Langevin approach to non-adiabatic molecular dynamics

Jing Tao Lü[1], Mads Brandbyge[1], Per Hedegård[2]

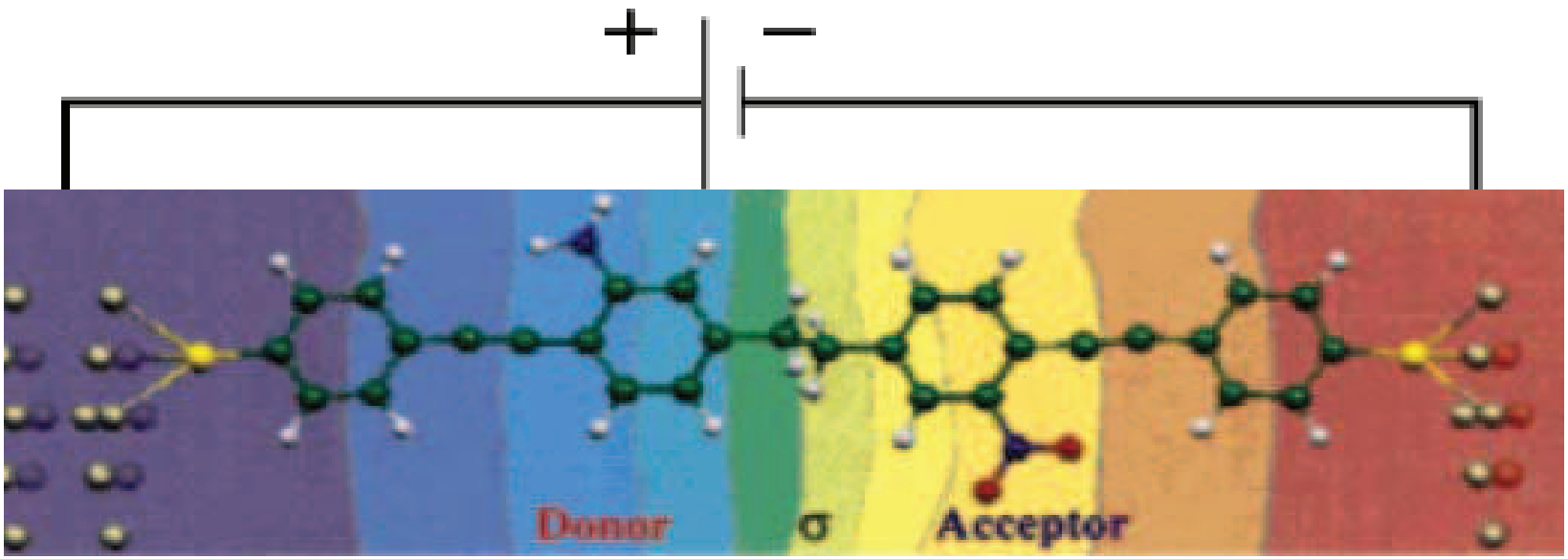
1. Department of Micro- and Nanotechnology, Technical University of Denmark
2. Niels Bohr institute, University of Copenhagen

Joint ICTP-IAEA Workshop on
Non-adiabatic Dynamics and Radiation Damage in Nuclear Materials,
Trieste, Italy

