Statistical methods in Atomistic Computer Simulations

2. Thermostats and Langevin dynamics

Michele Ceriotti

MSE 639 - EPFL - EDMX

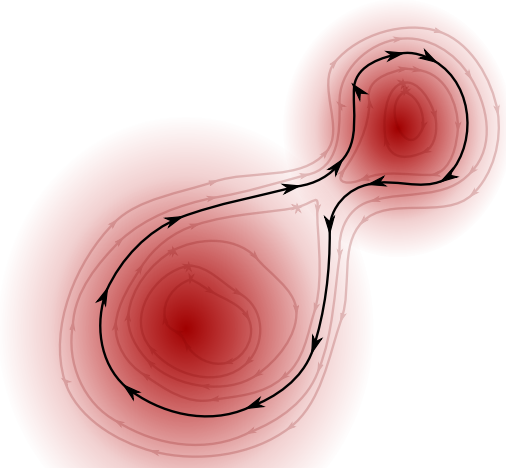
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Outline

1. Sampling the canonical ensemble in atomistic simulations: Monte Carlo, correlation functions, ergodicity
2. Thermostatting MD efficiently: white and colored-noise Langevin dynamics
3. Rare events: transition state theory and the transition state ensemble
4. Statistical re-weighting, biased sampling, metadynamics
5. Linear and non-linear dimensionality reduction: determining automatically order parameters

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

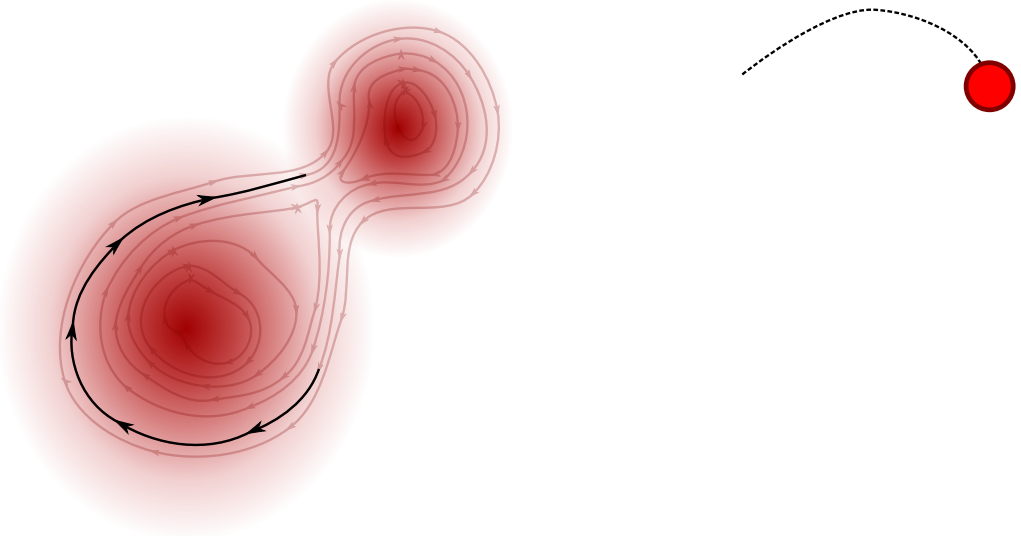


$$dH/dt = 0$$

Andersen, J. Chem. Phys. 1980

Constant-temperature molecular dynamics

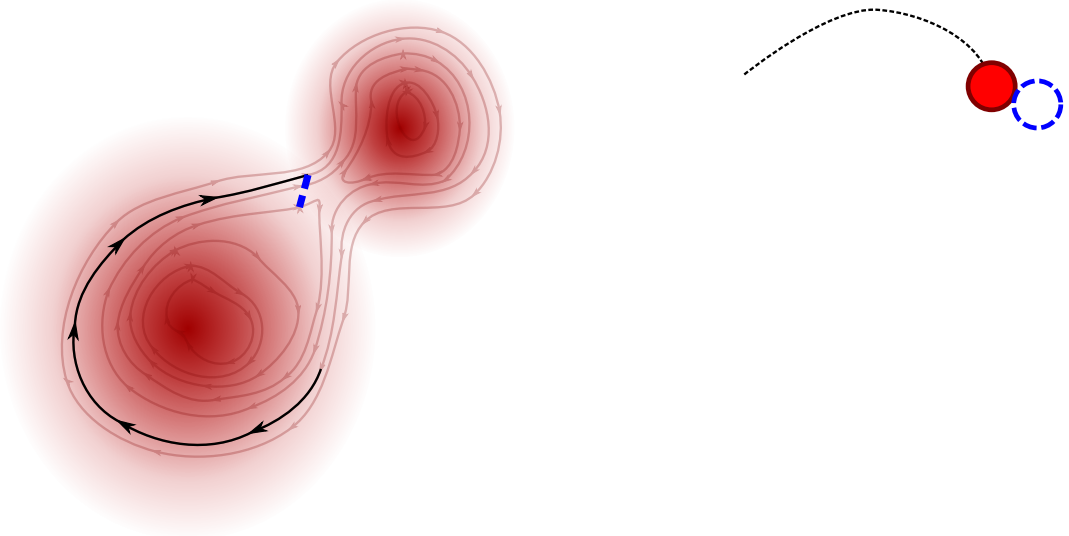
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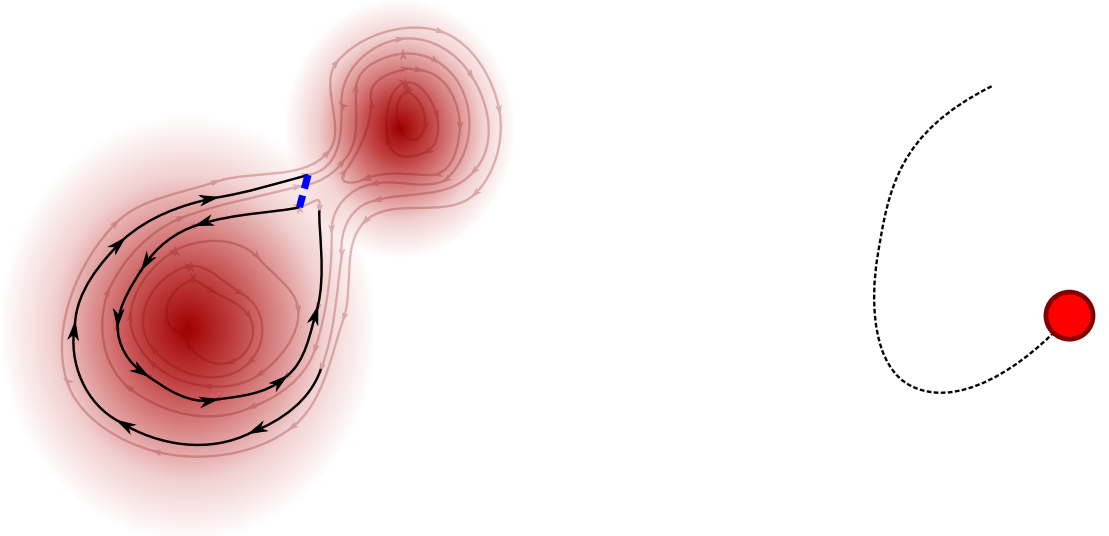
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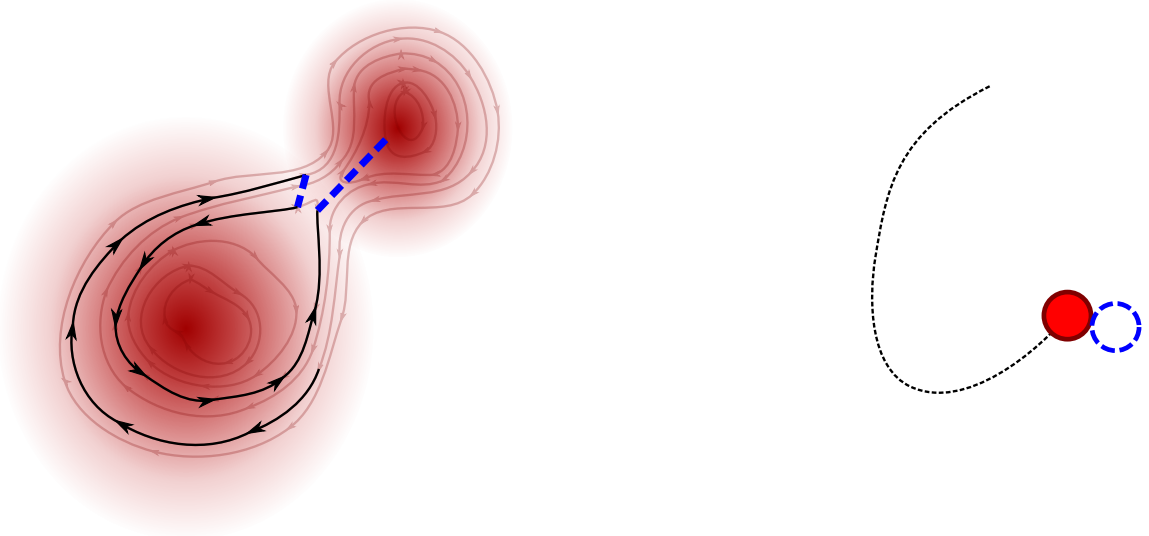
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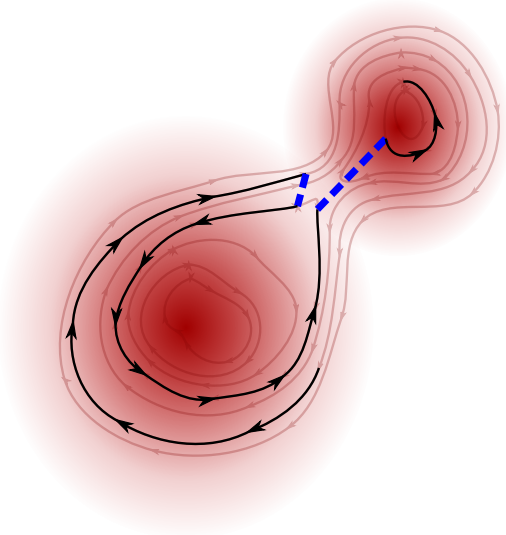
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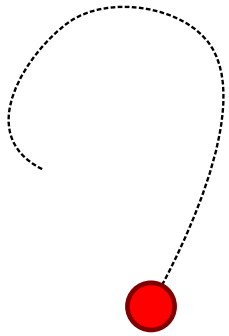


