Università degli Studi di Milano

Dissipative quantum dynamics of H adsorption on graphene/graphite

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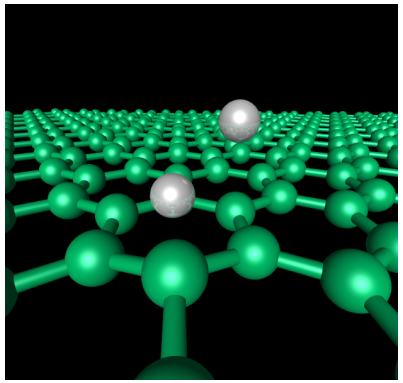
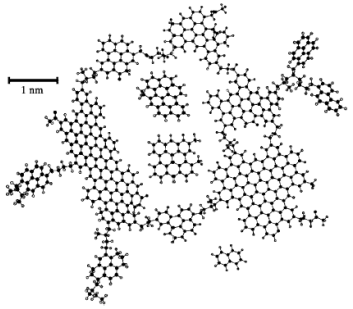
Friday June 19th, 2015

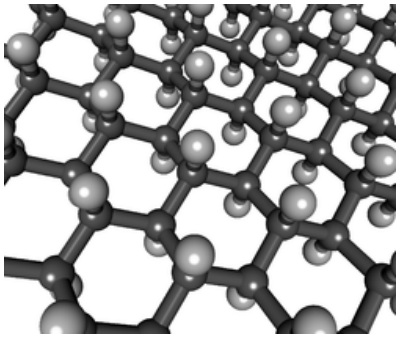
H on Graphene: technology and astrochemistry

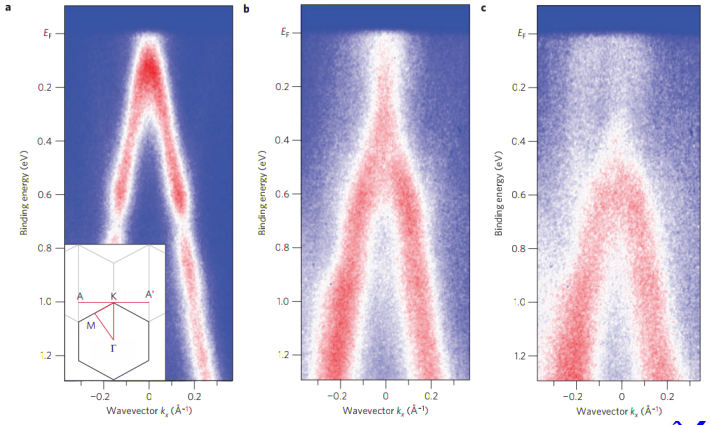


H_2 in the Interstellar Medium is formed at the surface of carbonaceous particles

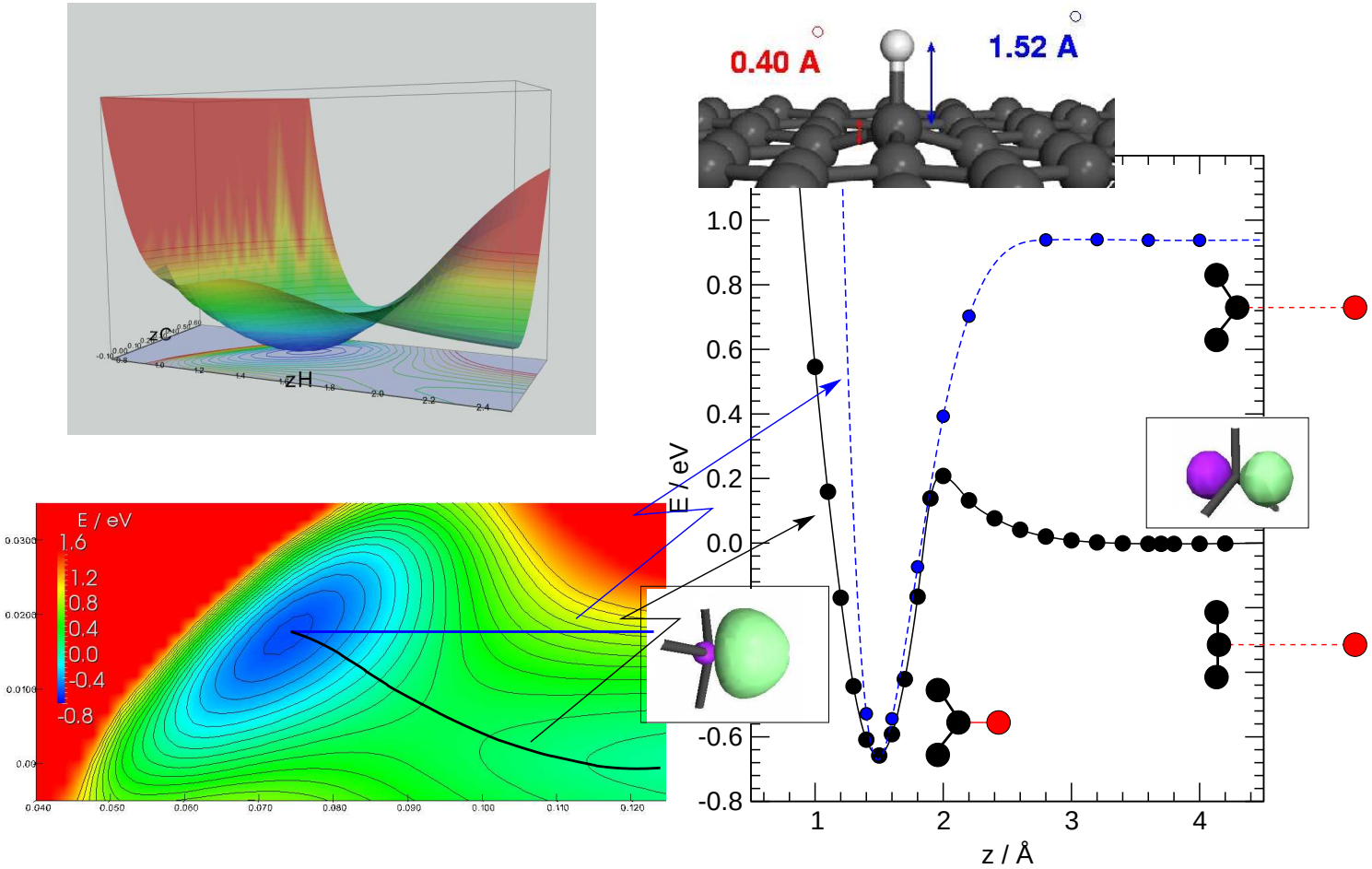


Chemical functionalization of graphene: band-gap opening





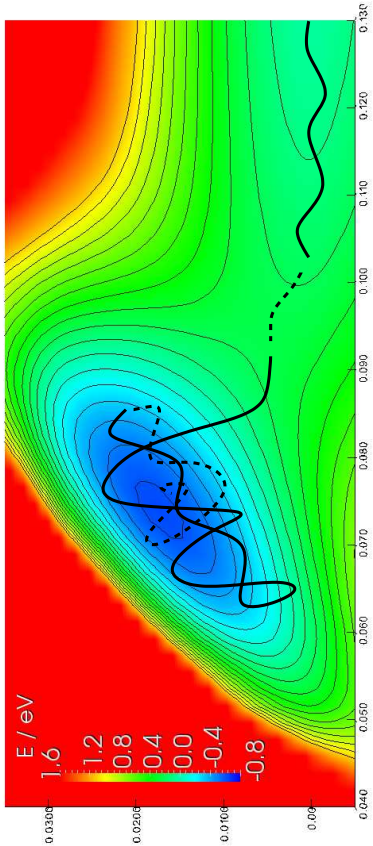
Chemisorption of a H atom

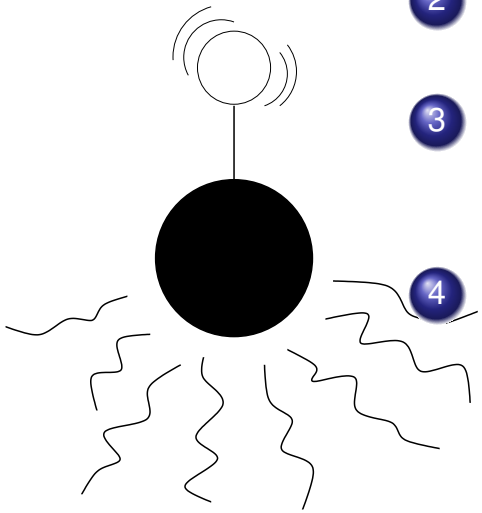


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)

X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

H sticking dynamics on graphene





Challenging problem...

1. fast surface reconstruction induced by the sp^2–sp^3 rehybridization
   $\Rightarrow$ C and H strongly coupled
2. steering mechanism
   $\Rightarrow$ importance of non-collinear geometries
3. fast dissipation to graphene phonons
   $\Rightarrow$ explicit thermal bath exchanging an arbitrary amount of E
4. tunneling for $E_{coll} \leq 0.2$
   $\Rightarrow$ quantum dynamics is needed

$\Rightarrow$ **high dimensional quantum model**

Outline

1. System-bath Dynamics
   - Dissipative dynamics with Independent Oscillator Models
2. H-Sticking Model Construction
   - Modeling of Graphene-H
   - Spectral Density
3. High-Dimensional Quantum Dynamics
   - Vibrational Relaxation
   - Sticking

Outline

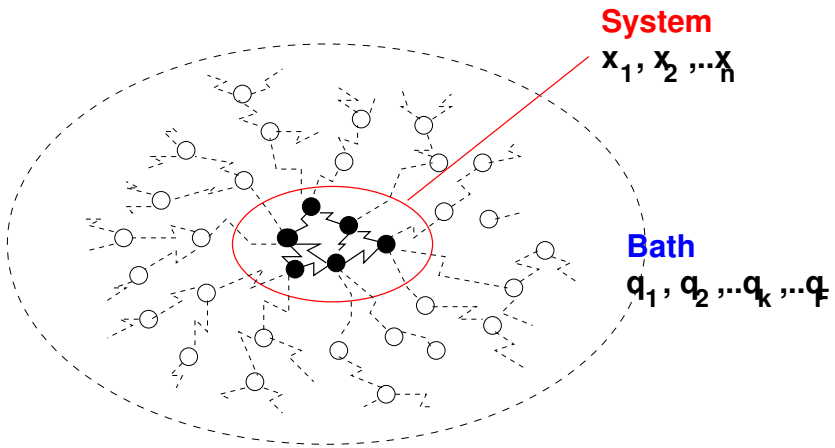
System-bath dynamics

- System: relevant part, experimentally probed

  $\Rightarrow$ Few, important DOFs

- Bath: irrelevant part, but responsible for energy transfer

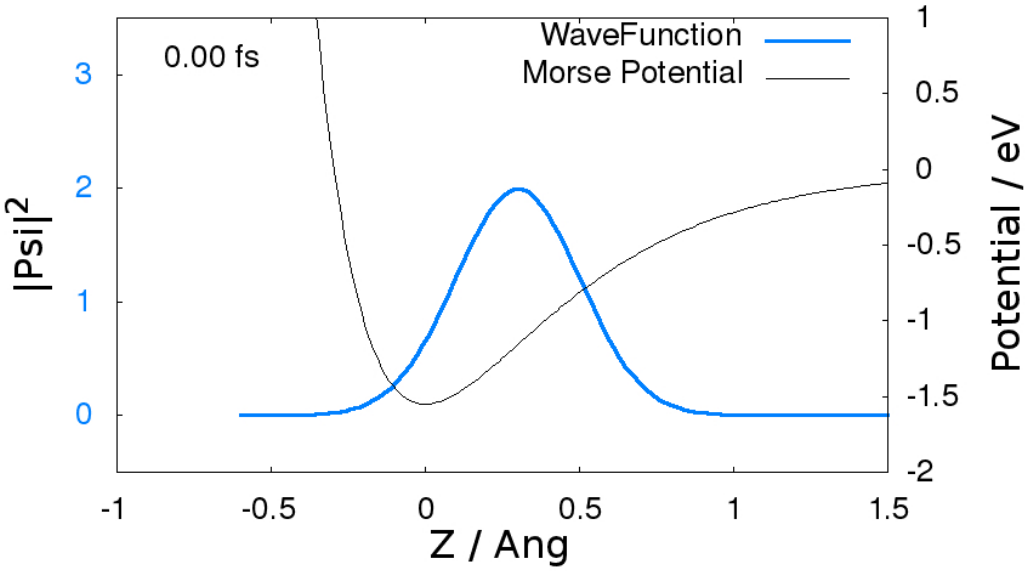
  $\Rightarrow$ Large number of DOFs of non-direct relevance



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

Independent Oscillator (IO) Model

- system coupled to a thermal bath of HO
- simple but general model of system bath dynamics
- energy fluctuation and dissipation



Independent Oscillator (IO) Model

Independent Oscillator Hamiltonian

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

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

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

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

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

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

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

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

Generalized Langevin Equation (GLE)

H_{IO} is equivalent to the GLE in the limit N$\rightarrow \infty$

$$M\ddot{s} = -V'(s) + F^{\text{env}}$$

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

where

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

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

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

Spectral Density $J(\omega)$

density of state of the environment "weighted" by the coupling with the system

$J(\omega) \Rightarrow$ GLE fluctuation-dissipation

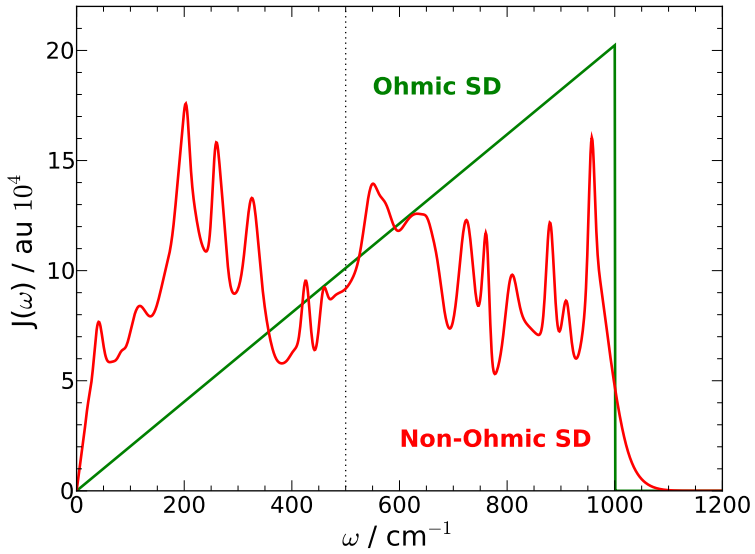
$$\gamma(|t|) = \frac{1}{m}\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{J(\omega)}{\omega} e^{-i\omega t} d\omega$$

$$\langle \xi(t)\xi(0)\rangle = \frac{\hbar}{\pi}\int_{-\infty}^{+\infty} \frac{J(\omega)}{1-e^{-\hbar\beta\omega}} e^{-i\omega t} d\omega$$

