Advanced Molecular Dynamics. Thermostats, Barostats and Nuclear Quantum Effects

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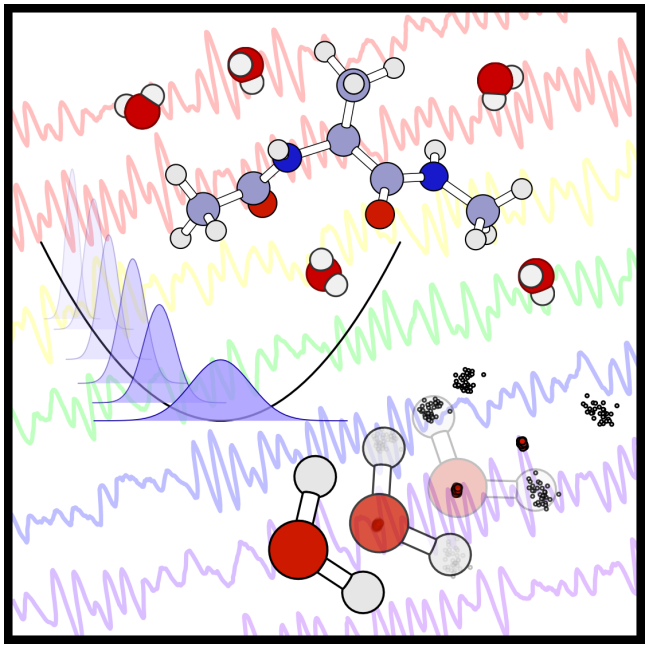
Materials Simulations using Quantum Espresso, Jan 2017

Outline

1. Efficient constant-temperature sampling:
   - White and colored-noise Langevin dynamics
   - Multiple time stepping, replica exchange
2. Sampling different ensembles: barostats
3. Path integral molecular dynamics: accurate modelling of quantum nuclear fluctuations
4. Examples



Checklist of approximations

- Classical dynamics of a system of atoms with positions $\mathbf{q}$ and momenta $\mathbf{p}$, described by the Hamiltonian

$$H(\mathbf{p},\mathbf{q}) = K(\mathbf{p}) + V(\mathbf{q}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q})$$

  - We assume V is given (force fields, electronic structure calculation)
  - In all cases, strictly Born-Oppenheimer
- Want to generate $(\mathbf{p},\mathbf{q})$ configurations consistent with given thermodynamic conditions
  - We focus (mostly) on the canonical (NVT) ensemble

$$P(\mathbf{p},\mathbf{q}) = e^{-\beta H(\mathbf{p},\mathbf{q})} \Big/ \int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}\, e^{-\beta H(\mathbf{p},\mathbf{q})}$$

Sampling by molecular dynamics

- Hamilton's equations can be used to generate a trajectory

$$\dot{\mathbf{p}} = -\partial V/\partial \mathbf{q}, \qquad \dot{\mathbf{q}} = \mathbf{p}/m$$

- Fulfills the *necessary*, "global" condition for sampling the canonical ensemble,

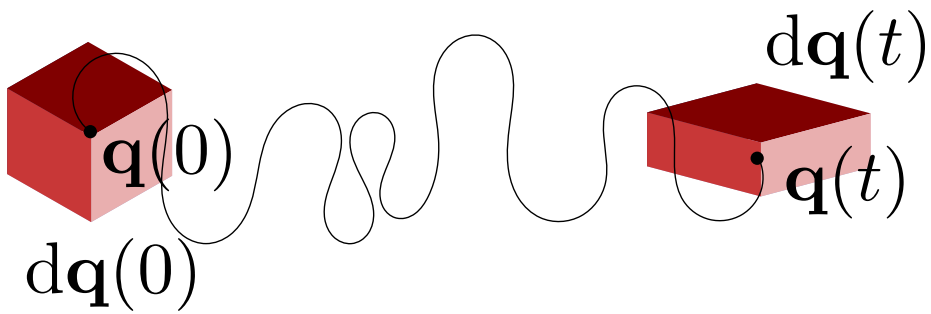
$$\int \mathrm{d}\mathbf{q}\, P(\mathbf{q}, \boldsymbol{p})\, p(\mathbf{q}, \mathbf{p} \to \mathbf{q}', \mathbf{p}') = P(\mathbf{q}', \mathbf{p}')\,.$$

  Clean proof with a Liouville operator formalism. The ingredients are:

  - Conservation of probability density

$$\frac{dP}{dt} \propto e^{-\beta H}\frac{dH}{dt}, \qquad \frac{dH}{dt} = \frac{\partial H}{\partial \mathbf{p}}\cdot\dot{\mathbf{p}} + \frac{\partial H}{\partial \mathbf{q}}\cdot\dot{\mathbf{q}} = -\frac{\partial H}{\partial \mathbf{p}}\cdot\frac{\partial H}{\partial \mathbf{q}} + \frac{\partial H}{\partial \mathbf{q}}\cdot\frac{\partial H}{\partial \mathbf{p}} = 0$$

  - Conservation of phase-space volume (symplectic property)



Ergodicity of sampling

- Underlying assumption behind importance sampling (by MD or MC) is **ergodicity**:

$$\lim_{M\to\infty} \frac{1}{M} \sum_i A(\mathbf{q}_i) = \int \mathrm{d}\mathbf{q}\, P(\mathbf{q})\, A(\mathbf{q})$$

  - This is an additional condition, that is very hard to prove in practice.
  - We always have a finite M, so the question is: *how much* ergodic is the trajectory? How can we "measure" ergodicity?
- The key tool to assess the ergodicity of a trajectory for computing $\langle A \rangle$ is the autocorrelation function

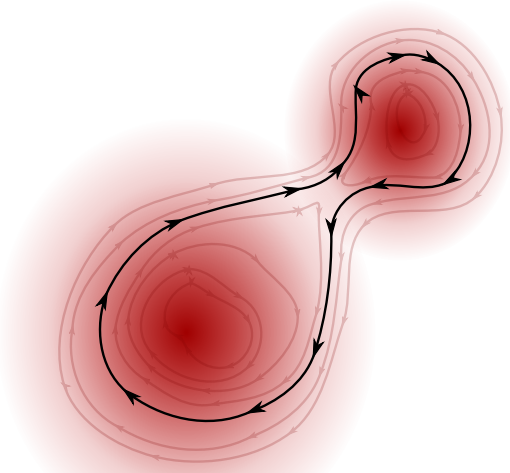
$$c_{AA}(t) = \langle A(0)\, A(t) \rangle$$

- Direct link with the error in the mean of a trajectory of length T

$$\epsilon_A^2(T) = \frac{\sigma_A^2}{T} \int_{-T}^{T} \mathrm{d}\Delta\, c_{AA}(\Delta) \left(1 - \frac{|\Delta|}{T}\right)$$

Constant-temperature molecular dynamics

- Plain, Hamiltonian MD conserves energy and is not ergodic
- Must modify the dynamics to model the interaction with a heat bath (**thermostats**)
- Andersen thermostat: randomize atomic velocities every now and then
  - Exploits factorization of the canonical partition function
  - Simple, physically sound and effective



$$dH/dt = 0$$

Andersen, J. Chem. Phys. 1980

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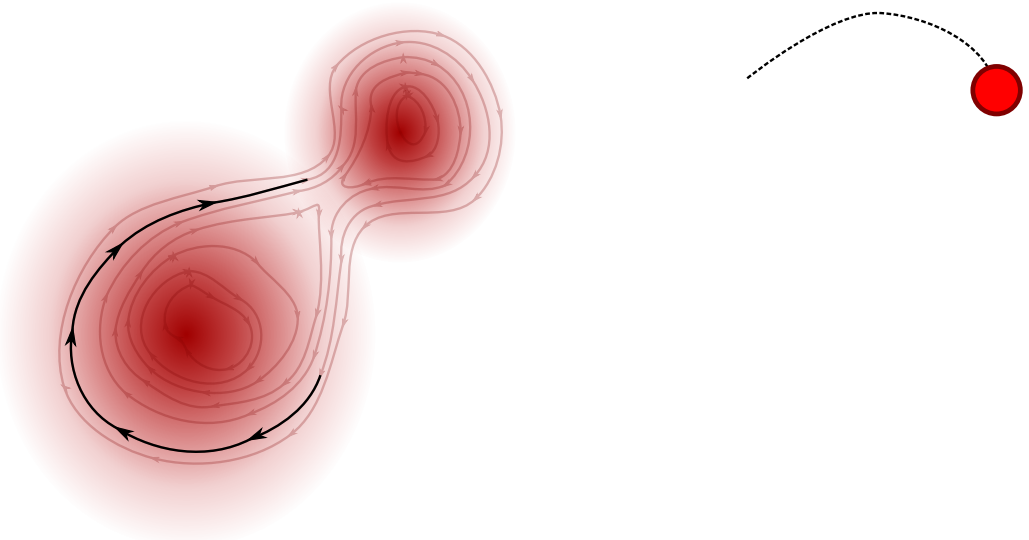

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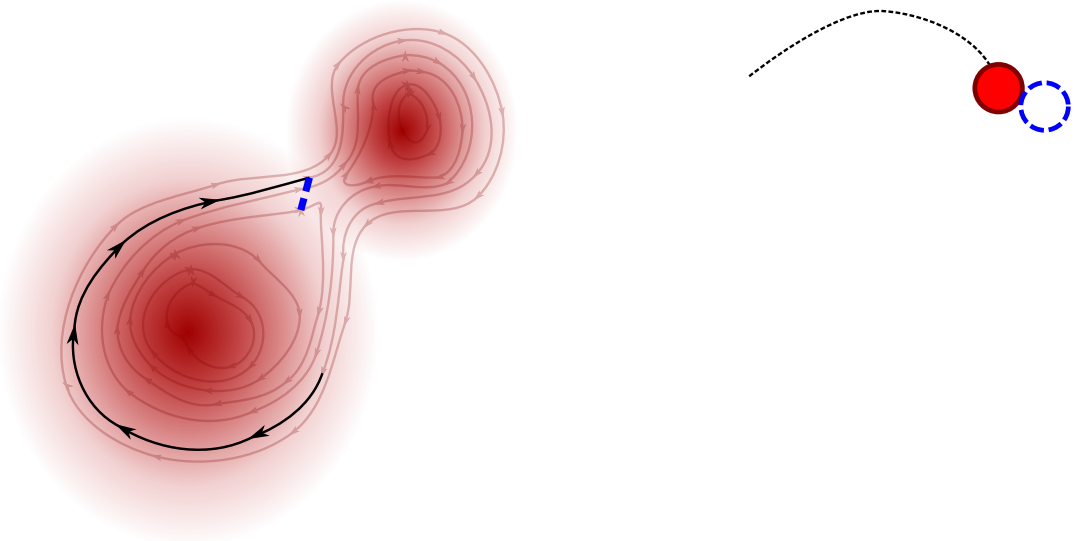

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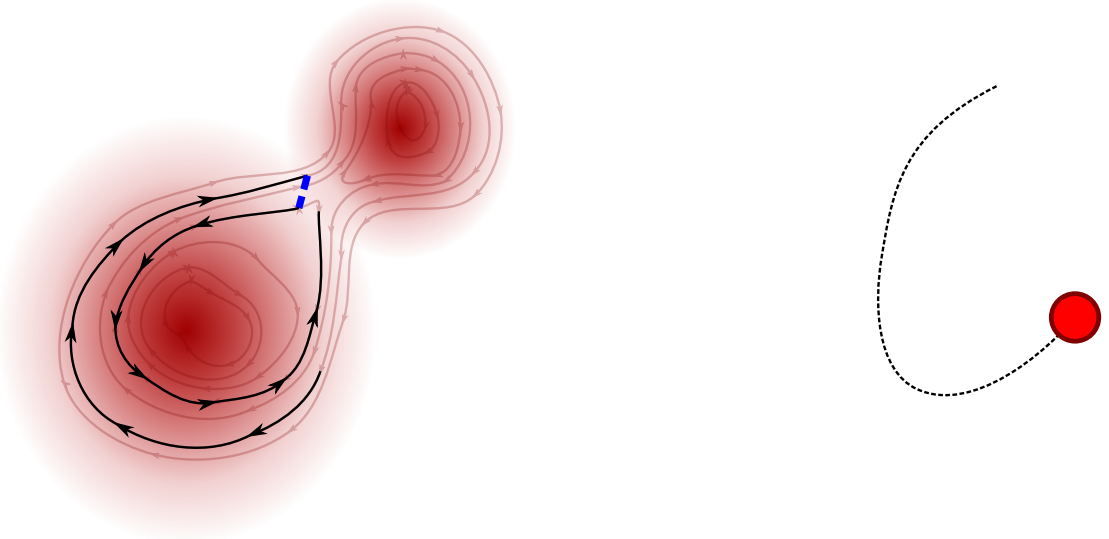

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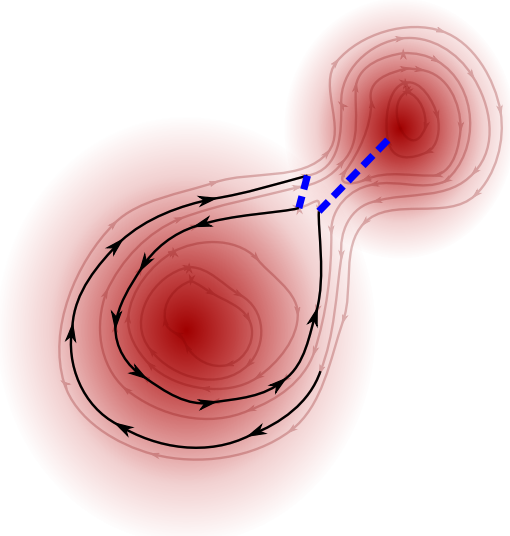

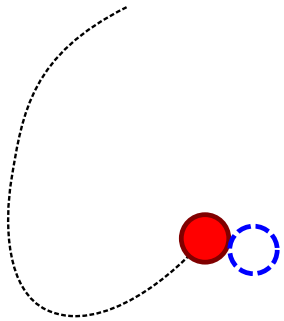

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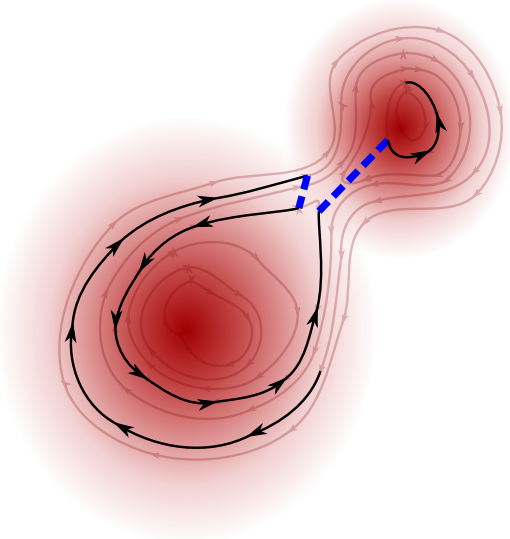
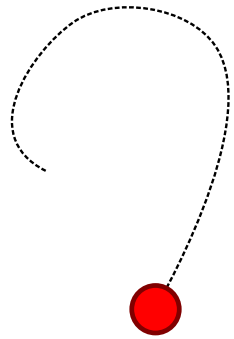




Andersen, J. Chem. Phys. 1980

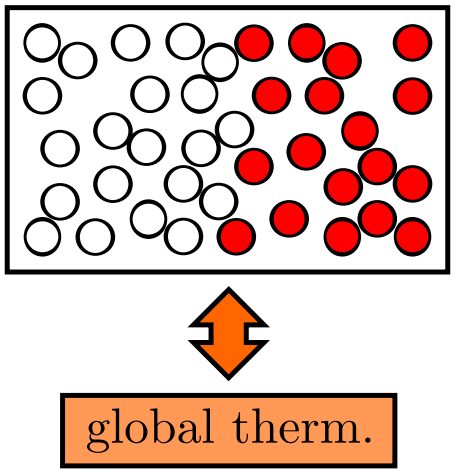
Getting a conserved quantity

- Having a conserved quantity is handy to monitor integration
- Thermostats implement ergodic canonical sampling, so total energy fluctuates
- Very general solution: keep track of the heat flow to the bath
  - Compute kinetic energy before and after the thermostat, K_0 and K_f
  - Accumulate $\Delta H \leftarrow \Delta H + K_0 - K_f$
  - Conserved quantity is $\tilde{H} = H + \Delta H$
- This works best with symmetric-split velocity Verlet
  1. Apply thermostat for $dt/2$, keep track of ΔH
  2. Symmetric-split Hamiltonian evolution of $(\mathbf{p}, \mathbf{q})$
  3. Apply thermostat for $dt/2$, keep track of ΔH

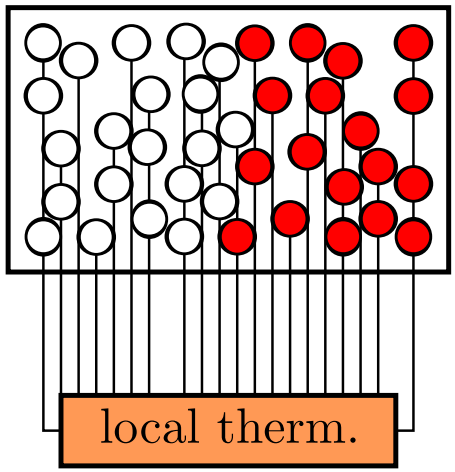
Bussi, Donadio, Parrinello, J. Chem. Phys 2007

Local and global thermostats

- "Global" thermostats enforce the correct distribution of the *total* kinetic energy (Berendsen[1], Nosé-Hoover, Bussi)
  - Gentle on the dynamics, but rely on the intrinsic Hamiltonian dynamics to relax internal degrees of freedom
- "Local" thermostats enforce the correct distribution of *each component* of the momentum (Andersen, Langevin, massive NHC)
  - More aggressive, slower collective dynamics, but also effective for poorly ergodic systems (e.g. crystals)



$$P(K) \propto K^{3N/2-1} e^{-\beta K}$$



$$P(\mathbf{p}) \propto e^{-\beta \mathbf{p}^2/2m}$$

[1] **Does not give proper canonical sampling!**

Deterministic and stochastic thermostats

- Nosé-Hoover thermostat: extended-Lagrangian approach, **deterministic** equations of motion

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial V}{\partial q} - p\frac{p_s}{Q}, \quad \dot{p}_s = \frac{p^2}{m} - \frac{1}{\beta}, \quad \dot{s} = \frac{p_s}{Q}$$

  - Not ergodic, must introduce chains to make the dynamics chaotic
  - The local version is not rotationally invariant
  - Integration is not straightforward, must use multiple time step

- Langevin-style thermostats: intrinsically **stochastic** dynamic

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial V}{\partial q} - \gamma p + \sqrt{2m\gamma/\beta}\xi, \quad \langle \xi(t)\,\xi(0) \rangle = \delta(t)$$

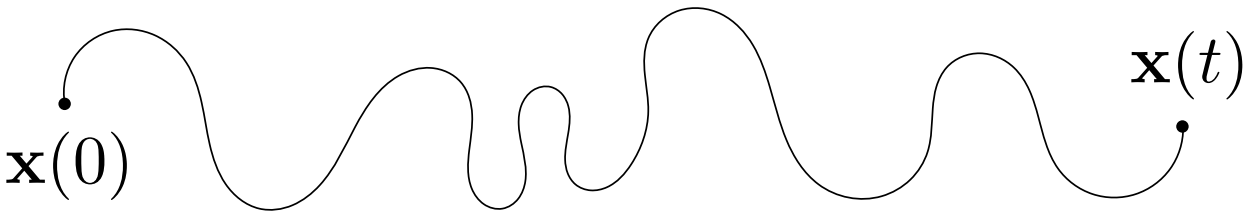
  - Ergodic, very natural model for coupling to a heat bath
  - Linear equations, very stable and easy to integrate
  - Require some care with the random number generator (parallelism!)

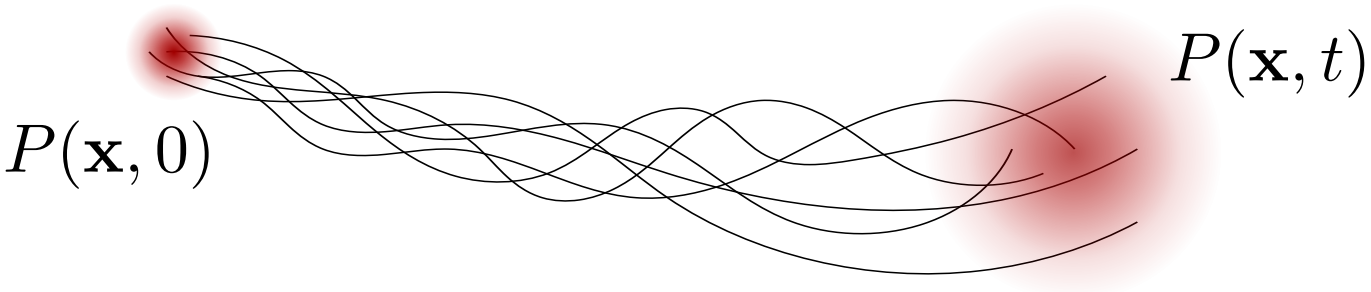
Nosé, J. Chem. Phys. 1984; Hoover, Phys. Rev. A 1985; Schneider & Stoll, Phys. Rev. B 1978

Stochastic differential equations

- Stochastic differential equations e.g. $\dot{x} = a(x,t) + b(x,t)\,\xi$, where $\xi(t)$ is a "Gaussian white noise" term can be integrated with some rigor using Ito/Stratonovich calculus
- They are best understood in terms of the associated Fokker-Planck equation for the time evolution of the probability distribution

$$\frac{\partial}{\partial t} P(x,t|x_0,t_0) = -\frac{\partial}{\partial x}\left[a(x,t)\,P\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[b(x,t)^2\,P\right]$$





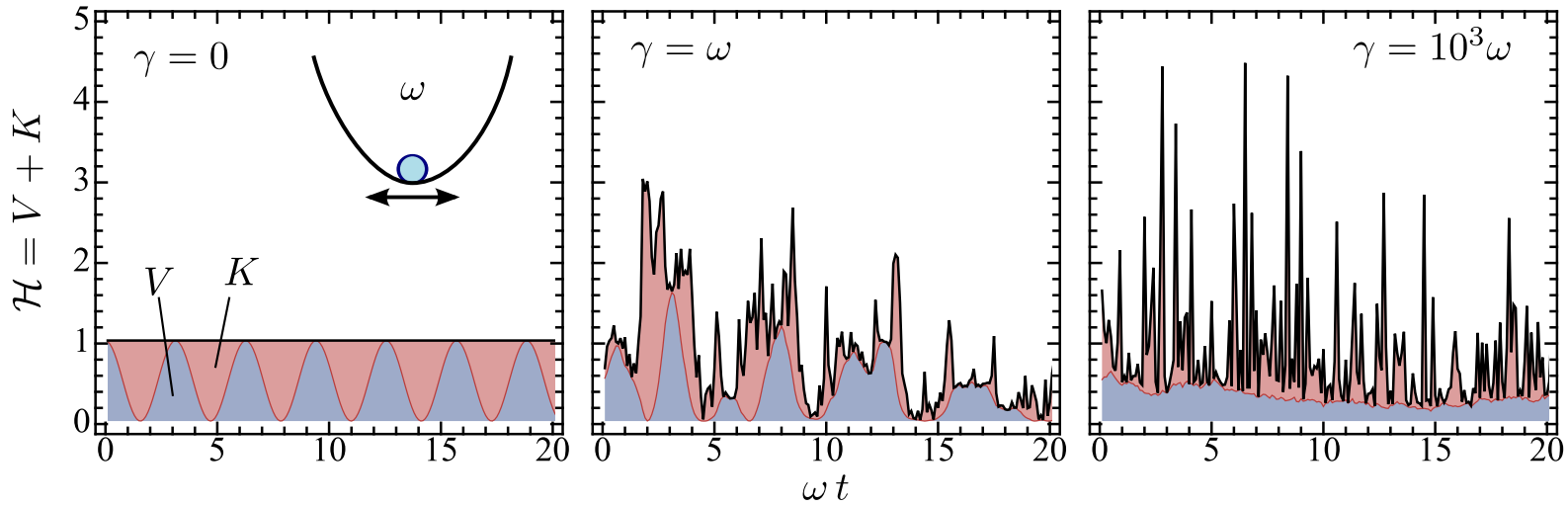
Gardiner, Handbook of Stochastic Methods

Langevin equation in atomistic simulations

- Langevin dynamics models the interaction with a thermal bath

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial V}{\partial q} - \gamma p + \sqrt{2 m \gamma k_B T}\,\xi, \quad \langle \xi(t)\,\xi(0) \rangle = \delta(t)$$

- Can be used in molecular dynamics to sample configurations consistent with constant temperature
- Crucial aspect: how efficient is that? Use autocorrelation time $\tau_V = \int_0^\infty \langle V(t)\,V(0) \rangle \, \mathrm{d}t$



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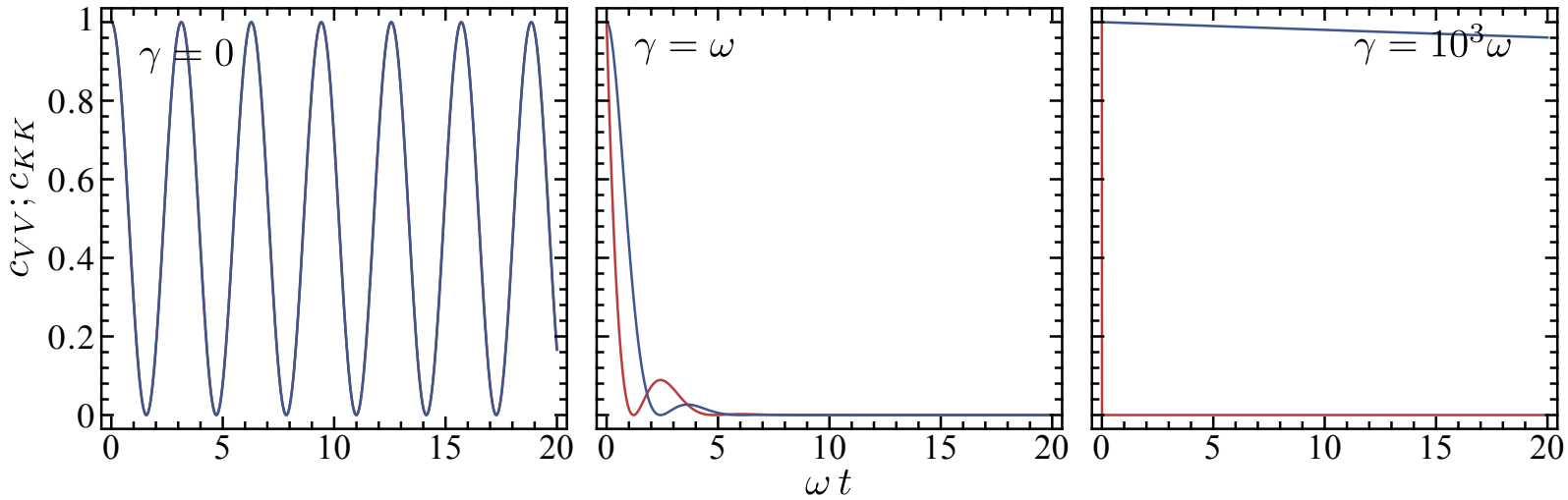
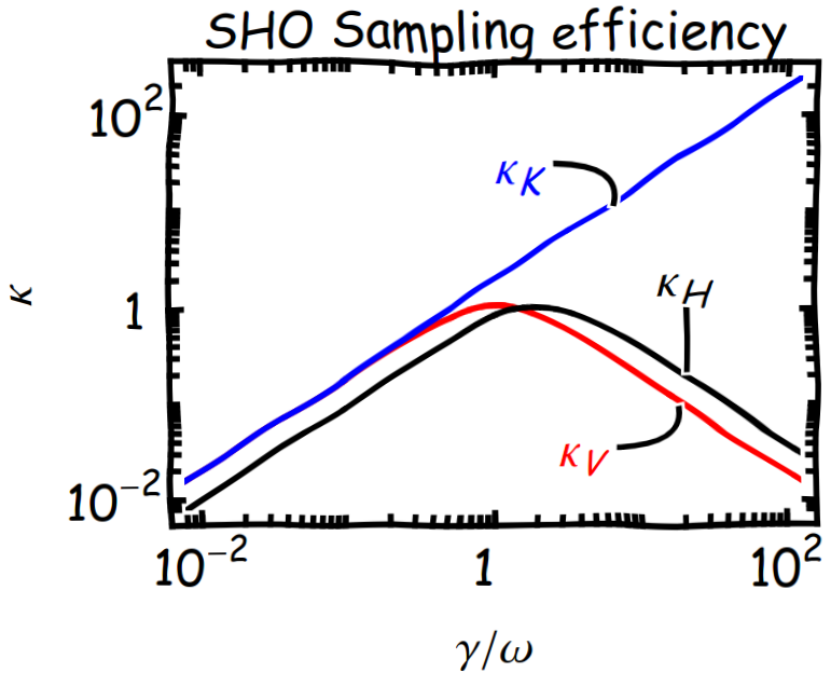


Sampling efficiency of Langevin dynamics

- Sampling efficiency: the intrinsic time scale divided by the correlation time $\kappa = 2/\tau\omega$. The efficiency κ is smaller than one
- $\gamma \ll \omega$: underdamping; $\gamma \gg \omega$: overdamping; $\gamma \approx \omega$: critical damping
- PB: atomistic simulations involve vibrational modes spanning multiple time scales – how can we pick just one value of γ?



