Universiteit Leiden

Independent Oscillator Models in System-Bath Quantum Dynamics

modeling energy dissipation in H scattering on surfaces

Matteo Bonfanti

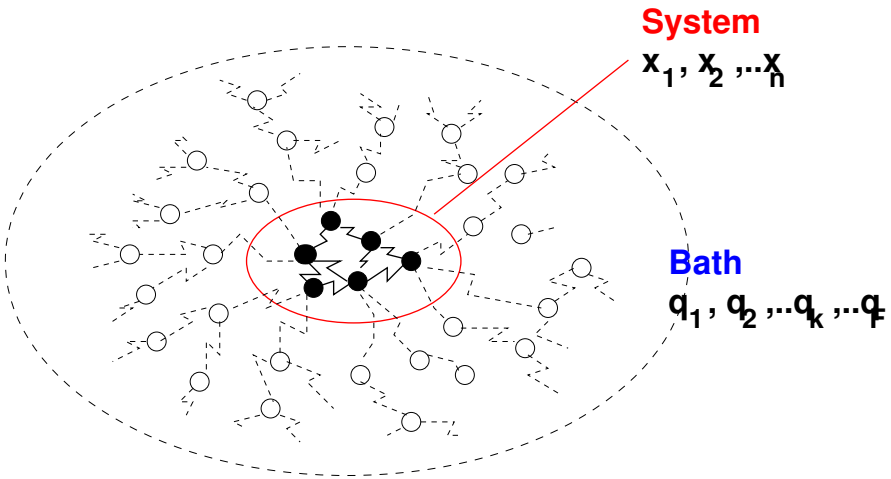
Theoretical Chemistry Group
Leiden Institute of Chemistry

Thursday February 9th, 2012

Outline

System-bath dynamics

- System: relevant part, experimentally probed
  $\Rightarrow$ Few, important DOFs
- Bath: irrelevant part, but responsible for energy transfer
  $\Rightarrow$ Large number of DOFs of non-direct relevance



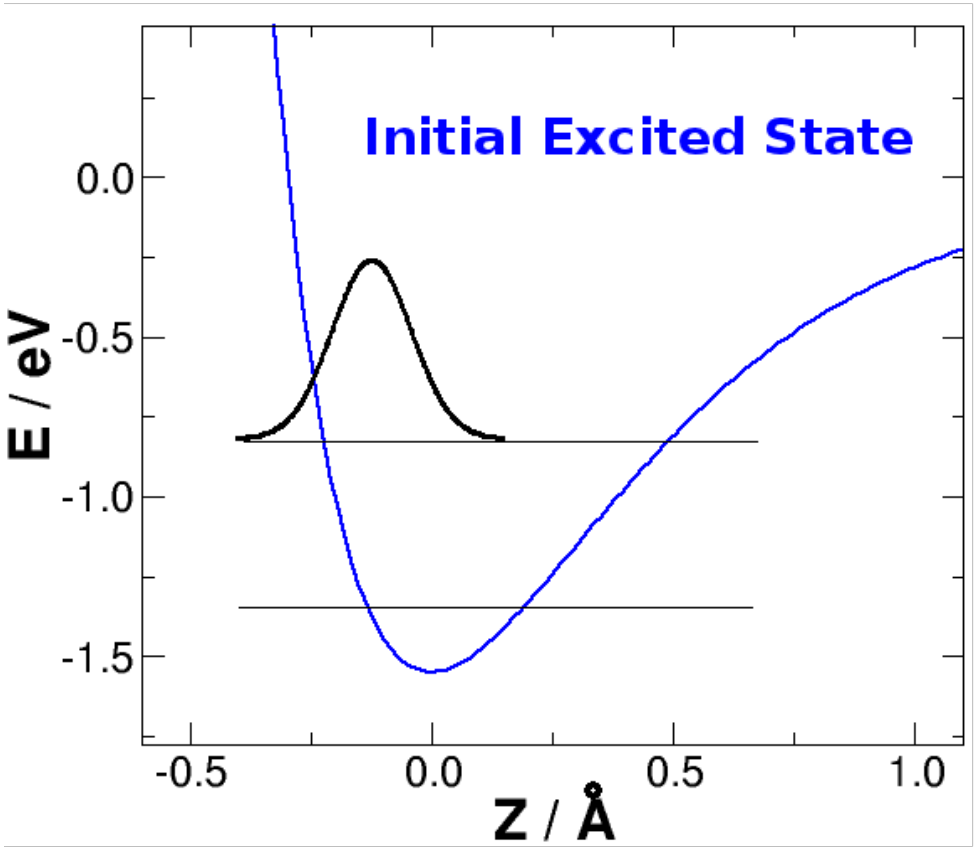
Quantum description is mandatory for inherently quantum systems and/or low-temperature baths..

