A novel framework for enhanced molecular dynamics based on the generalized Langevin equation

Michele Ceriotti

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- Simulation of the trajectories of a system at the atomic level
  - Hamilton's equation (classical dynamics)
  - Model of the interatomic potential (force field/ab initio)

$$\dot{\mathbf{q}} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}}, \qquad \dot{\mathbf{p}} = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}} = -\frac{\partial V}{\partial \mathbf{q}}$$

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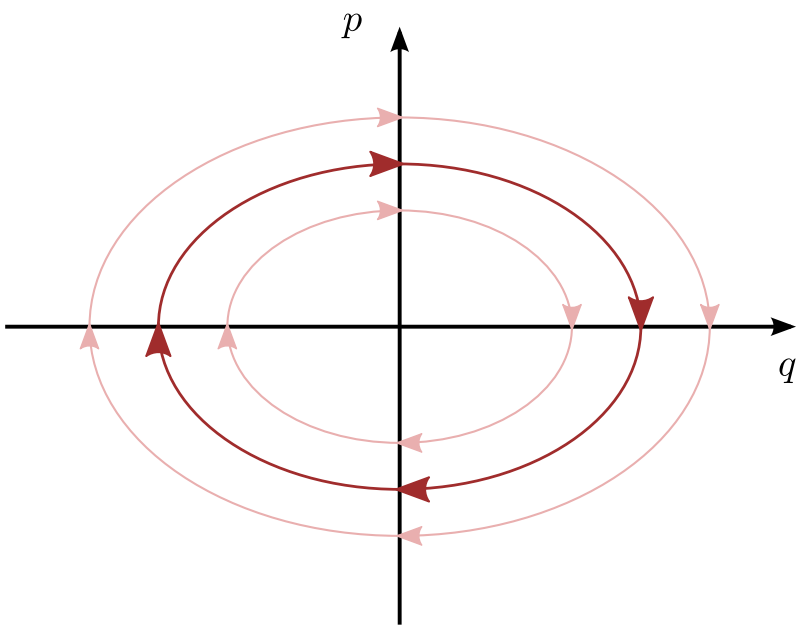

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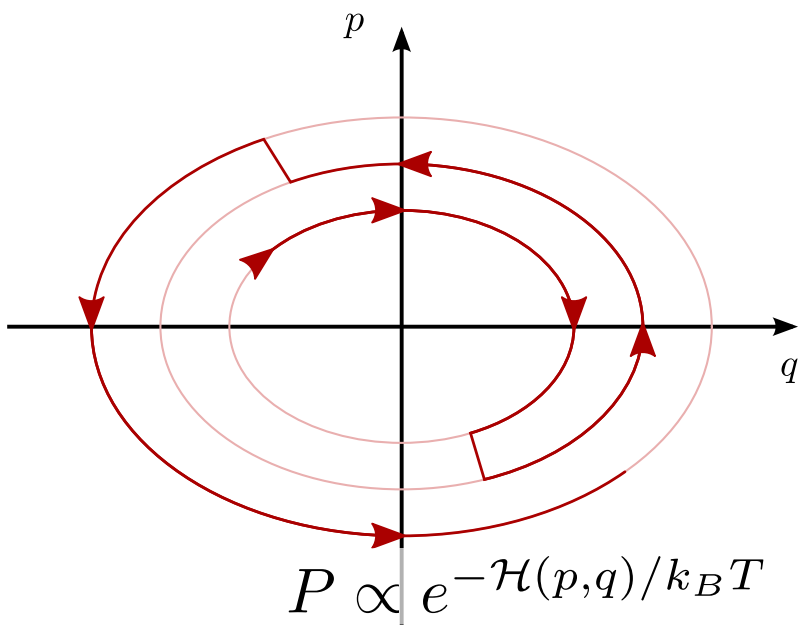

Langevin dynamics

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- Originally, physical model for Brownian motion containing a viscous friction and noisy force term

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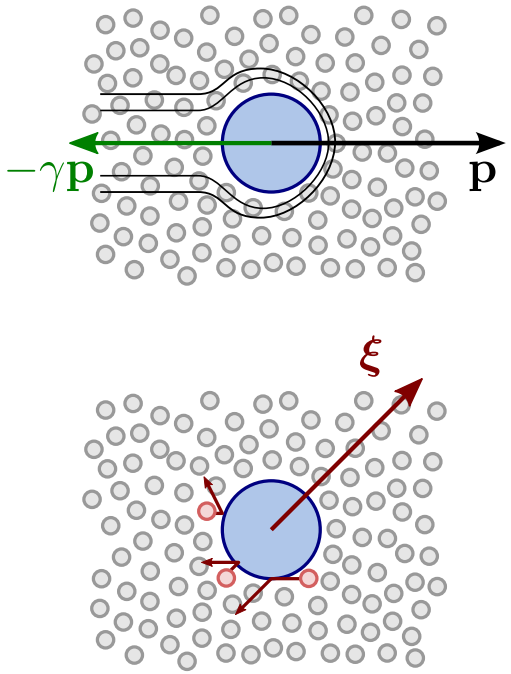

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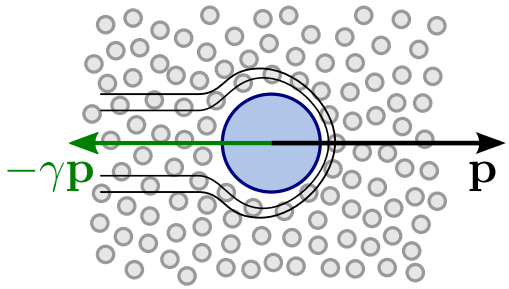
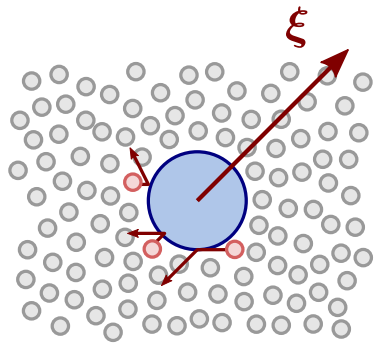
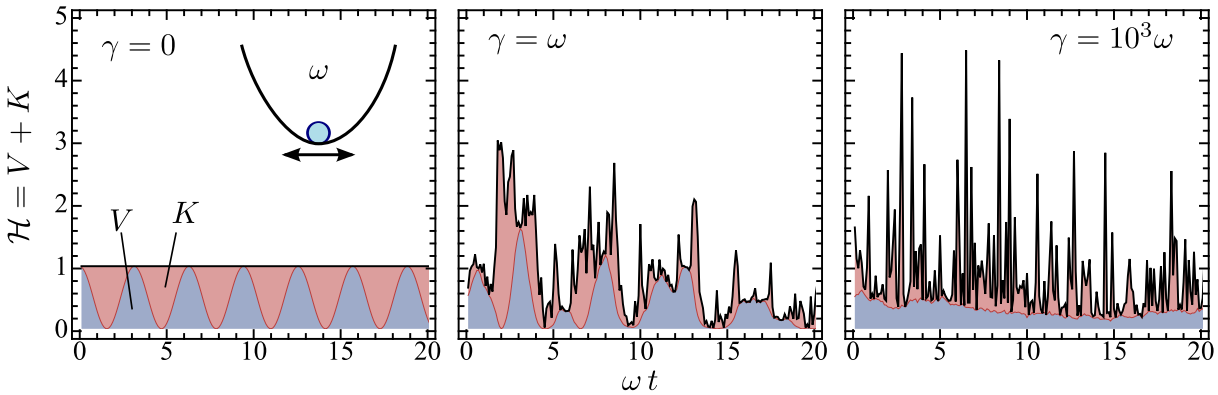
- Used routinely in MD simulations to achieve canonical sampling: how efficient?







Sampling efficiency depends on γ!

- The Langevin equation: a Markovian stochastic differential equation for the momenta

$$\dot{p}(t) = -\gamma p(t) + \sqrt{2m\gamma T}\xi(t), \ \langle \xi(t)\xi(0)\rangle = \delta(t)$$

Colored-noise Langevin equation

- The Langevin equation: a Markovian stochastic differential equation for the momenta
- What if one considers a **non-Markovian** equation?

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

Details of the noise **dramatically change dynamics!**

The trajectories of a particle subject to white and colored-noise LE with the same diffusion coefficient yield very different short-times behavior.

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- Non-Markovian generalized Langevin equations are used in many contexts as a physical model
  - Can we exploit the flexibility to manipulate the sampling properties of a molecular dynamics trajectory?
  - Can we make it as general and "user-friendly" as possible?

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- A large class of non-Markovian dynamics can be mapped onto a Markovian dynamics in an extended phase space

Non-Markovian GLE

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

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- The Markovian GLE corresponds to a (possibly complex) exponential memory kernel $K(t) = a_{pp}\delta(t) - \mathbf{a}_p^T e^{-\mathbf{A}t}\bar{\mathbf{a}}_p$

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- 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** $\dot{\mathbf{u}} = -\mathbf{A}\mathbf{u} + \mathbf{B}\boldsymbol{\xi}$ which can be solved analytically.

