Effective mode representation of structured environments: towards *first principles* quantum dynamics of hydrogen atoms on graphene

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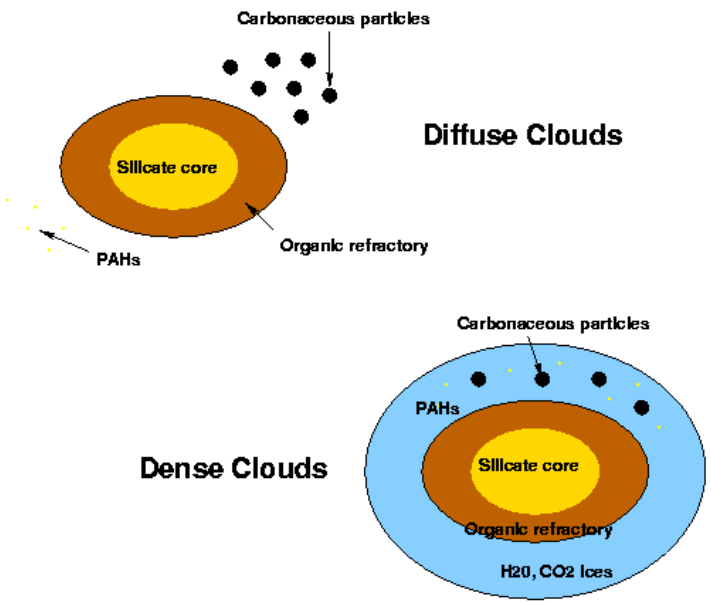
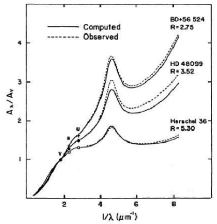
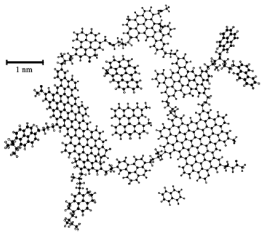
H_2 in the ISM

- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

$f_{grain}=n_{grain}/n_H \sim 10^{-12}$ i.e. $\sim$1% of ISM mass





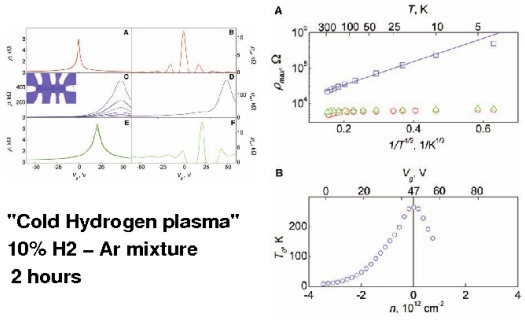


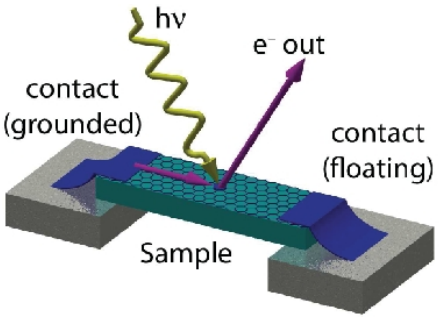
Hydrogen-graphite(graphene) is an important model for understanding H_2 formation in ISM

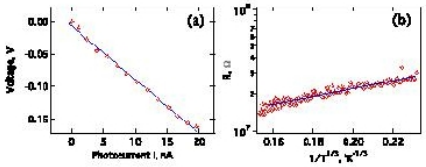
Graphene physics

Graphene is a true 2D-electron gas (2DEG) system with pseudo-relativistic charge-carriers

MIT occurs when hydrogenating graphene







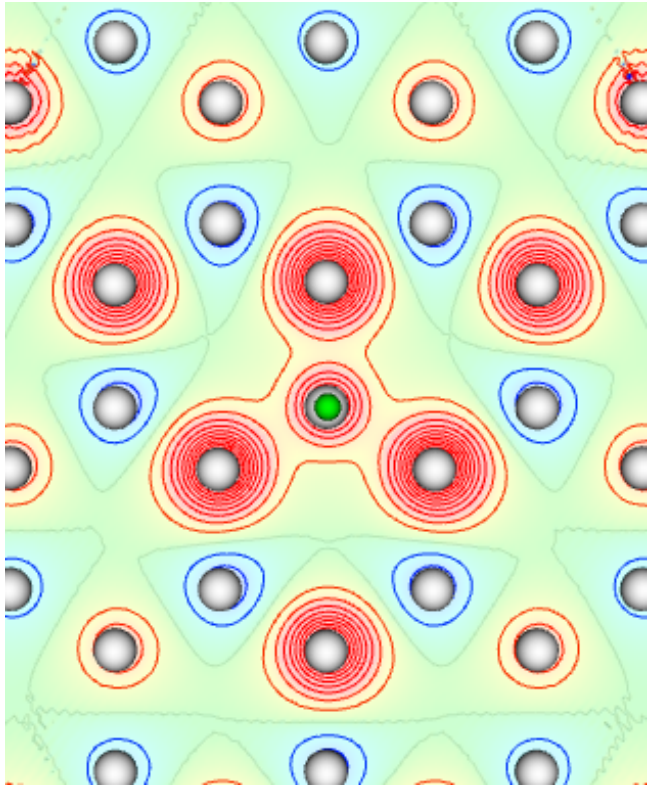
UHV (p ~ 10^{-9} torr)
T(H_2) ~ 2000 C

..σ *vs* T agrees well with VRH in two dimensions

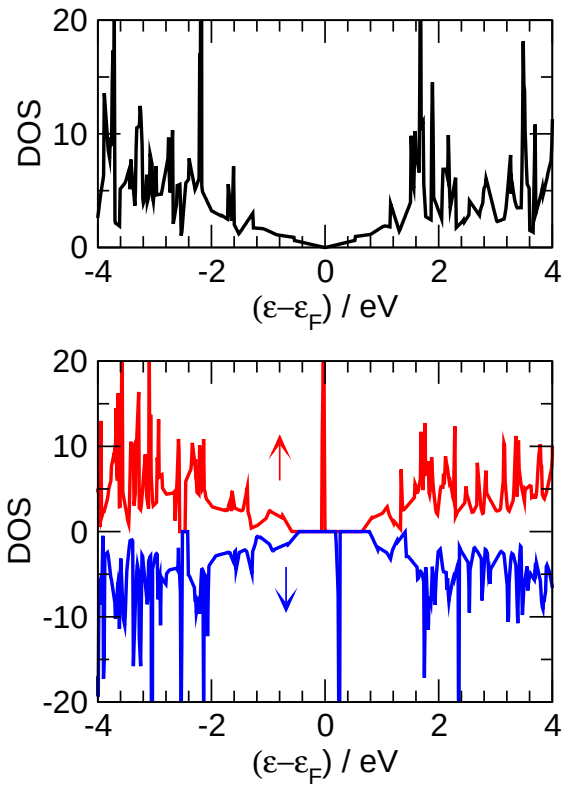
High n_H : D. C. Elias *et al.*, *Science* **323**, 610 (2009)

Low n_H : A. Bostwick *et al.*, *Phys. Rev. Lett.* **103**, 056404 (2009)

Midgap states: p_z vacancies



..*patterned* spin-density

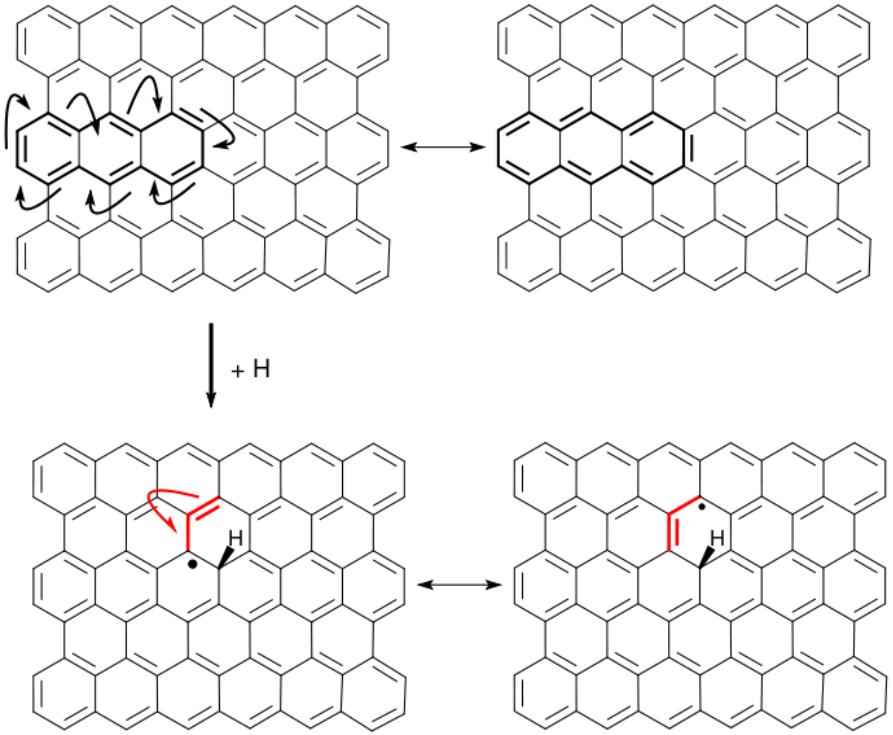


Graphene

+ H

H-Graphene

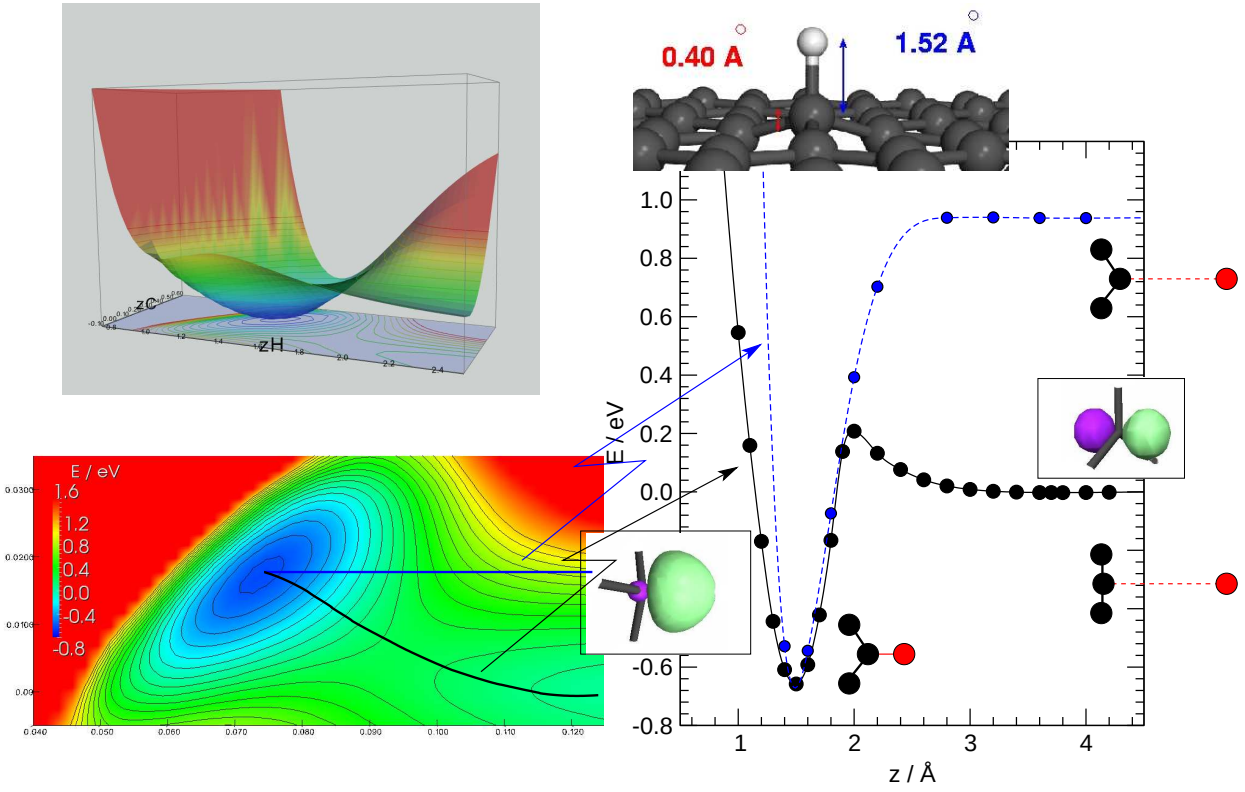
Midgap states: p_z vacancies



Resonating Valence Bond

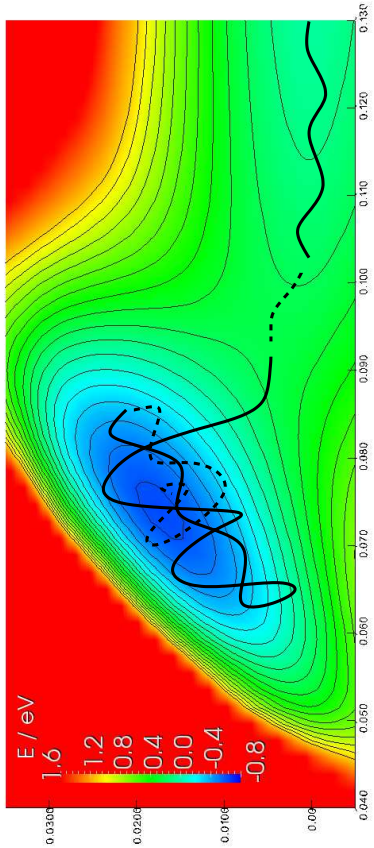
- **Transport**: resonant scatterers explain behavior of σ_{DC} at zero and finite electron densities
- **Magnetism**: local magnetic moments responsible for the observed paramagnetic response
- **Chemistry**: preferential sticking leading to dimer and cluster formation

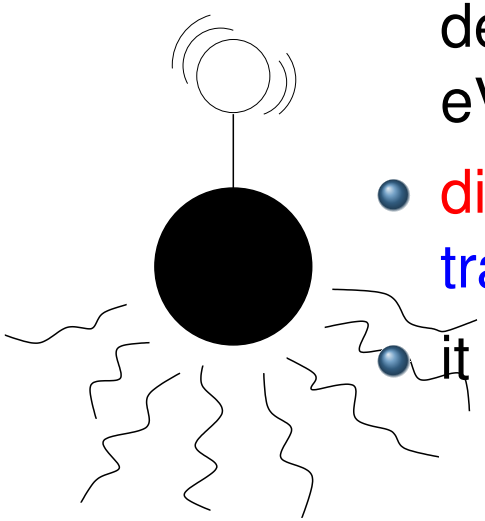
H chemisorption on graphene



L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

H chemisorption on graphene

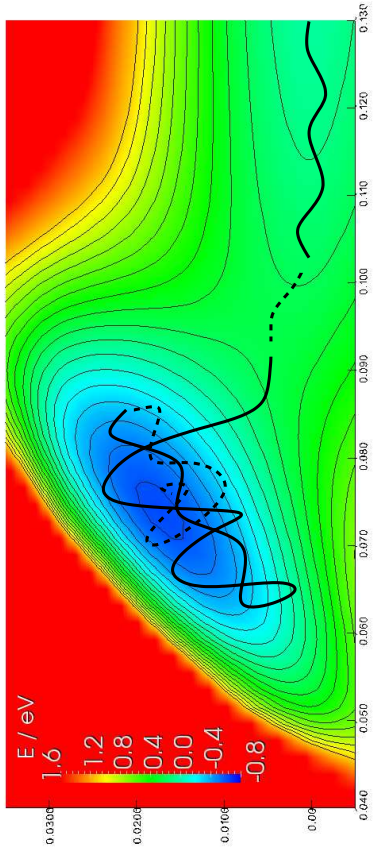


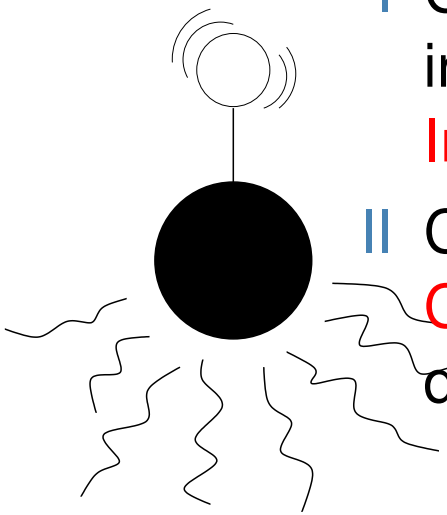


Challenging problem..