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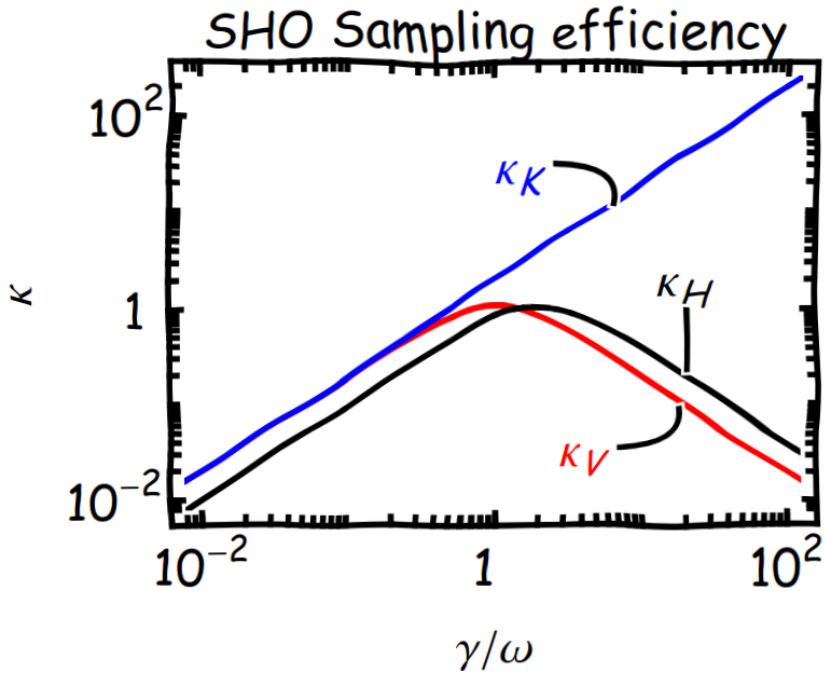

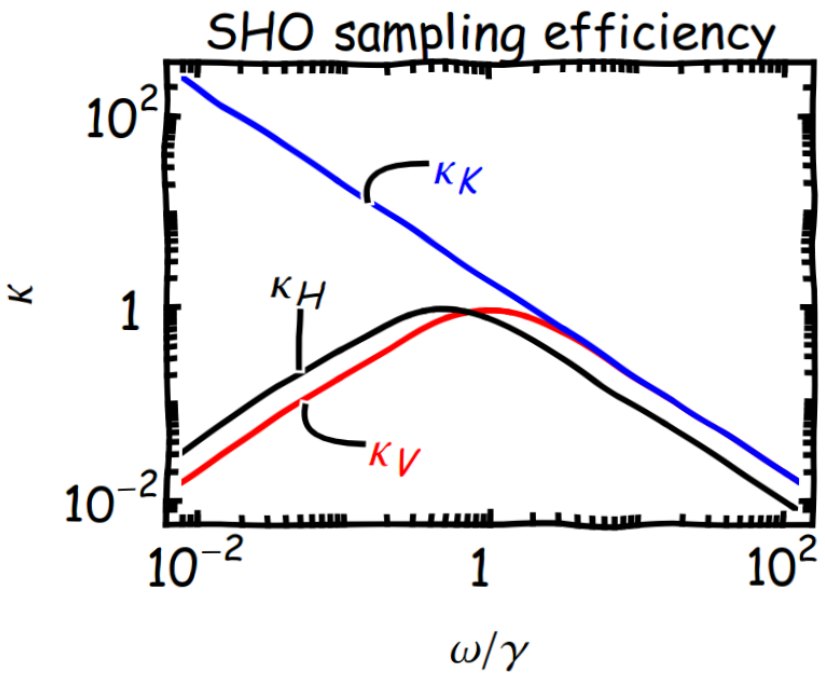

A Generalized Langevin Equation

- **Langevin equation**: modify Newton's equations with a viscous friction and white-noise force term.
  - A GLE framework based on **colored noise**
    - Markovian formulation - dynamics and sampling can be estimated analytically
    - One can tune the parameters based on these estimates, and obtain all sorts of useful effects

$$\dot{q} = p/m \quad \dot{p} = f(q)$$

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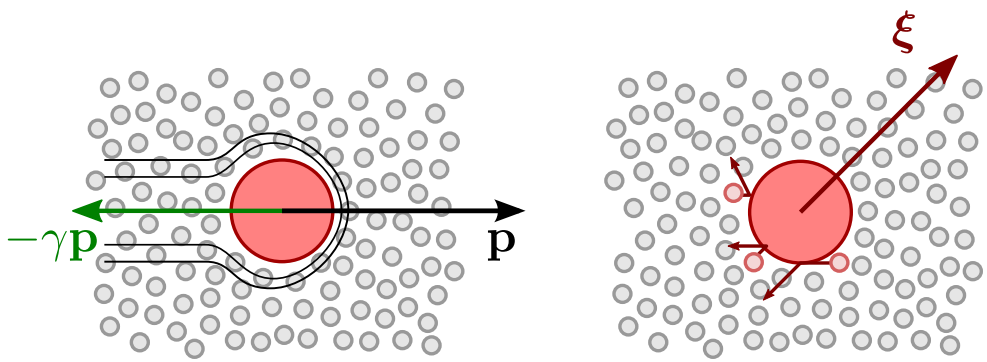

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$$\dot{p}(t) = f(q) - \int_0^\infty K(s)\, p(t-s)\, \mathrm{d}s + \sqrt{2mk_BT}\,\zeta(t),\ \langle \zeta(t)\,\zeta(0)\rangle = K(t)$$

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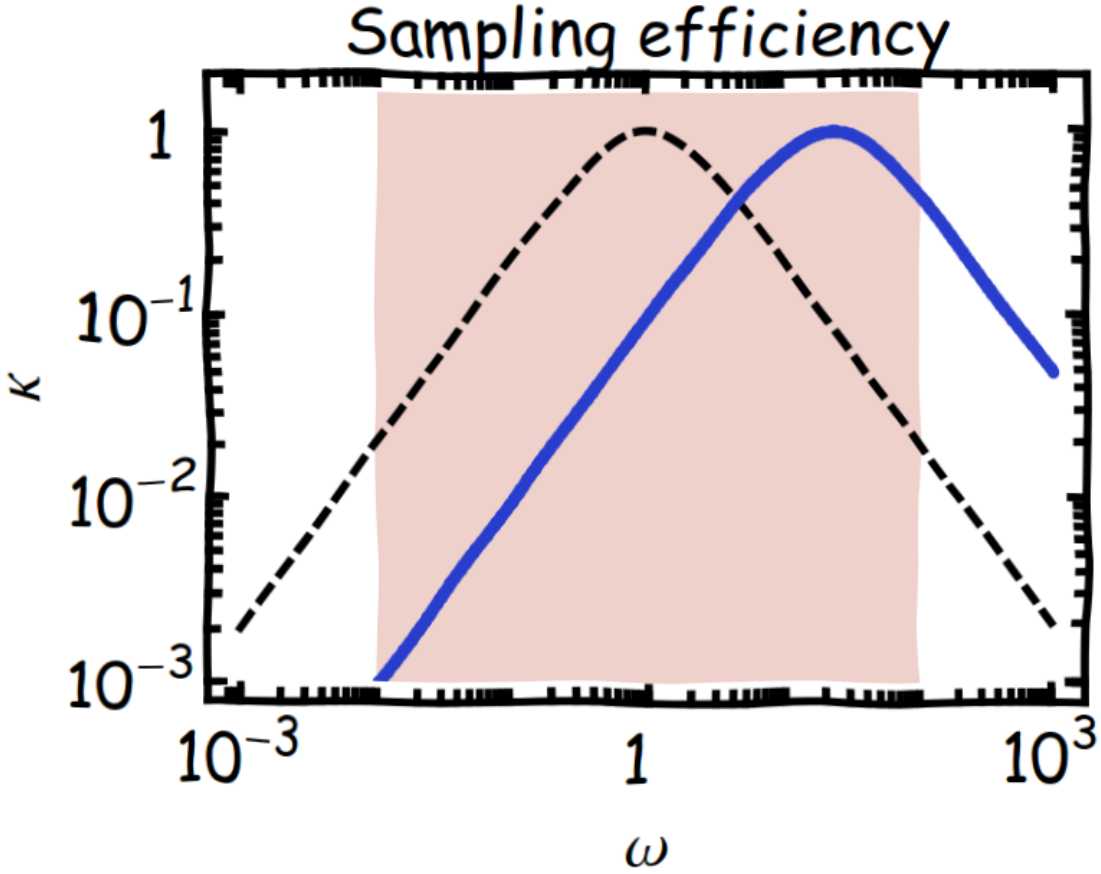
$$\begin{aligned} \dot{q}(t) &= p(t)/m \\ \begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} &= \begin{pmatrix} -V'(q) \\ \mathbf{0} \end{pmatrix} - \begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\xi \end{aligned}$$

Ceriotti, Bussi, Parrinello PRL 102 (2009)
Ceriotti, Bussi, Parrinello JCTC 6(2010)
Morrone, Markland, Ceriotti, Berne JCP 134 (2011)

Optimal sampling by colored noise

- Revisit the problem of canonical sampling of a system with many normal modes
- Start off with a random (bad!) choice of colored-noise parameters
- Iteratively optimize. . .



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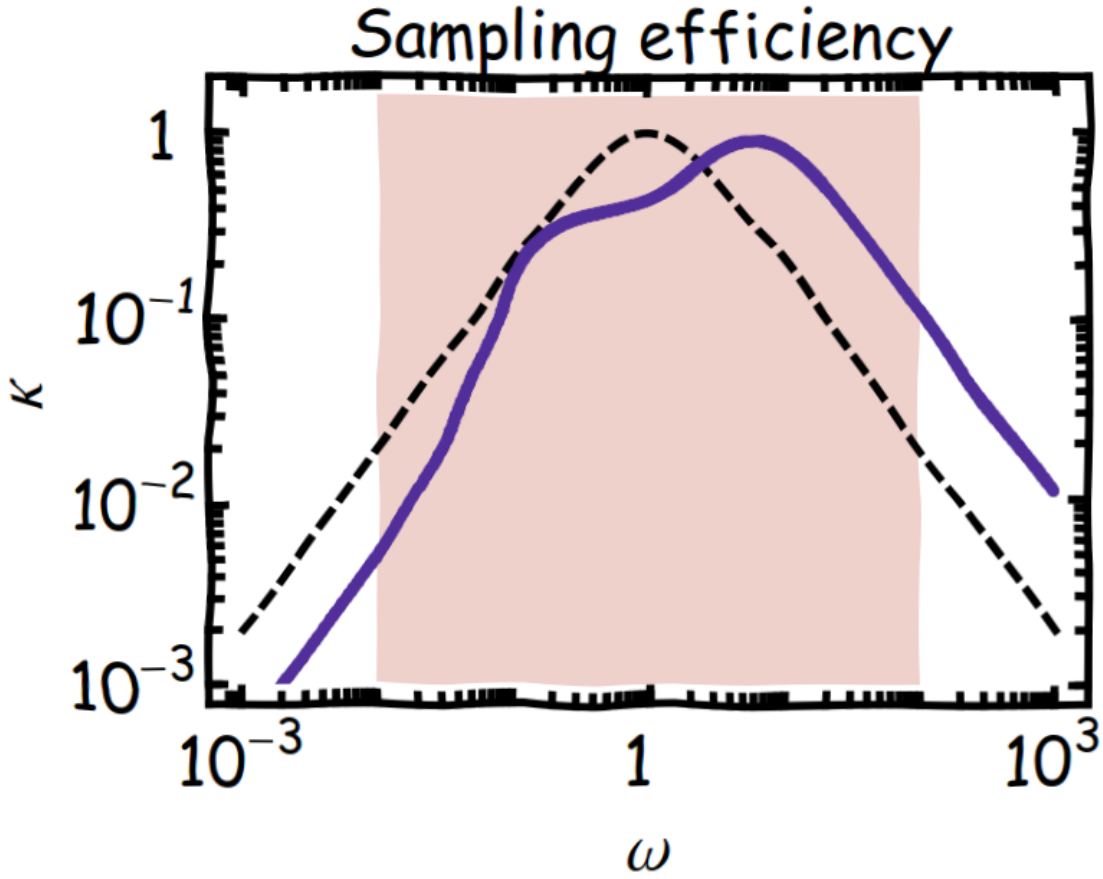

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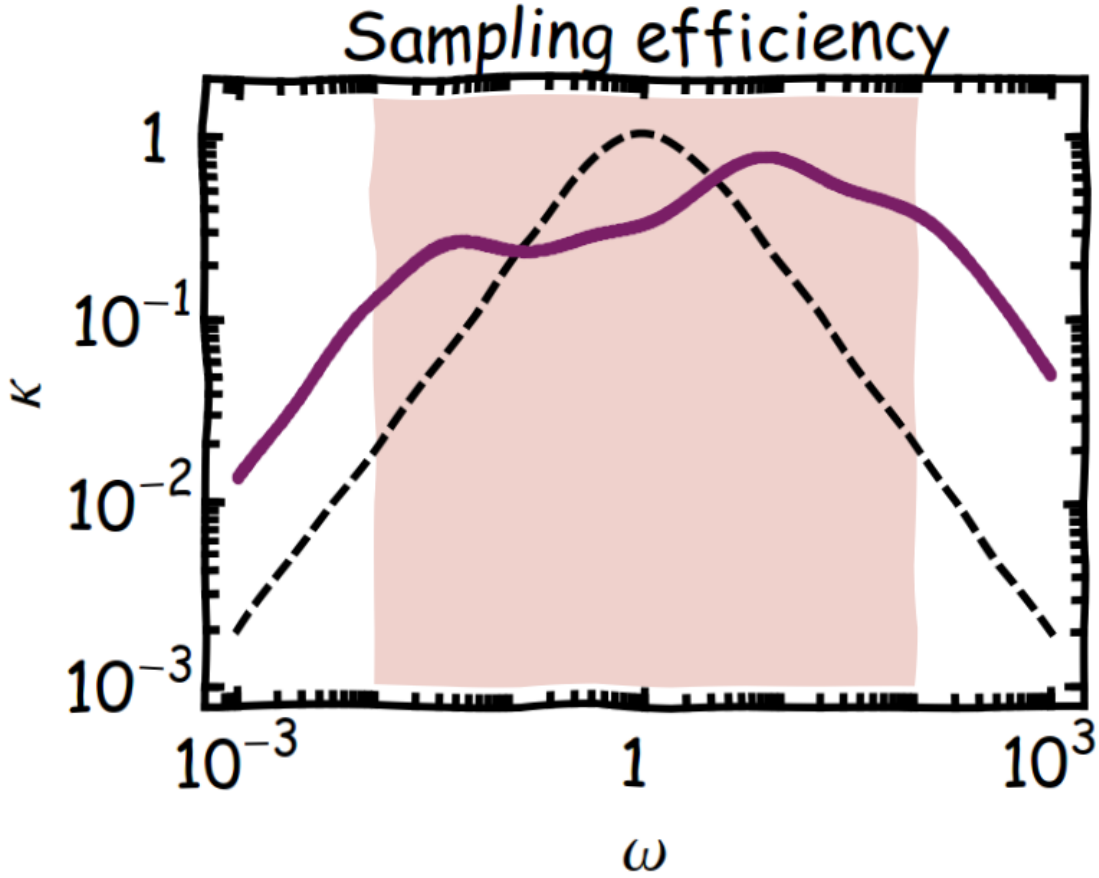

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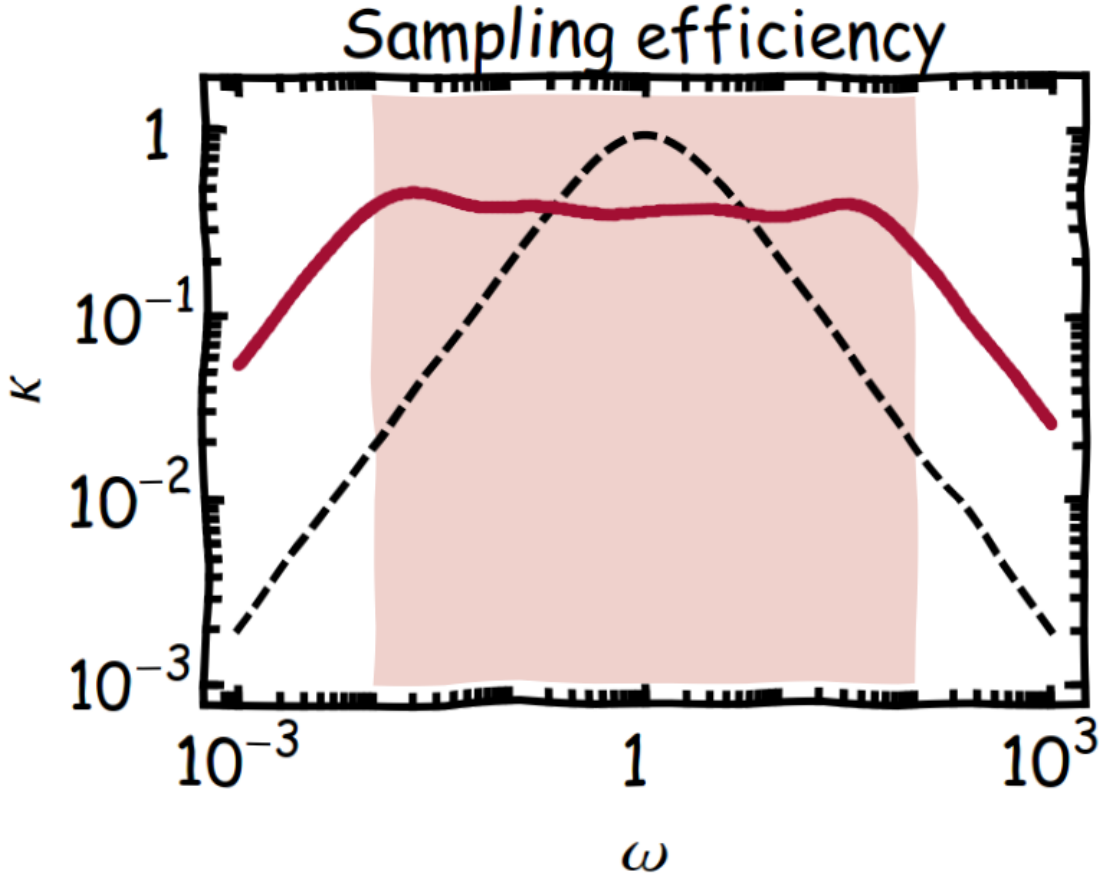

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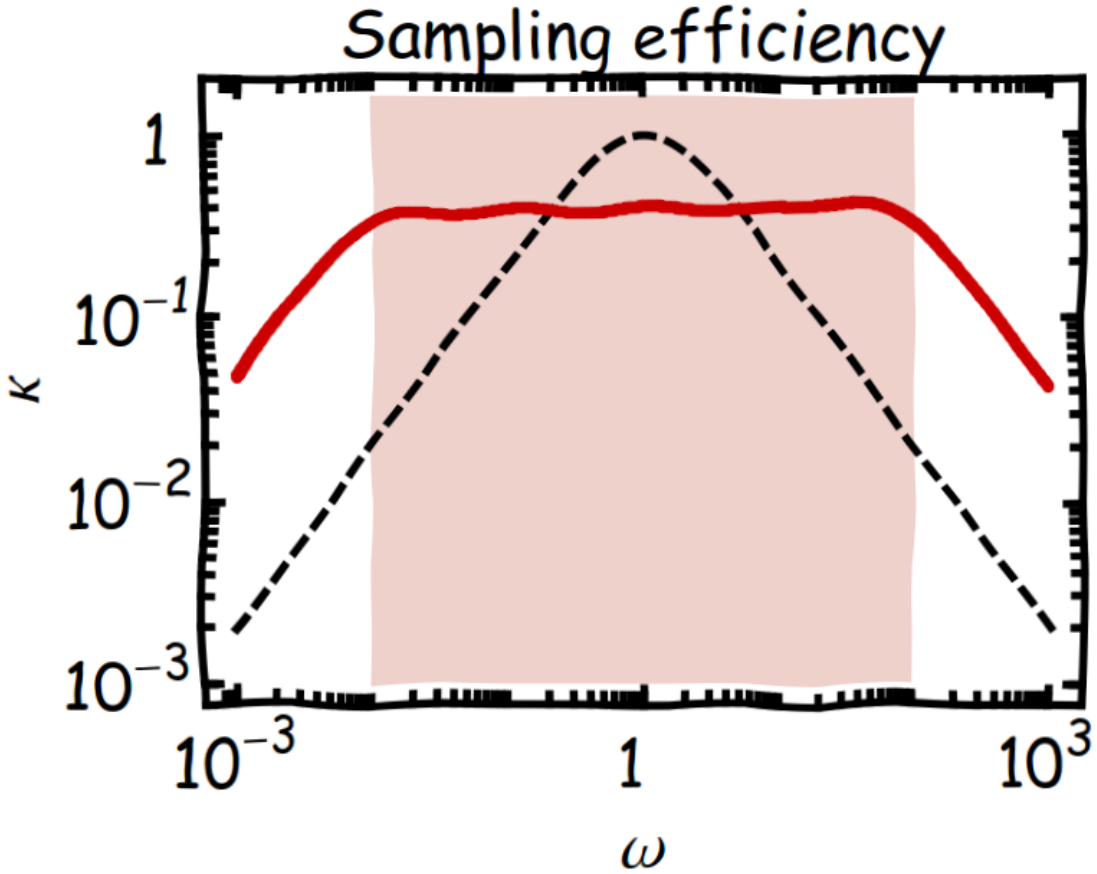

Beyond canonical GLE

- It is possible to generalize further the GLE framework, by breaking the fluctuation-dissipation theorem: $K(t) \neq \langle \zeta(t)\zeta(0) \rangle$
- Simple non-eq. example: two thermostats at different temperature and different coupling curves
  - A steady state will be reached with frequency-dependent T

$T_1 \gg$

$T_2 \ll$

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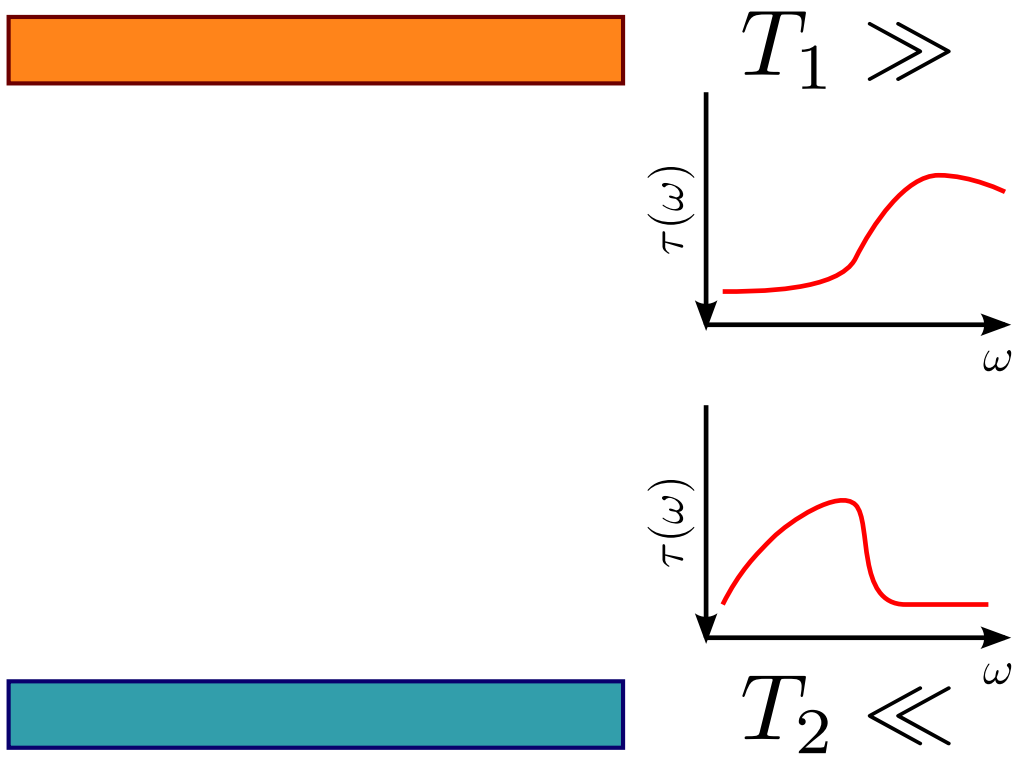

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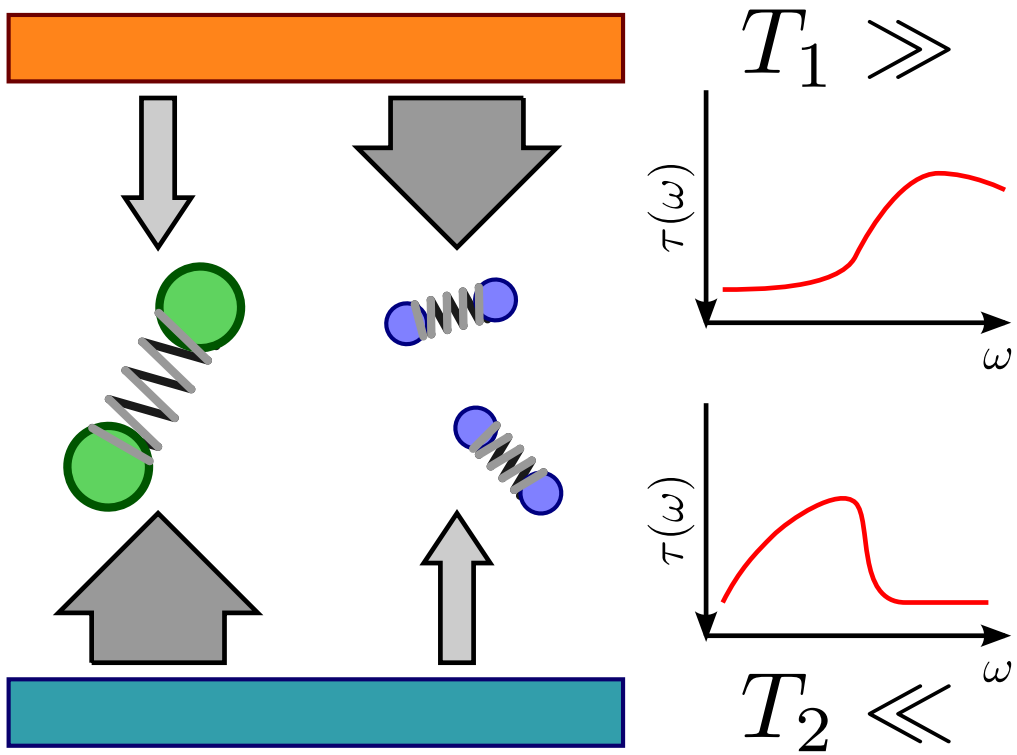