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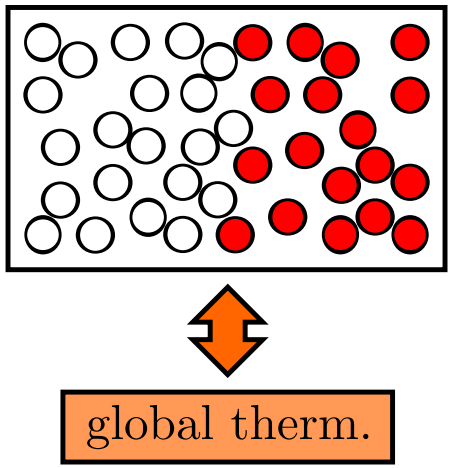
Getting a conserved quantity

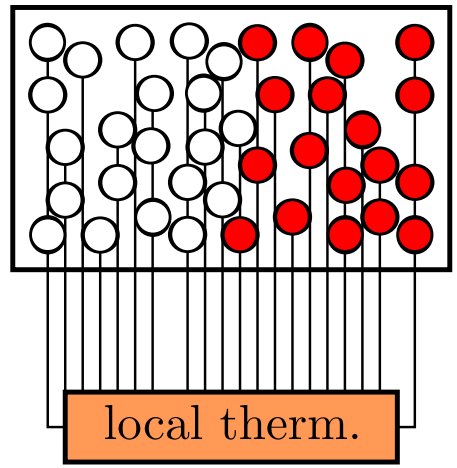
- Having a conserved quantity is handy to monitor integration
- Thermostats implement ergodic canonical sampling, so total energy fluctuates
- Very general solution: keep track of the heat flow to the bath
  - Compute kinetic energy before and after the thermostat, K_0 and K_f
  - Accumulate $\Delta H \leftarrow \Delta H + K_0 - K_f$
  - 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, 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)





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

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

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

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

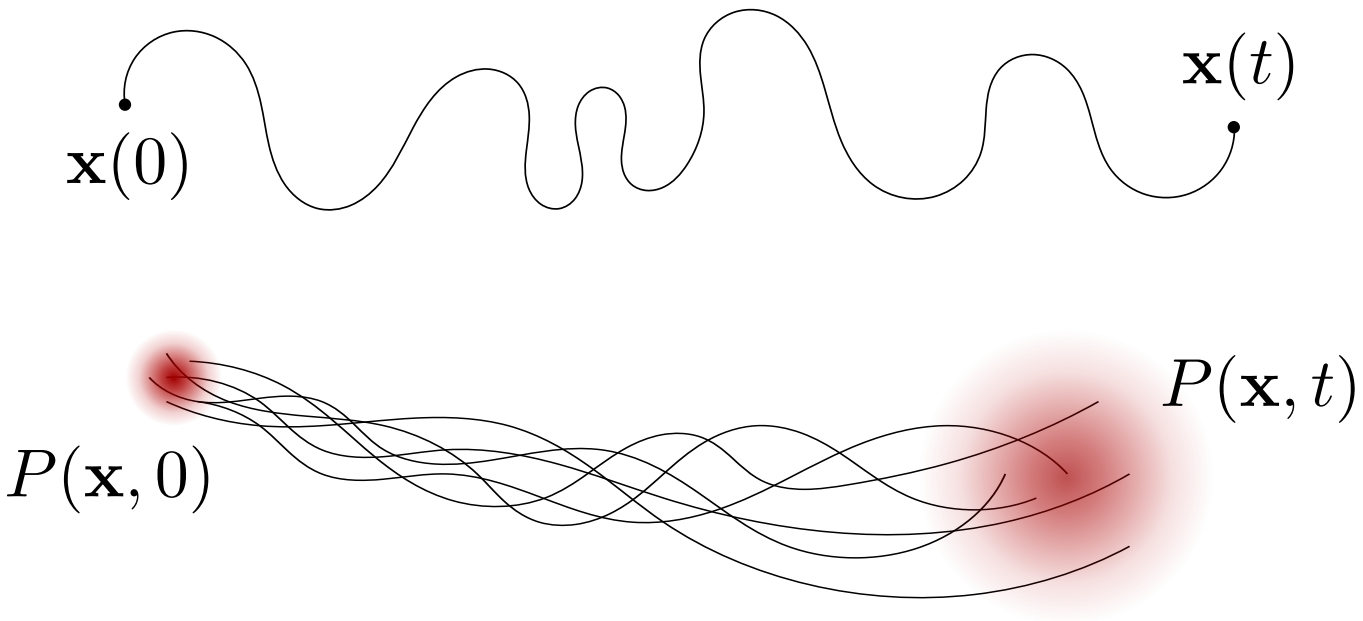
  - Ergodic, very natural model for coupling to a heat bath
  - Linear equations, very stable and easy to integrate
  - Require some care with the random number generator (parallelism!)

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

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



Sample paths and probabilistic descriptions

- Assume we have an ensemble of trajectories labeled by an index ω. We can understand *some* of the physics based on a probability distribution that evolves in time $P(\mathbf{x}, t) \propto \int \delta(\mathbf{x}_\omega(t) - \mathbf{x})\, \mathrm{d}\omega$
- More information is contained in *joint* probability distributions, that look at the position at different times

$$P(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) \propto \int \delta(\mathbf{x}_\omega(t_1) - \mathbf{x}_1)\, \delta(\mathbf{x}_\omega(t_2) - \mathbf{x}_2)\, \mathrm{d}\omega$$

  - **Stationary** assumption: P only depends on time differences $P(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) = P(\mathbf{x}_1, t_1 - t_2; \mathbf{x}_2, 0)$
  - Conditional probability $P(\mathbf{x}_1, t_1 | \mathbf{x}_2, t_2) = P(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) / P(\mathbf{x}_2, t_2)$
  - **Markovian** assumption: conditional probabilities only depend on most recent time $P(\mathbf{x}_1, t_1; \ldots; \mathbf{x}_k, t_k | \mathbf{x}_{k+1}, t_{k+1}; \ldots; \mathbf{x}_n, t_n) = P(\mathbf{x}_1, t_1; \ldots; \mathbf{x}_k, t_k | \mathbf{x}_{k+1}, t_{k+1})$
  - The two-point conditional probability determines completely a Markovian stationary process.

Liouville equation and Newtonian MD

- In the deterministic case $b(x,t) = 0$. We want to relate

$$\dot{x} = a(x,t) \quad \text{and} \quad \frac{\partial}{\partial t} P(x,t|x_0,t_0) = -\frac{\partial}{\partial x}\left[a(x,t)\,P\right]$$

  - Take a test function $f(x)$ and define $\langle \square \rangle = \int \mathrm{d}x\, \square\, P(x,t|x_0,0)$.

$$\frac{\partial}{\partial t} f(x) = f'(x)\,\dot{x} = f'(x)\,a(x,t)$$

  - Integrating the right-hand side gives (integrating by parts)

$$\int \mathrm{d}x\, f'(x)\,a(x,t)\,P(x,t|x_0,0) = -\int \mathrm{d}x\, f(x)\,\frac{\partial}{\partial x}\left[a(x,t)\,P(x,t|x_0,0)\right]$$