- quantum dynamics is needed to describe tunneling for $E_{coll} \leq 0.2$ eV
- dissipation is required to turn trapping into sticking
- it involves scattering dynamics

H chemisorption on graphene





Challenging huge dimensional, strongly coupled quantum problem..

I Convert the H-graphene problem into a dynamically *equivalent* Independent Oscillator (IO) model

II Convert the IO bath to a Linear Chain (LC) form suited for large dimensional quantum calculations

Outline

Outline

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Generalized Langevin Equation

$$M\ddot{s}(t) + M\int_{-\infty}^{\infty}\gamma(t-t')\dot{s}(t')dt' + V'(s(t)) = \xi(t)$$

- $V'(s)$: deterministic force
- $\gamma(t)$: dissipative memory kernel
- $\xi(t)$: Gaussian, stationary stochastic noise

GLE: Spectral density

$$J_0(\omega) = M\omega \mathrm{Re}\tilde{\gamma}(\omega)$$

- $J_0(\omega)$ is a real, odd function of ω
- $J_0(\omega) \geq 0$ for $\omega \geq 0$ — Positivity
- $\gamma(t) = \frac{\Theta(t)}{\pi M} \int_{-\infty}^{+\infty} \frac{J(\omega)}{\omega} e^{-i\omega t} d\omega$ — Kramers-Kronig
- $\langle \xi(t)\xi(0) \rangle = M k_B T \gamma(|t|)$ — Fluctuation-Dissipation

IO 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

IO Hamiltonian

$$M\ddot{s}(t) + M\int_{t_0}^{\infty}\gamma(t-t')\dot{s}(t')dt' + V'(s(t)) = \xi(t)$$

$$\rho(x_1, x_2, \dots p_1, p_2, \dots) = \frac{1}{Z}\mathrm{e}^{-\beta H_{z_0}^{\mathrm{env}}}$$

$$H_{z_0}^{\mathrm{env}} = \sum_k \left\{ \frac{p_k^2}{2} + \frac{\omega_k^2}{2}\left(x_k - \frac{c_k z(t_0)}{\omega_k^2}\right)^2 \right\}$$

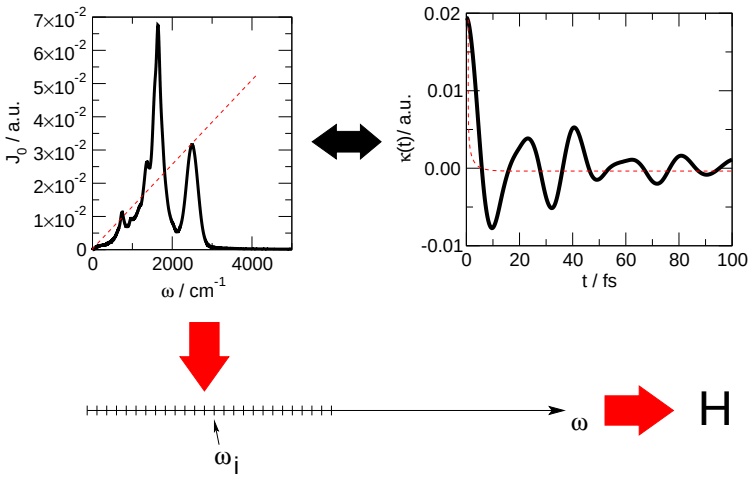
$$\langle \xi(t) \rangle = 0, \qquad \langle \xi(t)\xi(0) \rangle = \frac{k_B T}{M}\kappa(t)$$

$$\Rightarrow \quad J_0(\omega) = \frac{\pi}{2}\sum_k \frac{c_k^2}{\omega_k}\left(\delta(\omega-\omega_k) - \delta(\omega+\omega_k)\right)$$

IO Hamiltonian

...

$$J_0(\omega) \Rightarrow \omega_k = k\Delta\omega \text{ and } c_k = \sqrt{\frac{2\omega_k \Delta\omega J_0(\omega_k)}{\pi}} \; (k = 1, \ldots N)$$



..discretized model which is equivalent to the GLE for times less than the Poincaré recurrence time,

$$t < T_{rec} = \frac{2\pi}{\Delta\omega} = \frac{2\pi}{\omega_N} N$$

Effective modes

$$H^{\text{int}} = -\sum_k c_k x_k s = -D_0 X_1 s$$

- $D_0^2 = \sum_k c_k^2$: effective mode coupling
- $X_1 = \sum_k x_k T_{k1}, \ (T_{k1} \equiv c_k)$: effective mode
- $(X_1, X_2, .., X_N) = (x_1, x_2, .., x_N)\, \boldsymbol{T}$: (quasi-arbitrary) orthogonal transformation
- $\left(\boldsymbol{T}^t \boldsymbol{\omega}^2 \boldsymbol{T}\right)_{ij} = \boldsymbol{\Omega}_{ij}^2 \ \ i, j = 2, N$: frequency matrix of the "residual" bath

$$\Rightarrow \ \boldsymbol{T} \text{ can be fixed by requiring } \boldsymbol{\Omega}_{ij}^2 = \delta_{ij} \bar{\Omega}_i^2$$

Effective modes

$$H = \left(\frac{p^2}{2M} + V(s)\right) + \Delta V(s) - D_0 s X_1 + \left(\frac{P_1^2}{2} + \frac{\Omega_1^2 X_1^2}{2}\right) - X_1 \sum_{k=2}^{N} C_k X_k + \\ + \sum_{k=2}^{N} \left(\frac{P_k^2}{2} + \frac{\bar{\Omega}_k^2 X_k^2}{2}\right)$$

In the continuum limit $N \to \infty$ (with $N\Delta\omega \equiv \omega_c$):

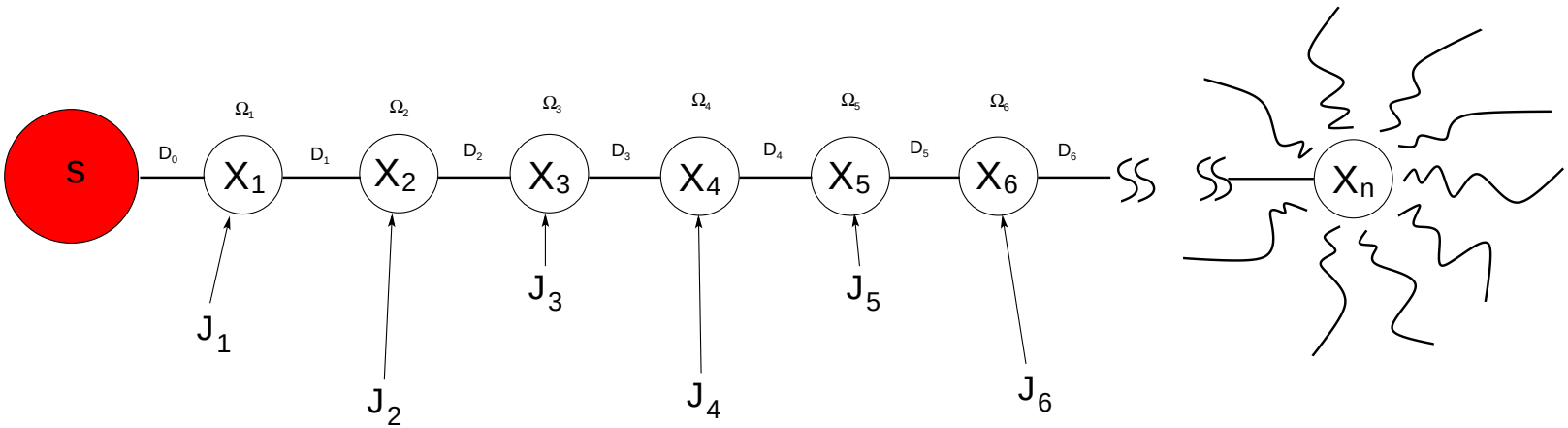
$$D_0^2 \to \frac{2}{\pi} \int_0^{+\infty} J_0(\omega)\omega d\omega$$

$$\Omega_1^2 \to \frac{2}{\pi D_0^2} \int_0^{+\infty} J_0(\omega)\omega^3 d\omega$$

..and the procedure can be indefinitely iterated
without knowing the eigenfrequencies at each step

Effective modes

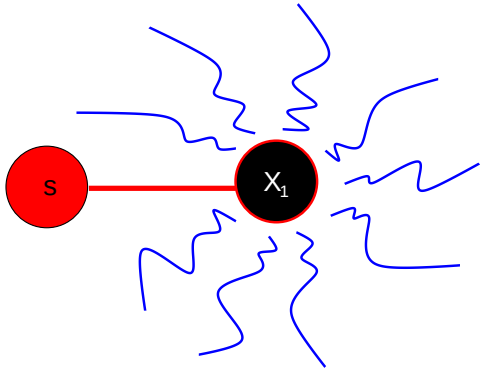
$$H = \left(\frac{p^2}{2M} + V(s)\right) + \Delta V(s) - D_0 s X_1 - \sum_{n=1}^{\infty} D_n X_n X_{n+1} + \sum_{n=1}^{\infty}\left(\frac{P_n^2}{2} + \frac{\Omega_n^2 X_n^2}{2}\right)$$



- How to obtain $J_{n+1}(\omega)$ from $J_n(\omega)$?
- What is the limiting spectral density?

A recursive relation

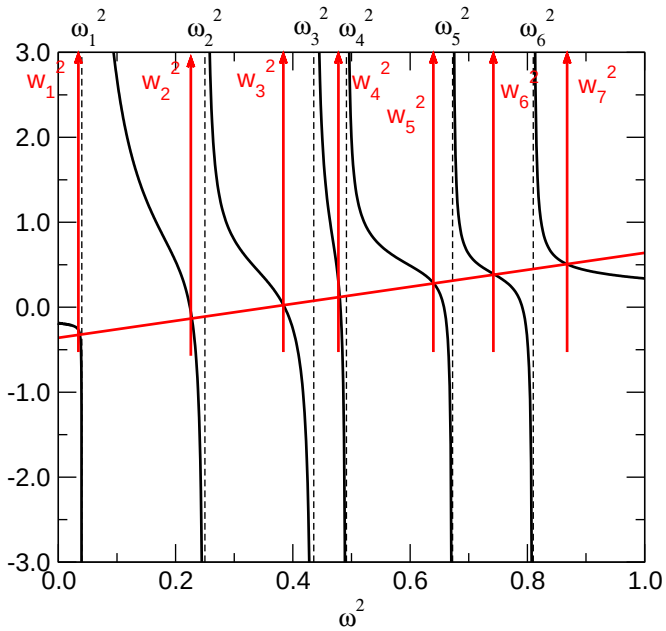
$$H = \left(\frac{p^2}{2M} + V(s)\right) + \Delta V(s) - D_0 s X_1 + \left(\frac{P_1^2}{2} + \frac{\Omega_1^2 X_1^2}{2}\right) - X_1 \sum_{k=2}^{N} C_k X_k + \\ + \sum_{k=2}^{N} \left(\frac{P_k^2}{2} + \frac{\bar{\Omega}_k^2 X_k^2}{2}\right)$$



We can use the Leggett's trick[1] to obtain $J_0(\omega)$ from $J_1(\omega)$

[1] A.J. Leggett, *Phys. Rev. B* **30**, 1208 (1984); A. Garg, J.N. Onuchic and V. Ambegaokar, *J. Chem. Phys.* **83**, 4491 (1985); K.H. Hughes, C.D. Christ, and I. Burghardt, *J. Chem. Phys.* **131**, 024109 (2009); *ibid.* 131, 124108 (2009)

A recursive relation



$$\omega_1^2 \leq \bar{\Omega}_2^2 \leq \omega_2^2 \leq \bar{\Omega}_3^2 \ldots \bar{\Omega}_N^2 \leq \omega_N^2$$

$$J_0(\omega) = \lim_{\epsilon\to 0} \operatorname{Im} W_0(\omega + i\epsilon)$$

$$W_0(z) = \frac{D_0^2}{\Omega_1^2 - z^2 - W_1(z)}$$

where

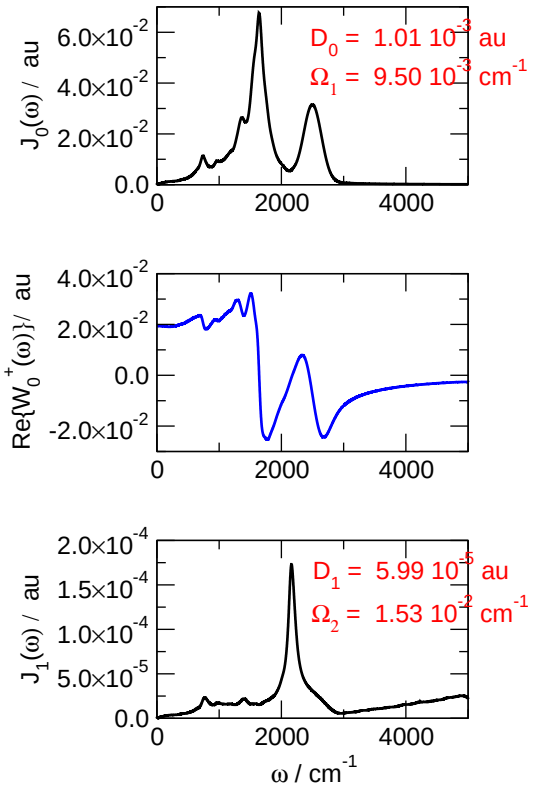
$$W_1(z) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{J_1(\omega)}{\omega - z} d\omega$$

$$(J_1(\omega) = \lim_{\epsilon\to 0} \operatorname{Im} W_1(\omega + i\epsilon))$$

$W_0(z)$ analytic in $\mathbb{C}^{\pm}$, $W_0(z) \sim z^{-2}$ as $z \to \infty$

$$\Rightarrow W_0(z) \equiv \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{J_0(\omega)}{\omega - z} d\omega$$

