EFFICIENT MOLECULAR DYNAMICS: THERMOSTATS, BAROSTATS AND MULTIPLE TIME STEPS

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COMPUTATIONAL SCIENCE AND MODELLING

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

OUTLINE

1. Why molecular dynamics ?

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2. How to integrate equations of motion ?

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3. How to sample a NVT Ensemble ?

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4. How to sample a NPT Ensemble ?

WHAT ARE WE CALCULATING ?

$\mathrm{P}(\vec{\mathrm{p}}, \vec{\mathrm{q}})$ is the probability distribution at a given thermodynamic condition.

$$\langle \mathrm{A}(\vec{\mathrm{q}}) \rangle = \frac{\int \mathtt{d}\vec{\mathrm{q}} \ \mathtt{d}\vec{\mathrm{p}} \ \mathrm{A}(\vec{\mathrm{q}}) \ \mathrm{P}(\vec{\mathrm{p}}, \vec{\mathrm{q}})}{\int \mathtt{d}\vec{\mathrm{q}} \ \mathtt{d}\vec{\mathrm{p}} \ \mathrm{P}(\vec{\mathrm{p}}, \vec{\mathrm{q}})}$$

WHAT ARE WE CALCULATING ?

6N dimensional integral !

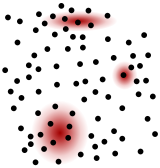

Figure : Integral by quadrature

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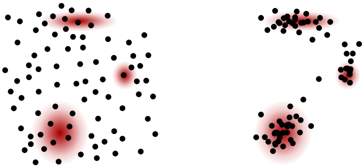

Figure : Integral by importance sampling

WHAT ARE WE CALCULATING ?

$$\langle A(\vec{q})\rangle = \frac{\int d\vec{q}\ \ d\vec{p}\ \ A(\vec{q})\ \ P(\vec{p},\vec{q})}{\int d\vec{q}\ \ d\vec{p}\ \ P(\vec{p},\vec{q})} = \langle A(q(\vec{t}))\rangle_t$$

t should be "long enough"!

Boltzmann's Ergodic Conjecture (1871)

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IS MY SIMULATION TIME LONG ENOUGH ?

$$c_{AA}(\Delta) = \langle A(t) \cdot A(\Delta + t) \rangle_t$$

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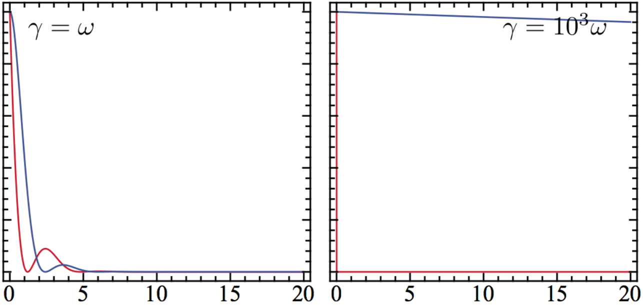

Figure : Auto correlation function for the potential and kinetic energy

WHY NOT MARKOV CHAIN MONTE CARLO ?

Probability of acceptance in MCMC :

$$\boxed{\mathtt{a}(q \to q') = \mathtt{min}(1, e^{-\beta[V(q') - V(q)]})}$$

Metropolis *et al.* JCP (1953)

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1. High acceptance vs "making things happen".

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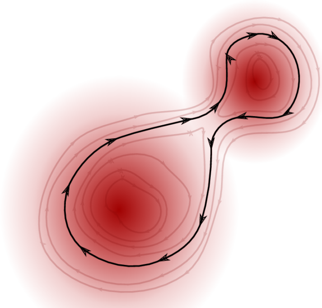
1. High acceptance vs "making things happen".
2. Curse of large system size.
3. Generalized "smart moves".