Predicting and fitting

- In the **harmonic limit**, exact propagator for the OU process:
  - Thanks to **rotational invariance**, response is the same when independent GLEs are applied to Cartesian coordinates or in normal mode representation!
- 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 $\mathbf{B}_p$

Optimal sampling...

- Measure statistical sampling efficiency by the correlation time, i.e. $\tau_{\mathcal{H}} = \int_0^\infty \langle H(t) H(0) \rangle \, \mathrm{d}t$
  - "Normalized" sampling efficiency $\kappa(\omega) = [\tau(\omega)\omega]^{-1}$

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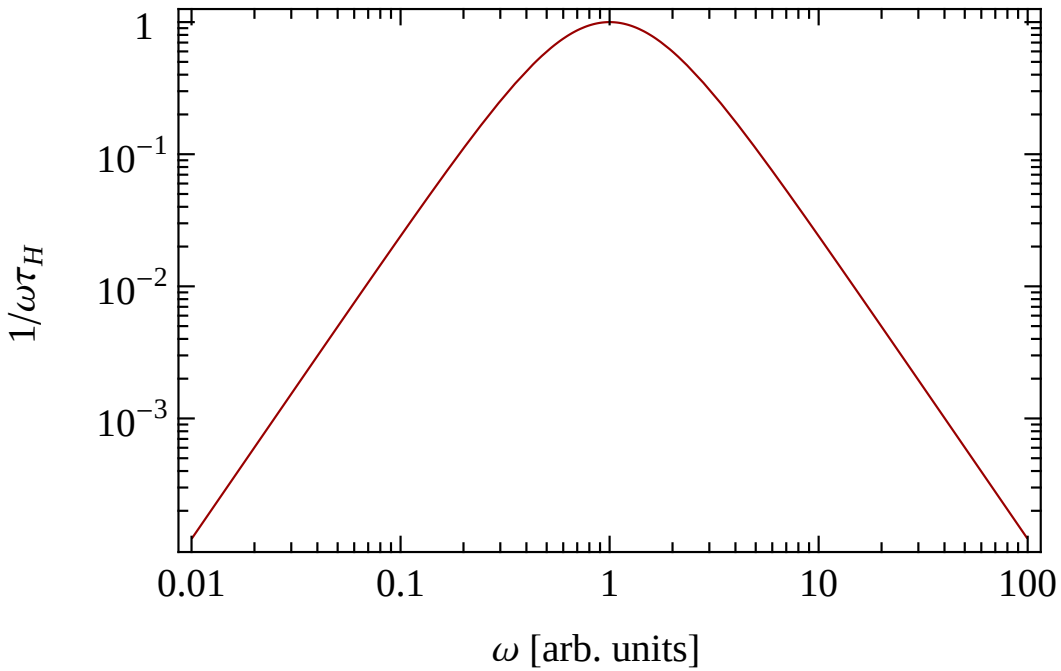
  - Severe degradation for $\omega \neq \omega_{opt}$: choice of γ?



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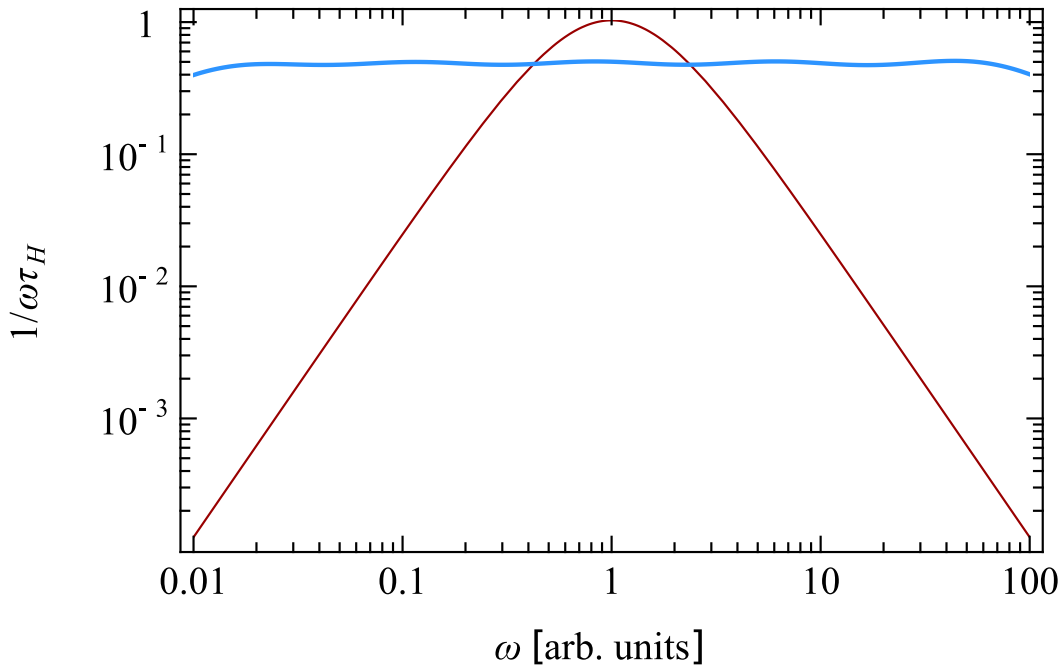

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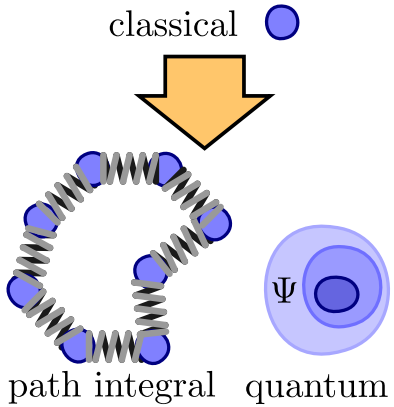
White noise ($\gamma = 0.1$) vs optimal sampling. Anisotropic 2D harmonic oscillator ($\omega_1 = 0.01$, $\omega_2 = 1$). Relaxation of probability density starting from δ.

- Path integral methods allow computing expectation values in quantum systems
  - Isomorphism between the quantum partition function and that of a classical ring polymer.
  - Many replicas of the system, corresponding particles connected by harmonic springs
- **Difficult sampling problem**: non-ergodic stiff modes together with the ones of the classical system



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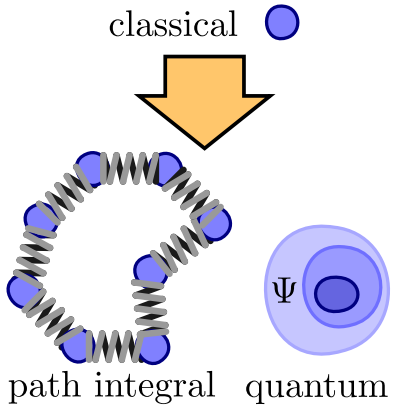

- **Difficult sampling problem**: non-ergodic stiff modes together with the ones of the classical system
- GLE allows to sample nearly-optimally the whole spectrum...
- ...hence, better sampling performance than white noise, for different observables

τ [ps]	WN	GLE
Kinetic En.	0.036	0.020
Potential En.	2.24	1.20
Cell dipole	32	14

... and much more!

- Application to **Car-Parrinello dynamics**
- Evaluate quantitatively the disturbance induced on dynamics
  - "η" parameter, based on the predicted smearing of the power spectrum
  - **Localize disturbance** on few normal modes

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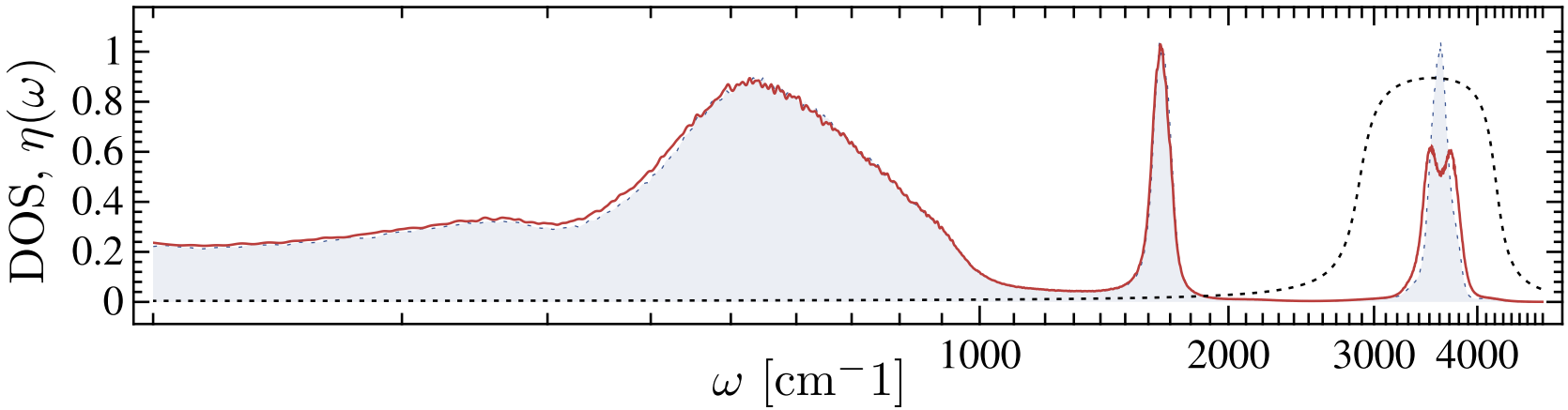

Comparison between NVE and "localized disturbance" power spectrum for liquid water.