Vibrational Relaxation and Atomic Sticking

- Energy transfer to the sorrounding
- Challenging problems: large set of degrees of freedom

Vibrational Relaxation

- Morse Potential for Graphite-H
- System Energy in time



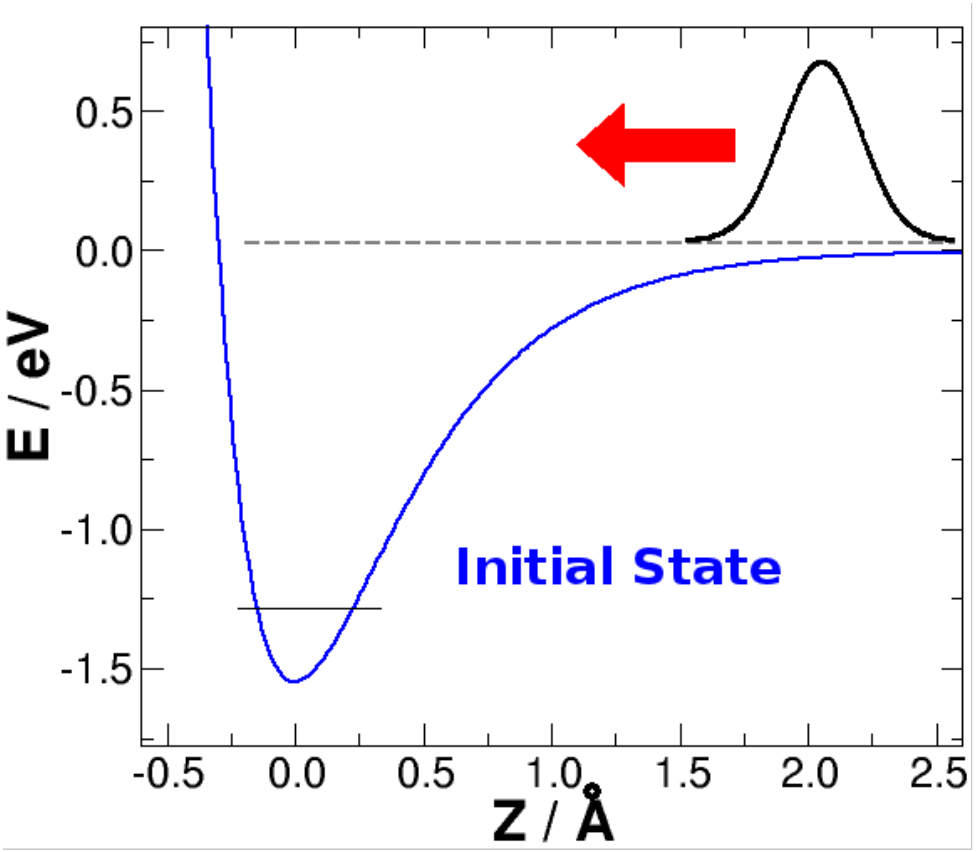
[a] G. A. Worth, H.-D. Meyer and L. S. Cederbaum, J.Chem.Phys. **109**, 3518 (1998)
[b] M. Nest and H.-D. Meyer, J.Chem.Phys. **119**, 24 (2003)

Vibrational Relaxation and Atomic Sticking

- Energy transfer to the sorrounding
- Challenging problems: large set of degrees of freedom

Sticking

- Morse Potential for Graphite-H
- Sticking Probability, *i.e.* fraction of trapped norm



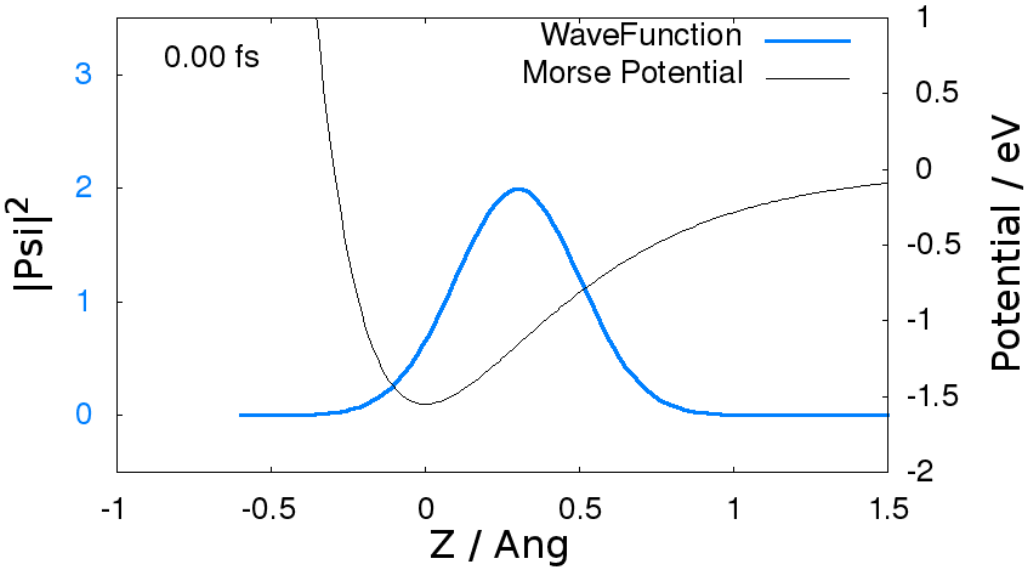
[a] G. A. Worth, H.-D. Meyer and L. S. Cederbaum, J.Chem.Phys. **109**, 3518 (1998)

[b] M. Nest and H.-D. Meyer, J.Chem.Phys. **119**, 24 (2003)

Independent Oscillator Model

- Quantum Model of dissipation
- System exchanges energy with a thermal bath of HO

$$H_{CL} = H_{system} + \sum_n \left\{ \frac{p_n}{2\mu_n} + \frac{1}{2}\mu_n \omega_n^2 q_n^2 \right\} + coupling$$



