A tunable, all-purpose, colored-noise thermostat

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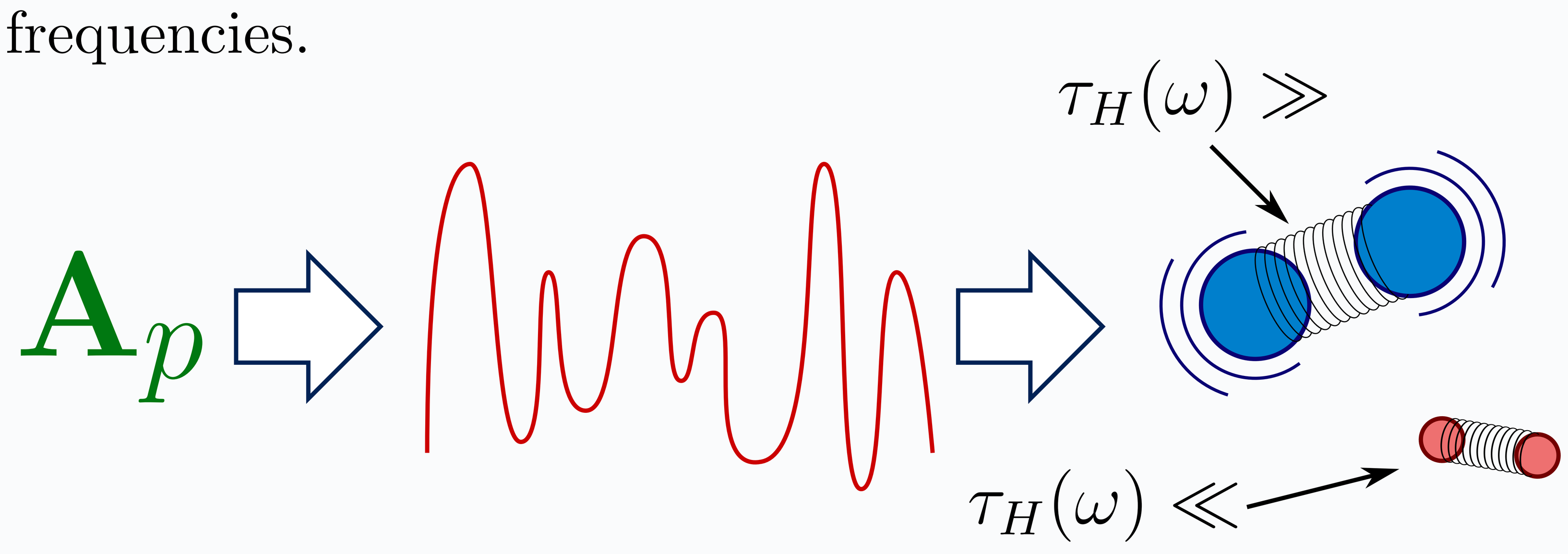
How do you get a tunable and *predictable* thermostat? We use a generalized version of the Langevin equations, which includes a set of additional degrees of freedom[1,3]:

$$\dot{q} = -p, \quad \begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = -\begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}_p \boldsymbol{\xi} \qquad (1)$$

with $\mathbf{B}\mathbf{B}^T = k_B T \left(\mathbf{A}_p + \mathbf{A}_p^T\right)$. This corresponds to a non-Markovian Langevin equation,

$$\dot{p}(t) = -\int_{-\infty}^{t} K(t-s)p(s)\mathrm{d}s + \zeta(t)$$
$$K(t) = 2a_{pp}\delta(t) - \mathbf{a}_p^T e^{-|t|\mathbf{A}}\mathbf{a}_p, \qquad (2)$$
$$\langle \zeta(t)\zeta(0)\rangle = k_B T K(t)$$

