High-order averaging schemes for molecular dynamics simulations

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Joint work with Eric Cancès, Claude Le Bris, Gabriel Turinici (CERMICS, ENPC and INRIA) and François Castella, Philippe Chartier and Erwan Faou (INRIA)

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Molecular Dynamics to compute phase space averages

System energy: $$H(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{M} \frac{p_i^2}{2m_i} + V(q_1,\ldots,q_M)$$

Thermodynamical properties (radial distribution, elastic constants, ...):

$$\langle A \rangle_{NVE} = \frac{\displaystyle\int_{\Omega\times\mathbb{R}^{3M}} A(\mathbf{q},\mathbf{p})\,\delta(H(\mathbf{q},\mathbf{p}) - H_0)\,d\mathbf{q}\,d\mathbf{p}}{\displaystyle\int_{\Omega\times\mathbb{R}^{3M}} \delta(H(\mathbf{q},\mathbf{p}) - H_0)\,d\mathbf{q}\,d\mathbf{p}}$$

MD computations:

$$\langle A \rangle_{NVE} = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(\mathbf{q}(t),\mathbf{p}(t))\,dt \approx \frac{1}{N}\sum_{n=1}^{N} A(\mathbf{q}_n,\mathbf{p}_n)$$

Outline of the talk

- Rate of convergence of the time average to the spatial average?
- Is it possible to improve the convergence rate?

  $\longrightarrow$ a new averaging scheme
- What is the effect of the discretization?
- Numerical experiments

Toy model: a particle in a harmonic potential

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$$H(q,p) = \frac{1}{2}p^2 + \frac{1}{2}\omega^2 q^2$$

Trajectory of the Newton's equations:

$$q(t) = C_0\ \cos(\omega t + \phi), \quad p(t) = -C_0\,\omega\ \sin(\omega t + \phi)$$

Time average:

$$\frac{1}{T}\int_0^T A(q(t),p(t))\,dt = \frac{1}{T}\int_0^T A(C_0\ \cos(\omega t + \phi), -C_0\,\omega\ \sin(\omega t + \phi))\,dt$$

Toy model: a particle in a harmonic potential

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Fourier expansion of $\theta \mapsto A(C_0\ \cos\theta, -C_0\,\omega\ \sin\theta)$:

$$A(C_0\ \cos\theta, -C_0\,\omega\ \sin\theta) = \sum_{k\in\mathbb{Z}} a_k \exp(ik\theta)$$

Ergodic theorem

$$\langle A\rangle^{(1)}(T) = \frac{1}{T}\int_0^T A(q(t),p(t))\,dt \quad = \quad \frac{1}{T}\int_0^T \sum_{k\in\mathbb{Z}} a_k \exp(ik\phi)\exp(ik\omega t)\,dt$$

$$= \quad a_0 + \sum_{k\neq 0} a_k \exp(ik\phi)\frac{1}{T}\frac{e^{ik\omega T}-1}{ik\omega}$$

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$$= \quad a_0 + \sum_{k\neq 0} a_k \exp(ik\phi)\frac{1}{T}\frac{e^{ik\omega T}-1}{ik\omega}$$

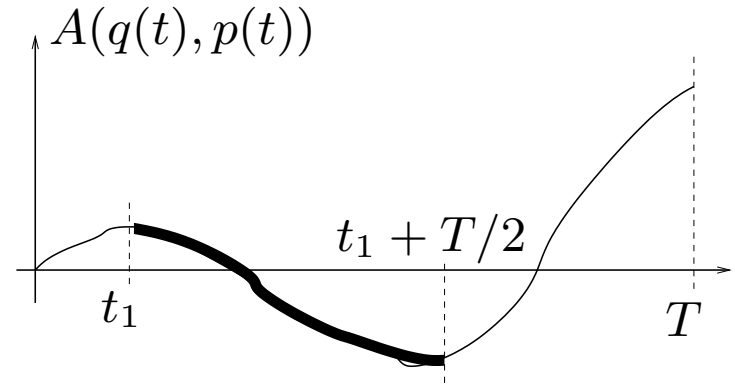
$$a_0 = \frac{1}{2\pi}\int A(C_0\,\cos\theta, -C_0\,\omega\,\sin\theta)d\theta \quad = \quad \langle A\rangle_{NVE}$$

So

$$\frac{1}{T}\int_0^T A(q(t),p(t))\,dt = \langle A\rangle_{NVE} + O\left(\frac{1}{T}\right)$$

Convergence rate improvement

Averaging over initial conditions:



$$\langle A \rangle^{(2)}(T) = \left(\frac{2}{T}\right)^2 \int_0^{T/2} \int_0^{T/2} A(q(t_1 + t_2), p(t_1 + t_2))\, dt_1\, dt_2$$

Convergence rate improvement

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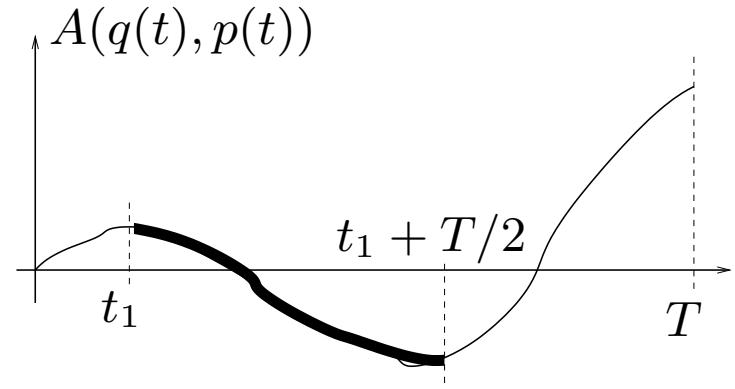

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Plug previous Fourier expansion:

$$\begin{aligned} &= \left(\frac{2}{T}\right)^2 \int_0^{T/2} \int_0^{T/2} \sum_{k\in\mathbb{Z}} a_k \exp(ik\phi) \exp(ik\omega(t_1+t_2))\, dt_1\, dt_2 \\ &= a_0 + \sum_{k\neq 0} a_k \exp(ik\phi) \left(\frac{2}{T}\int_0^{T/2} \exp(ik\omega t)\, dt\right)^2 \\ &= \langle A \rangle_{NVE} + O\left(\frac{1}{T^2}\right) \end{aligned}$$

Signal filtering (a first example)

$$\langle A \rangle^{(2)}(T) = \left(\frac{2}{T}\right)^2 \int_0^{T/2} \int_0^{T/2} A(q(t_1+t_2), p(t_1+t_2))\, dt_1\, dt_2$$

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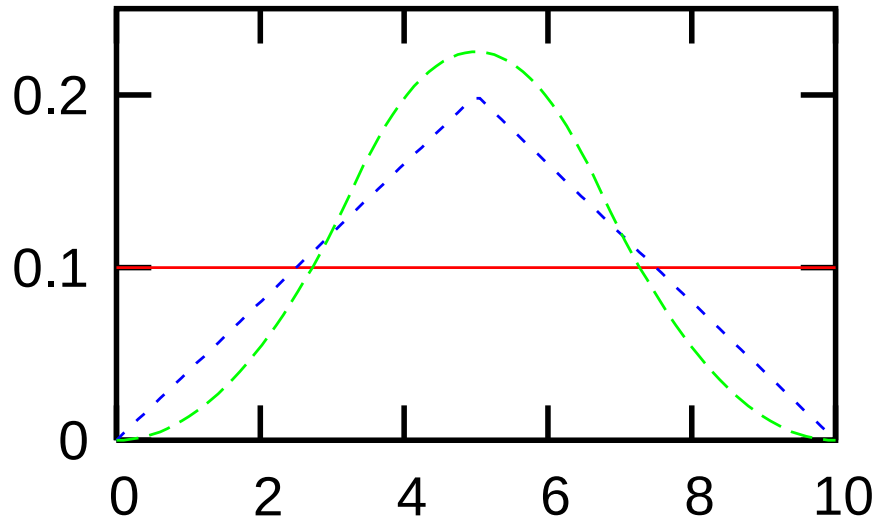
With window function $\chi_T(t) = \frac{1}{T}\mathbf{1}_{[0,T]}(t)$:

$$\langle A\rangle^{(2)}(T) = \int_{\mathbb{R}} A(q(t), p(t))\ \chi_{T/2} * \chi_{T/2}(t)\, dt$$

Averaging over initial conditions amounts to filtering of signal $t \mapsto A(t)$



First result (M particles in 3D)

$$\langle A\rangle^{(k)}(T) = \left(\frac{k}{T}\right)^k \int_{t_1=0}^{T/k} .. \int_{t_k=0}^{T/k} A(\mathbf{q}(t_1+\ldots+t_k), \mathbf{p}(t_1+\ldots+t_k))\, dt_1 .. dt_k$$

Under strong assumptions on the Hamiltonian H (complete integrability + non resonance condition):

$$\langle A\rangle^{(k)}(T) = \langle A\rangle_{NVE} + O\left(\frac{1}{T^k}\right)$$

Completely integrable system: there exists a symplectic map ψ such that

$$(\mathbf{q}(t), \mathbf{p}(t)) = \psi(\mathbf{a}_0, \theta_0 + \omega t)$$

and $\psi(\mathbf{a}_0, \cdot)$ is periodic.

