An adaptive Langevin thermostat for non-equilibrium molecular dynamics simulations

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Outline

Why do we do MD simulations?

- To calculate observables - static, dynamic
- To see what happens

Changing Ensemble

- MD is nominally energy conserving - NVE ensemble
- Usually more interested in NVT or NPT ensemble
- Need temperature regulation - Thermostat

Thermostatted MD

- A thermostat alters the forces and/or velocities
- These alterations can be deterministic or stochastic

Non-equilibrium MD

Non-equilibrium simulations or bad equilibrium simulations generate heat:

- Non-Hamiltonian
- QM/MM with discontinuous force calculation
- $F \neq -\nabla U$

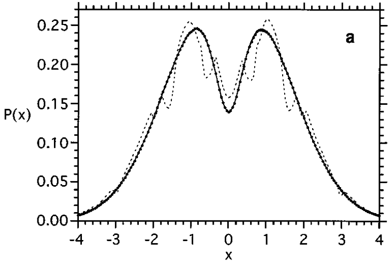
Here we can only hope a thermostat gives the correct average temperature.

Deterministic	Stochastic
Rescaling Rescale velocities such that $$E_k = \frac{1}{2} N_{\mathrm{dof}} k_B T$$	Andersen Every M steps choose a particle and reassign its velocity from Maxwellian distribution
Nosé-Hoover Hoover, PhysRevA **31** 1695 $$\dot{r}_i = \frac{p_i}{m_i}$$ $$\dot{p}_i = F_i - \xi p_i$$ $$Q\dot{\xi} = \sum_i \frac{p_i^2}{m_i} - N_{\mathrm{dof}} k_B T$$	Langevin Quigley, Probert, JChemPhys **120**(24) 11432 $$\dot{r}_i = \frac{p_i}{m_i}$$ $$\dot{p}_i = F_i - \gamma p_i + \sqrt{\Gamma}\tilde{A}_i(t)$$ $$\Gamma = 2\gamma m_i k_B T \quad \left\langle \tilde{A}_i(t) \right\rangle = 0$$ $$\left\langle \tilde{A}_i(t)\tilde{A}_j(t') \right\rangle = \delta_{ij}\delta(t-t')$$

Deterministic	Stochastic
Rescaling Temp. gradients Rescale velocities such that $$E_k = \frac{1}{2} N_{\mathrm{dof}} k_B T$$	Andersen Unphysical (MC) Every M steps choose a particle and reassign its velocity from Maxwellian distribution
Nosé-Hoover Bad sampling Hoover, PhysRevA **31** 1695 $$\dot{r}_i = \frac{p_i}{m_i}$$ $$\dot{p}_i = F_i - \xi p_i$$ $$Q\dot{\xi} = \sum_i \frac{p_i^2}{m_i} - N_{\mathrm{dof}} k_B T$$	Langevin No feedback Quigley, Probert, JChemPhys **120**(24) 11432 $$\dot{r}_i = \frac{p_i}{m_i}$$ $$\dot{p}_i = F_i - \gamma p_i + \sqrt{\Gamma}\tilde{A}_i(t)$$ $$\Gamma = 2\gamma m_i k_B T \quad \left\langle \tilde{A}_i(t) \right\rangle = 0$$ $$\left\langle \tilde{A}_i(t)\tilde{A}_j(t') \right\rangle = \delta_{ij}\delta(t - t')$$

Nosé-Hoover Thermostat

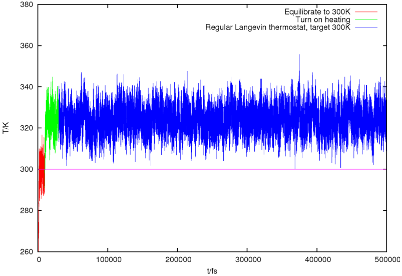
The Nosé-Hoover thermostat relies on chaotic trajectories

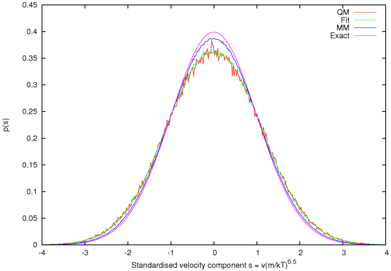


R.G. Winkler et. al., JChemPhys **102**(22) 9018

Langevin Thermostat

The Langevin thermostat cannot be used when there is heating - incorrect average temperature:





1728 Si atoms, with Stillinger-Weber potential

Requirements

- Feedback - Nosé-Hoover
- Stochastic - Langevin
- Modified Fluctuation-Dissipation relation
  Kühne et al., PRL **98** 066401 (2007)

Equations of Motion

$$\dot{r}_i = \frac{p_i}{m_i}$$

$$\dot{p}_i = F_i - \gamma p_i + \sqrt{\Gamma}\tilde{A}(t)$$

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$$\dot{p}_i = F_i - \gamma p_i + \sqrt{\Gamma}\tilde{A}(t)s(t)$$

$$\dot{s} = \left(1 - \frac{\langle T_k \rangle_\tau}{T}\right)\beta$$

$$\langle f(t) \rangle_\tau = \frac{1}{\tau}\int_{-\infty}^{t} e^{\frac{t'-t}{\tau}} f(t')dt'$$

Choose β such that oscillations in s, and so $\langle T_k \rangle$, are critically damped (approximately)

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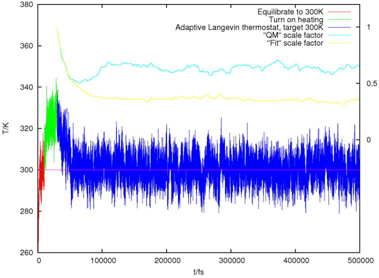
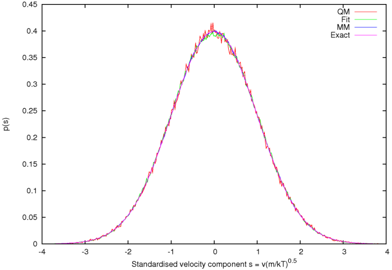
Choose β such that oscillations in s, and so $\langle T_k \rangle$, are critically damped (approximately)
Caveat: $s < 0$ makes no sense ($\tilde{A}$ and $-\tilde{A}$ have same properties)

Results


Equilibrate to 300K
Turn on heating
Adaptive Langevin thermostat, target 300K
"QM" scale factor
"Fit" scale factor
T/K
Scale factor
t/fs
380
360
340
320
300
280
260
0
100000
200000
300000
400000
500000
1
0.5
0


QM
Fit
MM
Exact
p(s)
Standardised velocity component s = v(m/kT)^0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-4
-3
-2
-1
0
1
2
3
4

Conclusions and Further Work

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Further Work:

- Recover Newtonian dynamics when temperature is OK

  Leimkuhler et al., JChemPhys **128** 074105
- Re-derive using Fokker-Planck equation in extended phase-space

Thank-you for listening!

Any questions?

Nosé-Hoover-Langevin Thermostat?

$$\dot{r}_i = \frac{p_i}{m_i}$$

$$\dot{p}_i = F_i - \xi p_i$$

$$Q\dot{\xi} = \left[\sum_i \frac{p_i^2}{m_i} - Nk_B T\right] - \gamma Q\xi + \sqrt{\Gamma}\tilde{A}(t)$$

$$\Gamma = 2\gamma Q k_B T$$

- Gives canonical probability density in equilibrium simulations
- Has feedback to deal with non-equilibrium simulations
- When temperature has stabilised ξ decays - dynamics is more Newtonian