- All applications so far had fluctuation-dissipation theorem satisfied,

$$\langle \zeta(t)\,\zeta(0)\rangle = TK(t)$$

- Simple non-eq. example: two thermostats at different temperature and different coupling curves

$T_1 \gg$

$T_2 \ll$

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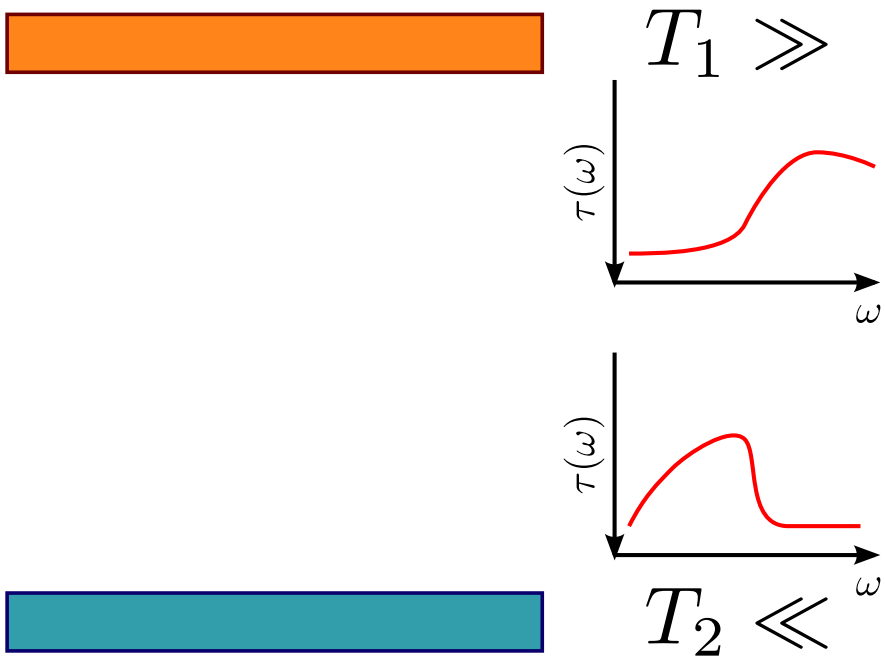

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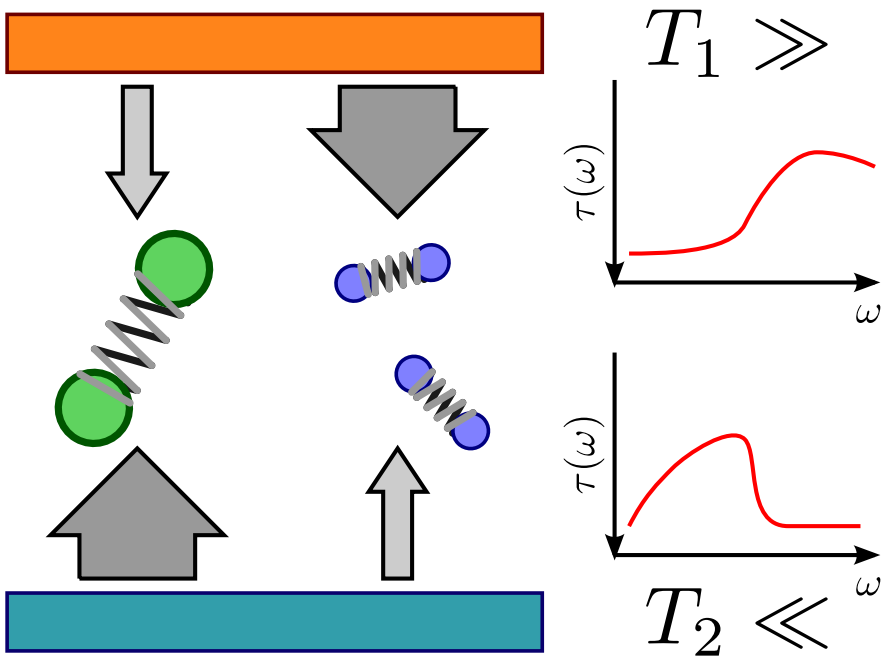

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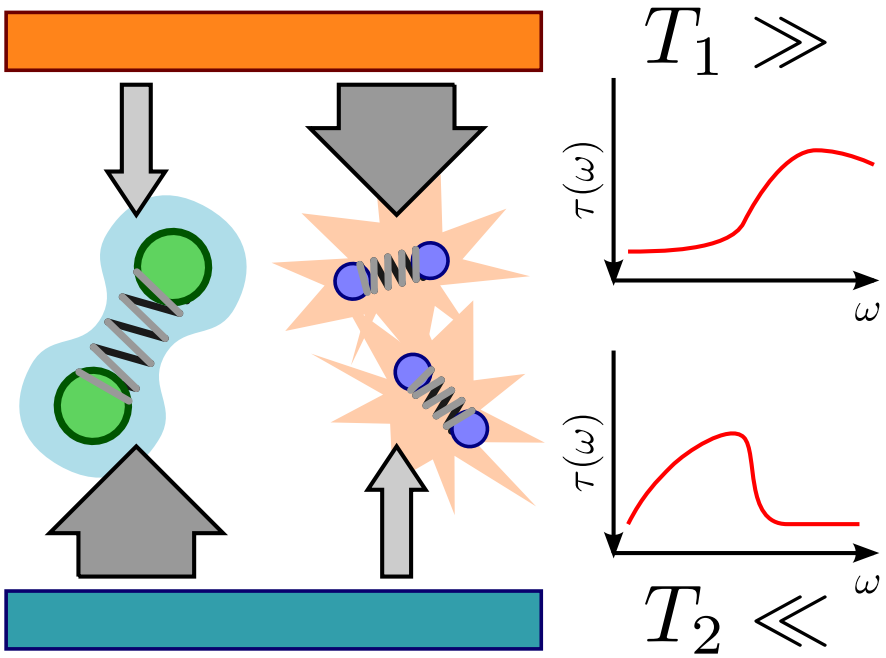
  - A steady state will be reached with frequency-dependent T



The δ-thermostat

- A simple application: the δ-thermostat
  - Thermalize the normal modes in a narrow frequency window, keep all the others frozen
  - No need to know normal modes in advance!
  - A stochastic vibrational spectroscopy and $\mathcal{O}(N)$ eigensolver

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.

The quantum thermostat

- The finite-temperature density for a quantum harmonic oscillator is a Gaussian, with a frequency and temperature dependent width
  - This is the same as a classical distribution at the effective temperature $T^\star(\omega) = (\hbar\omega/2k_B)\coth(\hbar\omega/2k_B T)$
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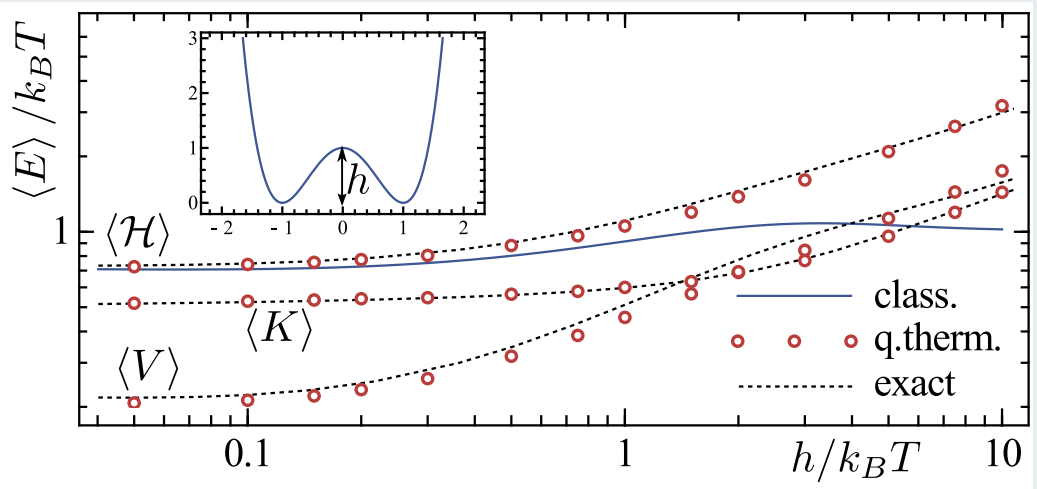
Quartic double well