Outline

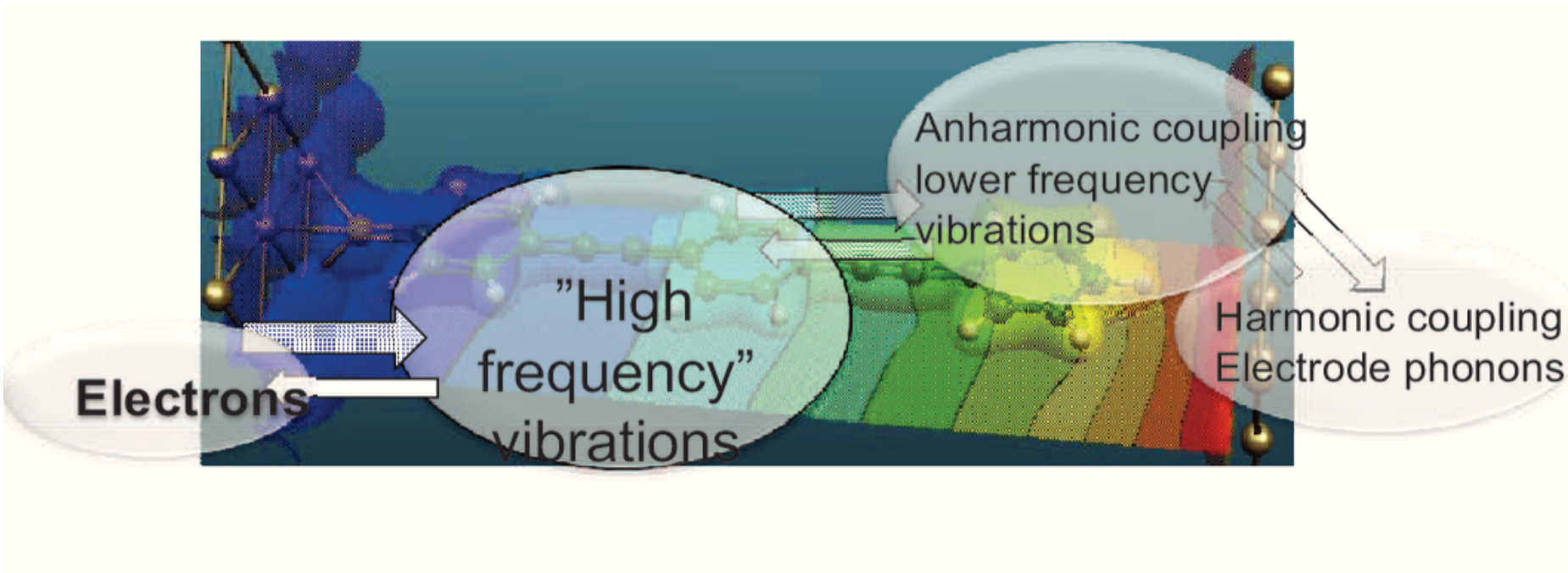
Outline

Molecular electronics



Seminal paper in molecular electronics
"Molecular Rectifiers" , A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277

Joule heating, Current-induced forces



Molecular dynamics in the presence of current!

Adiabatic (Born-Oppenheimer) dynamics

Hamiltonian for a system of electrons and ions:

$$\hat{H} = \hat{T}_e + \hat{T}_{ph} + V_e(\hat{r}) + V_{eph}(\hat{r}, \hat{R}) + V_{ph}(\hat{R})$$

Born-Oppenheimer approximation:

$$\hat{H}_{BO} = \hat{H} - \hat{T}_{ph}$$

Adiabatic (Born-Oppenheimer) dynamics

Electrons only see static ions:

$$\hat{H}_{BO}(R,r)\Phi_i(R,r) = \varepsilon_i(R)\Phi_i(R,r)$$

Forces to the ions:

$$m\ddot{R} = -\langle\Phi_0|\nabla_R\hat{H}_{BO}(R,r)|\Phi_0\rangle$$

Adiabatic (Born-Oppenheimer) dynamics

Electrons only see static ions:

$$\hat{H}_{BO}(R,r)\Phi_i(R,r) = \varepsilon_i(R)\Phi_i(R,r)$$

Forces to the ions:

$$m\ddot{R} = -\langle\Phi_0|\nabla_R\hat{H}_{BO}(R,r)|\Phi_0\rangle$$

No energy transfer between electron and phonon subsystems!

