Adaptive Particle Methods for Molecular Dynamics: Classical Liouville Equation

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Computational Task

Classical Liouville equation:

$$\partial_t \rho(t;p,q) = L\,\rho(t;p,q)$$
$$\rho(0;p,q) = \rho_0$$

with $$L = -M^{-1} p^T \nabla_q + (\nabla_q V(q))^T \nabla_p$$

Properties

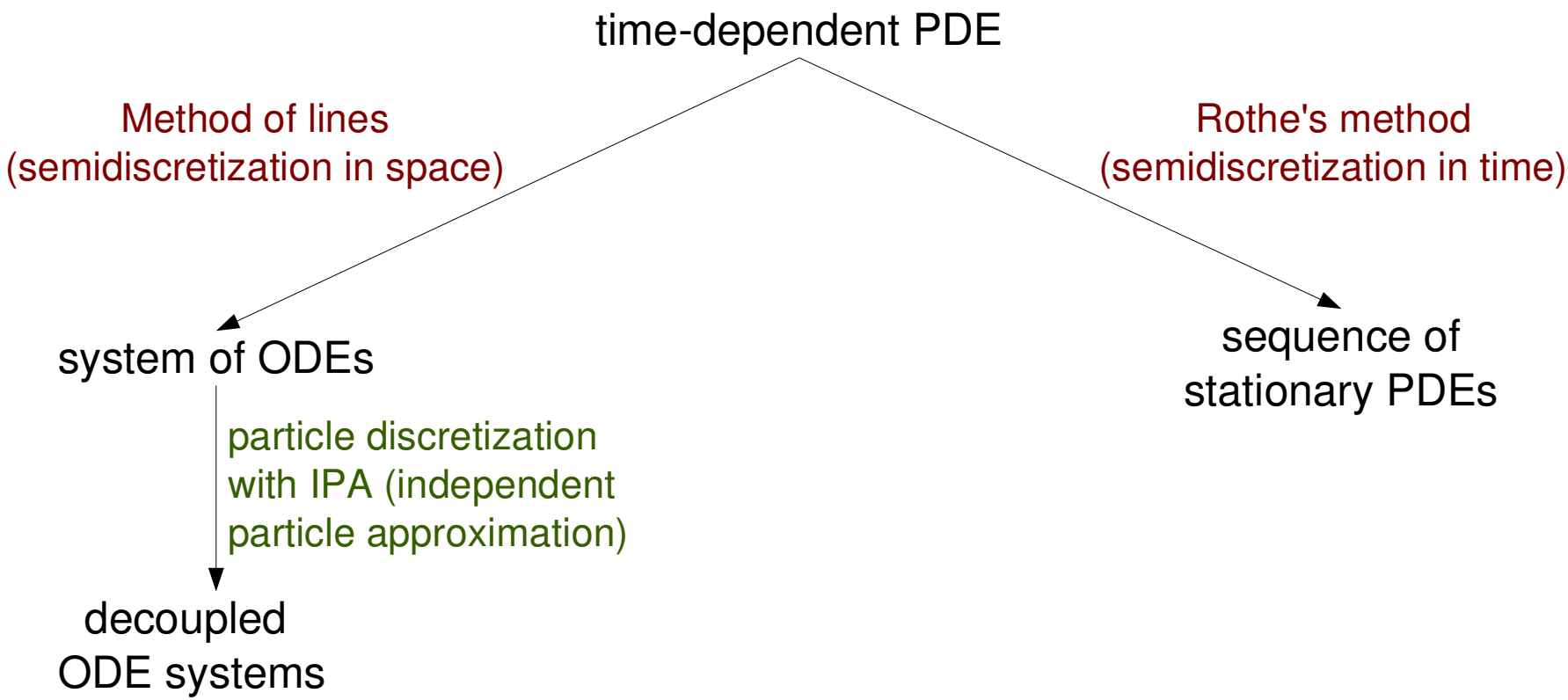
- linear time-dependent PDE
- purely imaginary spectrum
- conserves volume and energy

$$\text{volume} = \int_{\mathbb{R}^{2N}} \rho \; dp \; dq$$
$$\text{energy} = \int_{\mathbb{R}^{2N}} \rho\,(p^T M\, p + V(q)) \; dp \; dq$$