Issues related to discretization

$$\langle A\rangle^{(k)}(T) = \left(\frac{k}{T}\right)^k \int_{t_1=0}^{T/k} .. \int_{t_k=0}^{T/k} A(\mathbf{q}(t_1+\ldots+t_k), \mathbf{p}(t_1+\ldots+t_k))\, dt_1 .. dt_k$$

Discretization: with $T/k = N\delta t$,

$$\begin{aligned}
\langle A\rangle^{(k)}_{num}(\delta t, T) &= \frac{1}{N^k} \sum_{n_1=0}^{N-1} \ldots \sum_{n_k=0}^{N-1} A\left(\mathbf{q}_{n_1+\ldots+n_k}, \mathbf{p}_{n_1+\ldots+n_k}\right) \\
&= \sum_{n=0}^{k(N-1)} C(k, N-1, n)\, A\left(\mathbf{q}_n, \mathbf{p}_n\right) \quad \rightarrow \text{ issues } \ldots
\end{aligned}$$

Signal filtering: a better choice

Generalization of the filtering function:

$$\langle A \rangle^{(k)}(T) = \int_0^T A(q(t), p(t))\ f_k\left(\frac{t}{T}\right) dt$$

with $\quad f_k(x) \quad \propto \quad x^{k-1}\,(1-x)^{k-1}$ $\qquad$ (bell-shaped)

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Discretization: with $T = \mathcal{N}\delta t$,

$$\langle A \rangle^{(k)}_{num}(\delta t, T) = \frac{\displaystyle\sum_{j=0}^{\mathcal{N}-1} A\left(\mathbf{q}_j, \mathbf{p}_j\right) f_k\left(\frac{j}{\mathcal{N}}\right)}{\displaystyle\sum_{j=0}^{\mathcal{N}-1} f_k\left(\frac{j}{\mathcal{N}}\right)}$$

f_k is a polynomial function $\rightarrow$ recursive computation of $\langle A \rangle^{(k)}_{num}(\delta t, T)$

Main result

Assume we use a symplectic integration scheme (of order r_0):

$$\left| \langle A \rangle_{num}^{(k)}(\delta t, T) - \langle A \rangle_{NVE} \right| \leq C(k, r_0) \left(\frac{1}{T^k} + \delta t^{r_0} \right)$$

- symplectic scheme: the numerical trajectory with $H \approx$ the exact trajectory of a modifi edhamiltonian dynamics $H_{\delta t}$;
- $H_{\delta t}$ has quasi-invariants that are very close to the invariants of H;
- the manifold sampled by the numerical trajectory is close to the manifold sampled by the exact trajectory.

$\longrightarrow$ For any arbitrary k, possible to design a filter such that polynomial decay of the error ($1/T^k$).
$\longrightarrow$ This decay is made possible because the values $A\left(\mathbf{q}_j, \mathbf{p}_j\right)$ are correlated in time.

Numerical experiments

- Kepler problem

General case: non-integrable Hamiltonian functions:

- Lennard-Jones crystal
- alkane chains
- a double well problem in 2D

Kepler problem

Hamiltonian function:

$$H = \frac{\mathbf{p}^2}{2} - \frac{1}{|\mathbf{q}|}.$$

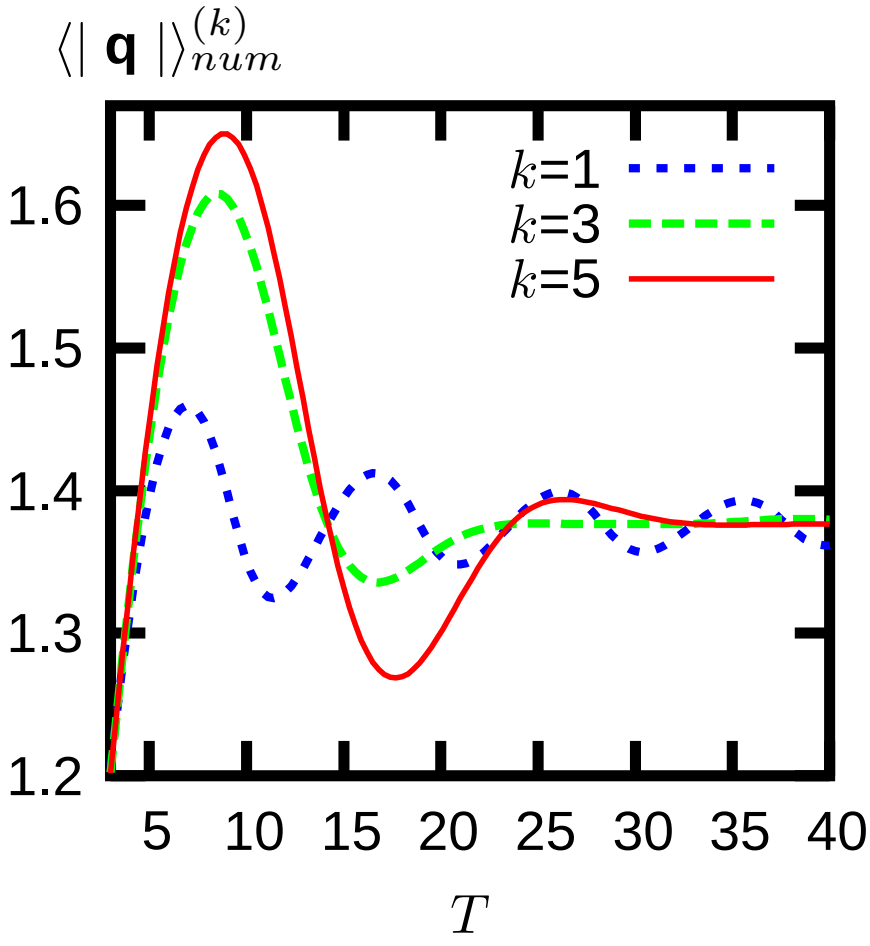
Observable:

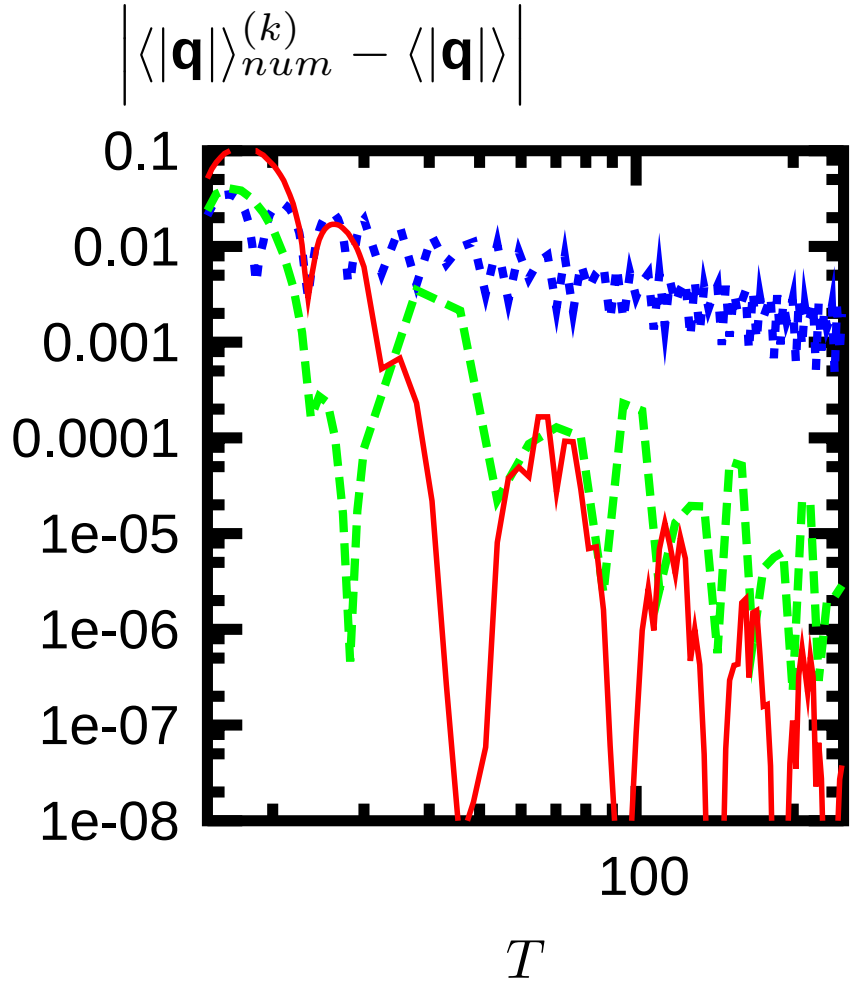
$$A = |\mathbf{q}|$$

Spatial average is known:

$$\langle |\mathbf{q}| \rangle_{NVE} = \frac{3 + 2\,E_0 L_0^2}{4\,|E_0|}$$

Kepler problem (period: 9.5)