Metropolis *et al.* JCP (1953)

$$H = \sum_{i=0}^{3N} \frac{{p_i}^2}{2m_i} + V(q_1, .., q_{3N}); \quad \dot{\vec{p}} = -\frac{\partial V}{\partial \vec{q}} \quad \& \quad \dot{\vec{q}} = \frac{\vec{p}}{\vec{m}}$$



$$dH/dt = 0$$

Figure : Dynamics conserves energy

Rahman PR (1964)

HOW TO INTEGRATE EQUATIONS OF MOTION?

$$
\begin{aligned}
\dot{\vec{x}} &= \frac{d}{dt} \; \vec{x} \\
&= [\dot{\vec{q}} \cdot \frac{\partial}{\partial \vec{q}} + \dot{\vec{p}} \cdot \frac{\partial}{\partial \vec{p}}] \; \vec{x} \\
&= [\frac{\vec{p}}{\vec{m}} \cdot \frac{\partial}{\partial \vec{q}} - \frac{\partial V}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}}] \; \vec{x} \\
&= iL_H \; \vec{x}
\end{aligned}
$$

$$\dot{\vec{x}} = iL_H \; \vec{x} \implies \vec{x}(t) = e^{iL_H t} \; \vec{x}(0)$$

$$\boxed{iL_H = \frac{\vec{p}}{\vec{m}} \cdot \frac{\partial}{\partial \vec{q}} - \frac{\partial V}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} = iL_q + iL_p}$$

HOW TO INTEGRATE EQUATIONS OF MOTION?

Phase space vector :
$\vec{x} = (p_1, .., p_{3N}, q_1, .., q_{3N})$.

How to evolve $\vec{p}$ & $\vec{q}$?

Tuckerman *et al.* JCP (1992)

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The classical propagator!

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The classical propagator!

$$\begin{aligned}
\vec{x}(t) &= e^{iL_H t} \; \vec{x}(0) \\
&= [e^{iL_H \frac{t}{M}}]^M \; \vec{x}(0) \\
&= [e^{iL_q \Delta t + iL_p \Delta t}]^M \; \vec{x}(0) \\
&\approx [e^{iL_p \Delta t/2} \cdot e^{iL_q \Delta t} \cdot e^{iL_p \Delta t/2}]^M \; \vec{x}(0)
\end{aligned}$$

$$e^{\tau(A+B)} = [e^{\Delta\tau/2A} \cdot e^{\Delta\tau B} \cdot e^{\Delta\tau/2A}]^M + \mathcal{O}(\Delta\tau^{-3}) \qquad \Delta\tau = \tau/M$$

Tuckerman *et al.* JCP (1992), Trotter PAMS (1959)

HOW TO INTEGRATE EQUATIONS OF MOTION?

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Tuckerman *et al.* JCP (1992)

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Given that:

$$e^{iL_q \Delta t} = e^{+\frac{\vec{p}}{\vec{m}} \Delta t \cdot \frac{\partial}{\partial \vec{q}}}$$

$$e^{iL_p \Delta t} = e^{-\frac{\partial V}{\partial \vec{q}} \Delta t \cdot \frac{\partial}{\partial \vec{p}}}$$

$$e^{c \frac{\partial}{\partial x}} \ f(x, y) = f(x + c, y)$$

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$$\begin{cases} \vec{p} \to \vec{p} - \frac{\partial V}{\partial \vec{q}} \Delta t/2 \\ \\ \end{cases}$$

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$$\begin{cases} \vec{p} \rightarrow \vec{p} - \frac{\partial V}{\partial \vec{q}} \Delta t/2 \\ \vec{q} \rightarrow \vec{q} + \frac{\vec{p}}{\vec{m}} \Delta t \\ \end{cases}$$

Tuckerman *et al.* JCP (1992)

HOW TO INTEGRATE EQUATIONS OF MOTION?

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The Velocity Verlet algorithm!

Tuckerman *et al.* JCP (1992)

HOW TO CHOOSE THE TIME STEP?