$J(\omega) \Rightarrow$ IO model parameters

$$\omega_k = k\Delta\omega$$

$$c_k = \sqrt{\frac{2\omega_k \Delta\omega J(\omega_k)}{\pi}}$$



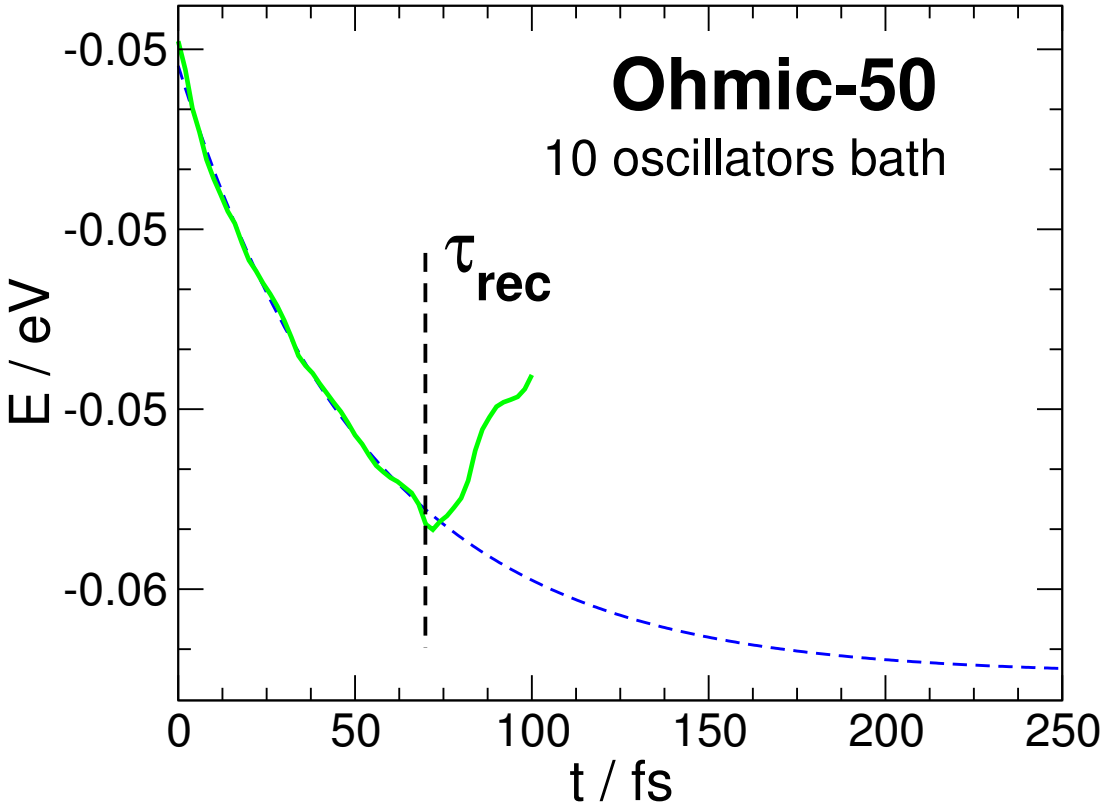
Recurrence Time

In simulations, we adopt a finite set of HO

$\Downarrow$

Poincaré's recurrence

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

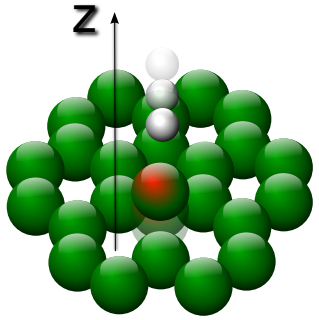


Outline

System-bath modeling: our strategy

Fully atomistic models

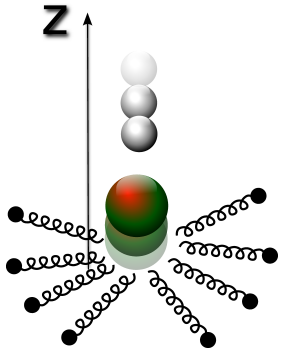
- Accurate representation of adsorbate-lattice interactions and of lattice dynamics
- Complicated form of the potential, inadequate for HD Quantum Dynamics



$$H_{latt} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}) + \sum_i \frac{p_i^2}{2m_i}$$

System-bath models

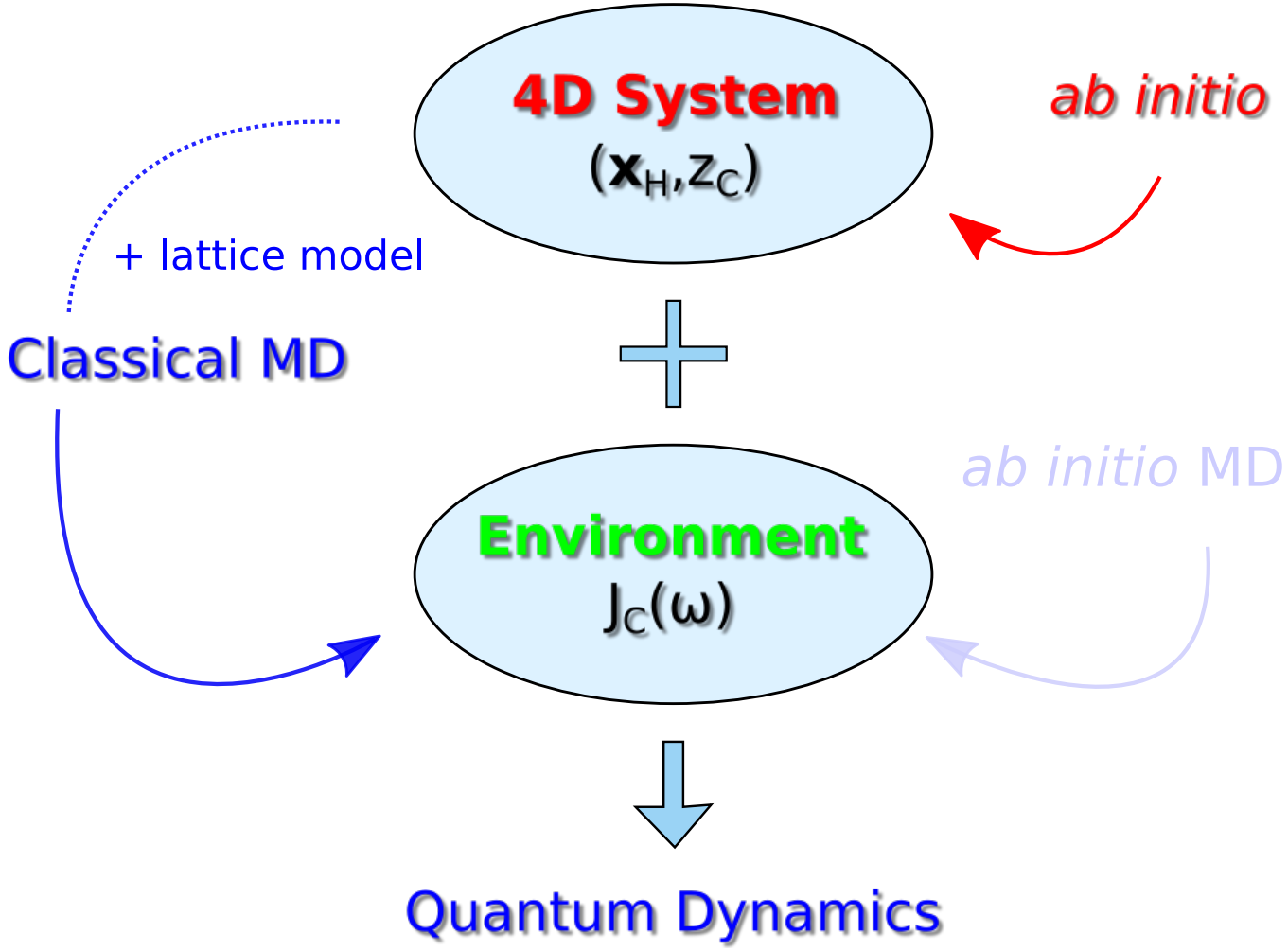
- Limited applicability, though fine iff a Generalized Langevin description of the dynamics holds
- Simplest possible form for an environment, suited to HD QD



$$H_{sb} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq}) + \sum_k \left[\frac{p_k^2}{2} + \frac{\omega_k^2}{2}\left(q_k - \frac{c_k}{\omega_k^2} z_C\right)^2 \right]$$

$$\gamma(t) \Leftrightarrow J(\omega) \Leftrightarrow \omega_k, c_k$$

System-bath modeling: our strategy



Atomistic model of Graphene-H: System

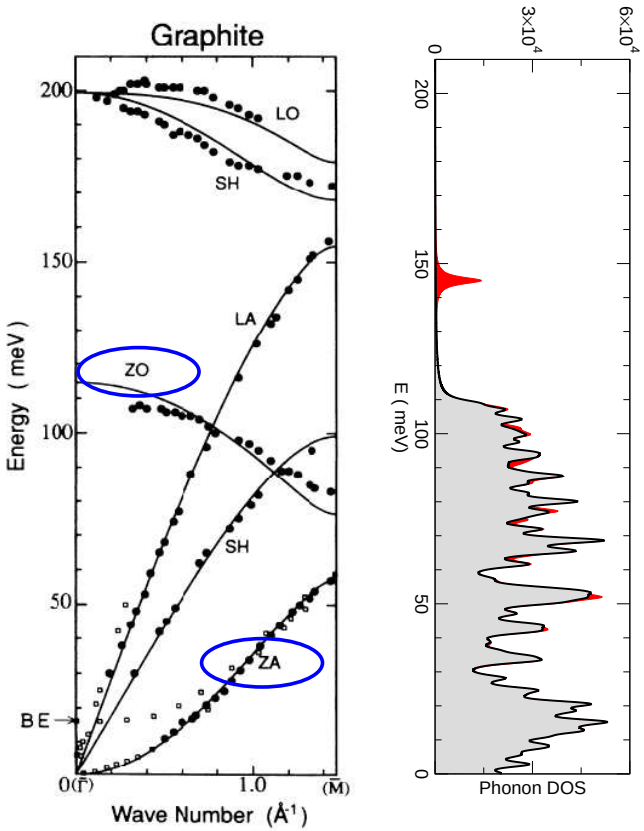
System

$$H_{sys} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq})$$

- Plane-wave DFT PW91
- Dense grid on x_H, y_H, z_H, z_C, for fixed coordinates of the remaining lattice atoms
- 12-parameter fit to LEPS functional form
- normal modes
  1. C–H stretching, 2550 cm^{-1}
  2. CH–surface stretching, 466 cm^{-1}
  3. C–H bending, doubly degenerate, 1170 cm^{-1}