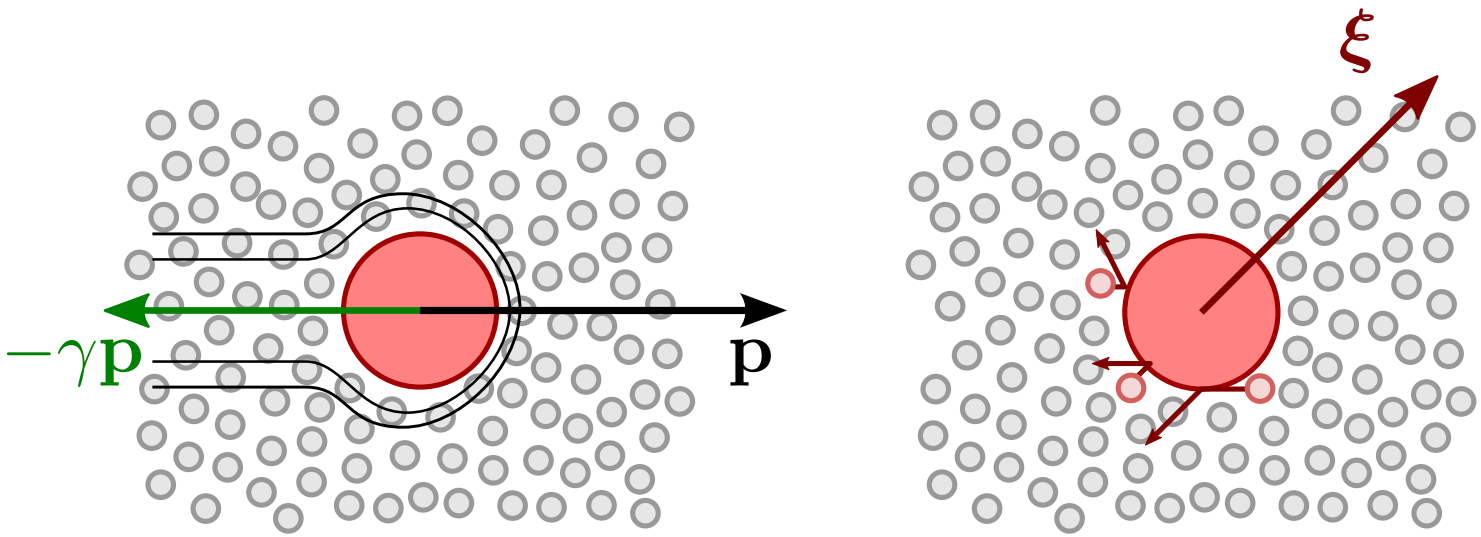
  - Exchanging derivative and integral on the left side one gets

$$\frac{\partial}{\partial t}\langle f(t)\rangle = \int \mathrm{d}x\, f(x)\,\frac{\partial}{\partial t} P(x,t|x_0,0)$$

The Langevin equation

- **Langevin equation**: modify Newton's equations with a viscous friction and white-noise force term.

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



Free-particle Langevin dynamics

$$\dot{p} = -\gamma p + \sqrt{2m\gamma/\beta}\xi, \quad \dot{P}(p,t|p_0,0) = \gamma \frac{\partial}{\partial p}(pP) + \frac{m\gamma}{\beta}\frac{\partial^2 P}{\partial p^2}$$

- Find the stationary probability distribution for $\dot{P} = 0$: Boltzmann!

$$\frac{\partial P}{\partial p} = -\frac{\beta}{m} pP \qquad \Rightarrow \qquad P(p) \propto e^{-\beta \frac{p^2}{2m}}$$

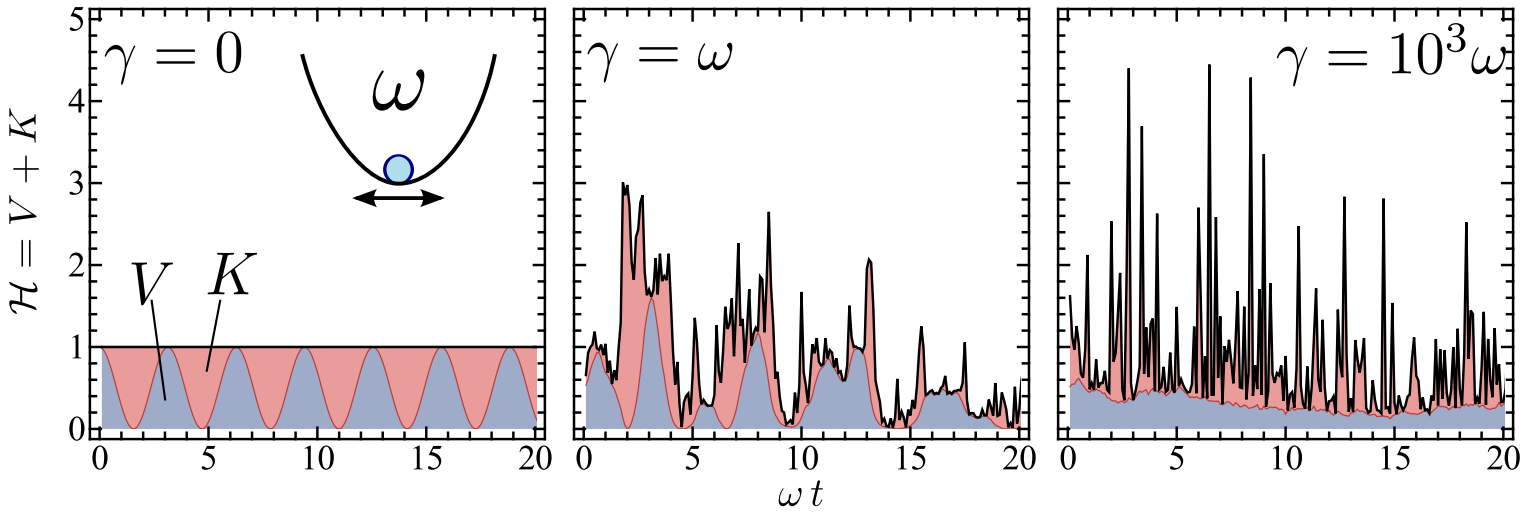
- Solution of the FP equation: still a Gaussian, with time-dependent width

$$P(p,t|p_0,0) \propto \exp -\frac{\beta}{2m} \frac{\left(p - p_0 e^{-\gamma t}\right)^2}{\sqrt{1 - e^{-2\gamma t}}}$$

  - This provides a very simple finite-time propagator:

$$p(t) = e^{-\gamma t} p(0) + \sqrt{m/\beta}\sqrt{1 - e^{-2\gamma t}}\xi, \quad \langle \xi \rangle = 0, \langle \xi^2 \rangle = 1$$

Langevin dynamics for a harmonic oscillator



What is the optimal friction γ for a Langevin dynamics to sample phase space for a Harmonic oscillator of frequency ω?

Langevin dynamics for a harmonic oscillator

- The force is linear in q, so the dynamics can be cast as a linear SDE

$$\begin{pmatrix}\dot{q}\\ \dot{p}\end{pmatrix} = -\begin{pmatrix}0 & -m^{-1}\\ m\omega^2 & \gamma\end{pmatrix}\begin{pmatrix}q\\ p\end{pmatrix} + \begin{pmatrix}0 & 0\\ 0 & \sqrt{2m\gamma/\beta}\end{pmatrix}\begin{pmatrix}0\\ \xi\end{pmatrix} = -\mathbf{A}\begin{pmatrix}q\\ p\end{pmatrix} + \mathbf{B}\begin{pmatrix}0\\ \xi\end{pmatrix}$$

  - Stationary probability distribution: Boltzmann!
    $P(q,p) \propto \exp -\beta (q,p)\,\mathbf{C}^{-1}\,(q,p)^T/2$, $C_{pp} = m/\beta$, $C_{qq} = 1/m\beta\omega^2$, $C_{qp} = C_{pq} = 0$
  - Finite-time propagator:

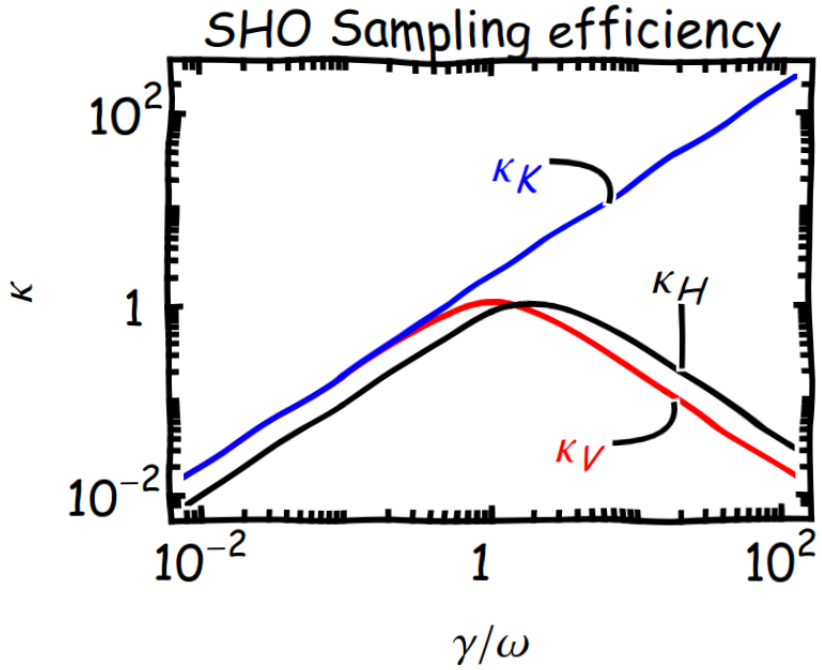
$$\begin{pmatrix}q(t)\\ p(t)\end{pmatrix} = \mathbf{T}(t)\begin{pmatrix}q(0)\\ p(0)\end{pmatrix} + \mathbf{S}(t)\begin{pmatrix}0\\ \xi\end{pmatrix},\ \mathbf{T} = e^{-\mathbf{A}t},\ \mathbf{SS}^T = \mathbf{C} - \mathbf{TCT}^T$$

  - Can use this result to obtain any correlation function. Correlation functions for q^2 and p^2 are quite complicated, but one can eventually get simple expressions for the correlation times:

$$\tau_V = \frac{1}{\gamma} + \frac{\gamma}{\omega^2}, \quad \tau_K = \frac{1}{\gamma}, \quad \tau_H = \frac{2}{\gamma} + \frac{\gamma}{2\omega^2}$$