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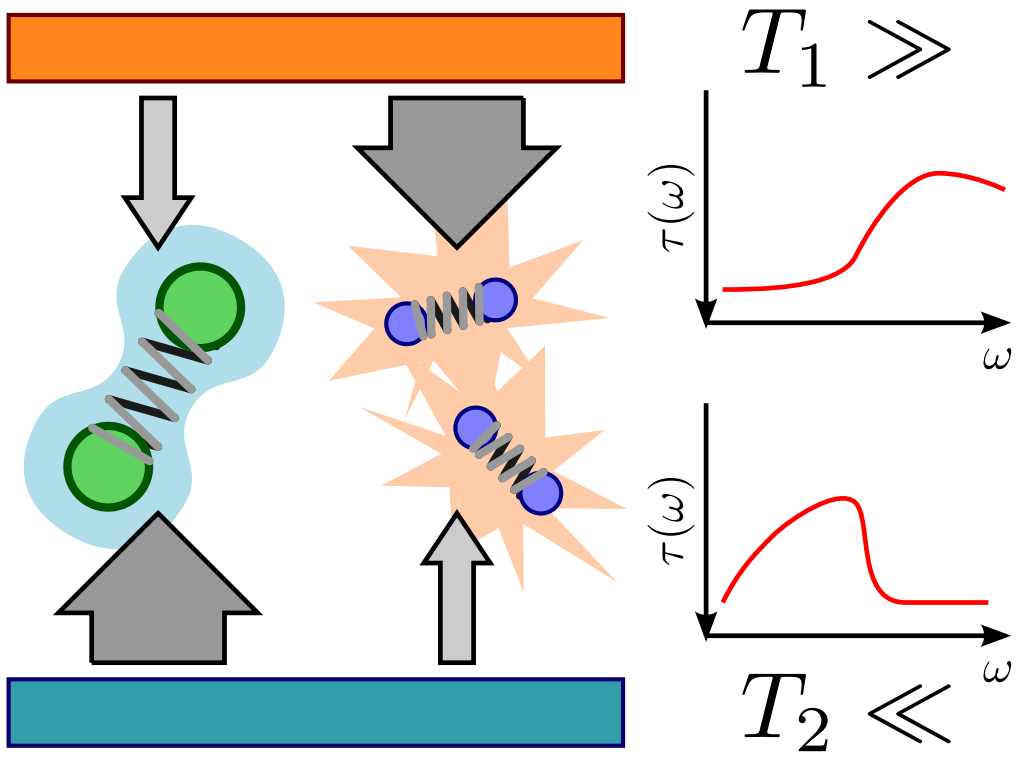
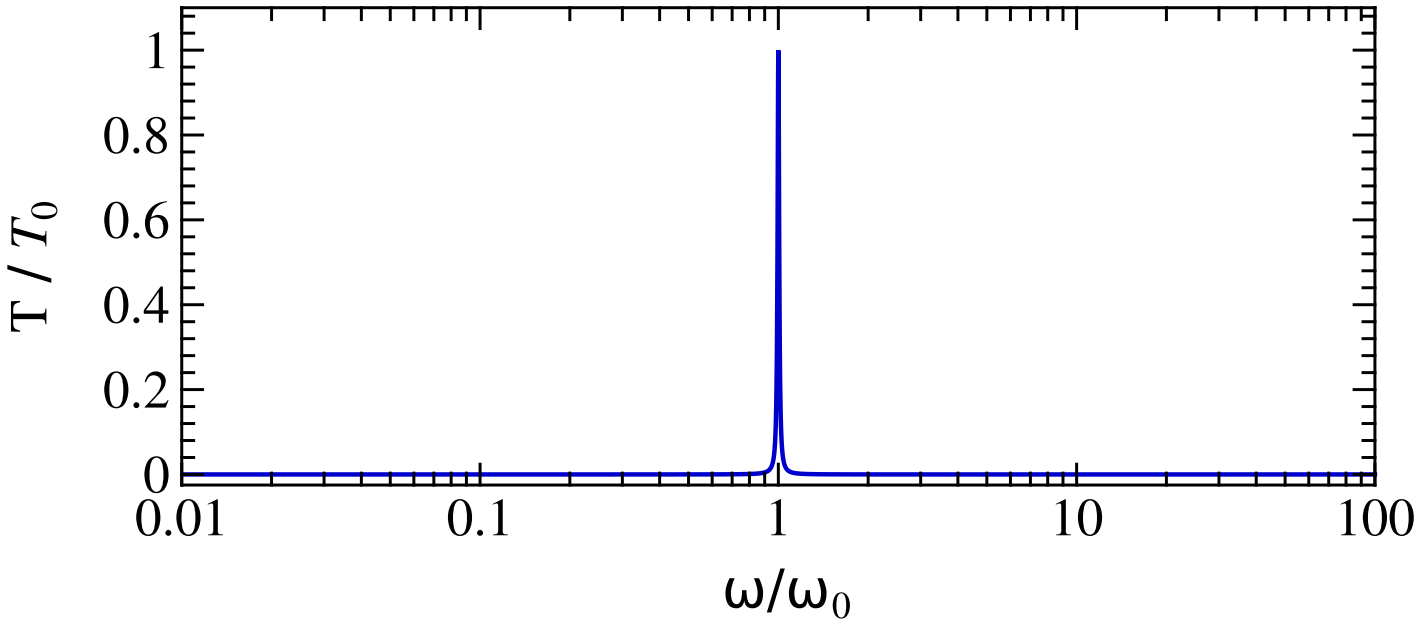


A δ-thermostat

- Thermalize the normal modes in a narrow frequency window, keep all the others frozen. No need to know normal modes in advance! Work in progress to extend this approach to model more physically excitations over a constant-T background



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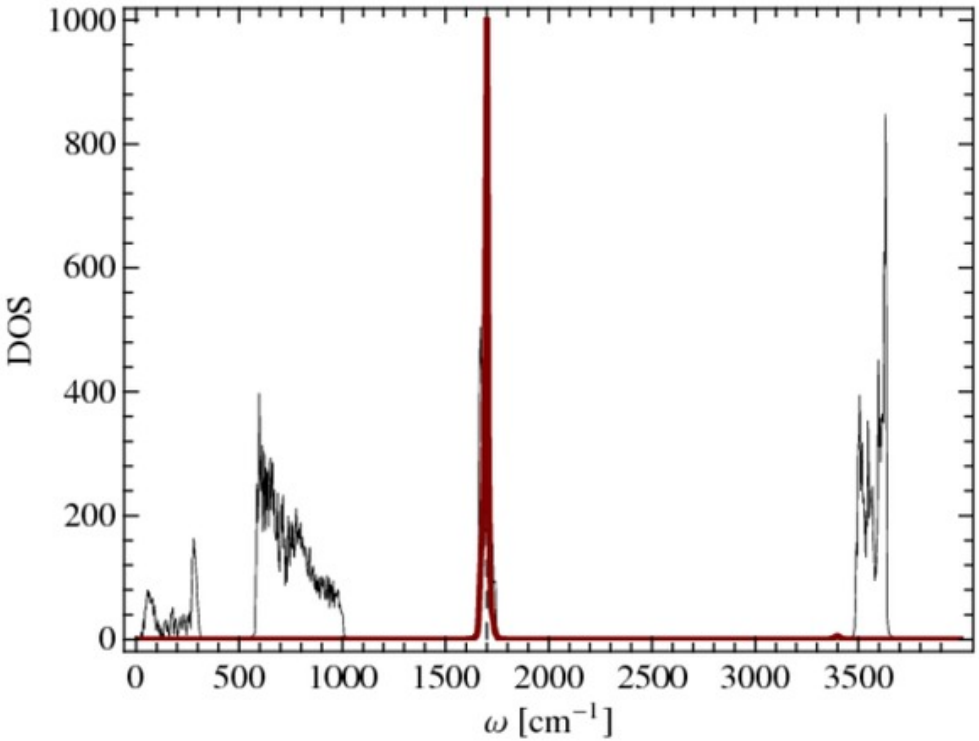
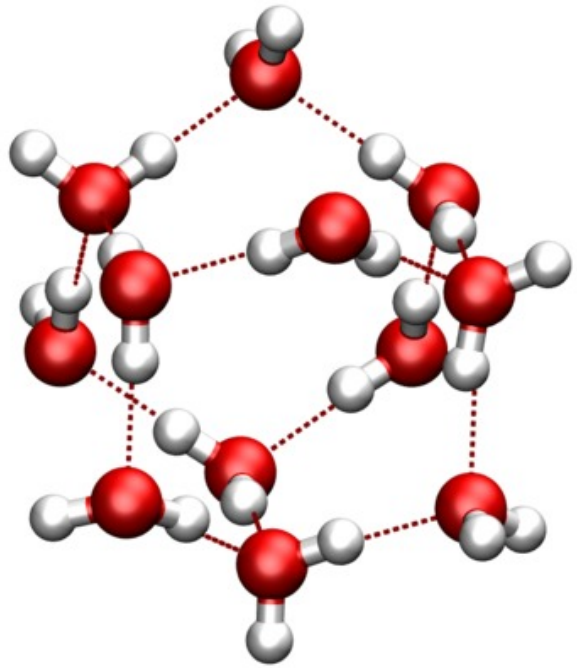


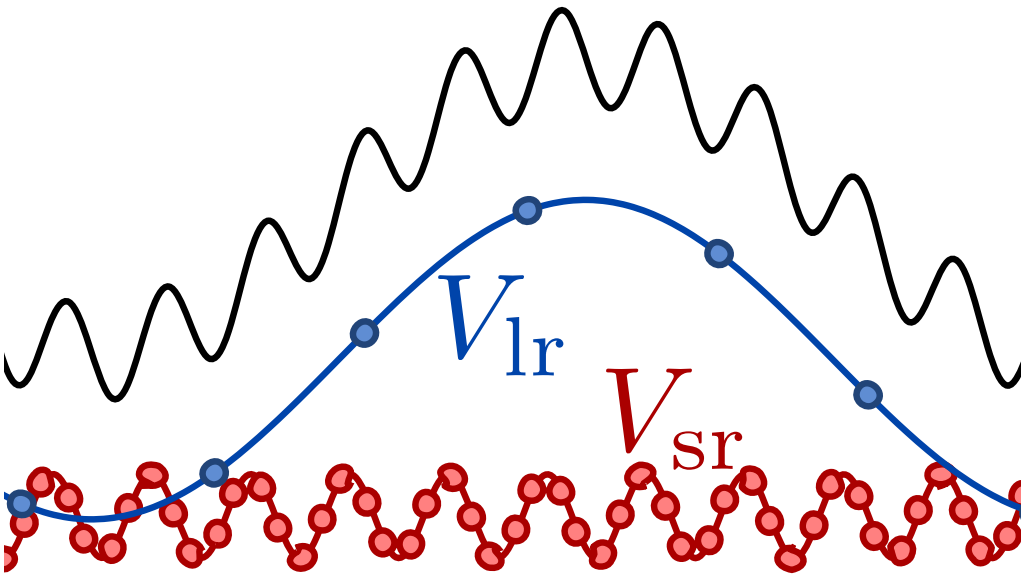


Selective NM excitation in hexagonal ice. Comparison of the NVE density of states and that obtained by targeted δ-thermostats. Atomic displacements have been magnified for clarity.

Multiple time stepping

- Can we make force evaluation cheaper?
- Idea: multiple time stepping: if we can break the potential into a cheap short-range part and an expensive long-range part $V = V_{\text{sr}} + V_{\text{lr}}$ we can use different time steps for the two components
- Simmetric splitting preserves important symmetries and is most stable

$$e^{i\mathcal{L}\Delta t} \approx e^{i\mathcal{L}_{\text{lr}}\Delta t/2}\left[e^{i\mathcal{L}_{\text{sr}}\Delta t/2M}e^{i\mathcal{L}_{q}\Delta t/M}e^{i\mathcal{L}_{\text{sr}}\Delta t/2M}\right]^{M}e^{i\mathcal{L}_{\text{lr}}\Delta t/2}$$



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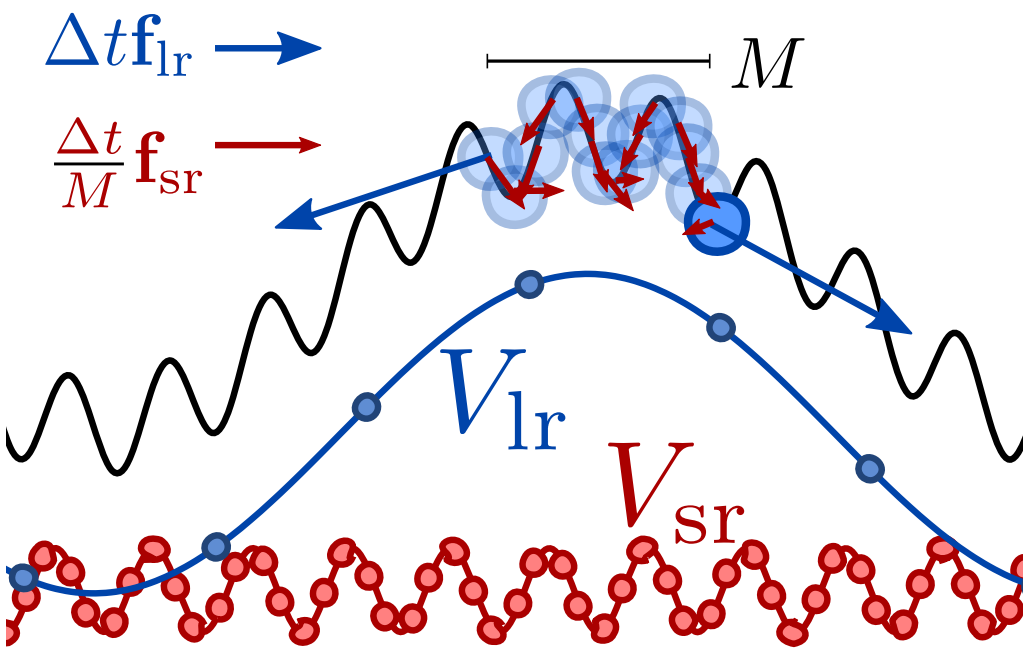

Tuckerman, Berne, Martyna, JCP (1992)

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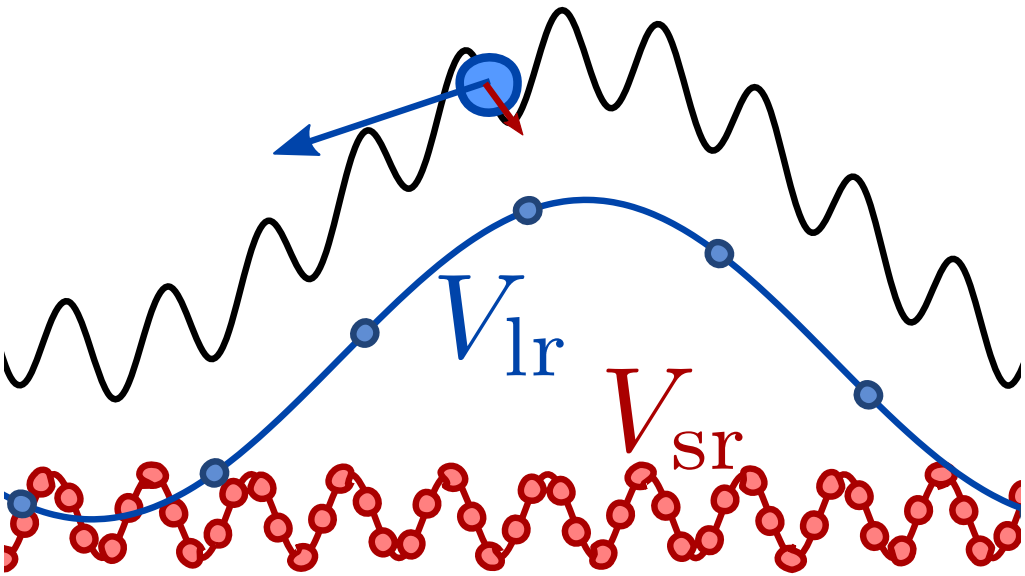

$$p \leftarrow p + f_{\text{lr}}\frac{\Delta t}{2}$$

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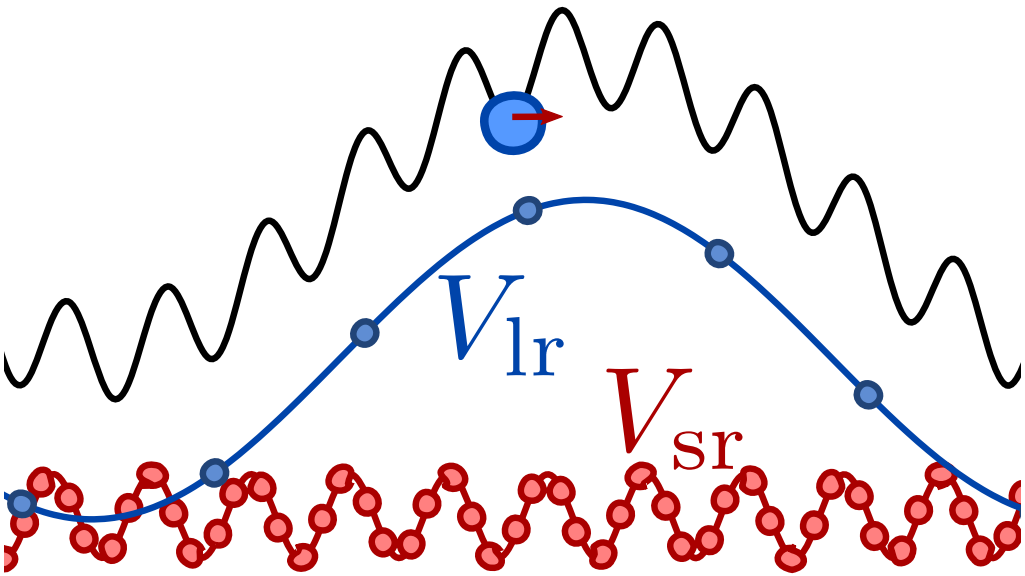

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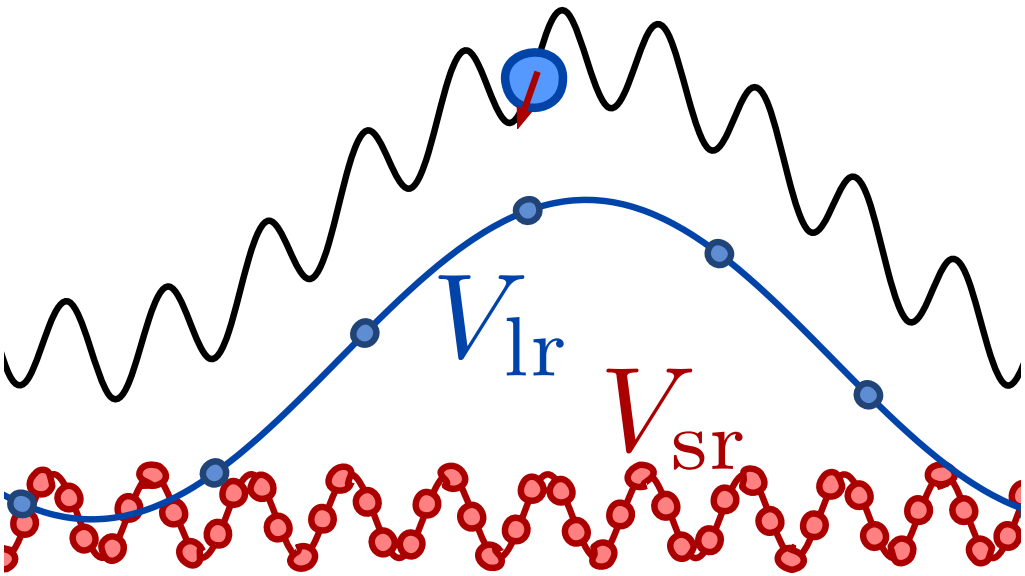

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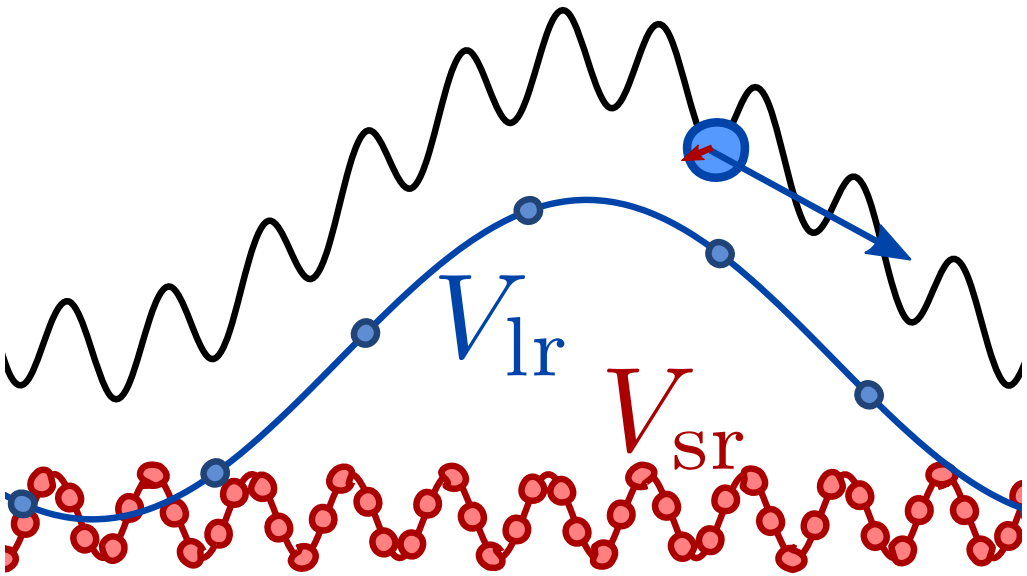

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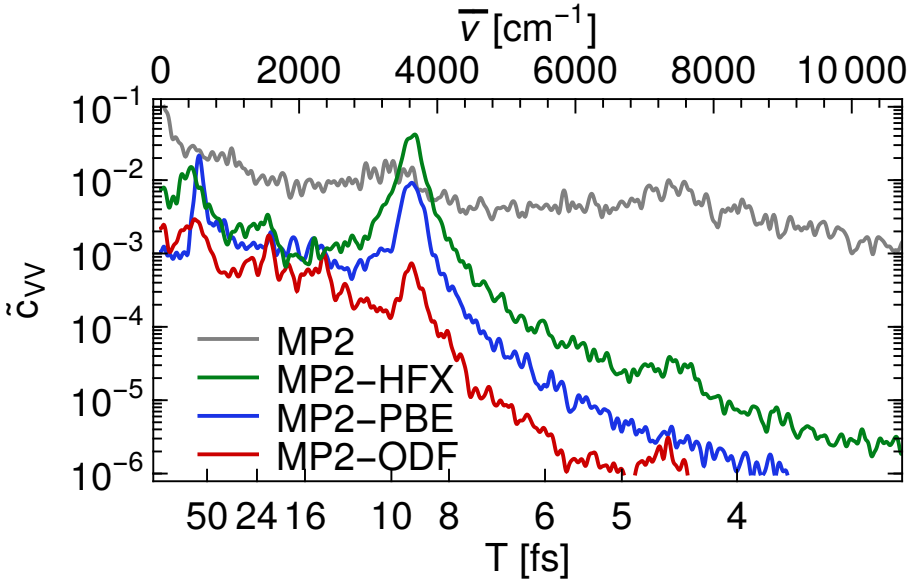
- How to deal with a first-principles setting? "Simple" if you can compute a cheap and an expensive version of V whose difference is "long-range":

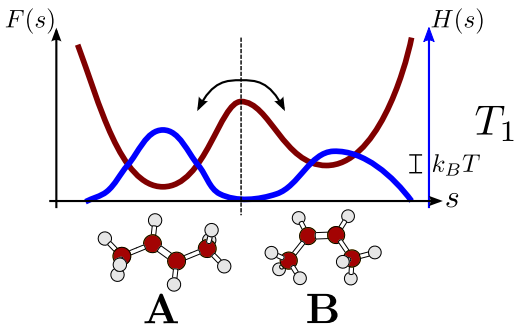
$$V = V_{\text{cheap}\equiv\text{sr}} + \left(V_{\text{exp.}} - V_{\text{cheap}}\right)_{\equiv lr}$$



Iftimie, Schofield JCP 2011; Marsalek, Markland JCP 2016; Kapil, Vandevondele, Ceriotti JCP 2016

Sampling many T with replica exchange

- Higher temperature would allow for faster sampling of activated events, but reweighing to low T would be very inefficient
- Solution is to add multiple replicas at intermediate temperature . . .
  - . . . stochastic exchanges drive simulations up and down the ladder
  - Exchanges are based on Monte Carlo criteria
  - All replicas are always consistent with their T



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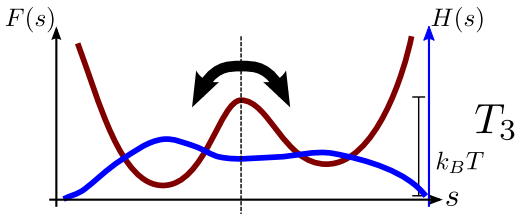

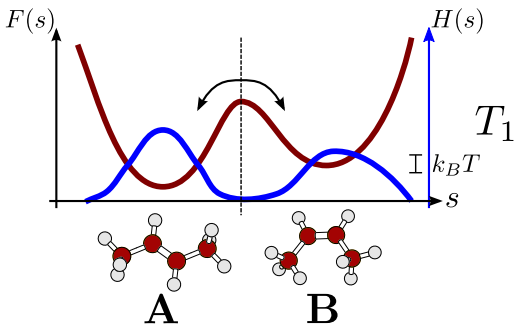

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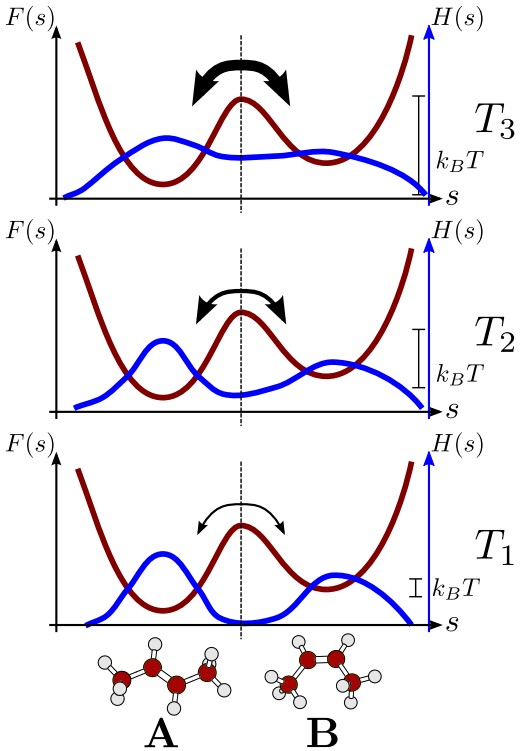