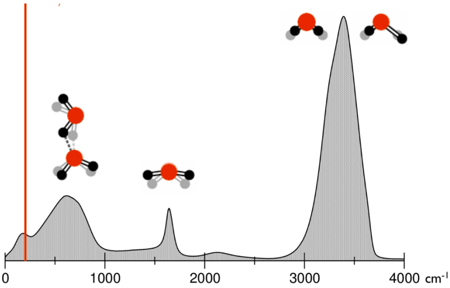


Figure : Presence of multiple time scales in a system

HOW TO INTEGRATE WITH MULTIPLE TIME STEPS

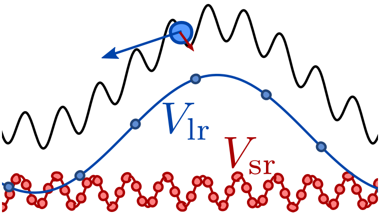
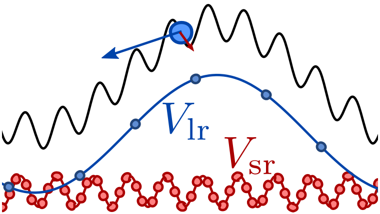


Figure : Separation of time scales

$$H = \sum_{i=0}^{3N} \frac{{p_i}^2}{2m_i} + V^{lr}(q_1, .., q_{3N}) + V^{sr}(q_1, .., q_{3N})$$

Tuckerman *et al.* JCP (1992)



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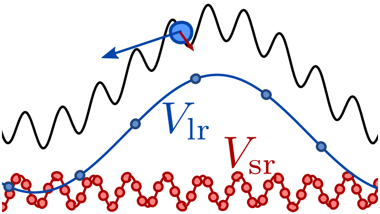
$$iL_H = \frac{\vec{p}}{\vec{m}} \cdot \frac{\partial}{\partial \vec{q}} - \frac{\partial V^{lr}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} - \frac{\partial V^{sr}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} = iL_q + iL_p^{lr} + iL_p^{sr}$$

Tuckerman *et al.* JCP (1992)

HOW TO INTEGRATE WITH MULTIPLE TIME STEPS



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$$
\begin{aligned}
\vec{x}(\Delta t) &= e^{iL_H \Delta t} \quad \vec{x}(0) \\
&= e^{i[iL_q + iL_p^{sr} + iL_p^{lr}]\Delta t} \quad \vec{x}(0) \\
&\approx e^{iL_p^{lr}} \Delta t/2 [e^{iL_p^{sr}\Delta t + iL_q \Delta t}] e^{iL_p^{lr}\Delta t/2} \quad \vec{x}(0)
\end{aligned}
$$

Tuckerman *et al.* JCP (1992)

HOW TO INTEGRATE WITH MULTIPLE TIME STEPS

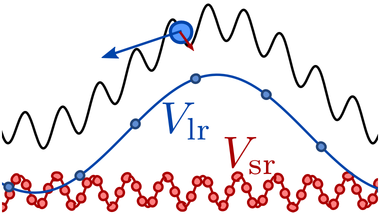

Figure : Separation of time scales

$$\begin{cases} p \rightarrow p - \frac{\partial V^{lr}}{\partial \vec{q}} \frac{\Delta t}{2} \\ \text{Velocity Verlet for } M \text{ steps with "short range" forces with } \Delta t/M. \\ p \rightarrow p - \frac{\partial V^{lr}}{\partial \vec{q}} \frac{\Delta t}{2} \end{cases}$$

Tuckerman *et al.* JCP (1992)

MTS: THE REALITY

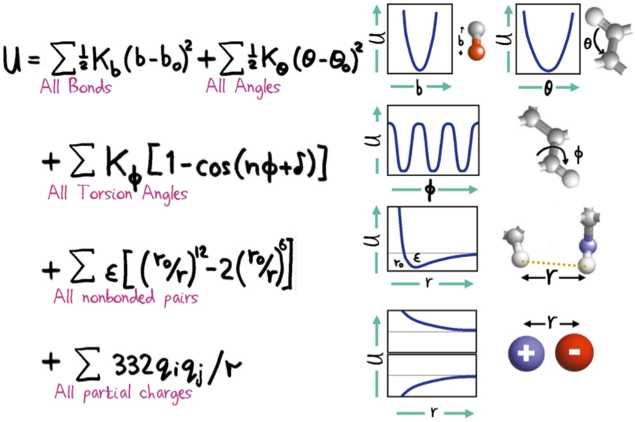

Figure : Range separation is trivial

[http://www.omnia.md/blog/2014/11/6/how-to-train-your-force-field]