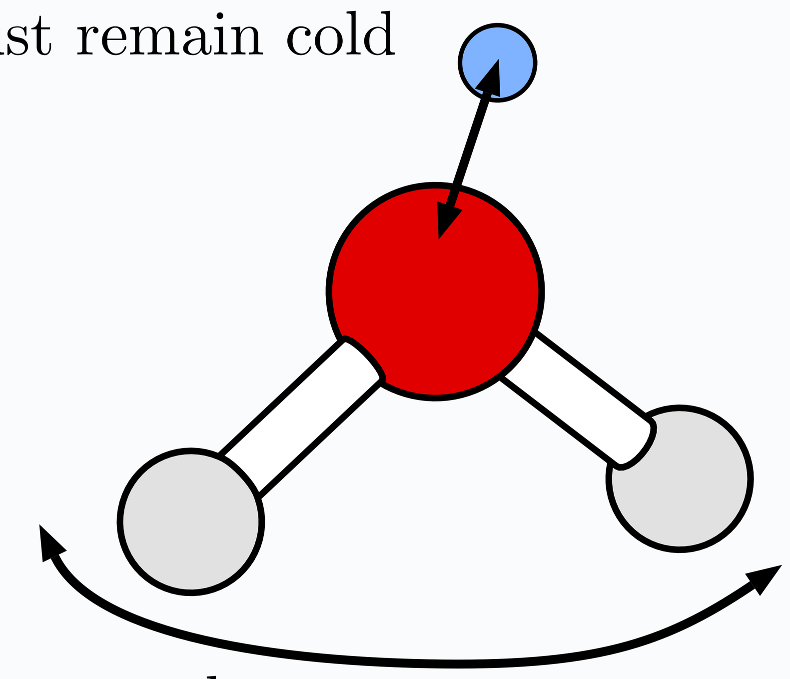
The dynamics of a harmonic oscillator can be solved exactly, and one can compute correlation functions which predict the response time of quasi-harmonic modes.
The correlation time of the total energy, $\tau_H(\omega)$ is a measure of the coupling with phonons of frequency ω.
By varying $\mathbf{A}_p$ one can tune $\tau_H(\omega)$, so as to optimize it, or to obtain a "filter" which prevents thermaliziation of some frequencies.