Ehrenfest dynamics

Time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{H}_{BO}(R(t), r)\Psi(t)$$

Force to the ions:

$$m\ddot{R} = -\langle\Psi(t)|\nabla_R\hat{H}_{BO}(R(t), r)|\Psi(t)\rangle$$

Ehrenfest dynamics

Time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{H}_{BO}(R(t), r)\Psi(t)$$

Force to the ions:

$$m\ddot{R} = -\langle\Psi(t)|\nabla_R\hat{H}_{BO}(R(t), r)|\Psi(t)\rangle$$

Energy transfer possible,
but not good enough for Joule heating problem

Joule heating: Simple perturbation analysis

- Suppose we have one harmonic oscillator (phonon), coupling with the electronic environment. Energy transfer between electrons and the phonon mode could be modelled by a rate equation,

$$\dot{N} = \mathcal{B}(N+1) - \mathcal{A}N,$$

with N the phonon occupation number.

- At steady state,

$$\dot{N} = 0 \rightarrow N = \frac{\mathcal{B}}{\mathcal{A}-\mathcal{B}} = \frac{1}{\frac{\mathcal{A}}{\mathcal{B}}-1}.$$

- For equilibrium electrons with temperature T_e, we have

$$\frac{\mathcal{A}}{\mathcal{B}} = \exp\left[\frac{\hbar\omega}{k_B T_e}\right].$$

Joule heating: Simple perturbation analysis

- Suppose we have one harmonic oscillator (phonon), coupling with the electronic environment. Energy transfer between electrons and the phonon mode could be modelled by a rate equation,

$$\dot{N} = \mathcal{B}(N+1) - \mathcal{A}N,$$

with N the phonon occupation number.

- At steady state,

$$\dot{N} = 0 \rightarrow N = \frac{\mathcal{B}}{\mathcal{A}-\mathcal{B}} = \frac{1}{\frac{\mathcal{A}}{\mathcal{B}}-1}.$$

- For equilibrium electrons with temperature T_e, we have

$$\frac{\mathcal{A}}{\mathcal{B}} = \exp\left[\frac{\hbar\omega}{k_B T_e}\right].$$

Joule heating: Simple perturbation analysis

- Suppose we have one harmonic oscillator (phonon), coupling with the electronic environment. Energy transfer between electrons and the phonon mode could be modelled by a rate equation,

$$\dot{N} = \mathcal{B}(N+1) - \mathcal{A}N,$$

with N the phonon occupation number.

- At steady state,

$$\dot{N} = 0 \rightarrow N = \frac{\mathcal{B}}{\mathcal{A}-\mathcal{B}} = \frac{1}{\frac{\mathcal{A}}{\mathcal{B}}-1}.$$

- For equilibrium electrons with temperature T_e, we have

$$\frac{\mathcal{A}}{\mathcal{B}} = \exp\left[\frac{\hbar\omega}{k_B T_e}\right].$$

Why Ehrenfest fails?

The energy transfer predicted from Ehrenfest dynamics

$$\dot{N} = \mathcal{B}N - \mathcal{A}N < 0$$

$\rightarrow$ The phonon keeps losing energy!

E. J. McEniry, Y. Wang, D. Dundas, T. N. Todorov, L. Stella, R. P. Miranda, A. J. Fisher, A. P. Horsfield, C. P. Race, D. R. Mason, W. M.C. Foulkes and A. P. Sutton, EPJB, 77, 305 (2010)

Outline

Semi-classical dynamics from influence functional

Influence functional approach:

- Start from the fully quantum-mechanical problem
- Split into the system (ions), and the bath/environment (electrons)
- Given configuration of the system, trace out the bath (electrons), and get an effective action for the system
- Semi-classical Langevin equation

References:
Phonon bath: Feynman&Vernon1963,Caldeira&Leggett1983, Schmid1982,
Electron bath: Chang&Chakravarty1985,Hedegård&Caldeira1987

Semi-classical dynamics from influence functional

Influence functional approach:

- Start from the fully quantum-mechanical problem
- Split into the system (ions), and the bath/environment (electrons)
- Given configuration of the system, trace out the bath (electrons), and get an effective action for the system
- Semi-classical Langevin equation