Independent Oscillator Hamiltonian

$$H = \frac{p^2}{2M} + V(s) + \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2} \left(x_k - \frac{c_k s}{\omega_k^2} \right)^2 \right\}$$

$$H \equiv H^{\text{sys}} + \Delta V(s) + H^{\text{int}} + H^{\text{bath}}$$

$H^{\text{sys}} = \frac{p^2}{2M} + V(s)$: system Hamiltonian

$\Delta V(s) = \frac{1}{2} \left(\sum_k \frac{c_k^2}{\omega_k^2} \right) s^2 = \frac{1}{2} M \delta \Omega^2 s^2$: "renormalization" potential

$H^{\text{int}} = -\sum_k c_k x_k s$: interaction term

$H^{\text{bath}} = \sum_k \frac{p_k^2}{2} + \frac{\omega_k^2}{2} x_k^2$: "bath " Hamiltonian

[a] A.O. Caldeira and A.J. Leggett, Phys.Rev.A **31**, 1059 (1985)

[b] G.W. Ford, J. T. Lewis and R. F. O'Connell Phys.Rev.A **37**, 4419 (1988)

Generalized Langevin Equation

Solving the classical IO Hamiltonian, the system experience a force due to the environment, given by

$$F^{\text{env}} = \xi(t) - M \int_{t_0}^{+\infty} \gamma(t - t')\dot{s}(t')\, dt'$$

where

$$\xi(t) = \sum_k \left\{ \left[x_k(t_0) - \frac{c_k}{\omega_k^2} s(t_0) \right] \cos(\omega_k t) + \frac{\dot{x}_k(t_0)}{\omega_k} \sin(\omega_k t) \right\} c_k$$

$$M\kappa(t) = \sum_k \frac{c_k^2}{\omega_k^2} \cos(\omega_k t)$$

$$\gamma(t) = \Theta(t)\kappa(t)$$

[c] R. Zwanzig, J.Stat.Phys. **9**, 215 (1973)