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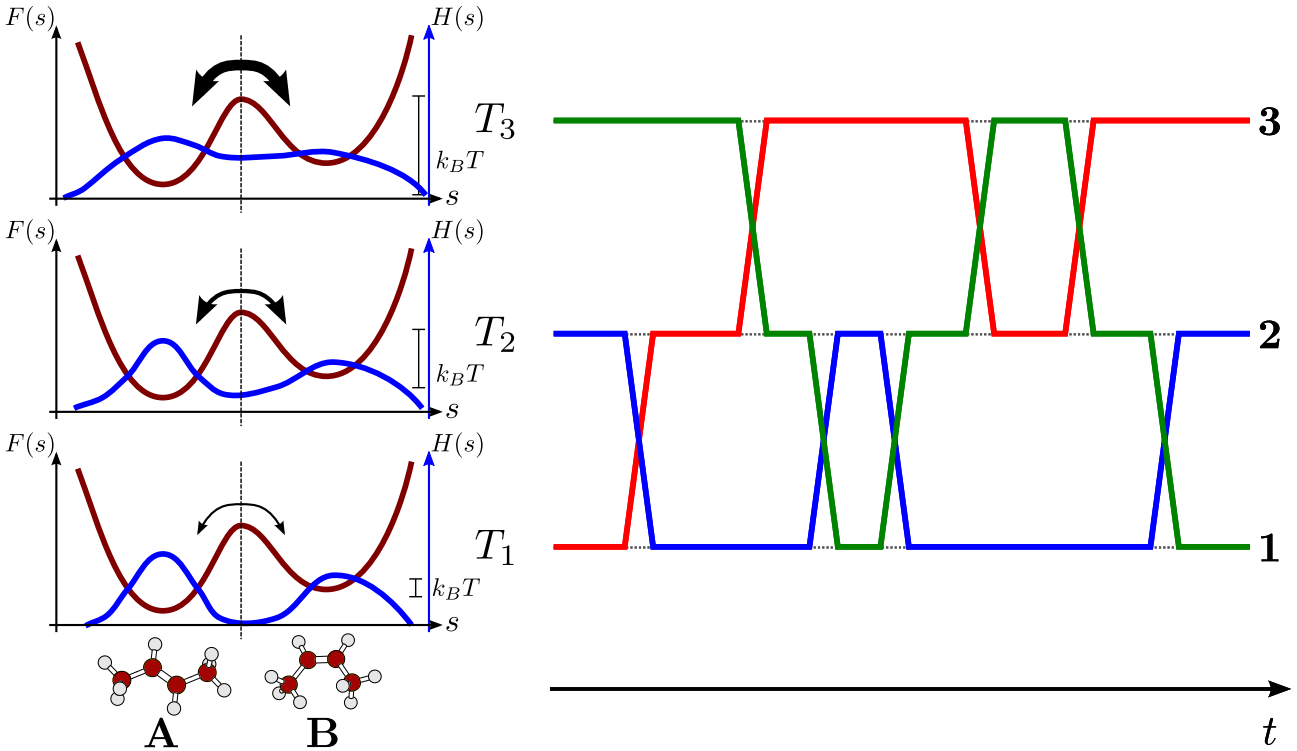

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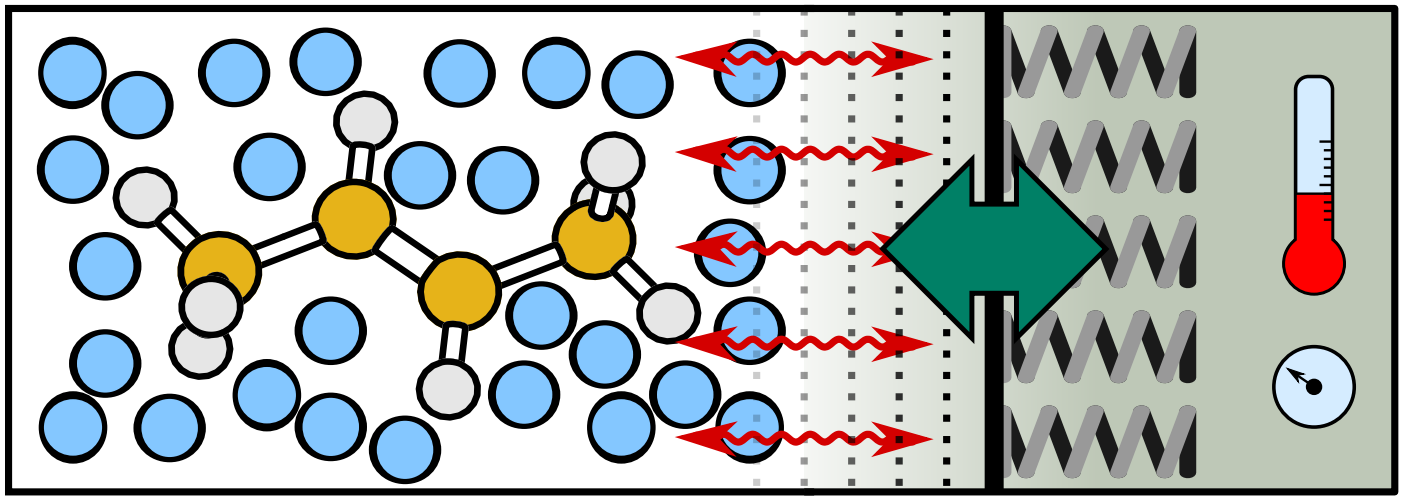
Sampling the isobaric ensemble

- How can one perform sampling consistent with constant-pressure conditions? General idea: modify the equations of motion to include the cell volume as a dynamical parameter, with a fictitious mass μ and a conjugate momentum α
- Requires evaluation of the internal pressure, that contains both a kinetic energy term, and a term coming from the virial of the potential - tricky in ab initio calculations!



$$P \propto e^{-\beta E} e^{-\beta p V}$$

HC Andersen, JCP 1980; Parrinello & Rahman, J.Appl.Phys. 1981, Bussi, Zykova & Parrinello, JCP 2009

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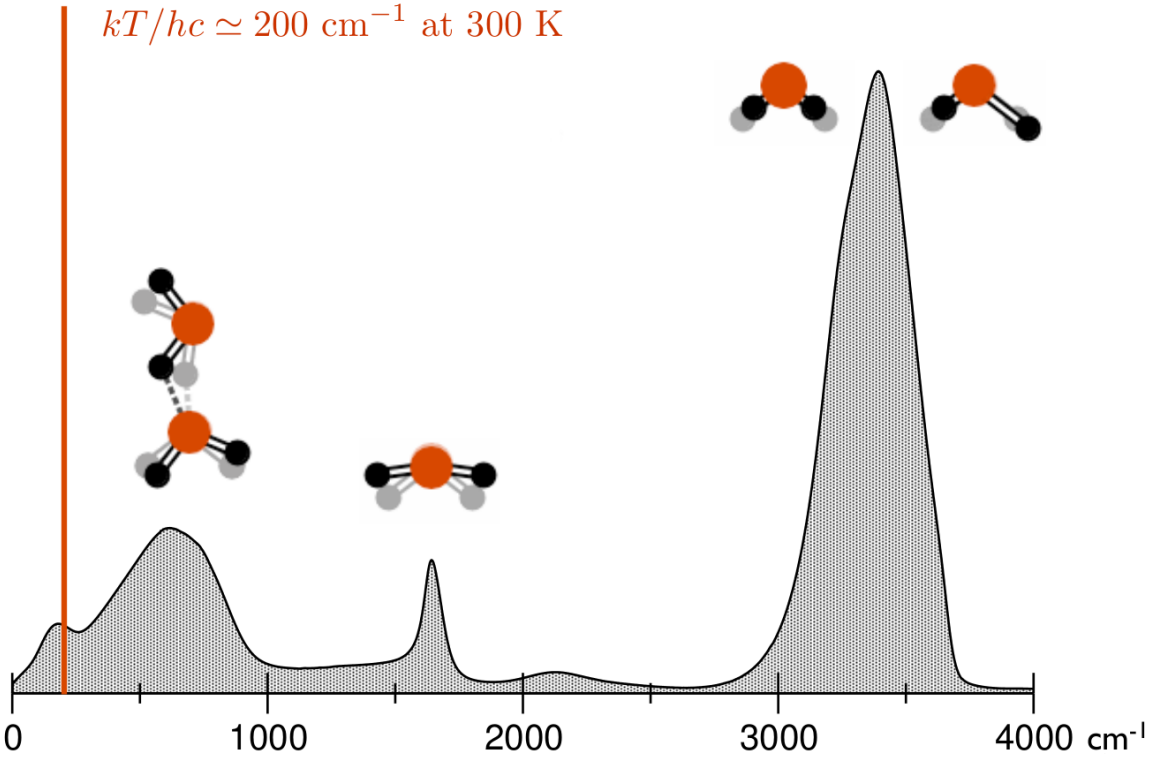
Nuclear quantum effects

- Light nuclei do not obey Newtonian mechanics
- Quantum nature of a vibrational mode of frequency ω becomes important when $\hbar\omega / k_B T > 1$.
  - Light nuclei have strong quantum behavior even at room temperature: $k_B T / \hbar \approx 200$ cm^{-1}!
  - Example: properties of isotopically-pure water
  - Isotope effects on rates for reactions involving hydrogen: massive effect (e.g. a factor of 60 for soybean lypoxigenase).



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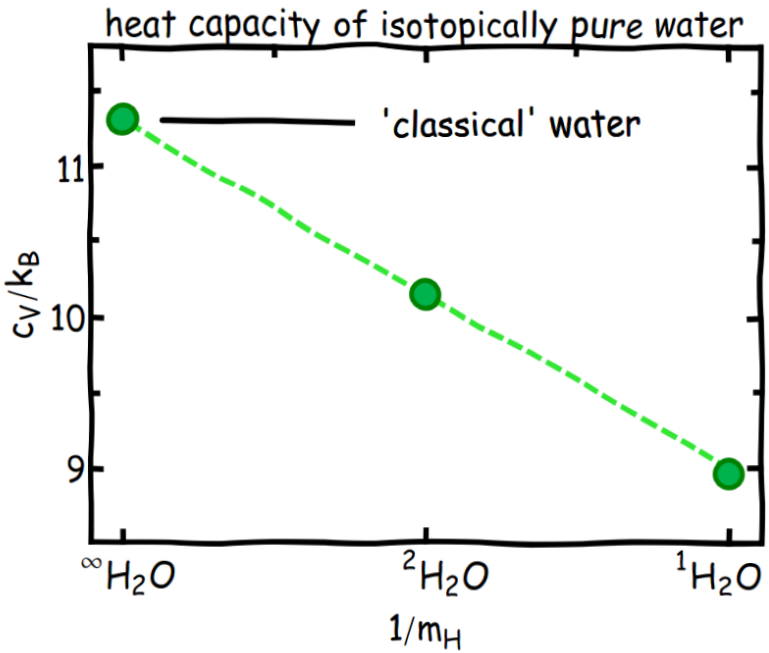

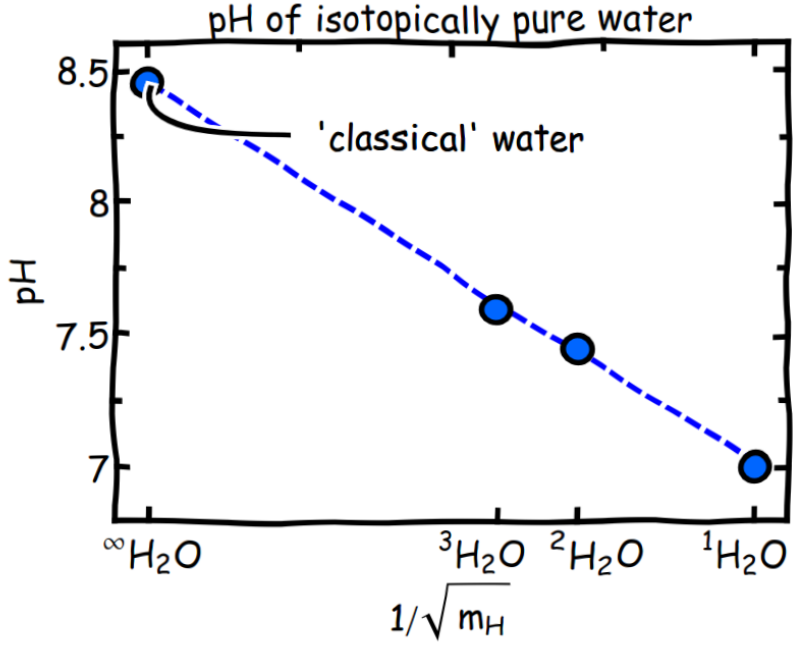

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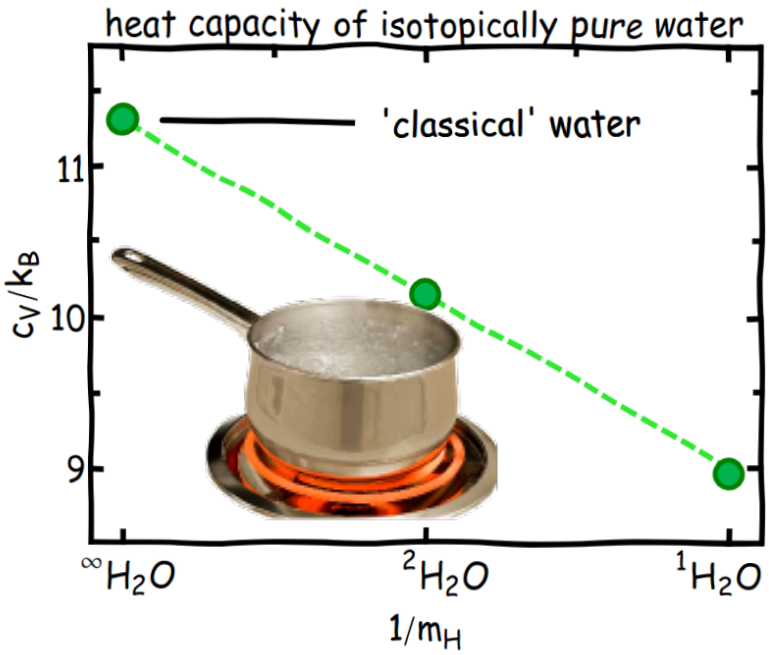

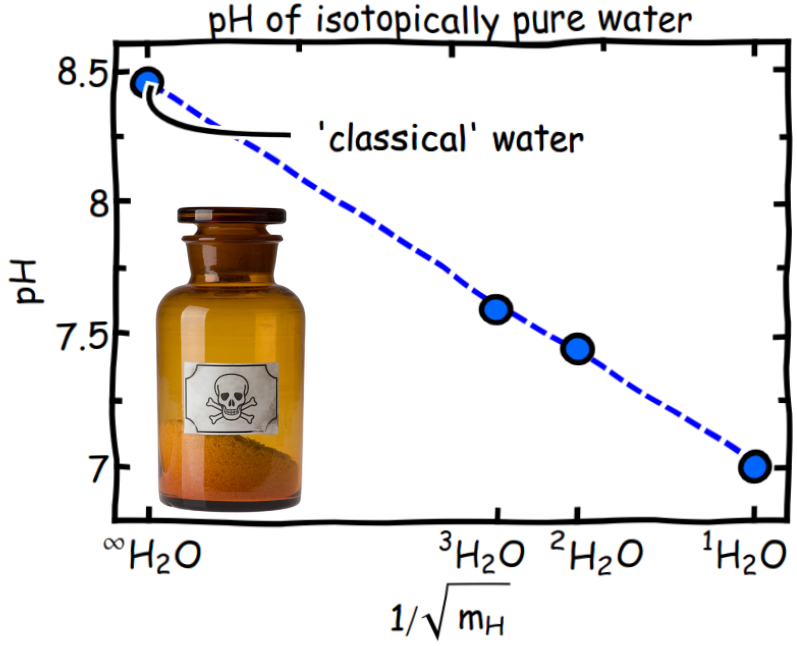

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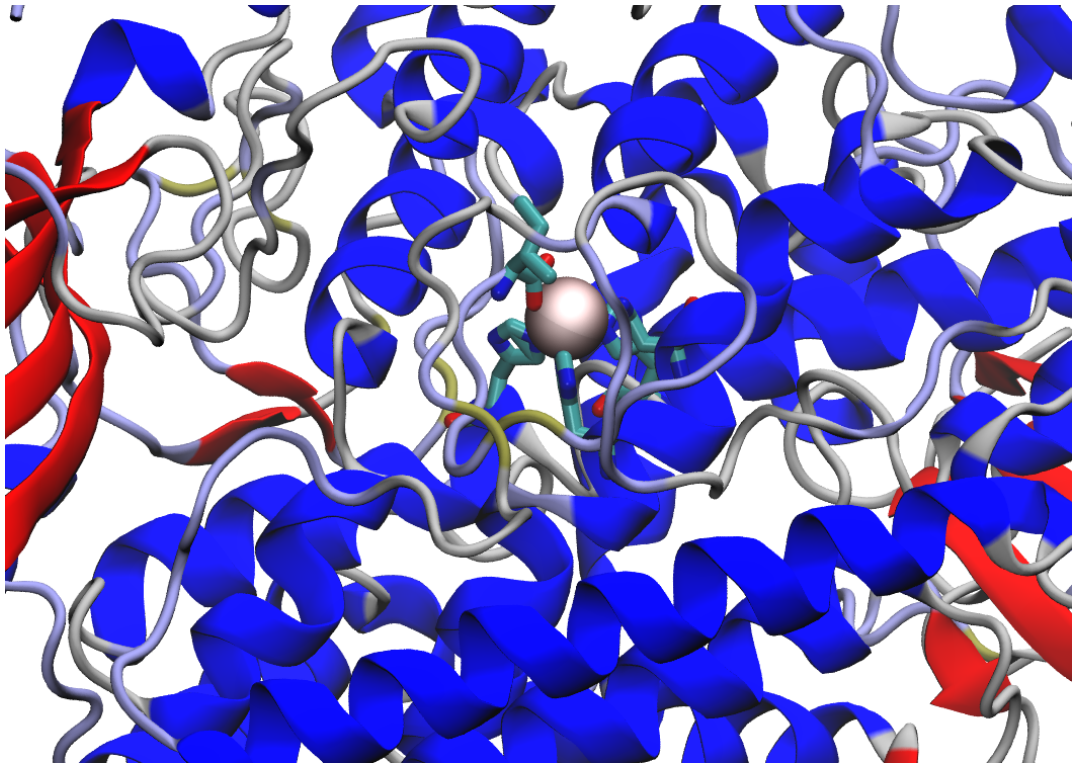

How to include NQEs in MD

- Solving the Schrödinger equation for the nuclei is impractical
- A connection exists between the statistical properties of a quantum system and those of a classical **ring polymer**

$$H_P = \sum_{i=1}^{P} \left[V(\mathbf{q}_i) + \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} m\omega_P^2 (\mathbf{q}_i - \mathbf{q}_{i-1})^2 \right]$$

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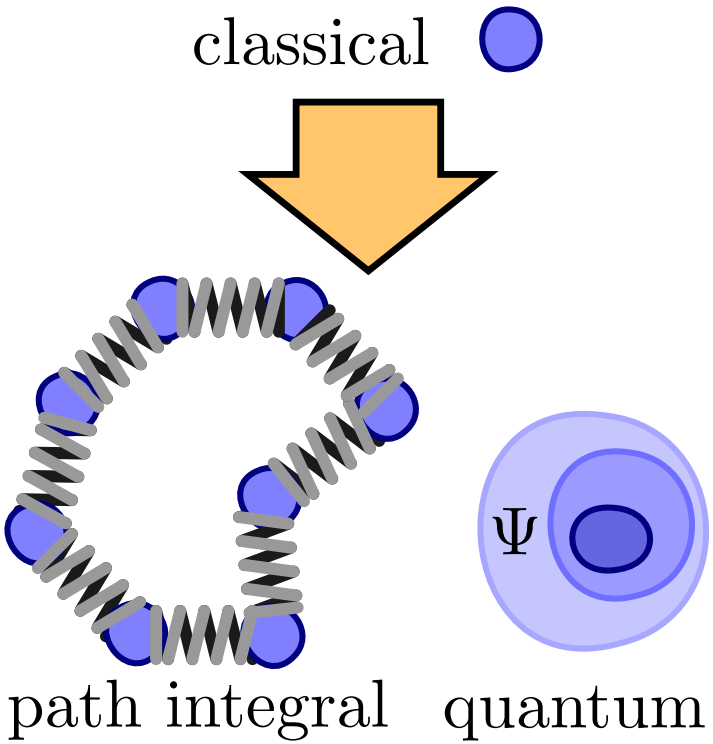

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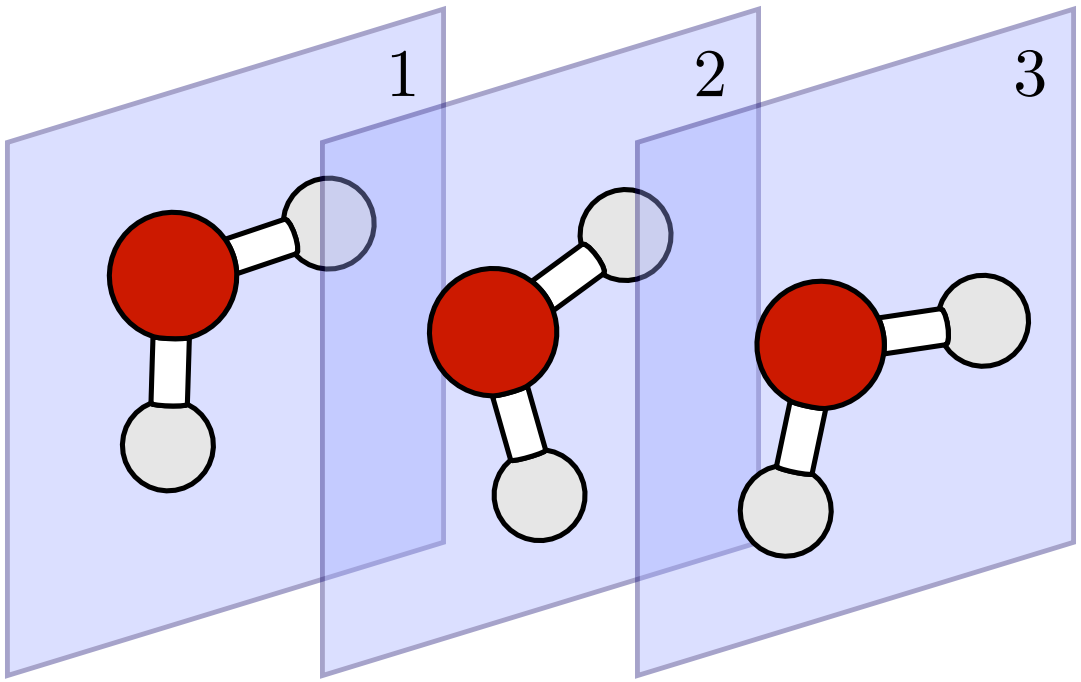

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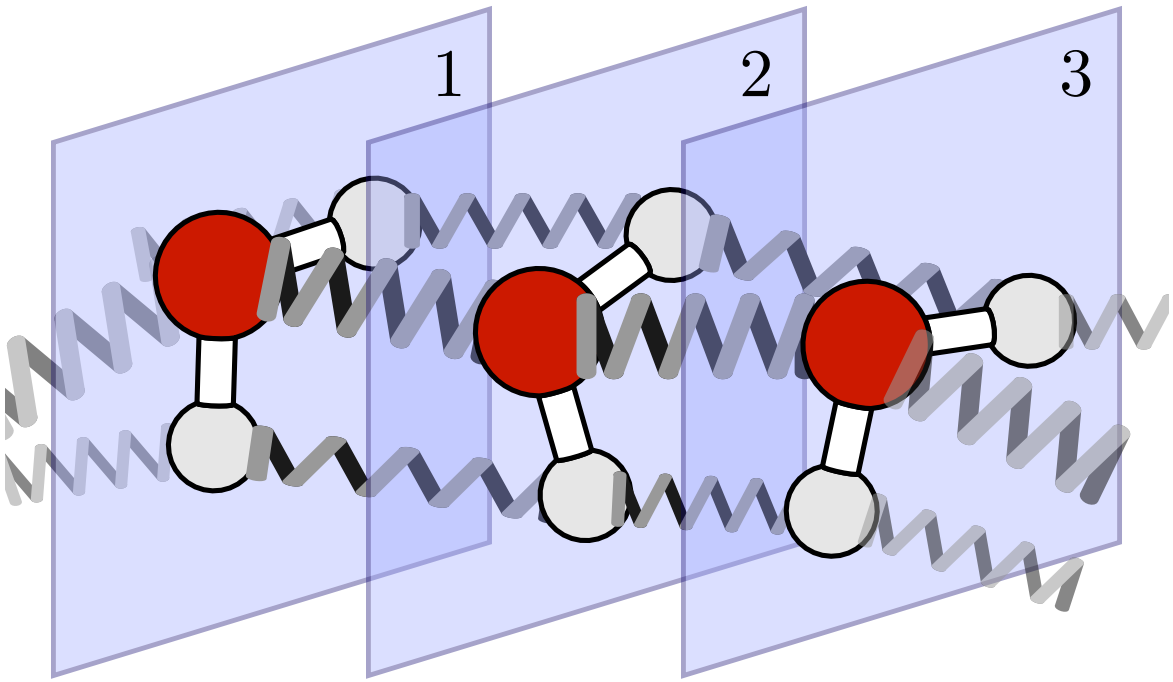

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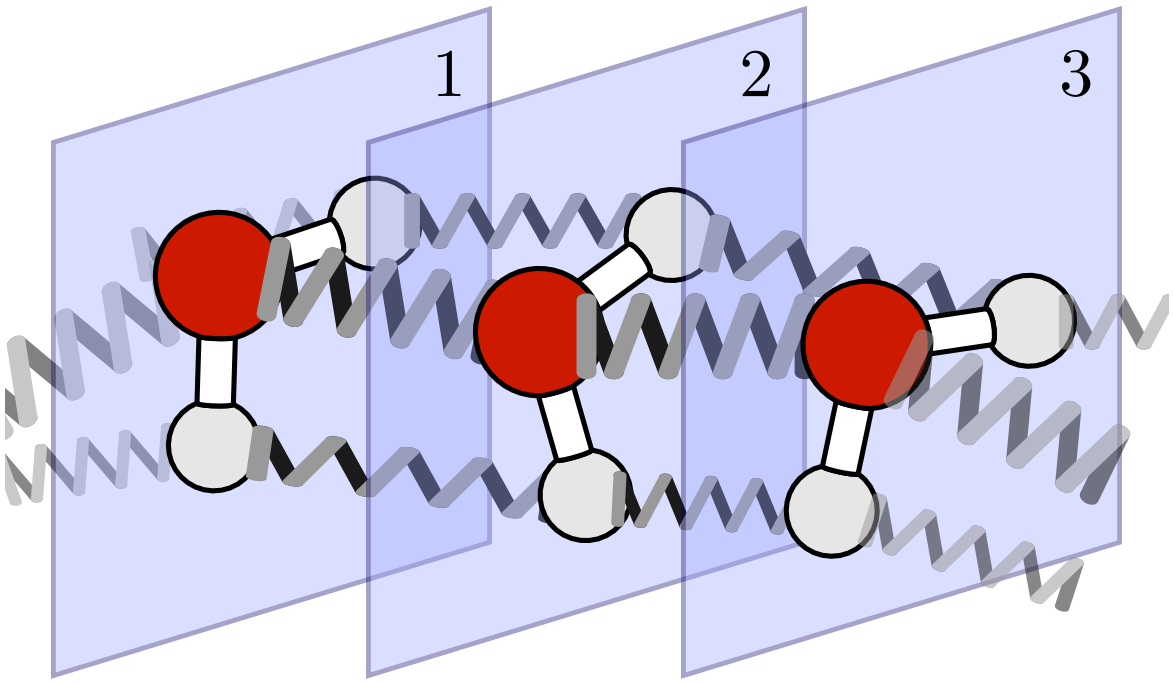
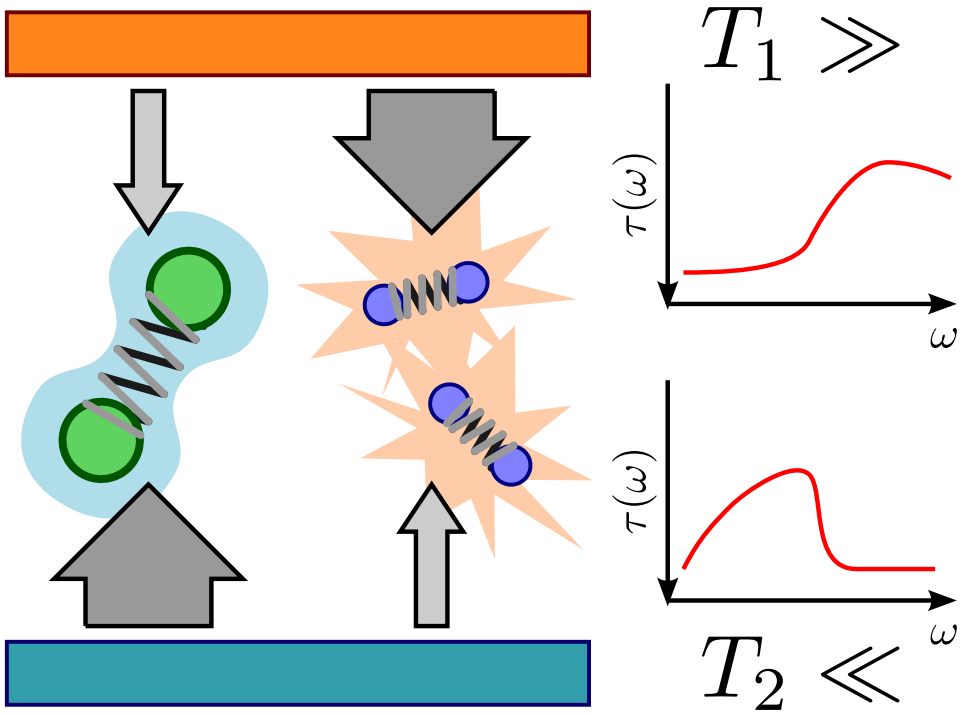