MTS: THE REALITY

What about the *ab inito* framework ?

$$[-\frac{-\hbar^2}{2\mathrm{m}}\nabla^2 + \mathrm{V}(\hat{\mathrm{r}})]\ \ \psi(\mathrm{r}) = \mathrm{E}\ \ \psi(\mathrm{r})$$

MTS: THE REALITY

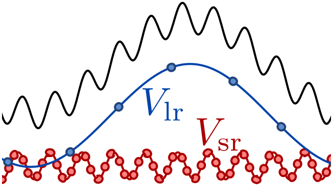

Figure : Separation of time scales

$$H = \sum_{i=0}^{3N} \frac{{p_i}^2}{2m_i} + V^{sr}(q_1, .., q_{3N}) + (V(q_1, .., q_{3N}) - V^{sr}(q_1, .., q_{3N}))$$

Kapil *et al.* JCP (2016), Marsalek *et al.* JCP (2016), John *et al.* PRE (2016)

MTS: THE REALITY

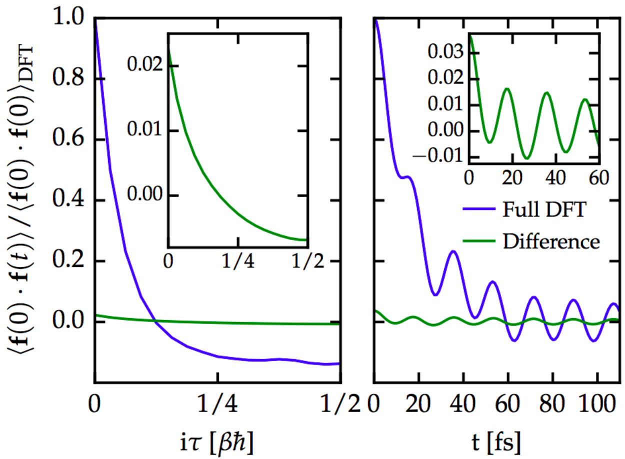

Figure : How to choose the "cheap potential"?

Kapil *et al.* JCP (2016), Marsalek *et al.* JCP (2016), John *et al.* PRE (2016)

HOW TO INTEGRATE EQUATIONS OF MOTION: WRAPPING UP

1. Velocity Verlet comes from the classical propagator.

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1. Velocity Verlet comes from the classical propagator.
2. Error decreases systematically as $(\Delta t)^{-2}$.
3. Further decomposition leads to a MTS integrator.
4. Time-reversible and symplectic.

How to sample a NVT ensemble for system given by the Hamiltonian ?

$$H(\vec{p}, \vec{q}) = \sum_{i=0}^{3N} \frac{{p_i}^2}{2m_i} + V(q_1, .., q_{3N})$$

Generate $(\vec{p}, \vec{q})$ such that:

$$\boxed{P(\vec{p}, \vec{q}) = \frac{e^{-\beta H(\vec{p}, \vec{q})}}{\int d\vec{p} d\vec{q} e^{-\beta H(\vec{p}, \vec{q})}}}$$

Do Hamilton's equations of motion conserve $P(\vec{p}, \vec{q})$?