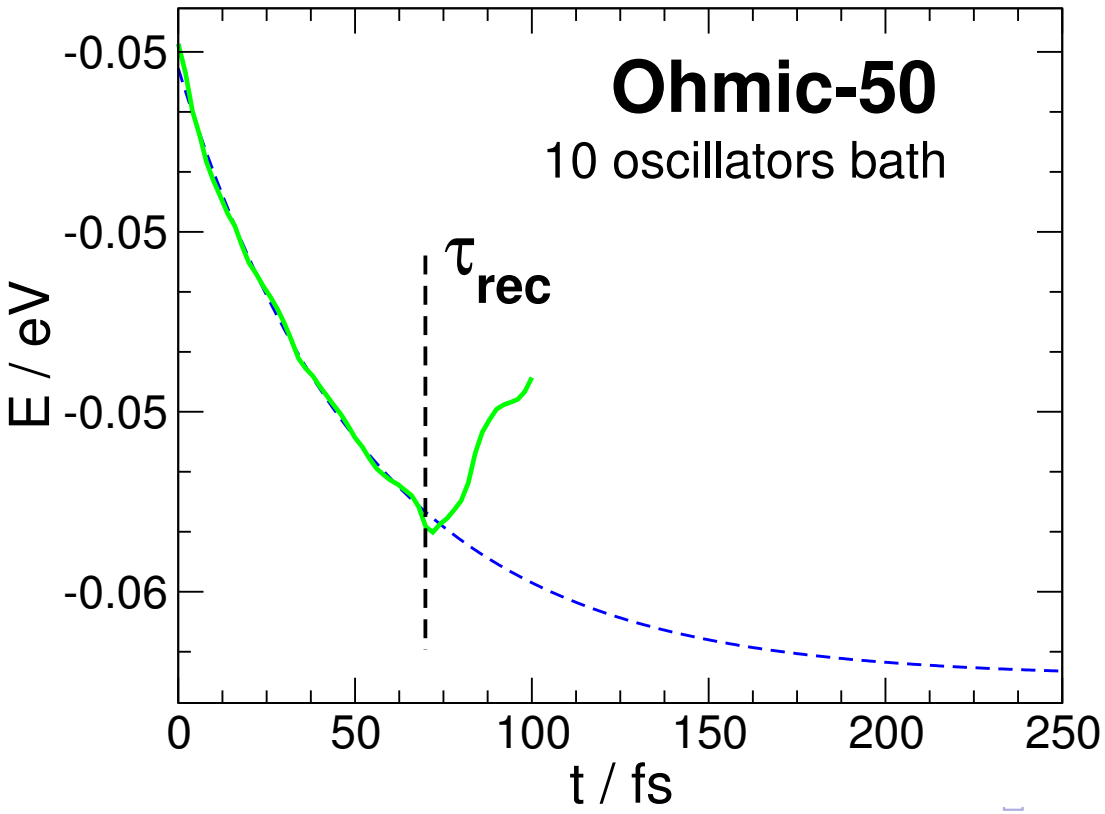
Recurrence Time

In simulations, we adopt a finite set of HO

$\Downarrow$

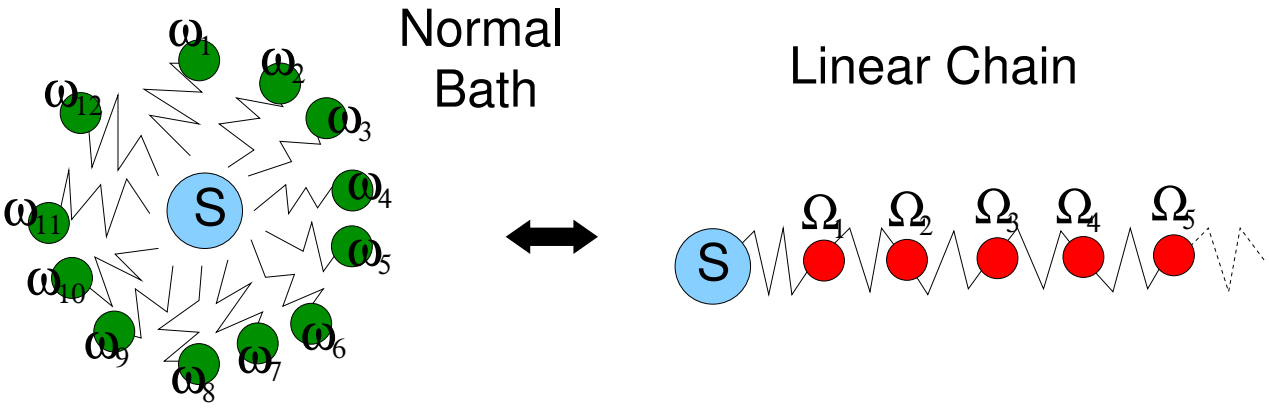
Poincaré's recurrence

After τ_{rec} the energy gets back to the system

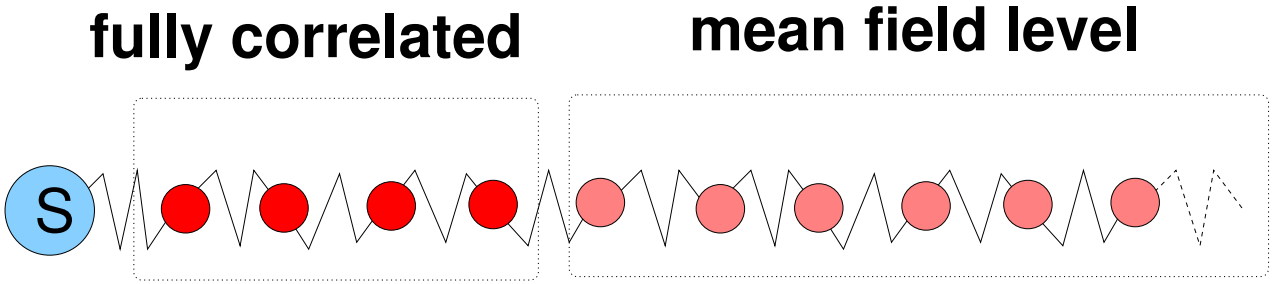


Linear Chain Representation of the Bath

Performing a normal model transformation...



Advantage: stronger approximation on the oscillators "far" from the system



[a] K. H. Hughes, C. D. Christ and I. Burghardt, J.Chem.Phys. **131**, 024109 (2009)

[b] R. Martinazzo, B. Vacchini, K. H. Hughes and I. Burghardt, J.Chem.Phys. **134**, 011101 (2011)

[c] R. Martinazzo, K. H. Hughes and I. Burghardt, Phys.Rev.E **84**, 030102 (2011)

Our project

Aim of the work

Check the accuracy and the computational performances of the linear chain representation

- Problems: vibrational relaxation and sticking
- Bath properties: different bath models (analytical / from literature)
- Linear chain: different degree of approximation (no. of correlated oscillators)
- Methodology: MCTDH[a] (Heidelberg's MCTDH Package[b])

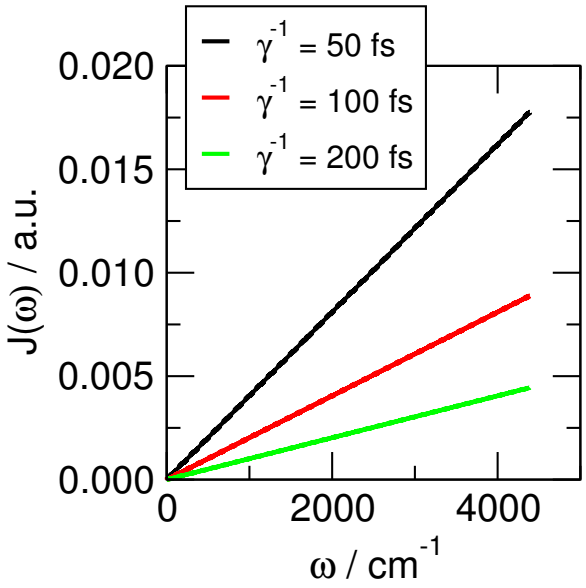
[a] H.-D. Meyer, U. Manthe and L. S. Cederbaum, Chem.Phys.Lett. **165**, 73 (1990)
M. H. Beck, A. Jäckle, G. A. Worth and H.-D. Meyer, Phys.Rep. **324**, 1 (2000)

[b] G. A. Worth, M. H. Beck, A. Jäckle and H.-D. Meyer, The MCTDH Package, Version 8.4 (2007)