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

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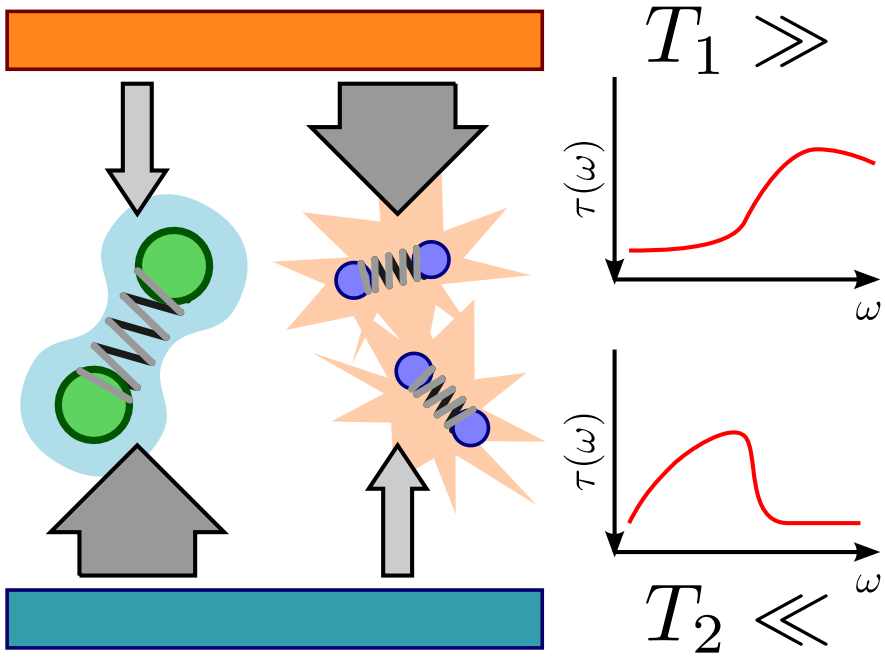
  - Works well also in anharmonic 1D examples
- The quantum thermostat costs as little as classical MD
  - $10\times$ to $100\times$ advantage over PI methods
- The momentum distribution can also be obtained

- A problem with multidimensional anharmonic systems



Anharmonicities and ZPE leakage

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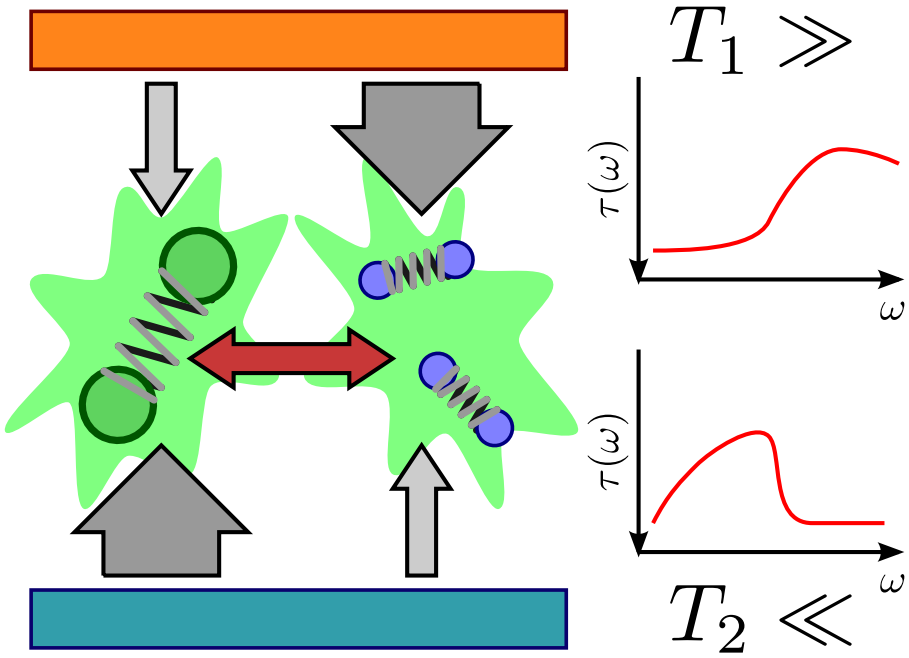

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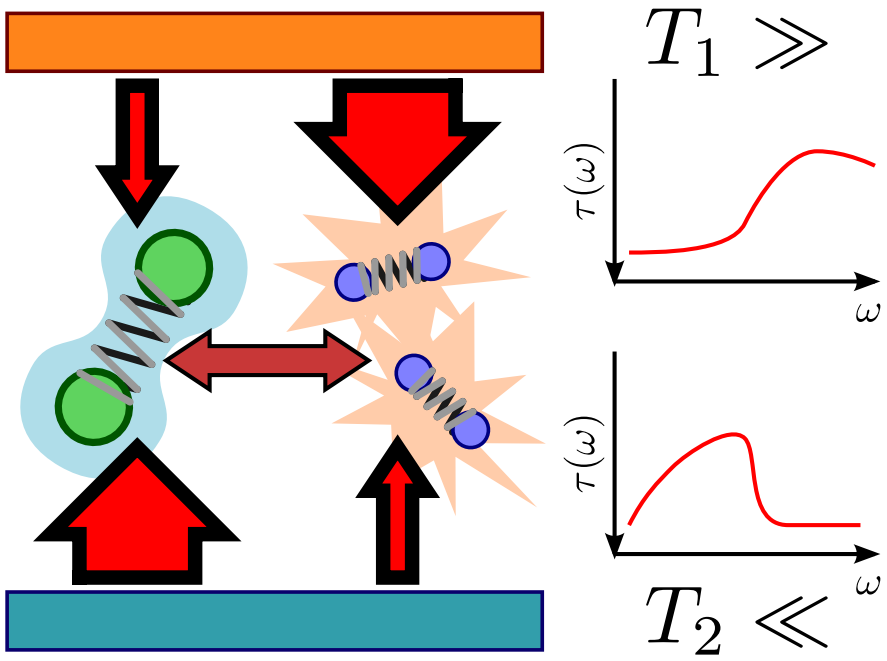

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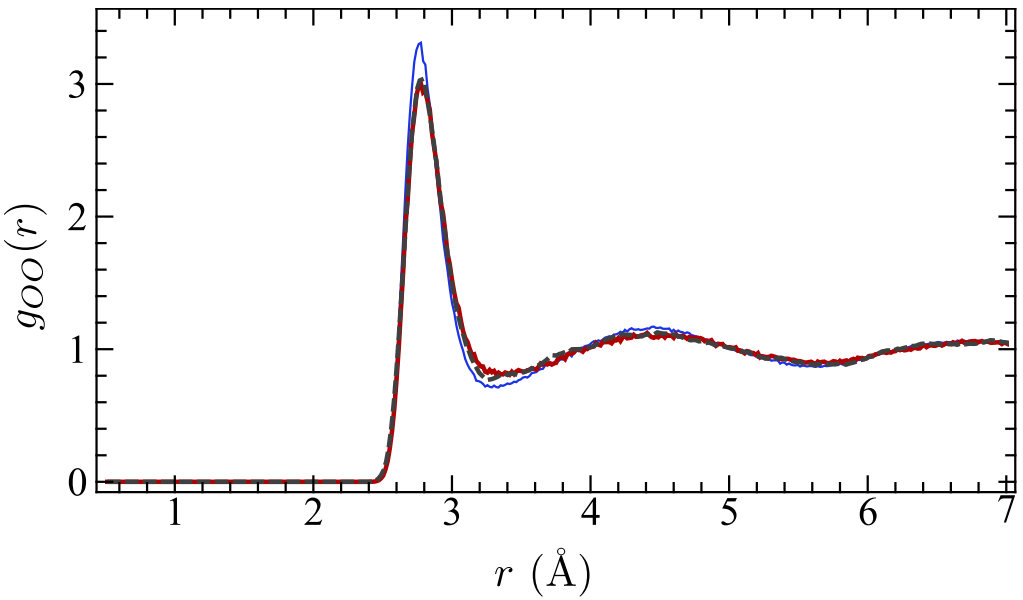

Oxygen-oxygen correlation function

Blue: classic MD, black: PIMD (exact), red: quantum thermostat.