References:
Phonon bath: Feynman&Vernon1963,Caldeira&Leggett1983, Schmid1982,
Electron bath: Chang&Chakravarty1985,Hedegård&Caldeira1987

Semi-classical dynamics from influence functional

Influence functional approach:

- Start from the fully quantum-mechanical problem
- Split into the system (ions), and the bath/environment (electrons)
- Given configuration of the system, trace out the bath (electrons), and get an effective action for the system
- Semi-classical Langevin equation

References:
Phonon bath: Feynman&Vernon1963,Caldeira&Leggett1983, Schmid1982,
Electron bath: Chang&Chakravarty1985,Hedegård&Caldeira1987

Semi-classical dynamics from influence functional

Influence functional approach:

- Start from the fully quantum-mechanical problem
- Split into the system (ions), and the bath/environment (electrons)
- Given configuration of the system, trace out the bath (electrons), and get an effective action for the system
- Semi-classical Langevin equation

References:
Phonon bath: Feynman&Vernon1963,Caldeira&Leggett1983, Schmid1982,
Electron bath: Chang&Chakravarty1985,Hedegård&Caldeira1987

Semi-classical dynamics from influence functional

Influence functional approach:

- Start from the fully quantum-mechanical problem
- Split into the system (ions), and the bath/environment (electrons)
- Given configuration of the system, trace out the bath (electrons), and get an effective action for the system
- Semi-classical Langevin equation

References:
Phonon bath: Feynman&Vernon1963,Caldeira&Leggett1983, Schmid1982,

Electron bath: Chang&Chakravarty1985,Hedegård&Caldeira1987

Outline

Hamiltonian

Hamiltonian for an ion moving in some potential:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$$

Evolution operator with path integral

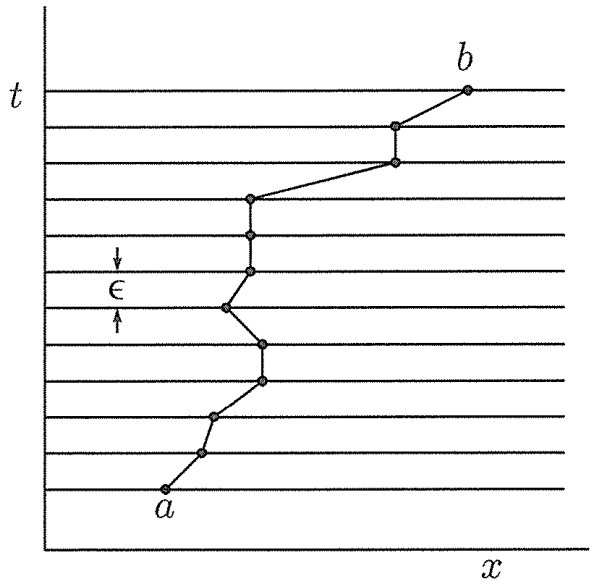
Evolution operator in coordinate basis:

$$\langle b|e^{-i\hat{H}t/\hbar}|a\rangle = \lim_{N\to+\infty}\langle b|\left(e^{-i\hat{H}\Delta t/\hbar}\right)^N|a\rangle$$

$$= \lim_{N\to+\infty}\prod_{j=1}^{N-1} dx_j\langle x_j|e^{-i\hat{H}\Delta t/\hbar}|x_{j-1}\rangle$$

with

$$x_N = b, \quad x_0 = a.$$



Evolution operator with path integral

$$\langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle$$

Evolution operator with path integral

$$\begin{aligned} & \langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle \\ \approx \quad & \langle x_j | e^{-i\hat{p}^2\Delta t/2m\hbar} e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \leftarrow \text{Trotter} \end{aligned}$$

Evolution operator with path integral

$$
\begin{aligned}
& \langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \langle x_j | e^{-i\hat{p}^2\Delta t/2m\hbar} e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \leftarrow \text{Trotter} \\
\approx\ & \int dp_j \int dp'_j \langle x_j | p_j \rangle \langle p_j | e^{-i\hat{p}^2\Delta t/2m\hbar} | p'_j \rangle \langle p'_j | e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle
\end{aligned}
$$