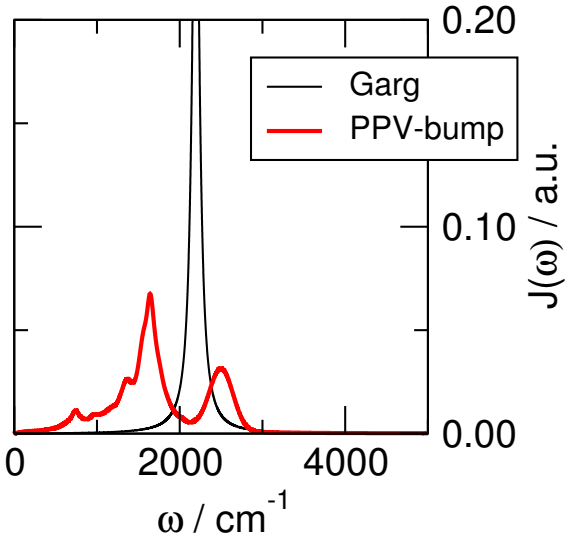
Bath models

- The properties of the bath are defined by ω_n and the coupling
- Sampling of the **spectral density** of the bath, *i.e.* dissipation in the frequency-domain
- We considered different model spectral densities

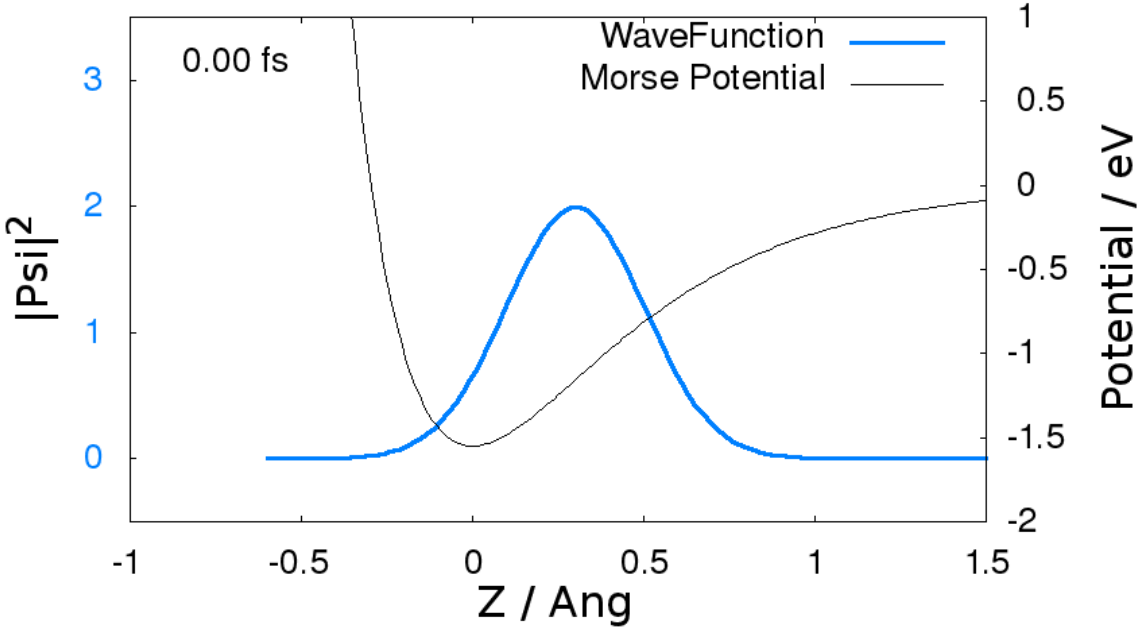
Ohmic Baths



Non Ohmic Baths

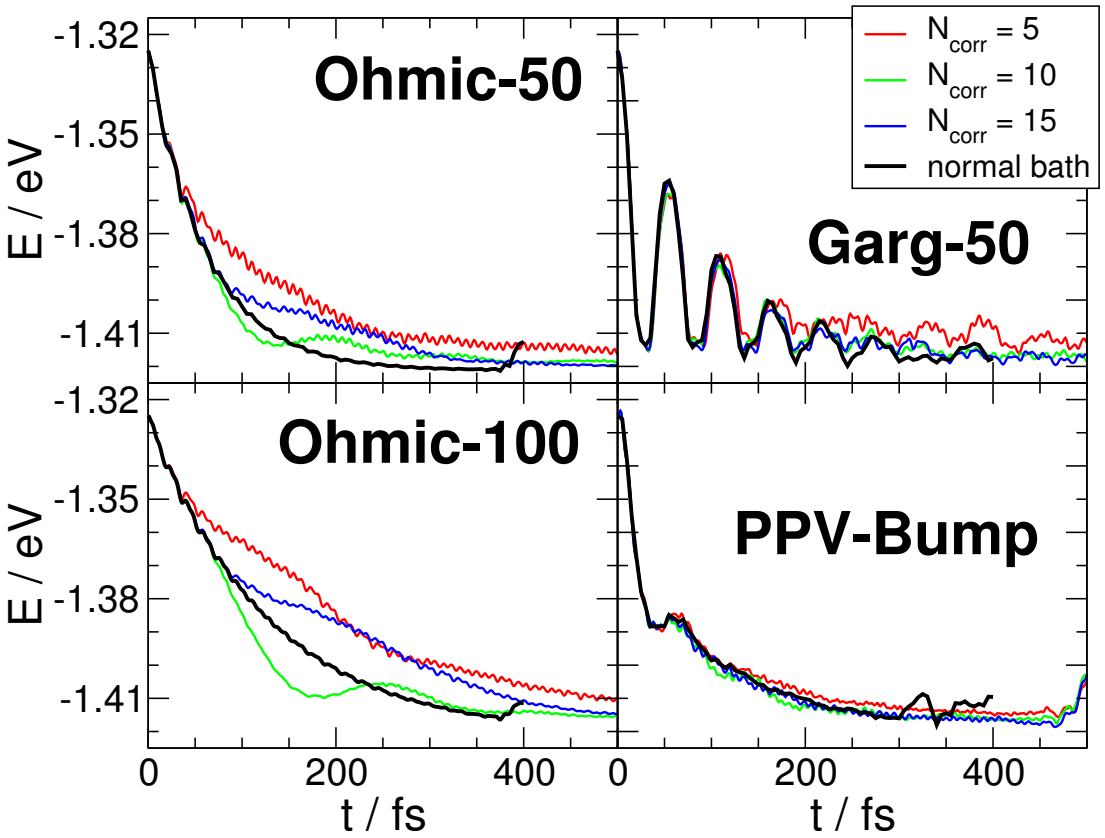


Example of Chain Dynamics



- WP Relaxation
- PPV Bath in chain form, 100 oscillators (15 fully correlated)