A "quantum" thermostat

- We can also make a "non-equilibrium" thermostat
  - **Frequency-dependent** thermalization $T^\star(\omega)$
- A quantum oscillator at temperature T behaves like a classical oscillator at temperature $T^\star(\omega) = (\hbar\omega/2k_B)\coth\hbar\omega/2k_BT$
  - This **quantum thermostat** is exact in the harmonic limit, and also works (approximately) in strongly anharmonic problems



Ceriotti, Bussi, Parrinello PRL 103 (2009)

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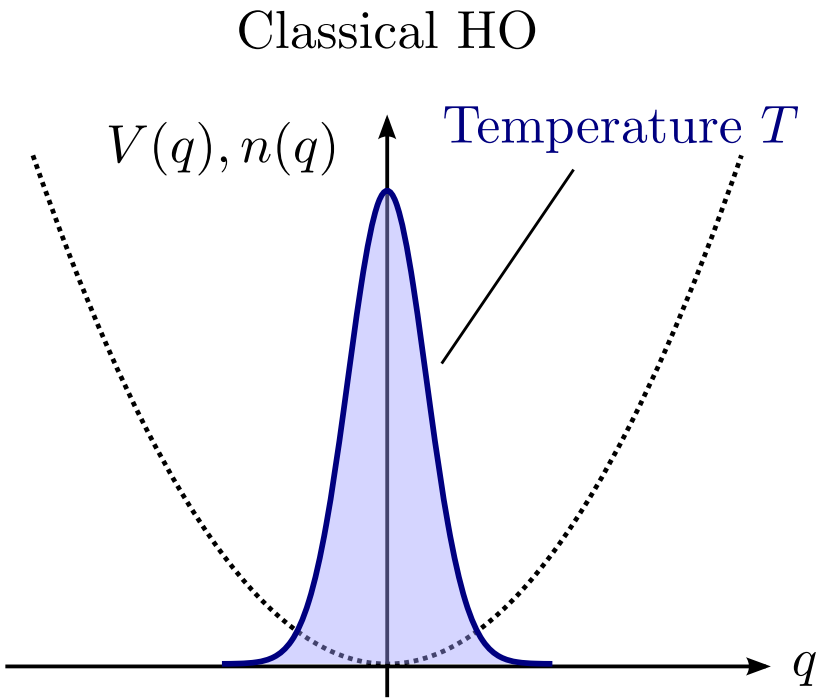

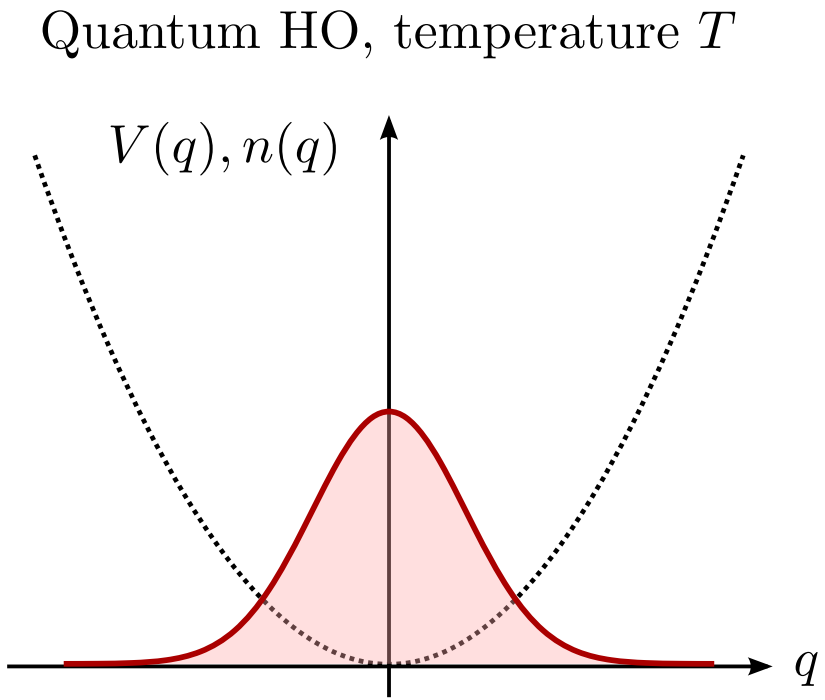

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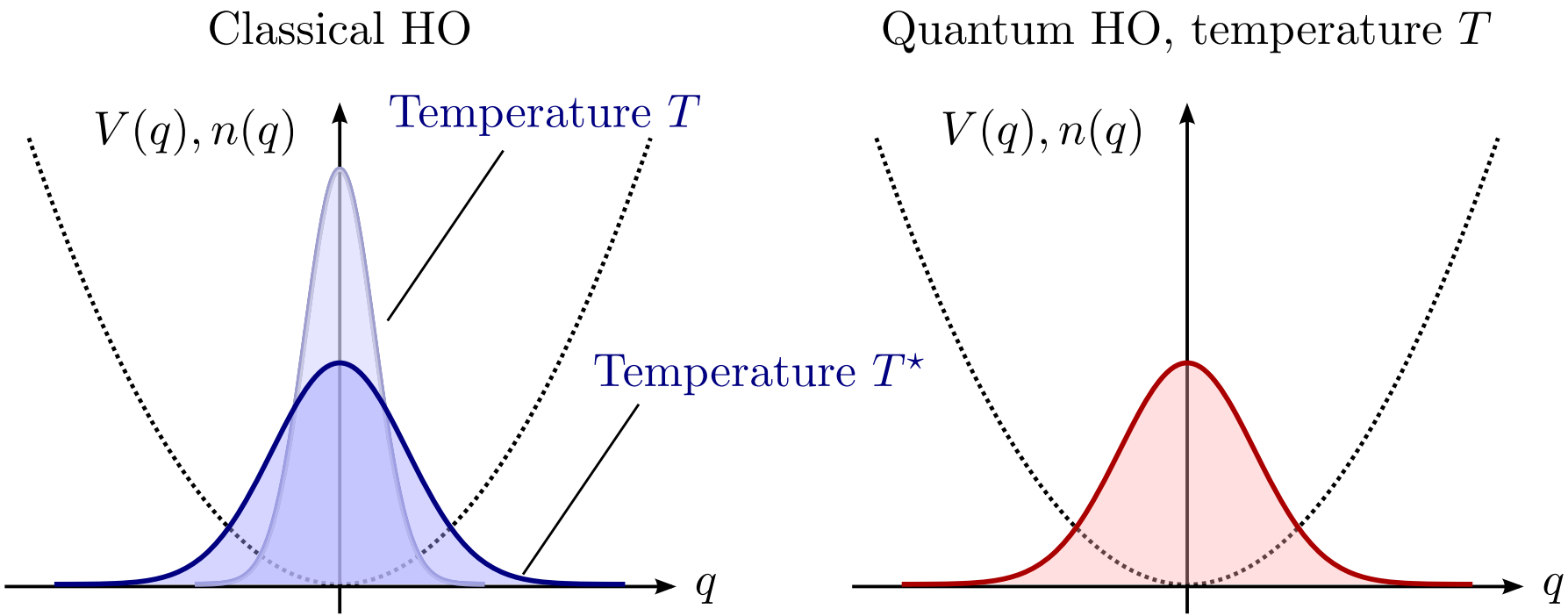
- A quantum oscillator at temperature T behaves like a classical oscillator at temperature $T^\star(\omega) = (\hbar\omega/2k_B)\coth\hbar\omega/2k_BT$
  - This **quantum thermostat** is exact in the harmonic limit, and also works (approximately) in strongly anharmonic problems



Ceriotti, Bussi, Parrinello PRL 103 (2009)

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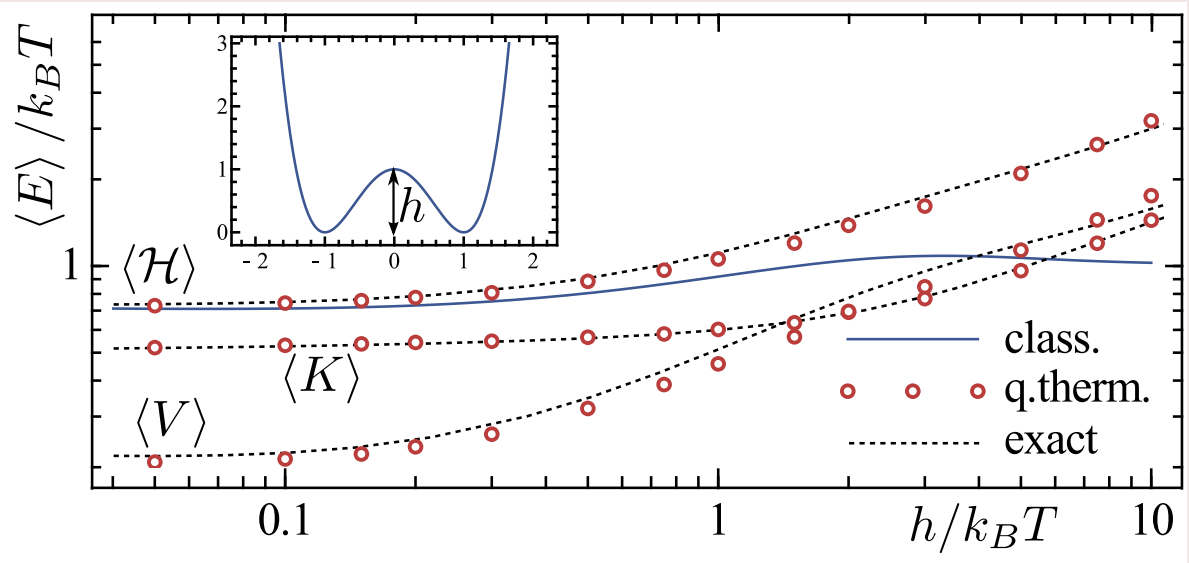
Quartic double well



Distance between minima: 1Å, comparison between exact and quantum thermostat results

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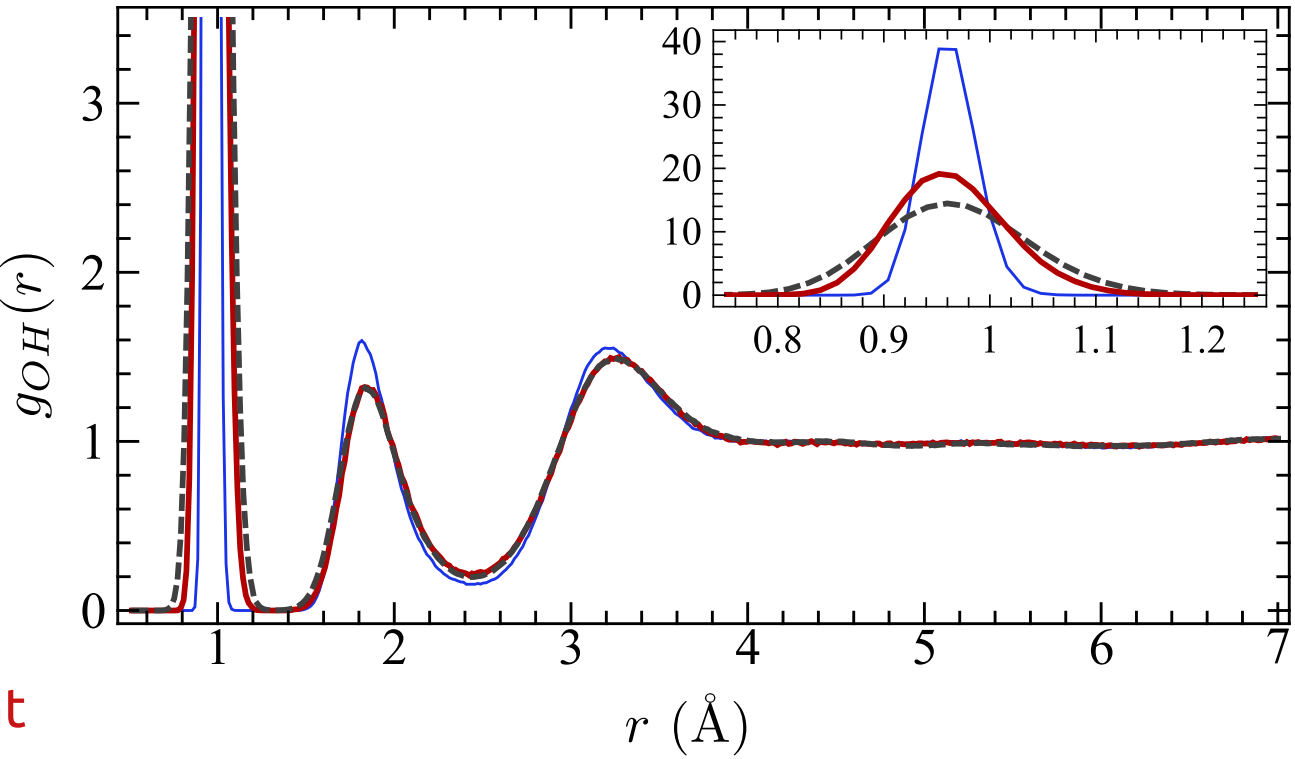
BLYP water at room temperature, CP2K, DZVP basis, GTH PP.

--- classical

- - - PIMD

--- quantum thermostat



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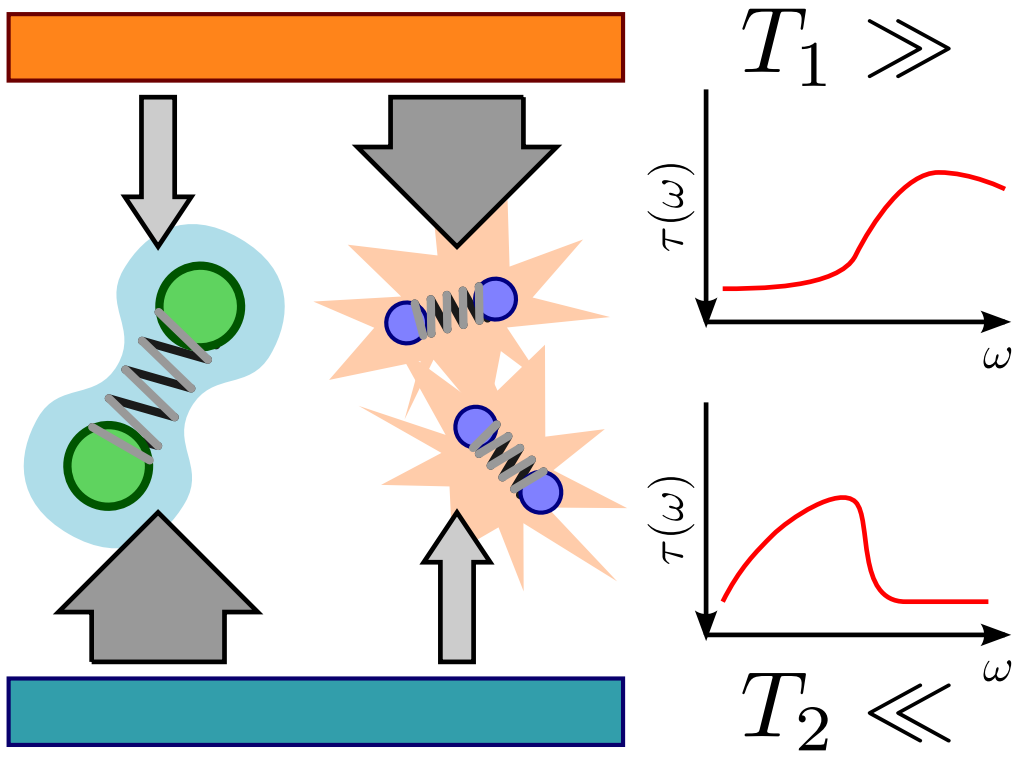
Anharmonicities and ZPE leakage

- A problem with multidimensional anharmonic systems
  - Zero-point energy leakage: common to many semiclassical approaches
  - Can be contrasted by tuning the strength of coupling!



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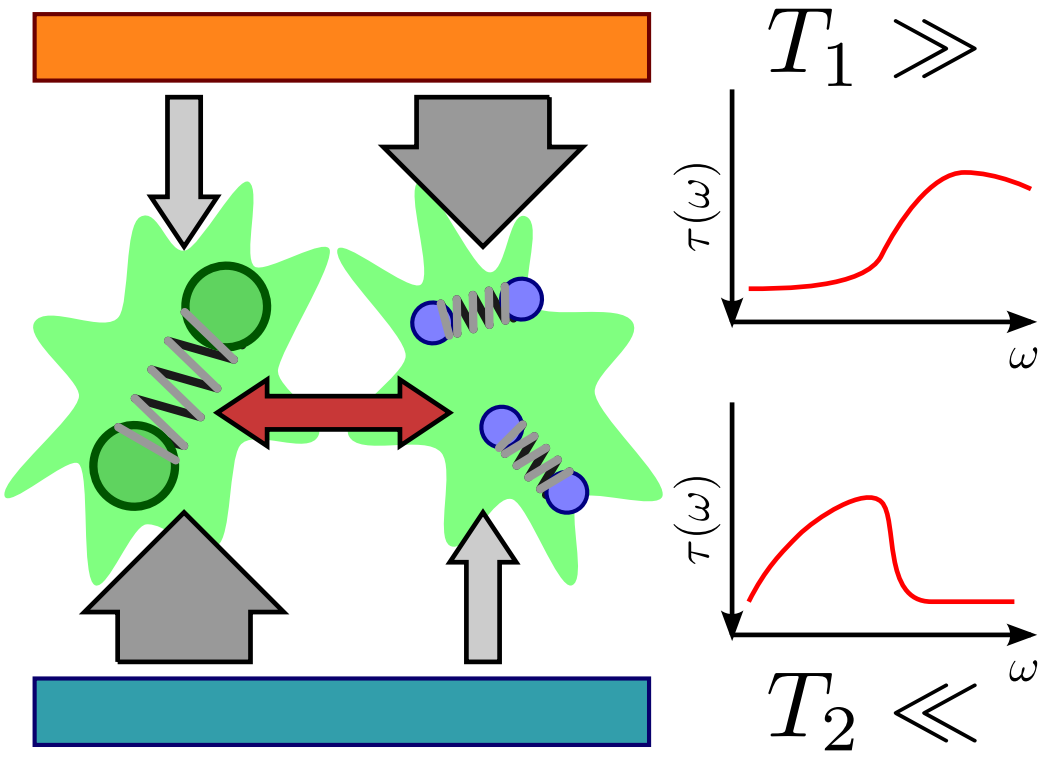

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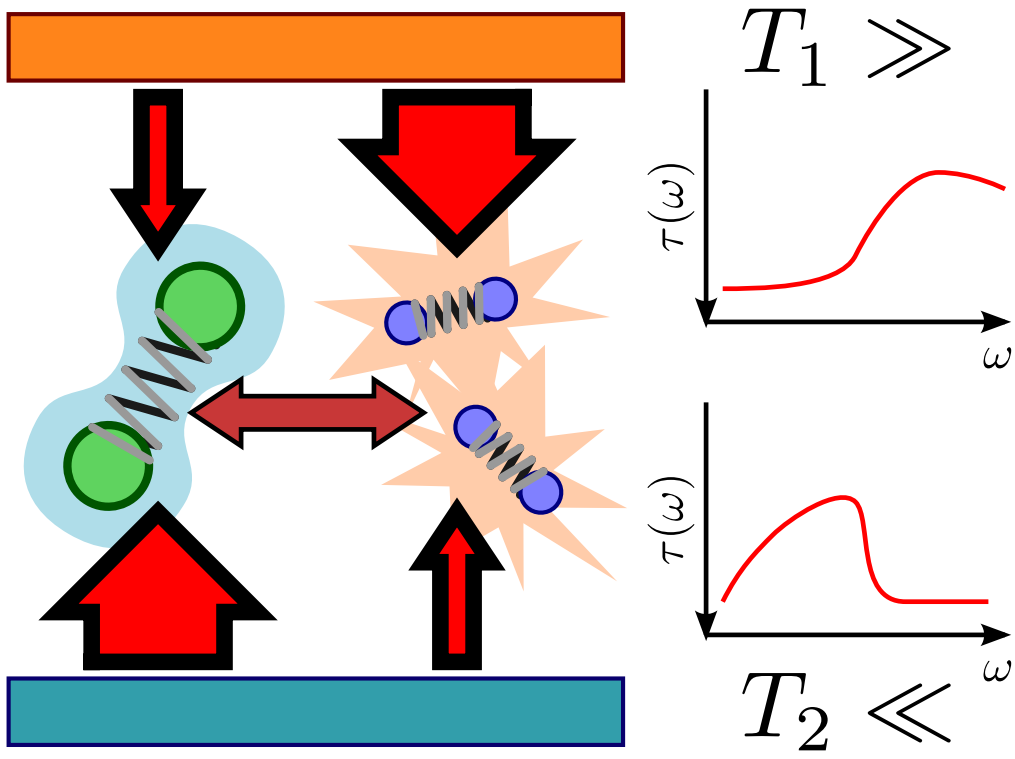
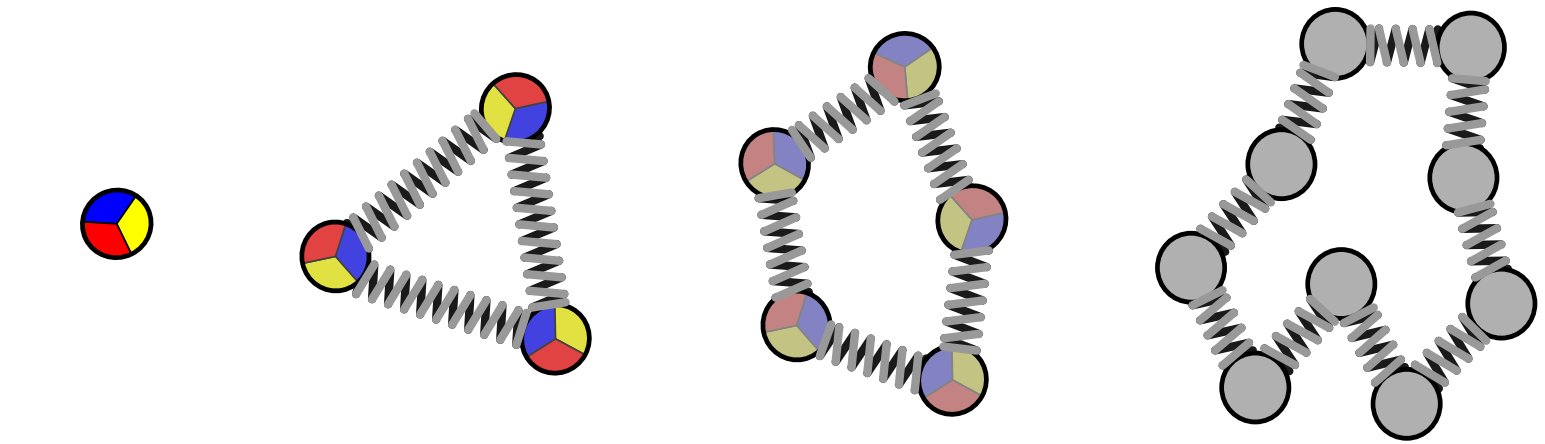


Systematic convergence with PIGLET

- Quantum thermostat ⇒ inexpensive but approximate;
  Path integrals ⇒ accurate but costly!
- **Can we get the best of both worlds?**
  - Devise "intermediate" forms of colored noise
  - Achieve systematic and accelerated convergence!



quantum thermostat

PI+GLE

path integral

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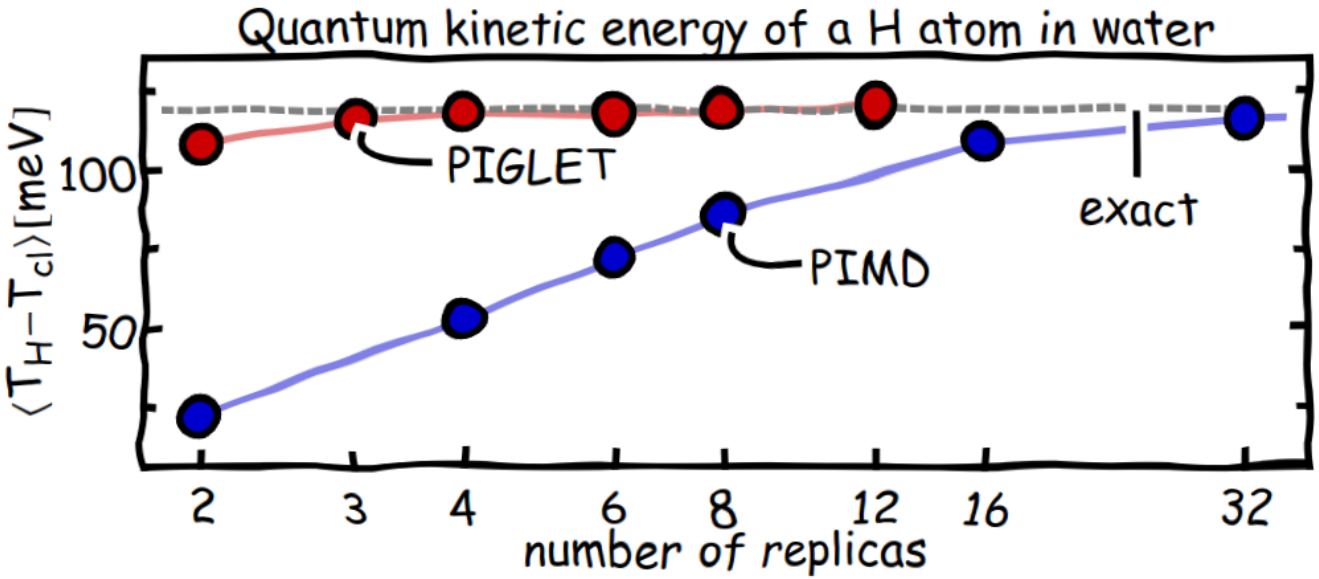