J. Kerwin, X. Sha and B. Jackson, *J. Phys. Chem. B*, 18811 **110** (2006)

Atomistic model of Graphene-H: Lattice



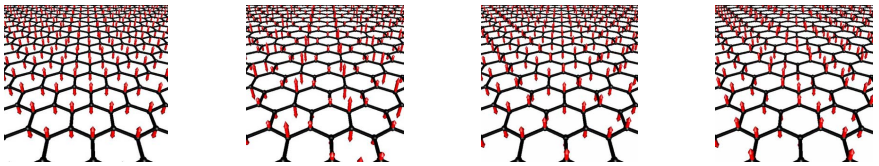
Lattice

$$H_{latt} = \sum_i^N \frac{p_i^2}{2m_i} + V_{latt}(z_1, z_2, \ldots z_N)$$

- Lattice model of graphene (Force Field)
- ZA, ZO branches only

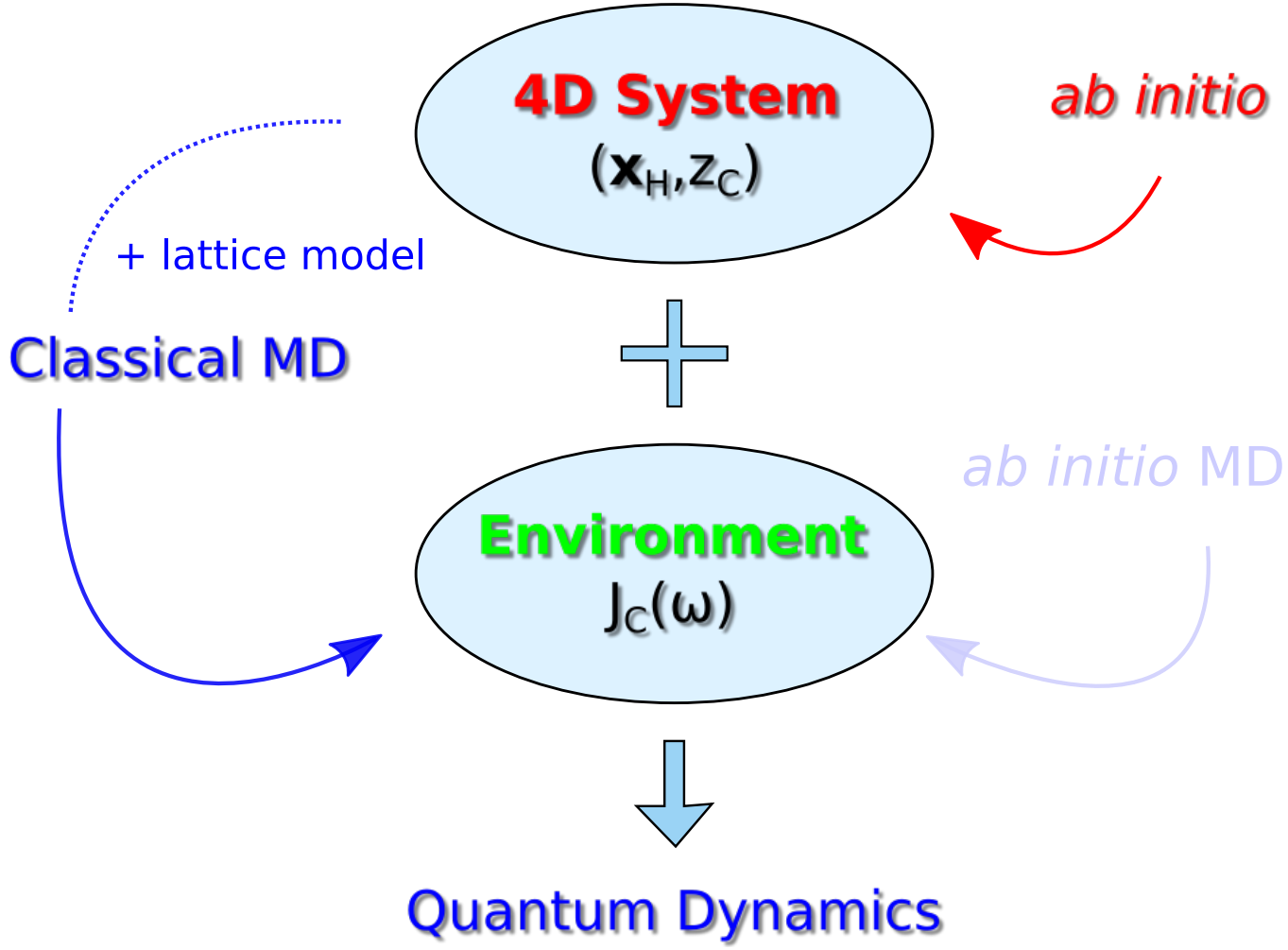
Coupling

$$V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq}) \Rightarrow$$
$$V(x_H, y_H, z_H - Q, z_C - Q, \boldsymbol{q}^{eq}) - \frac{k_C}{2}(z_C - Q)^2$$
$$Q = (z_1 + z_2 + z_3)/3$$

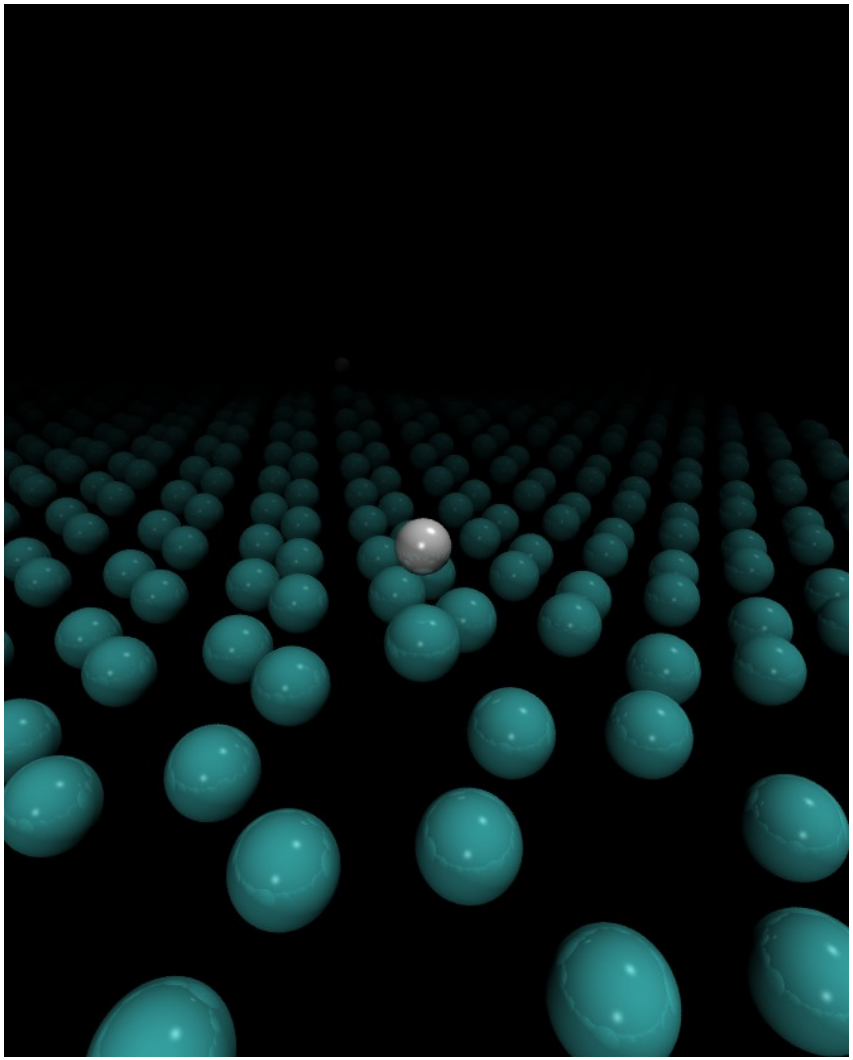


T. Aizawa *et al.*, *Phys. Rev. B*, 11469 **42** (1990)

System-bath modeling: our strategy



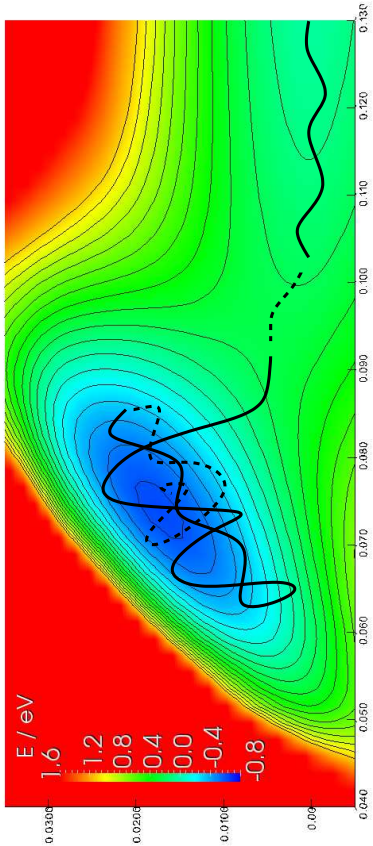
Classical Molecular Dynamics

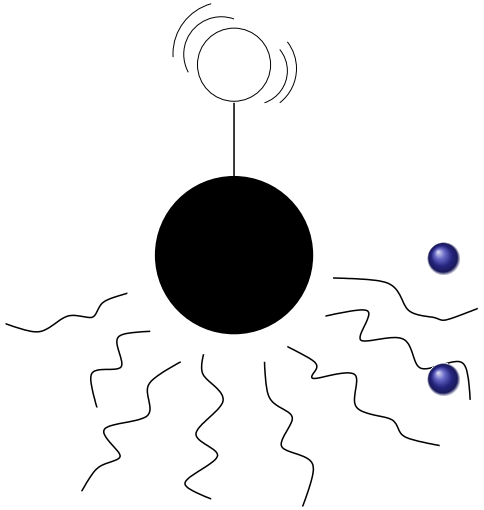


Canonical MD

- Finite slab with 120 carbon atoms
- Equilibration at different T
- 1000 trajectories with Langevin atoms at the slab edges
- $t_{fin} = 10$ ps

$J_C(\omega)$ from Molecular Dynamics





$\Rightarrow$ Canonical, classical dynamics:

$$\delta z_H^i(t)$$

$$C_{zz}(t) = < \delta z(t) \delta z(0) >$$

$$(\; C_{vv}(t) = < \dot{z}(t) \dot{z}(0) > \;)$$

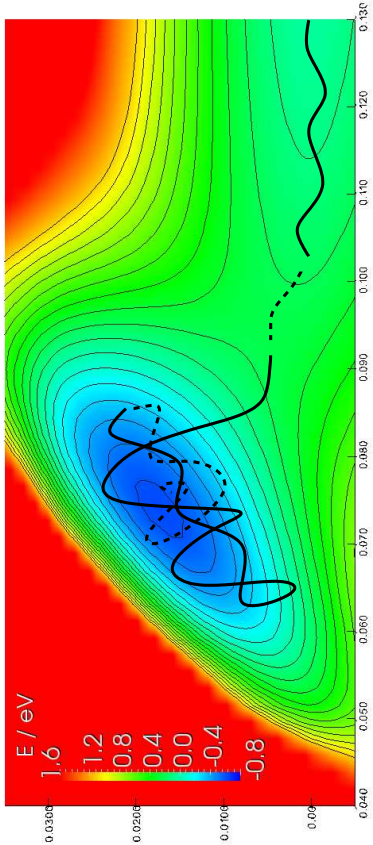
Environment

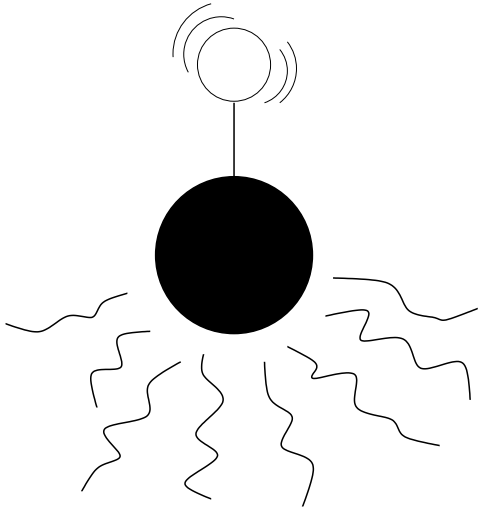
- dissipation mainly occurs at near-equilibrium configurations
- z_H couples only to z_C

H $\rightarrow$ C $\rightarrow$ lattice

$$\tilde{C}(\omega) \rightarrow J_H(\omega) \rightarrow J_C(\omega)$$

$J_C(\omega)$ from Molecular Dynamics





Environment

$$\delta\tilde{z}_H^i(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t}\delta z_H^i(t)dt$$

$$\tilde{C}(\omega) = \frac{1}{N}\sum_{i=1}^{N} |\delta\tilde{z}_H^i(\omega)|^2$$

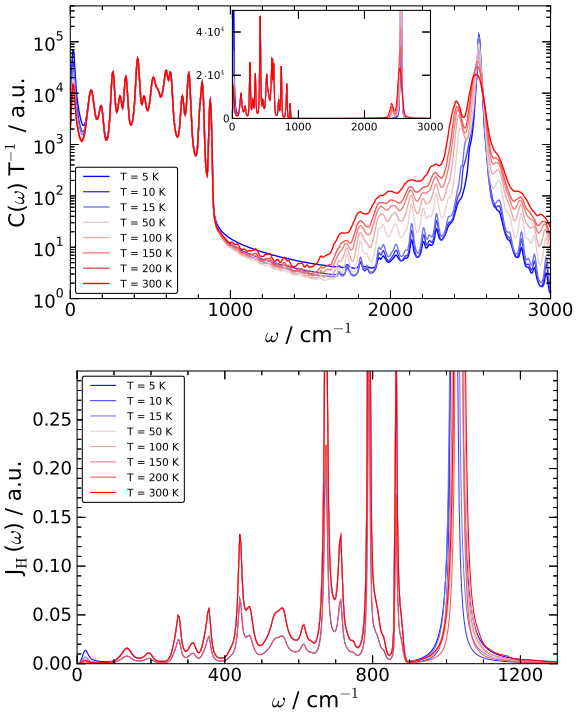
$$\sigma(\omega) = \tilde{C}(\omega)\omega/2$$

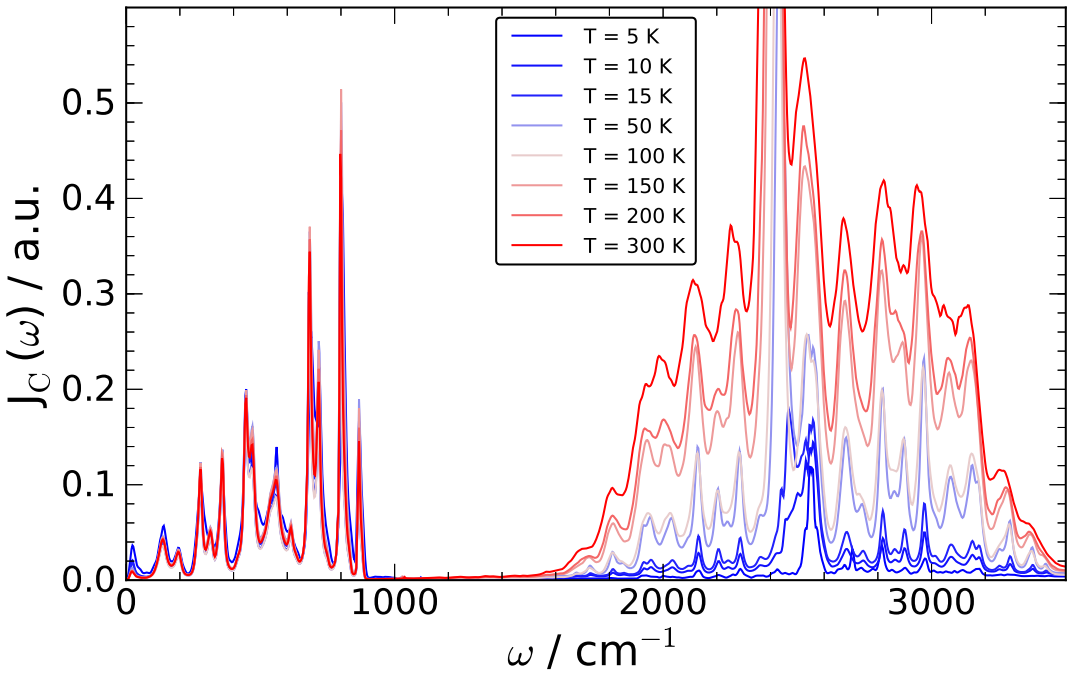
$$J_H(\omega) = k_B T \frac{\sigma(\omega)}{|S^+(\omega)|^2}$$