Lennard-Jones crystal

Hamiltonian function:

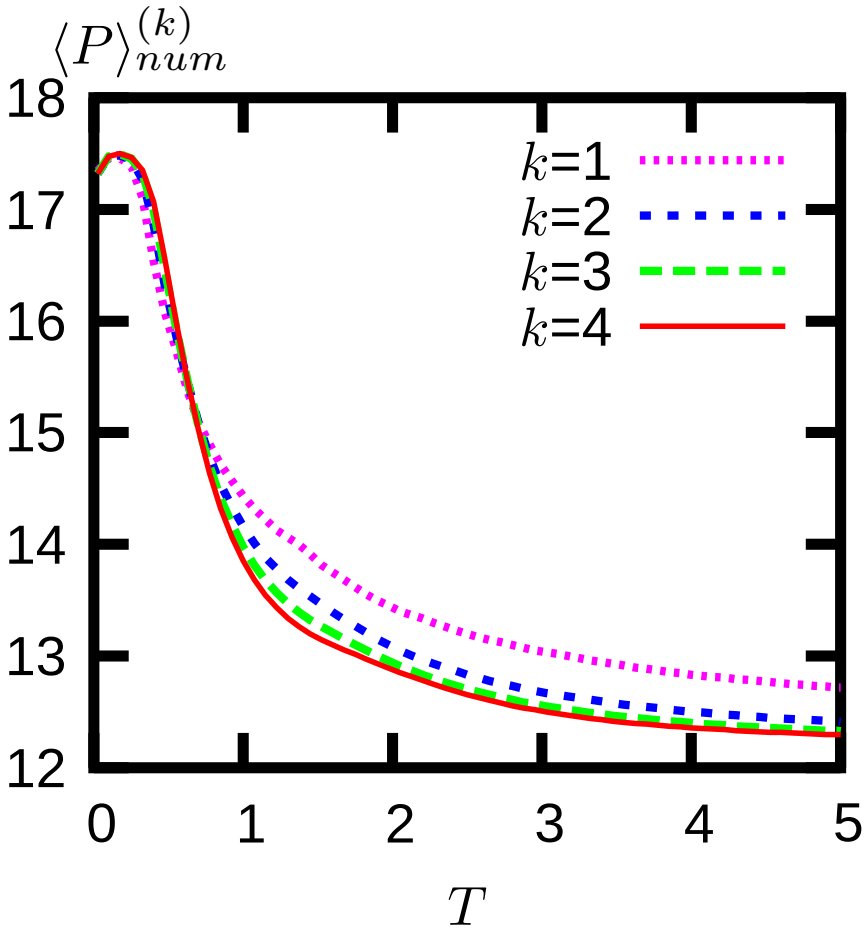
$$H(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{M} \frac{p_i^2}{2m_i} + \sum_i \sum_{j>i} V_{LJ}(|q_j - q_i|)$$

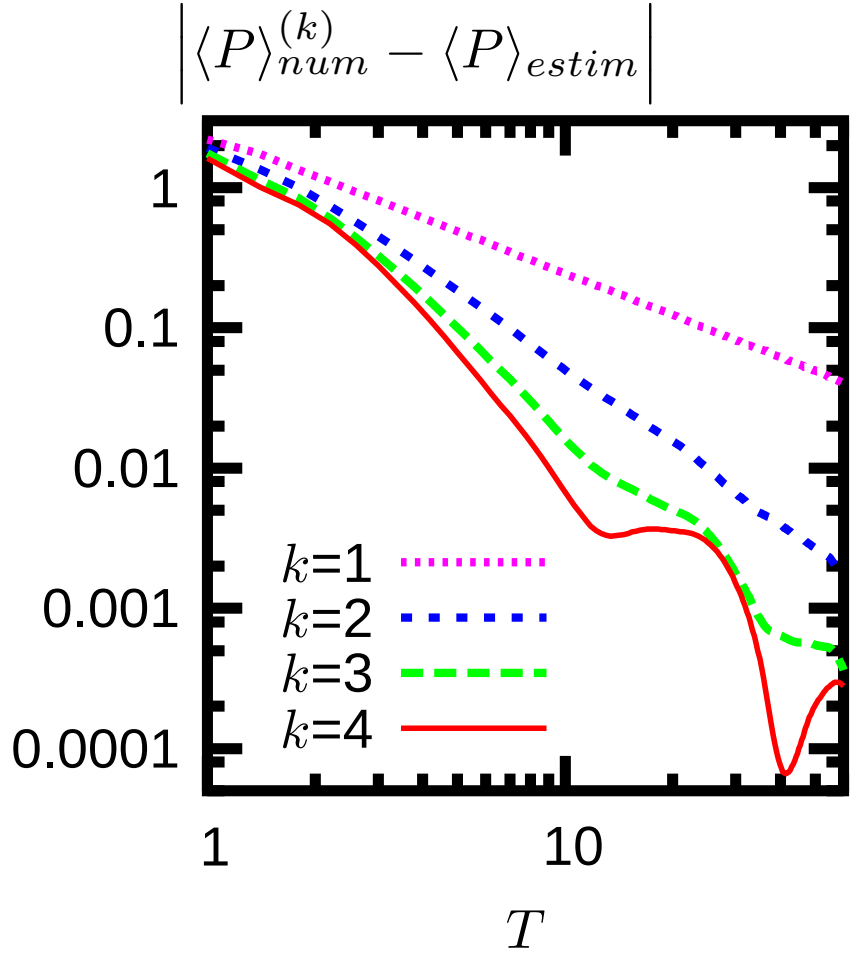
- Periodic boundary conditions,
- 288 particles in $[-3.17; 3.17]^3$, solid phase
- cutoff at $z = 3.08$, $V_{LJ}(z) = 4\left(\frac{1}{z^{12}} - \frac{1}{z^6}\right) - c_1 z - c_0$.

Observable: pressure of the system

$$A(\mathbf{q},\mathbf{p}) = P = \frac{1}{3V} \sum_{i=1}^{M} \left(\mathbf{p}_i^2 + \sum_{j>i} \mathbf{q}_{ij} \cdot \mathbf{F}_{ij} \right)$$

Lennard-Jones crystal



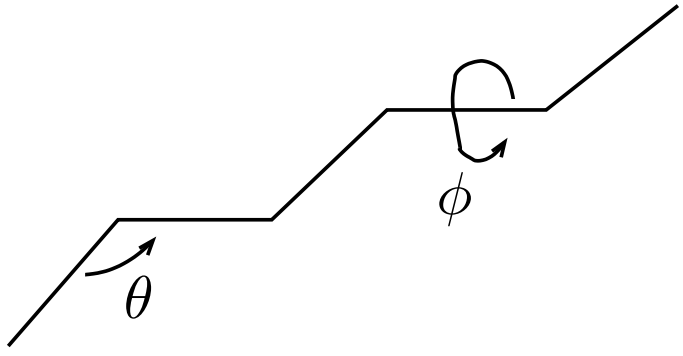


Alkane chains

United Atom (UA) model for alkane chain:

- bond length constraint: $d_{C-C} = 1.53A$
- bond angle potential $V_3(\theta)$ and dihedral angle potential $V_4(\cos\phi)$ according to Ryckaert-Bellemans model