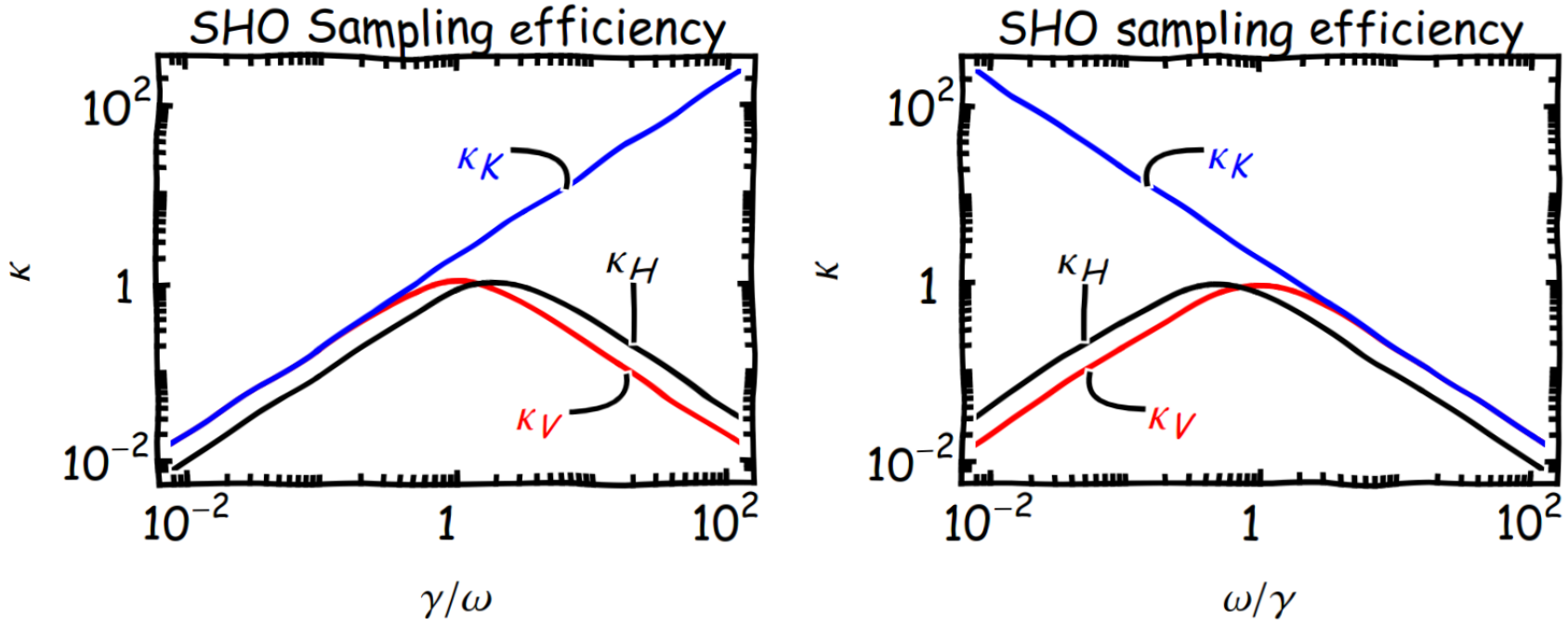
Sampling efficiency of Langevin dynamics

- 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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Colored-noise Langevin dynamics

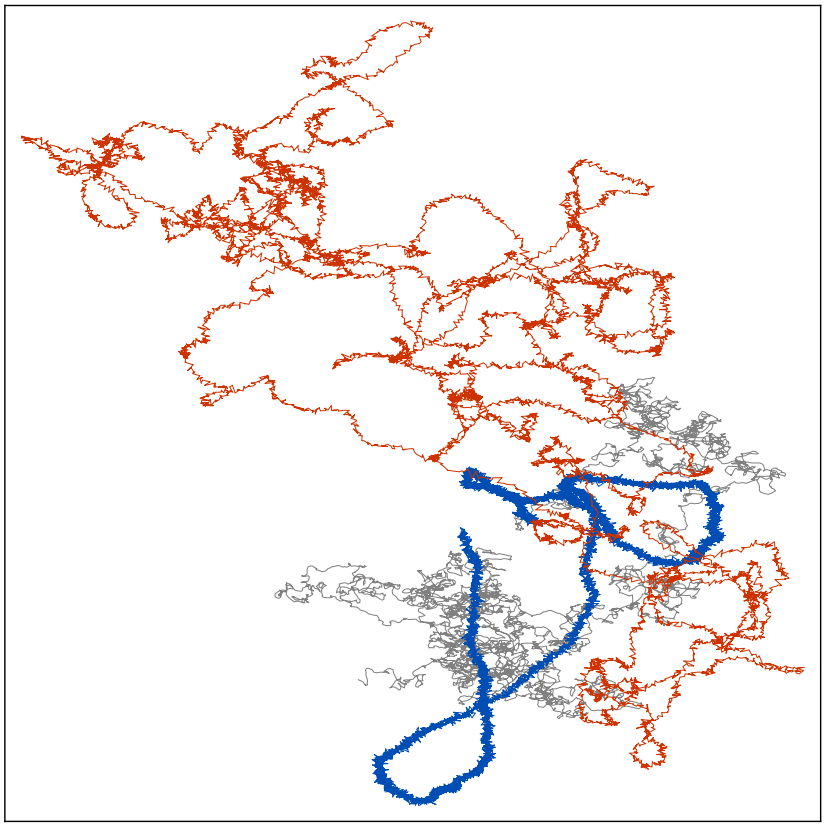
- The Langevin equation is Markovian: $\dot{p}(t)$ only depends on $p(t)$
- Can we generalize to a non-Markovian generalized Langevin equation?

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

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



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.

Colored-noise Langevin dynamics

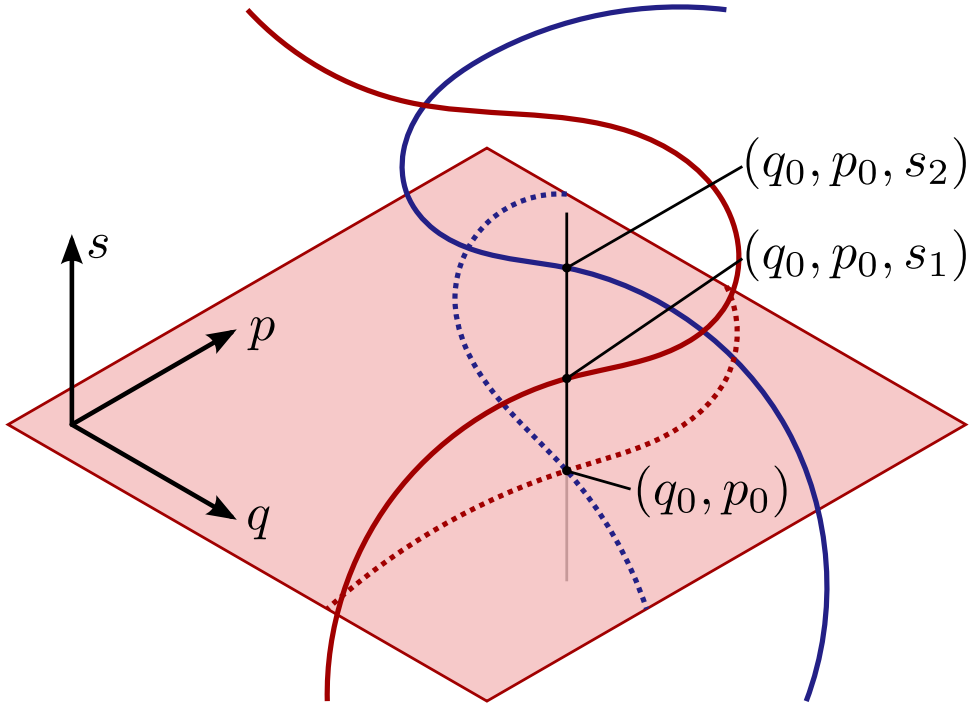
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- Non-Markovian generalized Langevin equations are used in many contexts as a physical model
  - Can we exploit the flexibility to manipulate the sampling properties of a molecular dynamics trajectory?
  - Can we make it as general and "user-friendly"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

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)