$$D_0^2 = \frac{2}{\pi}\int_0^{+\infty} J_H(\omega)\omega d\omega$$

$$J_C(\omega) = m_C \frac{D_0^2 J_H(\omega)}{|W^+(\omega)|^2}$$

$J_C(\omega)$ from Molecular Dynamics





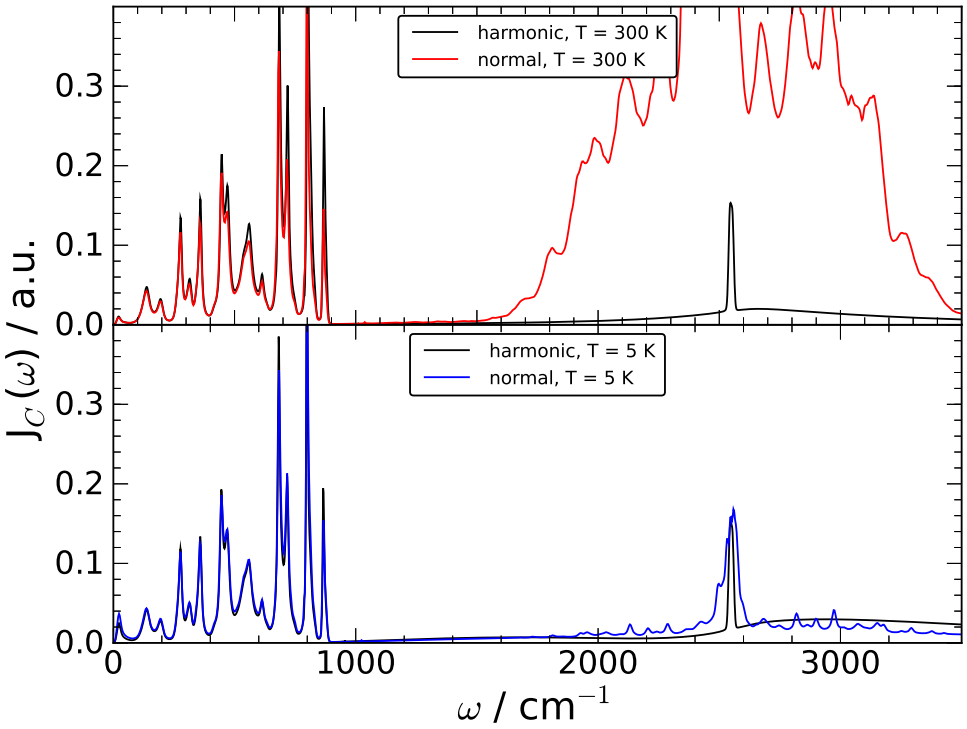
Both 2D and 4D models give the same results

$J_C(\omega)$ from Molecular Dynamics

T-dependent broad band at high ω ?

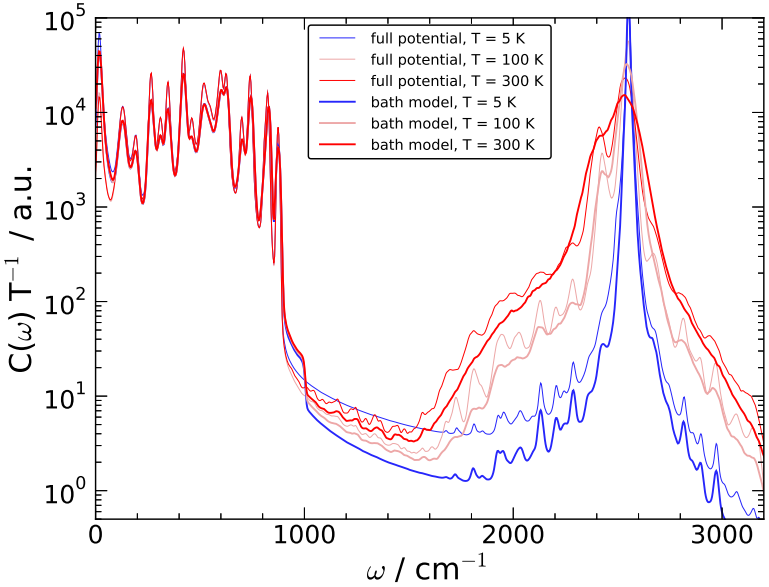
$$V(\boldsymbol{x}_H, z_C)$$
$$\Downarrow$$
harmonic expansion

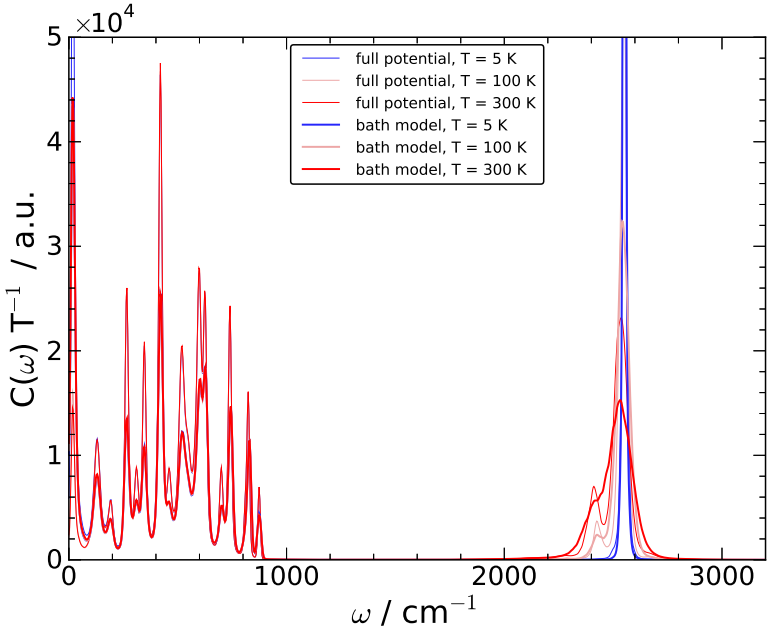
- not a spectral property of the bath
- decay of the $\tilde{C}(t)$ due to system anharmonicity



$J_C(\omega)$ from Molecular Dynamics

$$\tilde{C}(\omega) \xrightarrow{\text{inversion procedure}} J_H(\omega) \xrightarrow{\text{IO model MD}} \tilde{C}_{new}(\omega)$$

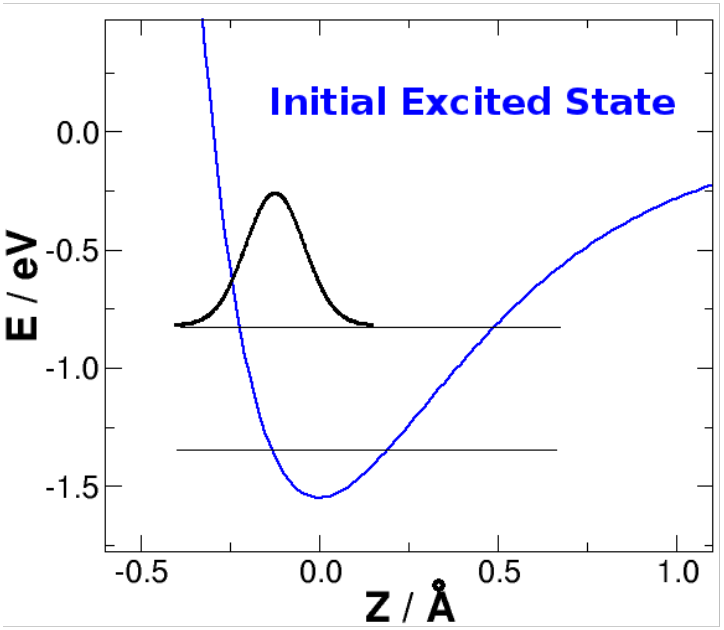




IO Bath with $J_{5K}(\omega)$ and $\omega_{\text{cutoff}} = 1000\ \text{cm}^{-1}$

Outline

Vibrational relaxation @ $T_s = 0$ K



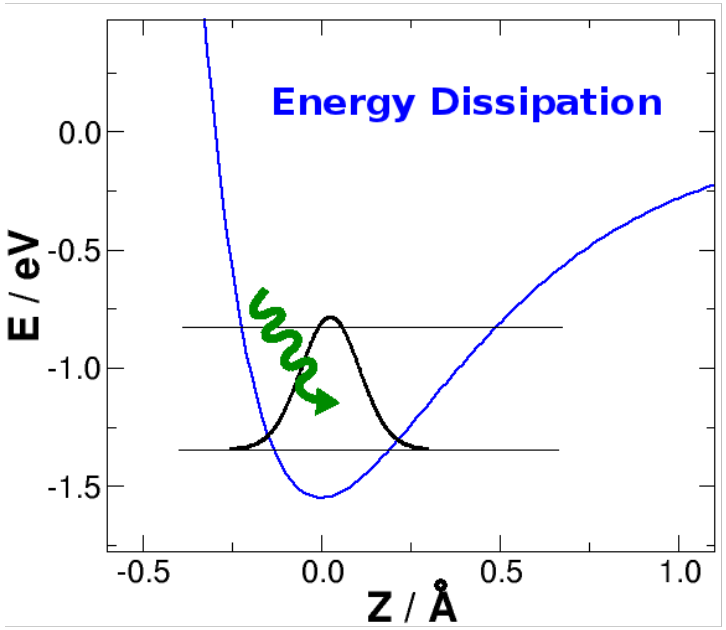
Multi Configurational Time-Dependent Hartree

$$\Psi(\mathbf{x}_H, z_C, \mathbf{Q}_1, .., \mathbf{Q}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}}\, \psi_{i_s}(\mathbf{x}_H, z_C)\phi^{(1)}_{i_1}(\mathbf{Q}_1)\ldots\phi^{(N)}_{i_N}(\mathbf{Q}_N)$$

- Hermite-DVR for system's spfs $\psi_{i_1}(\mathbf{x}_H, z_C)$
- Mode combination & Hermite-DVR for bath spfs $\phi^{(k)}_i(\mathbf{Q}_k)$
- Product initial state, $\psi_\nu(\mathbf{x}_H, z_C)\ldots\phi_{\nu=0}(q_k)\ldots$
- Lanczos diagonalization to obtain the 4D eigenvalues and eigenfunctions

M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

Vibrational relaxation @ $T_s = 0$ K



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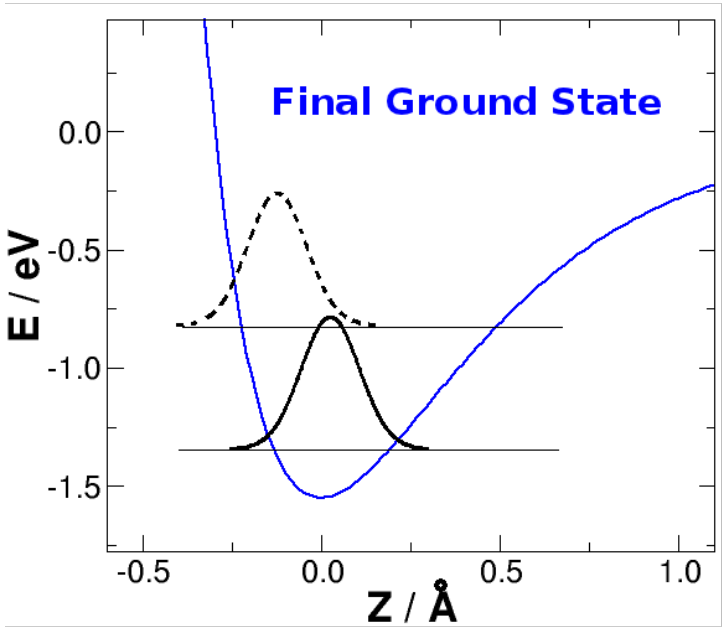

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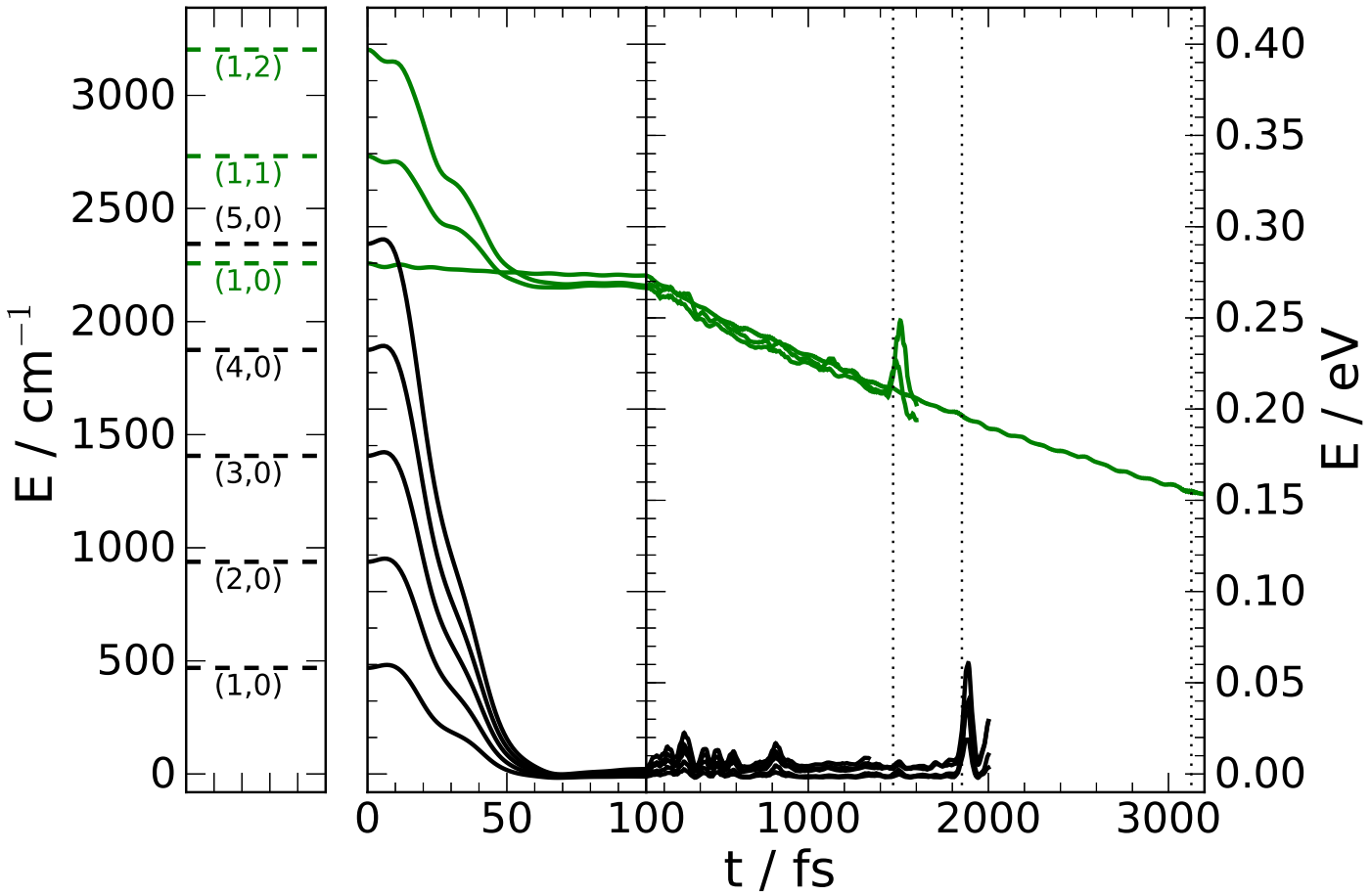
M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