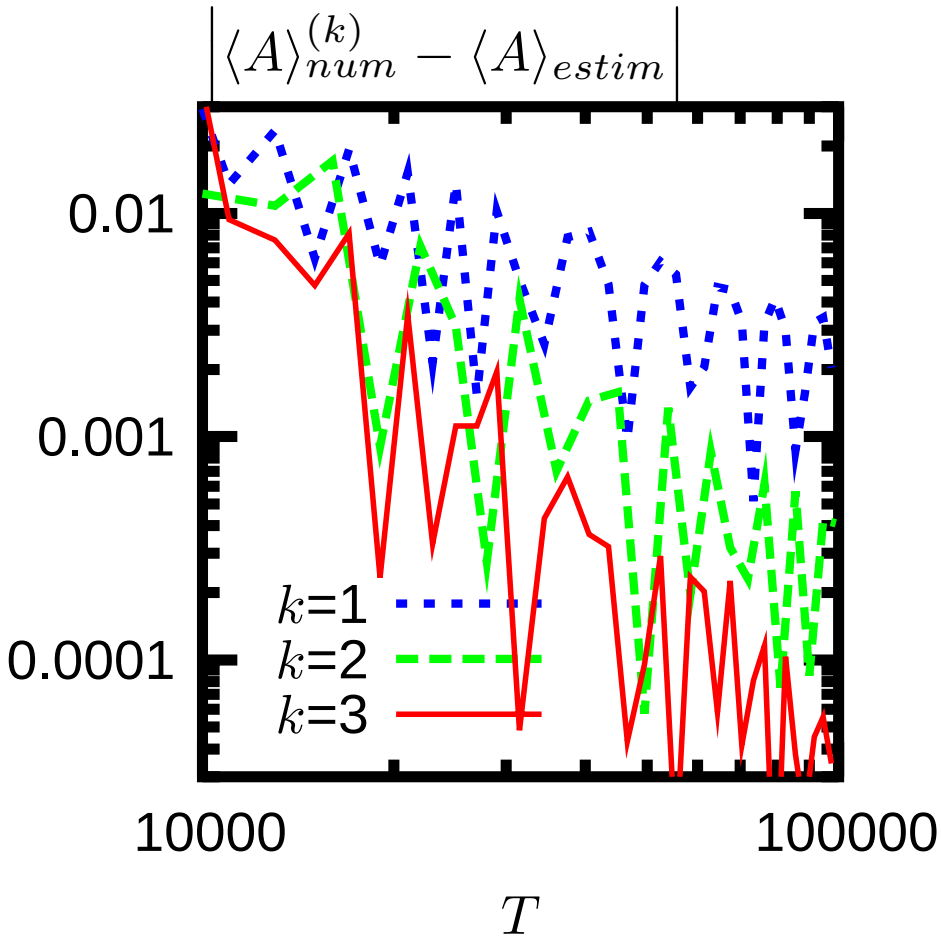
$$V(\mathbf{q}) = \sum_i V_2(q_{i+1} - q_i) + \sum_i V_3(\theta_i) + \sum_i V_4(\cos\phi_i)$$



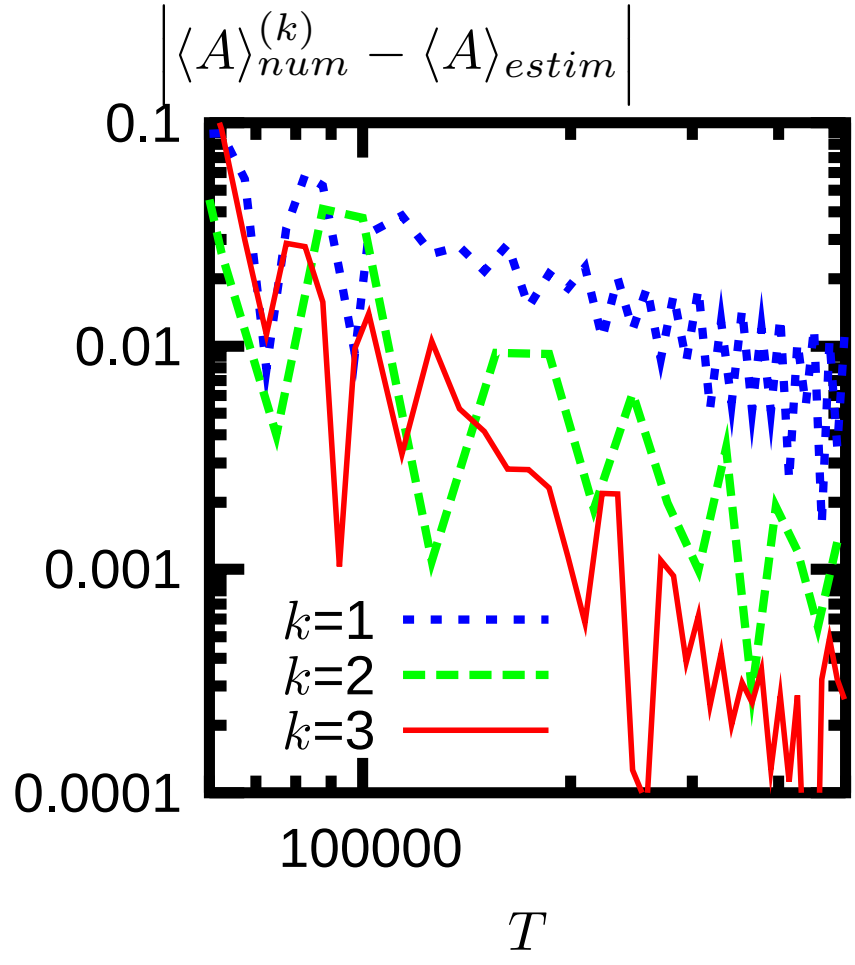
Observable: end-to-end distance

$$A(\mathbf{q}) = \frac{|\mathbf{q}_1 - \mathbf{q}_M|^2}{M d_{C-C}^2}.$$

Chains at very low energy



40 particles



100 particles

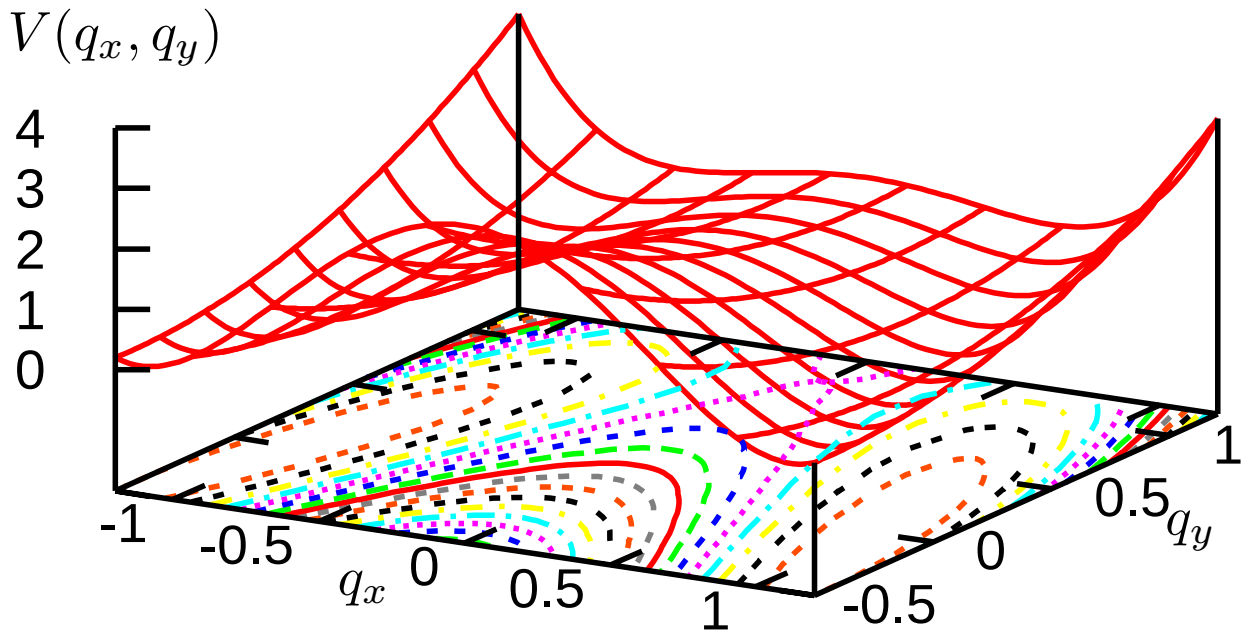
2D double well problem

Hamiltonian:

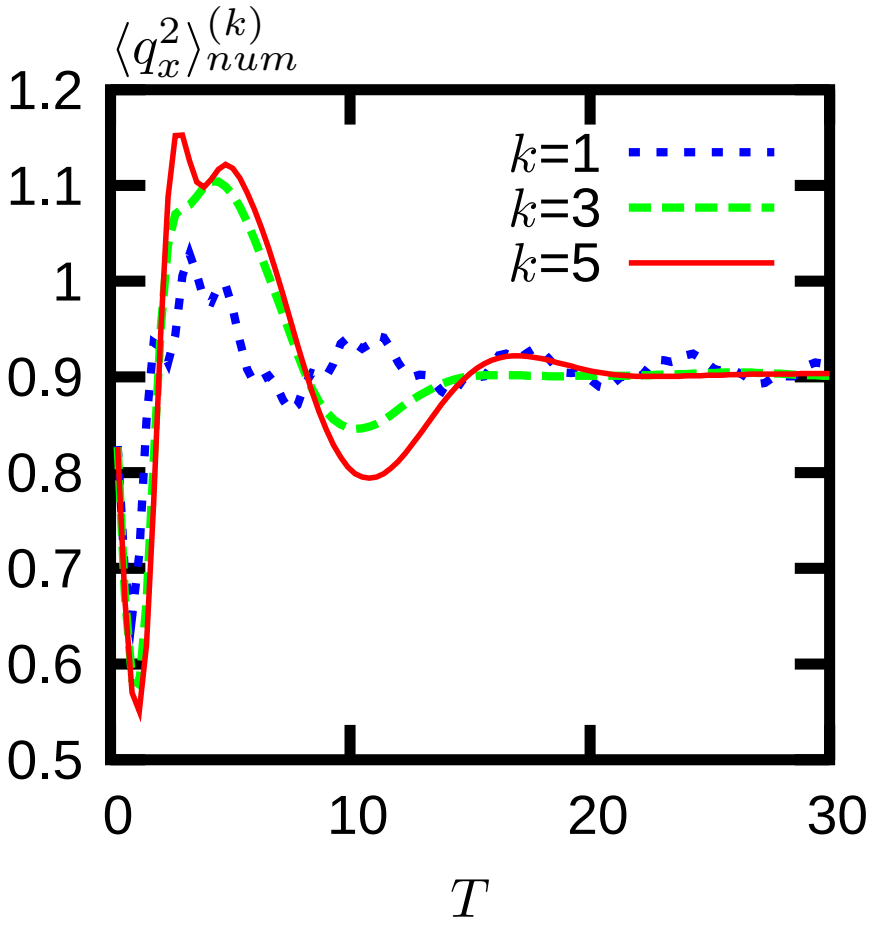
$$H = \frac{p_x^2}{2} + \frac{p_y^2}{2} + (q_x^2 - 1)^2 + (q_y + q_x^2 - 1)^2$$

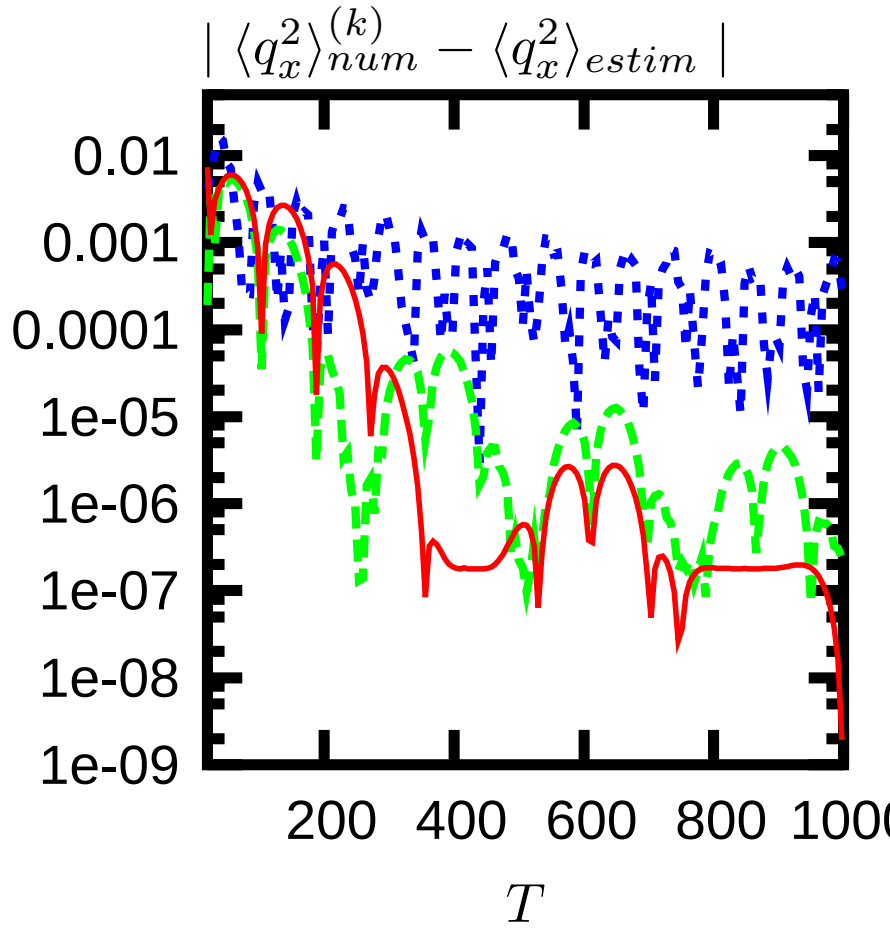
Potential energy:

- Two wells in $(\pm 1, 0)$ with $V(\pm 1, 0) = 0$,
- One saddle point in $(0, 1)$ with $V(0, 1) = 1$.



Double well problem, small energy case ($E_0 = 0.5$)





Do time averages converge to spatial average?

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Parametrization of the constant energy level-set ($E_0 < 1$, particle in the left well):

$$\begin{aligned} q_x &= -\sqrt{1+\sqrt{E_0}\cos\theta}, & q_y &= \sqrt{E_0}\ (\sin(\theta)\cos(\phi)-\cos(\theta)), \\ p_x &= \sqrt{2E_0}\ \sin(\theta)\sin(\phi)\cos(\psi), & p_y &= \sqrt{2E_0}\ \sin(\theta)\sin(\phi)\sin(\psi), \end{aligned}$$

with $(\theta, \phi, \psi) \in [0, \pi] \times [0, \pi] \times [0, 2\pi]$.

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with $(\theta, \phi, \psi) \in [0,\pi] \times [0,\pi] \times [0,2\pi]$.

Spatial average:

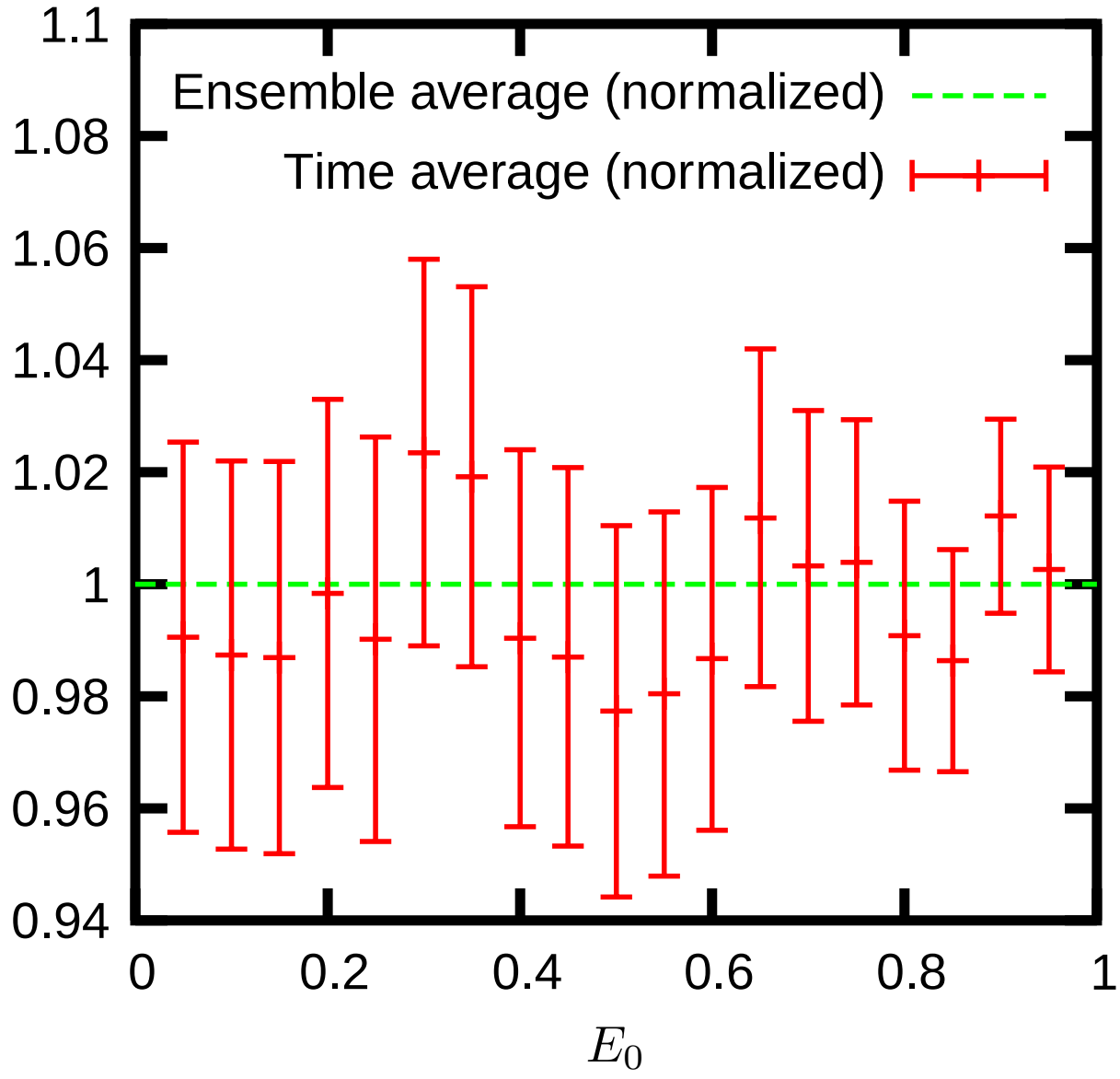
$$\langle A \rangle_{E_0} = \frac{\displaystyle\int_{[0,\pi]\times[0,\pi]\times[0,2\pi]} A\,(E_0,\theta,\phi,\psi)\ w_{E_0}(\theta,\phi)\ d\theta\, d\phi\, d\psi}{\displaystyle\int_{[0,\pi]\times[0,\pi]\times[0,2\pi]} w_{E_0}(\theta,\phi)\ d\theta\, d\phi\, d\psi}$$

Time averages do not converge to spatial average?!