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Do Hamilton's equations of motion conserve $P(\vec{p}, \vec{q})$?

$$\boxed{iL_H \; P(\vec{p}, \vec{q}) = 0}$$

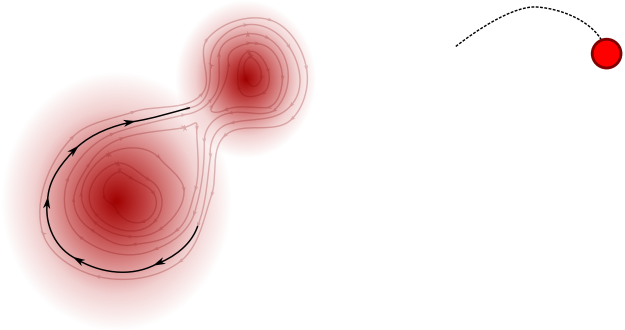


Figure : A problem of ergodicity

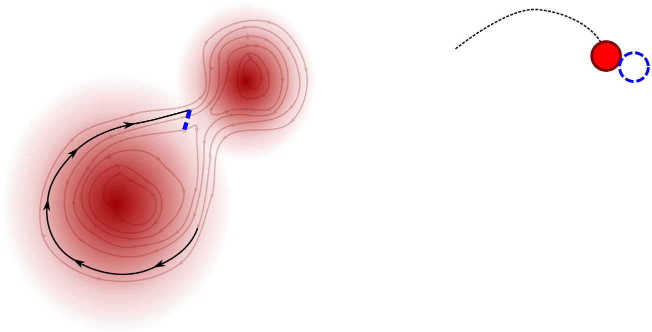
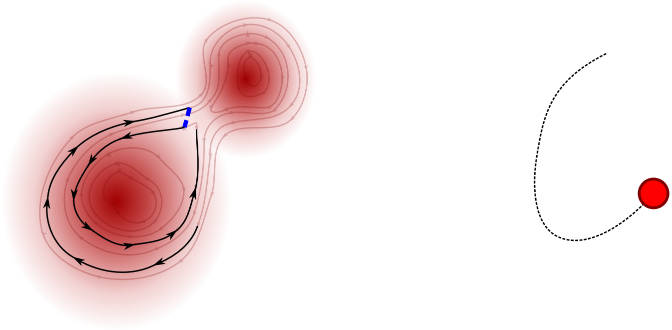


Figure : Andersen's thermostat

Andersen JCP (1980)



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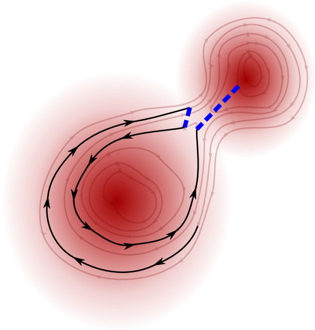

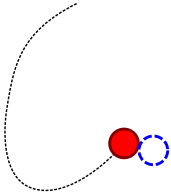

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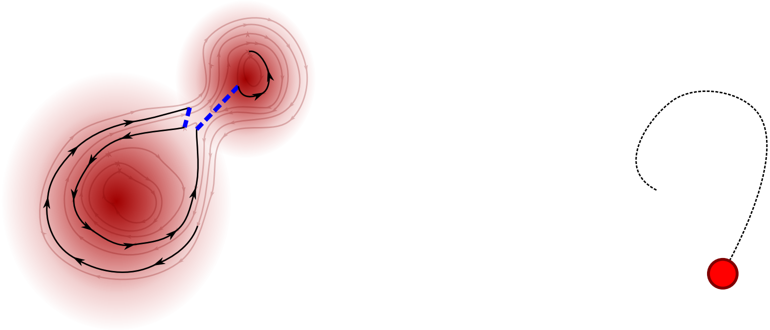
Andersen JCP (1980)

MOLECULAR DYNAMICS : AT CONSTANT TEMPERATURE



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Andersen JCP (1980)

Noseˊ Hoover thermostat:

$$\dot{\vec{q}} = \frac{\vec{p}}{\vec{m}}; \quad \dot{\vec{p}} = -\frac{\partial V}{\partial \vec{q}} - \vec{p}\frac{p_s}{Q}; \quad \dot{p_s} = \vec{p} \cdot \frac{\vec{p}}{\vec{m}}; \quad \dot{s} = \frac{p_s}{Q}$$

Nosé JCP (1984), Hoover PRA (1985)

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1. Not ergodic. Must use chains.