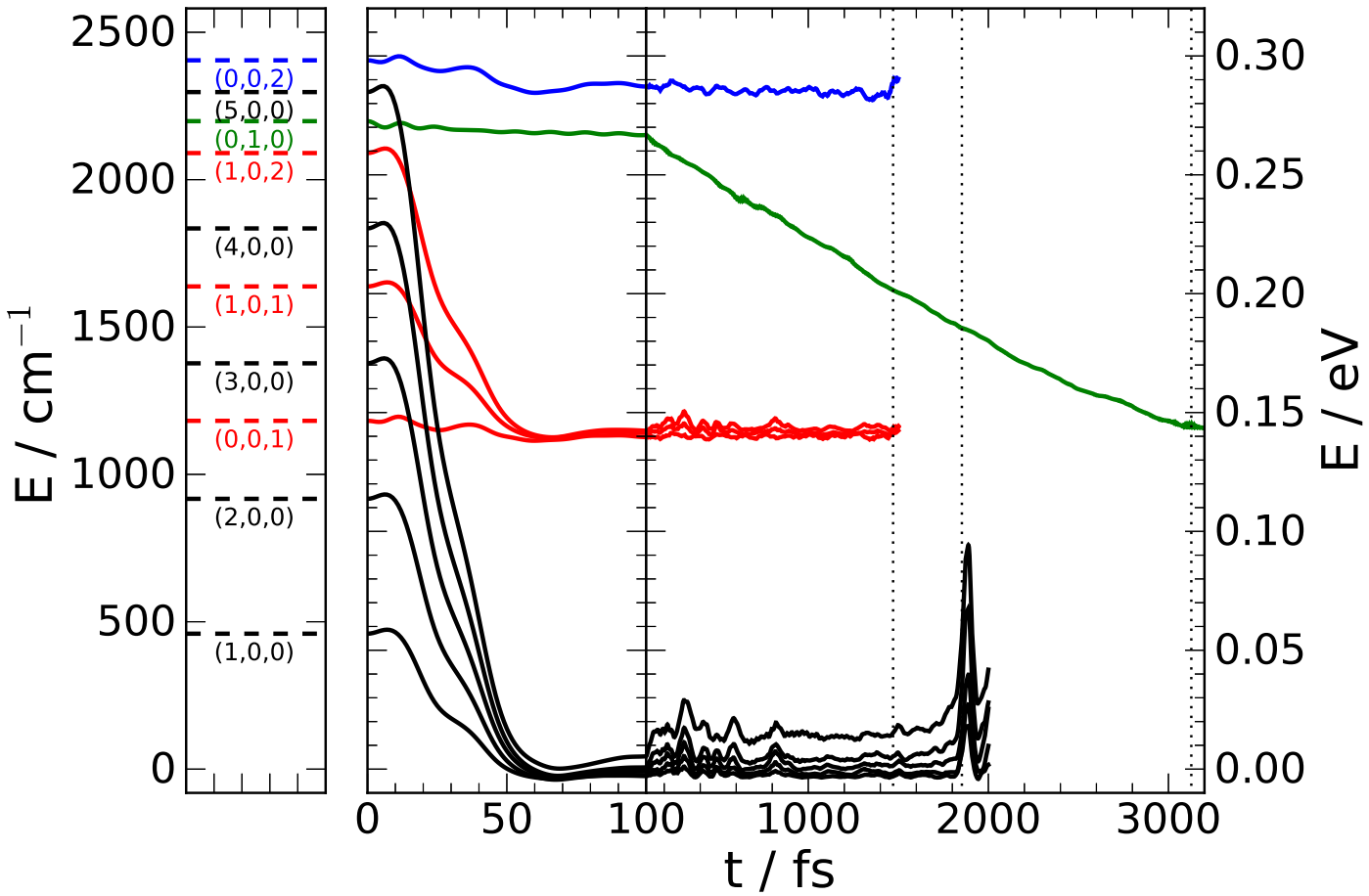
Vibrational relaxation - 2D collinear



(ν_{CH}, ν_{surf})

$\nu_{CH} \rightarrow$ C–H stretching
$\nu_{surf} \rightarrow$ surface–CH stretching

Vibrational relaxation - 4D with bending

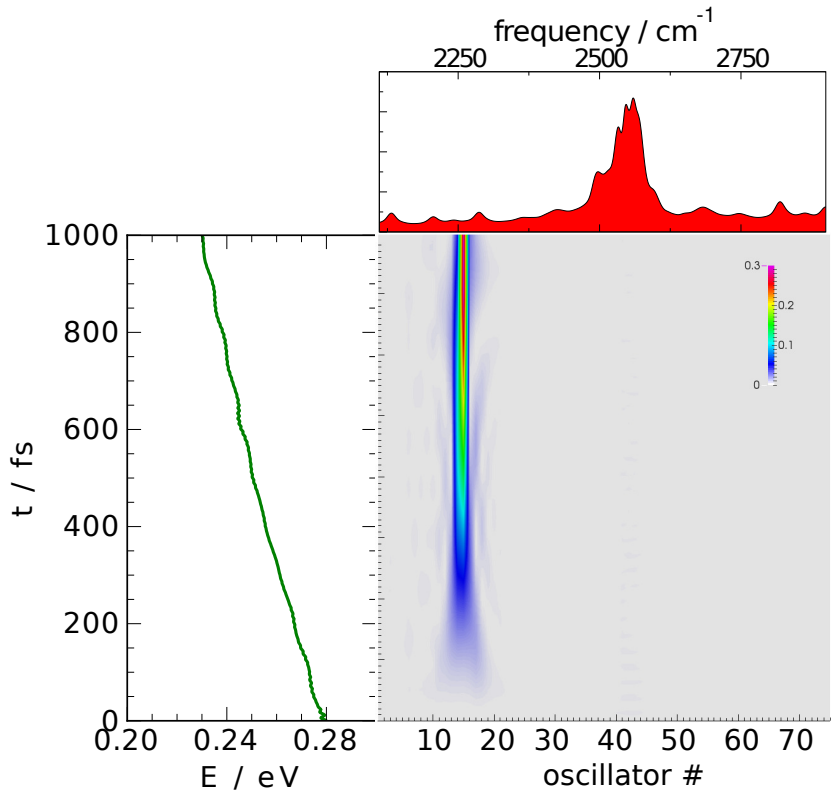


$(\nu_{CH}, \nu_{surf}, \nu_b)$

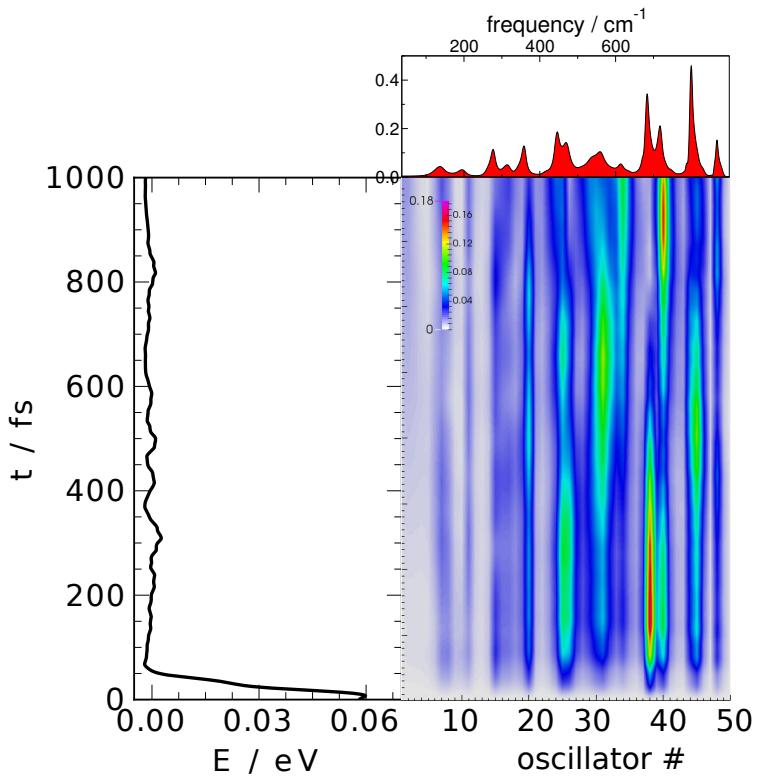
$\nu_{CH} \rightarrow$ C–H stretching
$\nu_{surf} \rightarrow$ surface–CH stretching
$\nu_b \rightarrow$ C–H bending

Vibrational relaxation

bath oscillators $\langle \nu \rangle$ over time



C–H stretching



surface–CH stretching

What makes ν_{CH} relaxing..?

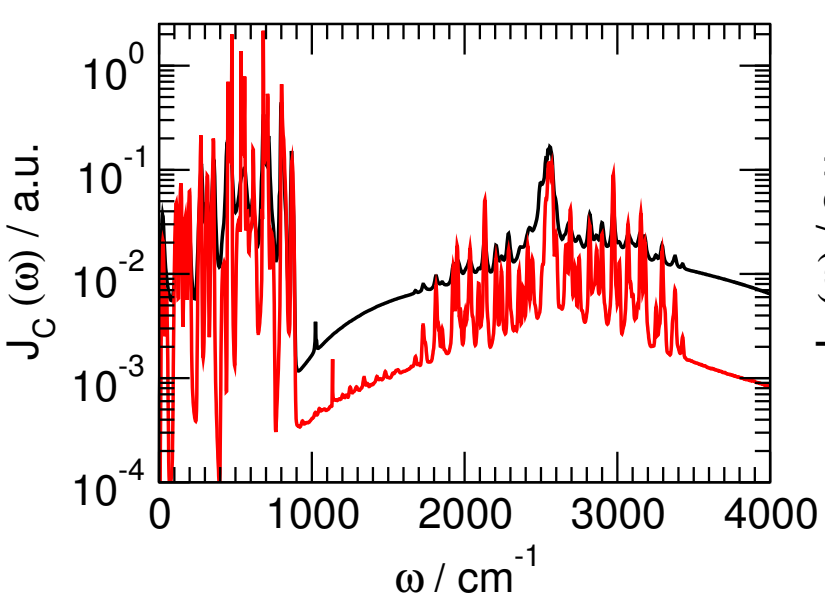
No graphene phonon mode is present at the stretching frequency..

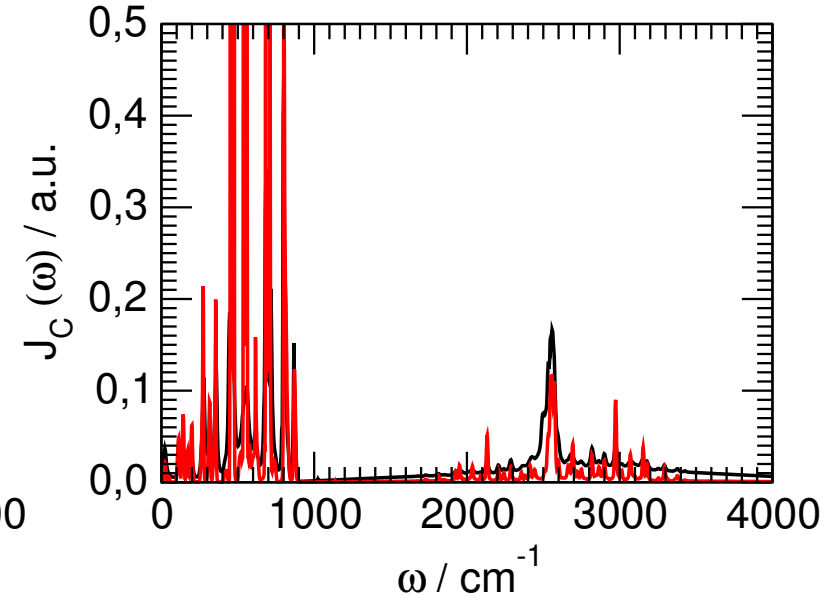
- Phonon bath is not graphene, rather vacant (and distorted) graphene..However, no significant change found
- Anharmonic coupling to bending might be at work in real world, but not in our model

$\Rightarrow$ check of the numerics (computing correlation functions in practice)

What makes ν_{CH} relaxing..?

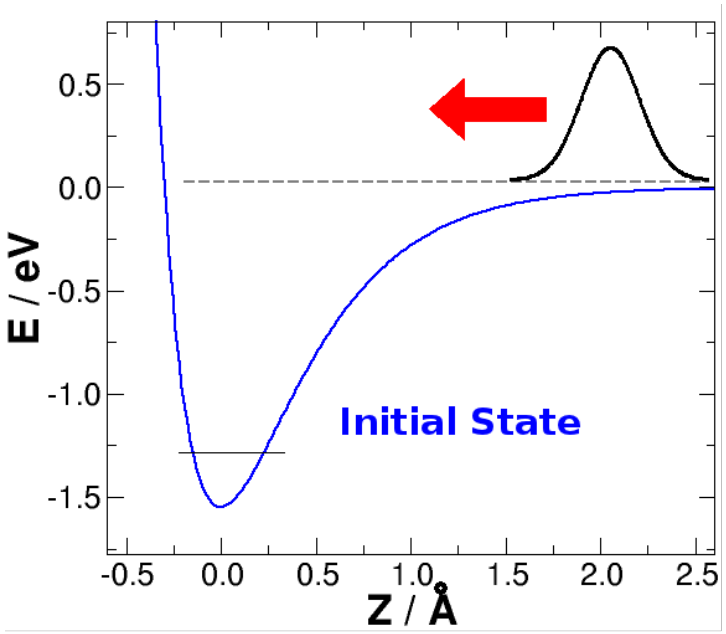
"More controlled" molecular dynamics and spectral analysis





... high-ω background comes from numerics of $J_C(\omega)$ inversion!