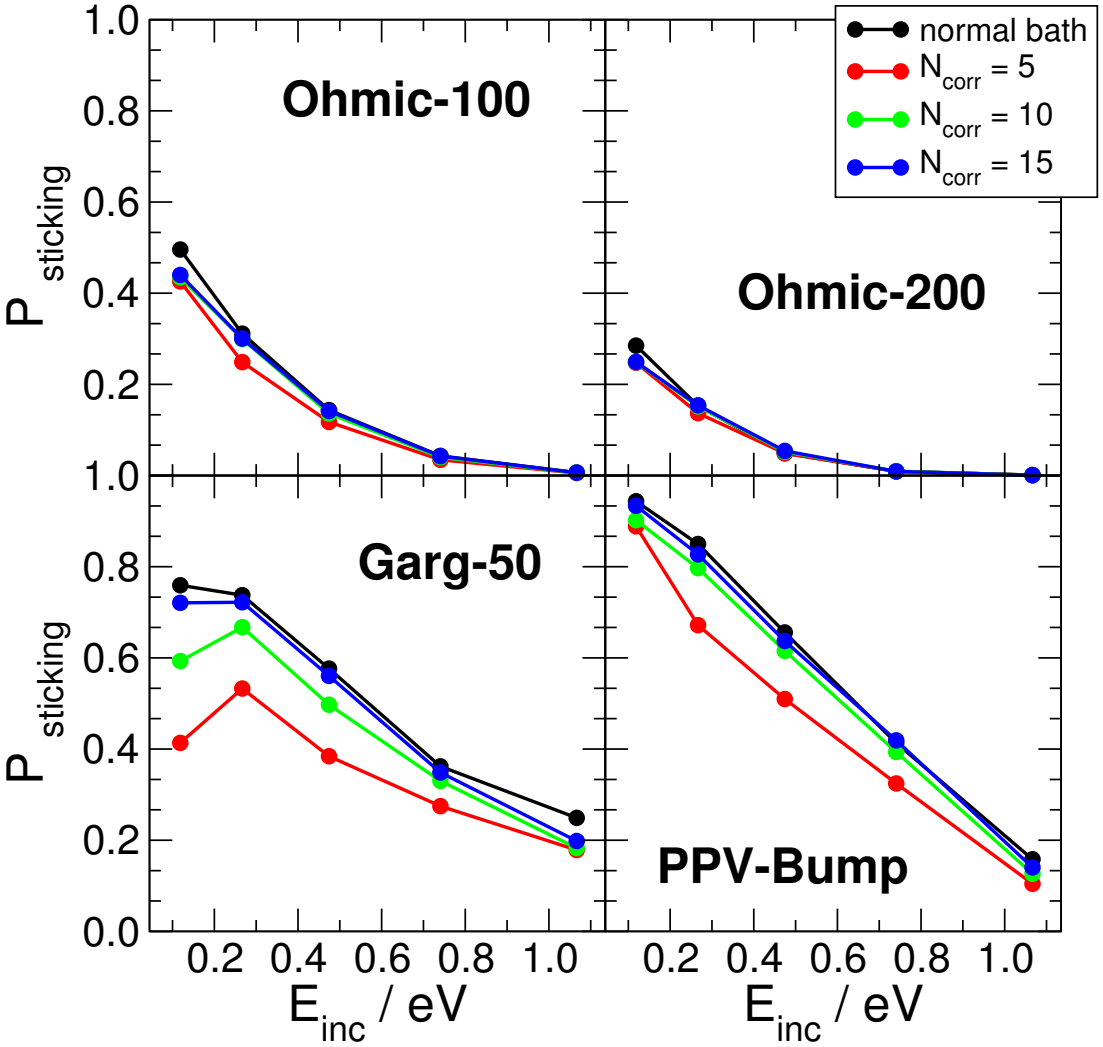
Results - Energy Relaxation



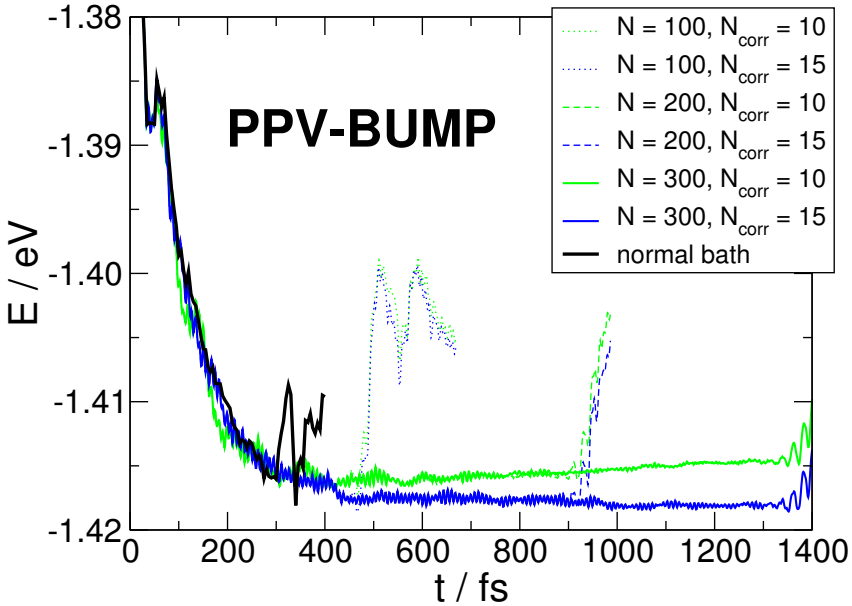
- Exact results at short time
- At longer time good qualitative behaviour
- Excellent agreement for non Ohmic Baths

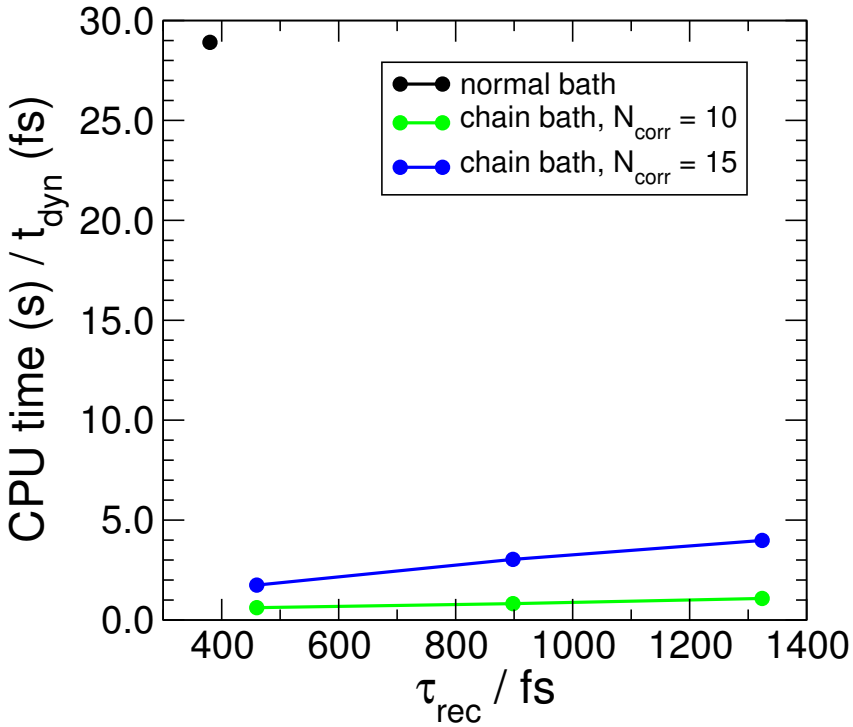
Results - Sticking

- P_{stick} decreases with increasing E_{inc}, as expected
- Excellent results with the chains
- For E_{inc} = 0.12 eV small error



Results - Long Time Relaxation





- For the same recurrence time, great reduction of CPU time
- The CPU time scales linearly with the recurrence time

Conclusions