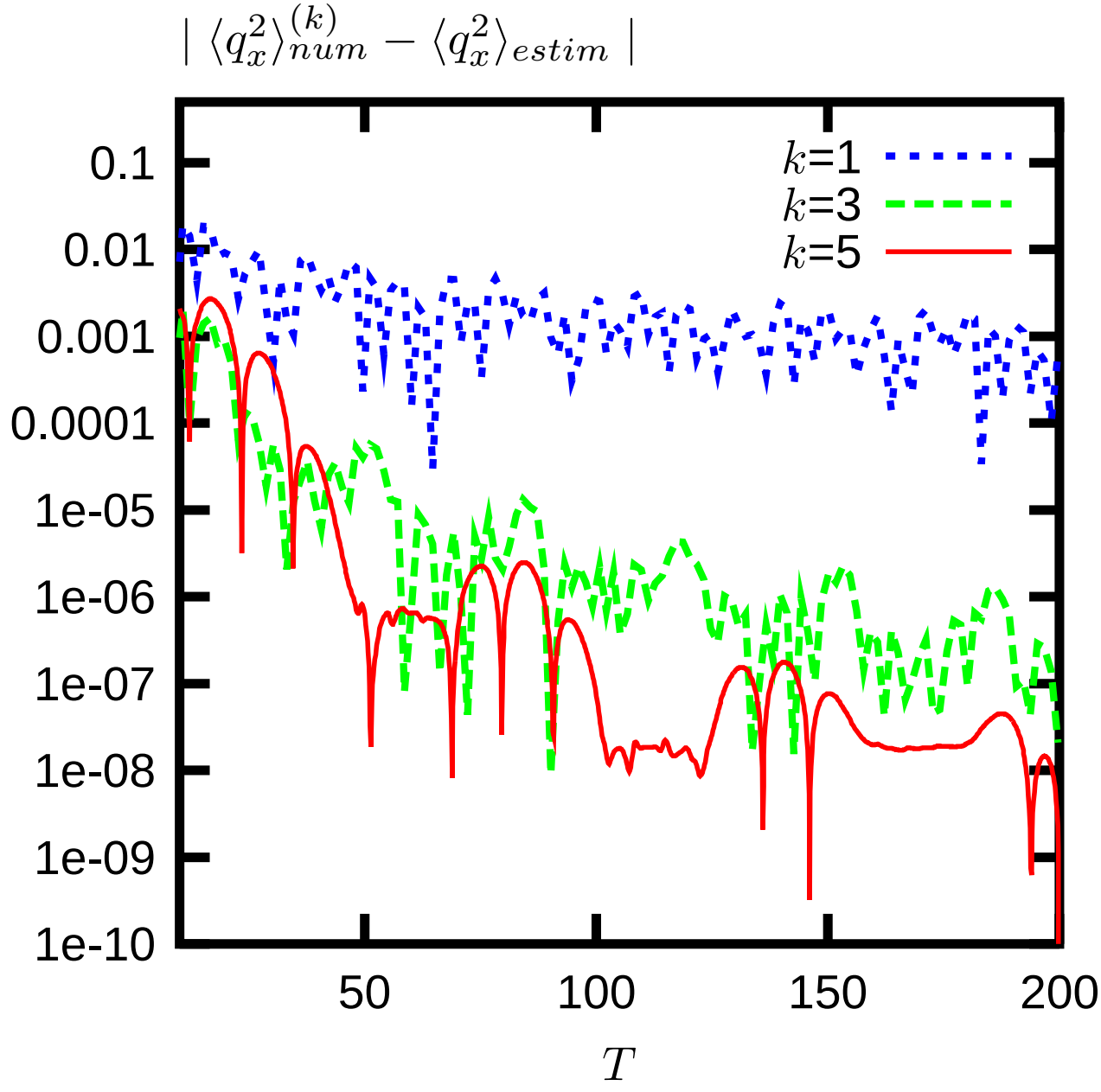
Test case for different initial conditions at $E_0 = 0.5$:

A	$\langle A \rangle^{NVE}$	$\langle A \rangle^{time}(\mathbf{q}_1^0, \mathbf{p}_1^0)$	$\langle A \rangle_2^{time}$	$\langle A \rangle_3^{time}$
q_x	-0.94459	-0.93118	-0.95585	-0.92386
q_x^2	0.92843	0.90077	0.95170	0.88565
q_x^4	0.98964	0.92855	1.04074	0.89565
q_y	0.071562	0.099221	0.048292	0.114346
q_y^2	0.25517	0.14298	0.34725	0.085192
p_x^2	0.24482	0.33949	0.16794	0.38717
p_x^2	0.24482	0.14615	0.32574	0.095278
$V(q_x, q_y)$	0.25517	0.25717	0.25315	0.25878

Mean value over initial conditions ($A = q_y^2$)



Double well problem, large energy case ($E_0 = 5.125$)



Case of an energy of 1.25 (just larger than the barrier)