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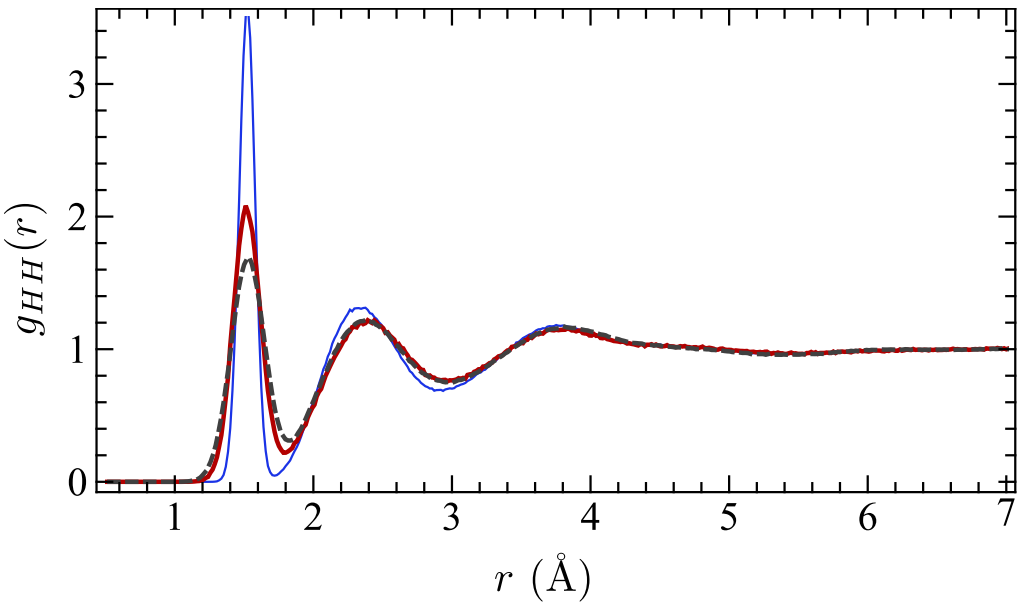

Hydrogen-hydrogen correlation function.

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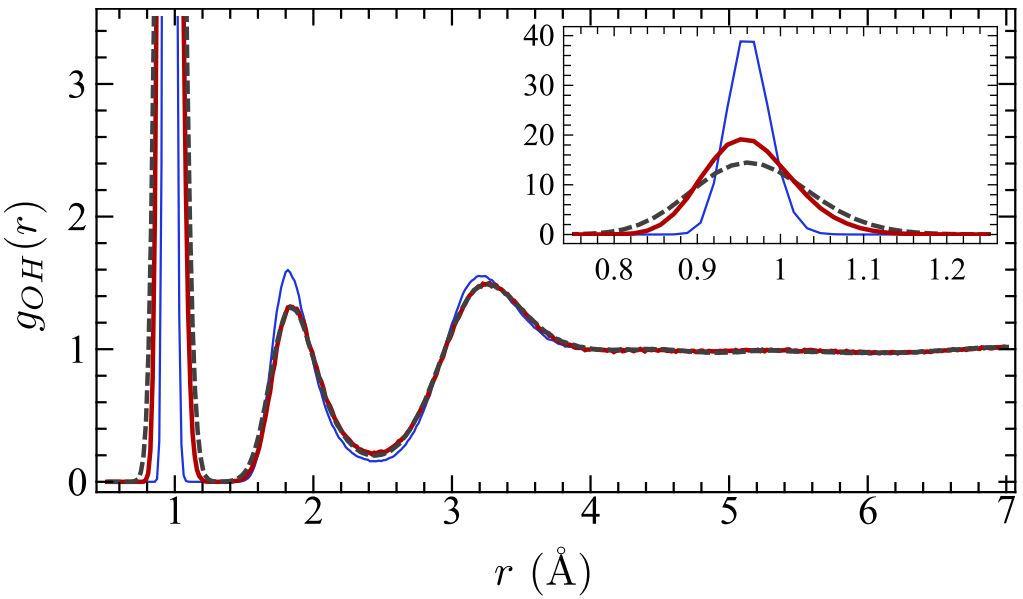

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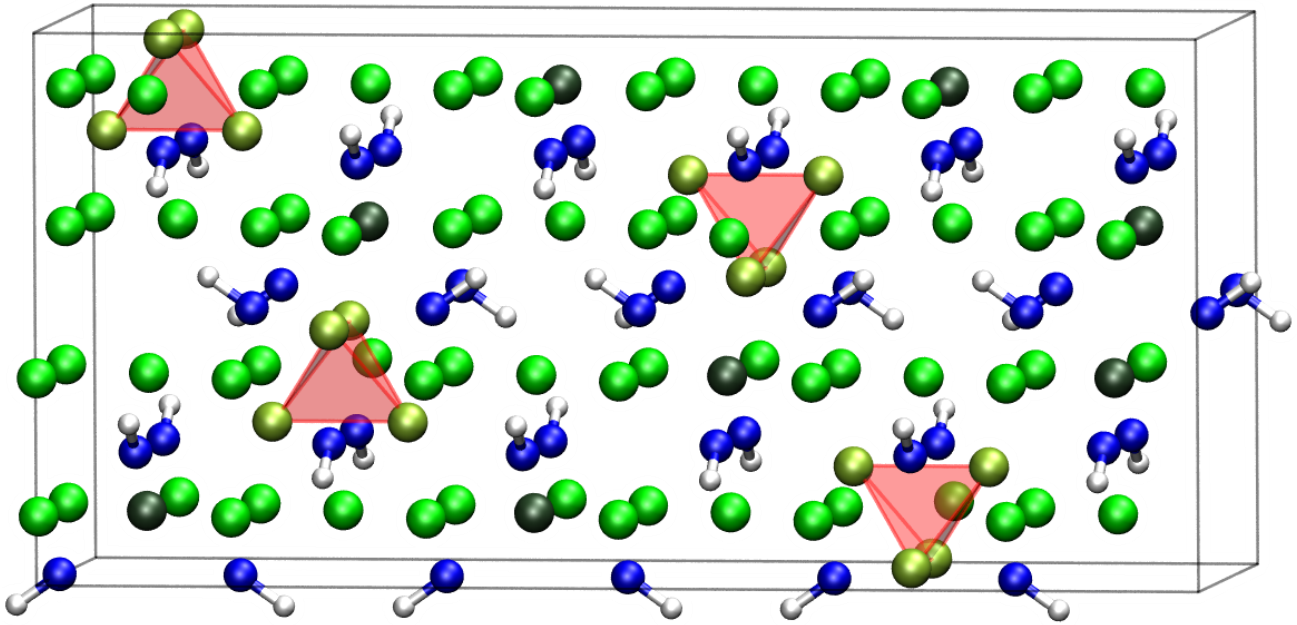
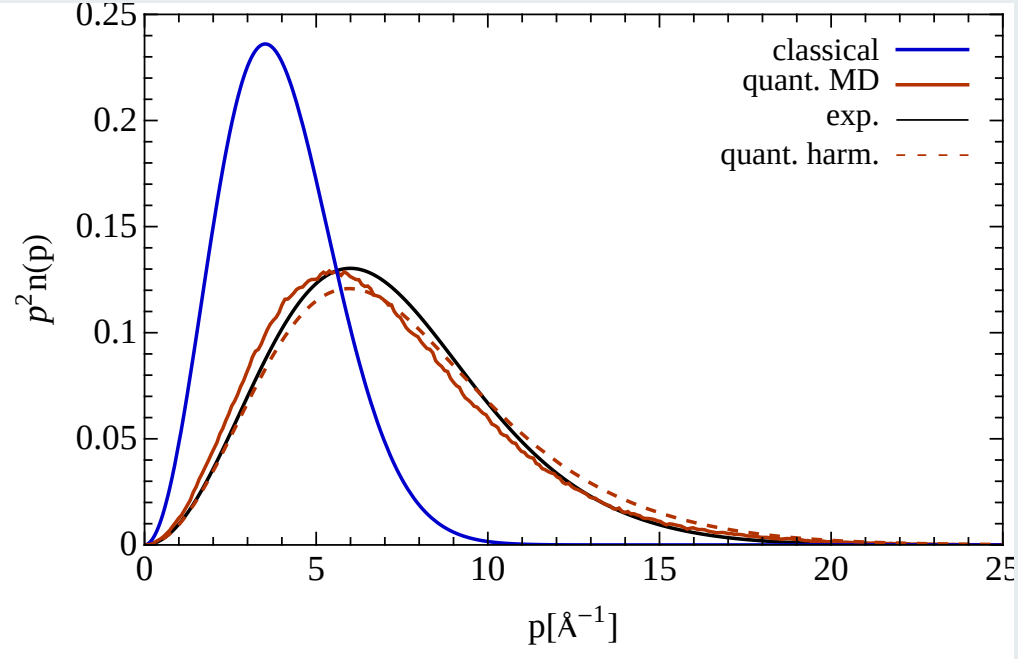
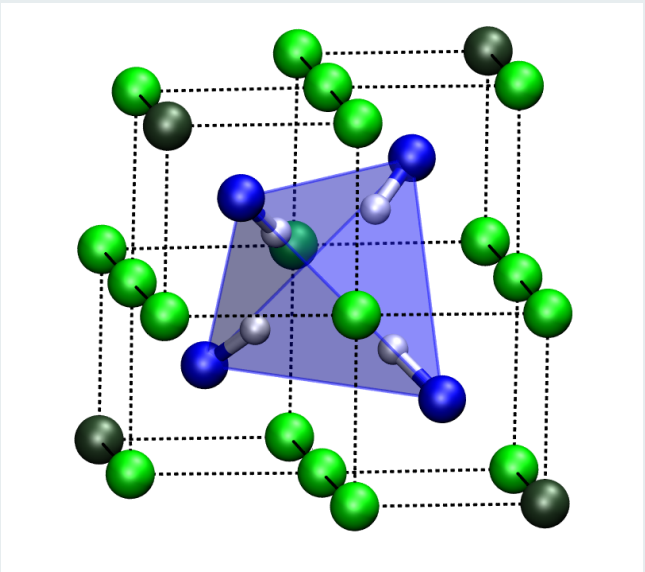