Difficulties

- Spatial dimension $2N$ of (p,q) possibly large.
- Potential $V(q)$ is nonquadratic.
- Computation of second derivative $\nabla_q^2 V(q)$ extremely expensive (for real life problems).
- Good continuous approximation of ρ desired

Discretization Concepts



- easy to implement
- spatial error estimation and spatial adaptivity difficult

- more complex
- spatial error estimation and adaptivity in each time step via PDE solver

Time Discretization

Integrator:

linear differential operator with purely imaginary spectrum: A-stable integrator

most simple scheme: implicit trapezoidal rule

$$\left(I - \frac{\tau}{2} L\right) \overline{\rho}(t+\tau) = \left(I + \frac{\tau}{2} L\right) \rho(t)$$

defines approximation $\overline{\rho}(t+\tau) \approx \Phi_\tau \rho(t)$

Error estimator: $[\overline{\epsilon_t}] := \left\| \overline{\rho}(t+\tau) - \Psi_\tau \rho(t) \right\| \approx \left\| \overline{\rho}(t+\tau) - \Phi_\tau \rho(t) \right\|$

for some cheaply computable comparison evolution Ψ_τ

Explicit propagation schemes based on LHA have consistence order 1!

Here: explicit Euler $\Psi_\tau = \left(I + \tau L\right)$

Stepsize selection: $\tau_{\text{opt}} = \sqrt{\dfrac{\sigma \, \text{TOL}_t}{[\overline{\epsilon_t}]}}$

algorithmic outline

Particle representation:

$$\rho(t;p,q) = \sum_{i=1}^{N} y_i(t)\; g(p_i(t), q_i(t), G_i(t))\,(p,q)$$

with Gaussian particles $$g(p_i, q_i, G_i)(p,q) = \exp\left(-\begin{pmatrix} p_i - p \\ q_i - q \end{pmatrix}^T G_i \begin{pmatrix} p_i - p \\ q_i - q \end{pmatrix} \right)$$

where G_i positive definite

Approximation of the trapezoidal rule:

$$\epsilon_x := \left\| \left(I - \frac{\tau}{2} L \right) \rho(t+\tau) - \left(I + \frac{\tau}{2} L \right) \rho(t) \right\| \leq \mathrm{TOL_x}$$

Approximation of integration by sampling at $K \geq N$ discrete points (ϕ_k, κ_k):

$$[\epsilon_x]^2 := \frac{1}{K} \sum_{k=1}^{K} \left(\left(I - \frac{\tau}{2} L \right) \rho(t+\tau) - \left(I + \frac{\tau}{2} L \right) \rho(t) \right) (\phi_k, \kappa_k)^2 \leq \mathrm{TOL}_x^2$$

spatial error estimator for trapezoidal rule

Minimization approach:

$$[\epsilon_x] = \min$$

Degrees of freedom:

y_i	amplitudes (linear)	n
p_i, q_i	centers (nonlinear)	$2Nn$
G_i	shapes (nonlinear)	$\frac{n}{2} N (N+1)$

For simplicity, robustness, and efficiency: fitting of amplitudes only

Predictors

Selection of particles and sample points:

"good" particle base needed for efficient and accurate representation of $\rho(t+\tau)$

generating all particles anew in every time step inefficient

move existing particles' centers and sample points with the flow,
possibly adjust shape, too

use explicit method based on LHA and IPA as *predictor.*

Linear least squares problem for amplitudes:

$$[\epsilon_x]^2 = \|Ay - b\|^2 = \min \quad \text{with} \quad A_{ki} = \left(\left(I - \frac{\tau}{2}L\right) g(p_i, q_i, G_i)\right)(\phi_k, \kappa_k)$$

$$b_k = \left(\left(I + \frac{\tau}{2}L\right)\rho(t)\right)(\phi_k, \kappa_k)$$

Numerically stable solution:

$A = QRP$ with column permutation P such that $|R_{ii}| \geq |R_{jj}|$ for $i \leq j$,

$$R = \begin{bmatrix} R_a & S_1 \\ 0 & R_c \\ 0 & 0 \end{bmatrix}, \quad Py = \begin{bmatrix} y_a \\ y_c \end{bmatrix}, \quad Q^T b = \begin{bmatrix} b_a \\ b_c \\ b_d \end{bmatrix},$$

and

$$\begin{aligned} \min |\operatorname{diag}(R_a)| \\ \geq \frac{1}{\kappa}|R_{11}| \\ > \max |\operatorname{diag}(R_c)|, \end{aligned}$$

κ maximum accepted subcondition

drop particles corresponding to y_c

Spatial Adaptivity: Refinement

Least-squares residual provides a local error indicator.

