

High-order averaging schemes for molecular dynamics simulations

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Molecular Dynamics to compute phase space averages

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

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

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

MD computations:

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

Outline of the talk

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

$$\begin{aligned}\langle A \rangle^{(1)}(T) &= \frac{1}{T} \int_0^T A(q(t), p(t)) dt = \frac{1}{T} \int_0^T \sum_{k \in \mathbb{Z}} a_k \exp(ik\phi) \exp(ik\omega t) dt \\ &= a_0 + \sum_{k \neq 0} a_k \exp(ik\phi) \frac{1}{T} \frac{e^{ik\omega T} - 1}{ik\omega}\end{aligned}$$

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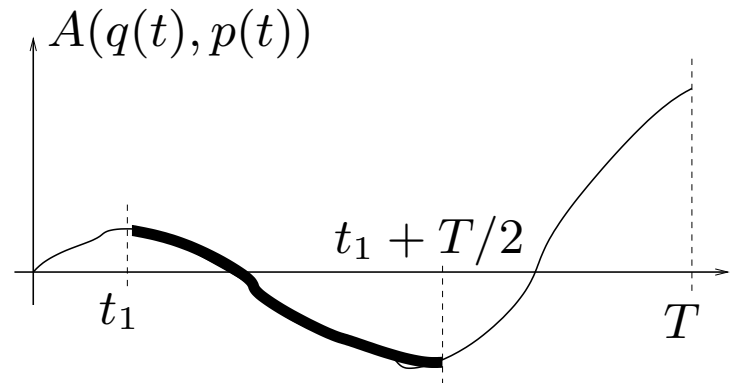
$$a_0 = \frac{1}{2\pi} \int A(C_0 \cos \theta, -C_0 \omega \sin \theta) d\theta = \langle A \rangle_{NVE}$$

So

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

Convergence rate improvement

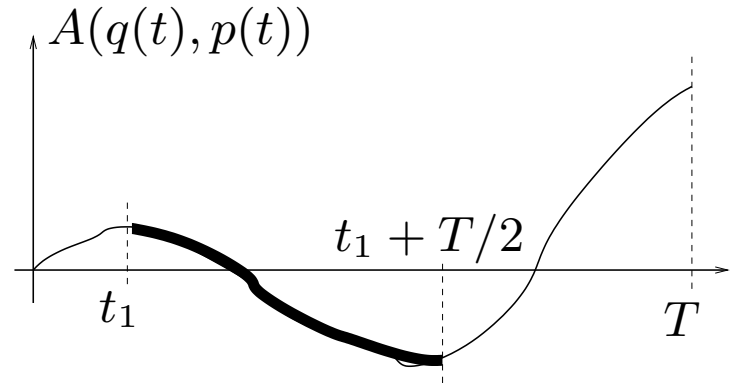
Averaging over initial conditions:



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

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Plug previous Fourier expansion:

$$= \left(\frac{2}{T} \right)^2 \int_0^{T/2} \int_0^{T/2} \sum_{k \in \mathbb{Z}} a_k \exp(ik\phi) \exp(ik\omega(t_1 + t_2)) dt_1 dt_2$$

$$= a_0 + \sum_{k \neq 0} a_k \exp(ik\phi) \left(\frac{2}{T} \int_0^{T/2} \exp(ik\omega t) dt \right)^2$$

$$= \langle A \rangle_{NVE} + O\left(\frac{1}{T^2}\right)$$

Signal filtering (a first example)

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

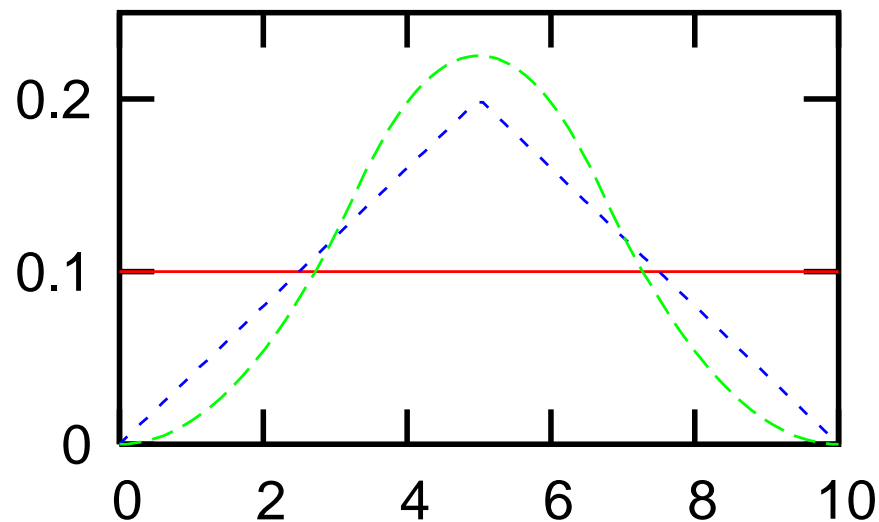
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With window function $\chi_T(t) = \frac{1}{T} \mathbf{1}_{[0,T]}(t)$:

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

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



First result (M particles in 3D)

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

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

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

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

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

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

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

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 $f_k(x) \propto x^{k-1} (1-x)^{k-1}$ (bell-shaped)

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

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

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

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 **modified** hamiltonian 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.

→ For any **arbitrary** k , possible to design a filter such that polynomial decay of the error ($1/T^k$).

→ This decay is made possible because the values $A(\mathbf{q}_j, \mathbf{p}_j)$ 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:

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

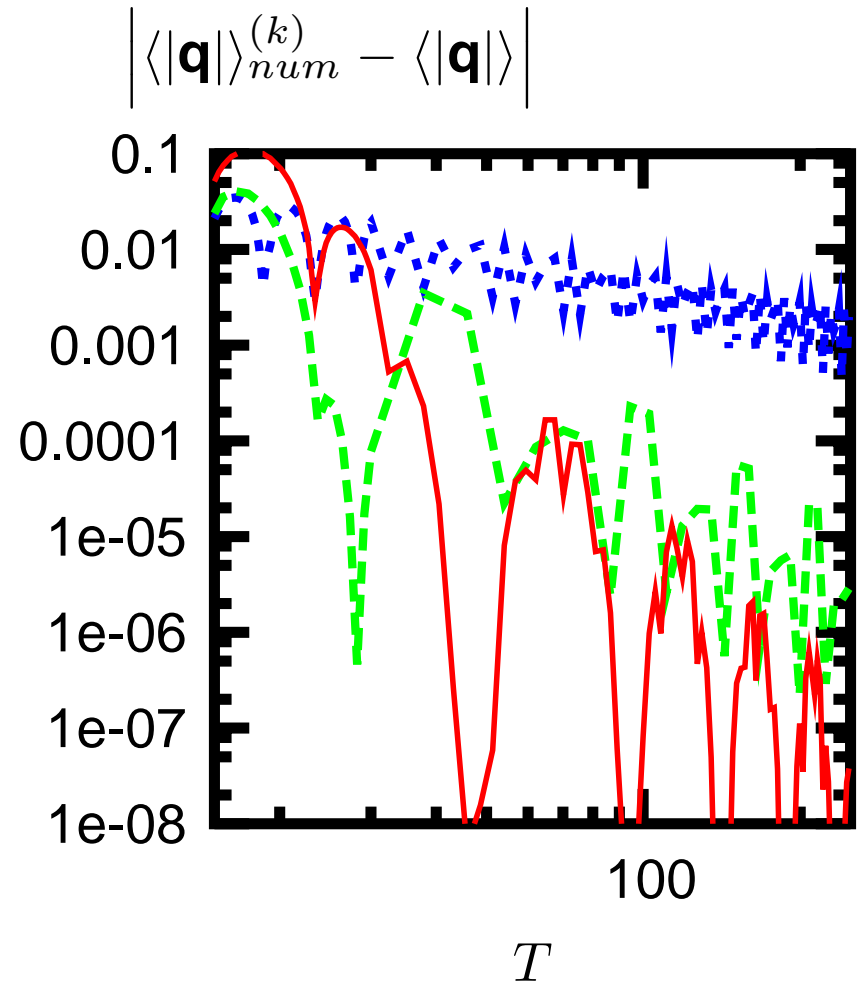
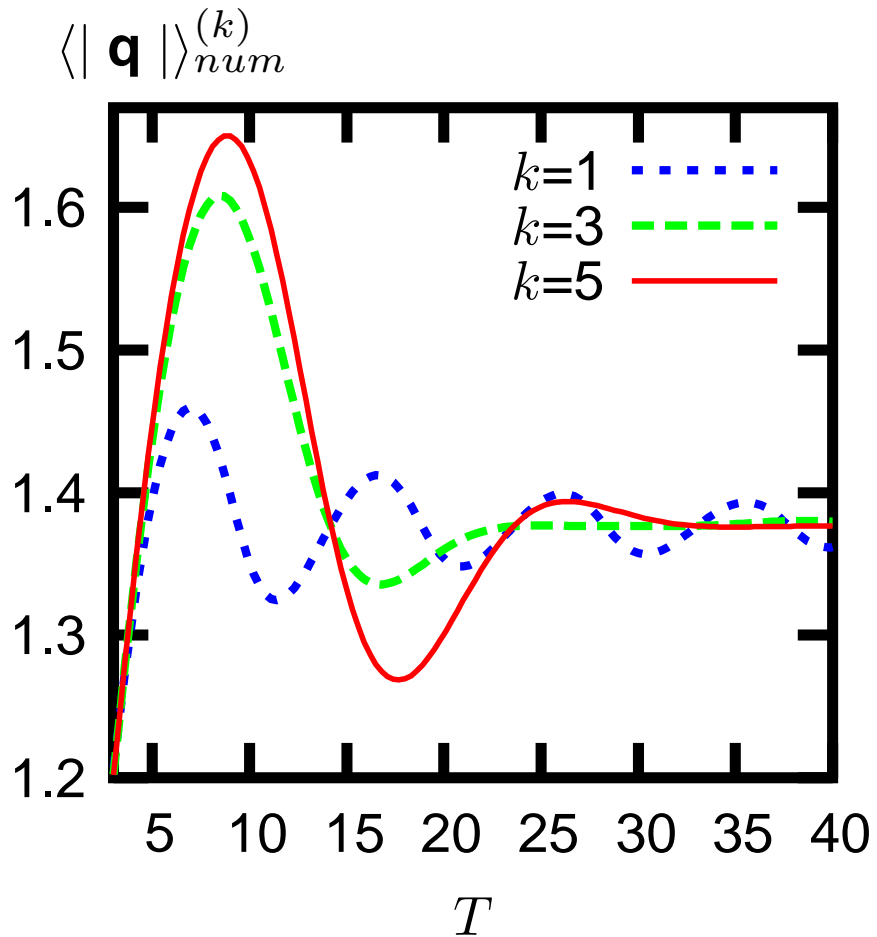
Observable:

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

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:

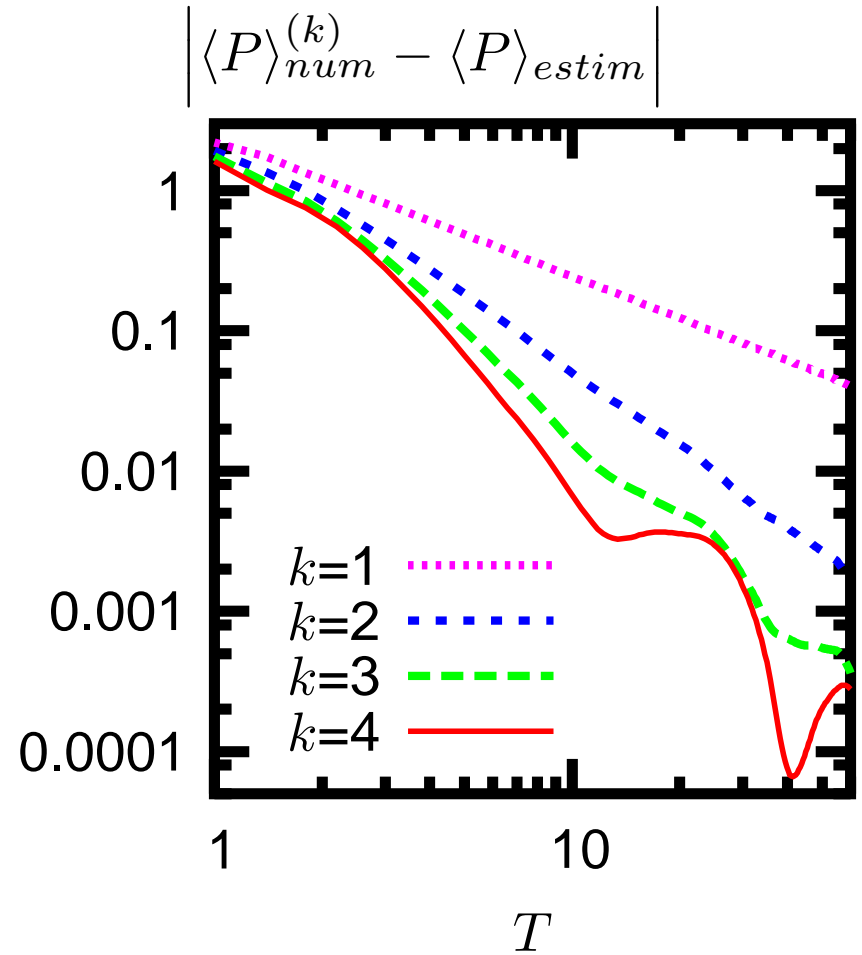
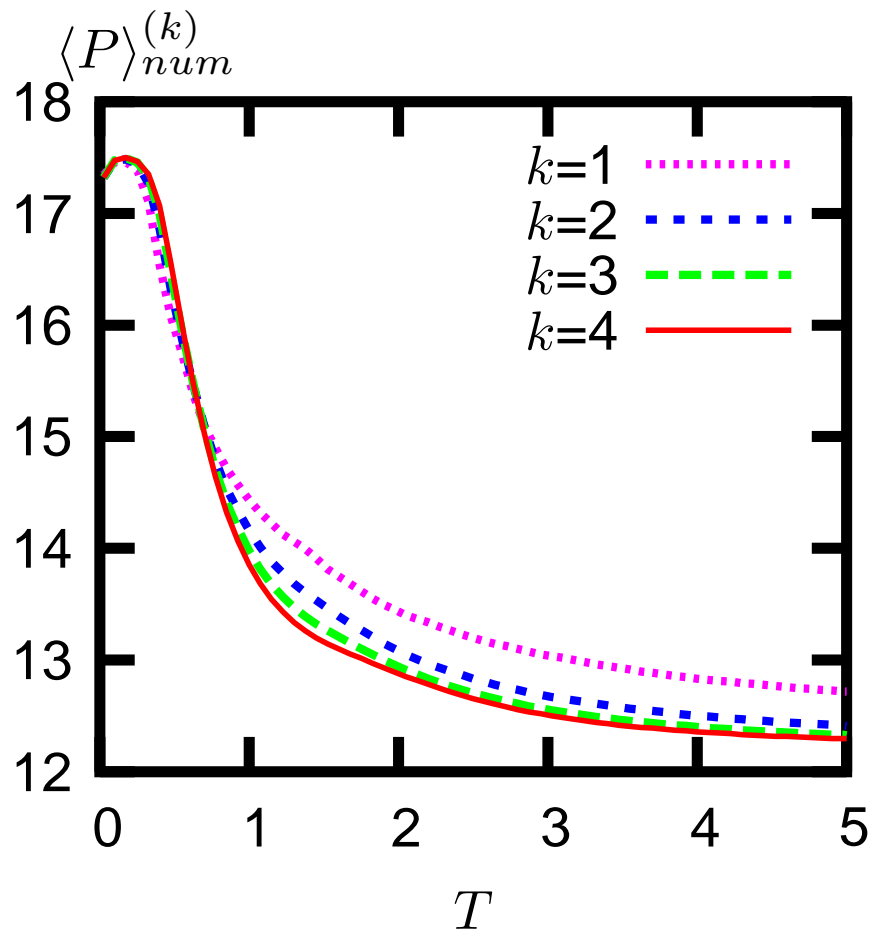
$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^M \frac{p_i^2}{2m_i} + \sum_i \sum_{j>i} V_{LJ}(|q_j - q_i|)$$