Car-Parrinello: heating everything but the electrons

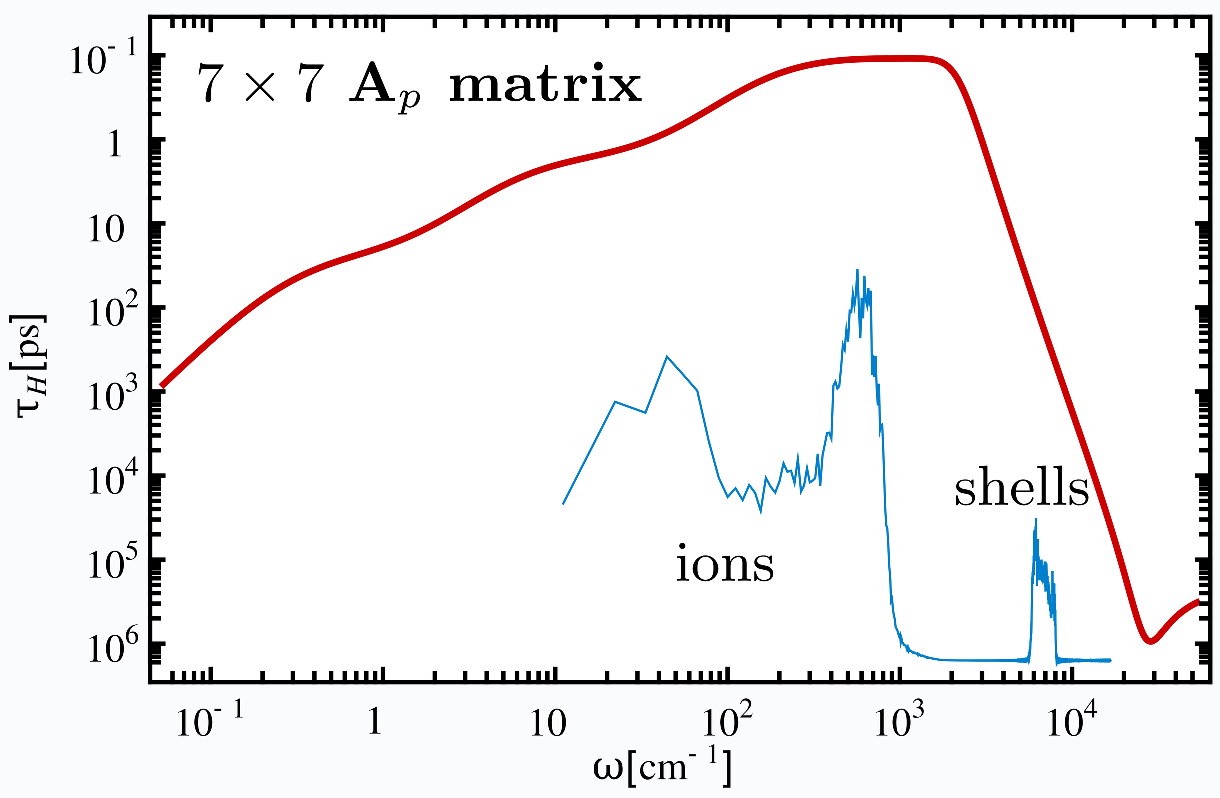
Polarizable water model

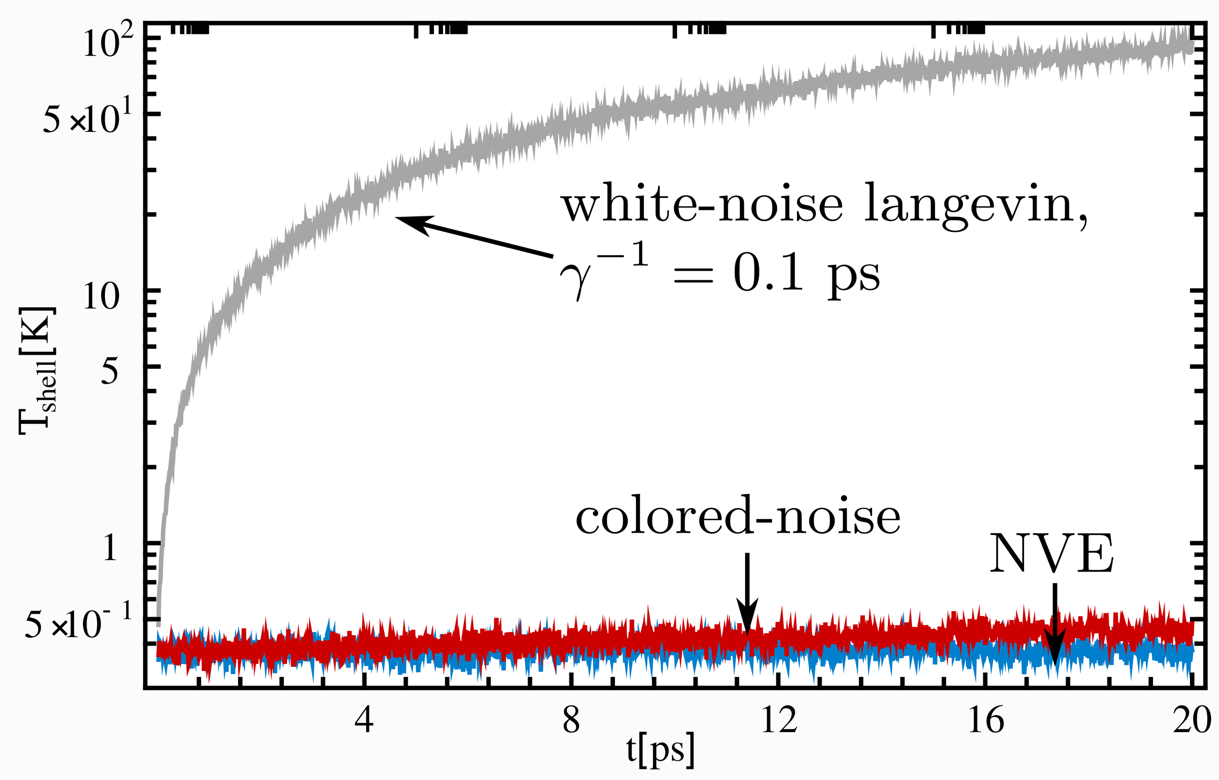
electronic degrees of freedom must remain cold



ions must be efficiently thermalized

We can tune $\tau_H(\omega)$ so as to design a **sharp** low-pass filter!