While $$[\epsilon_x]^2 = \frac{1}{K}\sum_{k=1}^{K}\left(\left(I-\frac{\tau}{2}L\right)\rho(t+\tau)-\left(I+\frac{\tau}{2}L\right)\rho(t)\right)(\phi_k,\kappa_k)^2 > \mathrm{TOL}_x^2$$

refine particle collection:

- generate new particle at sample point with maximum local residual $\left|(Ay-b)_k\right|$ (“greedy” refinement)
- generate new sample points in vicinity of new particle
- solve larger least squares problem using QR updates

Spatial Adaptivity: Coarsening

If $$\epsilon_x^2 = \frac{1}{K}\sum_{k=1}^{K}\left(\left(I-\frac{\tau}{2}L\right)\rho(t+\tau)-\left(I+\frac{\tau}{2}L\right)\rho(t)\right)(\phi_k,\kappa_k)^2 < \frac{1}{2}\mathrm{TOL}_x^2$$

Remove least important particles:

$$\|Ay-b\| = \min \qquad A = QRP$$ with column sorting

$$R=\begin{bmatrix} R_a & S_{ab} & S_{ac} \\ 0 & R_b & S_{bc} \\ 0 & 0 & R_c \\ 0 & 0 & 0 \end{bmatrix} \quad Py=\begin{bmatrix} y_a \\ y_b \\ y_c \end{bmatrix} \quad Q^T b=\begin{bmatrix} b_a \\ b_b \\ b_c \\ b_d \end{bmatrix}$$

such that $$\left\|\frac{1}{K}\left(b_b,b_c,b_d\right)\right\|^2 \le \frac{1}{2}\mathrm{TOL}_x^2$$

remove particles corresponding to (y_b, y_c)

Accuracy Matching

How to match TOL_x and TOL_t ?

Spatial error ϵ_x must be sufficiently small such that neither the time discretization nor its error estimator is impaired.

$$\epsilon_t = \left\| \overline{\rho}(t+\tau) - \Phi_\tau \rho(t) \right\| = O(\tau^3)$$

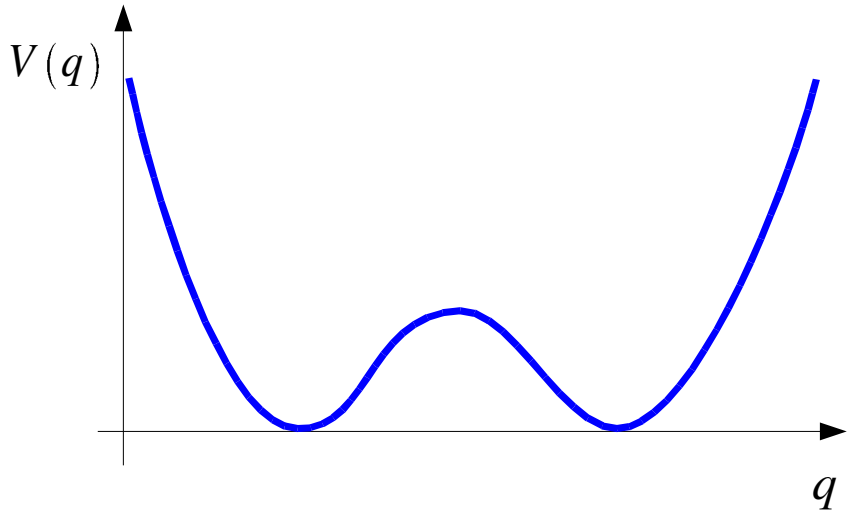
$$[\epsilon_t] = \| \rho(t+\tau) - \Psi_\tau \rho(t) \| = O(\epsilon_x) + O(\tau^2)$$