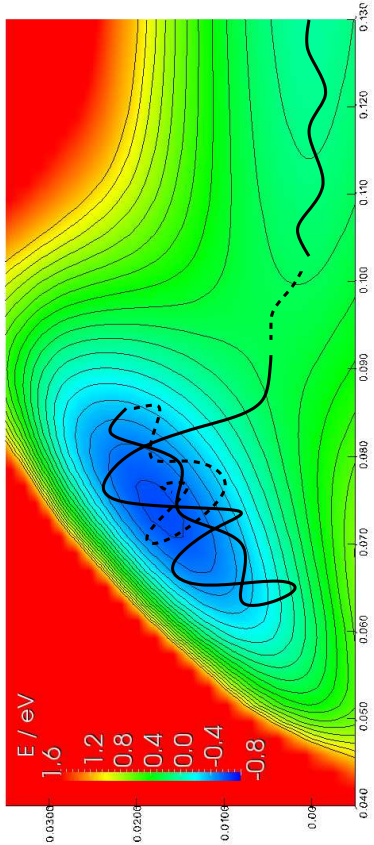
- Very good results: even in the worse case qualitatively consistent behaviour
- Excellent agreement for realistic bath (including memory effects)
- Achieved a reduction of the computational cost of the simulation
- The recurrence time of the bath can be increased at a reasonable computational cost

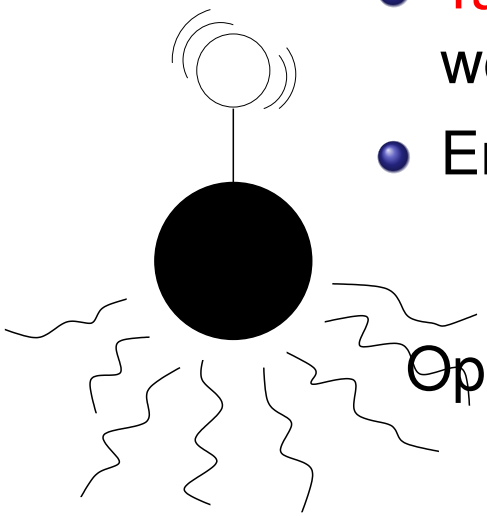
[a] M.Bonfanti, R.Martinazzo, K.H.Hughes, I.Burghardt and G.F.Tantardini *Effective mode based wavefunctions for system bath quantum dynamics*, in preparation (2011)

Further developments

In future...

