An adaptive Langevin thermostat for non-equilibrium molecular dynamics simulations

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ESDG
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Outline

Molecular Dynamics

Thermostats

Adaptive Langevin thermostat

Conclusions and Further Work
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.
<table>
<thead>
<tr>
<th>Deterministic</th>
<th>Stochastic</th>
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<td><strong>Andersen</strong></td>
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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

\[
\dot{r}_i = \frac{p_i}{m_i}
\]

\[
\dot{p}_i = F_i - \gamma p_i + \sqrt{\Gamma} \tilde{A}(t)
\]
Equations of Motion

\[ \dot{r}_i = \frac{p_i}{m_i} \]

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

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

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

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

Conclusions:

- Adding simple feedback to Langevin thermostat allows it to deal with non-equilibrium systems
- Canonical velocity distributions are recovered

Further Work:

- Recover Newtonian dynamics when temperature is OK
- Re-derive using Fokker-Planck equation in extended phase-space
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- Adding simple feedback to Langevin thermostat allows it to deal with non-equilibrium systems
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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?

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

- Gives canonical probability density in equilibrium simulations
- Has feedback to deal with non-equilibrium simulations
- When temperature has stabilised, \( \xi \) decays - dynamics is more Newtonian