A recursive relation



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

$$\Omega_{n+1}^2 = \frac{2}{\pi D_n^2}\int_0^{+\infty} J_n(\omega)\omega^3 d\omega$$

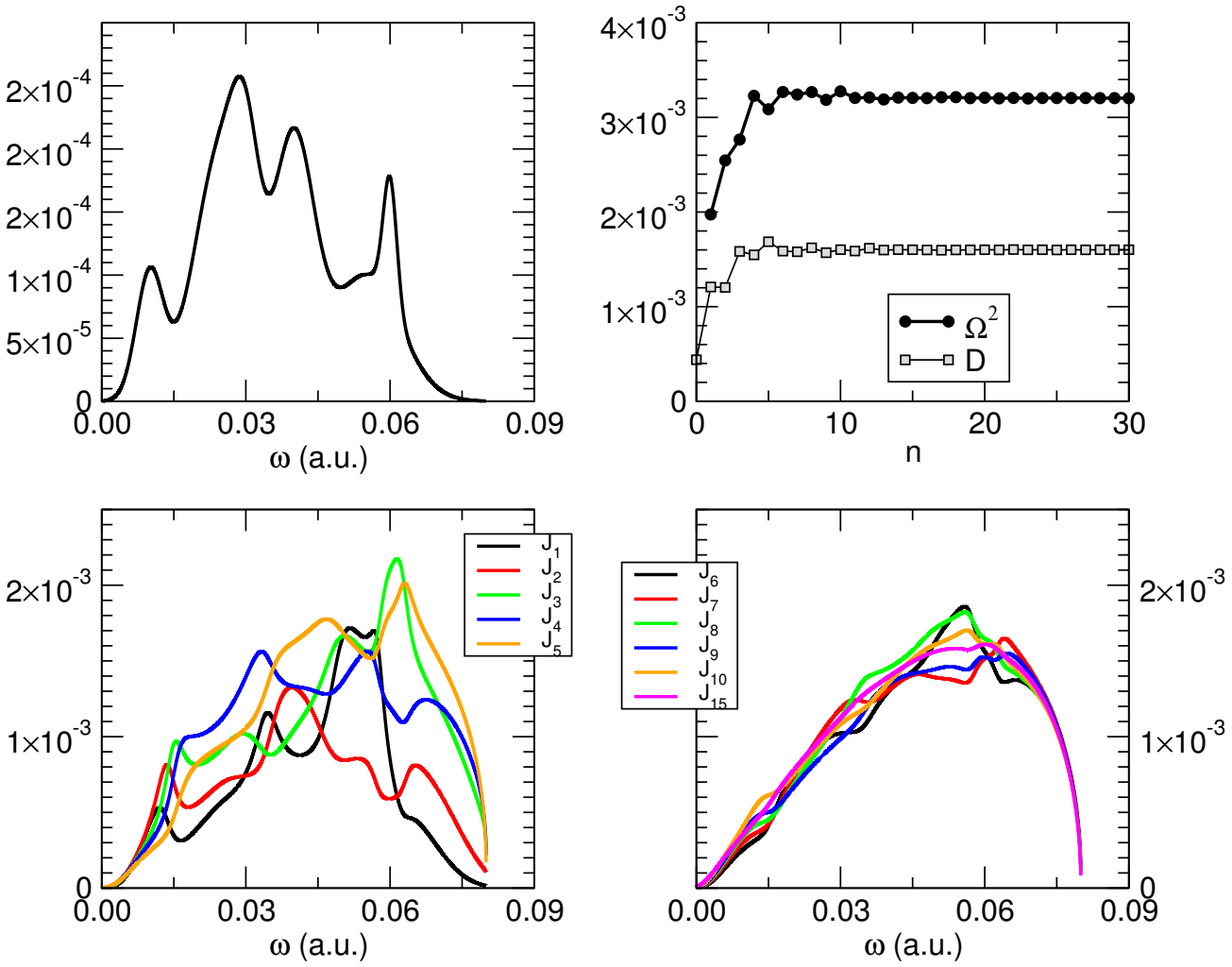
$$W_n(z) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{J_n(\omega)}{\omega - z} d\omega$$

$$W_{n+1}(z) = \Omega_{n+1}^2 - z^2 - \frac{D_n^2}{W_n(z)}$$

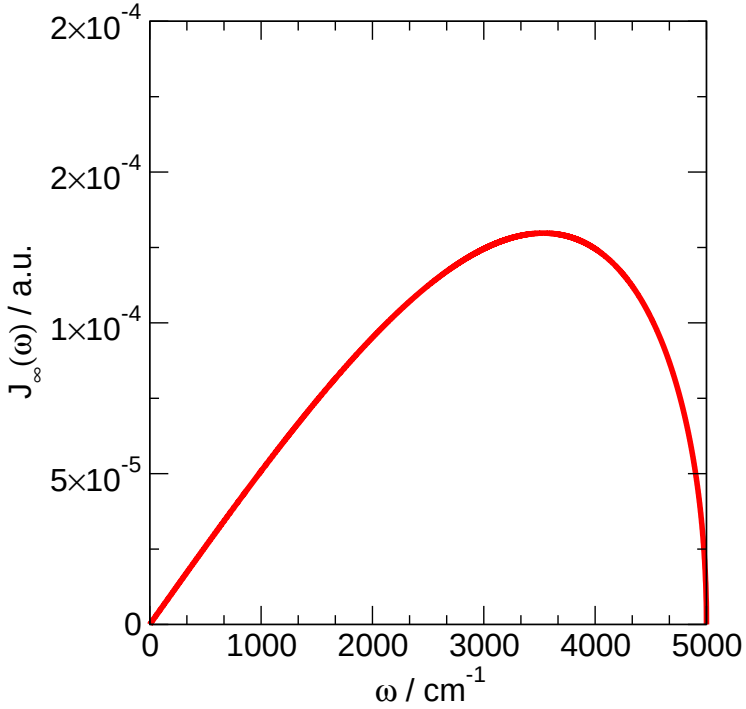
$$J_{n+1}(\omega) = \lim_{\epsilon\to 0} \mathrm{Im}\, W_{n+1}(\omega + i\epsilon)$$

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

A recursive relation



Limiting behaviour



Provided $D_n, \Omega_n \to D, \Omega$
the limiting chain is uniform

$$W_\infty(z) = \Omega^2 - z^2 - \frac{D^2}{W_\infty(z)}$$

i.e. if $J_0(\omega) > 0$ in $(0, +\omega_c)$ one gets the Rubin SD

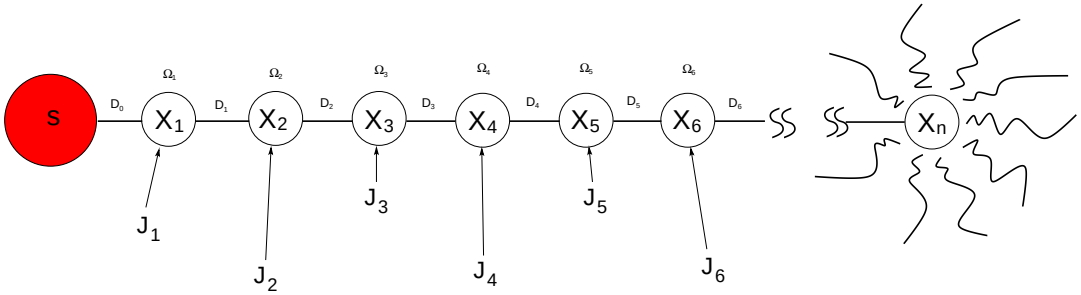
$$J_\infty(\omega) = \frac{\omega\omega_c}{2}\sqrt{1 - \frac{\omega^2}{\omega_c^2}}\Theta(\omega_c - \omega)$$

where $\Omega^2 = 2D = \frac{\omega_c^2}{2}$ and the chain is translationally invariant

(Quasi)-Ohmic behaviour

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

Short-time behaviour



$$J_{n+1}(\omega) \Rightarrow J_n(\omega), \cdots \Rightarrow J_0(\omega)$$

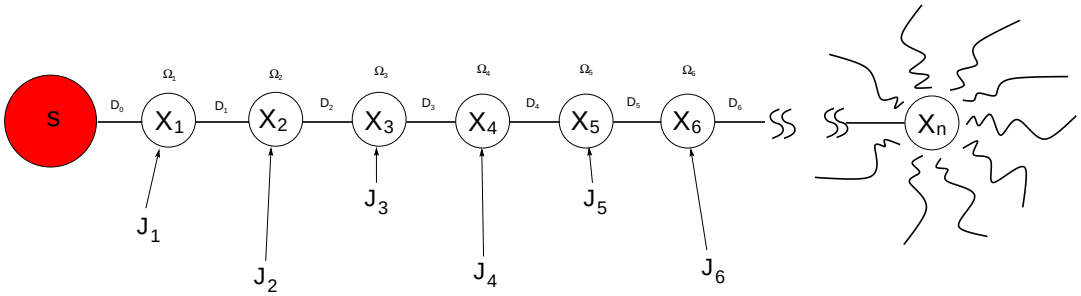
K.H. Hughes, C.D. Christ, and I. Burghardt, *J. Chem. Phys.* **131**, 024109 (2009); *ibid.* 131, 124108 (2009)

$$W_0(z) = \cfrac{D_0^2}{\Omega_1^2 - z^2 - \cfrac{D_1^2}{\Omega_2^2 - z^2 - \cfrac{D_2^2}{\Omega_3^2 - z^2 - W_4(z)}}}$$

What if **truncating** or **closing** the chain after introducing n modes?

$$W_{n+1} \to .. \Rightarrow W_0(z) \to W_0(z) + \delta W_0(z)$$

Short-time behaviour



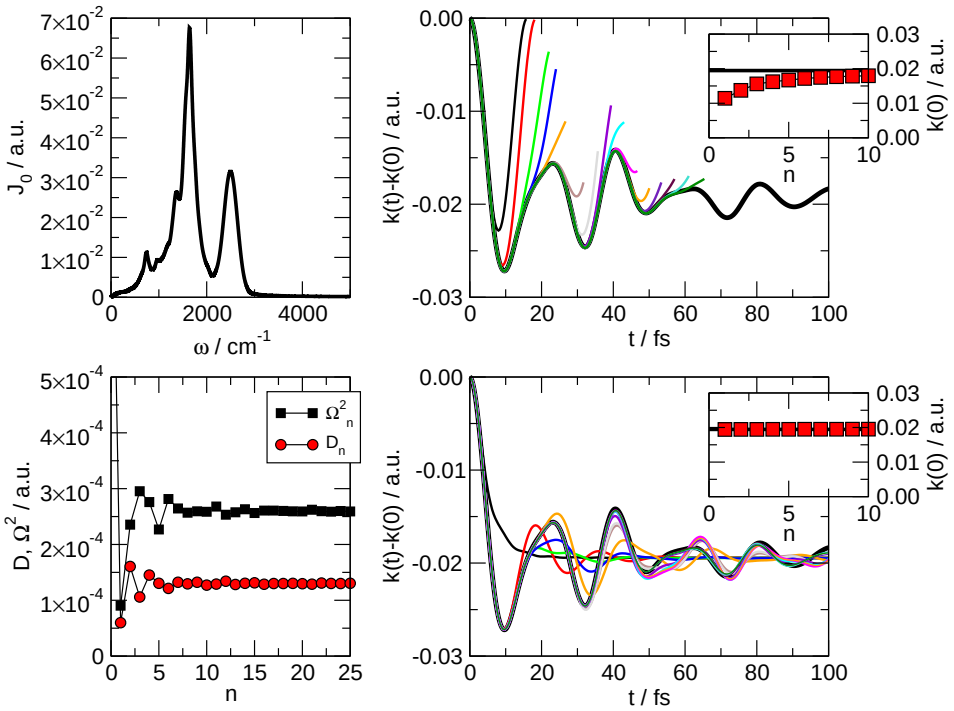
For $z \to \infty$ where $W_n(z) \to 0$, 'errors' propagate as

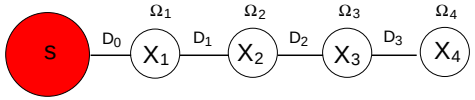
$$\delta W_{n-1}(z) \approx D_{n-1}^2 \left(\frac{1}{z}\right)^4 \delta W_n(z)$$

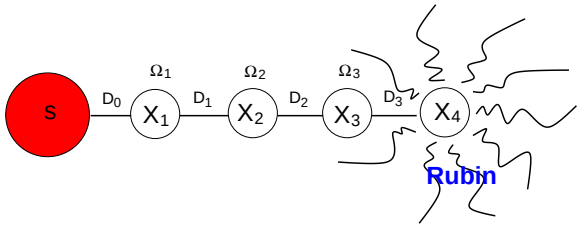
i.e. with n modes $W_0(z) = a_2 \left(\frac{1}{z}\right)^2 + a_4 \left(\frac{1}{z}\right)^4 + ..$ is correct up to the $4n$-th order

Short-time behaviour

$$\kappa(t) - \kappa(0) = \kappa_n(t) - \kappa_n(0) + \mathcal{O}(t^{4n})$$



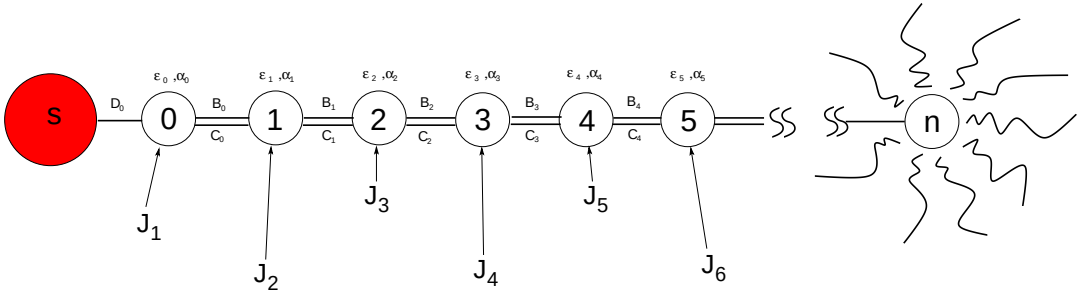




R. Martinazzo, K.H. Hughes and I. Burghardt, *Phys. Rev. E* **84**, 030102(R) (2011)

General linear chain transformations

$$
\begin{aligned}
H &= H_s + D_0 s \left(b_0 + b_0^\dagger\right) + \sum_{n=0}^{\infty} \epsilon_n b_n^\dagger b_n + \sum_{n=0}^{\infty} A_n \left(b_n^\dagger b_n^\dagger + b_n b_n\right) + \\
&\quad + \sum_{n=0}^{\infty} B_n \left(b_n^\dagger b_{n+1}^\dagger + b_n b_{n+1}\right) + \sum_{n=0}^{\infty} C_n \left(b_n^\dagger b_{n+1} + b_n b_{n+1}^\dagger\right)
\end{aligned}
$$



J. Prior, A. W. Chin, S. F. Huelga and M. B. Plenio, *Phys. Rev. Lett* **105**, 050404 (2010)
A. W. Chin, A. Rivas, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **51**, 092109 (2010)
M. P. Woods, R. Groux, A. W. Chin, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **55**, 032101 (2014)