Application to a realistic sticking problem





H Sticking on Graphene

Low energy H atoms:

- Tunneling into the chemisorption well
- Energy relaxation

$\Downarrow$

Open-system quantum problem

Acknowledgments

- Gian Franco Tantardini, Dr. Rocco Martinazzo, Università degli Studi di Milano, Italy

Università degli Studi di Milano

- Irene Burghardt, Institute of Physics and Theoretical Chemistry, Goethe University Frankfurt, Germany
- Keith Hughes, School of Chemistry, Bangor University, United Kingdom

... and thank you, for your attention!

Leiden Institute of Chemistry

Acknowledgments

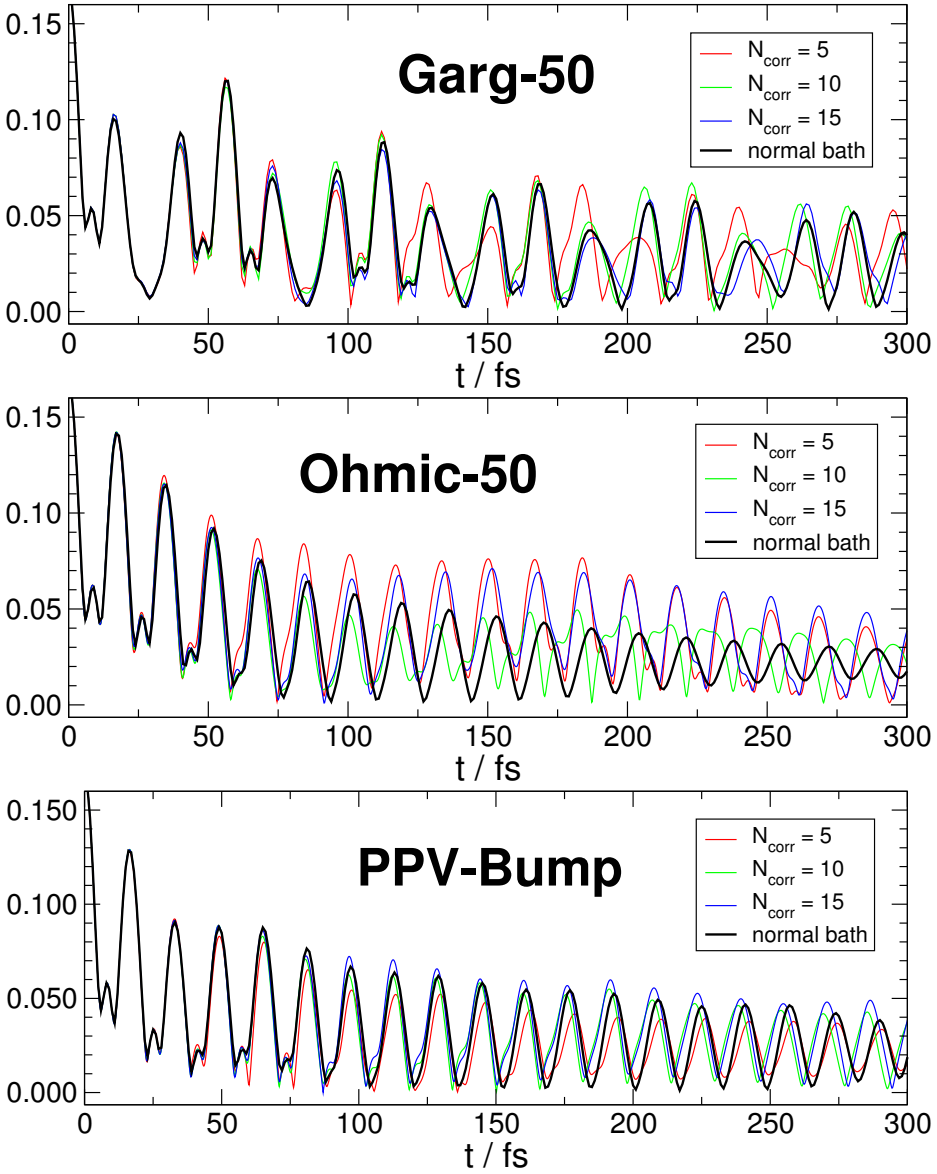
- Gian Franco Tantardini, Dr. Rocco Martinazzo, Università degli Studi di Milano, Italy

Università degli Studi di Milano

- Irene Burghardt, Institute of Physics and Theoretical Chemistry, Goethe University Frankfurt, Germany
- Keith Hughes, School of Chemistry, Bangor University, United Kingdom

... and thank you, for your attention!

Position correlation function



Bound State Probability