- 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

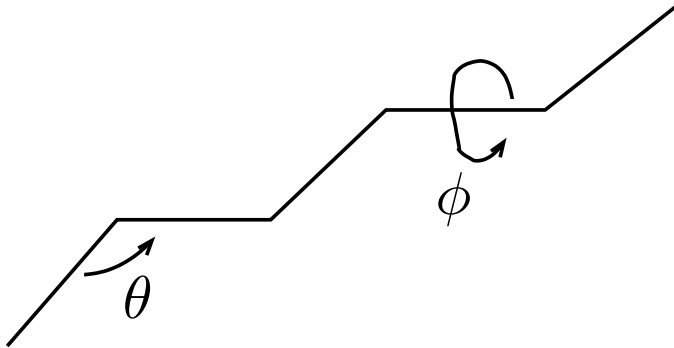


Alkane chains

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

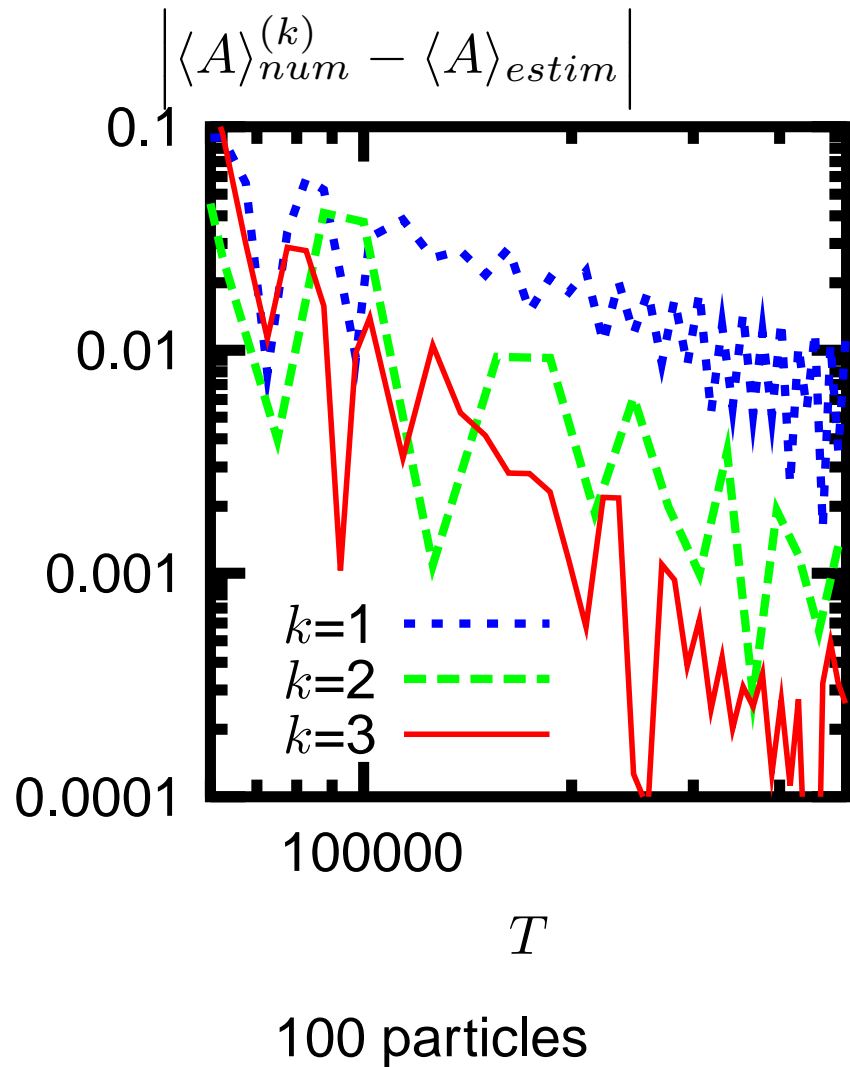
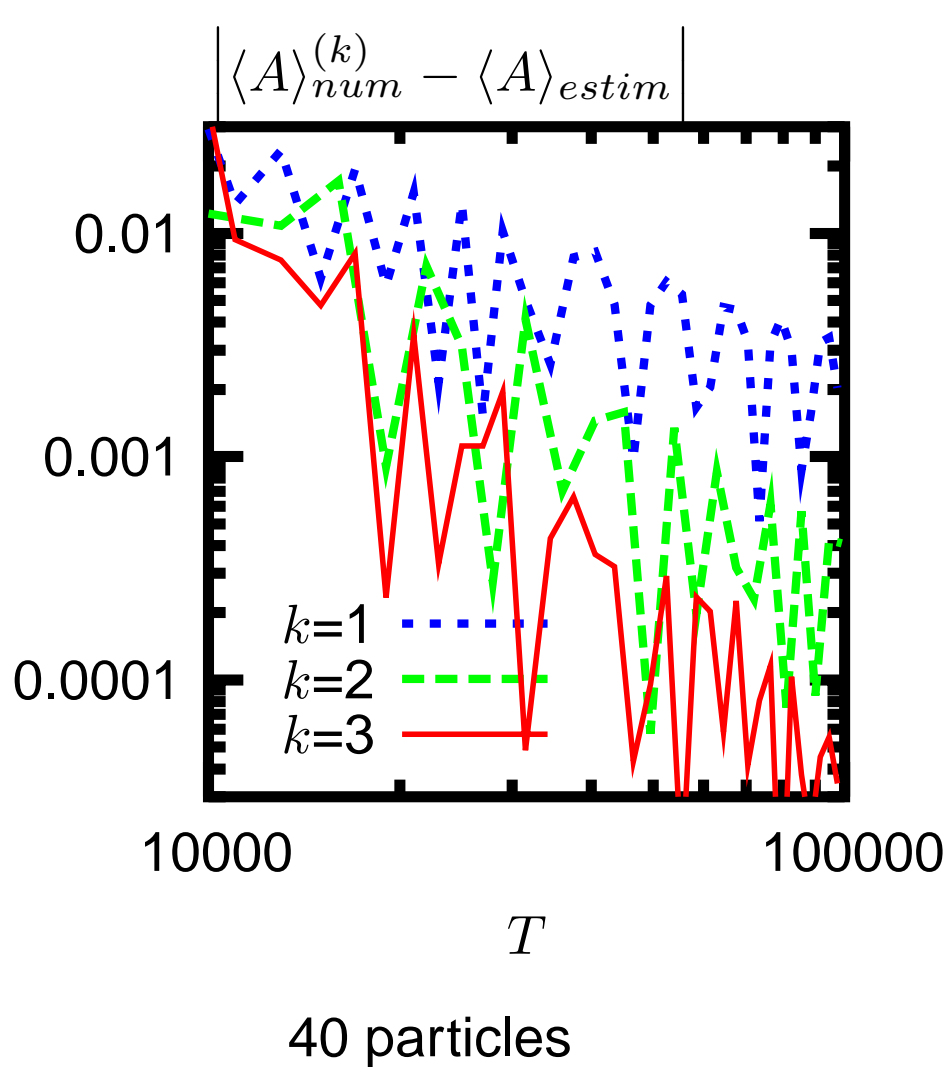
$$V(\mathbf{q}) = \sum_i V_2(q_{i+1} - q_i) + \sum_i V_3(\theta_i) + \sum_i V_4(\cos \phi_i)$$