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DETERMINISTIC THERMOSTATS

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1. Not ergodic. Must use chains.
2. Not rotationally invariant.

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1. Not ergodic. Must use chains.
2. Not rotationally invariant.
3. Integrating equations of motion is not pretty.

Nosé JCP (1984), Hoover PRA (1985)

STOCHASTIC THERMOSTATS

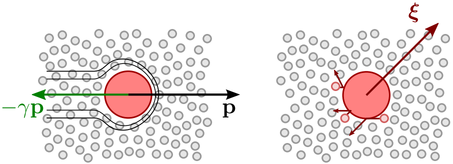

Figure : A white noise Langevin thermostat

Langevin thermostat:

$$\dot{\vec{q}} = \frac{\vec{p}}{\vec{m}}; \quad \dot{\vec{p}} = -\frac{\partial V}{\partial \vec{q}} - \gamma\vec{p} + \vec{m}^{1/2}\sqrt{2\gamma\beta^{-1}}\vec{\xi}; \quad \langle\vec{\xi}(t)\cdot\vec{\xi}(0)\rangle = \delta(t)$$

Schneider *et al.* PRB (1978), Bussi *et al.* JCP (1992)

STOCHASTIC THERMOSTATS

Langevin thermostat:

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1. Ergodic

Schneider *et al.* PRB (1978), Bussi *et al.* JCP (1992)

STOCHASTIC THERMOSTATS

Langevin thermostat:

$$\dot{\vec{q}} = \frac{\vec{p}}{\vec{m}}; \quad \dot{\vec{p}} = -\frac{\partial V}{\partial \vec{q}} - \gamma \vec{p} + \vec{m}^{1/2}\sqrt{2\gamma\beta^{-1}}\vec{\xi}; \quad \langle \vec{\xi}(t) \cdot \vec{\xi}(0) \rangle = \delta(t)$$

1. Ergodic
2. Linear equations

Schneider *et al.* PRB (1978), Bussi *et al.* JCP (1992)

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$$e^{iL\Delta t} \approx e^{iL_\gamma \Delta t/2} \; e^{iL_H \Delta t} \; e^{iL_\gamma \Delta t/2}$$

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$$\tilde{H} = \Delta H + \Delta K$$

$\Delta H =$ Change in total energy during the Hamiltonian step

$\Delta K =$ Change in kinetic energy during the thermostat step

Schneider *et al.* PRB (1978), Bussi *et al.* JCP (1992)

SAMPLING EFFICIENCY

Can we measure how efficient a Langevin thermostat is ?