General linear chain transformations

Stieltjies transform

$$J_0(\omega) \Rightarrow \mu_0 \qquad S_0(z) = \int \frac{d\mu_0(x)}{z-x}$$

- connection to moment problems, orthogonal polynomials, Padé approximants
- secondary measures and continued fractions

M. P. Woods, R. Groux, A. W. Chin, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **55**, 032101 (2014)

General linear chain transformations

$$S_0(z) = d_0 \frac{\rho_{n+1}(z) - \rho_n(z) S_{n+1}(z)}{\pi_{n+1}(z) - \pi_n(z) S_{n+1}(z)}$$

- for $n = 0, 1, ..$ $\bar{d}_n = d_n$ $\bar{\omega}_{n+1} = \omega_{n+1}$
- explicit expression for $S_n(z)$ ($J_n(\omega)$) in terms of $S_0(z)$ ($J_0(\omega)$)

Note:

- $T_{n+1}(z) = \rho_{n+1}(z)/\pi_{n+1}(z)$ corresponds to a truncated chain with $n+1$ modes and exactly gives the first $2(n+1)$ moments of $d\mu_0$
- spectral densities with gaps can also be mapped into two or more chains

M. P. Woods, R. Groux, A. W. Chin, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **55**, 032101 (2014)

Outline

Quantum dynamics with MCTDH

$$\Psi(x_1, x_2, .., x_N) = \sum_{i_1,i_2,\ldots i_N} c_{i_1,i_2,\ldots i_N}\, \phi_{i_1}^{(1)}(x_1)\phi_{i_2}^{(2)}(x_2)\ldots\phi_{i_N}^{(N)}(x_N)$$

- $c_{i_1,i_2,\ldots i_N} = c_{i_1,i_2,\ldots i_N}(t)$ are time-evolving amplitudes for the configurations
- $\phi_i^{(k)}(x) = \phi_i^{(k)}(x,t)$ are time-evolving single-particle functions
- $\langle \phi_i^{(k)} | \phi_j^{(k)} \rangle = \delta_{ij}$ for any $k = 1, ..N$

Equations of motion from DF variational principle

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

A simple MCTDH *ansatz*

System + Primary + Secondary modes

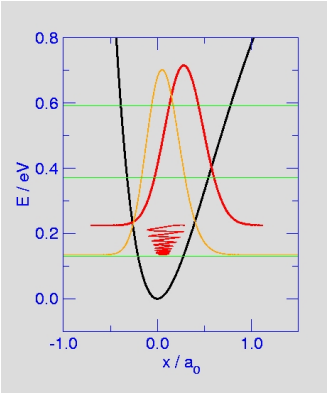
$$\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \sum_{IJ} c_{IJ}\, \phi_{i_1}(x_1) .. \phi_{j_1}(y_1) .. \psi_1(z_1)\psi_2(z_2) .. \psi_N(z_N)$$

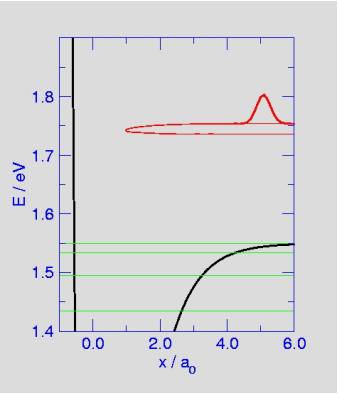
- Linear scaling
- Accuracy depends on the primary modes only
- Recurrence times can be enormously increased
- Effective-mode based variants for G-MCTDH[1], LCSA[2], etc. are possible

[1] I. Burghardt *et al.*, *J. Chem. Phys.* **111** 29727 (1999)
[1] R. Martinazzo *et al.*, *J. Chem. Phys.* **125** 194102 (2006)

Model systems

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



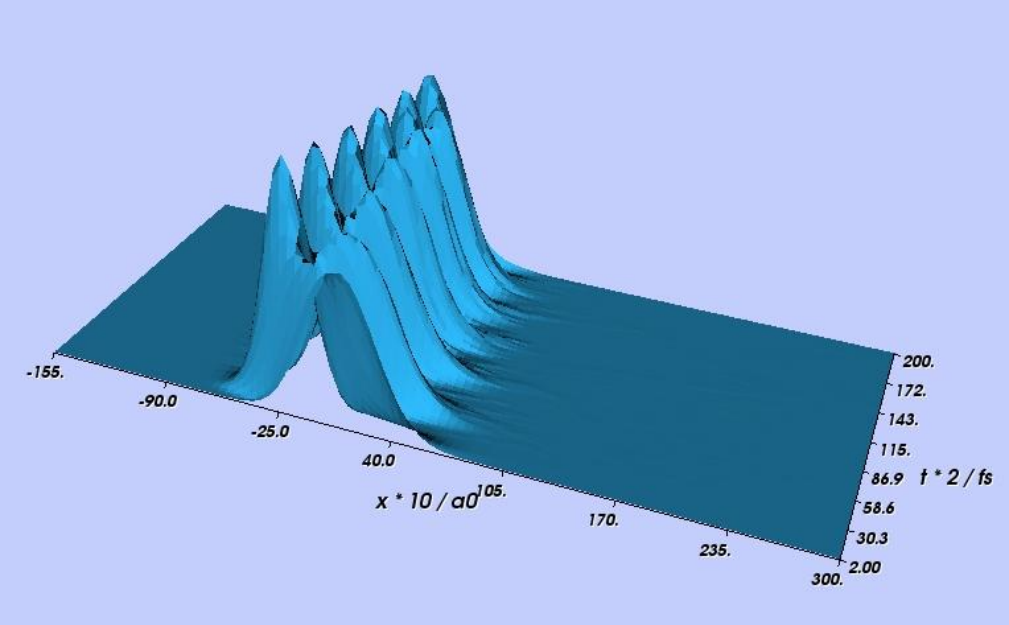


- $f(s) = \frac{1-e^{-\alpha s}}{\alpha} \to s$ for $s \to 0$
- $V(s) = D_e e^{-\alpha s}(e^{-\alpha s} - 2)$, with $D_e = 1.55eV$
- $M = m_H$
- Several $J(\omega)$s

Model systems

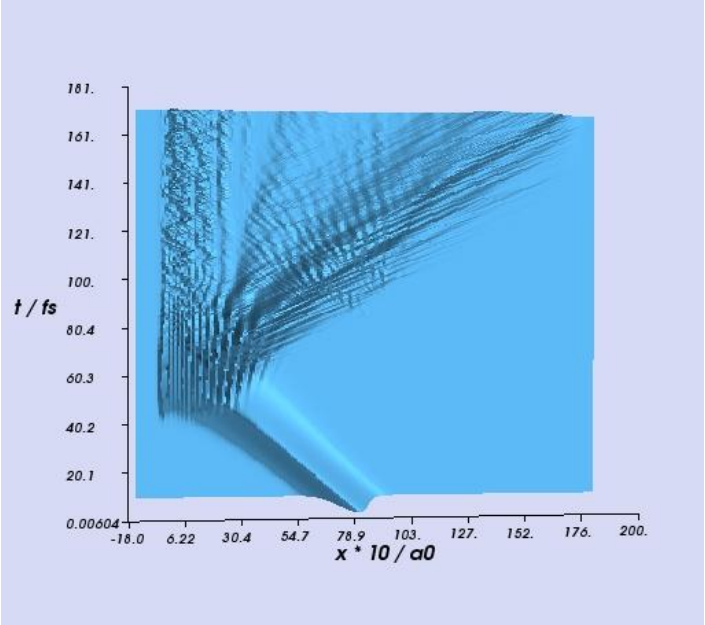
Vibrational relaxation

$\rho_t(s|s)$

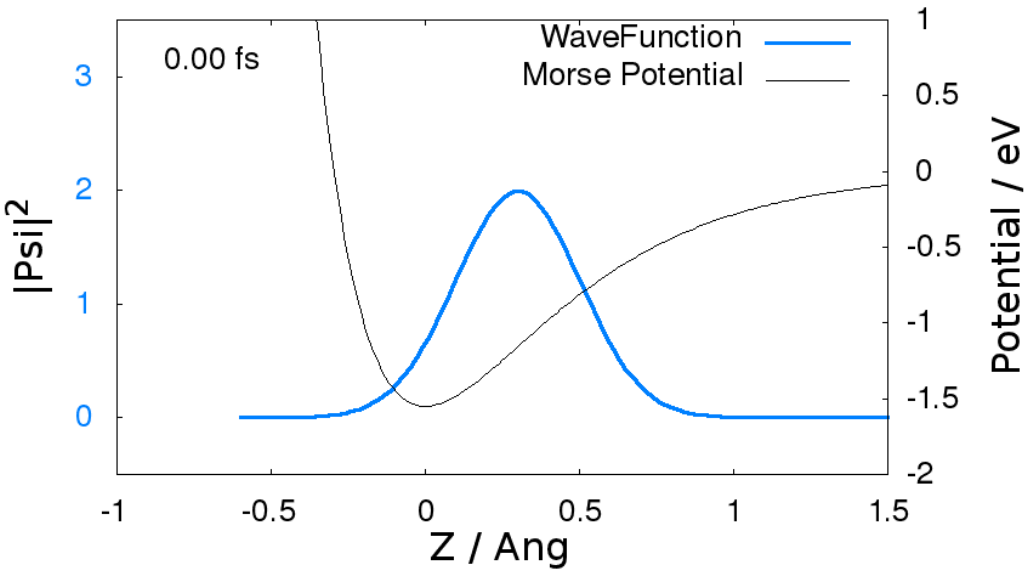


Sticking

$\rho_t(s|s)$

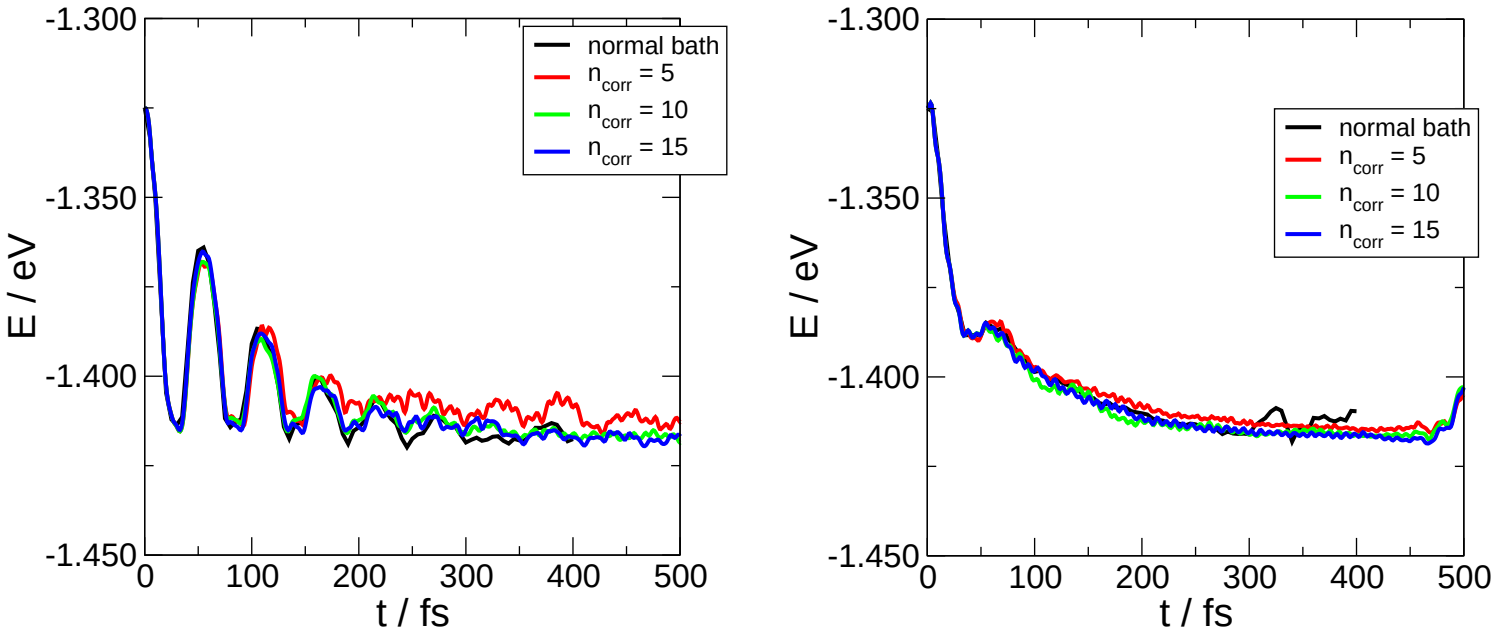


Chain dynamics: an example



A simple MCTDH *ansatz*: vib relax

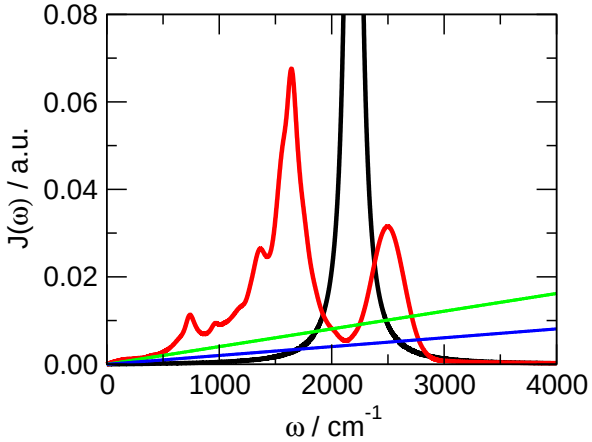
Non-Markovian SDs, $N = 100$

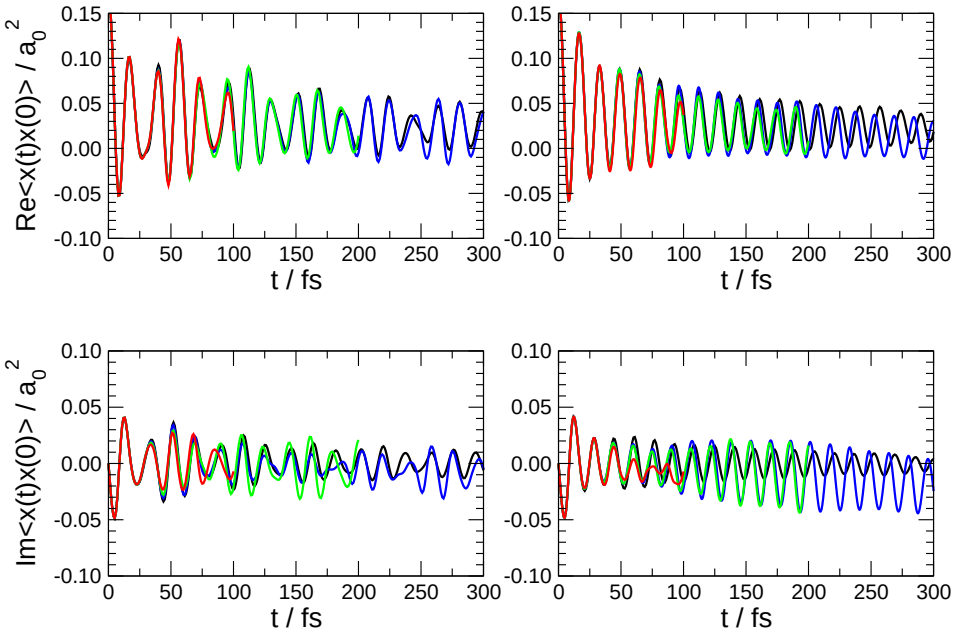


M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 **116** (2012)