Sticking @ $T_s = 0$ K



Multi Configurational Time-Dependent Hartree

$$\Psi(\mathbf{x}_H, z_C, \mathbf{Q}_1, .., \mathbf{Q}_N) = \sum_{\mathbf{I}} c_{\mathbf{I}}\, \psi_{i_s}(\mathbf{x}_H, z_C)\phi^{(1)}_{i_1}(\mathbf{Q}_1)\ldots\phi^{(N)}_{i_N}(\mathbf{Q}_N)$$

- Fourier grid representation of system's spfs $\psi_{i_1}(\mathbf{x}_H, z_C)$
- Mode combination & Hermite-DVR for bath spfs $\phi^{(k)}_i(\mathbf{Q}_k)$
- Product initial state, $\psi_{scatt}(\mathbf{x}_H, z_C)\ldots\phi_{\nu=0}(q_k)\ldots$
- Time–energy mapping and flux analysis

M.H. Beck, A. Jackle, G.A. Worth, H.-D. Meyer, *Phys. Rep.* **324** 1 (2000)

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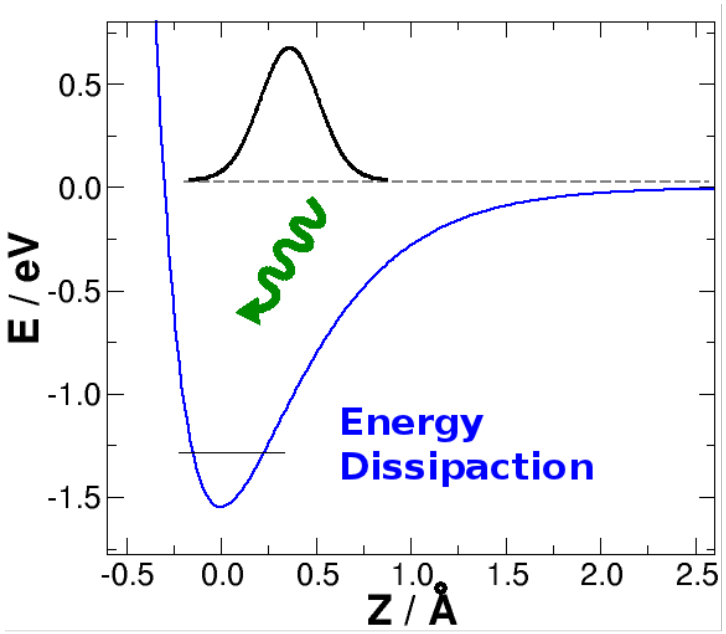

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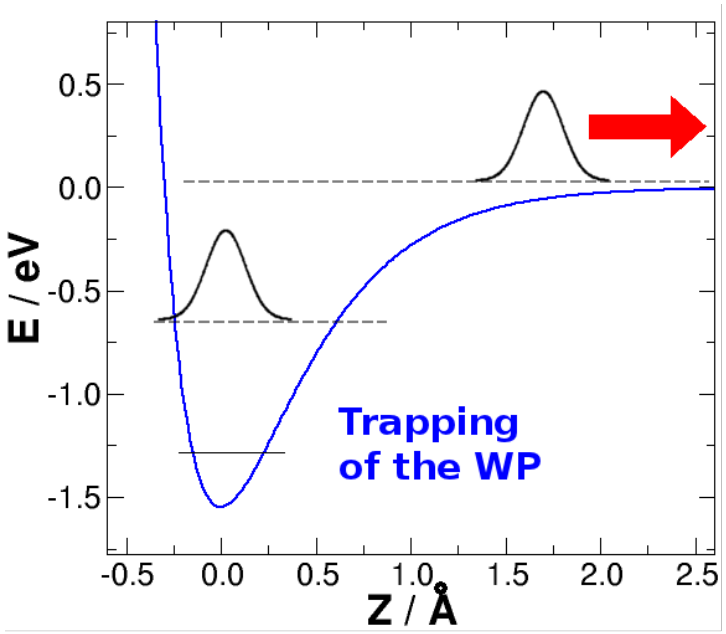

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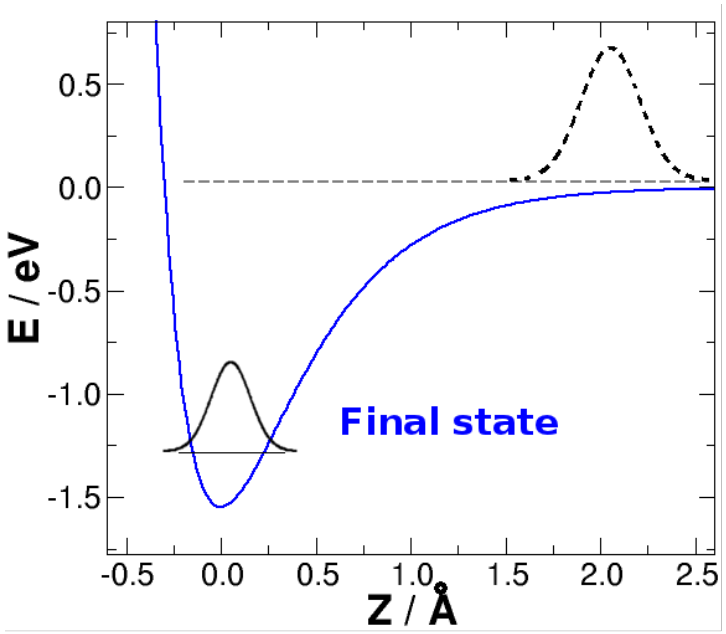

Multi Configurational Time-Dependent Hartree

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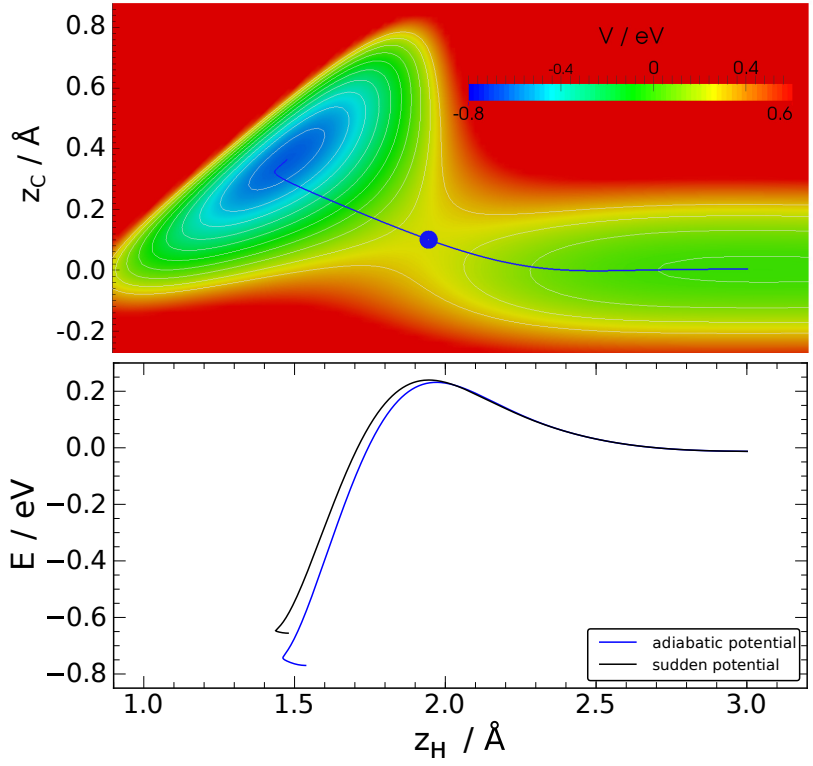
Minimum Energy Path



2 limiting definitions of the 4D system potential

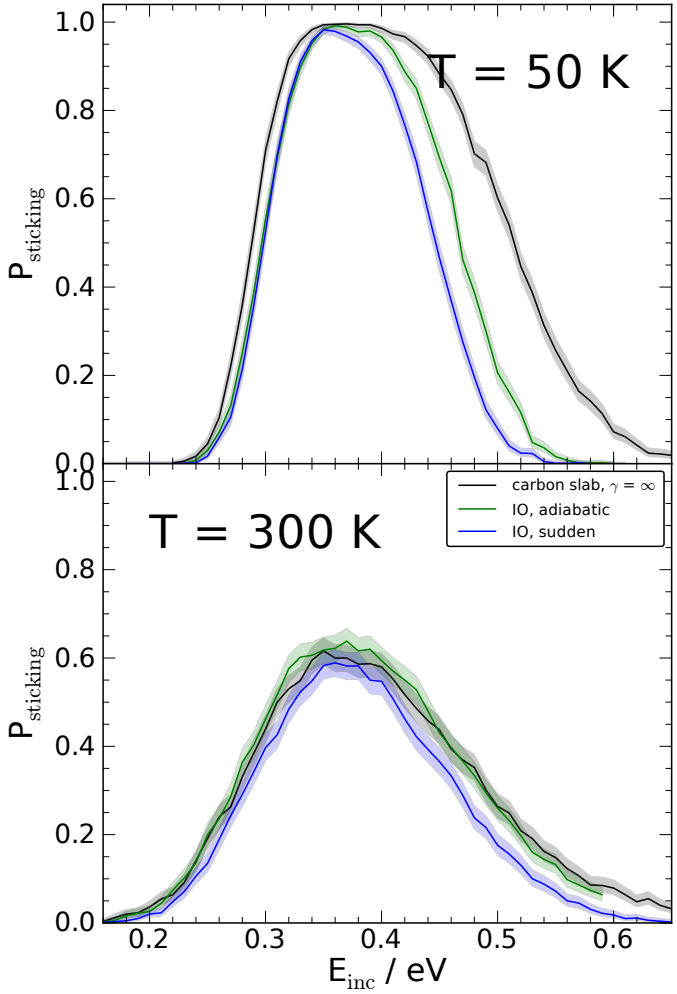
- sudden potential

  $V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{asy})$
  $\boldsymbol{q}^{asy} \Rightarrow$ planar graphene

- adiabatic potential

  $\min_{\boldsymbol{q}} V(\boldsymbol{x}_H, z_C, \boldsymbol{q})$
  substrate in minimum configuration at fixed $\boldsymbol{x}_H, z_C$

Classical sticking (2D + bath)

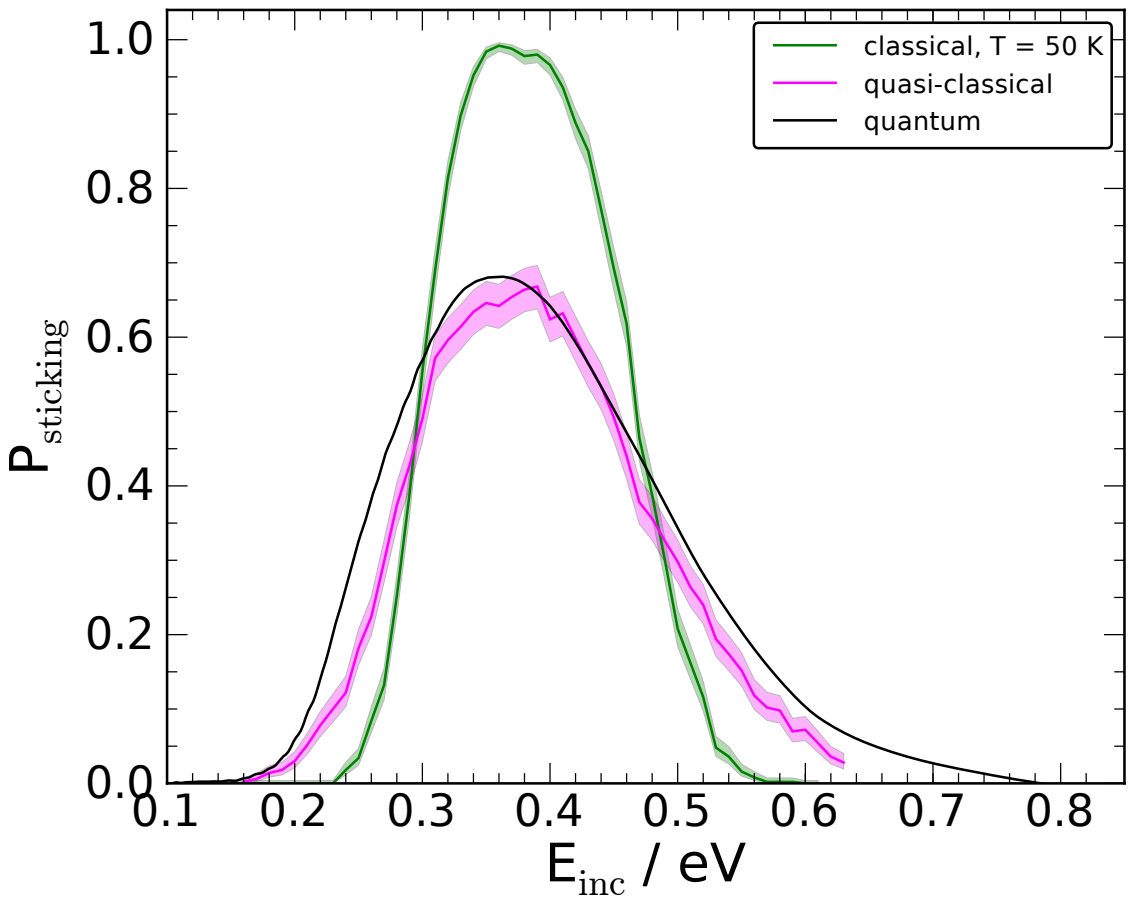


classical molecular dynamics

- **atomistic model** vs IO model (adiabatic/sudden)
- 500/1000 microcanonical trajs per E_{inc}
- bath/lattice initially in thermal equilibrium at given T