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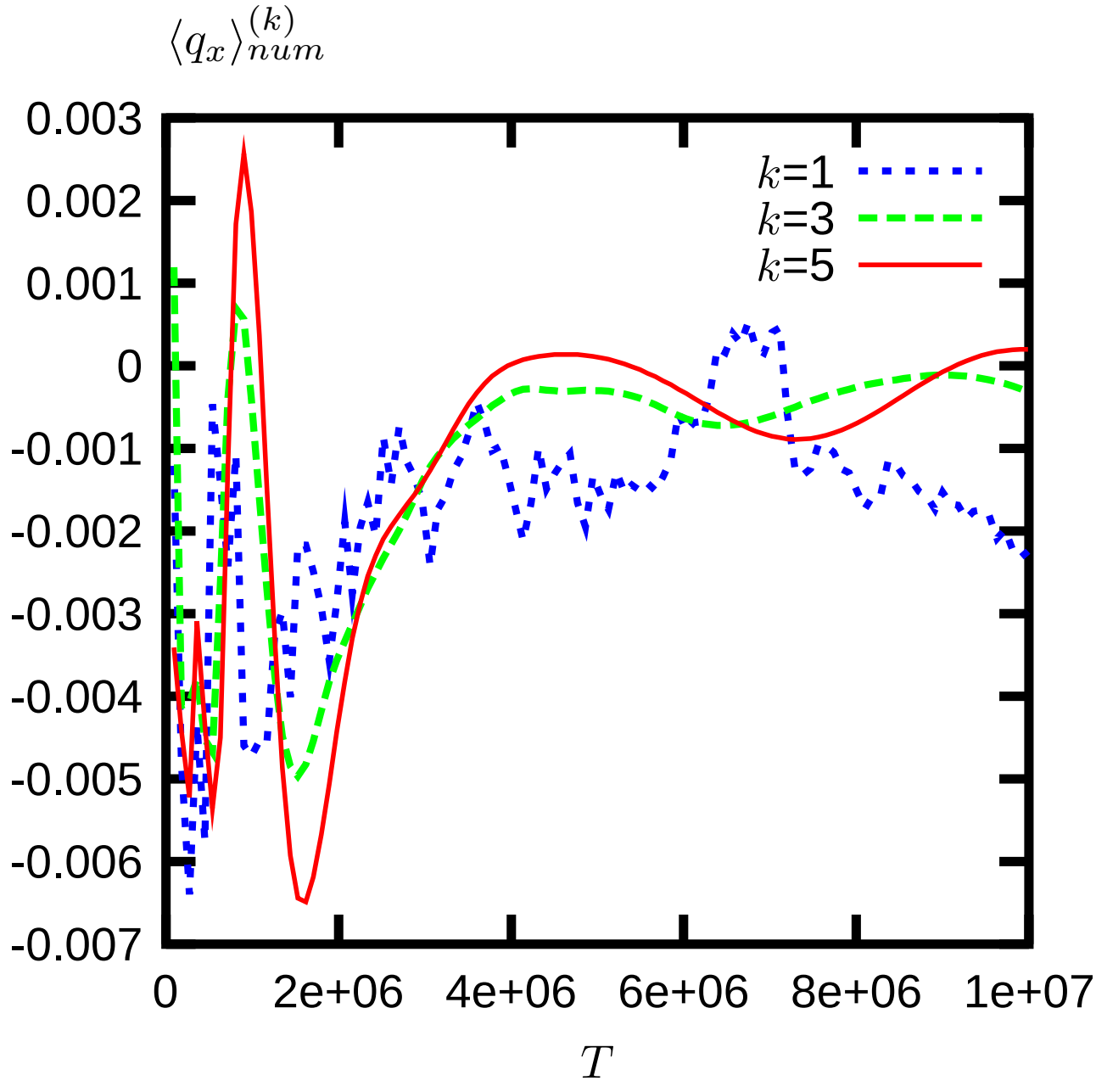
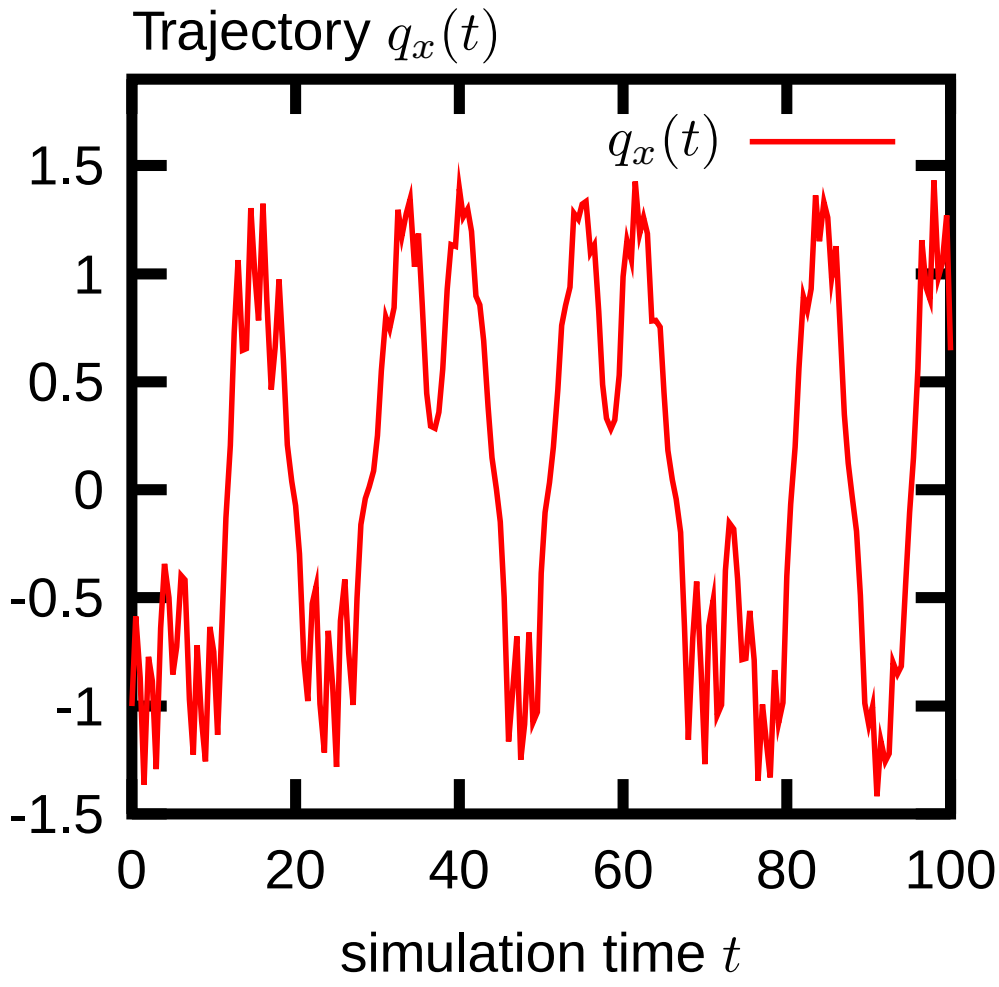


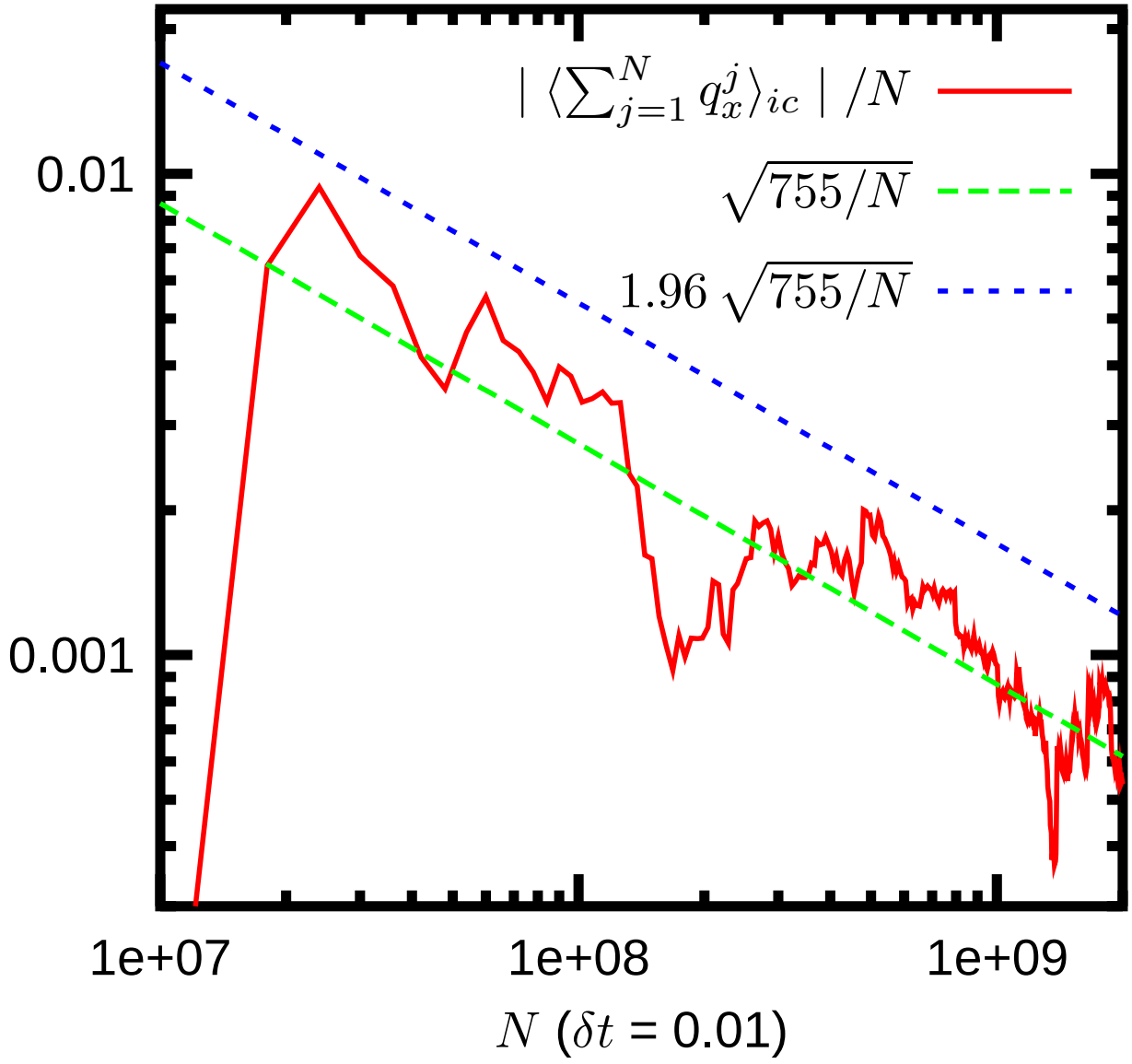
Determination of a well residence time



In 50% of the events, well separation line crossing after a residence time of 7.55.

A stochastic model

Convergence rate of $\frac{1}{N}\sum_{j=1}^{N} q_x^j$ to 0



What do we learn from this simple example?