A simple MCTDH *ansatz*: vib relax

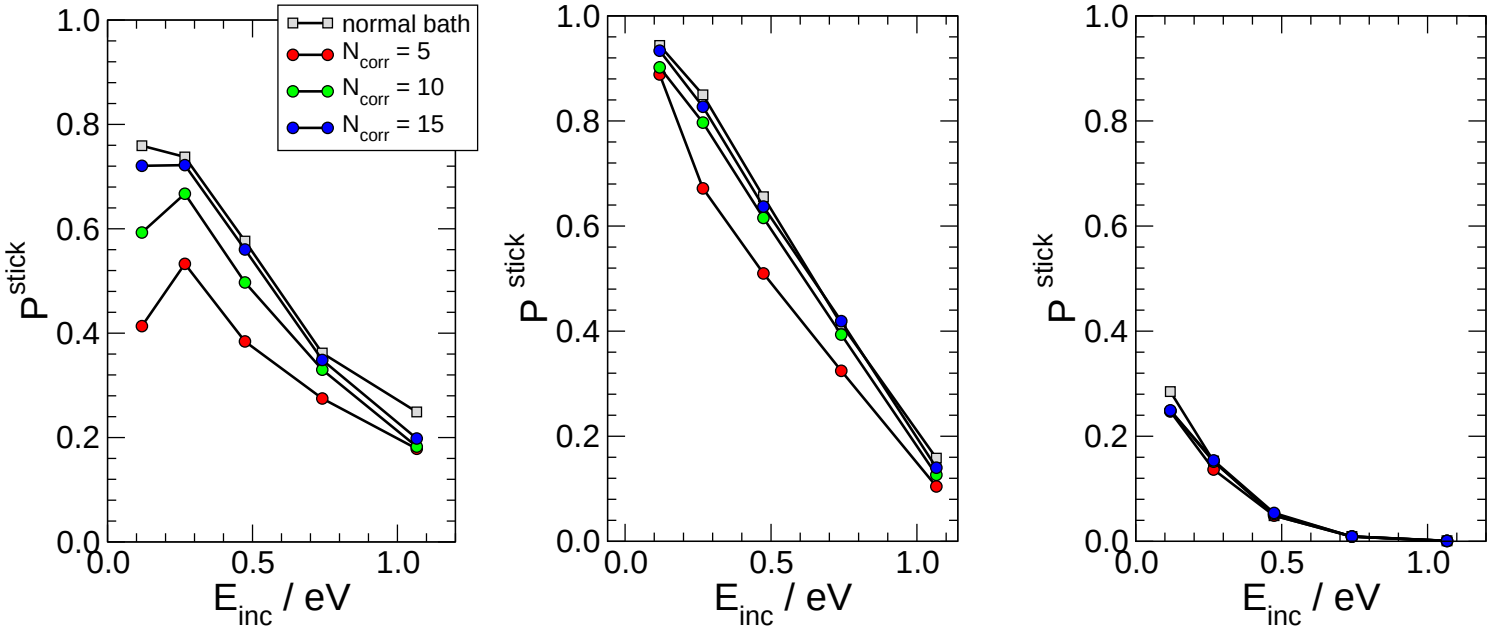
Non-Markovian SDs, $N = 100$





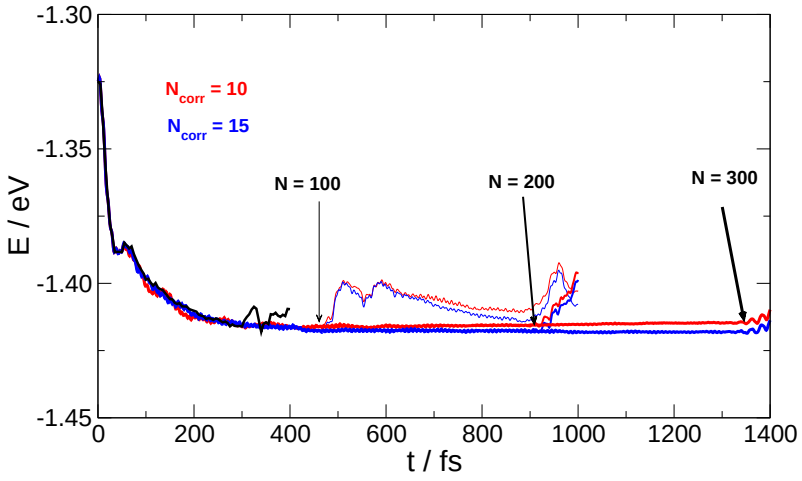
M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 **116** (2012)

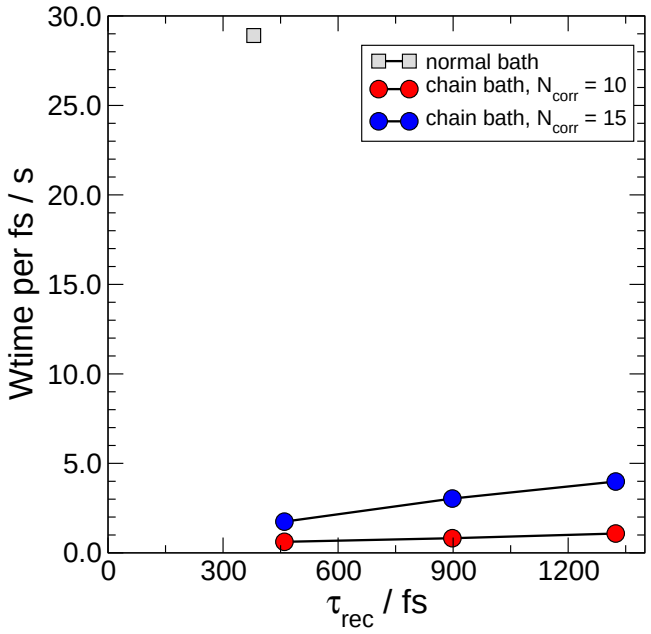
A simple MCTDH *ansatz*: sticking



M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 **116** (2012)

A simple MCTDH *ansatz*: timings

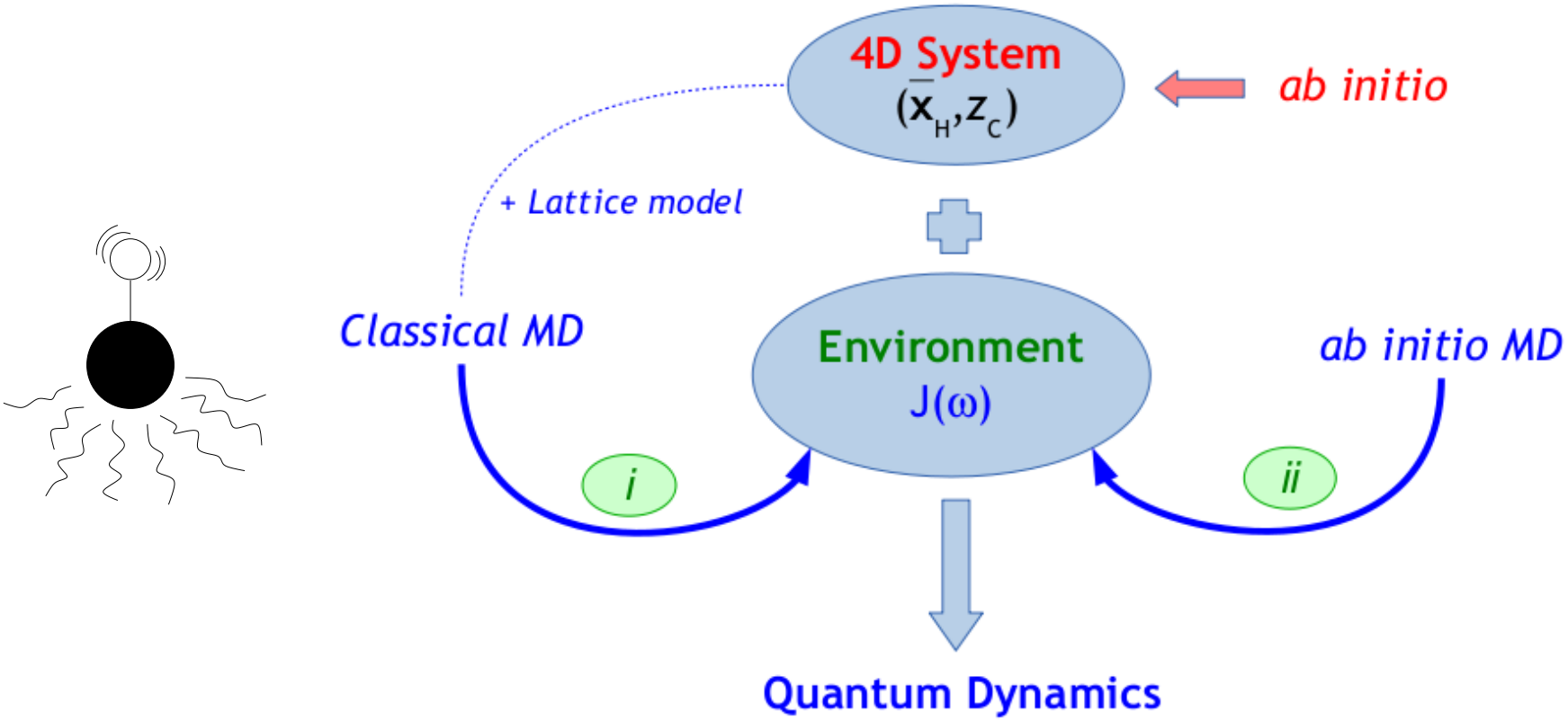




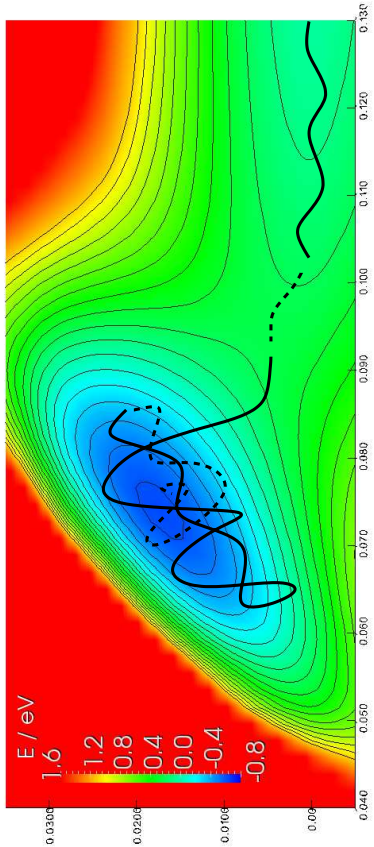
M. Bonfanti, G.F. Tantardini, K.H. Hughes, R. Martinazzo and I. Burghardt, *J. Phys. Chem. A*, 11406 **116** (2012)

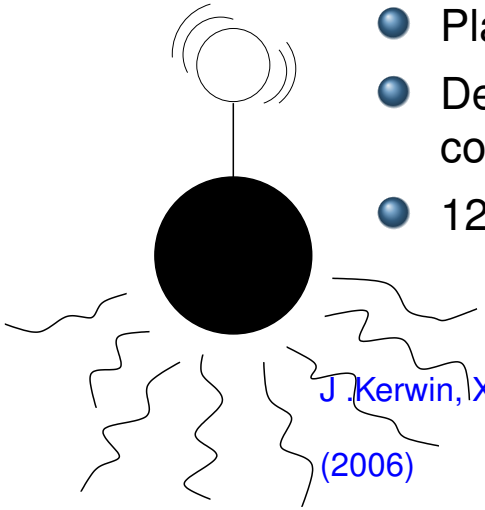
Outline

System-bath modeling



System-bath modeling





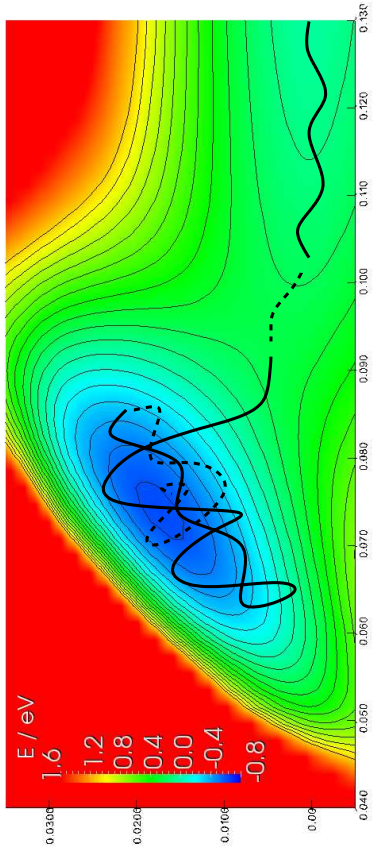
System

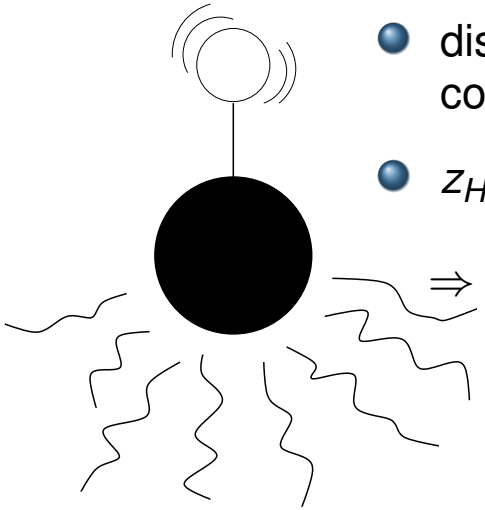
$$H_{sys} = \frac{\boldsymbol{p}_H^2}{2m_H} + \frac{p_C^2}{2m_C} + V(\boldsymbol{x}_H, z_C, \boldsymbol{q}^{eq})$$

- 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

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

System-bath modeling





Environment

H → C → lattice

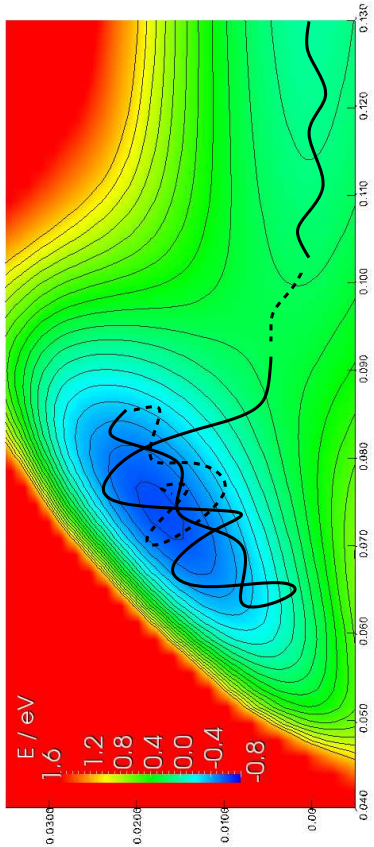
- dissipation mainly occurs at near-equilibrium configurations
- z_H couples only to z_C