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



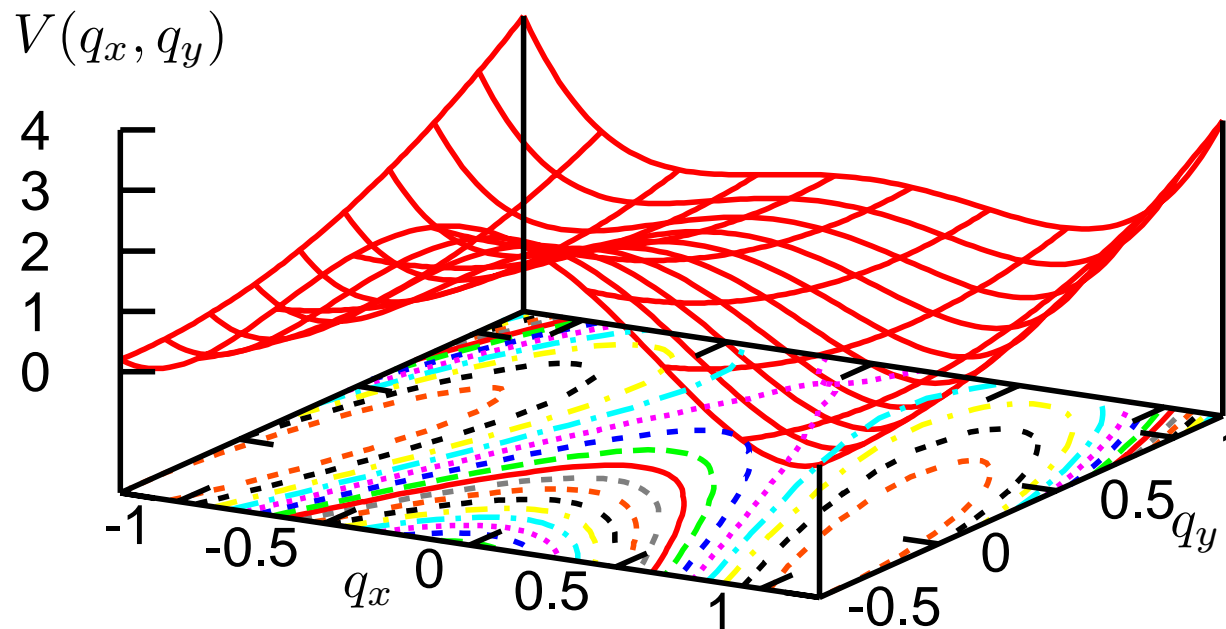
2D double well problem

Hamiltonian:

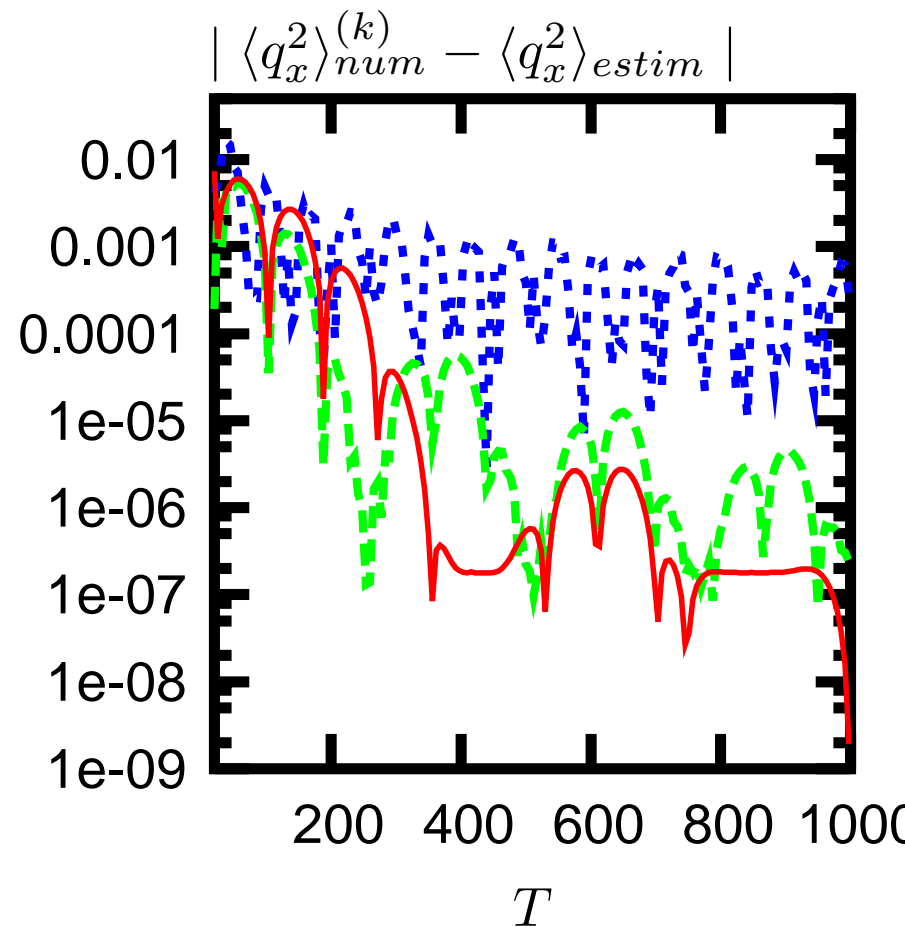
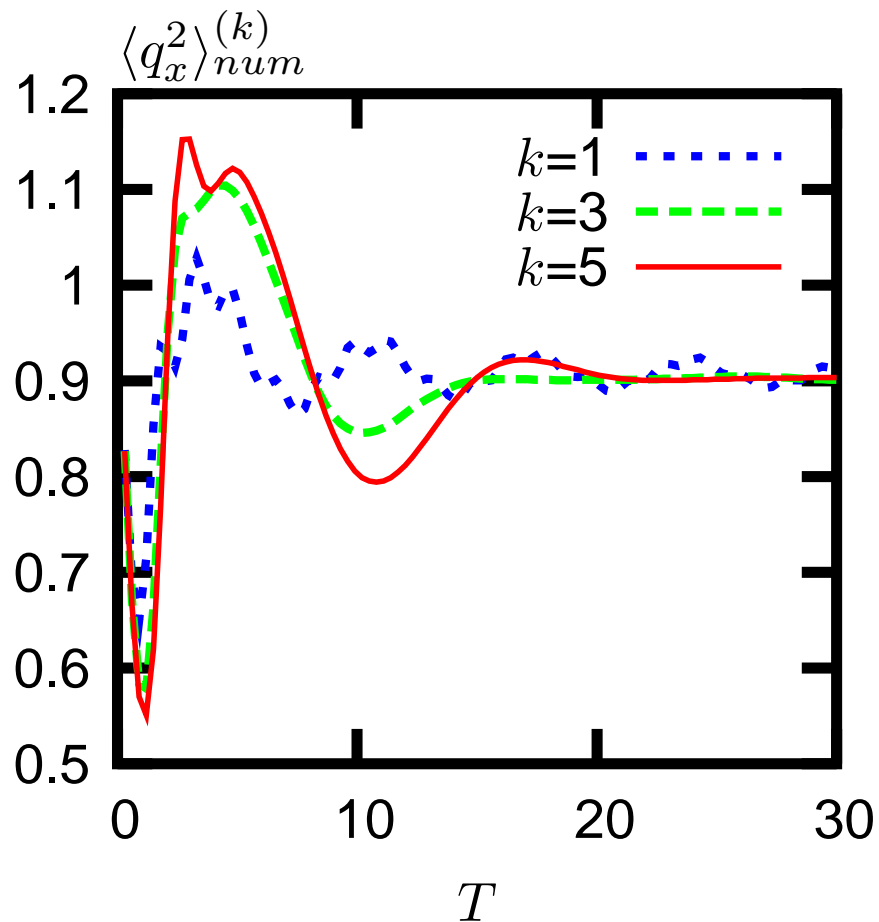
$$H = \frac{p_x^2}{2} + \frac{p_y^2}{2} + (q_x^2 - 1)^2 + (q_y + q_x^2 - 1)^2$$