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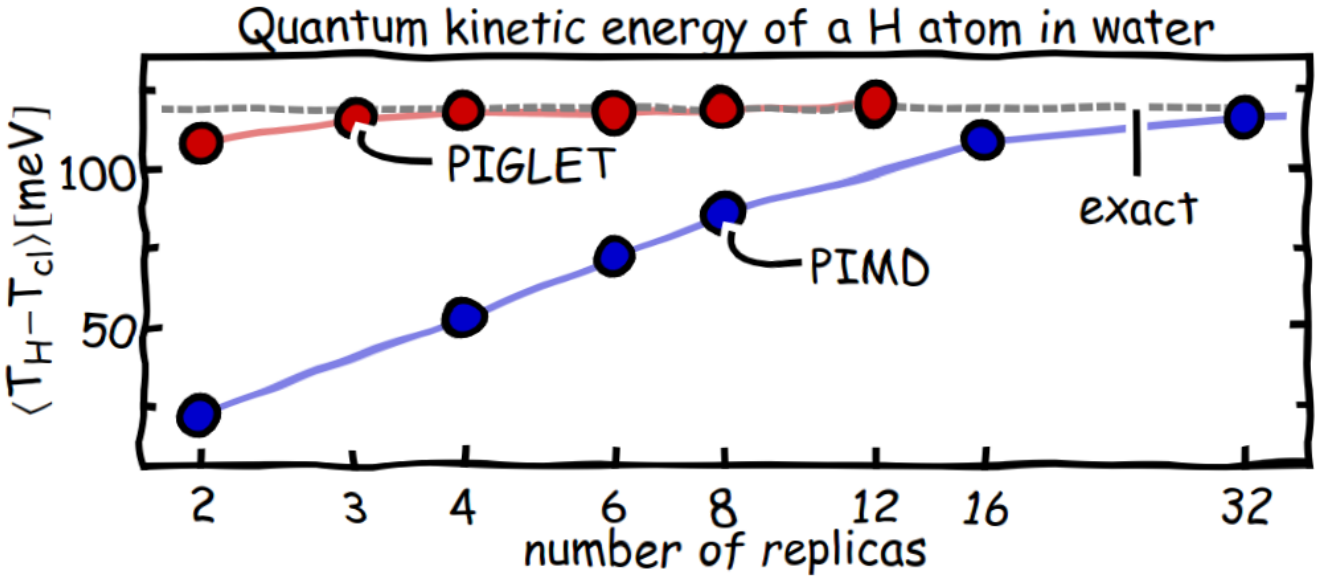

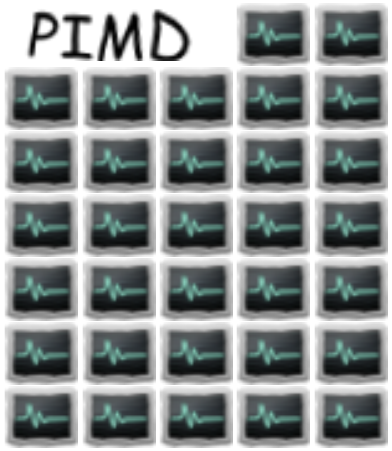

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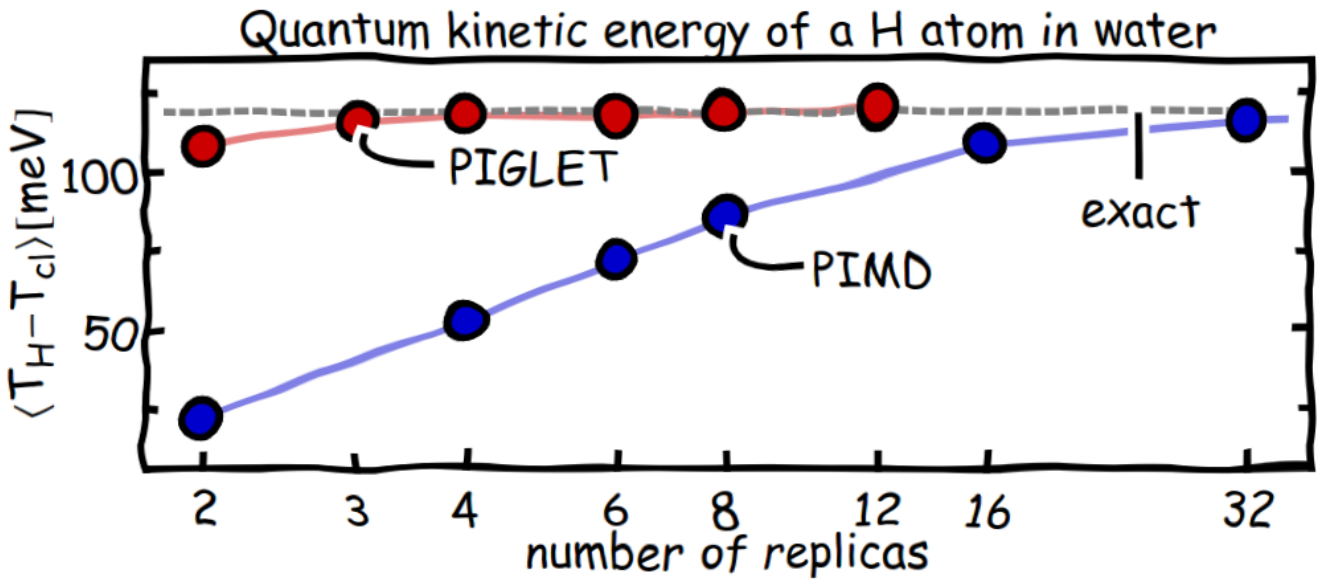

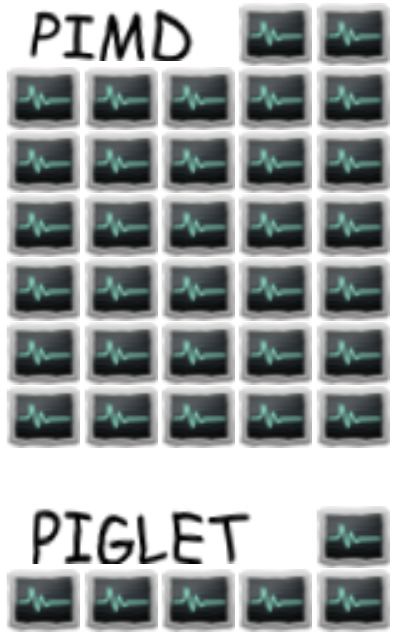

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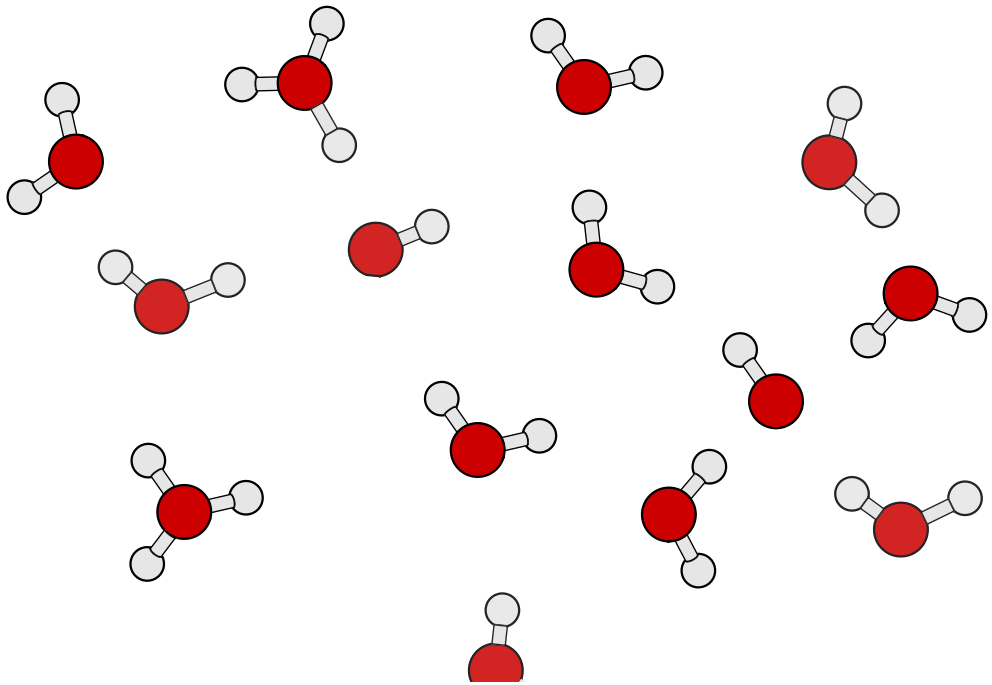
Self dissociation at 10GPa, 750K

- Pressure promotes water dissociation. Presence of a large concentration of charged species, particularly with NQEs
- These are real dissociations, leading to proton exchanges
- Quantum effects have a small (but noticeable) effect on density



Schwegler, Galli, Gygi, Hood, PRL 2001

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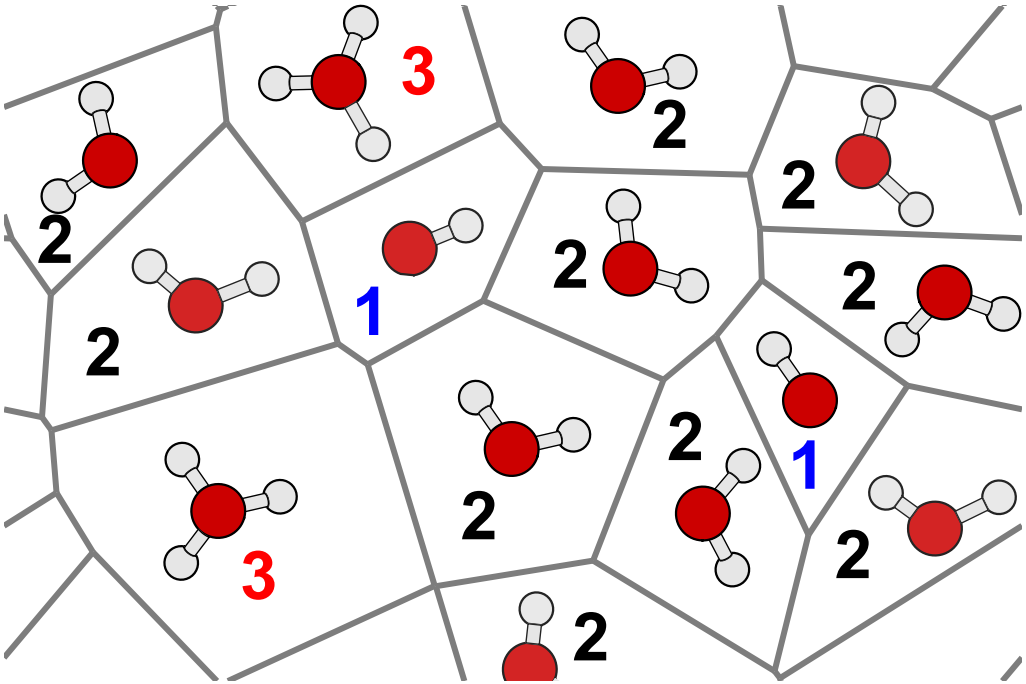

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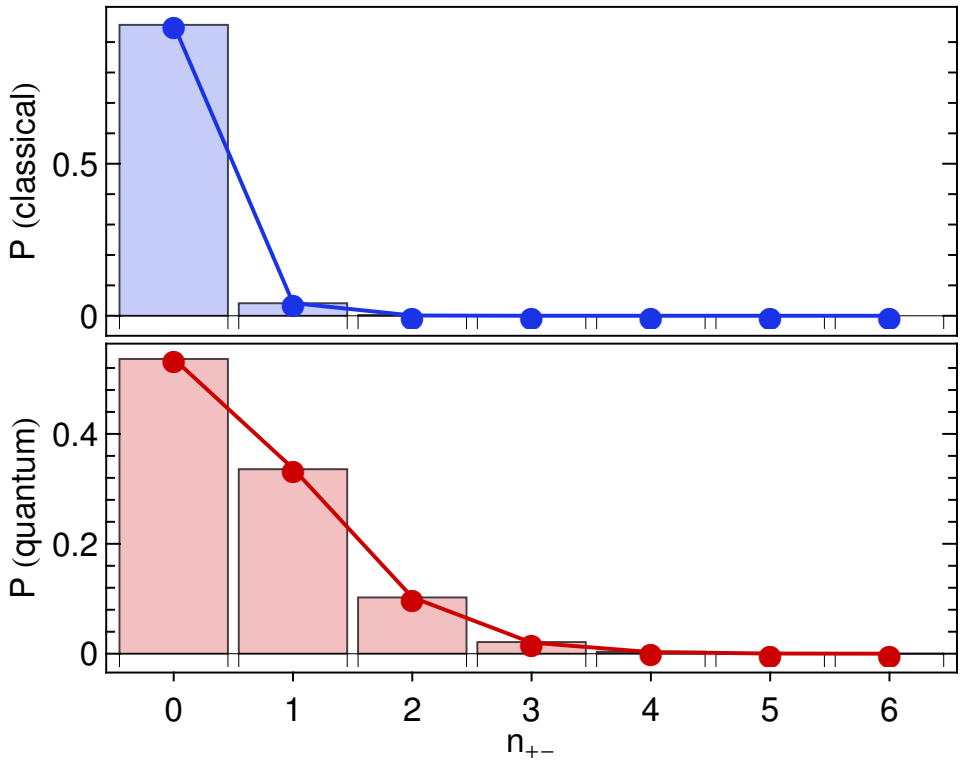

BLYP+D3, NpT PIGLET, CP2K; Ceriotti, More, Manolopoulos, Comp. Phys. Comm. 2014

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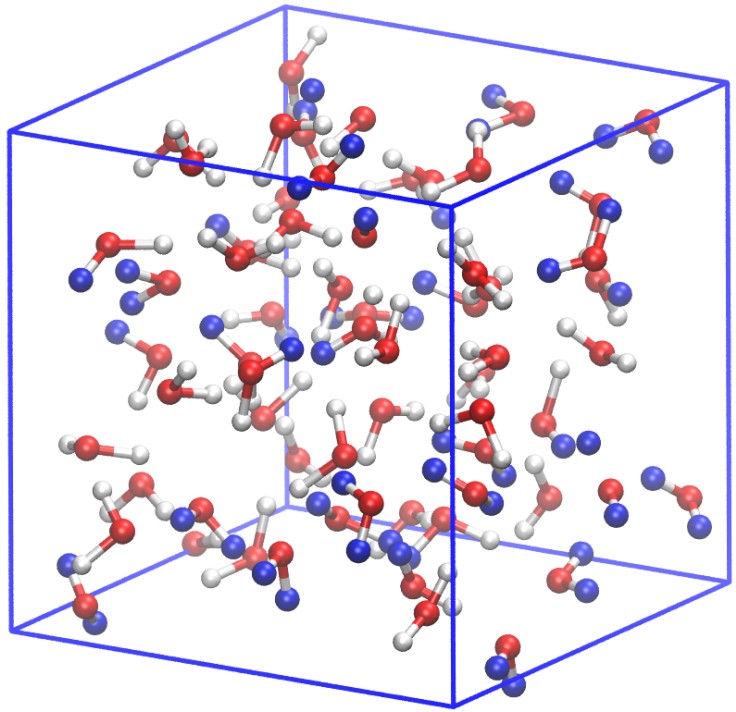

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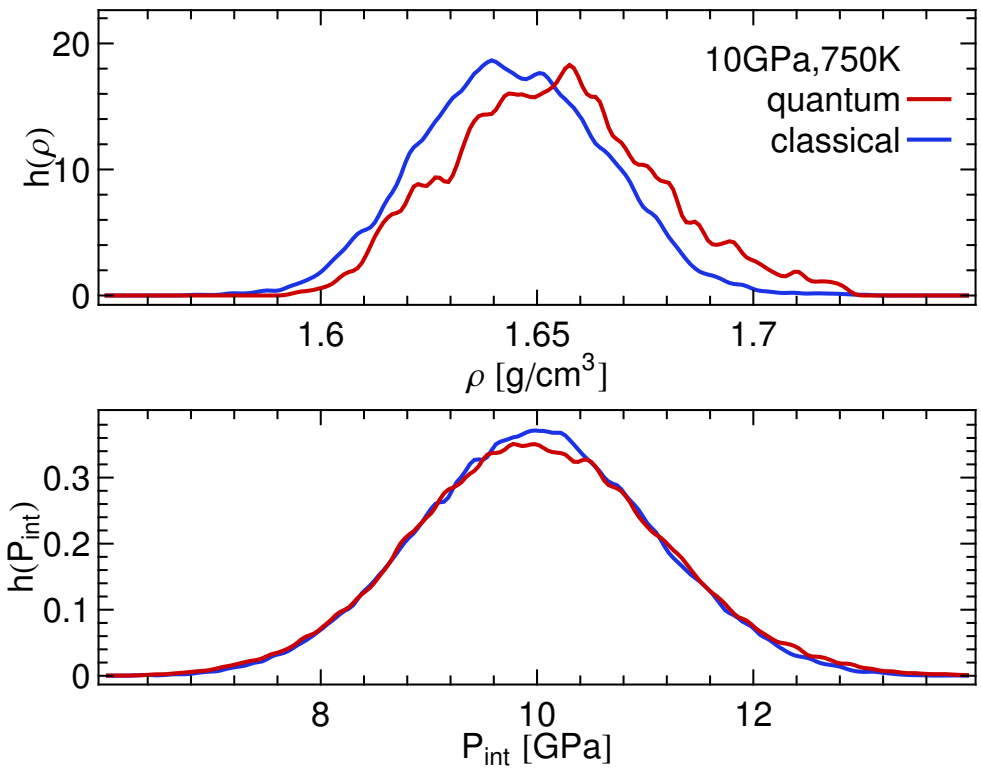

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Isotope fractionation in DFT water

- Different phases in equilibrium contain different fractions of light and heavy isotopes

$$\mathrm{H}_{phase1} + \mathrm{D}_{phase2} \overset{\Delta G}{\rightleftharpoons} \mathrm{D}_{phase1} + \mathrm{H}_{phase2}$$

  - Very useful for geochemistry and atmospheric sciences: extremely accurate experimental data available
  - Very demanding calculations, but can be made cheaper with a few tricks

$$\Delta G \propto \int_{m_\mathrm{H}}^{m_\mathrm{D}} \frac{T_1(\mu)}{\mu} - \frac{T_2(\mu)}{\mu} \mathrm{d}\mu$$

- Purely quantum mechanical effect, would be zero for classical nuclei – Ideal test of the quality of DFT functionals
  - Because of quantum fluctuations, the simulations probe different regions of the potential energy surface

Ceriotti & Markland, JCP 2013

A comparison of different functionals

- Comparison of fractionation ratios with different functionals
  - Break down in different contributions give more insight
  - Comparison of (virtually) exact results in the gas phase, infer reference value for ΔA_l (CCSD(T) PES for the monomer)
- Temperature dependence for BLYP – qualitatively predicts inversion

	PBE	BLYP	BLYP-D3	PBE0	B3LYP	B3LYP-D3	**Exp**
$-10^3 \Delta G / k_B T$	-17	62	48	90	102	95	**73**
O-H	-409	-292	-272	-241	-199	-205	-
Plane	114	104	90	99	88	87	-
Orthogonal	278	250	230	232	213	213	-

Partridge & Schwenke, JCP 1997; Wang, Ceriotti & Markland, JCP 2014

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(meV)	PBE	BLYP	BLYP-D3	PBE0	B3LYP	B3LYP-D3	**Exact**
K_v	147.1	145.6	145.8	152.3	149.5	149.5	**151.1**
ΔA_v	-88.1	-87.2	-87.3	-91.1	-89.6	-89.6	**-90.4**
K_l	146.7	148.3	147.5	155.6	153.7	153.3	**-**
ΔA_l	-87.7	-88.8	-88.5	-93.4	-92.3	-92.1	**-92.3**

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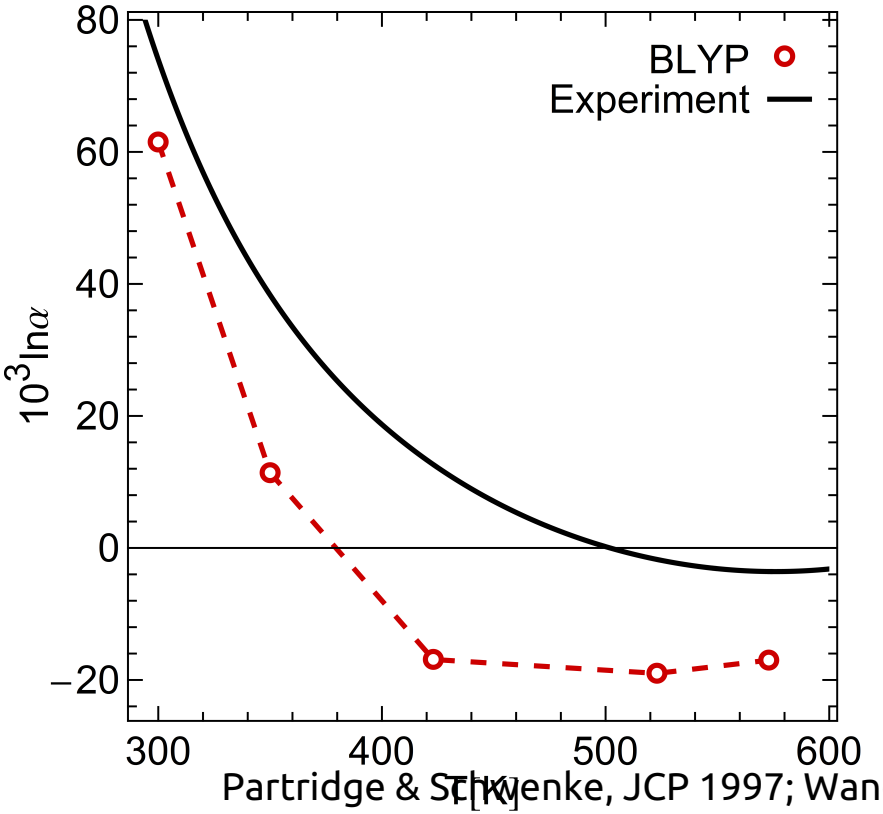

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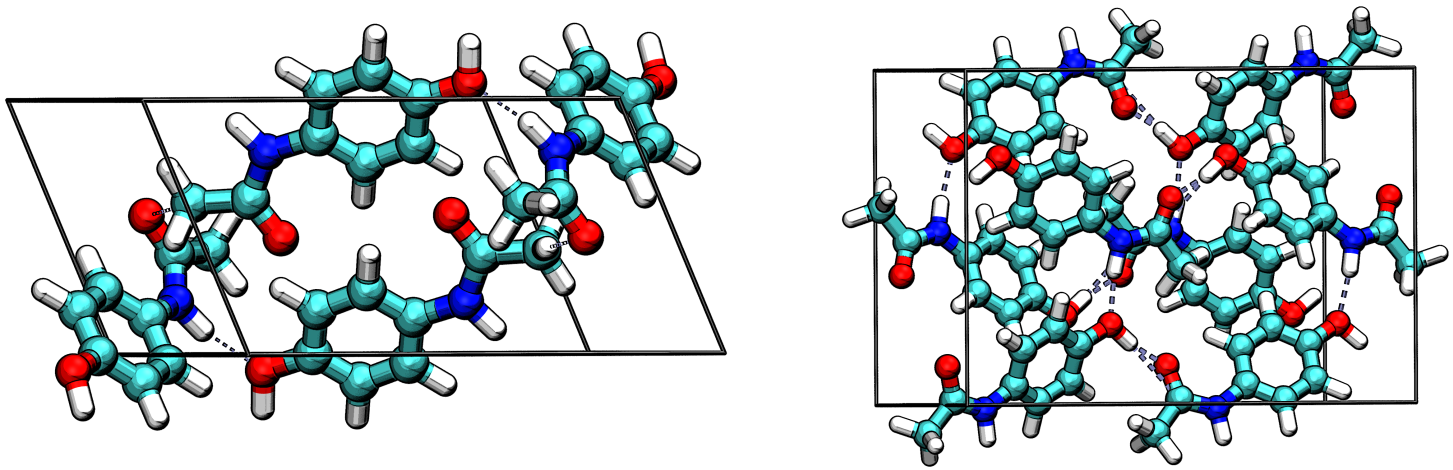
Quantum effects in molecular crystals

- Csomputing quantum and anharmonic contributions to the stability of paracetamol form I and II
- A complex combination of thermodynamic integration steps:
  - PIMD with multiple time step and GLE acceleration
  - Phonon calculations and thermodynamic integration
- Bottom line: quantum nuclear effects and anharmonic free energy are as important as the details of the electronic structure calculation (PBE+D3)



Rossi, Gasparotto, Ceriotti, PRL 2016

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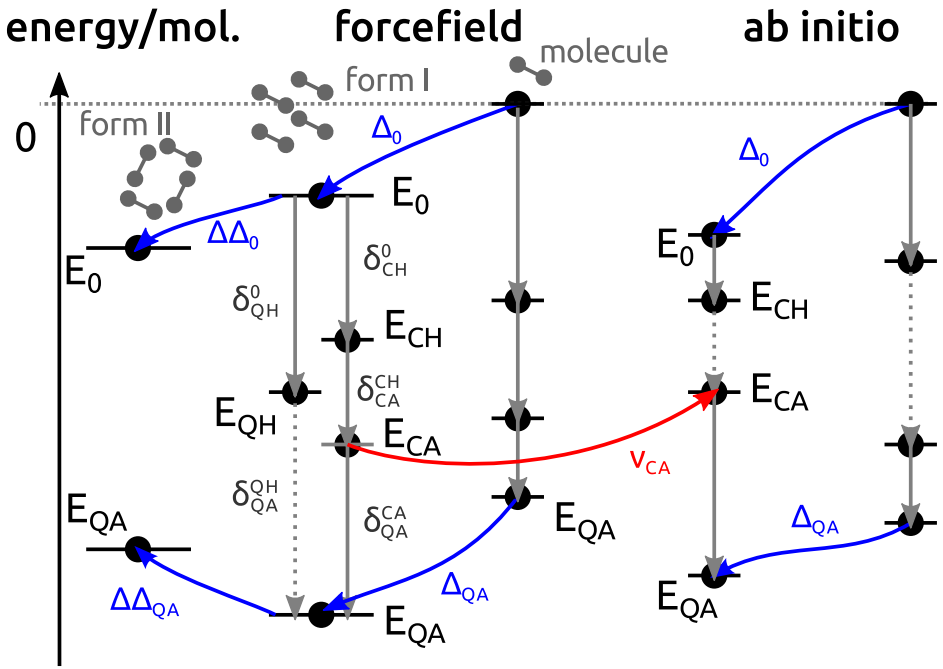

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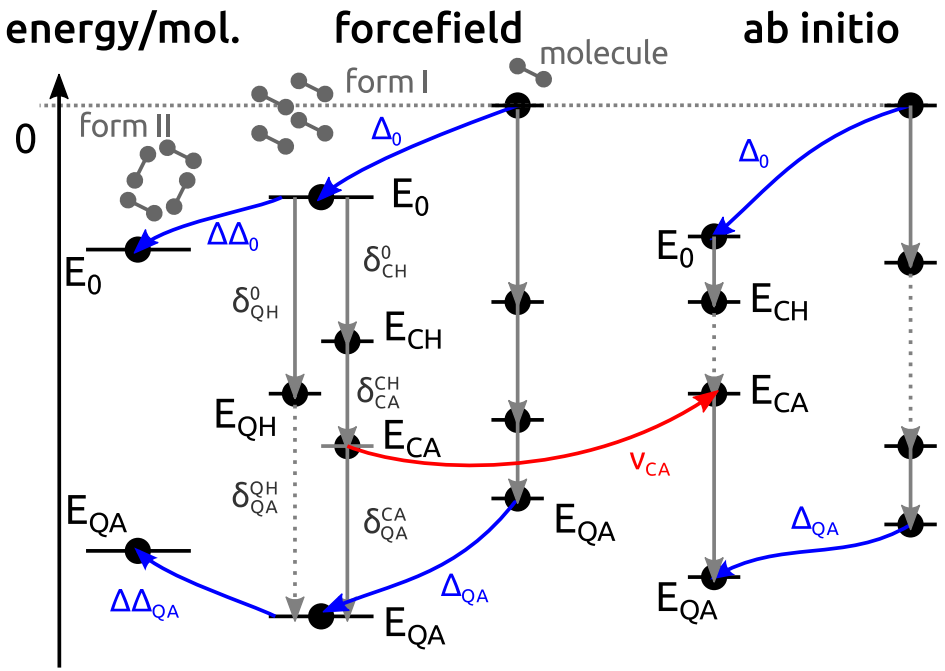
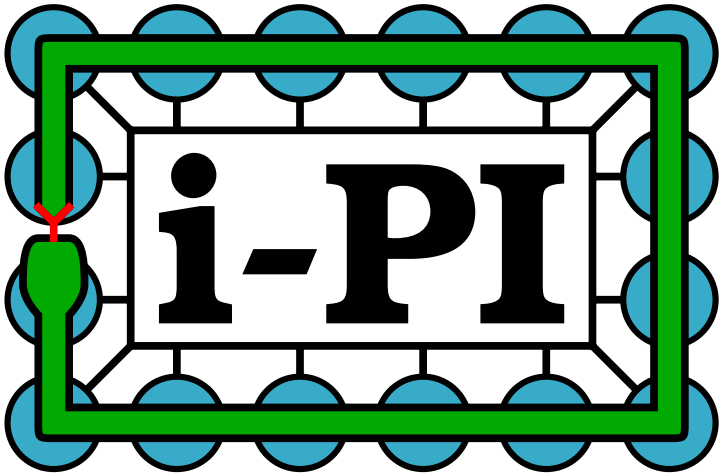