Accuracy matching: $\epsilon_x = O(\tau^3)$

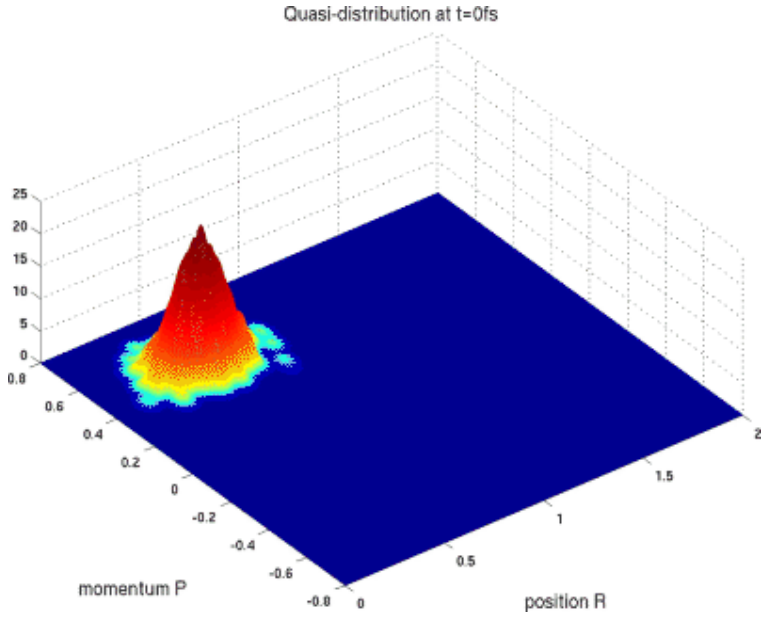
$$\mathrm{TOL}_x := \tau\, \mathrm{TOL}_t$$