→ good agreement at $E_{inc} \sim E_{barrier}$
→ complex comparison at high E_{inc}

Quantum sticking (2D + bath)

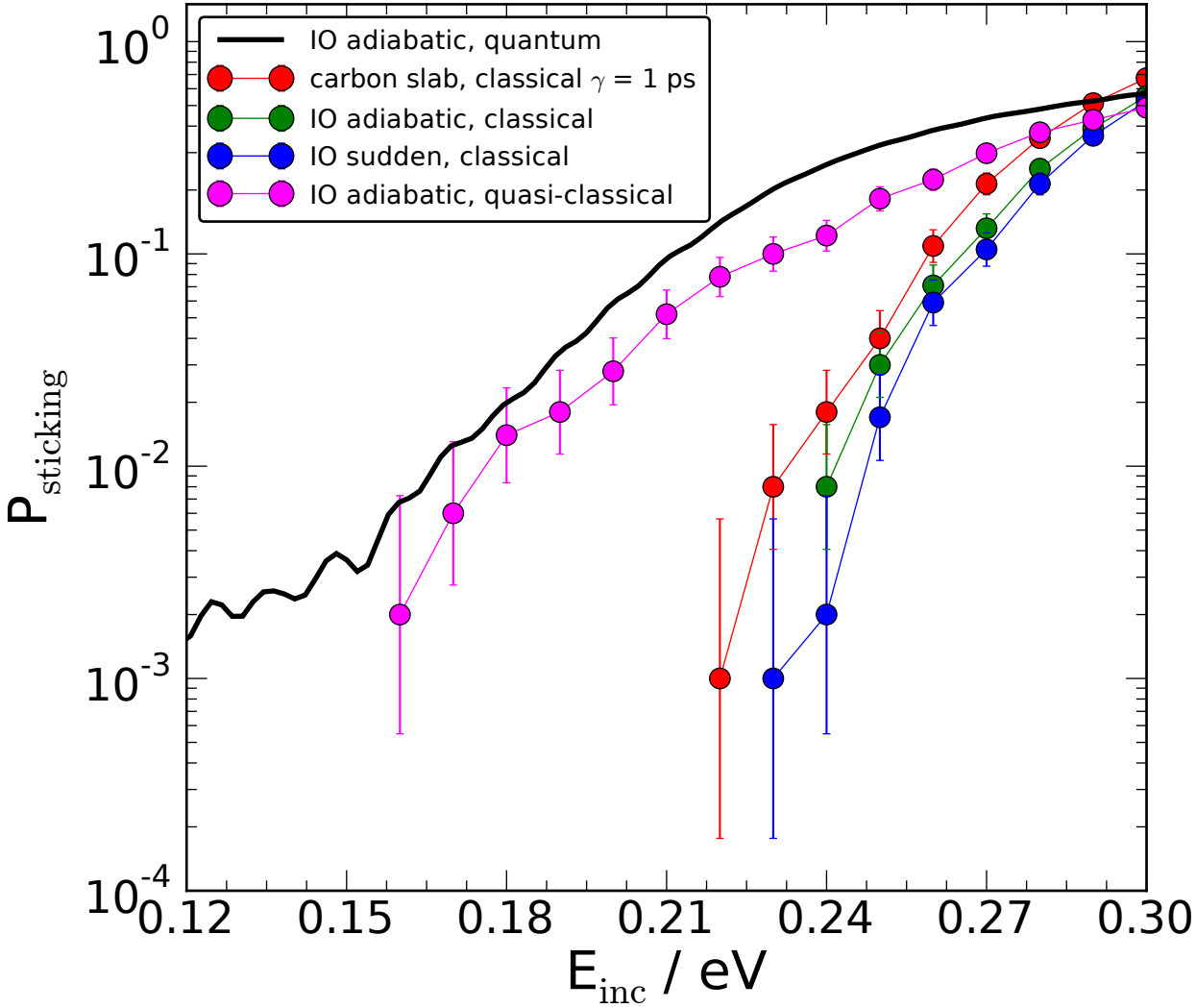


classical @ T = 50 K

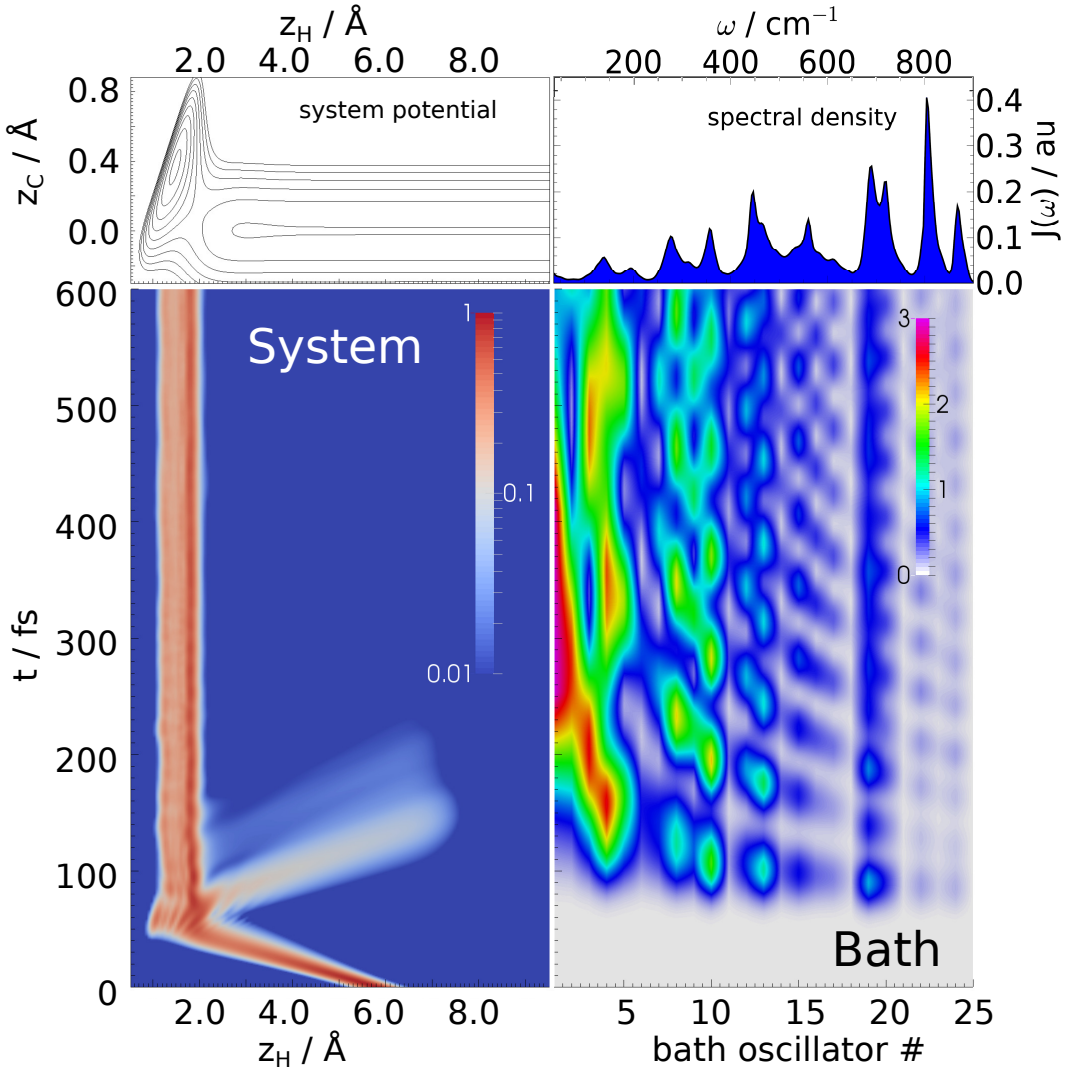
quasi–classical initial bath with ZPE

quantum dynamics

Quantum sticking (2D + bath)



Quantum sticking (2D + bath)



Summary

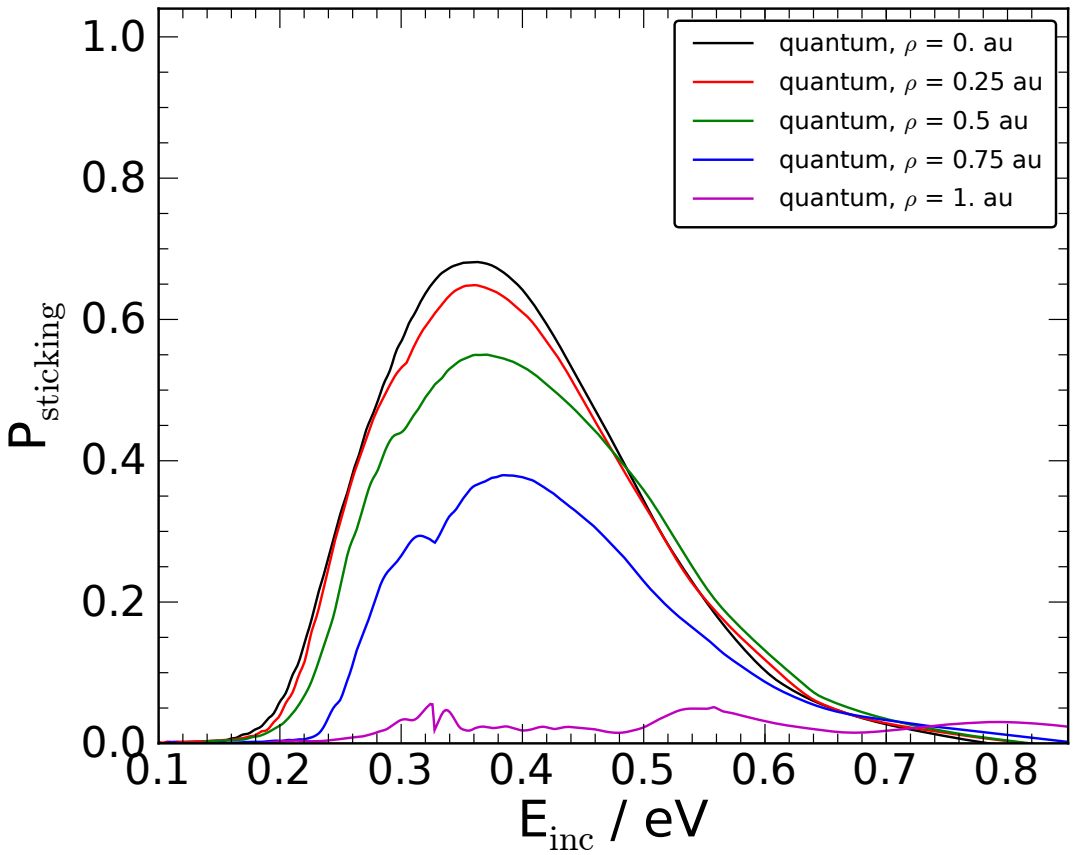
- Mapping of a fully atomistic model to a system-bath IO model, by computing environmental spectral density $J(\omega)$
- Fast vibrational relaxation of low frequency surface surface–CH mode
- Classical, quasi–classical and quantum dynamics of collinear sticking

Inclusion of ρ

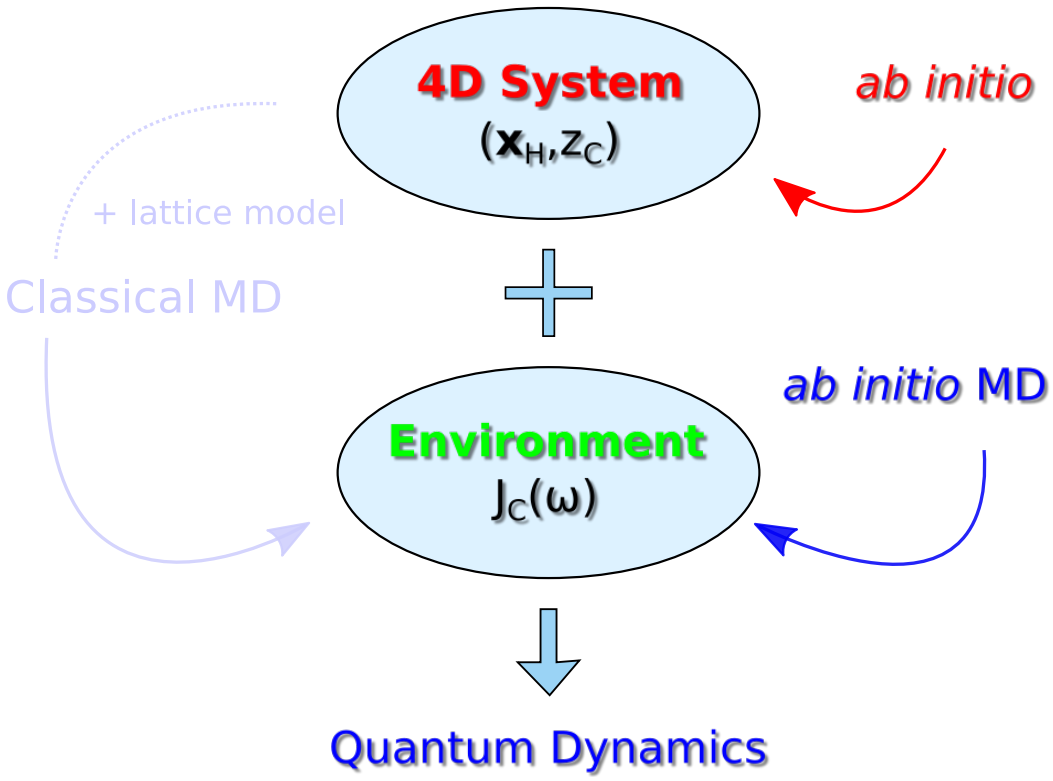
evidence for steering in previous theoretical modes