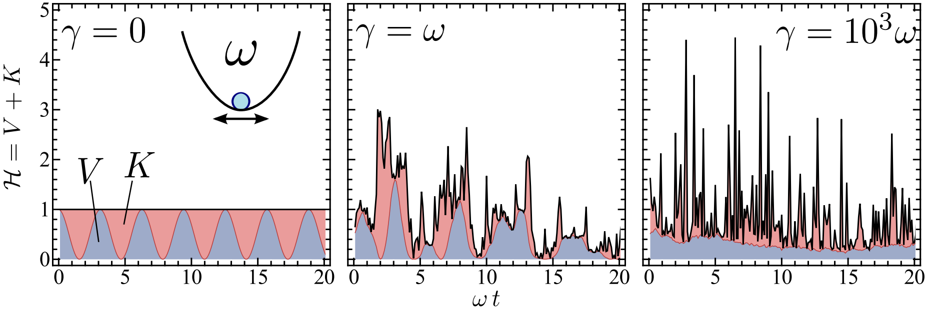

Figure : Under damped, optimally damped and over damed regimes

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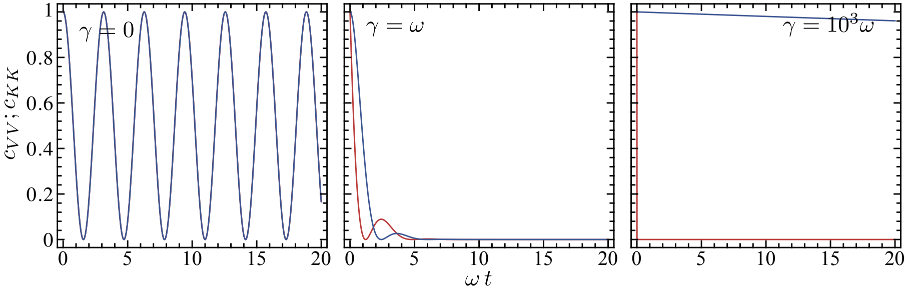

Figure : Under damped, optimally damped and over damed regimes

A GENERALIZED LANGEVIN EQUATION

$$\dot{\vec{q}} = \frac{\vec{p}}{\vec{m}}$$

$$\dot{\vec{p}} = -\frac{\partial V}{\partial \vec{q}} - \int ds \;\; K(s) \;\; \vec{p}(t-s) + \vec{m}^{1/2}\sqrt{2\beta^{-1}}\vec{\xi}; \quad \langle \vec{\xi}(t) \cdot \vec{\xi}(0) \rangle = H(t)$$

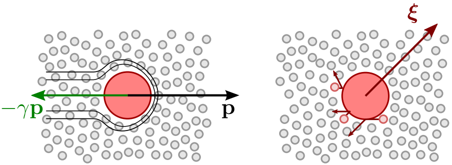

Figure : A generalized Langevin equation (GLE)thermostat

Zwanzig, Nonequilibrium statistical mechanics (2001)

A GENERALIZED LANGEVIN EQUATION

$$\dot{q} = p$$

$$\begin{pmatrix} \dot{p} \\ \dot{s} \end{pmatrix} = \begin{pmatrix} -V'(q) \\ 0 \end{pmatrix} - \begin{pmatrix} a_{pp} & a_p^T \\ \bar{a}_p & A \end{pmatrix} \begin{pmatrix} p \\ s \end{pmatrix} + \begin{pmatrix} b_{pp} & b_p^T \\ \bar{b}_p & B \end{pmatrix} \begin{pmatrix} \boldsymbol{\xi} \end{pmatrix}$$

$K(t)$ and $H(t)$ can be expressed in terms of the drift and the diffusion matrix.

Zwanzig, Nonequilibrium statistical mechanics (2001)

Sampling efficiency over a wide frequency range?

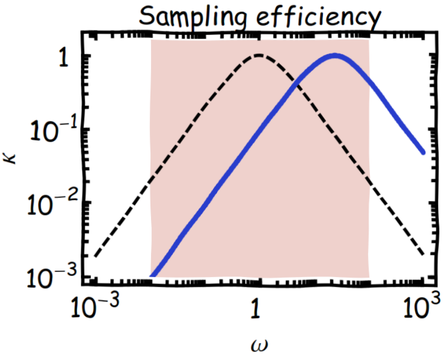

Figure : Optimizing a merit function of sampling efficiency

Ceriotti *et al.* JCTC (2010)

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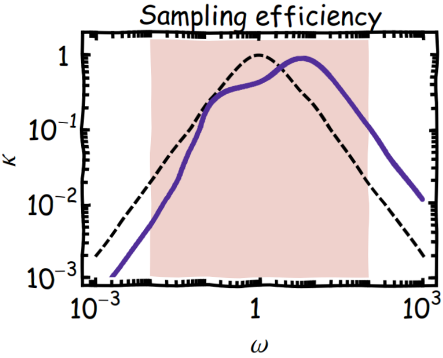

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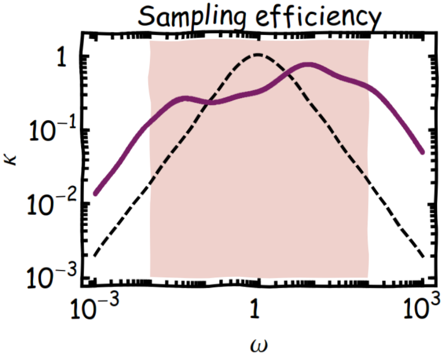