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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Spatial average:

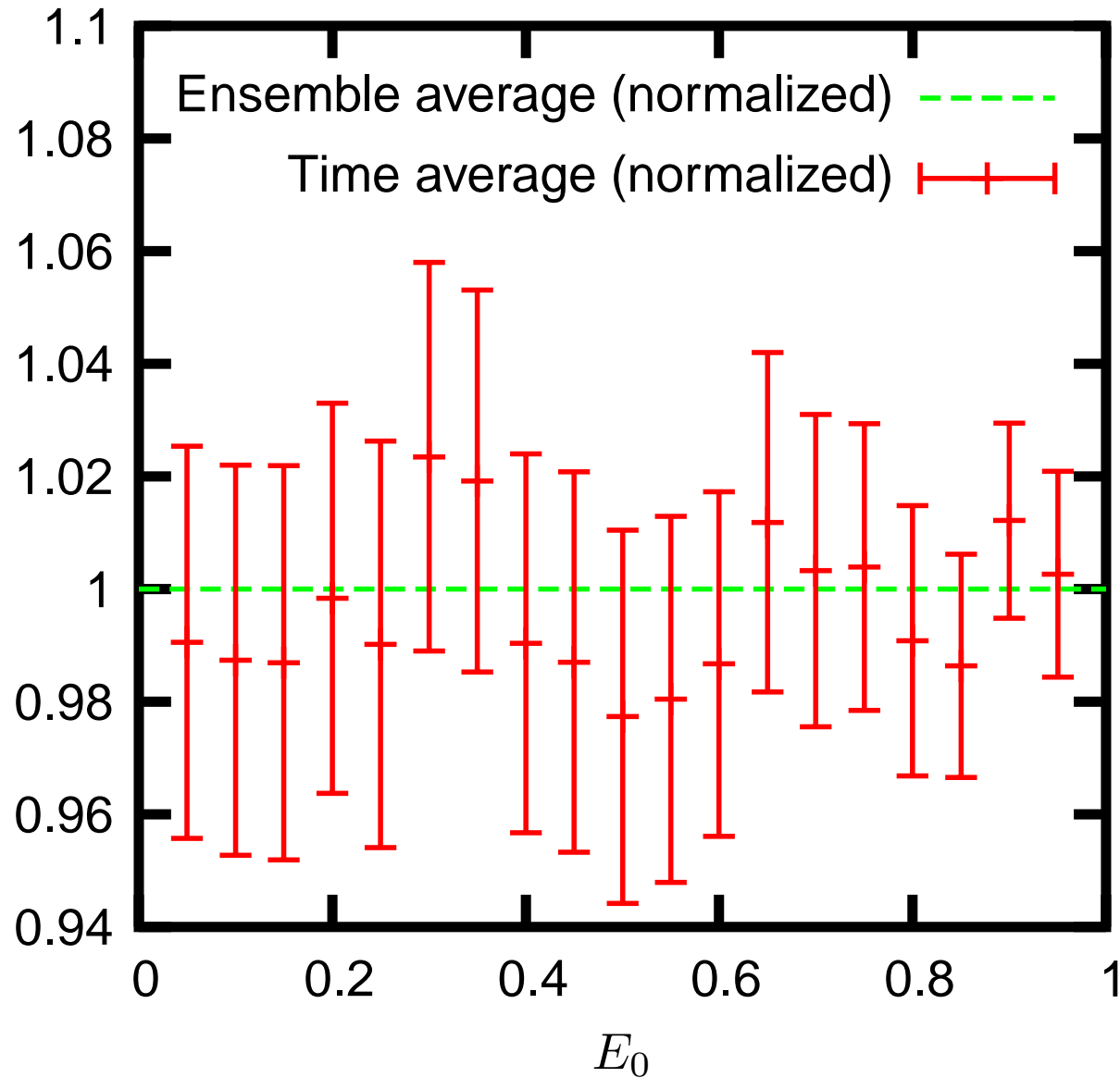
$$\langle A \rangle_{E_0} = \frac{\int_{[0, \pi] \times [0, \pi] \times [0, 2\pi]} A(E_0, \theta, \phi, \psi) w_{E_0}(\theta, \phi) d\theta d\phi d\psi}{\int_{[0, \pi] \times [0, \pi] \times [0, 2\pi]} w_{E_0}(\theta, \phi) d\theta d\phi d\psi}$$

Time averages do not converge to spatial average?!