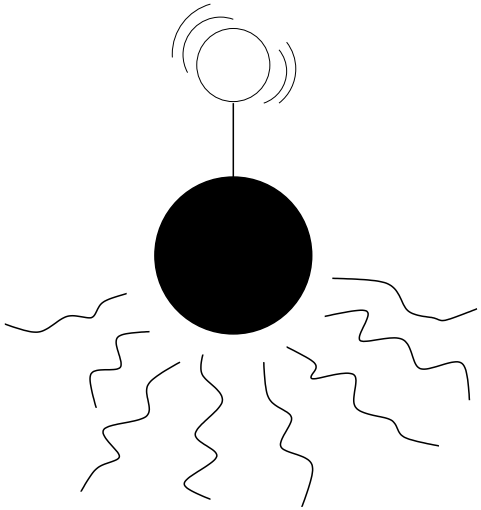
$\Rightarrow$ Canonical, classical dynamics: $\delta z_H^i(t)$

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

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

System-bath modeling





Environment

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

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

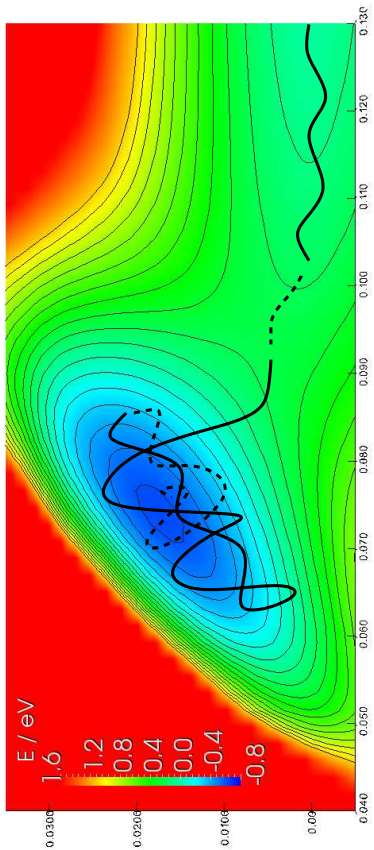
$$\sigma(\omega) = \tilde{C}(\omega)\omega/2$$

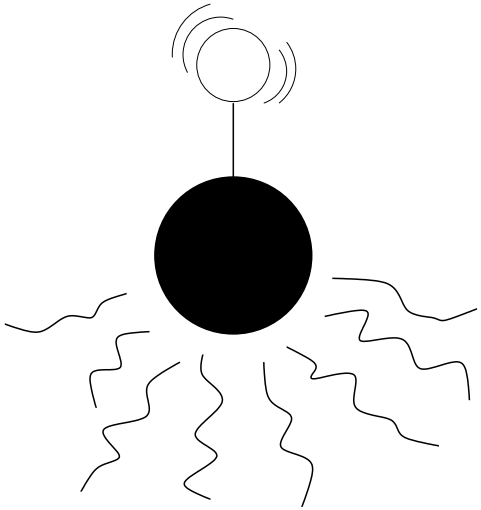
$$J_H(\omega) = k_B T \frac{\sigma(\omega)}{|S^+(\omega)|^2}$$

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

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

System-bath modeling



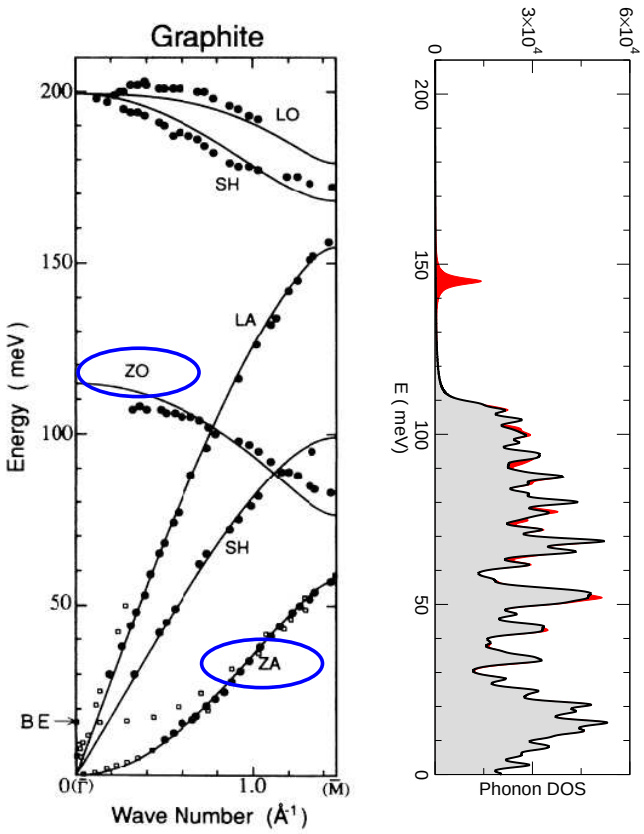


System-bath

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

$$\omega_k, c_k \Leftrightarrow J_C(\omega)$$

Environment (i)



Lattice

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

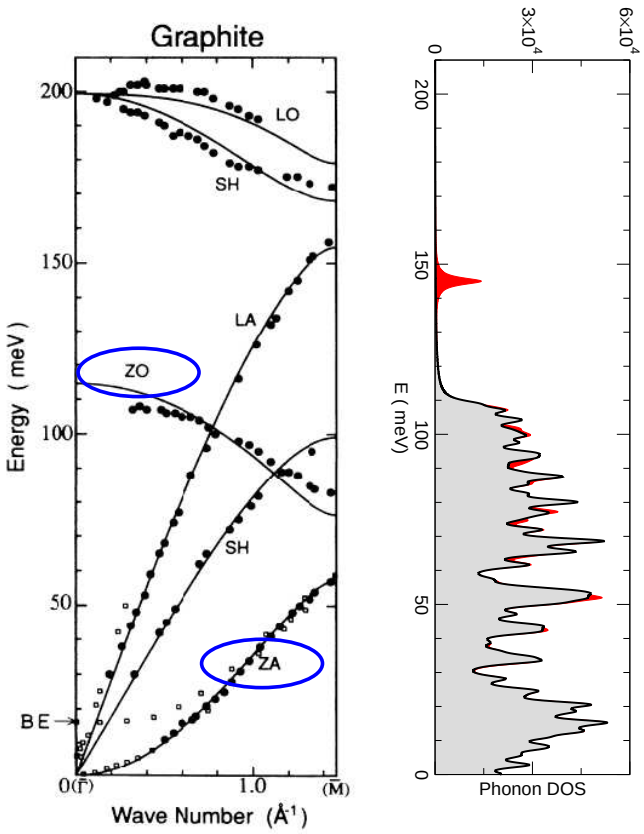
- Lattice model to graphene containing stretching, bending, twisting modes
- ZA, ZO branches only

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

Coupling

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

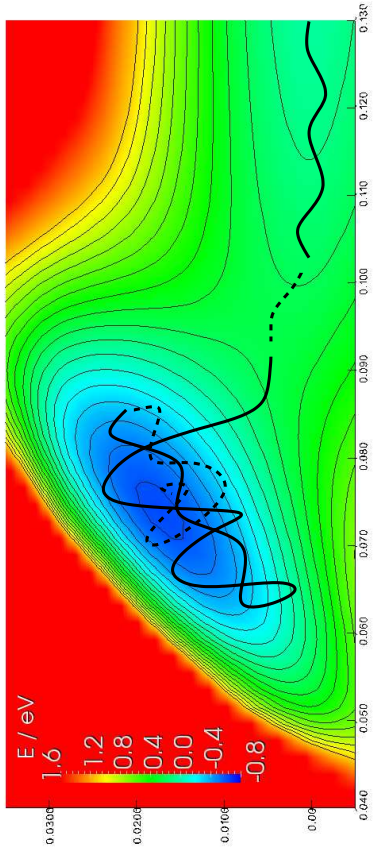
Environment (i)

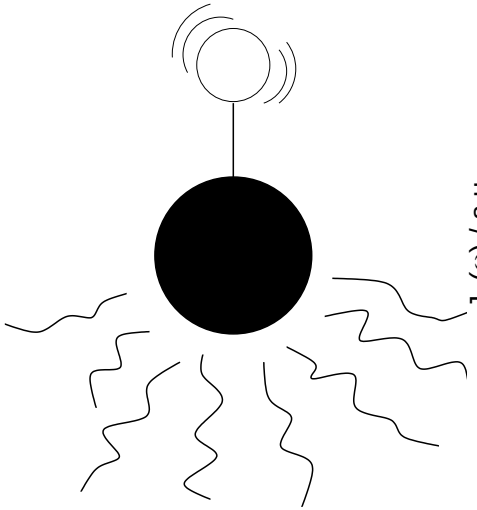


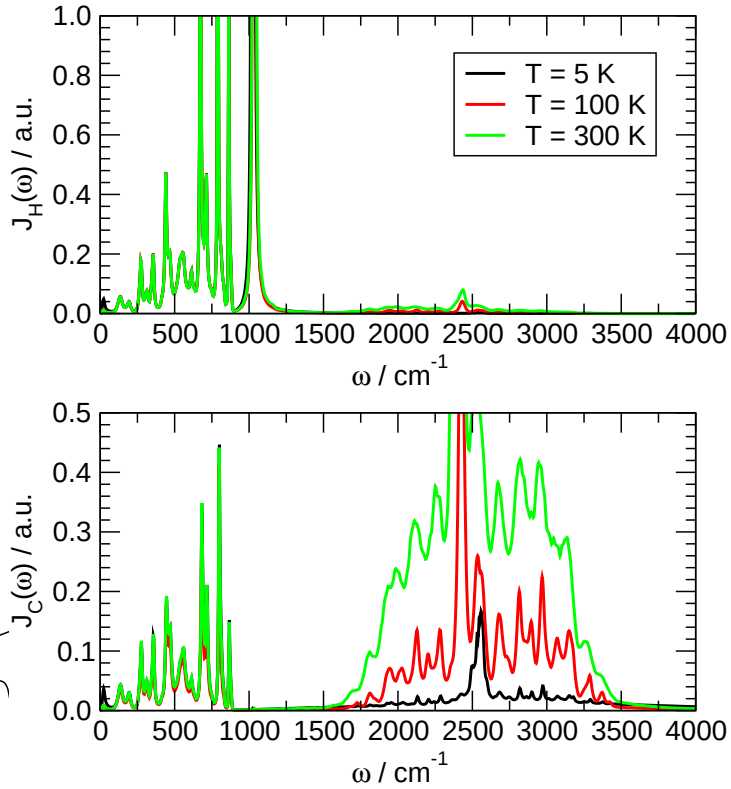
Canonical MD

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

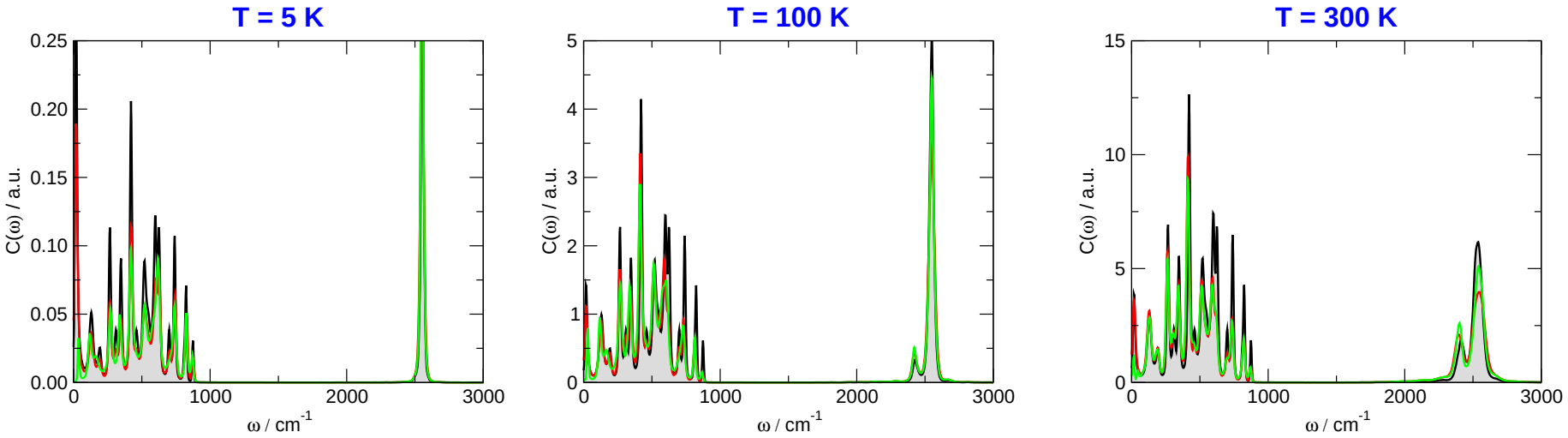
Environment (i)





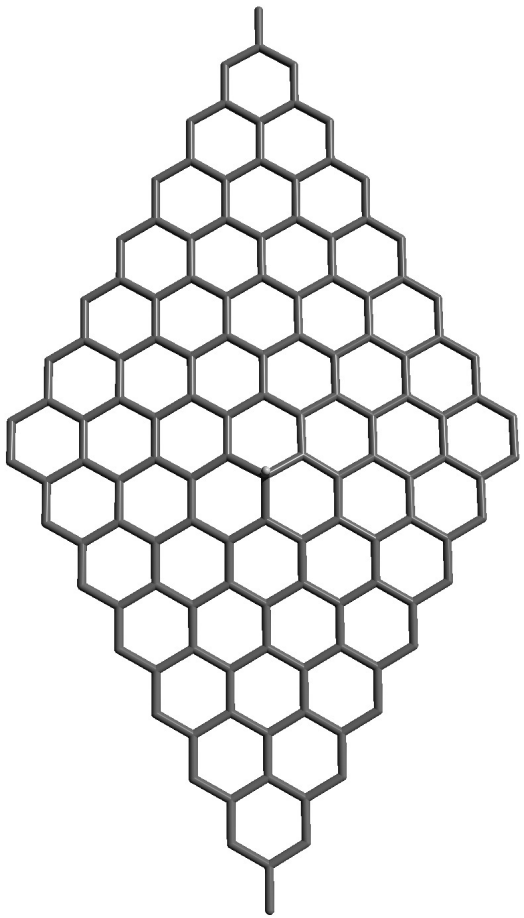


Environment (i)



Lattice - Normal Bath - Linear Chain

Environment (ii)