Evolution operator with path integral

$$
\begin{aligned}
& \langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \langle x_j | e^{-i\hat{p}^2\Delta t/2m\hbar} e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \leftarrow \text{Trotter} \\
\approx\ & \int dp_j \int dp_j' \langle x_j | p_j \rangle \langle p_j | e^{-i\hat{p}^2\Delta t/2m\hbar} | p_j' \rangle \langle p_j' | e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \int dp_j \langle x_j | p_j \rangle e^{-ip_j{}^2\Delta t/2m\hbar} \langle p_j | x_{j-1} \rangle e^{-iV(x_{j-1})\Delta t/\hbar} \leftarrow \langle x_j | p_j \rangle = e^{ip_j x_j/\hbar}
\end{aligned}
$$

Evolution operator with path integral

$$
\begin{aligned}
& \langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \langle x_j | e^{-i\hat{p}^2\Delta t/2m\hbar} e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \leftarrow \text{Trotter} \\
\approx\ & \int dp_j \int dp_j' \langle x_j | p_j \rangle \langle p_j | e^{-i\hat{p}^2\Delta t/2m\hbar} | p_j' \rangle \langle p_j' | e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \int dp_j \langle x_j | p_j \rangle e^{-ip_j{}^2\Delta t/2m\hbar} \langle p_j | x_{j-1} \rangle e^{-iV(x_{j-1})\Delta t/\hbar} \leftarrow \langle x_j | p_j \rangle = e^{ip_j x_j/\hbar} \\
\approx\ & \int dp_j e^{-ip_j{}^2\Delta t/2m\hbar} e^{-iV(x_{j-1})\Delta t/\hbar} e^{i(x_j - x_{j-1})p_j/\hbar}
\end{aligned}
$$

Evolution operator with path integral

$$
\begin{aligned}
& \langle x_j | e^{-i\hat{H}\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \langle x_j | e^{-i\hat{p}^2\Delta t/2m\hbar} e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \leftarrow \text{Trotter} \\
\approx\ & \int dp_j \int dp_j' \langle x_j | p_j \rangle \langle p_j | e^{-i\hat{p}^2\Delta t/2m\hbar} | p_j' \rangle \langle p_j' | e^{-iV(\hat{x})\Delta t/\hbar} | x_{j-1} \rangle \\
\approx\ & \int dp_j \langle x_j | p_j \rangle e^{-ip_j{}^2\Delta t/2m\hbar} \langle p_j | x_{j-1} \rangle e^{-iV(x_{j-1})\Delta t/\hbar} \leftarrow \langle x_j | p_j \rangle = e^{ip_j x_j/\hbar} \\
\approx\ & \int dp_j e^{-ip_j{}^2\Delta t/2m\hbar} e^{-iV(x_{j-1})\Delta t/\hbar} e^{i(x_j - x_{j-1})p_j/\hbar} \\
\approx\ & \mathcal{N} \exp\left\{ \frac{i}{\hbar} \left[\frac{m}{2} \left(\frac{x_j - x_{j-1}}{\Delta t} \right)^2 - V(x_{j-1}) \right] \Delta t \right\}
\end{aligned}
$$

Evolution operator with path integral

Evolution operator in coordinate basis:

$$\begin{aligned}
\langle b|e^{-i\hat{H}t/\hbar}|a\rangle &= \lim_{N\to+\infty}\prod_{j=1}^{N-1}\int dx_j \exp\left\{\frac{i}{\hbar}\sum_{j=1}^{N}\left[\frac{m}{2}\left(\frac{x_j-x_{j-1}}{\epsilon}\right)^2 - V(x_{j-1})\right]\right. \\
&\equiv \int \mathcal{D}x \exp\left\{\frac{i}{\hbar}\int dt\left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right\} \\
&\equiv \int \mathcal{D}x \exp\left\{\frac{i}{\hbar}S(\dot{x},x)\right\}
\end{aligned}$$

