynamic Thermostats

\[ \dot{z} = u(z, \xi) \]

\[ \dot{\xi} = v(z, \xi) \]

invariant measure:

\[ \tilde{\rho} = \tilde{\rho}(z, \xi) \]

\[ \int_{\mathcal{R}} \varphi(T(z, \xi)) \tilde{\rho}(z, \xi) d\xi_1 d\xi_2 \ldots d\xi_k = \varphi(z) \rho_{\beta}(z) \]
Bulgac-Kusnezov

\[ \dot{z} = u(z, \xi) \]
\[ \dot{\xi} = v(z) \]

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

e.g. Nosé Hoover

\[ \dot{q} = p \]
\[ \dot{p} = -U'(q) - \xi p \]
\[ \mu \dot{\xi} = p^2 - \beta^{-1} \]

\[ H = \frac{p^2}{2} + U(q) \]
Ex: Butane

Error due to discretization + lack of ergodicity

![Graphs showing error due to discretization and lack of ergodicity](image)

- h=6fs
- h=4fs
- h=2fs

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

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

pseudo-microcanonical dynamics

\[ \begin{align*}
\dot{q} &= p \\
\dot{p} &= -U'(q) - \xi p \\
\mu \dot{\xi} &= p^2 - \beta^{-1} 
\end{align*} \]

Nosé-Hoover

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

→ symplectic methods
Generalized Distributions

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

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

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

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

semi-implicit reversible scheme

(or symplectic alternative)
Why Symplectic Methods?

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

- **Stability**

  - 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

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).
backward error analysis for Verlet

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

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

2nd order BEA for discretized Nosé Poincaré

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

\[
\omega \propto \exp \left\{ -\frac{\hbar^2}{24k_BT} \left[ \sum_j \sum_k \frac{2p_j p_k V_{q_j q_k}}{m_j m_k} - \sum_j \frac{V_{q_j}^2}{m_j} - \frac{1}{\mu} \left( \sum_j \frac{p_j^2}{m_j} - gk_BT \right) \right] \right\}.
\]

- 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 \((\text{BL + Laird, Sweet})\)

\[ H_{GN} = H(q, p/\Pi_\sigma \alpha) + H_G(\sigma_1, \sigma_2, \ldots, \sigma_m, \pi_1, \pi_2, \ldots, \pi_m) \]

Various coupling structures
\[ \tilde{\rho}(z, \xi) = e^{-\beta H} e^{-\beta w(\xi)} \]
\[ \dot{z} = J \nabla H(z) + \Phi(z, \xi) \]
\[ \dot{\xi} = g(z) \]

**Examples**

\[ \Phi = \xi G(z), \quad \eta = \xi^2 / 2 \]
\[ \Phi = (\xi I + S(\xi)) \nabla H, \quad \eta = \xi^2 / 2 \quad S = -S^T \]
\[ \Phi = Q(\xi + S(\xi)) Q \nabla H, \quad \eta = \xi^2 / 2 \]
\[ S = -S^T \quad Q = Q^T = Q^2 \]
Projective Thermostatting

Separate thermostats in “reaction coordinate”, transverse directions

\[ \dot{\hat{R}}(q) = I - \frac{\nabla \xi \nabla \xi^T}{|\nabla \xi|^2} \]

\[ \dot{q} = p, \]
\[ \dot{p} = -\nabla U(q) - \xi \hat{R}p - \xi_\perp \hat{R}p \]
\[ \dot{\xi} = p^T \hat{R}p - \theta, \]
\[ \dot{\xi}_\perp = p^T \hat{R}p - \theta(m - 1), \quad \theta = \beta^{-1} \]

Also configurational thermostats...
Generalized BK Thermostat

\[ \dot{z} = u(z, \xi) \]
\[ \dot{\xi} = v(z, \xi) \]

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

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 $a,b$:

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

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

D. Smith: \textit{erf}-based thermostat for self-guided MD
Stochastic Dynamics

\[ \dot{z} = u(z, \xi) + \text{noise} + \text{dissipation} \]
\[ \dot{\xi} = v(z, \xi) + \text{noise} + \text{dissipation} \]

- 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”

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

\[
\langle \beta \xi^2 \rangle = 1
\]

- Part of force field is activated by the auxiliary variable
- Inertial part: reversible (non-Hamiltonian) dynamics
A “Barrier Thermostat”

\[
\begin{align*}
\dot{q} & = p \\
\dot{p} & = -\tilde{U}'(q) + \beta \xi^2 F(q) \\
\dot{\xi} & = \beta \xi p \cdot F - \gamma \xi + \sqrt{2\gamma \beta^{-1}} \dot{W}
\end{align*}
\]
A “Barrier Thermostat”

\[ \beta \xi^2 = 1 \]
\[ \xi = 0 \]

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

\[ kT = 1/4 \]
Gentle Stochastic Thermostats
Hoover-Langevin


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

a method suggested by *Samoletov, Dettmann & Chaplain*

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

Fokker-Planck Equation

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

\(\mathcal{L}^*\) Hypoelliptic:
- Elliptic only in some components
- Mixing

\[\Rightarrow\] Stationary solutions are smooth
Uniqueness of invariant measure

stochastic analysis literature
Mattingley, Stuart, E...
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

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

Difficult to verify globally in general setting, due to high order Lie brackets.
Linear system w/o resonance

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

\[ A = M^{-1} B, \quad A \varphi_k = \omega_k \varphi_k \]

\[ \omega_k \neq \omega_l, \quad k \neq l \]

Theorem: Hoover-Langevin is ergodic for this problem.

Example: clamped harmonic spring chain.
Linear system w/o resonance

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

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

\[ \overline{X}_0 = X_0 - (\|p\|^2 - n) - \frac{1}{2}\xi) X_1 = (p, -Bq - \xi p, 0), \]

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

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

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

generates a sequence of vectors that span \( R^{2n} \)
Butane Momentum Distributions

Nose Hoover

H = 0.006

H = 0.004

H = 0.002

Hoover-Langevin

School of Mathematics
Comparisons

K.E. in 10K steps of simulation

K.E. in 20M steps of simulation
Near equilibrium

With Noorizadeh, Oliver Penrose:

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

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 $\xi$ 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

\begin{align*}
\text{NH} & \quad \text{h}=6\text{fs} & \quad \text{h}=4\text{fs} & \quad \text{h}=2\text{fs} \\
\text{Metropolis-Adjusted NH} & \quad \text{No Flip!}
\end{align*}
Butane Angle Distribution

\[ r_{12}, r_{11}, \delta, \gamma_1 \]

\[ \text{distribution} \]

\[ \text{dihedral angle} \]

\[ \text{exact distribution} \]

\[ 2M \text{ timesteps} \]

\[ 8M \text{ timesteps} \]

\[ 32M \text{ timesteps} \]
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