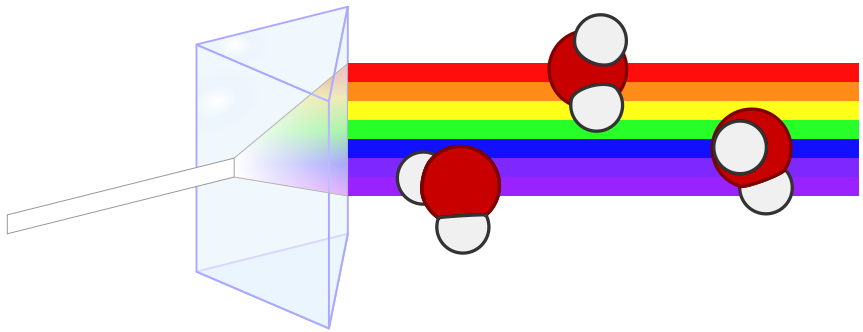
meV/mol	Δ(form I-form II)
Δ_0	-3
Δ_{CH}	-13
Δ_{CA}	-38
Δ_{QH}	-18
Δ_{QA}	-45

Rossi, Gasparotto, Ceriotti, PRL 2016

Outlook

- Molecular dynamics offers a very flexible framework to sample (thermo)dynamical properties of matter
- Stochastic dynamics provide a natural model for coupling to a bath - GLE thermostats are an exquisitely tunable incarnation of the idea
- Besides the constant-*T* classical dynamics, MD can be adapted to model constant-pressure conditions, quantum systems, and more!





http://epfl-cosmo.github.io/gle4md/

Introducing autocorrelation functions

- One can also define a version for discrete series,

$$c_{AA}(i) = \langle A(\mathbf{q}_0)\, A(\mathbf{q}_i)\rangle$$

- It is written $\langle A(0)\, A(t)\rangle$, but it really means

$$c_{AA}(t) = \frac{\langle (A(0) - \langle A\rangle)\,(A(t) - \langle A\rangle)\rangle}{\langle A^2\rangle - \langle A\rangle^2}$$

. . . and it *really* means

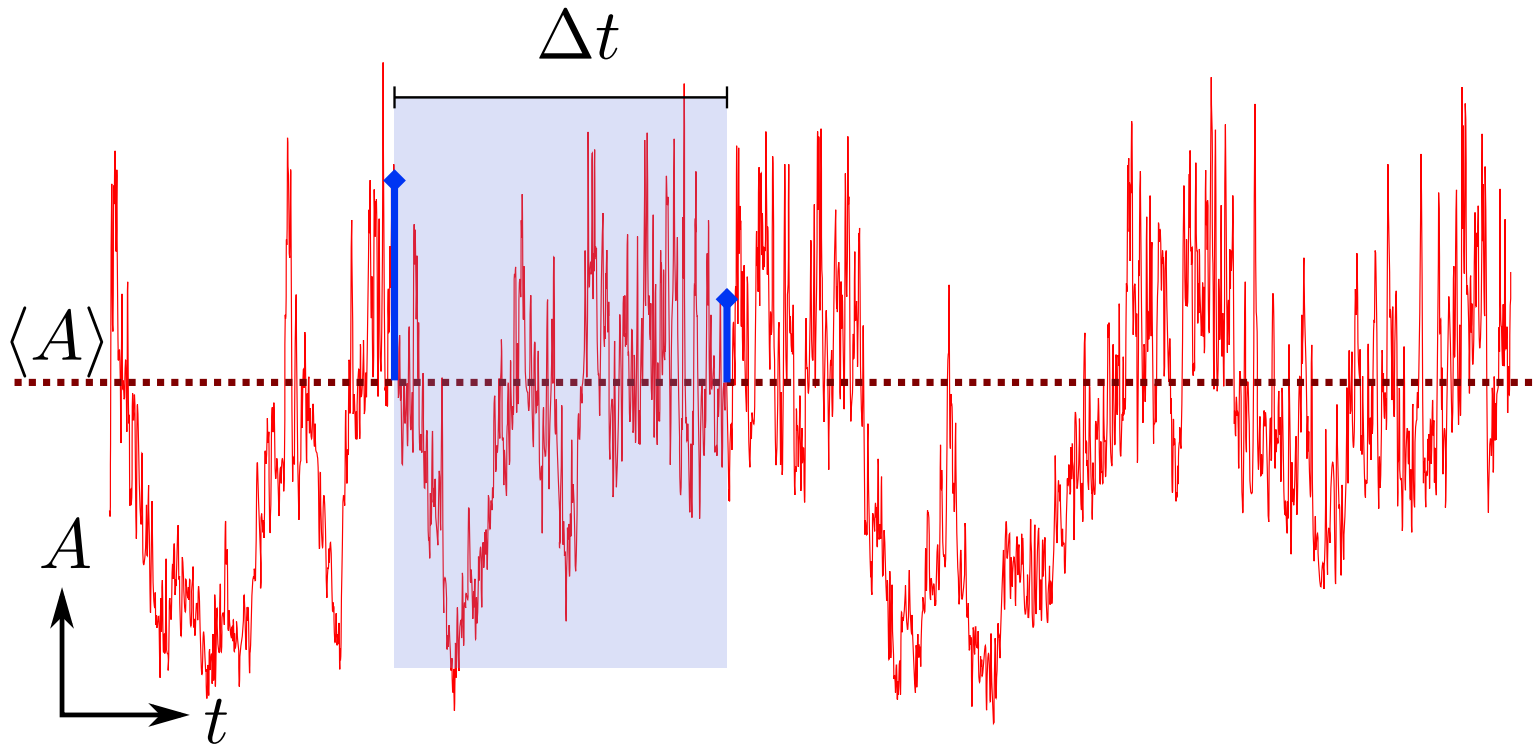
$$c_{AA}(t) = \frac{\int \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{q}'\, P(\mathbf{q})\, P(\mathbf{q}'; t|\mathbf{q}; 0)\, [A(\mathbf{q}) - \langle A\rangle]\, [A(\mathbf{q}') - \langle A\rangle]}{\int \mathrm{d}\mathbf{q}\, P(\mathbf{q})\, [A(\mathbf{q}) - \langle A\rangle]^2}$$

. . . and in practice it is computed from a trajectory $A(t)$ as

$$c_{AA}(t) = \frac{1}{\sigma_A^2} \lim_{T\to\infty} \frac{1}{T-t} \int_0^{T-t} \mathrm{d}t'\, [A(t') - \langle A\rangle]\, [A(t'+t) - \langle A\rangle]\,.$$

Autocorrelation function from a trajectory

$$c_{AA}(t) = \frac{1}{\sigma_A^2} \lim_{T\to\infty} \frac{1}{T-t} \int_0^{T-t} \mathrm{d}t' \left[A(t') - \langle A \rangle\right] \left[A(t'+t) - \langle A \rangle\right]$$



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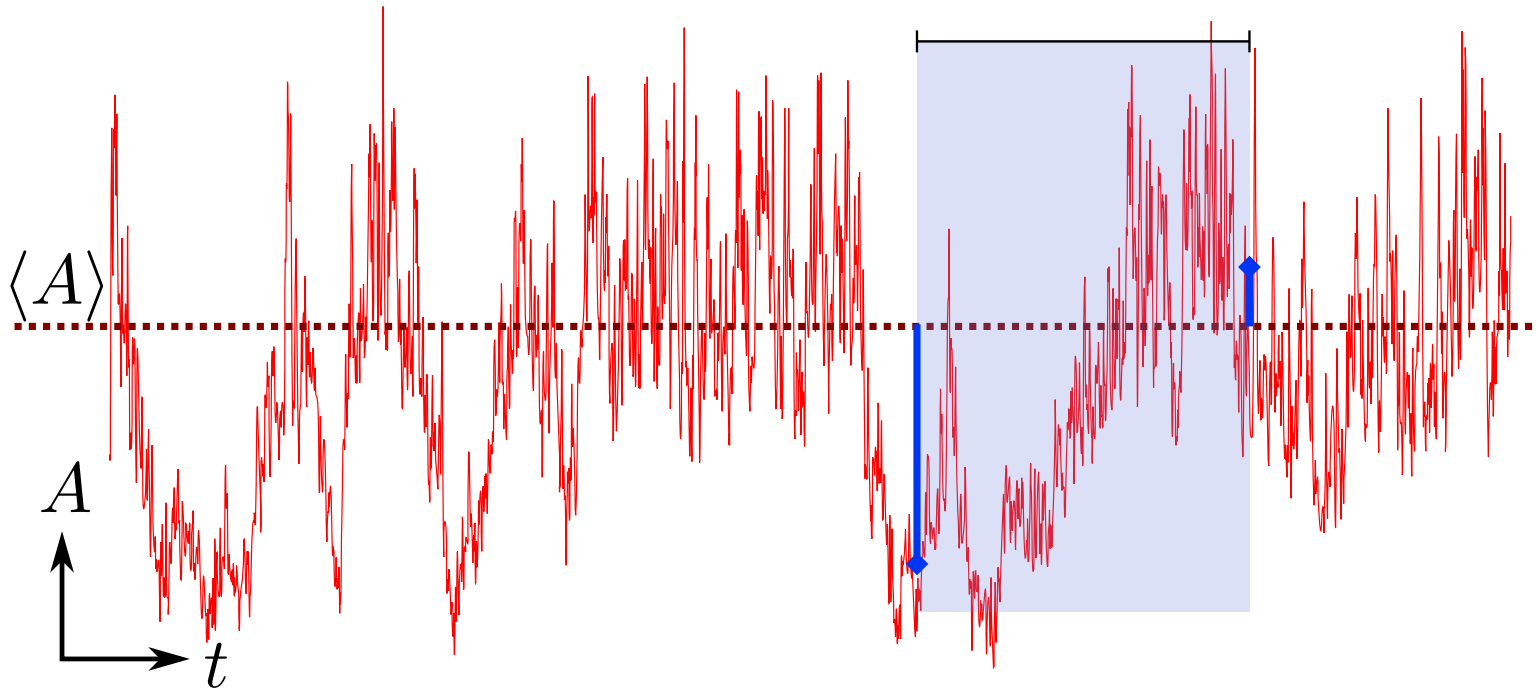

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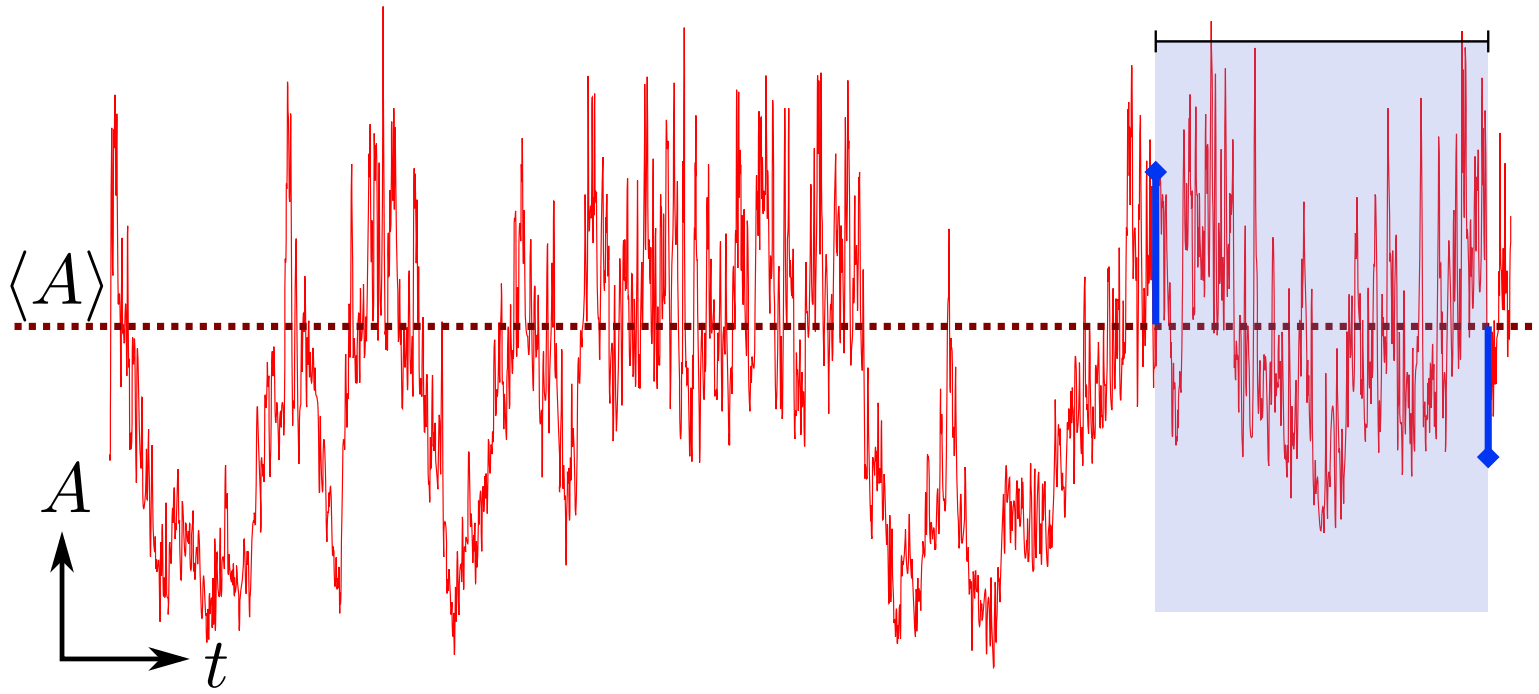
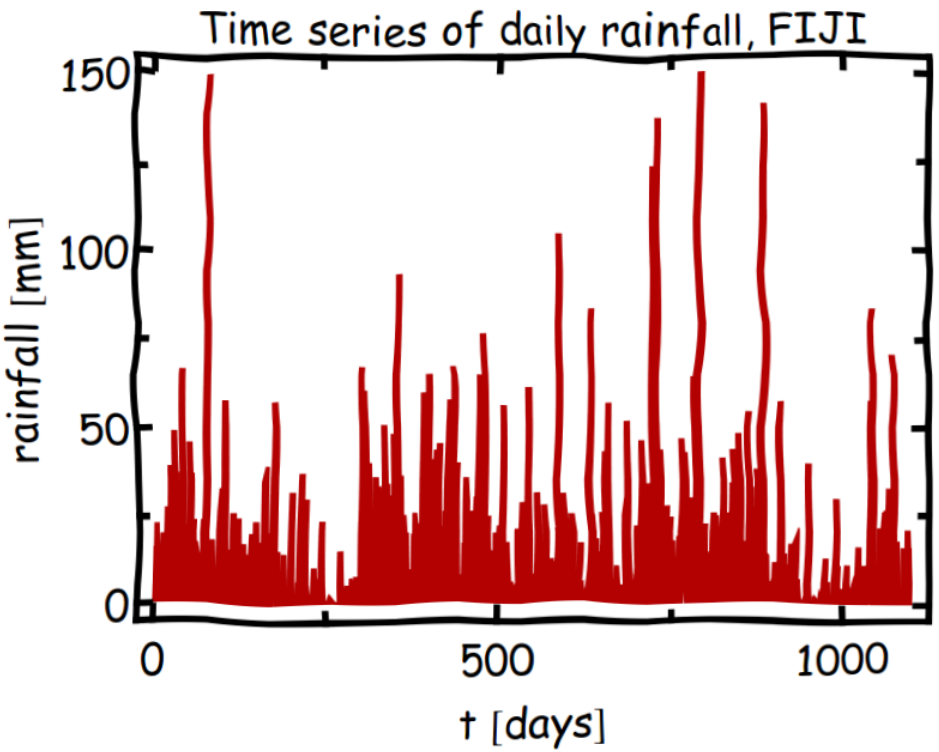


If it rained yesterday. . .

- $c_{AA}(t)$ tells you how much one can infer about the deviation of A from its mean at time t from its deviation at time 0.
- Example: daily rain fall on a small island in the Pacific: will it rain tomorrow? Multiple time scales can be identified.



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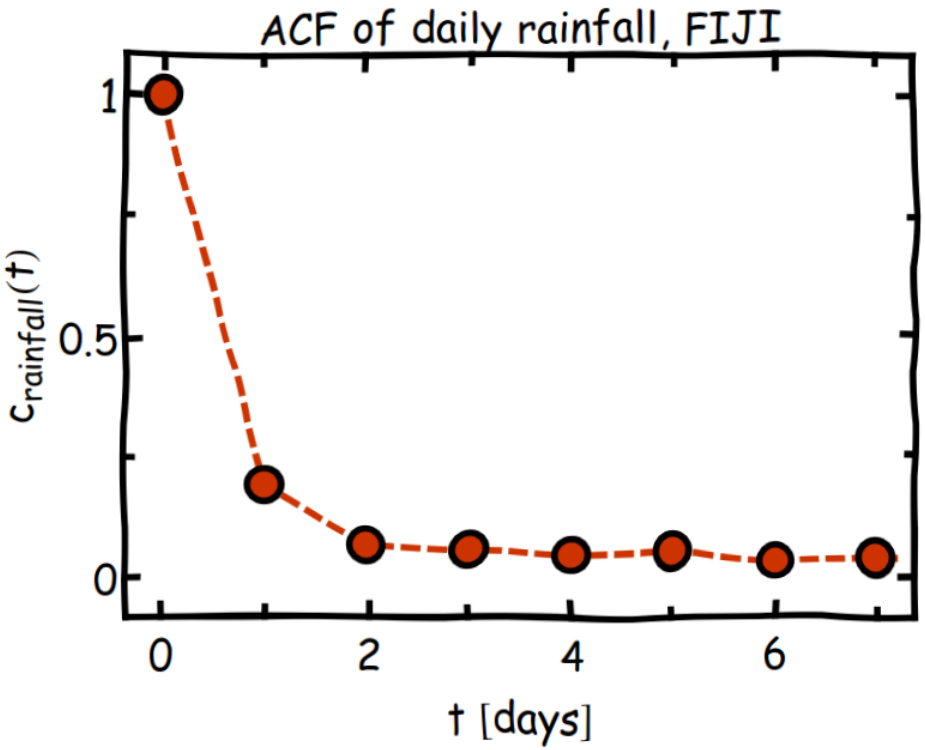

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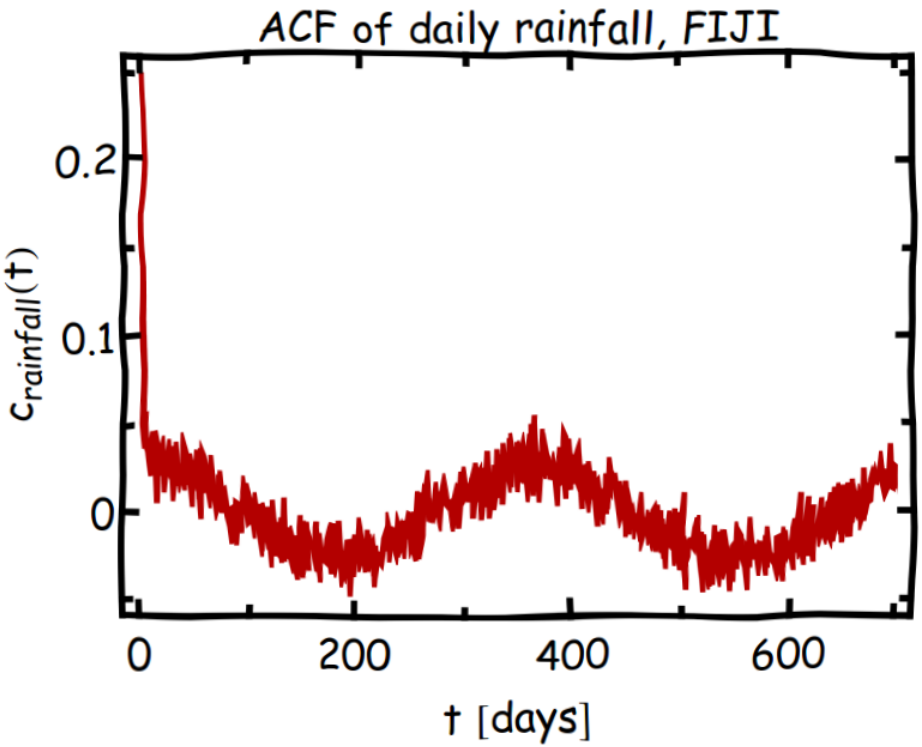

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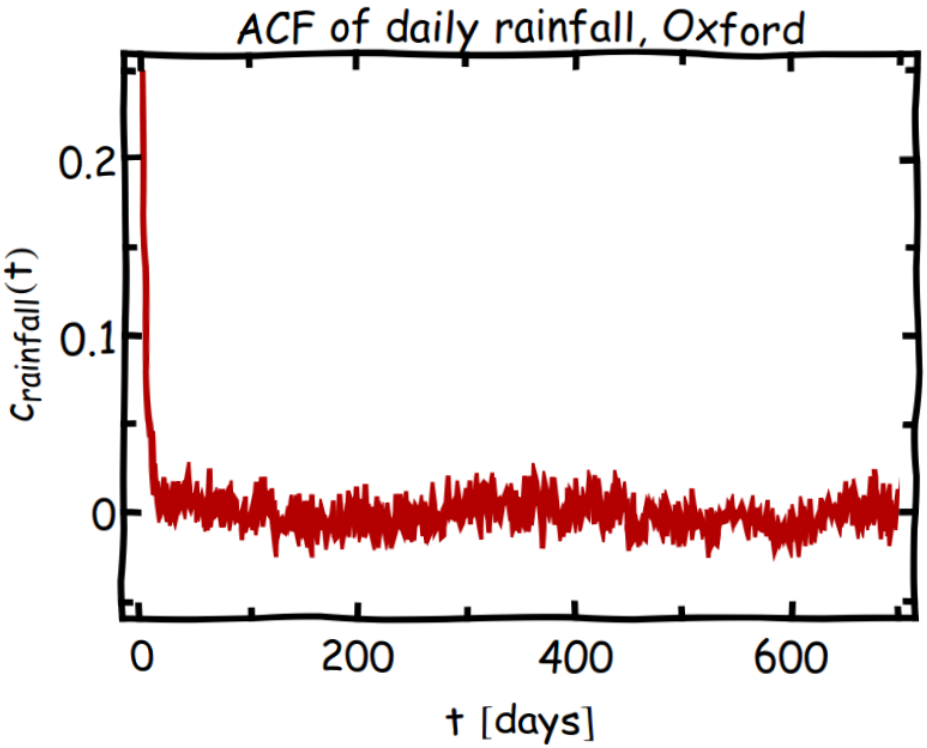

ACF and error in the mean

- Autocorrelation functions are closely related to the sampling efficiency
- The mean A computed from a run of length T is

$$\langle A \rangle_T = \frac{1}{T} \int_0^T A(t)\, \mathrm{d}t$$

- The mean square error in the mean $\epsilon_A^2(T)$ is then

$$\left\langle \left[\langle A \rangle_T - \langle A \rangle \right]^2 \right\rangle = \frac{1}{T^2} \int_0^T \mathrm{d}t \int_0^T \mathrm{d}t' \left\langle \left[A(t) - \langle A \rangle \right] \left[A(t') - \langle A \rangle \right] \right\rangle .$$

Noting that

$$\left\langle \left[A(t) - \langle A \rangle \right] \left[A(t') - \langle A \rangle \right] \right\rangle = \sigma_A^2 c_{AA}(t' - t) ,$$

one can do a change of variables $t' - t = \Delta$ and get

$$\epsilon_A^2(T) = \frac{\sigma_A^2}{T} \int_{-T}^T \mathrm{d}\Delta\, c_{AA}(\Delta) \left(1 - \frac{|\Delta|}{T} \right)$$

Correlation time and statistical efficiency

- For T much longer than the time scale on which $c_{AA}(t)$ decays to zero, $\epsilon_A^2(T) = \frac{\sigma_A^2}{T/\tau_A}$, where we introduced the **correlation time**

$$\tau_A = \int_{-\infty}^{\infty} c_{AA}(t)\,\mathrm{d}t$$

- Samples spaced by less than τ_A do not contribute to statistics

Correlation time and statistical efficiency

- For T much longer than the time scale on which $c_{AA}(t)$ decays to zero, $\epsilon_A^2(T) = \frac{\sigma_A^2}{T/\tau_A}$, where we introduced the **correlation time**

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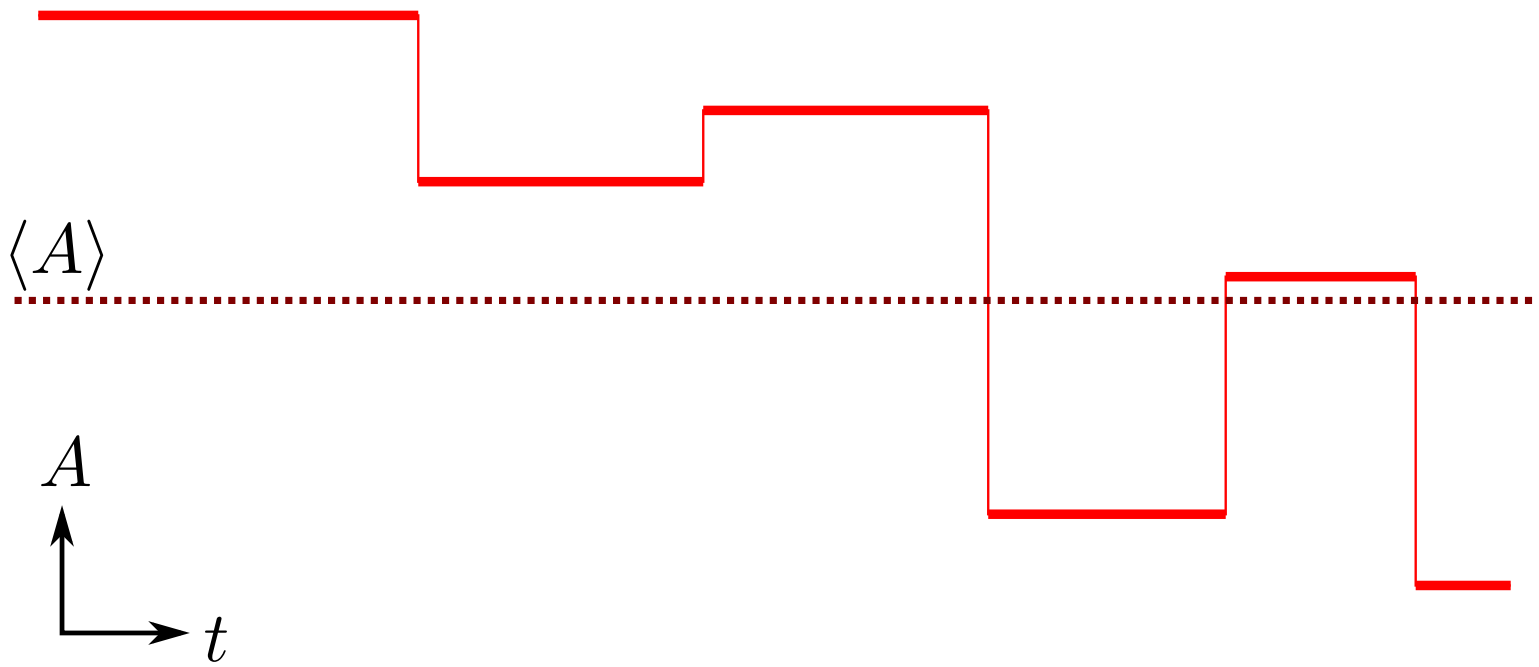