A GLE framework for molecular dynamics

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}\boldsymbol{\xi} \\
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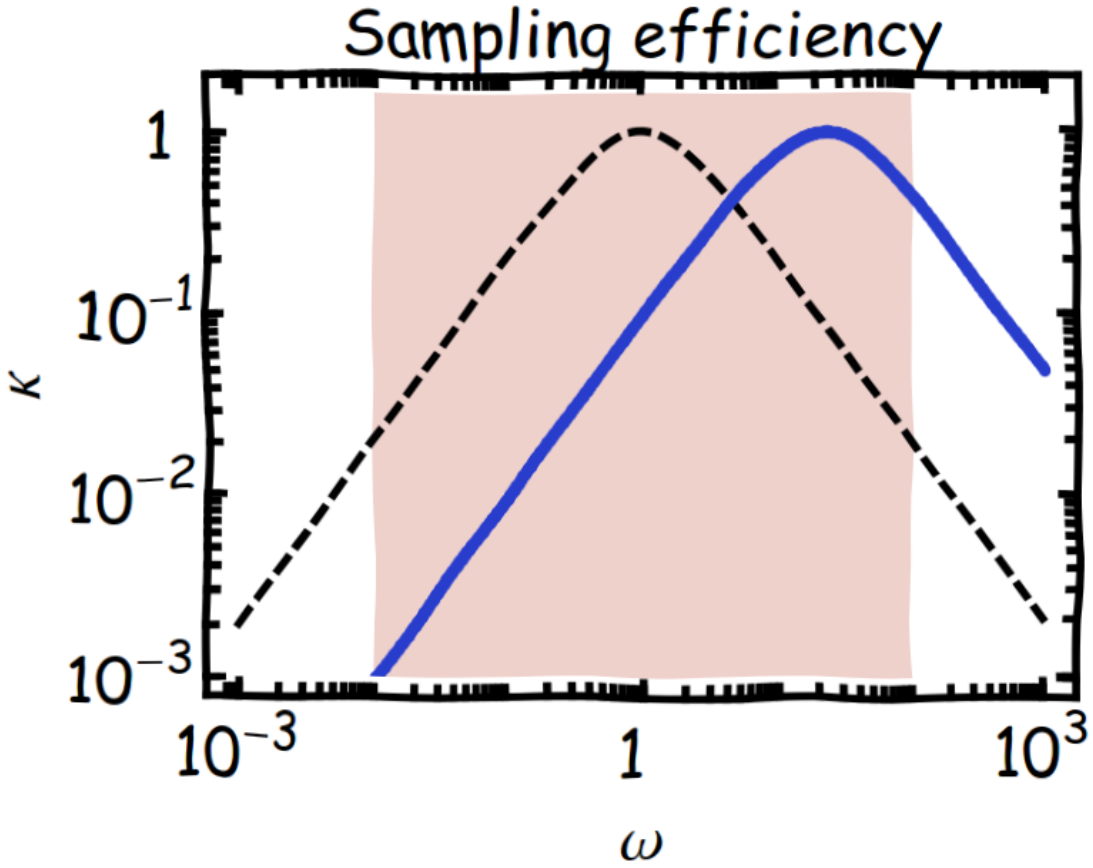
Predicting and fitting

- 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)

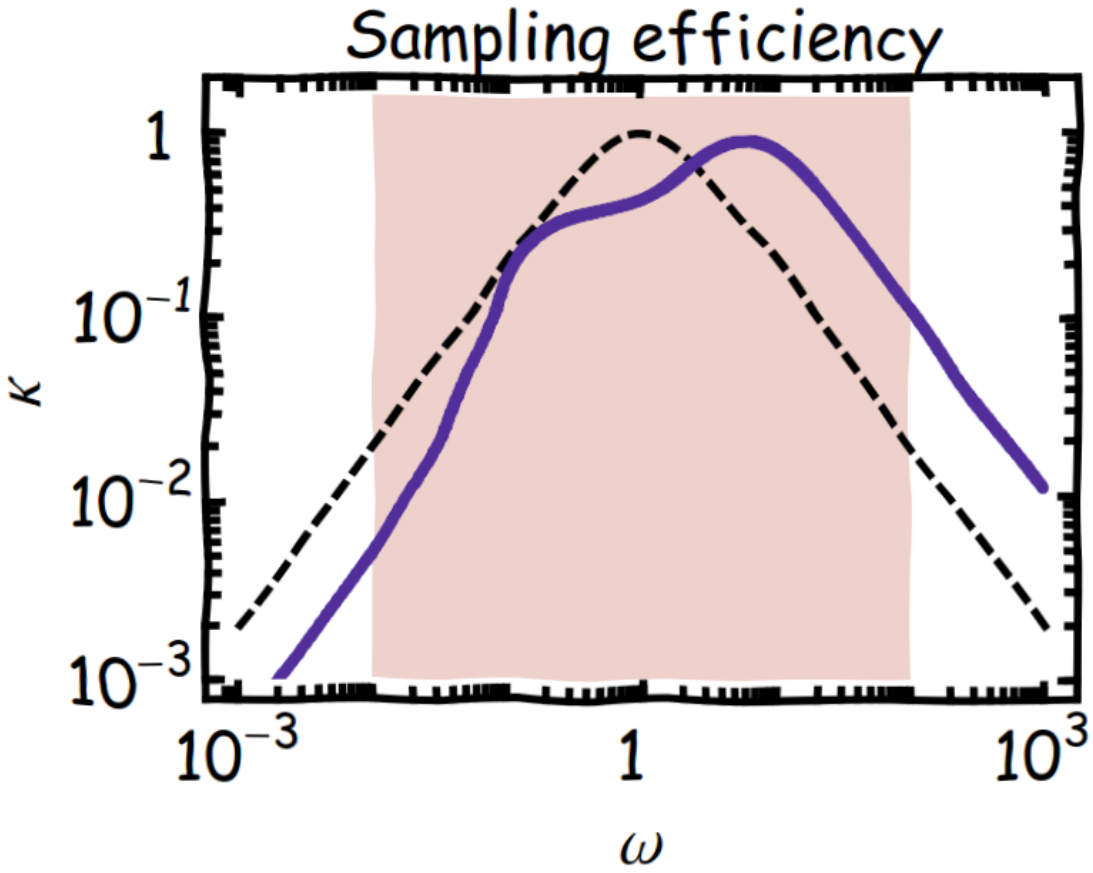
Optimal sampling by colored noise

- 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. . .