$\Downarrow$

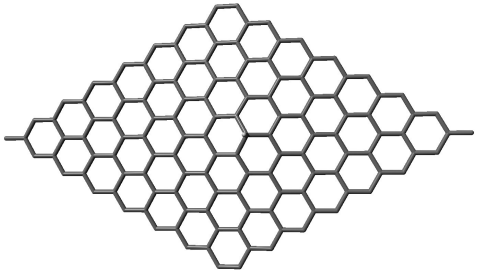
explicit inclusion of ρ in the quantum dynamics



Environment from AIMD



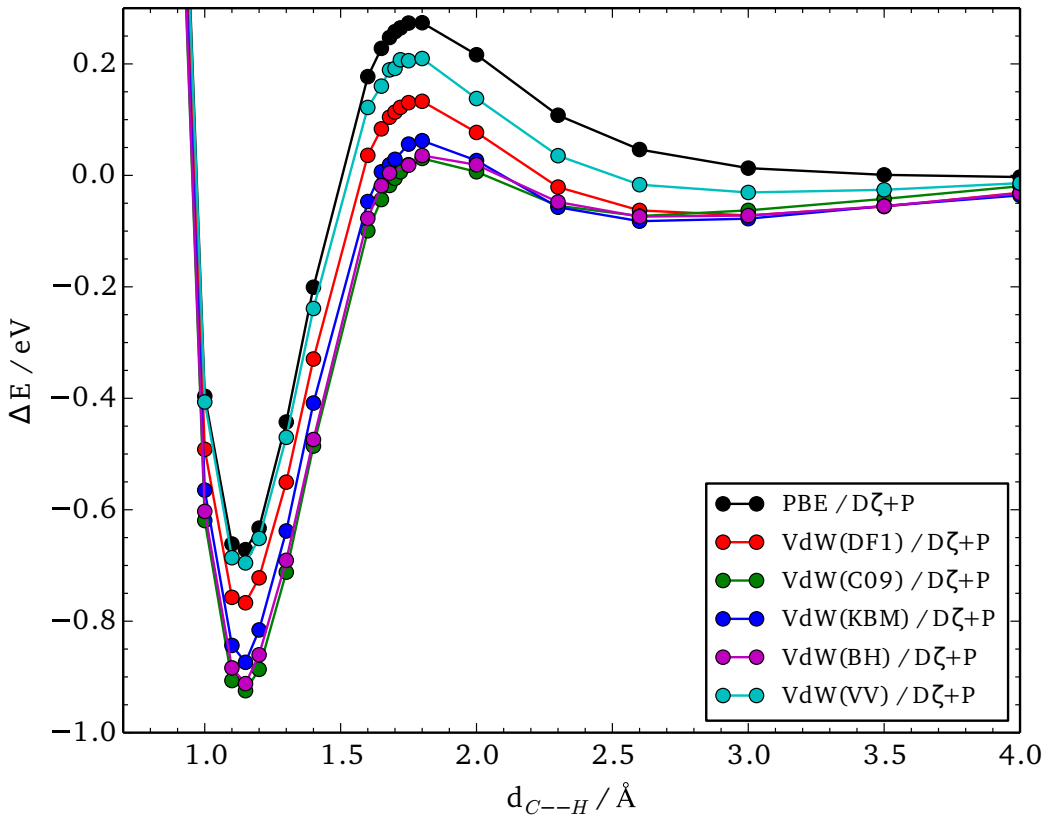
ab initio MD



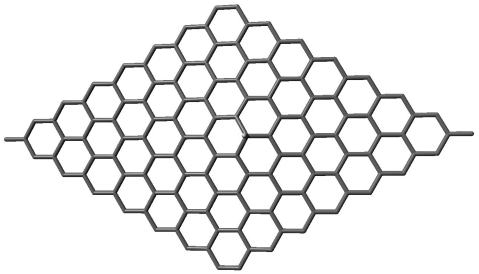
- 8×8 supercell (129 atoms)
- Atomic Orbital DFT PBE, Double-ζ + P
- Equilibration at several T (velocity rescaling)
- 128 trajectories in *NEV*
- $t_{fin} = 2.5$ ps

...in progress

Improved 4D system PES

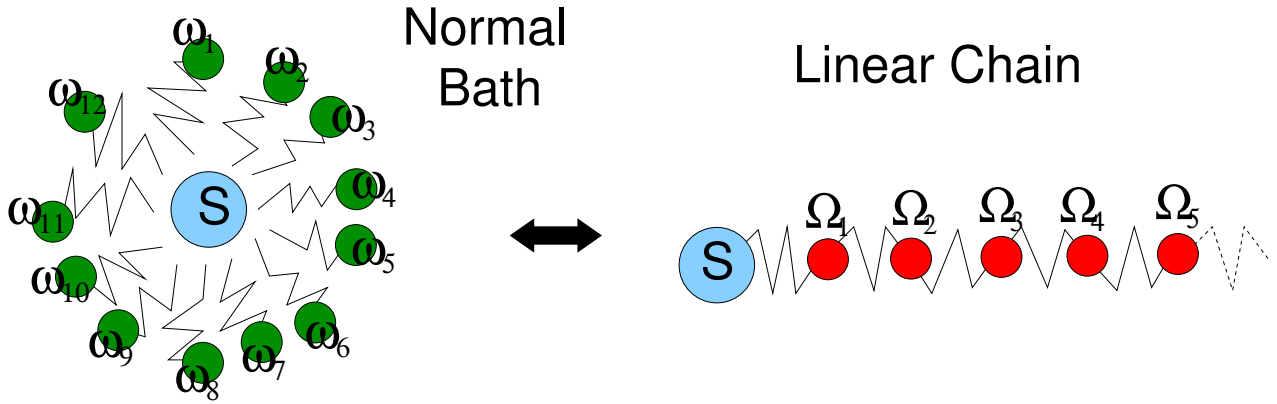


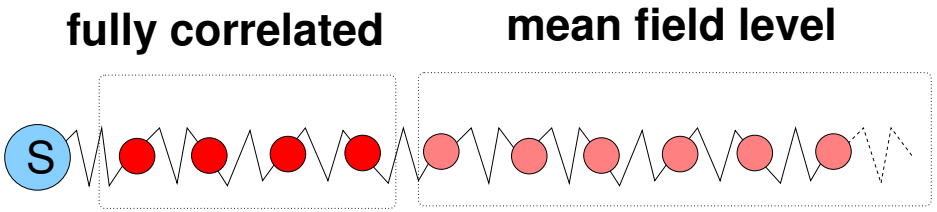
self-consistent VdW potentials



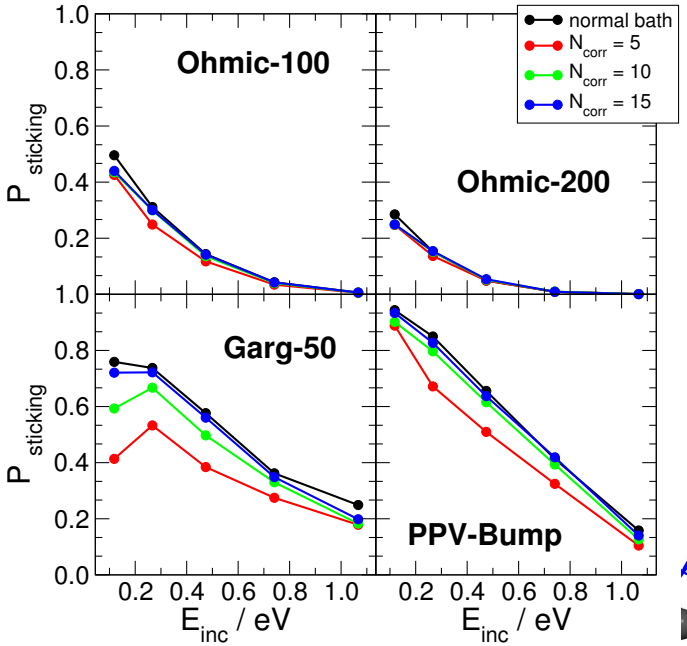
- 8×8 supercell (129 atoms)
- Atomic Orbital DFT, Double-ζ + P
- VdW corrected functionals
- full system ($\mathbf{r}_H$, z_C) dependence

Linear Chain Representation of the Bath





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



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

Acknowledgments

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Bret Jackson	University of Massachusetts, Amherst
Irene Burghardt	Goethe University Frankfurt
Keith Hughes	Bangor University, UK

... and thank you, for your attention!

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System-bath modeling: our strategy

$$\ddot{z}(t) + \int_{-\infty}^{+\infty} \gamma(t-\tau)\dot{z}(\tau)d\tau + \omega_0^2 z(t) = \xi(t)/m$$

$$\Downarrow$$

$$\delta\tilde{z}(\omega) = \frac{1}{m}\frac{\tilde{\xi}(\omega)}{\omega_0^2 - \omega^2 - i\omega\tilde{\gamma}(\omega)}$$

$$\Downarrow$$

$$\frac{1}{2}\omega\tilde{C}(\omega) = \frac{k_B T}{m}\,\mathrm{Im}\left(\frac{1}{\omega_0^2 - \omega^2 - i\omega\tilde{\gamma}(\omega)}\right)$$

$$\Downarrow$$

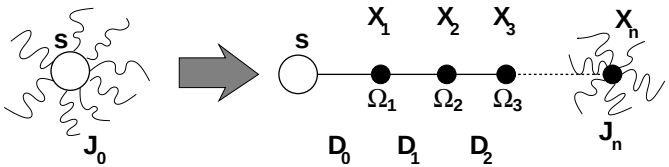
$$S(z) = iz\tilde{C}^{>}(z) + C(0) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\omega\tilde{C}(\omega)/2}{\omega - z}d\omega$$

$$\Downarrow$$

$$S(z) \equiv \frac{k_B T}{m}\frac{1}{\omega_0^2 - z^2 - iz\tilde{\gamma}(z)}$$

$$\Downarrow$$

$$J_H(\omega) = \frac{k_B T}{2}\frac{\omega\tilde{C}_H(\omega)}{|S^+(\omega)|^2}$$



$$D_C^2 = \frac{2m_C}{\pi}\int_0^{\infty} J_H(\omega)\omega d\omega$$

$$W_H(z) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{J_H(\omega)}{\omega - z}d\omega$$

$$W_H^+(\omega) = \lim_{\epsilon\to 0^+} W_H(\omega + i\epsilon)$$

$$\Downarrow$$

$$J_C(\omega) = \frac{D_C^2 J_H(\omega)}{|W_H^+(\omega)|^2}$$

System-bath modeling: our strategy

..justifying out choice of the system potential

$$V_s(s_1, s_2, ..s_N) = \mathrm{Min}_{\xi_1,\xi_2,..\xi_F} V(s_1, s_2, ..s_N, \xi_1, \xi_2, ..\xi_F)$$

In our case,

$$\xi_i \equiv z_i,\ s_1 = x_H,\ s_2 = y_H,\ s_3 = z_H - Q,\ s_4 = z_C - Q$$

where $Q = \sum_i z_i$ and

$$V = V_{4D}(s_1, s_2, s_3, s_4) + V_{latt}(s_4 + Q, z_1, z_2, ..z_F) - V_{puck}(s_4)$$

$$\Downarrow$$

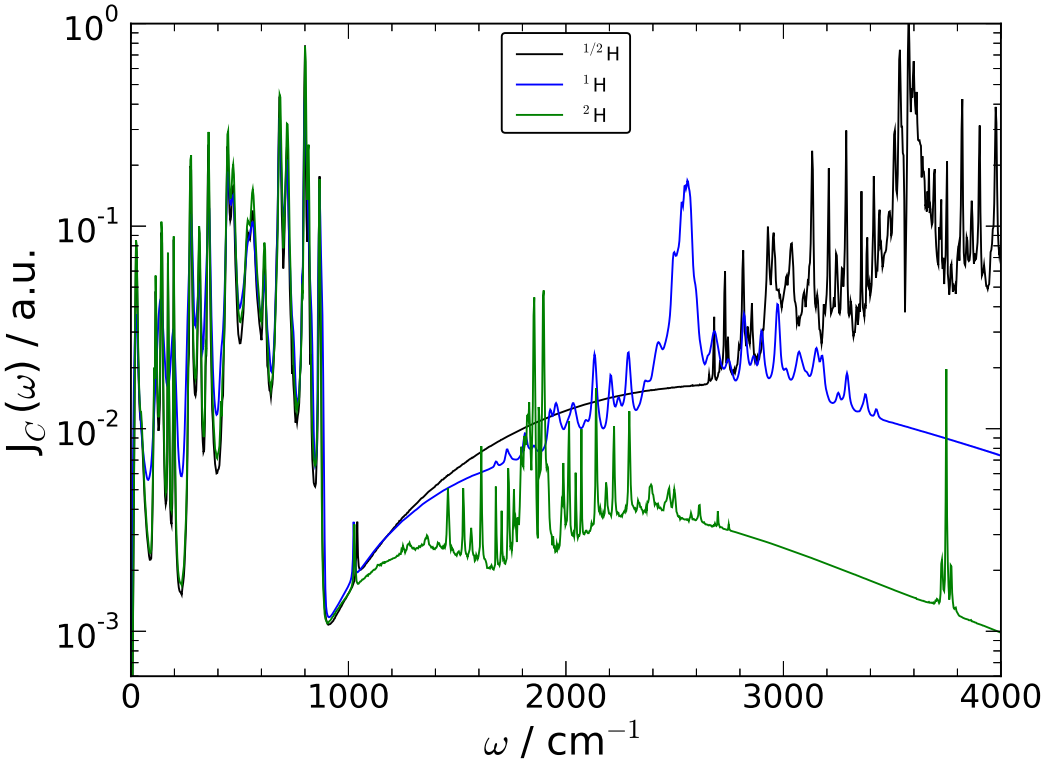
$$V_s(\boldsymbol{s}) \equiv V_{4D}(\boldsymbol{s}) - V_{puck}(s_4) + \mathrm{Min}_{z_1,z_2,..z_F} V_{latt}(s_4 + Q, z_1, z_2, ..z_F)$$

if $V_{puck}(s) := \mathrm{Min}_{z_1,z_2,..z_F} V_{latt}(s + Q, z_1, z_2, ..z_F) \approx \frac{k_C}{2} s^2$

$$V_s(\boldsymbol{s}) \equiv V_{4D}(\boldsymbol{s})$$

What makes ν_{CH} relaxing..?

Isotopic substitution



..high-ω background is artificial!

Sticking (2D + bath)