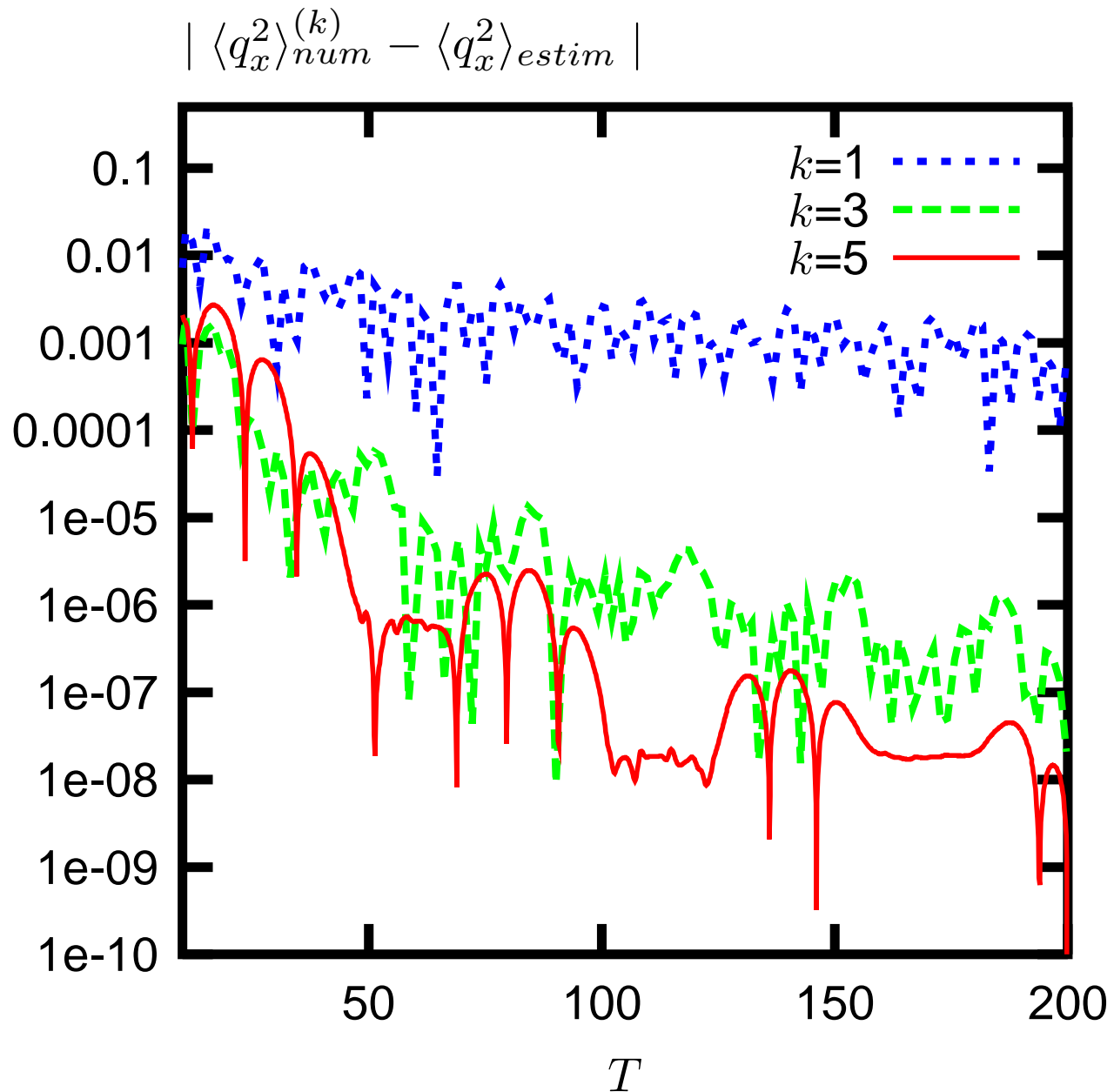
Test case for different initial conditions at $E_0 = 0.5$:

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 ($A = q_y^2$)

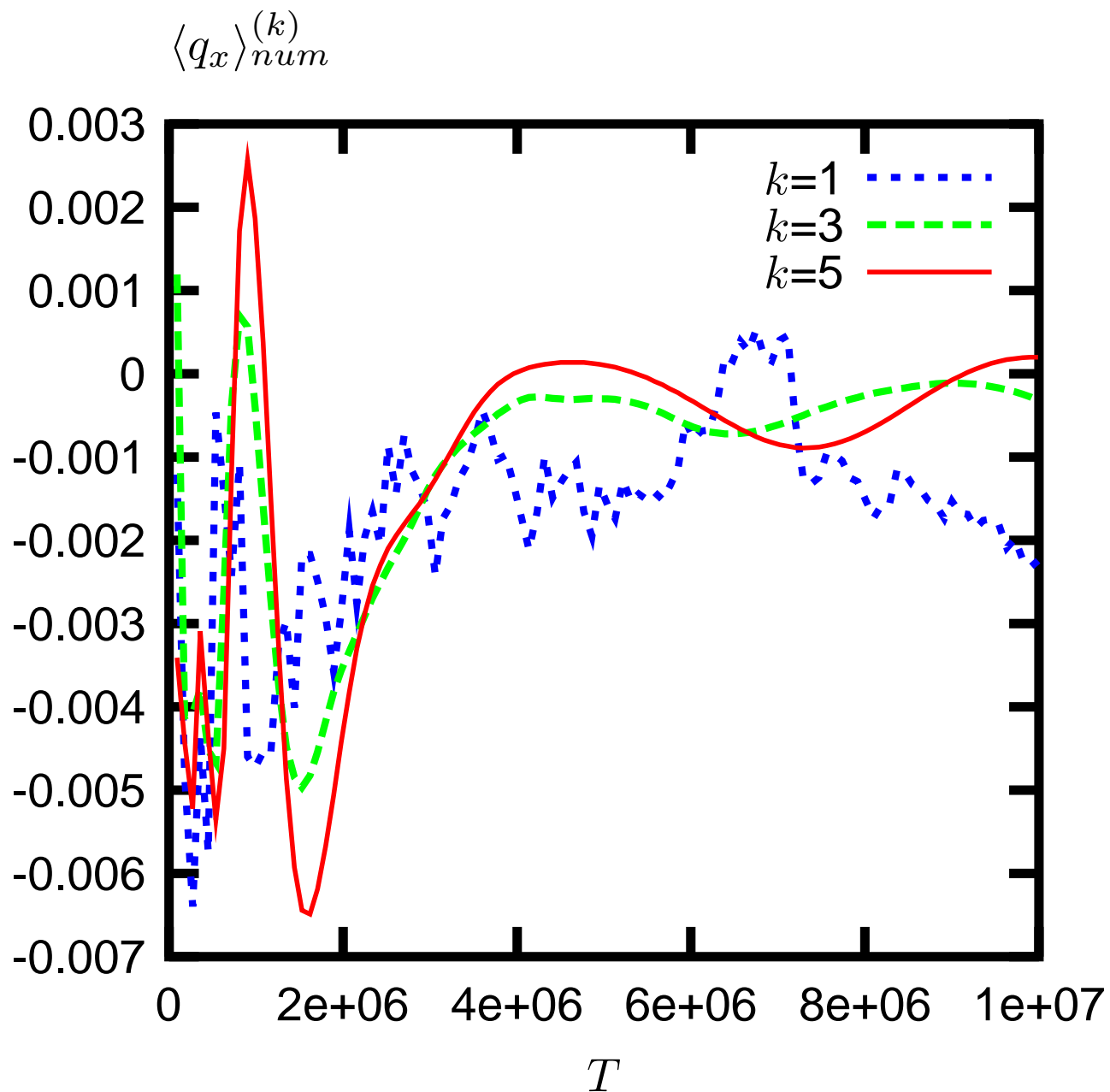


Double well problem, large energy case ($E_0 = 5.125$)