Quantum effects in lithium imide

- Ab initio analysis (no FF available), anharmonic system
- Non-Maxwellian momentum distribution is a purely quantum effect
  - Good agreement with inelastic neutron scattering experiments

Proton momentum distribution, theory & experiment





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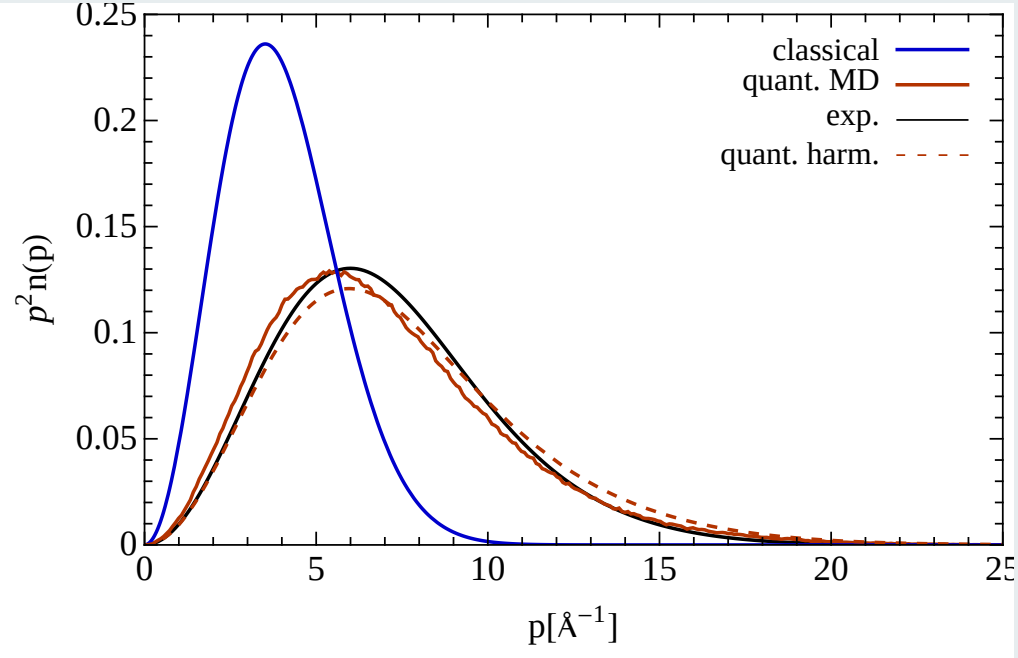

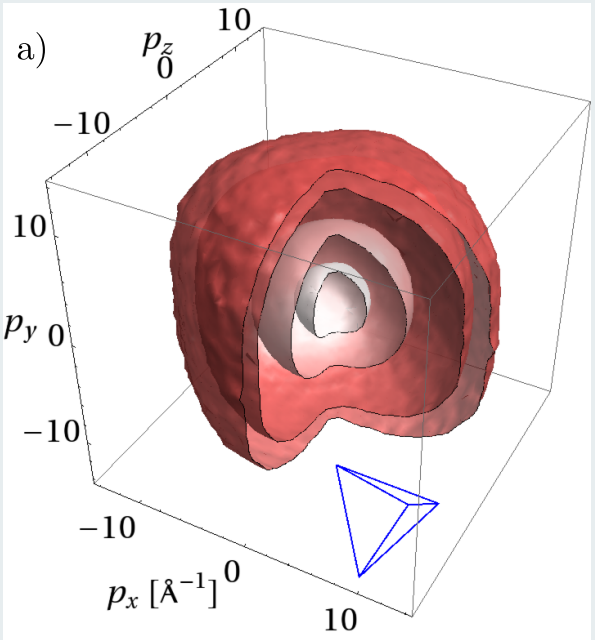

Conclusions

- Enhanced MD stochastic schemes based on GLEs
- Simple & robust: analytical predictions and fitting
- Flexible: many applications within the same framework
  - Canonical sampling (efficient, targeted, gentle on dynamics....)
  - Non-equilibrium GLE, unusual statistical ensembles (selected NM excitation, quantum thermostat)
- More to come: a long to-do list!
- A webpage with references, tutorials and sample code: **http://gle4md.berlios.de/**

Acknowledgments

- Michele Parrinello
- Giovanni Bussi
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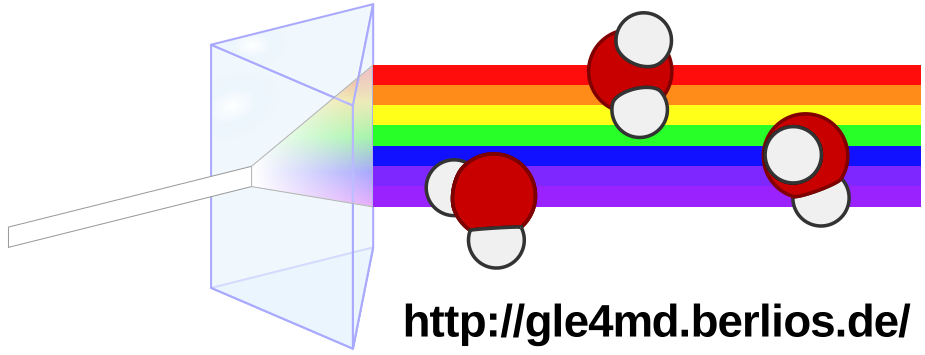
- Gareth Tribello
- Everyone @ RGP

THANKS!



http://gle4md.berlios.de/

- In a velocity-Verlet integrator, we can propagate stepwise the nonlinear (q, p) coupling, and treat $(p, \mathbf{s})$ exactly, using the free-particle propagator.

$$\dot{q} = p/m$$

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = \begin{pmatrix} f(q) \\ \mathbf{0} \end{pmatrix} - \mathbf{A} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\xi$$

Analytical propagator

- In a velocity-Verlet integrator, we can propagate stepwise the nonlinear (q, p) coupling, and treat $(p, \mathbf{s})$ exactly, using the free-particle propagator.
- We must then solve the forward Chapman-Kolmogorov equation, computing $P\left[(p, \mathbf{s}) ; \Delta t \middle| (p_0, \mathbf{s}_0) ; 0\right]$

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = -\mathbf{A} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\boldsymbol{\xi} \quad \Rightarrow \quad P\left[(p, \mathbf{s}), \Delta t \middle| (p_0; \mathbf{s}_0) ; 0\right]$$

- In a velocity-Verlet integrator, we can propagate stepwise the nonlinear (q, p) coupling, and treat $(p, \mathbf{s})$ exactly, using the free-particle propagator.
- We must then solve the forward Chapman-Kolmogorov equation, computing $P\left[(p, \mathbf{s}) ; \Delta t \middle| (p_0, \mathbf{s}_0) ; 0\right]$
- The distribution is Gaussian, so we can get the new position properly by knowing the new mean value and covariance matrix.

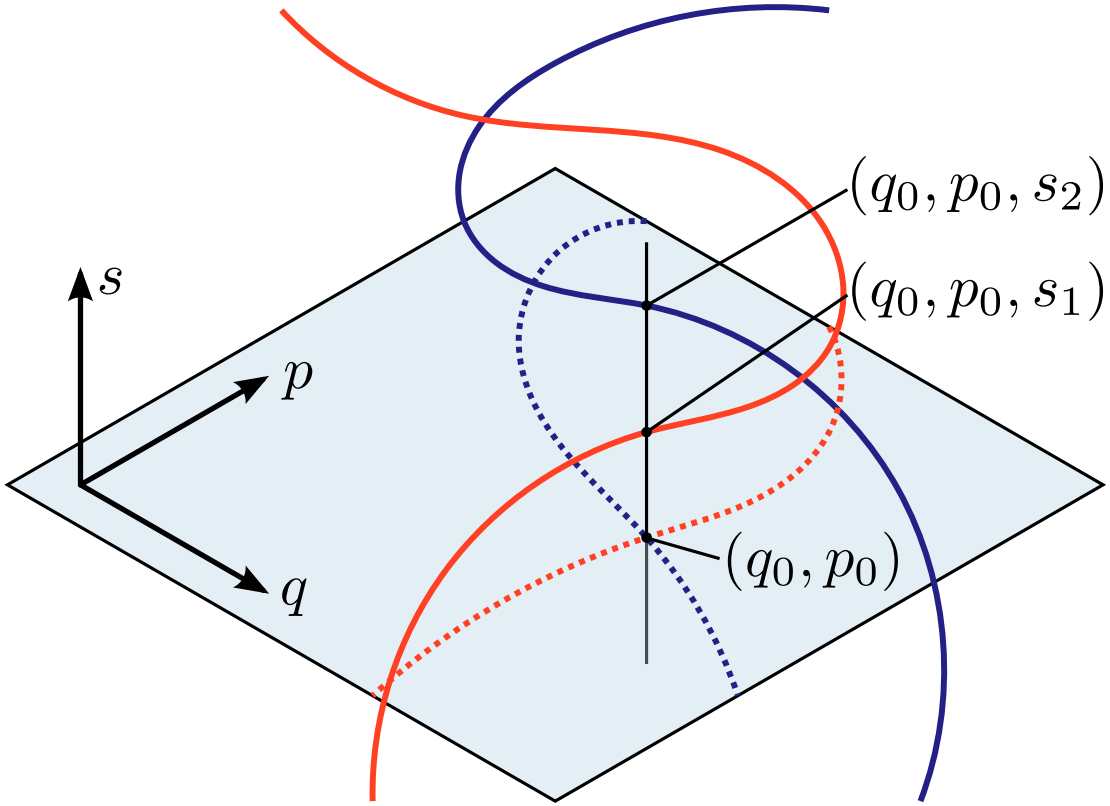
$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = -\mathbf{A} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\xi \quad \Rightarrow \quad P\left[(p, \mathbf{s}), \Delta t \middle| (p_0; \mathbf{s}_0) ; 0\right]$$