Semi-classical approximation

Evolution operator in coordinate basis:

$$\langle b|e^{-i\hat{H}t/\hbar}|a\rangle = \int \mathcal{D}x \exp\left\{\frac{i}{\hbar}\int dt\left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right\}$$

Pick out the classical path:

$$x = x_{cl} + \xi,$$

we get

$$\begin{aligned}\langle b|e^{-i\hat{H}t}|a\rangle &\approx \exp\left\{\frac{i}{\hbar}S_{cl}\right\} \\ &\times \int \mathcal{D}\xi \exp\left\{\frac{i}{\hbar}\int dt\left(\frac{1}{2}m\dot{\xi}^2 - V''(x_{cl})\xi^2\right)\right\} + \mathcal{O}(\xi^3)\end{aligned}$$

In the limit of $\xi^2 \gg \hbar$, classical path contributes the most.

Semi-classical approximation

Evolution operator in coordinate basis:

$$\langle b|e^{-i\hat{H}t/\hbar}|a\rangle = \int \mathcal{D}x \exp\left\{\frac{i}{\hbar}\int dt\left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right\}$$

Pick out the classical path:

$$x = x_{cl} + \xi,$$

we get

$$\begin{aligned}\langle b|e^{-i\hat{H}t}|a\rangle \quad &\approx \quad \exp\left\{\frac{i}{\hbar}S_{cl}\right\} \\ &\times \quad \int \mathcal{D}\xi \exp\left\{\frac{i}{\hbar}\int dt\left(\frac{1}{2}m\dot{\xi}^2 - V''(x_{cl})\xi^2\right)\right\} + \mathcal{O}(\xi^3)\end{aligned}$$

In the limit of $\xi^2 \gg \hbar$, classical path contributes the most.

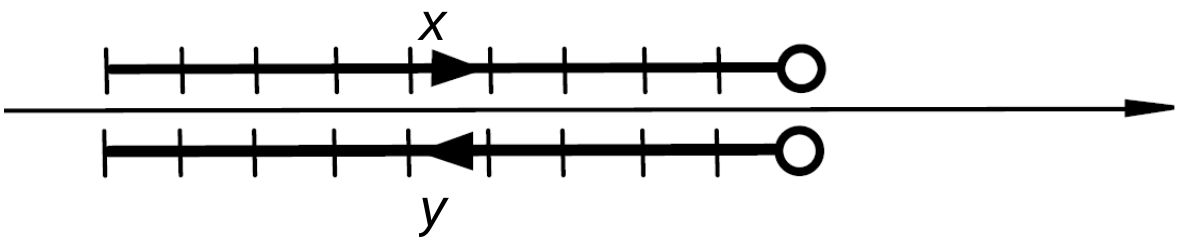
Evolution of Density matrix

Density matrix:

$$\hat{\rho}(t) = e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}$$

Evolution in coordinate basis:

$$\begin{aligned}\langle x_1|\hat{\rho}(t)|y_1\rangle &= \langle x_1|e^{-i\hat{H}t/\hbar}|x_0\rangle\langle x_0|\hat{\rho}(0)|y_0\rangle\langle y_0|e^{i\hat{H}t/\hbar}|y_1\rangle \\ &= \int \mathcal{D}[x,y]e^{i(S(x)-S(y))/\hbar}\langle x_0|\hat{\rho}(0)|y_0\rangle \\ &\equiv K(x_1,y_1;x_0,y_0)\langle x_0|\hat{\rho}(0)|y_0\rangle\end{aligned}$$