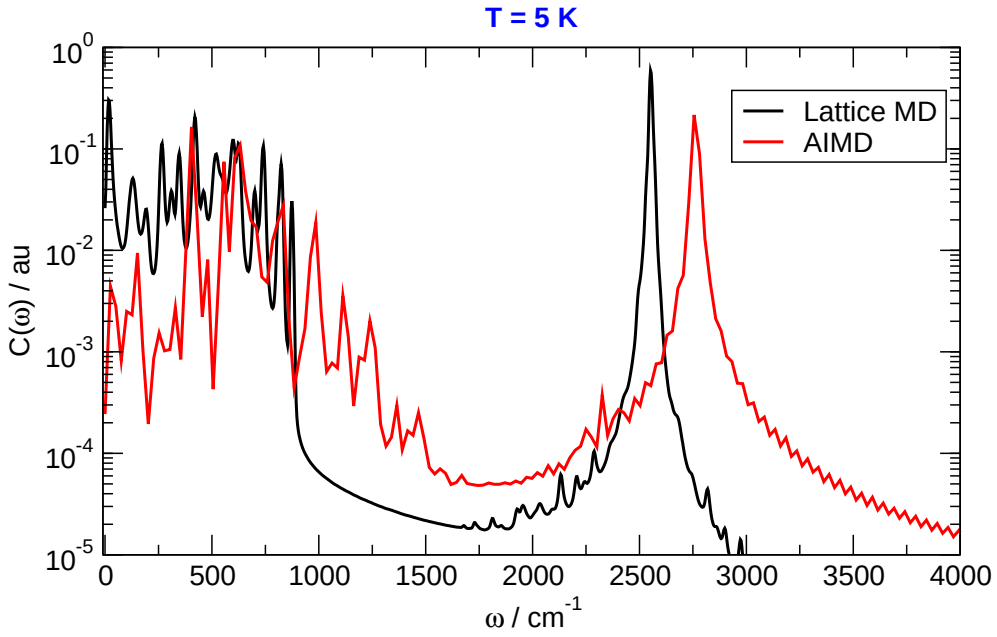


Canonical *ab initio* MD

- 8×8 supercell (129 atoms)
- Atomic Orbital DFT PBE, Double-ζ *plus* Polarization
- Equilibration at several T (velocity rescaling)
- 128 trajectories in *NEV*
- $t_{fin} = 1.3$ ps

...(so far)

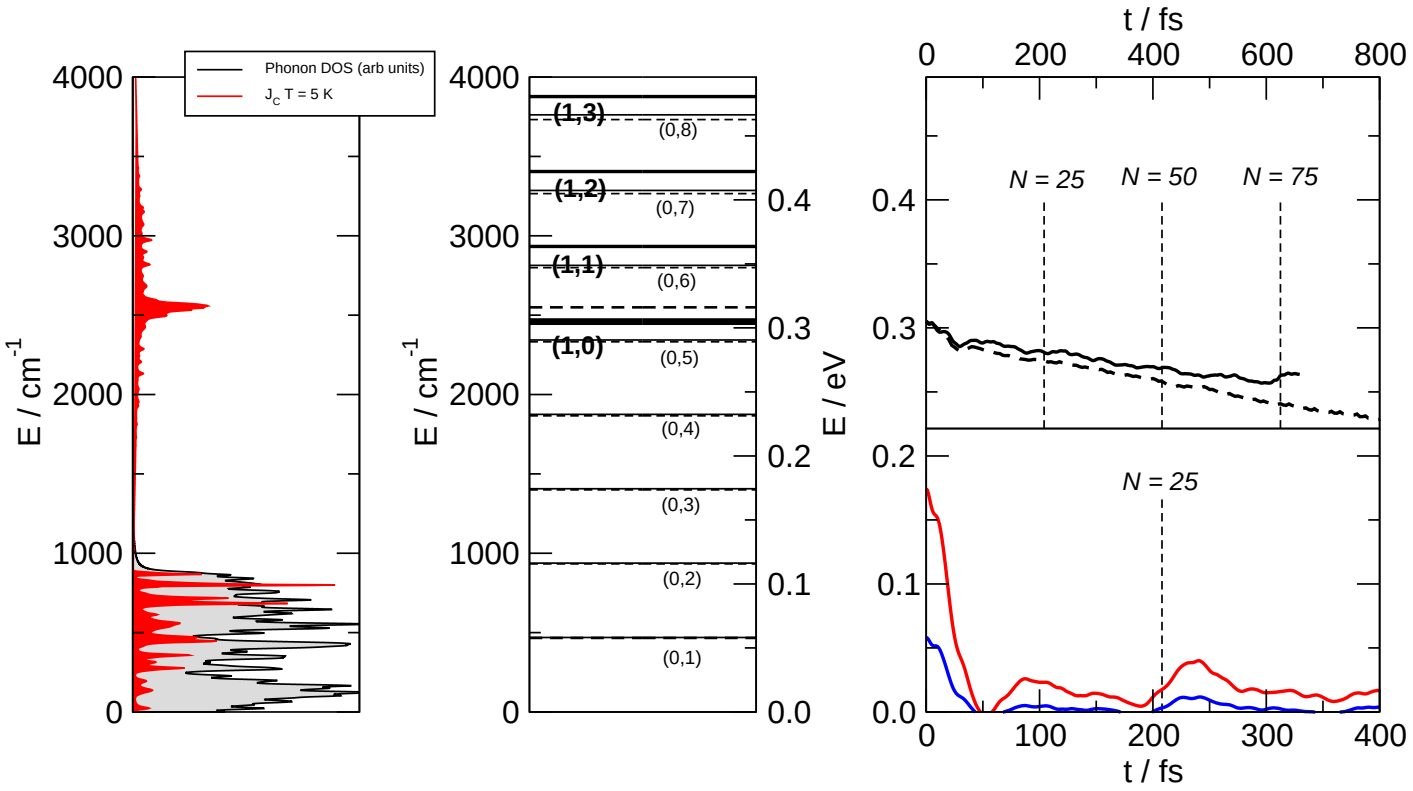
Environment (ii)



..

- ZA-ZO modes are sufficient
- coupling to the lattice is reasonable
- system potential has to be revised

Vibrational relaxation (2D)



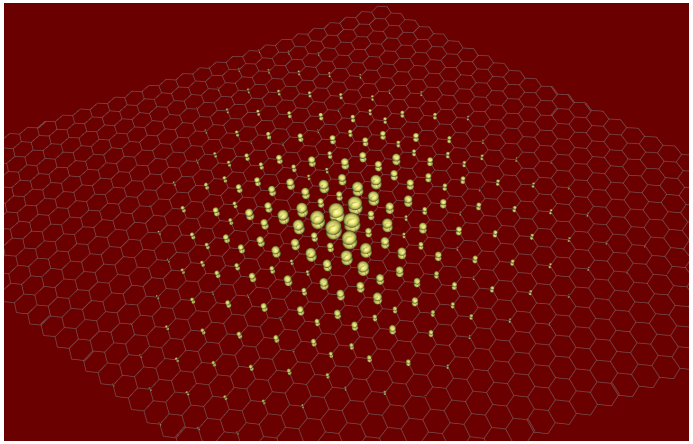
Summary

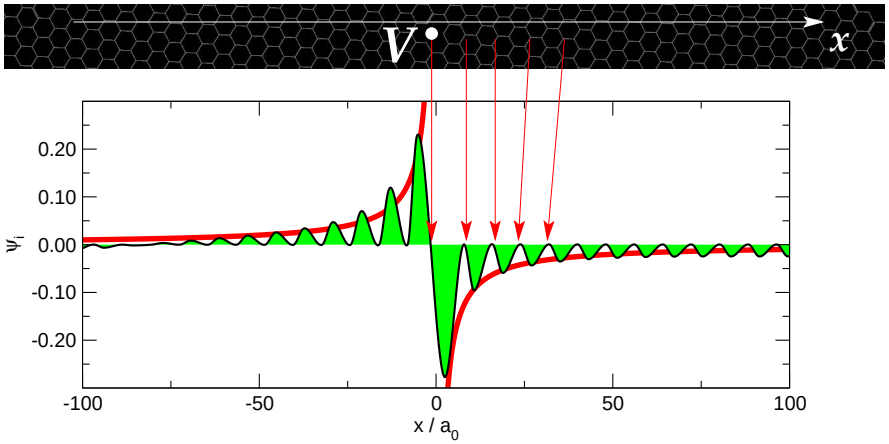
- The IO model can be handled with high-dimensional quantum methods
- Effective modes considerably enlarge the range of applicability of quantum IO models
- Classical mechanics can be used to build a quantum IO model
- No need to build a potential: (equilibrium) AIMD can be used to obtain the necessary correlation functions

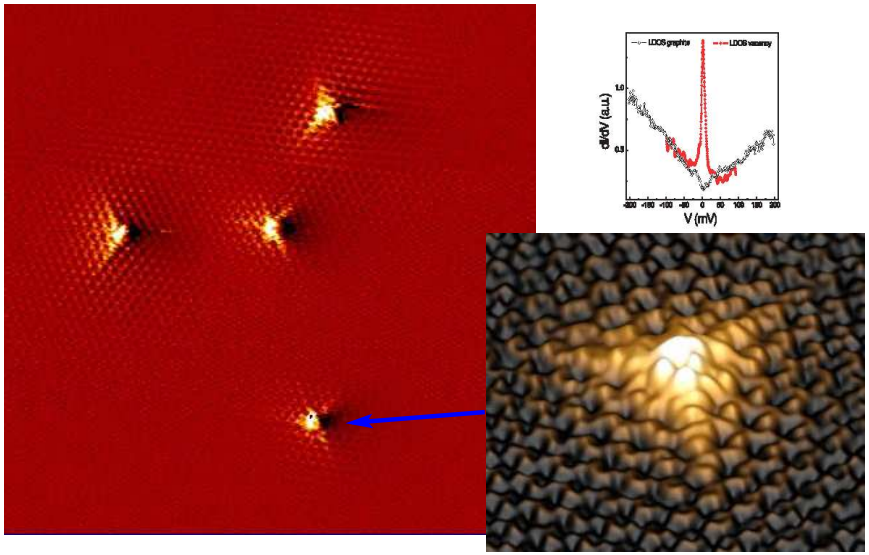
Acknowledgements

Thank you for your attention!

Midgap states: p_z vacancies







M.M. Ugeda *et al.*, *Phys. Rev. Lett.* **104**, 096804 (2010)

$$\psi(x, y, z) \sim 1/r$$

V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006); *Phys. Rev. B* **77**, 115109 (2008)

GLE: positivity

$$\mathrm{Re}\tilde{\gamma}(\omega) \geq 0$$

f external force, $u = \langle v \rangle$ average velocity

$$M\dot{u}(t) + M\int_{-\infty}^{\infty} \gamma(t-t')u(t')dt' = f(t)$$

$\dot{W} = u(t)f(t)$: power of the force f

$$W = \int_{-\infty}^{\infty} u(t)^{\dagger} f(t)dt = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{u}(\omega)^{\dagger}\tilde{f}(\omega)d\omega$$

Second Law of Thermodynamics: $W \geq 0$

$$\Downarrow$$

$$W = \frac{M}{2\pi}\int_{-\infty}^{\infty} \tilde{u}(\omega)^{\dagger}\mathrm{Re}\tilde{\gamma}(\omega)\tilde{u}(\omega)d\omega \geq 0$$

GLE: causality

$$\gamma(t) = 0 \text{ for } t < 0$$

$$\tilde{\gamma}(\omega) \equiv \int_0^{\infty} \gamma(t) e^{i\omega t} dt$$

$\omega \to z$ in the upper half complex plane ($\mathrm{Im} z > 0$)

$\Downarrow$

General Kramers-Kronig relation

$$\tilde{\gamma}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\mathrm{Im}\tilde{\gamma}(\omega)}{\omega - z} d\omega = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\mathrm{Re}\tilde{\gamma}(\omega)}{\omega - z} d\omega$$

GLE: Fluctuation-Dissipation

$$I(\omega) = 2Mk_BT\mathrm{Re}\tilde{\gamma}(\omega)$$

$$I(\omega) = \int_{-\infty}^{+\infty} \langle \xi(t)\xi(0) \rangle \, e^{i\omega t} dt$$

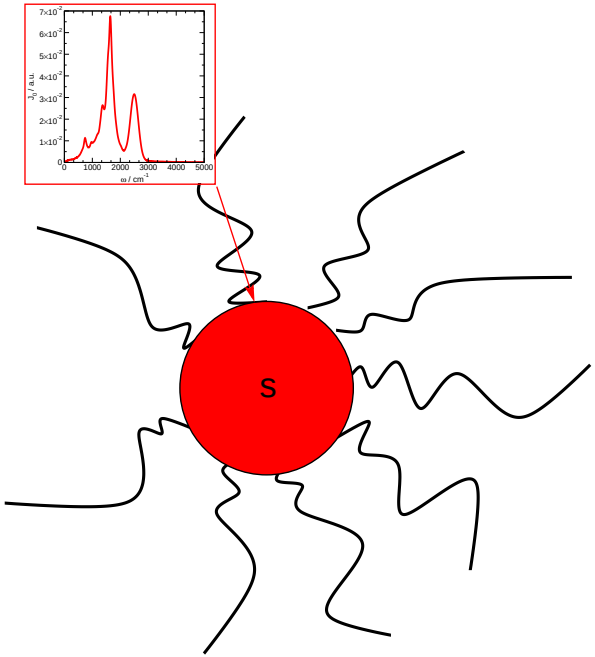
For a free particle ($V' \equiv 0$) in a stationary state (i.e. $t \to \infty$)

$$C(t) = \langle v(t)v(0) \rangle = \frac{1}{2\pi M^2} \int_{-\infty}^{+\infty} \frac{I(\omega)}{|-i\omega + \tilde{\gamma}(\omega)|^2} e^{-i\omega t} d\omega$$

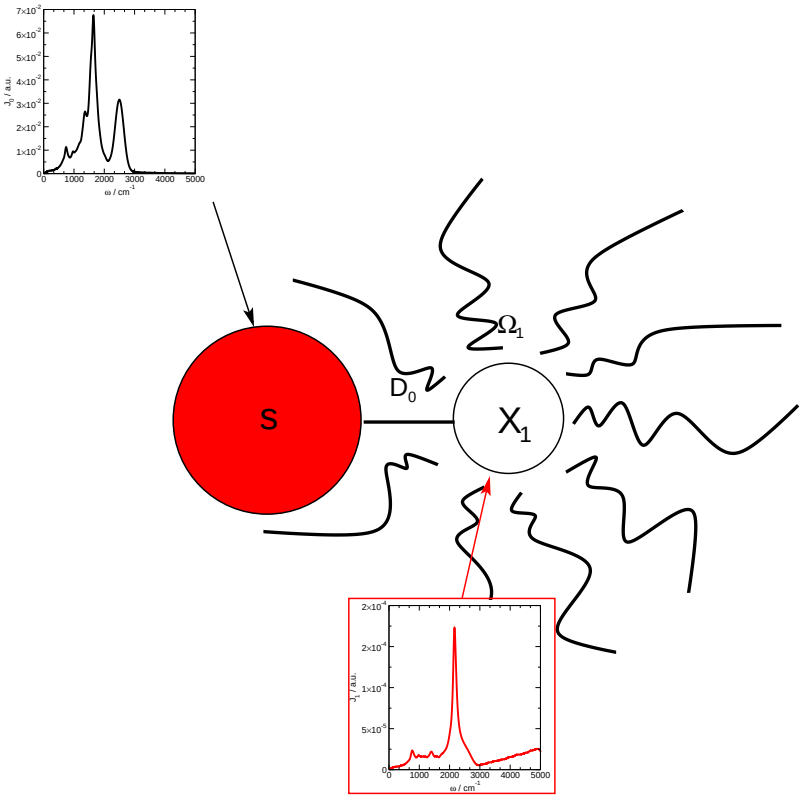
Equipartition Law: $C(0) \equiv \frac{k_BT}{M}$