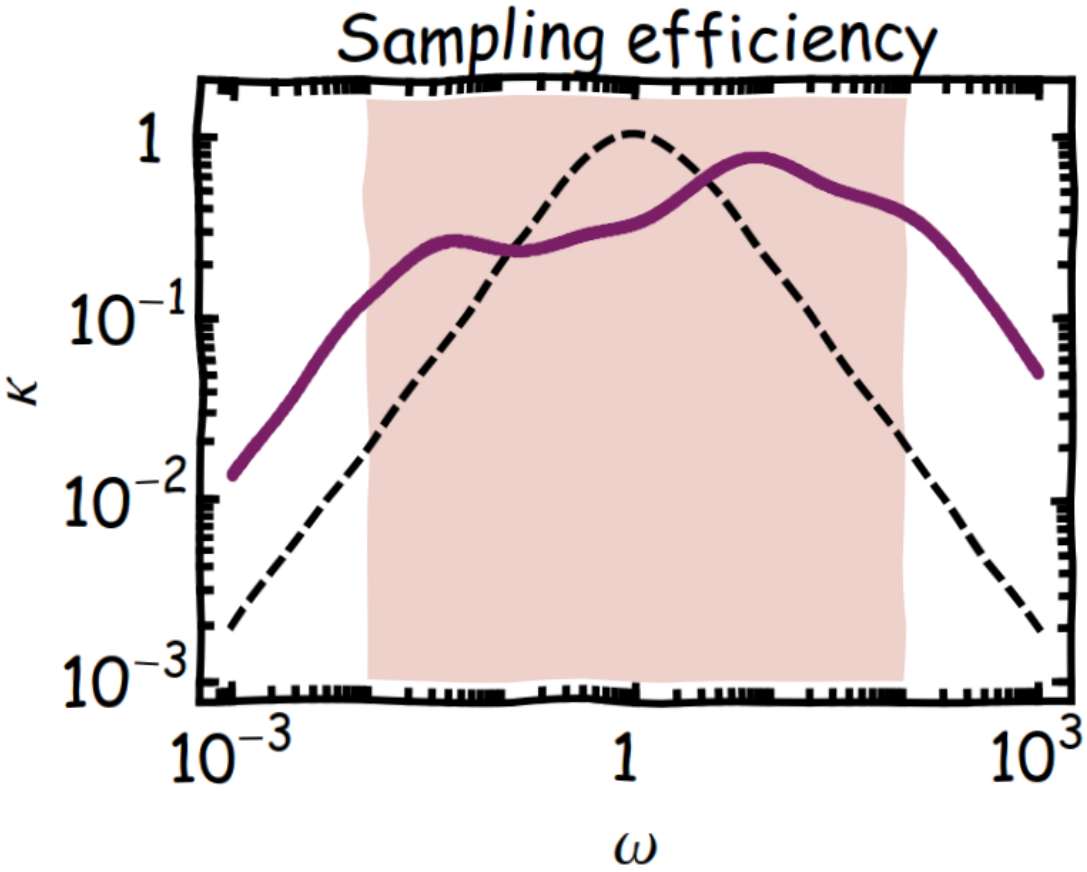
Optimal sampling by colored noise

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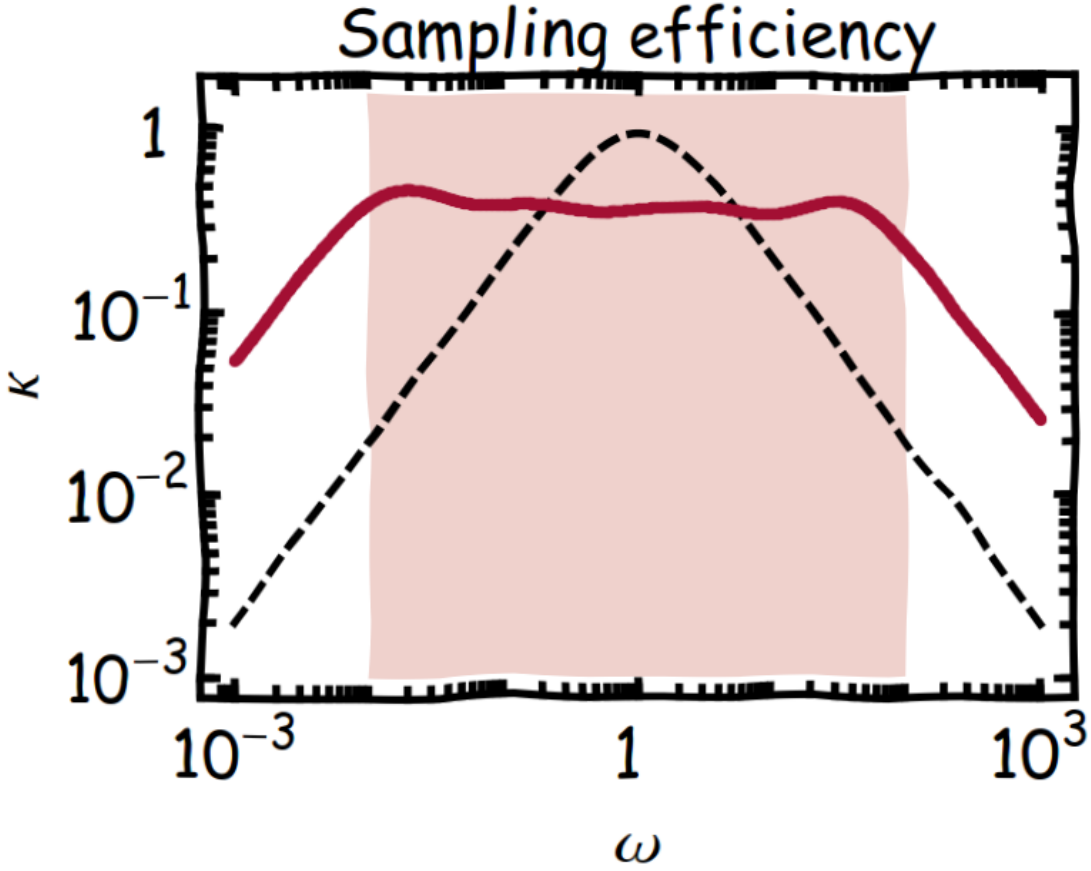
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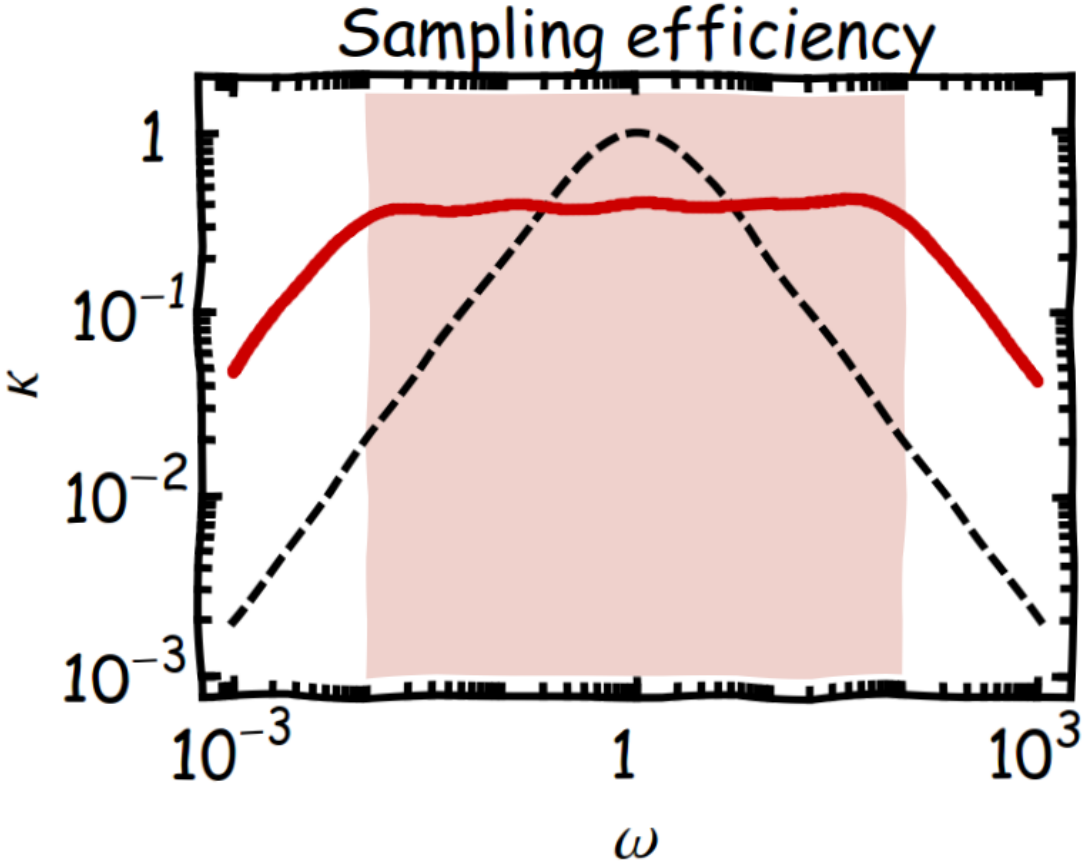
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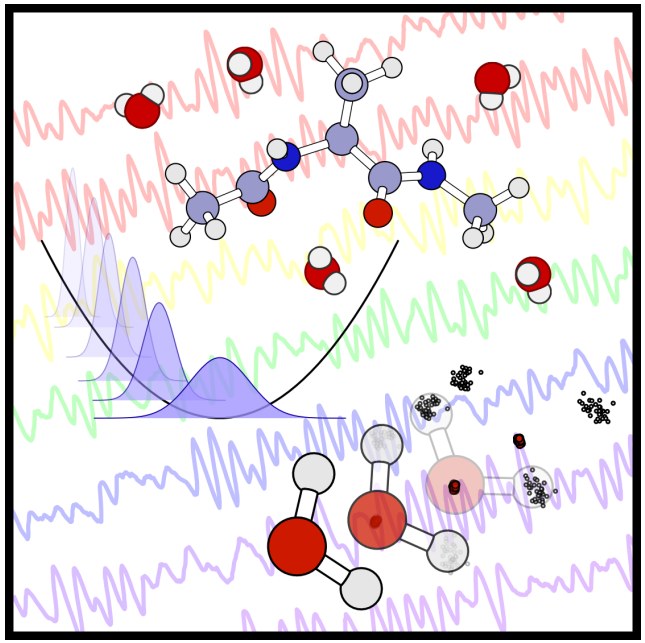
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- Start off with a random (bad!) choice of colored-noise parameters
- Iteratively optimize... until we get **constant sampling efficiency**



Canonical sampling GLE

- **Optimal sampling** for high statistical efficiency
- Thermostatting of path integral MD
- Evaluate quantitatively the disturbance induced on dynamics to **localize disturbance** on few normal modes
- Thermostatting of CPMD which doesn't disrupt adiabatic decoupling
- **GLE-RESPA** to stabilize multiple time-step dynamics without over-damping collective molecular motion



Ceriotti, Bussi, Parrinello, Phys. Rev. Lett. (2009)
Ceriotti, Markland, Manolopoulos and Parrinello, J. Chem. Phys. (2010)
Morrone, Markland, Ceriotti and Berne, J. Chem. Phys. (2011)