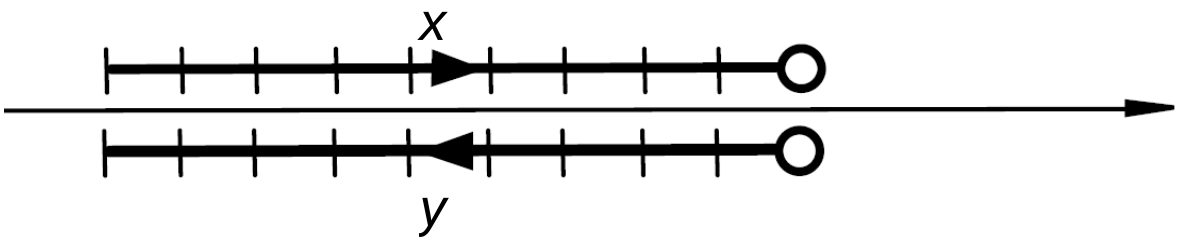
Evolution of Density matrix

Density matrix:

$$\hat{\rho}(t) = e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar}$$

Evolution in coordinate basis:

$$\begin{aligned}
\langle x_1|\hat{\rho}(t)|y_1\rangle &= \langle x_1|e^{-i\hat{H}t/\hbar}|x_0\rangle\langle x_0|\hat{\rho}(0)|y_0\rangle\langle y_0|e^{i\hat{H}t/\hbar}|y_1\rangle \\
&= \int \mathcal{D}[x,y]e^{i(S(x)-S(y))/\hbar}\langle x_0|\hat{\rho}(0)|y_0\rangle \\
&\equiv K(x_1,y_1;x_0,y_0)\langle x_0|\hat{\rho}(0)|y_0\rangle
\end{aligned}$$



Semi-classical approximation

Define $R \equiv \frac{1}{2}(x+y)$(classical),$\xi \equiv x-y$(quantum), we get

$$K(x_1,y_1;x_0,y_0) = \int \mathcal{D}[x,y]\exp\left\{\frac{i}{\hbar}(S(x)-S(y))\right\}$$

$$\approx \int \mathcal{D}[R,\xi]\exp\left\{-\frac{i}{\hbar}\int \xi(t)(m\ddot{R}(t)+V'(R(t)))dt\right\} + \mathcal{O}(\xi^3)$$

- Only odd in ξ terms contribute!

Think of $\int e^{ikx}\frac{dk}{2\pi} = \delta(x)$, integrate out ξ, we get

$$L_0(t) = m\ddot{R}(t) + V'(R(t)) = 0.$$

- Average path follows classical equation of motion
- Exact for quadratic potential

Semi-classical approximation

Define $R \equiv \frac{1}{2}(x+y)$(classical),$\xi \equiv x-y$(quantum), we get

$$K(x_1,y_1;x_0,y_0) = \int \mathcal{D}[x,y]\exp\left\{\frac{i}{\hbar}(S(x)-S(y))\right\}$$

$$\approx \int \mathcal{D}[R,\xi]\exp\left\{-\frac{i}{\hbar}\int \xi(t)(m\ddot{R}(t)+V'(R(t)))dt\right\}+\mathcal{O}(\xi^3)$$

- Only odd in ξ terms contribute!

Think of $\int e^{ikx}\frac{dk}{2\pi} = \delta(x)$, integrate out ξ, we get

$$L_0(t) = m\ddot{R}(t)+V'(R(t)) = 0.$$

- Average path follows classical equation of motion
- Exact for quadratic potential

Outline

Density matrix for system+bath model

- System variables: x, y, Bath variables: X, Y. The density matrix is

$$\langle x_1, X_1|\hat{\rho}(t)|y_1, Y_1\rangle = \langle x_1, X_1|e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}|y_1, Y_1\rangle$$

- Since we are only interested in the system, we want to look at the evolution of the reduced density matrix for the system only $\hat{\rho}_s$

Density matrix for system+bath model

- System variables: x, y, Bath variables: X, Y. The density matrix is

$$\langle x_1, X_1|\hat{\rho}(t)|y_1, Y_1\rangle = \langle x_1, X_1|e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}|y_1, Y_1\rangle$$