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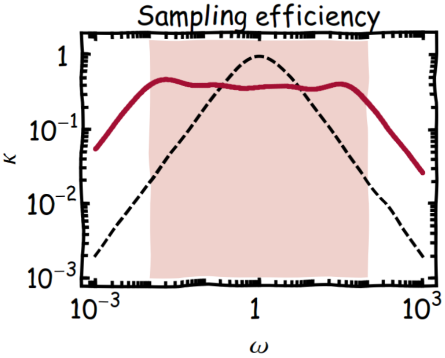

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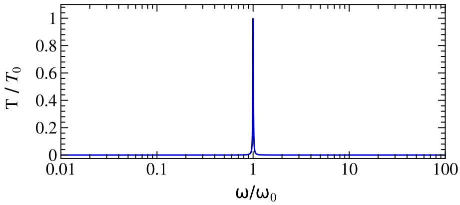
A GENERALIZED LANGEVIN EQUATION

Exciting a narrow range of frequencies?



Dettori *et al.* JCTC (2017)

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WRAPPING UP

1. System + bath gives canonical sampling.

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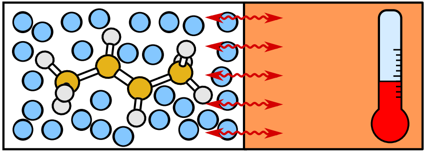
MOLECULAR DYNAMICS : AT CONSTANT PRESSURE



$$P \propto e^{-\beta E}\delta(V - \bar{V})$$

Figure : Sampling at constant volume

Andersen JCP (1980), Parinello *et al.* JAP (1981), Martyna JCP (1994), Bussi JCP (2009)

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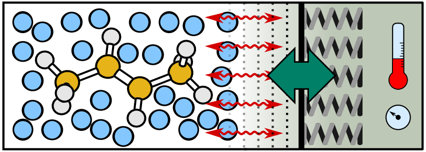

$$P \propto e^{-\beta E} e^{-\beta p V}$$

Figure : Sampling at constant pressure

Andersen JCP (1980), Parinello *et al.* JAP (1981), Martyna JCP (1994), Bussi JCP (2009)

$$\dot{\vec{\mathrm{q}}} = \frac{\vec{\mathrm{p}}}{\vec{\mathrm{m}}} + \alpha\vec{\mathrm{q}}$$

$$\dot{\vec{\mathrm{p}}} = -\frac{\partial \mathrm{V}}{\partial \vec{\mathrm{q}}} - \alpha\vec{\mathrm{p}}$$

$$\dot{\mathbb{V}} = 3\mathbb{V}\alpha$$

$$\dot{\alpha} = 3[\mathbb{V}\left(\mathrm{P}_{\mathtt{int}} - \mathrm{P}_{\mathtt{ext}}\right) + 2\beta^{-1}]\mu^{-1}$$

Andersen JCP (1980), Parinello *et al.* JAP (1981), Martyna JCP (1994), Bussi JCP (2009)

$$\mathrm{iL} = \mathrm{iL}_{\gamma} + \mathrm{iL}_{\tilde{\mathrm{H}}}; \quad \mathrm{iL}_{\gamma} \; \mathrm{P}_{\mathrm{NPT}}(\vec{\mathrm{p}}, \vec{\mathrm{q}}) = 0; \qquad \mathrm{iL}_{\tilde{\mathrm{H}}} \; \mathrm{P}_{\mathrm{NPT}}(\vec{\mathrm{p}}, \vec{\mathrm{q}}) = 0$$

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TAKE HOME

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1. Molecular Dynamics vs Monte Carlo.
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4. Density fluctuations, changes in cell, isotherms, stress-strain curves can be computed by sampling the NPT ensemble.