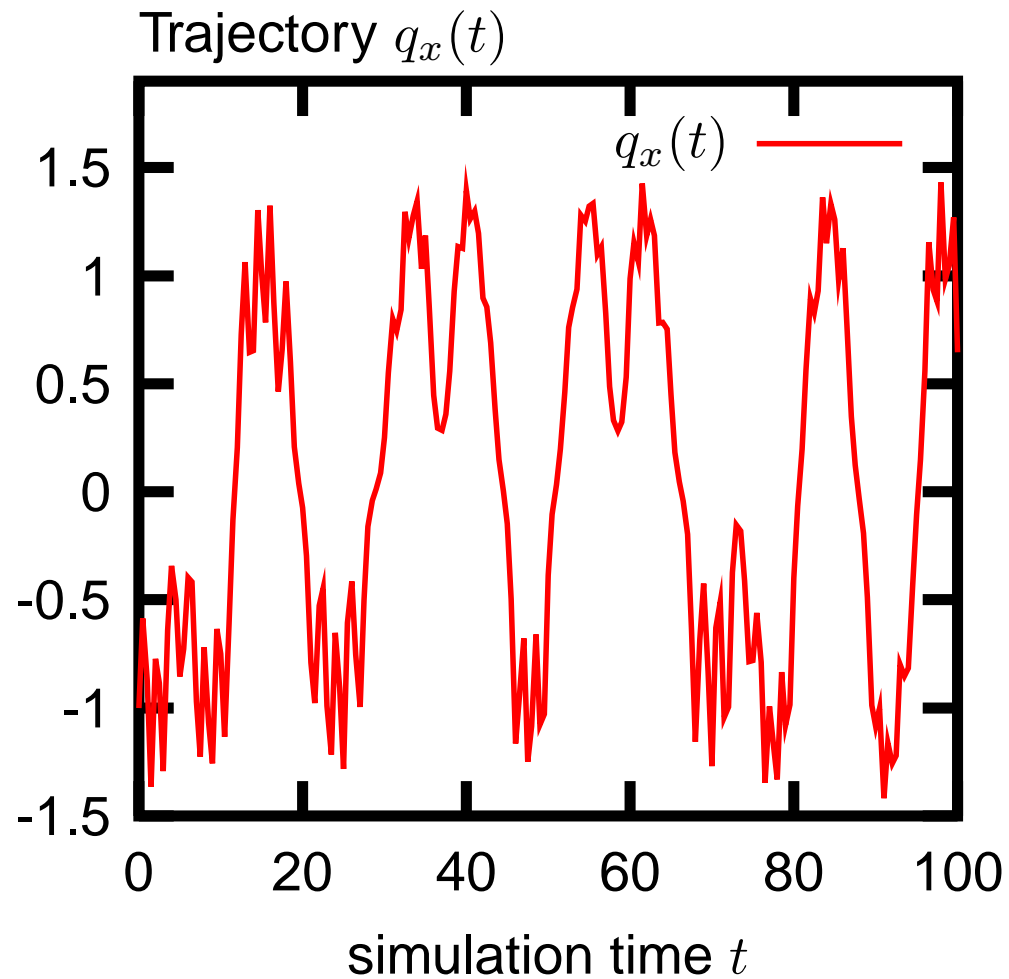


Case of an energy of 1.25 (just larger than the barrier)

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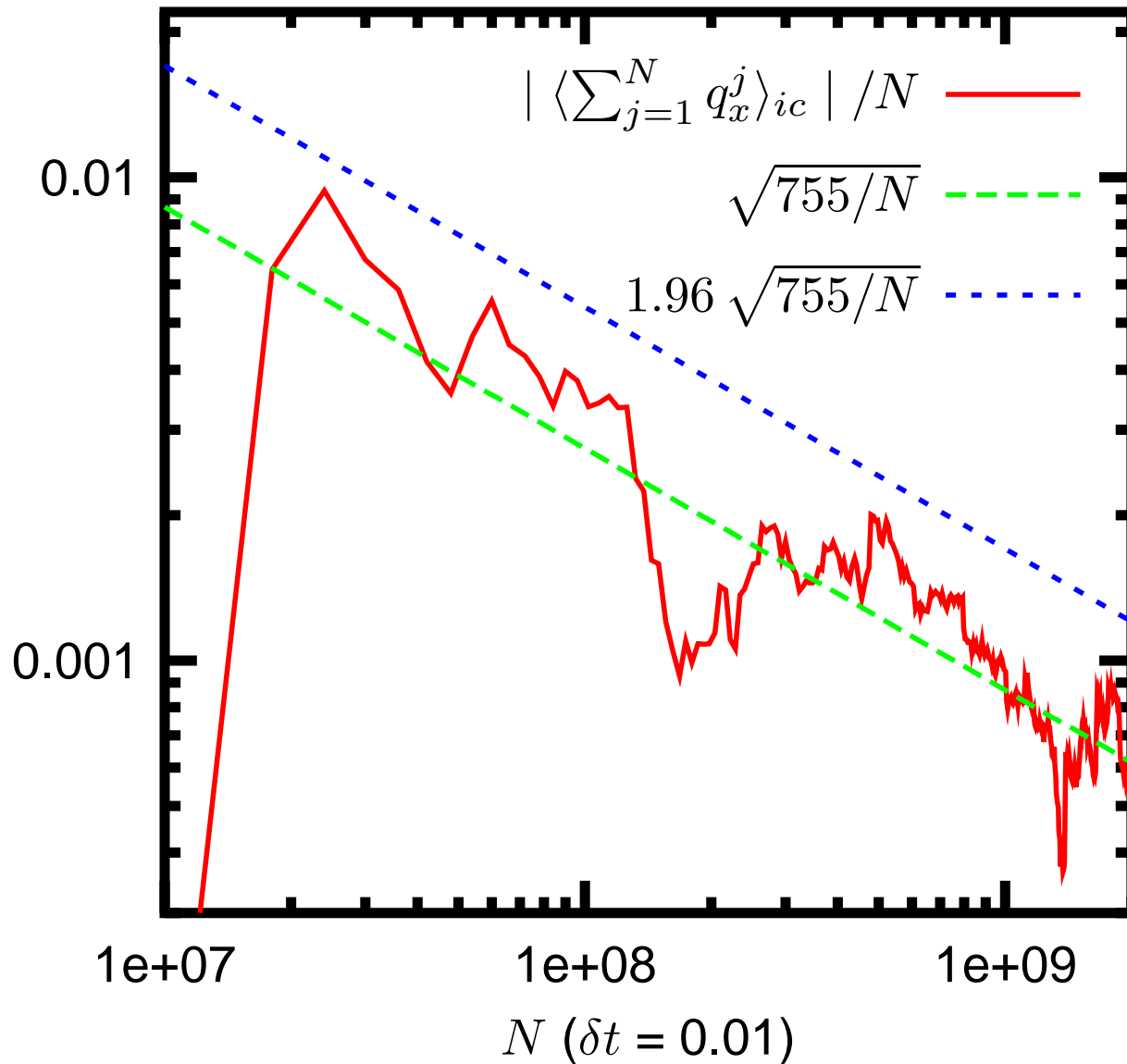
Determination of a well residence time



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:

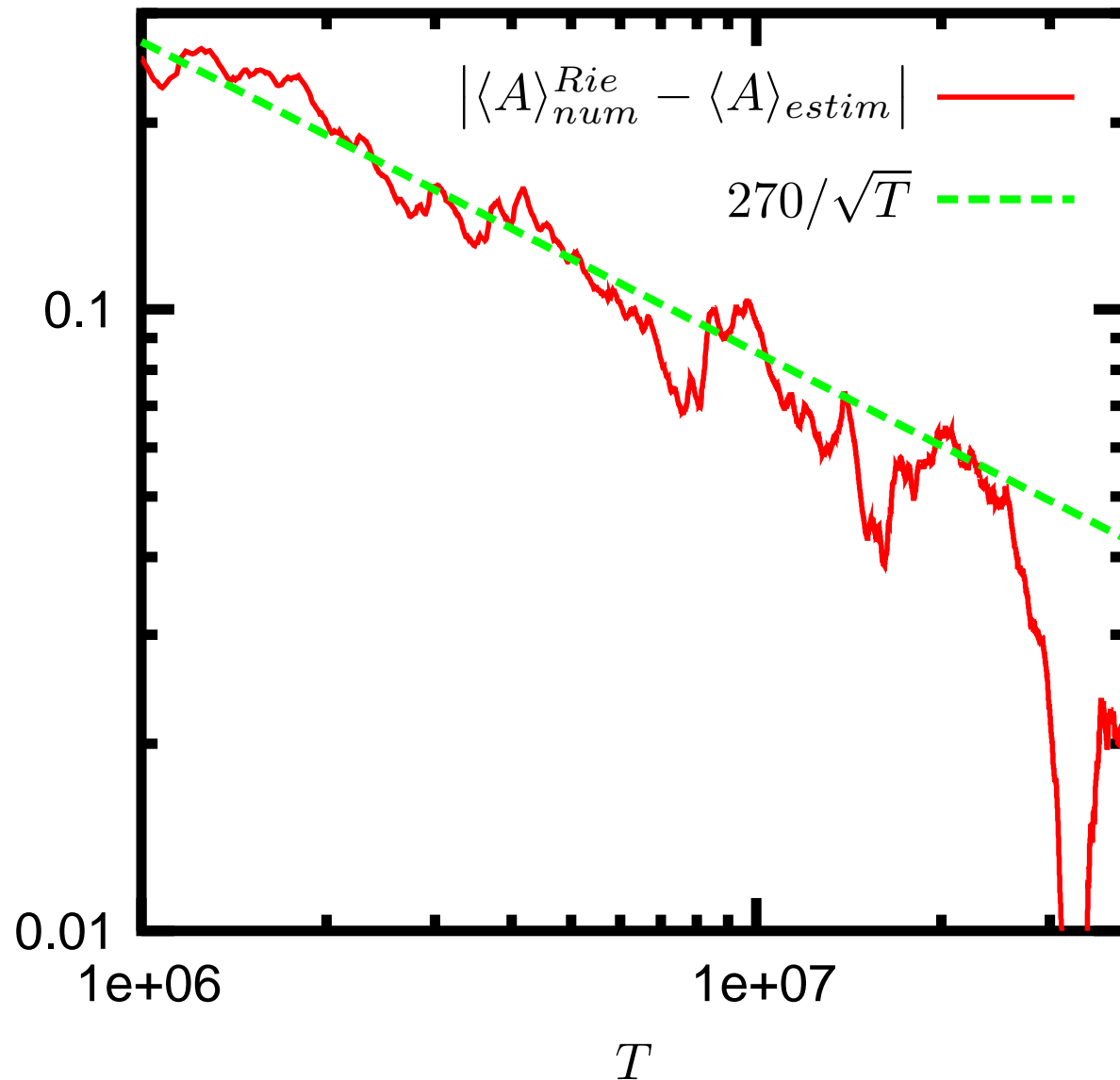
$$O\left(\frac{1}{T}\right) \mapsto O\left(\frac{1}{T^k}\right)$$

Second case:

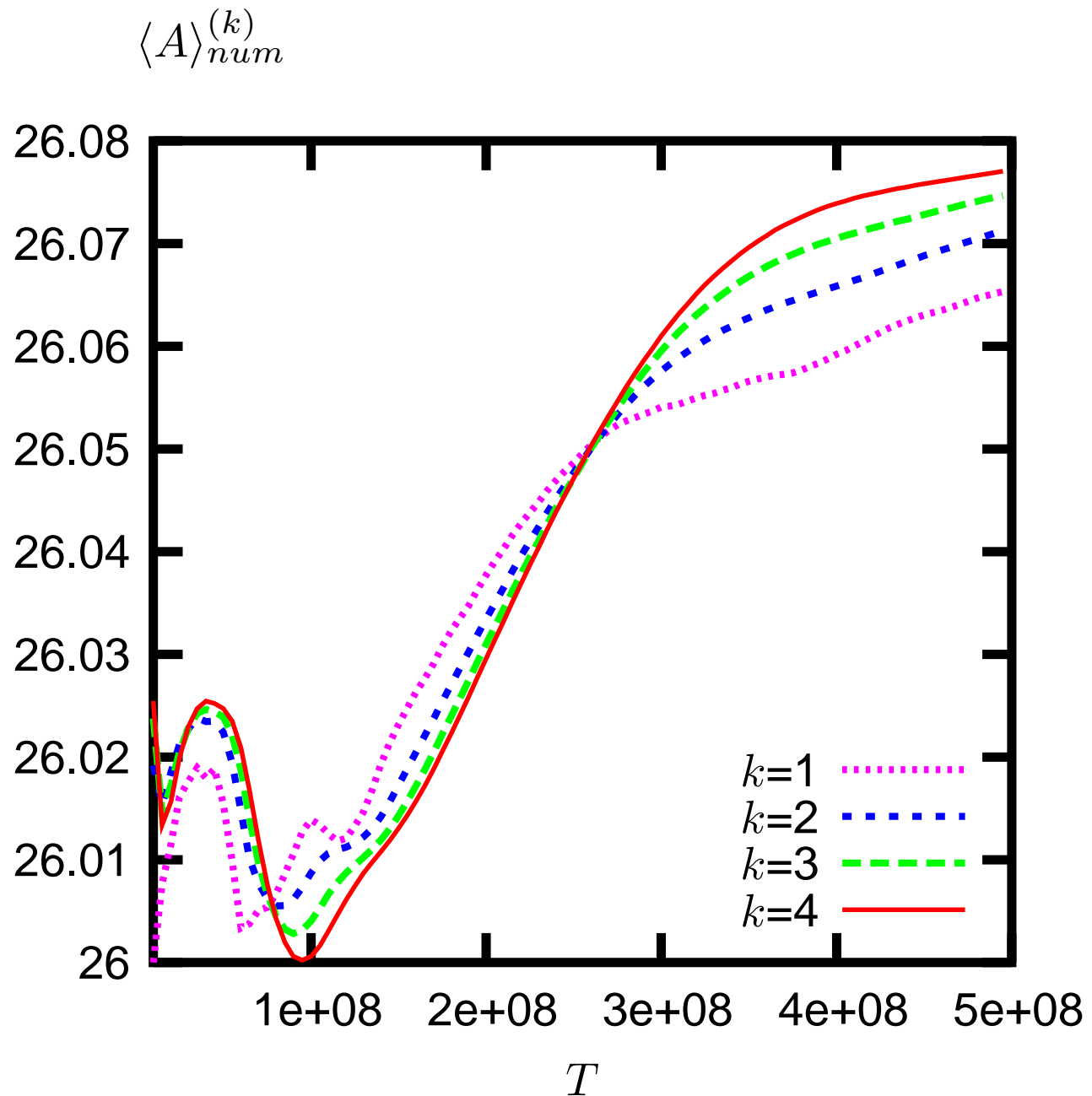
Residence time \gg transition time: convergence with rate $1/\sqrt{T}$.

→ 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.