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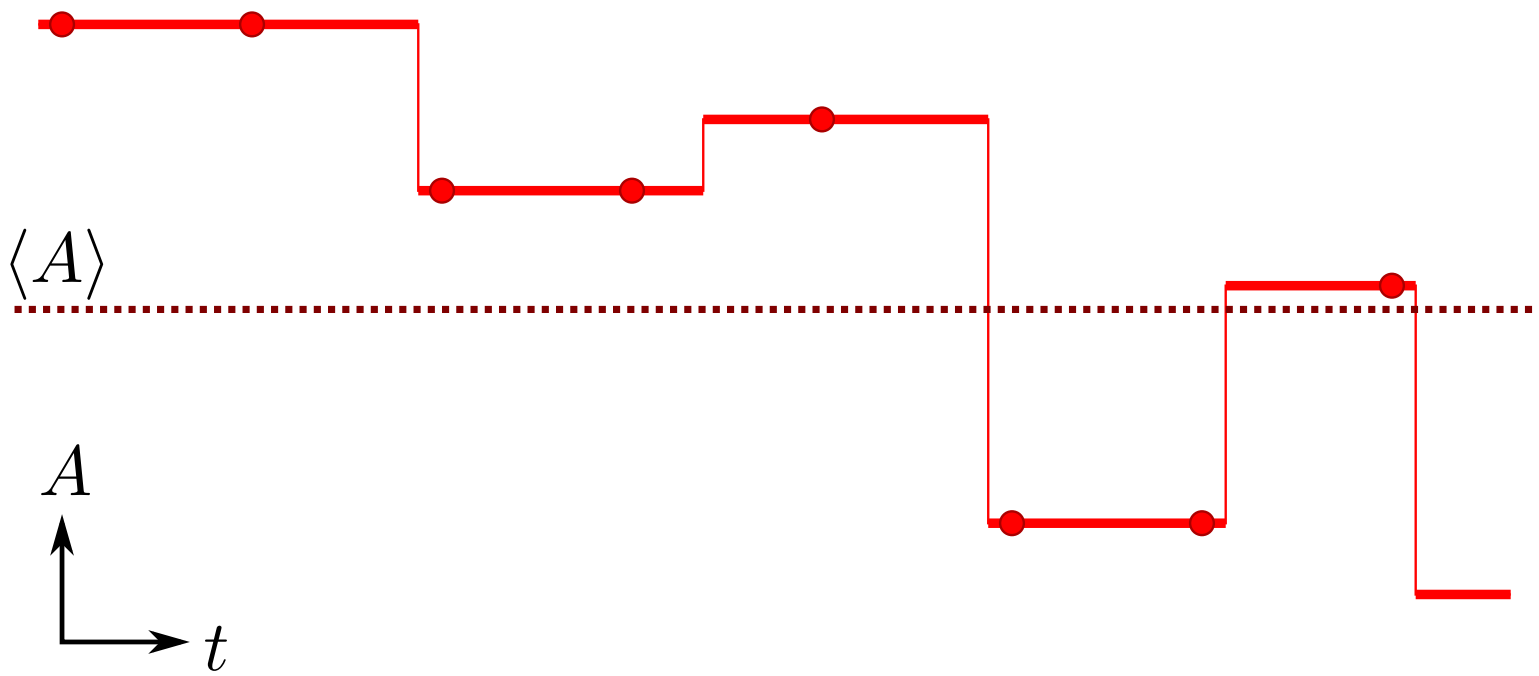

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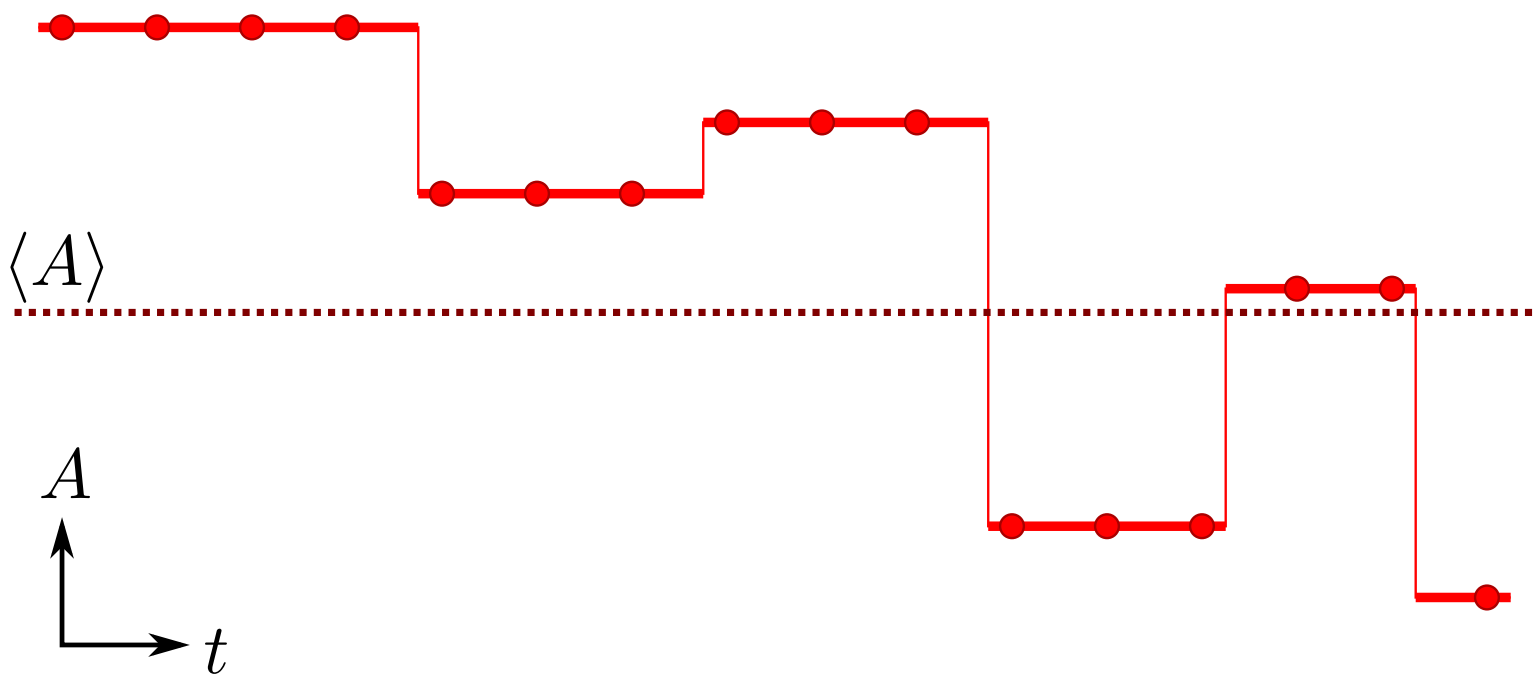

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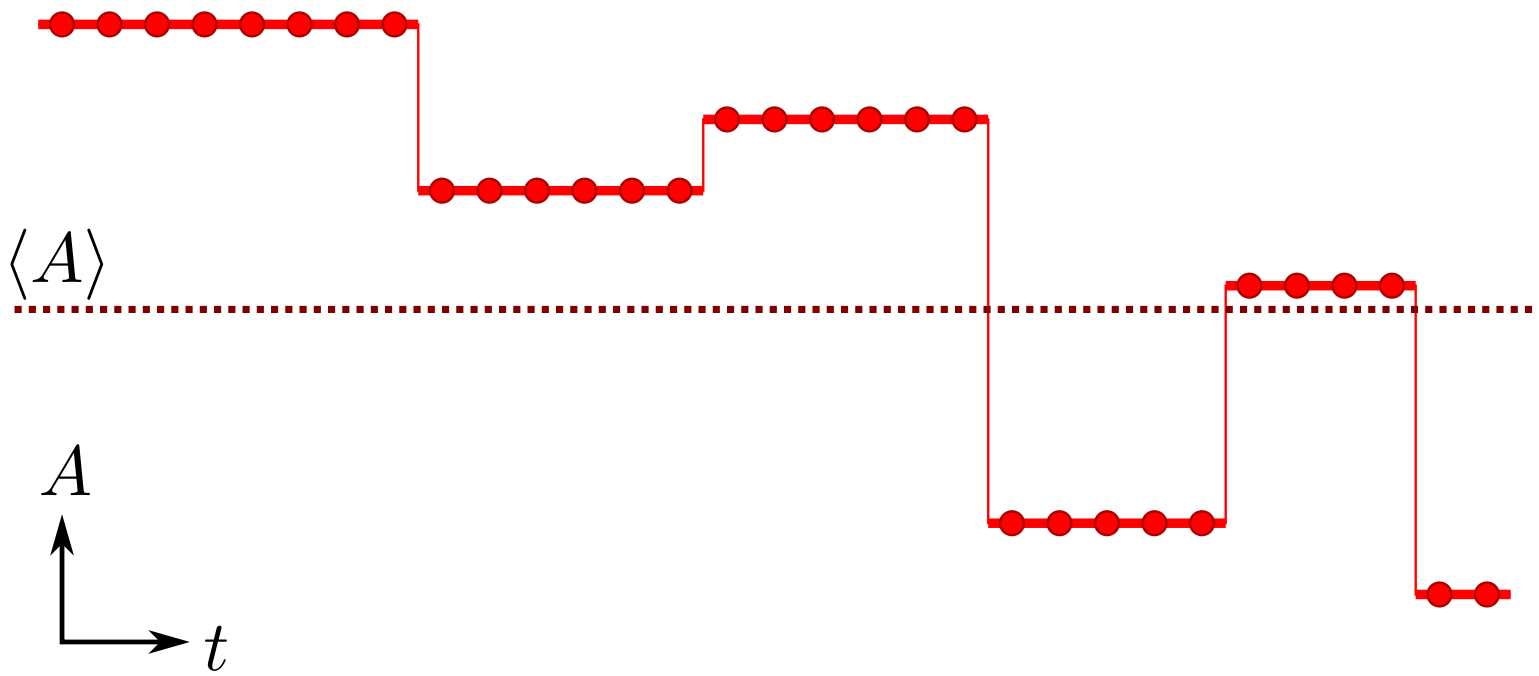

Practicalities of computing ACFs

- ACFs can be computed very efficiently with FFT
- There is a problem with the average entering the definition of c_{AA}
  - For $T \sim \tau_A$, $\langle A \rangle$ estimated from the trajectory is correlated with $A(t)$
  - The estimator for c_{AA} is biased (sort of $N \to N-1$ evaluating σ_A^2)
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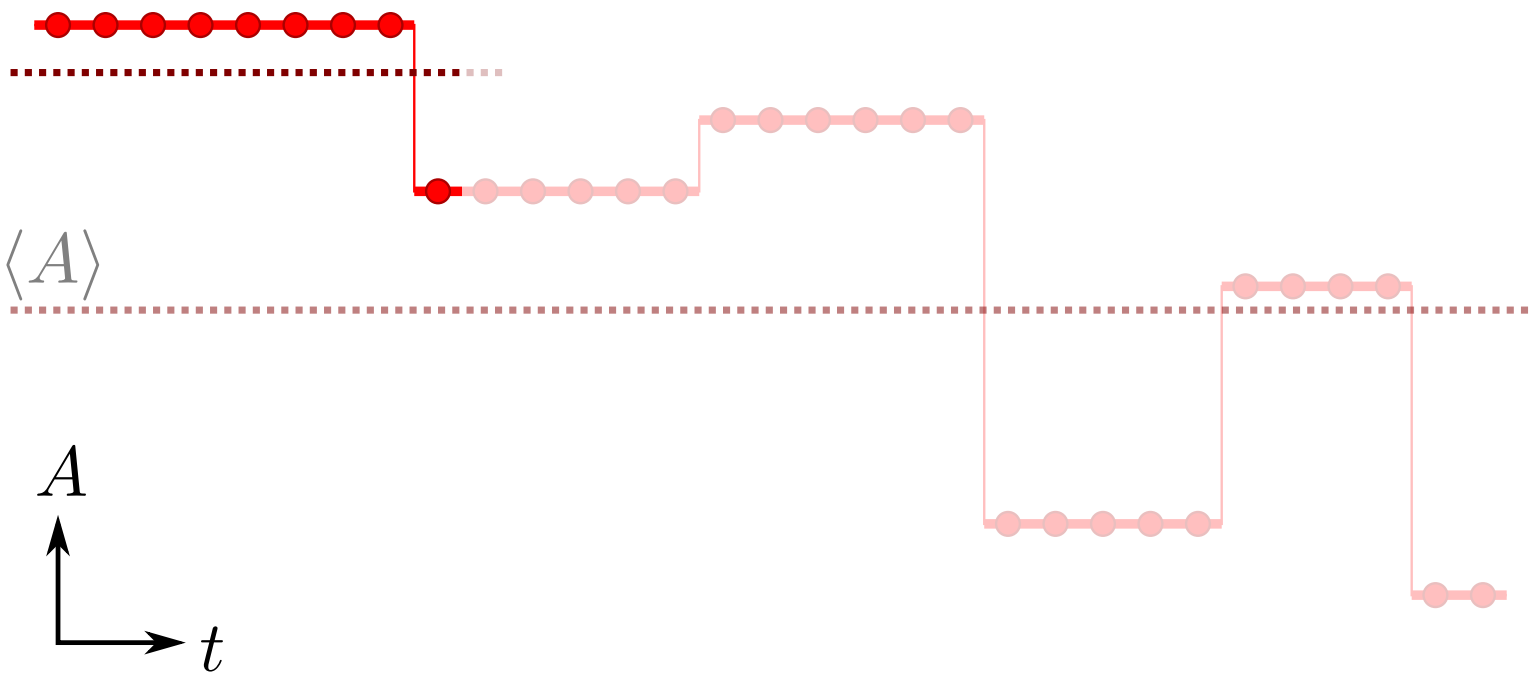

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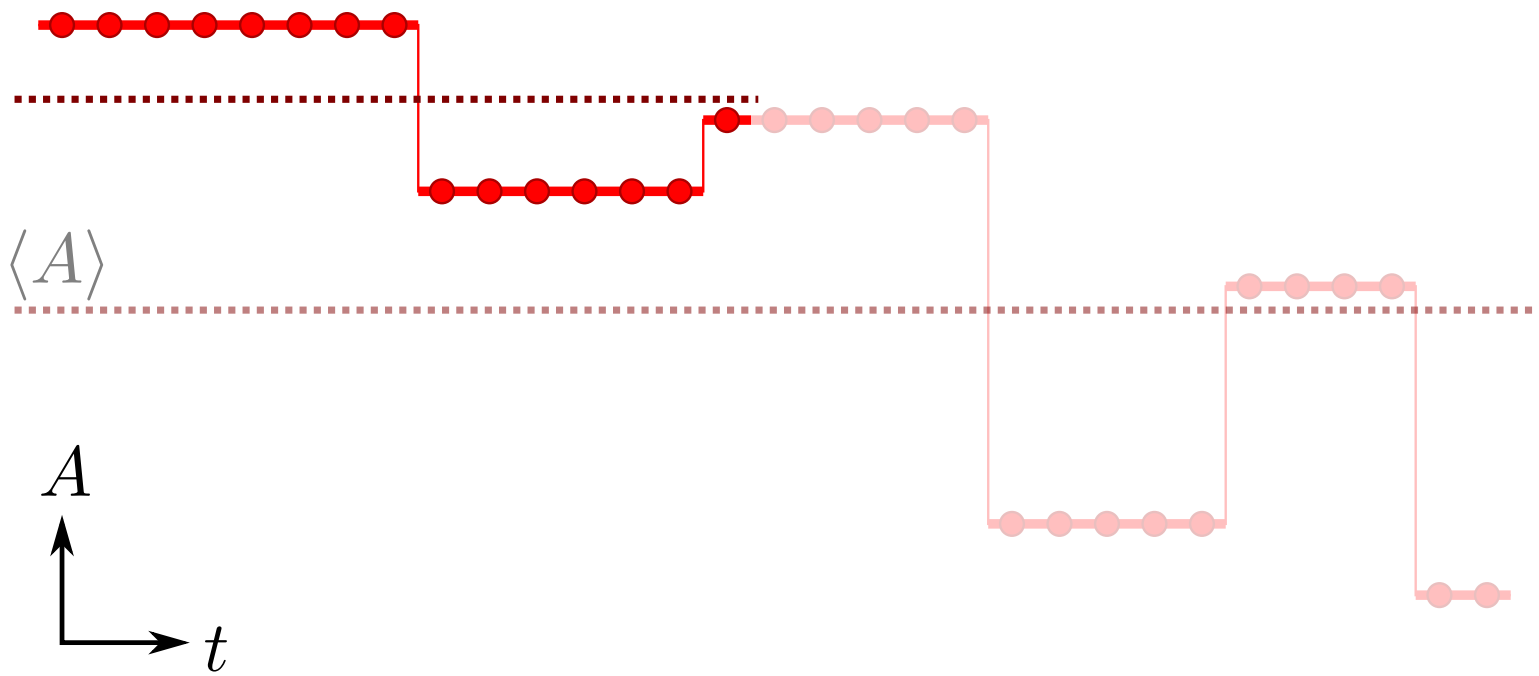

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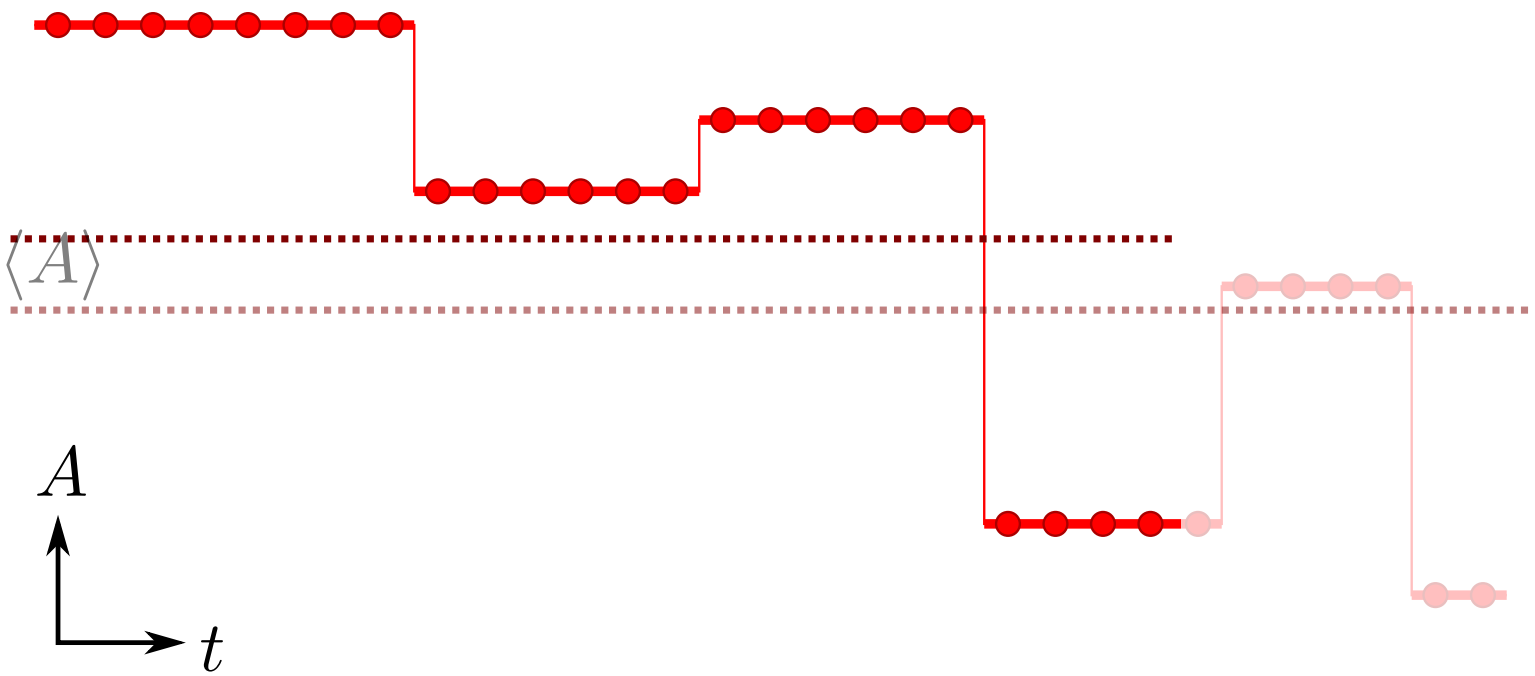
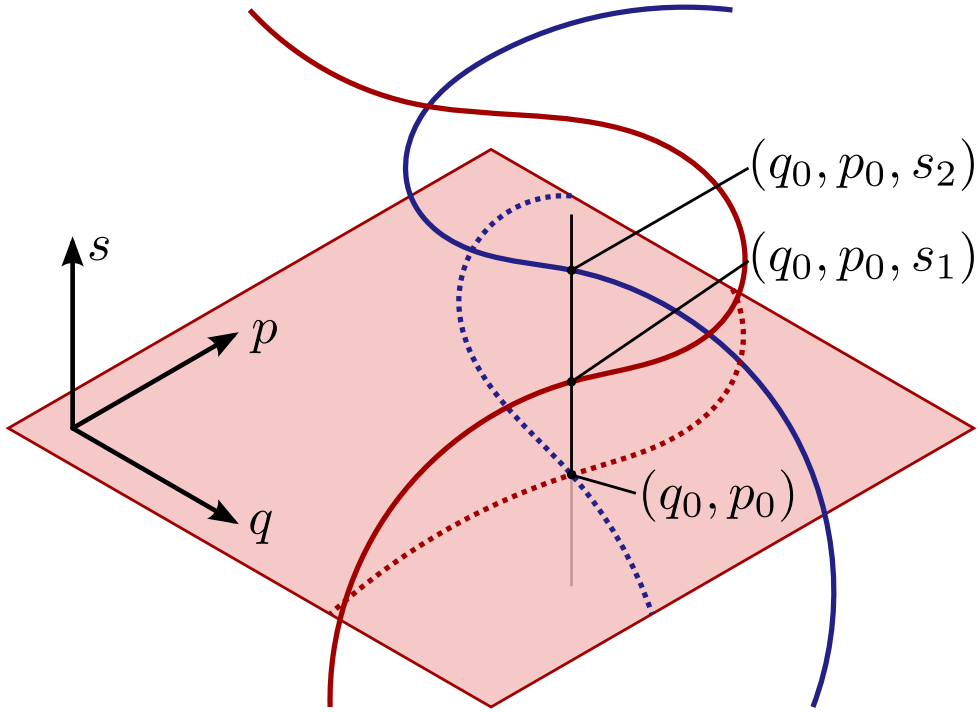


Markovian/non-Markovian dynamics

- A non-Markovian dynamics can be seen as the projection of a Markovian dynamics in an extended phase space
- With the appropriate formalism (Mori-Zwanzig), the effect of the extra degrees of freedom can be integrated out, and corresponds to a memory kernel in a generalized Langevin equation



A GLE framework for molecular dynamics

Non-Markovian GLE

$$\begin{aligned} \dot{q}(t) &= p(t)/m \\ \dot{p}(t) &= -V'(q) - \int_0^\infty K(t')\, p(t-t')\, \mathrm{d}t' + \sqrt{2mT}\,\zeta(t) \\ \langle \zeta(t)\,\zeta(0)\rangle &= TK(t) \end{aligned}$$

- We want to use a non-Markovian GLE, but it is inconvenient
- A large class of non-Markovian dynamics can be **mapped onto a Markovian dynamics** in an extended phase space
- The Markovian GLE corresponds to a (possibly complex) exponential memory kernel $K(t) = a_{pp}\delta(t) - \mathbf{a}_p^T e^{-\mathbf{A}t}\bar{\mathbf{a}}_p$
- Except for the non-linear potential, this stochastic differential equation is an **Ornstein-Uhlenbeck process** $\dot{\mathbf{u}} = -\mathbf{A}\mathbf{u} + \mathbf{B}\xi$ which can be solved analytically.

http://epfl-cosmo.github.io/gle4md; Ceriotti, Bussi, Parrinello, Phys. Rev. Lett. 102&103 (2009)

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Markovian GLE

$$\begin{aligned} \dot{q}(t) &= p(t)/m \\ \begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} &= \begin{pmatrix} -V'(q) \\ \mathbf{0} \end{pmatrix} - \begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\xi \\ \mathbf{B}\mathbf{B}^T &= T\left(\mathbf{A} + \mathbf{A}^T\right) \end{aligned}$$

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Predicting and fitting

- In the **harmonic limit**, exact propagator for the OU process (just as the Langevin propagator):
  - Static and dynamics properties can be predicted analytically
  - Thanks to **rotational invariance**, in the multidimensional case thermostats can be applied to Cartesian coordinates
- One can obtain **custom-tailored thermostats**:
  - Compute response properties over a frequency range as broad as the vibrational spectrum of the system
  - Modify the parameters of the GLE until the response matches requirements
- The fitting is a complex **nonlinear optimization** problem: must restrict the range of $\mathbf{A}_p$ and $\mathbf{B}_p$

Ceriotti, Bussi, Parrinello, Phys. Rev. Lett. 102&103 (2009); JCTC (2010)

Trotter Factorization

- Consider the QM partition function in the position representation

$$Z_{\mathrm{QM}} = \int \mathrm{d}q \left\langle q \middle| e^{-\beta \hat{H}} \middle| q \right\rangle$$

- At high temperature $e^{-\beta \hat{H}} \approx e^{-\beta \hat{V}} e^{-\beta \hat{T}}$, so we can get around this problem by a Trotter factorization

$$e^{-\beta \hat{H}} = \left(e^{-\beta \hat{H}/P} \right)^P \approx \left(e^{-\beta_P \hat{V}/2} e^{-\beta_P \hat{T}} e^{-\beta_P \hat{V}/2} \right)^P + \mathcal{O}\left(\beta_P^2\right),$$

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Fluctuations in a (quantum) HO

- A quantum harmonic oscillator of frequency ω has Gaussian fluctuations with amplitude

$$\left\langle q^2 \right\rangle(\omega) = \frac{\hbar}{2\omega} \coth \frac{\hbar\omega}{2k_B T}$$

- A ring polymer with P beads for a HO potential has normal modes with frequencies

$$\omega_k = \sqrt{\omega^2 + 4\omega_P^2 \sin^2(k\pi/P)}, \qquad \omega_P = Pk_B T/\hbar$$

  so the fluctuations of $\left\langle q^2 \right\rangle$ *with canonical sampling* can be written as

$$\left\langle q^2 \right\rangle_P(\omega) = \frac{1}{P} \sum_k \left\langle \tilde{q}_k^2 \right\rangle = k_B T \sum_k \frac{1}{\omega_k^2}$$

- For large P, $\left\langle q^2 \right\rangle_P(\omega) \to \frac{\hbar}{2\omega} \coth \frac{\hbar\omega}{2k_B T}$

PI+GLE

- The quantum thermostat enforces ω-dependent fluctuations that mimic quantum phase-space distribution of p and q for all the frequencies of interest
- PI+GLE idea: use colored noise to make sure that $\left\langle q^2 \right\rangle_P (\omega) = \frac{\hbar}{2\omega} \coth \frac{\hbar\omega}{2k_B T}$ **for any finite** P
  - The thermostat knows nothing about the necklace, only knows the frequency of each mode. So we are trying to find $c_{qq}(\omega)$ such that

$$\frac{1}{P} \sum_{k=0}^{P-1} c_{qq}(\omega_k) = \frac{\hbar}{2\omega} \coth \frac{\hbar\omega}{2k_B T}$$

  - ω_k depends from the physical frequency ω. This functional equation can be solved iteratively by casting it as a fixed-point iteration for c_{qq}, exploiting the fact that $\omega_0 = \omega$

$$c_{qq}(\omega) = \frac{\hbar P}{2\omega} \coth \frac{\hbar\omega}{2k_B T} - \sum_{k=1}^{P-1} c_{qq}(\omega_k)$$

Ceriotti, Manolopoulos, Parrinello, JCP 2011