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



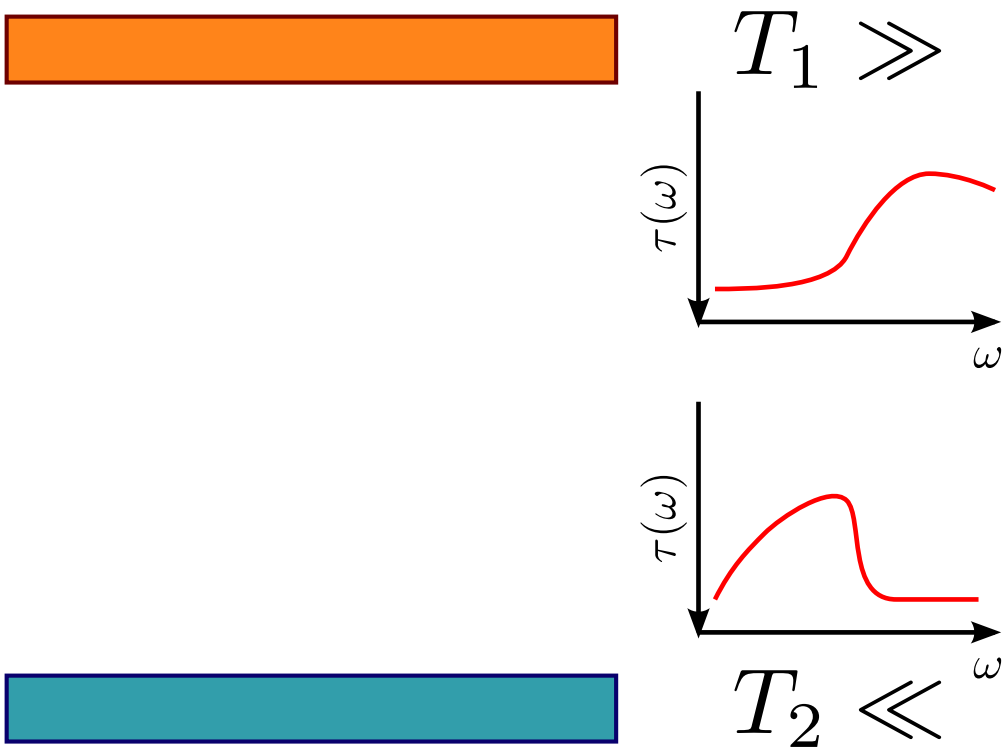
$T_1 \gg$



$T_2 \ll$

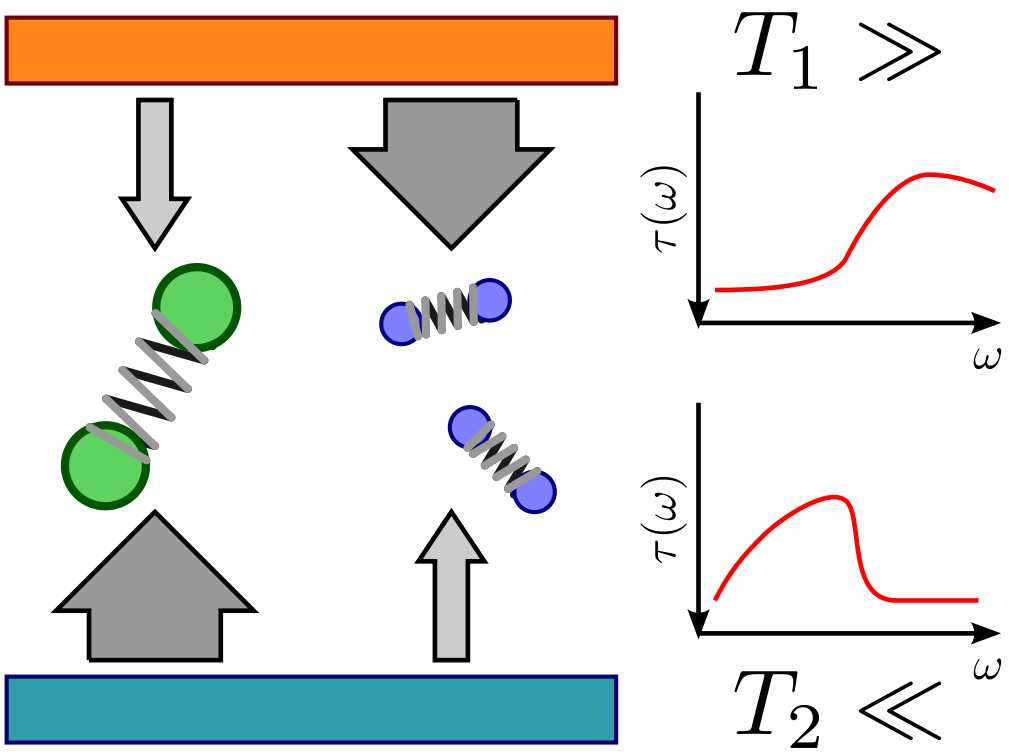
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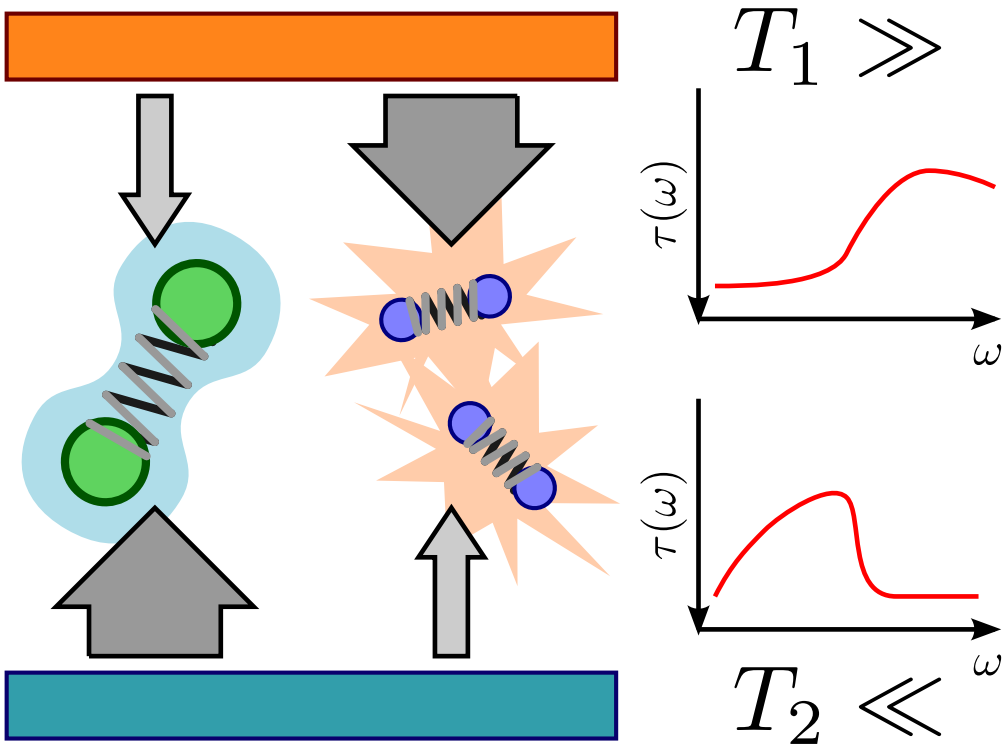
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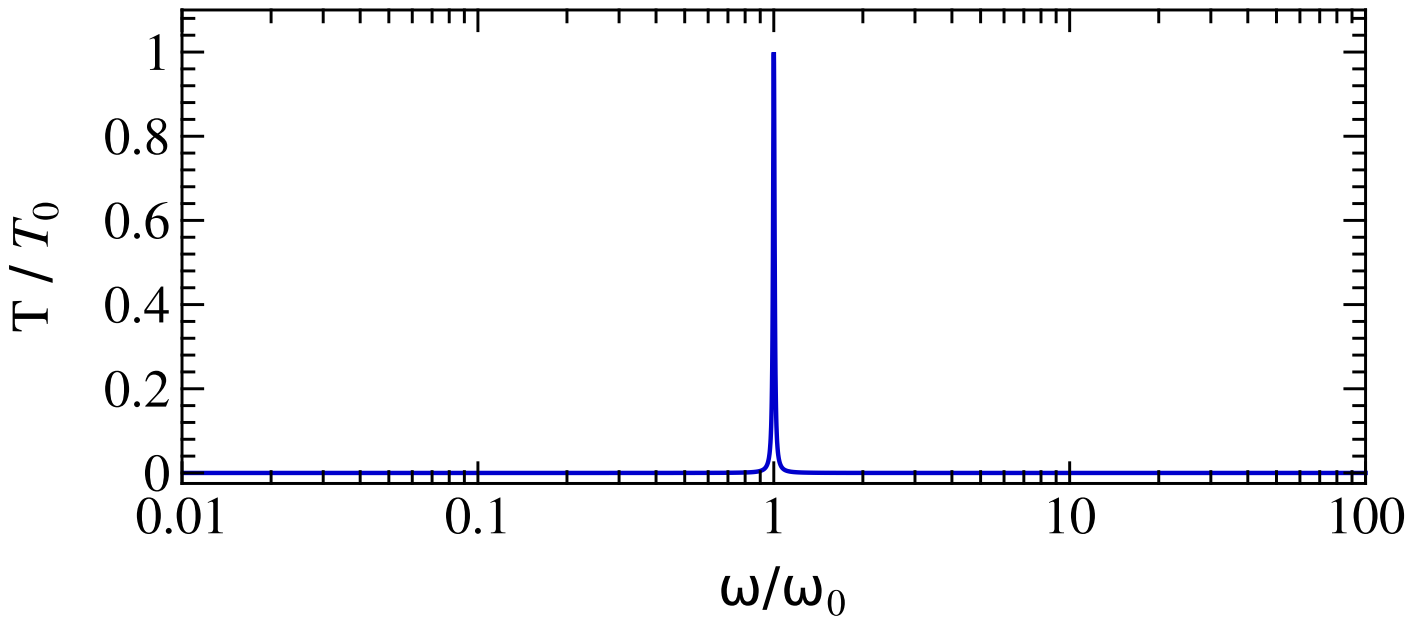
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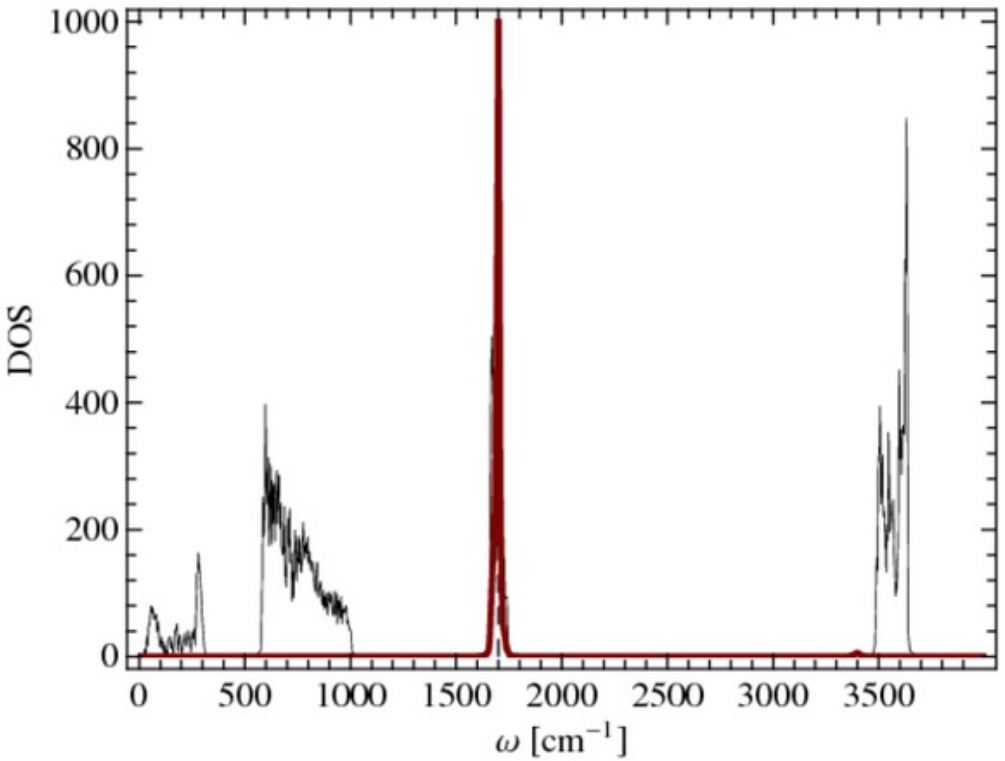
A δ-thermostat