First case:

- the MD trajectory explores a unique well,
- or all explored wells are considered as a single well (high energy case):

then

- time averages converge to ensemble averages with rate $1/T$,
- it is possible to speed-up the convergence by filtering the signal:

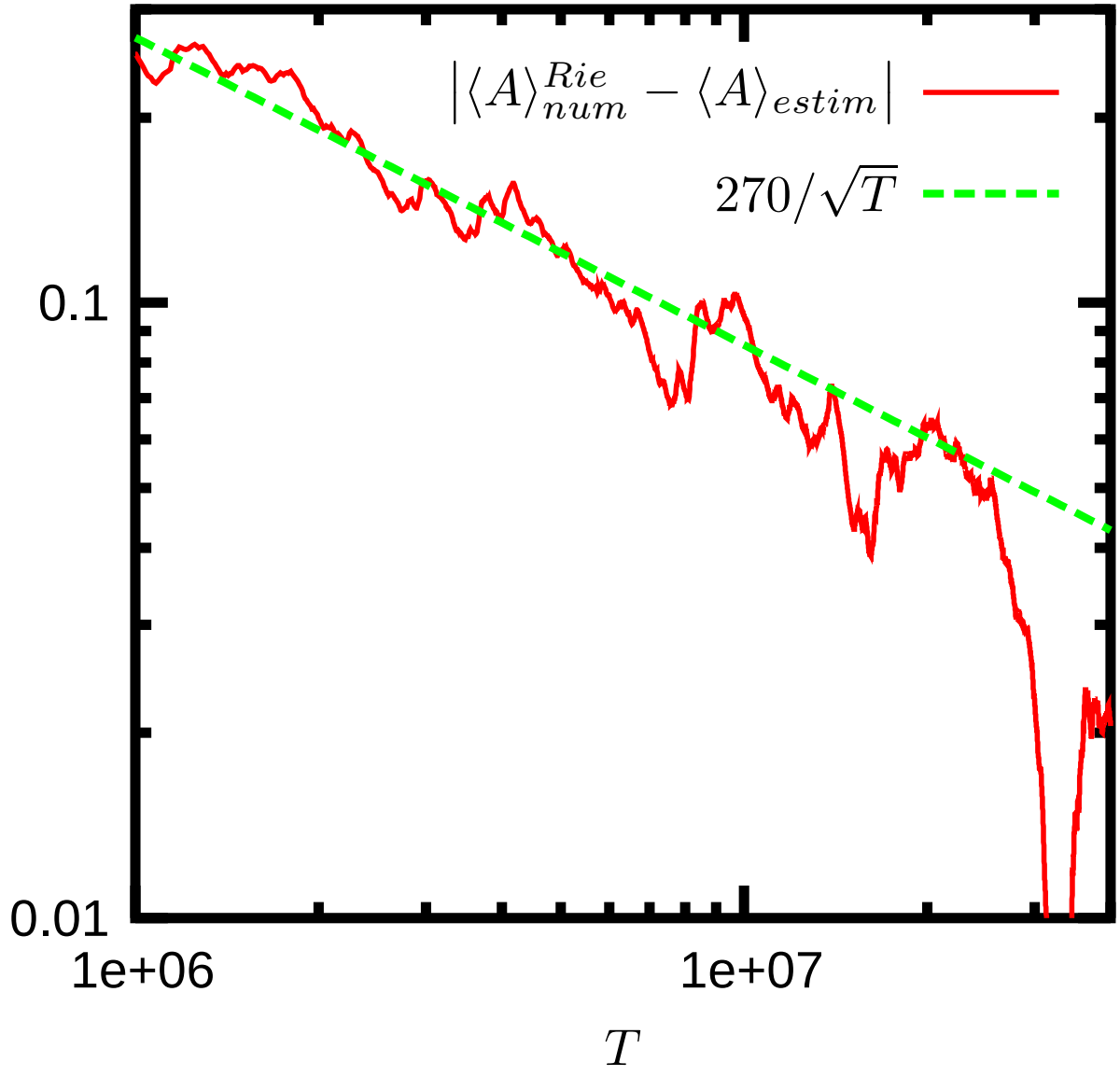
$$O\left(\frac{1}{T}\right) \mapsto O\left(\frac{1}{T^k}\right)$$

Second case:

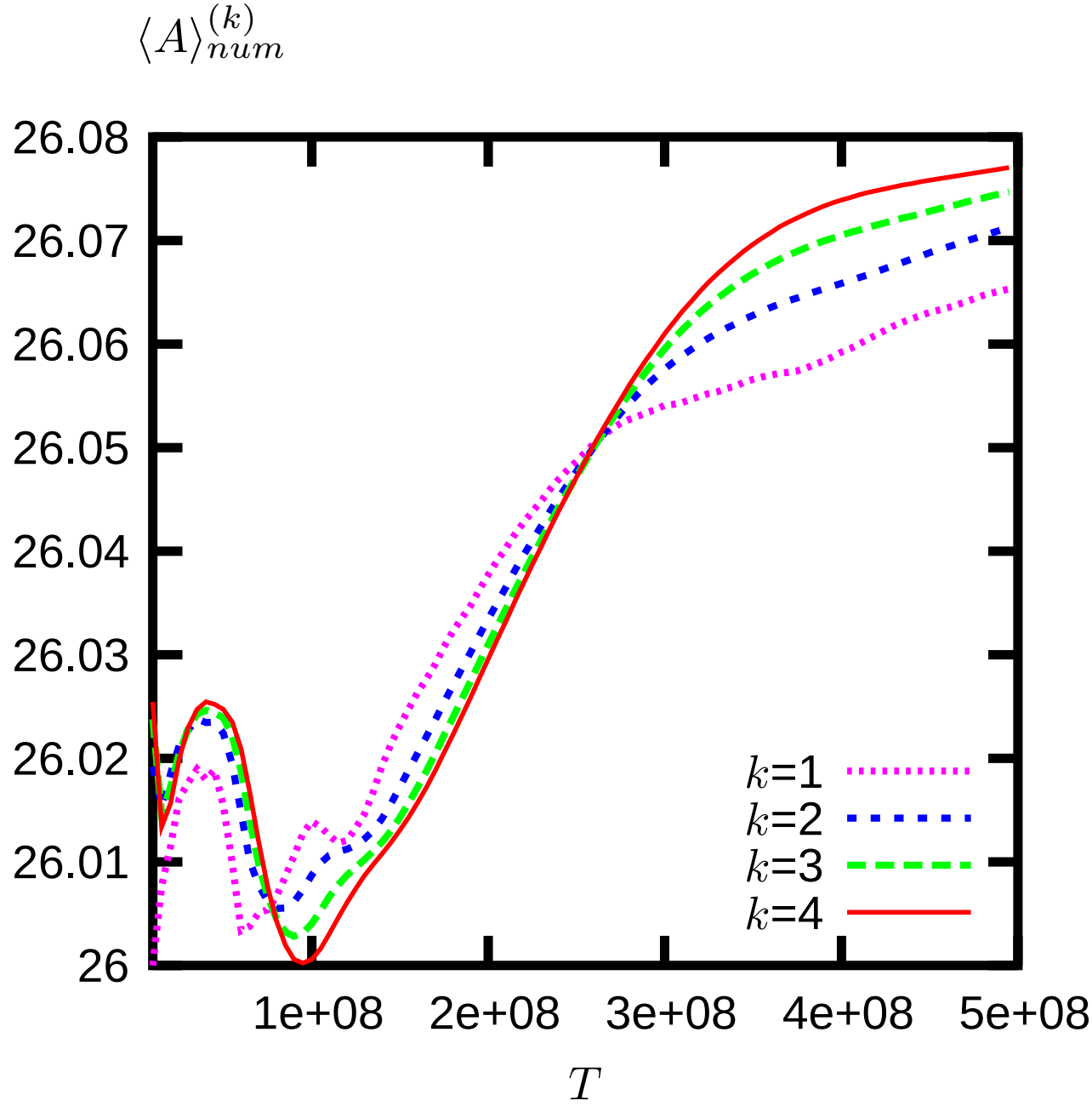
Residence time $\gg$ transition time: convergence with rate $1/\sqrt{T}$.

$\rightarrow$ Can it be generalized to alkane chains?

Chain of $M = 40$ atoms (kinetic temperature $= 135$ K)



Chain of $M = 40$ atoms (kinetic temperature $= 4.16$ K)



Conclusion on alkane chain example

- At low and high energy,
  - time averages converge
  - and it is possible to speed-up the convergence by filtering the signal:

$$O\left(\frac{1}{T}\right) \mapsto O\left(\frac{1}{T^k}\right)$$

- At medium energy, convergence of time averages is not very clear . . . (and rate is probably not better than Monte Carlo rate)

Unfortunately, the interesting temperature $\in$ medium energy case!

Cancès et al, J. Chem. Phys. **121** (21), 10346, 2004

Conclusions

The filtering method:

- is easy to implement,
- in the case when time averages converge, it speeds-up the convergence from $1/T$ to $1/T^k$ (for any k).

Future work:

- time correlation functions,
- NVT sampling: compare the efficiency of different methods.