$$\Downarrow$$

$$\begin{pmatrix} p(t+\Delta t) \\ \mathbf{s}(t+\Delta t) \end{pmatrix} = \mathbf{T}(\Delta t) \begin{pmatrix} p(t) \\ \mathbf{s}(t) \end{pmatrix} + \mathbf{S}(\Delta t)\,\xi$$

$$\mathbf{T} = e^{-\Delta t \mathbf{A}} \qquad \mathbf{S}\mathbf{S}^T = mT\left[1 - \mathbf{T}\mathbf{T}^T\right]$$

- Markovian trajectories can be mapped to non-Markovian ones in a lower-dimensionality phase-space



- Consider the free-particle GLE in Markovian form

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = -\begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\boldsymbol{\xi}$$

- Consider the free-particle GLE in Markovian form
- Ansatz for the additional momenta, assuming $\mathbf{s}(-\infty) = 0$

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$$\Downarrow$$

$$\mathbf{s}(t) = \int_{-\infty}^{t} e^{-(t-t')\mathbf{A}} \left[-p(t')\,\bar{\mathbf{a}}_p + \mathbf{B}\boldsymbol{\xi}(t')\right] \mathrm{d}t'$$

- Consider the free-particle GLE in Markovian form
- Ansatz for the additional momenta, assuming $\mathbf{s}(-\infty) = 0$
- Verify that the original GLE is satisfied, and that one can write $\dot{p}$ in non-Markovian form

$$\begin{pmatrix} \dot{p} \\ \dot{\mathbf{s}} \end{pmatrix} = -\begin{pmatrix} a_{pp} & \mathbf{a}_p^T \\ \bar{\mathbf{a}}_p & \mathbf{A} \end{pmatrix} \begin{pmatrix} p \\ \mathbf{s} \end{pmatrix} + \mathbf{B}\boldsymbol{\xi}$$

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$$\Downarrow$$

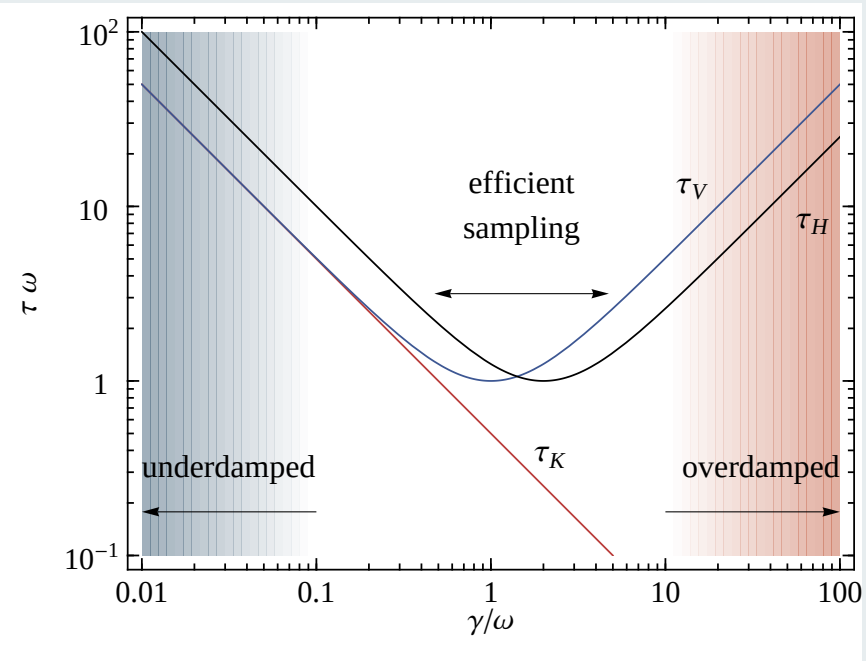
$$\dot{p} = \ldots = -\int_0^{\infty} K(t')\,p(t-t')\,\mathrm{d}t' + \sqrt{mT}\,\zeta(t)$$

$$K(t) = 2a_{pp}\delta(t) - \mathbf{a}_p^T e^{-|t|\mathbf{A}} \bar{\mathbf{a}}_p \qquad \zeta(t) = \ldots$$

Sampling by white noise

- Measure statistical sampling efficiency by the correlation time, i.e. $\tau_{\mathcal{H}} = \int_0^\infty \langle H(t)\, H(0)\rangle \, \mathrm{d}t$
- For white noise and harmonic potential, a simple closed-form expression can be found

White-noise correlation times



Correlation times of kinetic, potential and total energy:

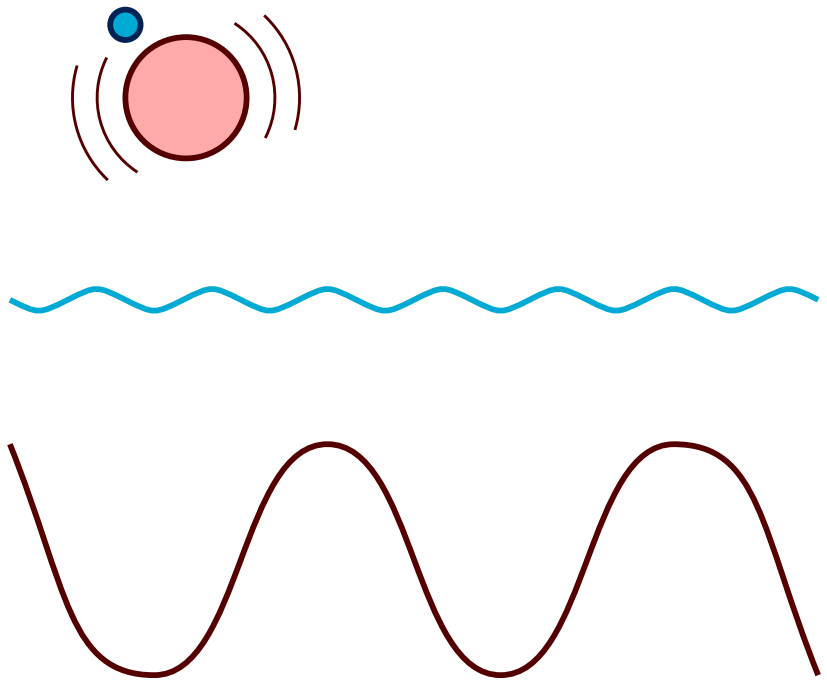
$$\tau_K = 1/2\gamma$$

$$\tau_V = 1/2\gamma + \gamma/2\omega^2$$

$$\tau_{\mathcal{H}} = 1/\gamma + \gamma/4\omega^2$$

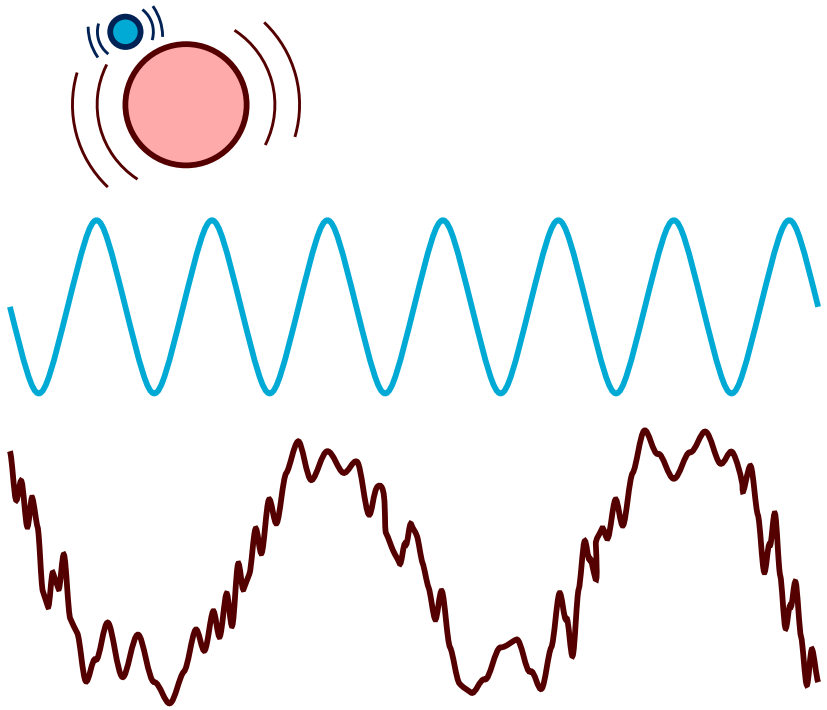
- Based on adiabatic separation: fast modes must remain cold