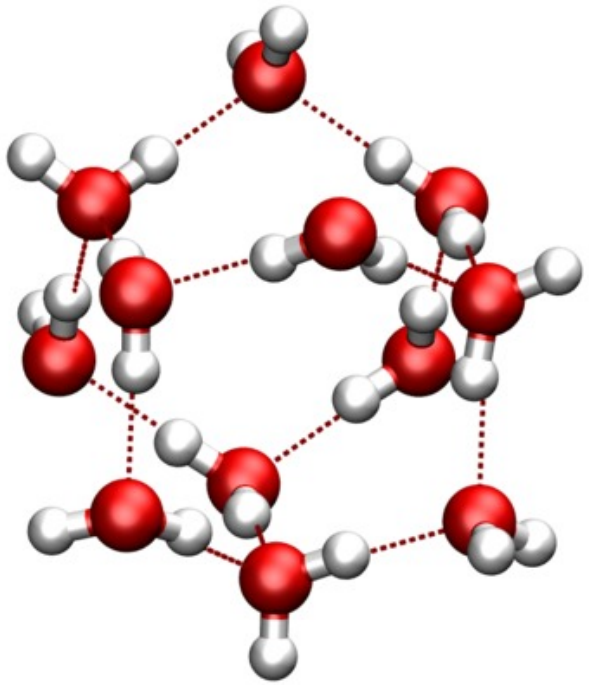
- Thermalize the normal modes in a narrow frequency window, keep all the others frozen. No need to know normal modes in advance!



A δ-thermostat

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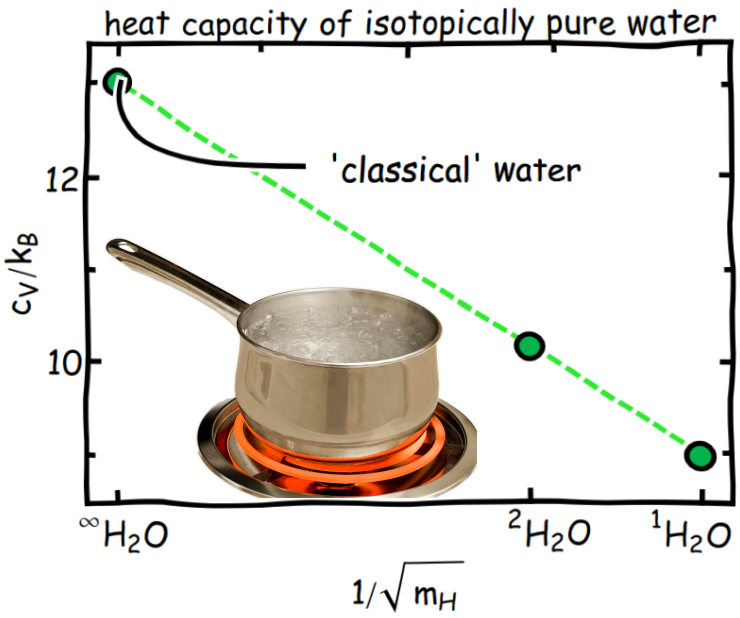


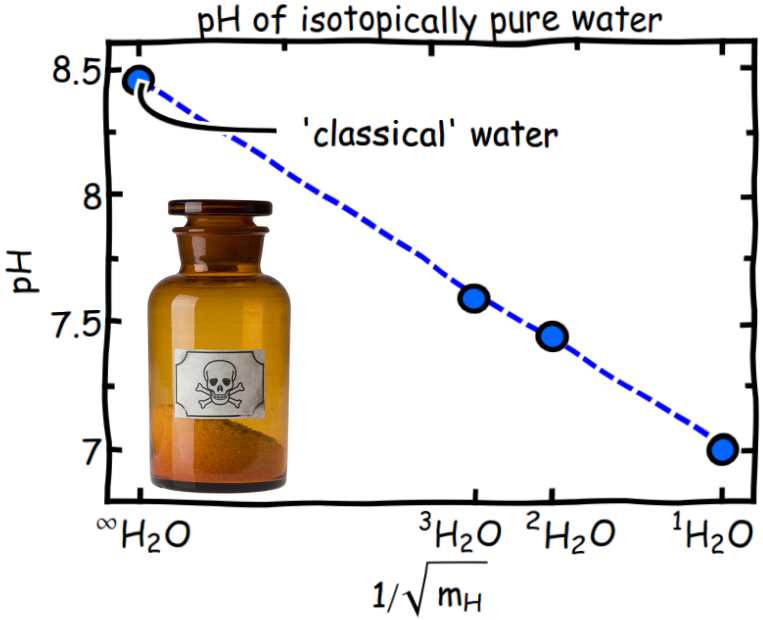


Selective NM excitation in hexagonal ice. Comparison of the NVE density of states and that obtained by targeted δ-thermostats. Atomic displacements have been magnified for clarity.

Quantum thermostats

- Beyond the scope of this lecture. Non-equilibrium GLE can be used to model approximately the quantum nature of light nuclei
- Can be combined with path integral molecular dynamics to obtain systematic convergence at a much reduced computational cost

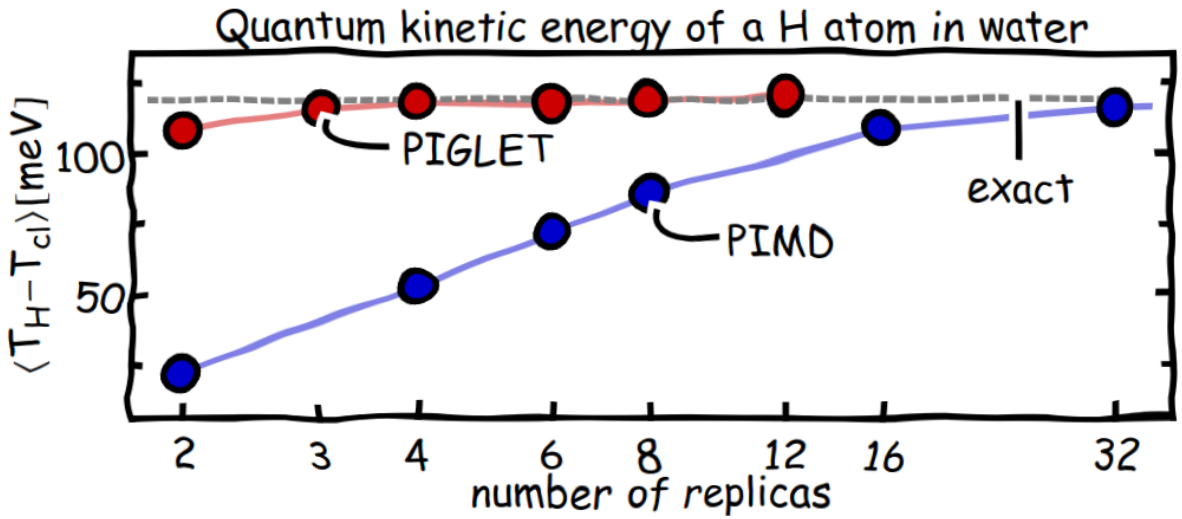


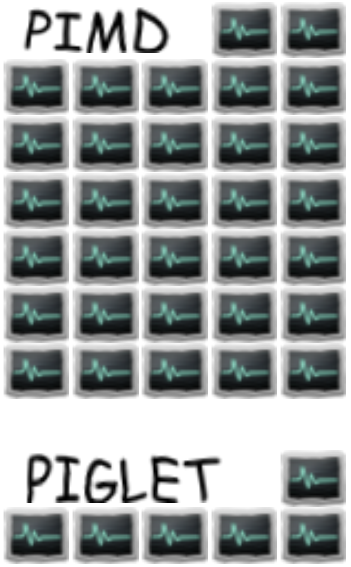


Ceriotti, Bussi, Parrinello, Phys. Rev. Lett. 2009
Ceriotti, Manolopoulos, Parrinello, J. Chem. Phys. 2011
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Wrap up and take home

- Molecular dynamics simulations require a thermostat to perform constant-temperature sampling efficiently
- Deterministic/stochastic thermostats: randomness is good
- Global thermostats for ergodic systems (e.g. liquids) [*Stochastic Velocity Rescaling*], local thermostats for solids or short simulations [*Generalized Langevin Thermostats*]
- GLE framework gives exquisite control over the sampling properties of the dynamics
  - Efficient, tunable sampling for constant-temperature simulations
  - Possibility of manipulating the target ensemble
  - Quantum thermostat for modelling of light ions

Bibliography

Gardiner, "Stochastic Methods"
Tuckerman, "Statistical Mechanics"
http://epfl-cosmo.github.io/gle4md