*

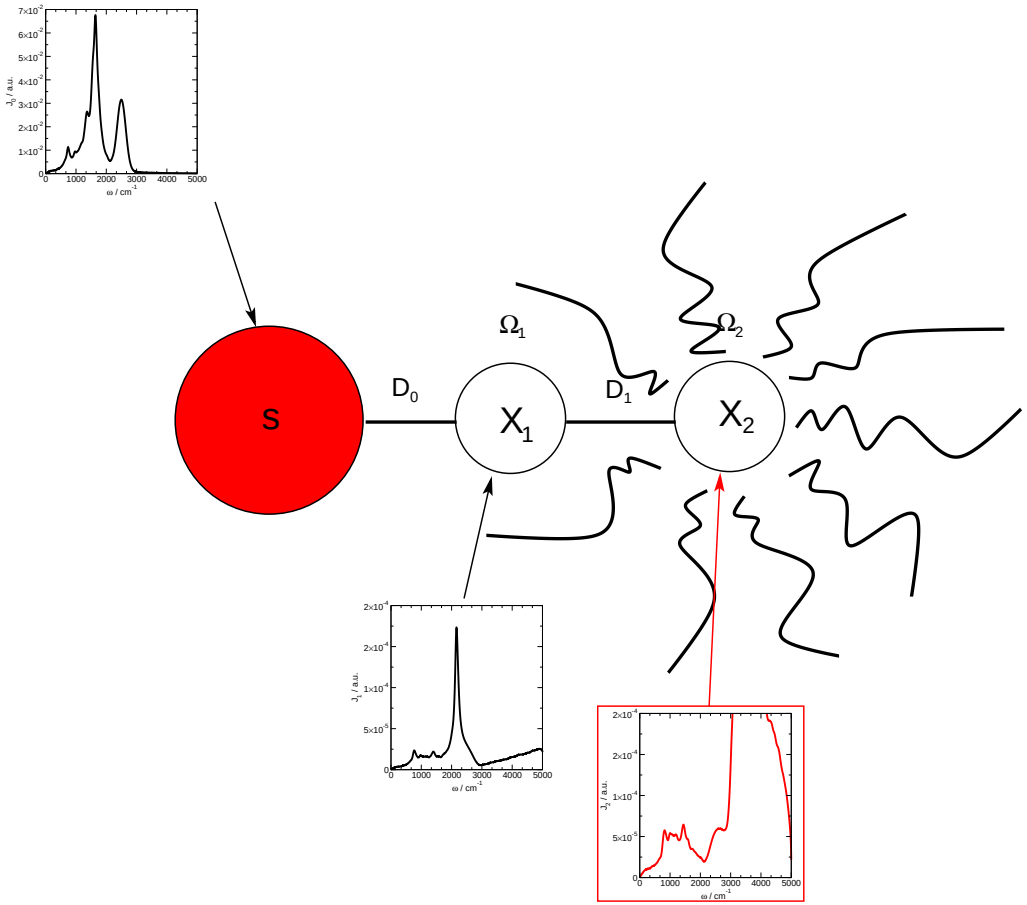
A recursive relation



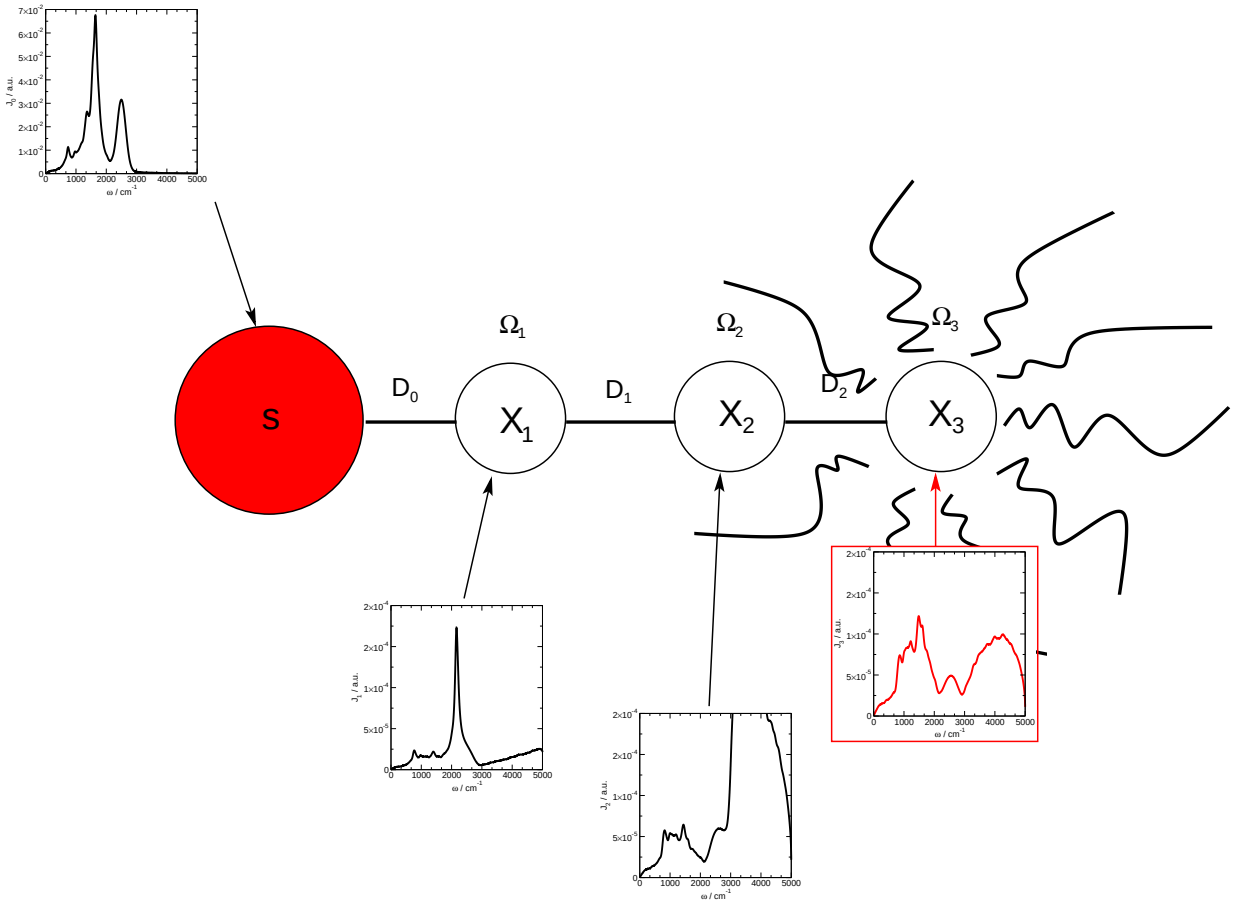
A recursive relation



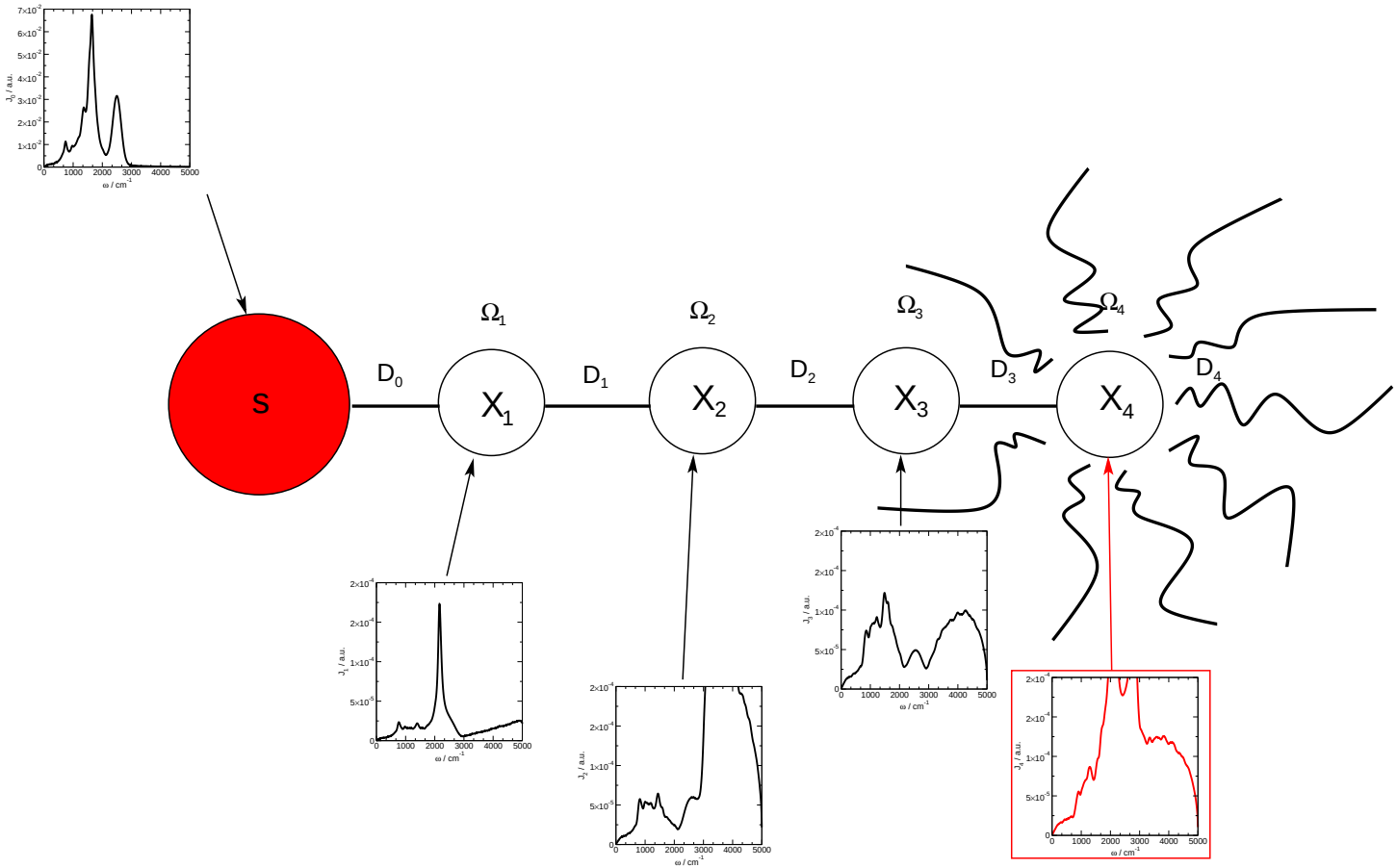
A recursive relation



A recursive relation



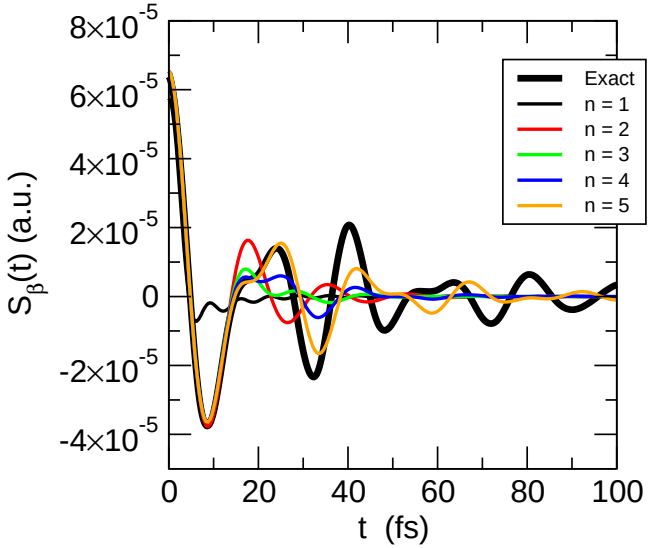
A recursive relation



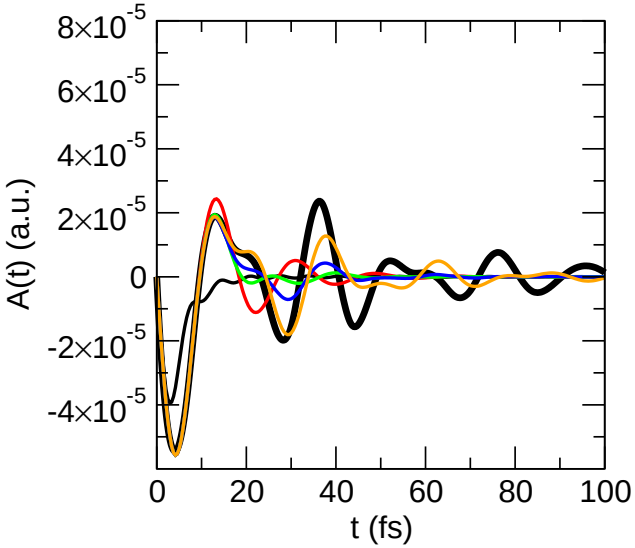
Short-time behaviour

$$\kappa(t) - \kappa(0) = \kappa_n(t) - \kappa_n(0) + \mathcal{O}(t^{4n})$$

$S_\beta(t) = \mathrm{Re}\,\langle \xi(t)\xi(0)\rangle$



$A(t) = \mathrm{Im}\,\langle \xi(t)\xi(0)\rangle$



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

General linear chain transformations

Moment problems and orthogonal polynomials

$$S_0(z) = d_0 \frac{\rho_{n+1}(z)}{\pi_{n+1}(z)} + \mathcal{O}\left(\frac{1}{z^{2n+3}}\right)$$

$$d_0 = \int d\mu_0 \quad d_n = \frac{(\pi_n|\pi_n)}{(\pi_{n-1}|\pi_{n-1})} \quad \omega_{n+1} = \frac{(\pi_n|x\pi_n)}{(\pi_n|\pi_n)}$$

$$\pi_{n+1}(z) = (z - \omega_{n+1})\pi_n(z) - d_n \pi_{n-1}(z)$$

$$\rho_n(z) = \int \frac{\pi_n(z) - \pi_n(x)}{z - x} d\mu_0(x)$$

M. P. Woods, R. Groux, A. W. Chin, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **55**, 032101 (2014)

General linear chain transformations

Sequence of secondary measures

$$\bar{d}_n = \int d\mu_n \quad \bar{\omega}_{n+1} = \frac{1}{\bar{d}_n} \int x d\mu_n$$

$$S_{n+1}(z) = z - \bar{\omega}_{n+1} - \frac{\bar{d}_n}{S_n(z)}$$

$$\bar{\mu}_{n+1}(x) = -\frac{1}{\pi} \mathrm{Im} S^+_{n+1}(x) \quad d\mu_{n+1}(x) = \bar{\mu}_{n+1}(x) dx$$

$$S_0(z) = \frac{\bar{d}_0}{z - \bar{\omega}_1 -} \frac{\bar{d}_1}{z - \bar{\omega}_2 -} .. \frac{\bar{d}_n}{z - \bar{\omega}_{n+1} - S_{n+1}(z)} \equiv d_0 \frac{u_{n+1}(z) - u_n(z) S_{n+1}(z)}{v_{n+1}(z) - v_n(z) S_{n+1}(z)}$$

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M. P. Woods, R. Groux, A. W. Chin, S. F. Huelga and M. B. Plenio, *J. Math. Phys.* **55**, 032101 (2014)

System-bath

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

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