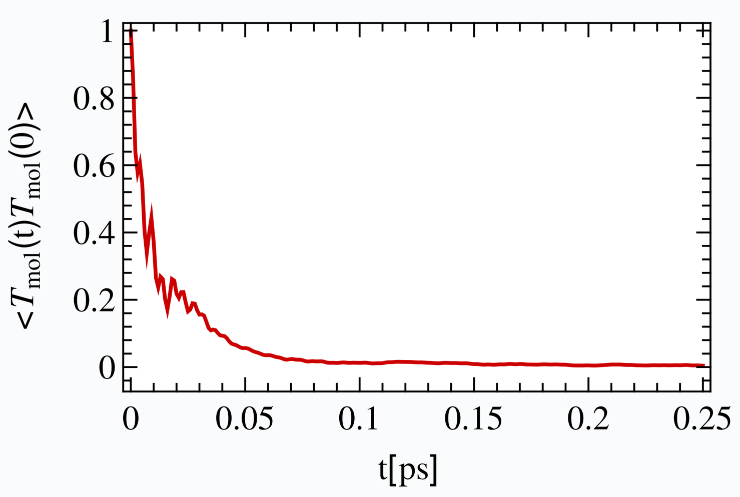




White noise disrupts adiabatic separation. The drift induced by the filtered noise is tiny, and can be easily compensated by a mild damping of the velocities of the shells.

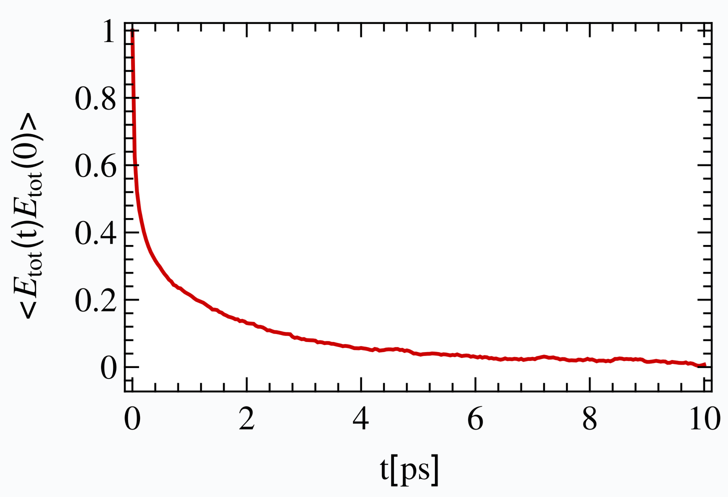
Efficient sampling without the headache

T_{mol} is the kinetic temperature of a single molecule. Gauges the efficiency in imposing equipartion.



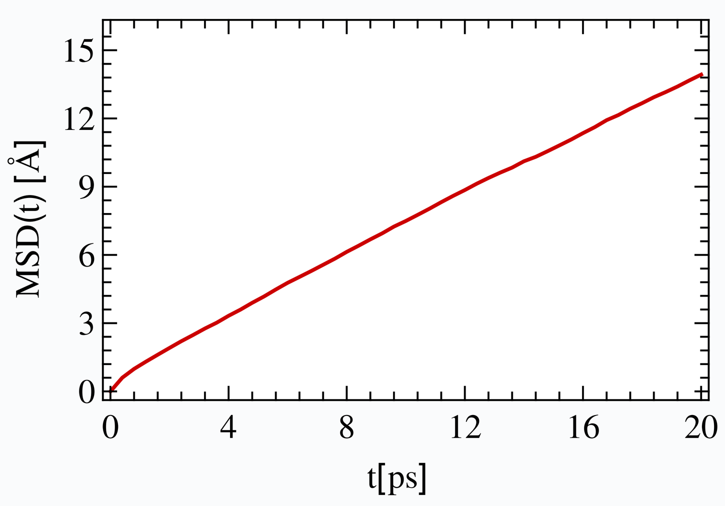
Correlation time (ps)	
col. noise	**0.03**
white noise	
$\gamma^{-1} = 10$ fs	**0.01**
$\gamma^{-1} = 0.1$ ps	0.05
$\gamma^{-1} = 1$ ps	0.12
$\gamma^{-1} = 10$ ps	0.16
global rescale[2]	
$\gamma^{-1} = 10$ fs	**0.16**
$\gamma^{-1} = 0.1$ ps	0.16
$\gamma^{-1} = 1$ ps	0.2
$\gamma^{-1} = 10$ ps	0.2

E_{tot} is the total (kinetic+potential) energy of the whole box. Gauges the efficiency in sampling global averages.