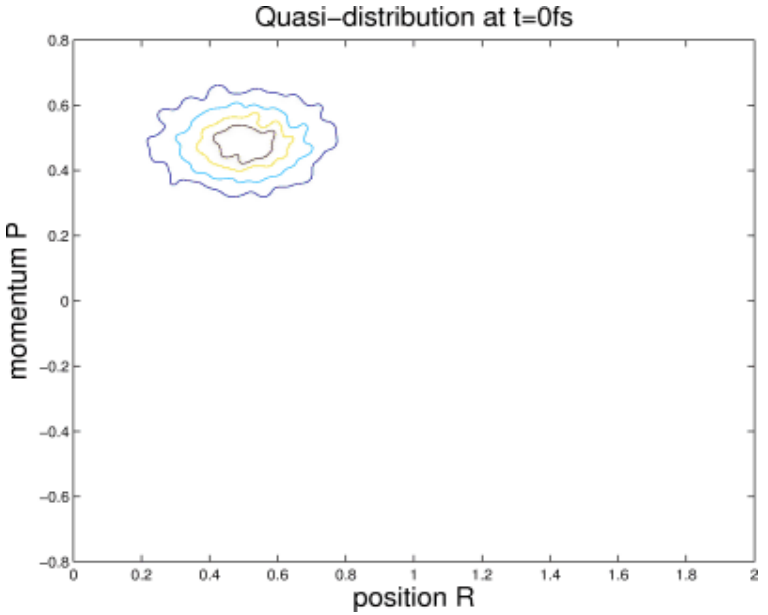
Numerical Example

A simple test case:
Double-well potential 1D



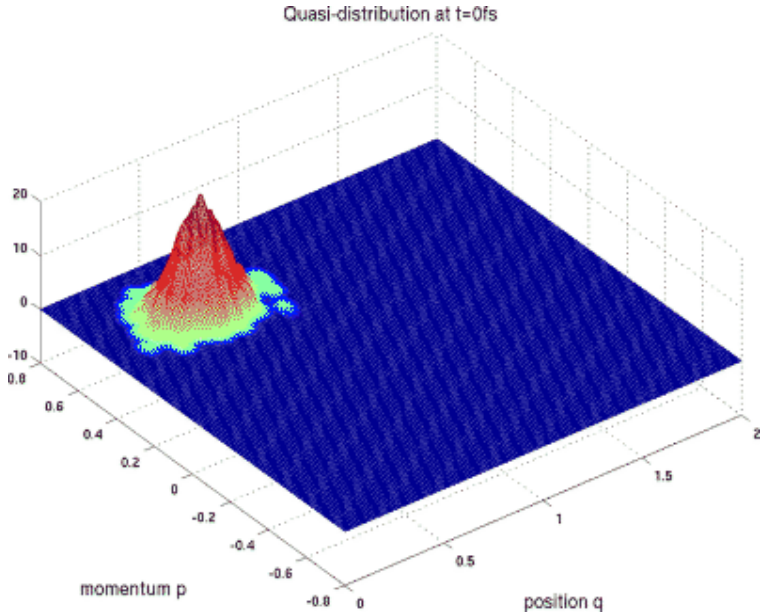
Almost exact solution computationally available (40fs):

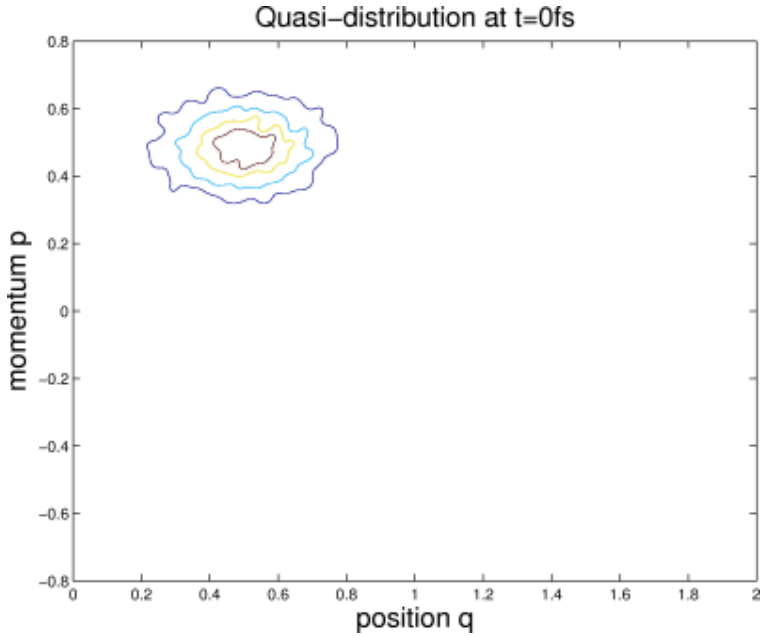




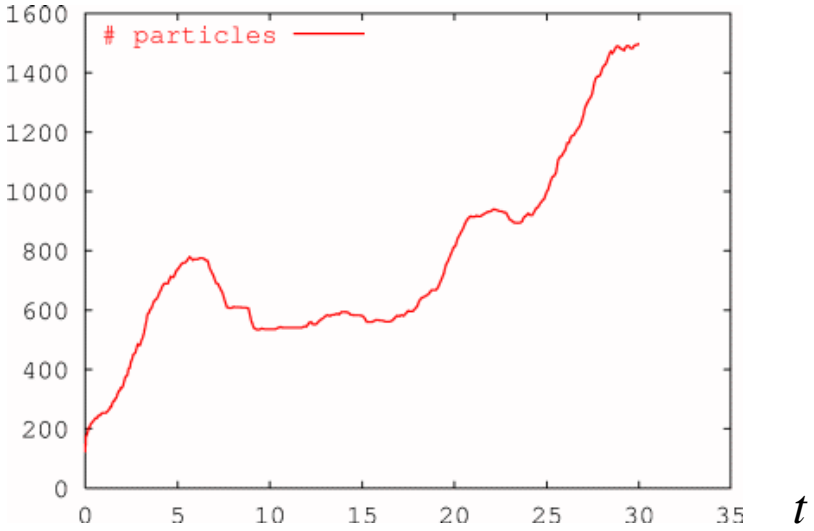
Numerical Results

Propagated density (30fs):





Spatial adaptivity:



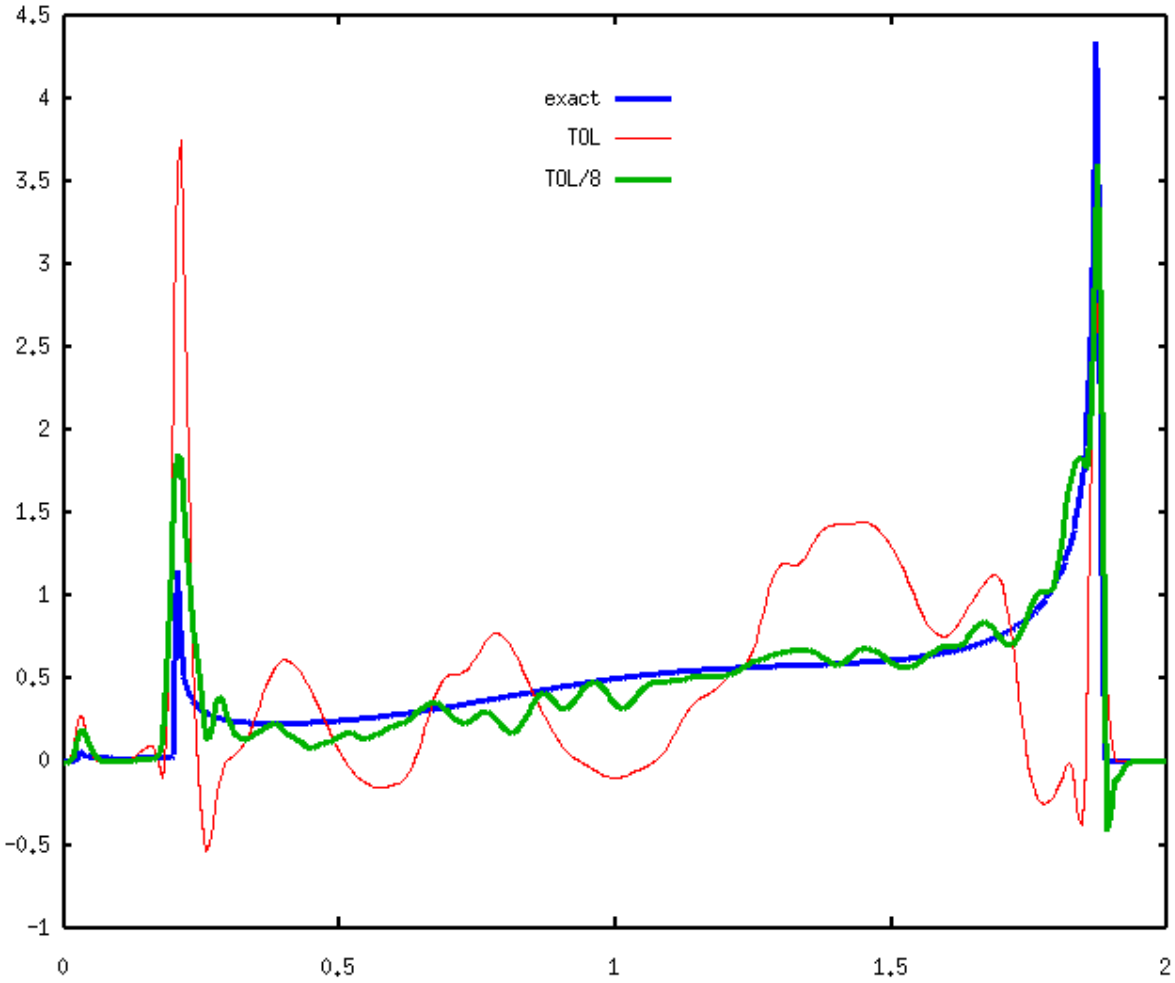
numerical example

Numerical Results

Spatial density for different tolerances (30fs):

spatial density

$$\int_{\mathbb{R}^N} \rho(t; p, q)\, dp$$



position q

numerical example

Conclusion

- fully adaptive particle method for Liouville type equations
- works for 1D test problem with highly local features
- efficient solution of large least squares problems needed (currently under investigation)
- testing on more and higher dimensional problems necessary