CPMD

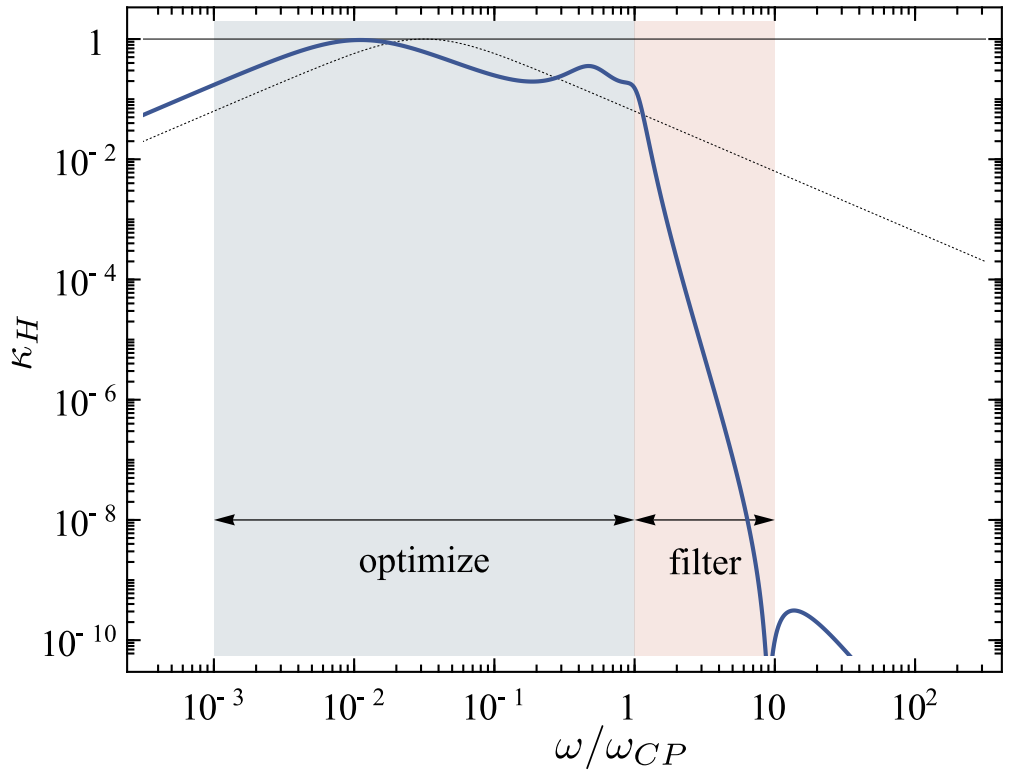


- Based on adiabatic separation: fast modes must remain cold
  - White noise quickly disrupts adiabatic behavior.

CPMD + noise



- Based on adiabatic separation: fast modes must remain cold
  - White noise quickly disrupts adiabatic behavior.
  - With GLE one can enforce *loose* coupling, and at the same time optimize sampling for ions



Response curve for a GLE fitted for CPMD

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  - White noise quickly disrupts adiabatic behavior.
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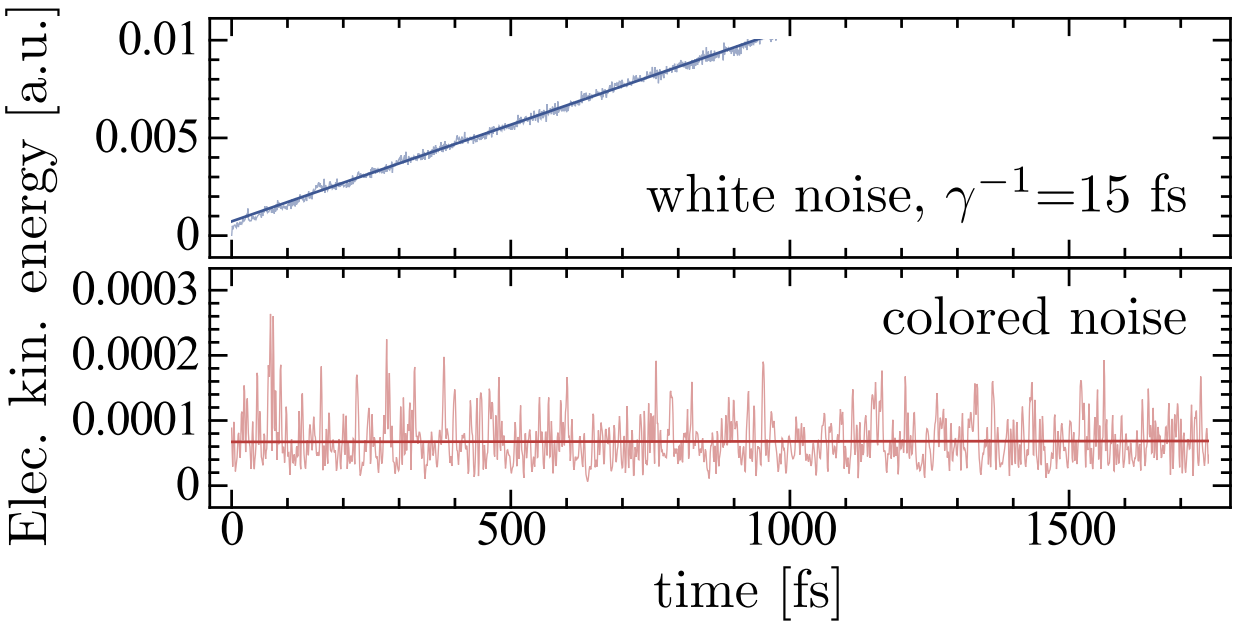
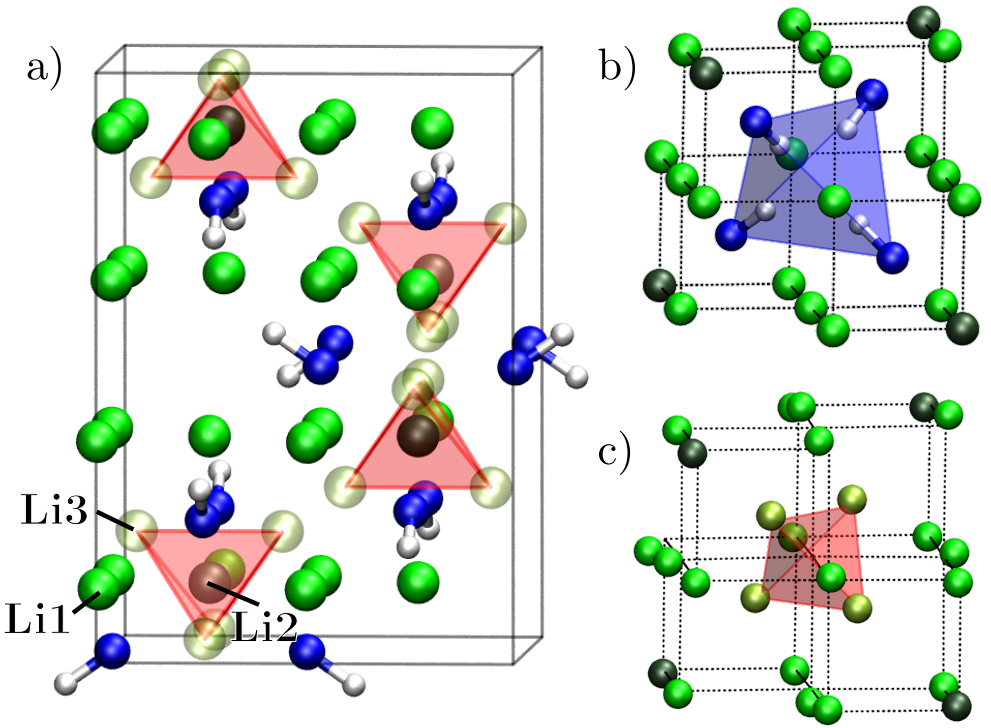


Drift of electronic temperature, white noise vs GLE (a water molecule in vacuum)

- Partially disordered structure with fractional occupations.
  - Intrinsic Li vacancies coordinated by imide groups
  - Tetrahedral clusters of interstitials key to explain local structure



Lithium imide: anharmonicity

- Strongly anharmonic system
  - Librations of NH groups.
  - Quasi-harmonic description is inadequate
  - Pronounced quantum effects on hydrogens

Distribution of hydrogens