Correlation time (ps)	
col. noise	**2.0**
white noise	
$\gamma^{-1} = 10$ fs	4.0
$\gamma^{-1} = 0.1$ ps	**3.0**
$\gamma^{-1} = 1$ ps	4
$\gamma^{-1} = 10$ ps	25
global rescale	
$\gamma^{-1} = 10$ fs	**1.5**
$\gamma^{-1} = 0.1$ ps	1.8
$\gamma^{-1} = 1$ ps	10
$\gamma^{-1} = 10$ ps	>30

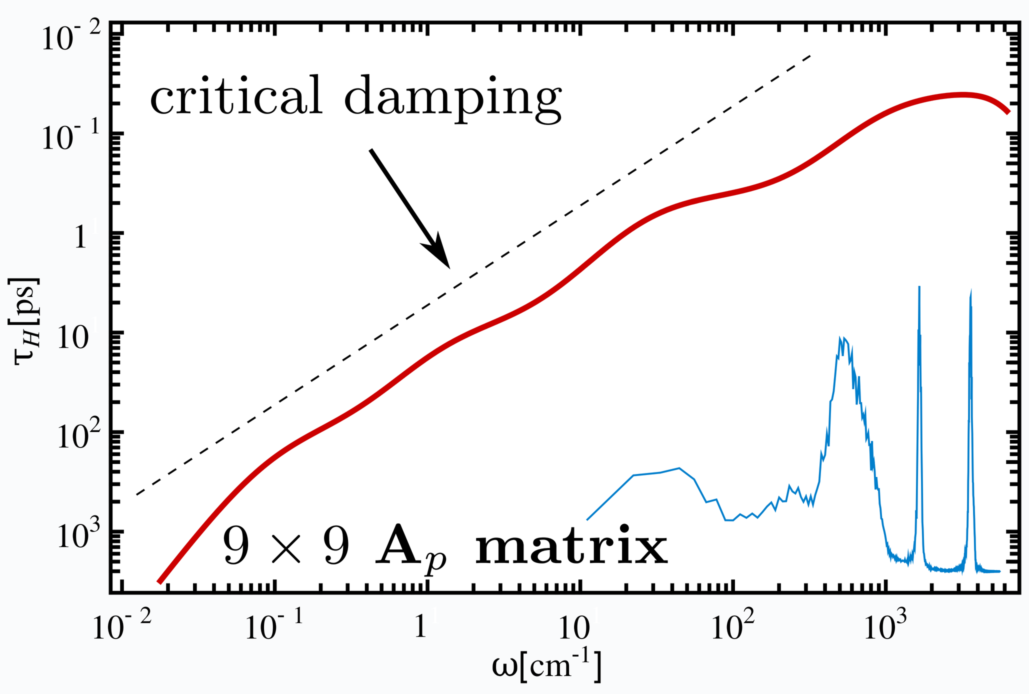
D is the diffusion coefficient. Gauges the efficiency in sampling diffusive degrees of freedom.



Diff. coeff. (Å^2/ps)	
col. noise	**0.33**
white noise	
$\gamma^{-1} = 10$ fs	0.05
$\gamma^{-1} = 0.1$ ps	0.26
$\gamma^{-1} = 1$ ps	0.49
$\gamma^{-1} = 10$ ps	**0.58**
global rescale	
$\gamma^{-1} = 10$ fs	0.57
$\gamma^{-1} = 0.1$ ps	0.55
$\gamma^{-1} = 1$ ps	**0.59**
$\gamma^{-1} = 10$ ps	0.58

1-ns simulation of 216 flexible-TIP4P water molecules.

Performance of standard thermostats varies depending on the parameters and on the observable. Expensive tests must be performed. Colored-noise thermostat can be fitted **beforehand** to give close-to-optimal $\tau_H \sim \omega^{-1}$ over an extended frequency range. **Without any preliminary simulation** one gets a very good efficiency. **No set of parameters performed better than colored-noise for all the observables at once.**
The fitting is performed down to very low frequency, so as to reduce damping of diffusive modes.



[1] *M. Ceriotti, G. Bussi, and M. Parrinello,* Phys. Rev. Lett. 102, 020601 (2009)
[2] *G. Bussi, D. Donadio, and M. Parrinello,* J. Chem. Phys. 126, 014101 (2007)
[3] *C. W. Gardiner,* Handbook of Stochastic Methods, Springer (Berlin, 2004)

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