- Since we are only interested in the system, we want to look at the evolution of the reduced density matrix for the system only $\hat{\rho}_s$

$$\langle x_1|\hat{\rho}_s(t)|y_1\rangle = \mathrm{Tr}_{X_1}\left[\langle x_1, X_1|\hat{\rho}(t)|y_1, Y_1\rangle\right]$$

Density matrix for system+bath model

- System variables: x, y, Bath variables: X, Y. The density matrix is

$$\langle x_1, X_1|\hat{\rho}(t)|y_1, Y_1\rangle = \langle x_1, X_1|e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}|y_1, Y_1\rangle$$

- Since we are only interested in the system, we want to look at the evolution of the reduced density matrix for the system only $\hat{\rho}_s$

$$\langle x_1|\hat{\rho}_s(t)|y_1\rangle = \mathrm{Tr}_{X_1}\left[\langle x_1, X_1|\hat{\rho}(t)|y_1, X_1\rangle\right]$$

Decoupling scheme

The total Hamiltonian

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{int}$$

Assume at $t = 0$,

$$\rho(0) = \rho_s(0) \oplus \rho_b(0)$$

then

$$\langle x_1|\rho_s(t)|y_1\rangle = F(x,y)U_s(x_1,x_0)\langle x_0|\rho_s(0)|y_0\rangle U_s^\dagger(y_0,y_1)$$

with the influence functional (F), phase (Φ)

Decoupling scheme

The total Hamiltonian

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{int}$$

Assume at $t = 0$,

$$\rho(0) = \rho_s(0) \oplus \rho_b(0)$$

then

$$\langle x_1|\rho_s(t)|y_1\rangle = F(x,y)U_s(x_1,x_0)\langle x_0|\rho_s(0)|y_0\rangle U_s^\dagger(y_0,y_1)$$

with the influence functional (F), phase (Φ)

Decoupling scheme

The total Hamiltonian

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{int}$$

Assume at $t = 0$,

$$\rho(0) = \rho_s(0) \oplus \rho_b(0)$$

then

$$\langle x_1|\rho_s(t)|y_1\rangle = F(x,y)U_s(x_1,x_0)\langle x_0|\rho_s(0)|y_0\rangle U_s^\dagger(y_0,y_1)$$

with the influence functional (F), phase (Φ)

$$F(x,y) \equiv e^{i\Phi(x,y)/\hbar} = \mathrm{Tr}_b\left[U_b(x)\rho_b(0)U_b^\dagger(y)\right]$$

Properties of F/Φ

From the definition of F

$$F(x,y) \equiv e^{i\Phi(x,y)/\hbar} = \mathrm{Tr}_b \left[U_b(x)\rho_b(0)U_b^\dagger(y) \right],$$

we have

- $F(x,y) = F^*(y,x)$,
- $F(x,x) = 1$,

or in terms of classical (R) and quantum (ξ) paths

- $F(R,\xi) = F^*(R,-\xi)$,
- $F(R,0) = 1$,

Properties of F/Φ

From the definition of F

$$F(x,y) \equiv e^{i\Phi(x,y)/\hbar} = \mathrm{Tr}_b \left[U_b(x)\rho_b(0)U_b^\dagger(y) \right],$$

we have

- $F(x,y) = F^*(y,x)$,
- $F(x,x) = 1$,

or in terms of classical (R) and quantum (ξ) paths

- $F(R,\xi) = F^*(R,-\xi)$,
- $F(R,0) = 1$,

Effect of the bath to the evolution

Recall in the semi-classical approximation, for system only, we have

$$K(x_1, y_1; x_0, y_0) \approx \int \mathcal{D}[R, \xi] \exp\left\{-\frac{i}{\hbar}\int \xi(t) L_0(t) dt\right\}.$$

What is the effect of the bath?

$$K(x_1, y_1; x_0, y_0) \approx \int \mathcal{D}[R, \xi] \exp\left\{-\frac{i}{\hbar}\int \left(\xi(t) L_0(t) - \Phi(t)\right) dt\right\}$$

Effect of the bath to the evolution

Recall in the semi-classical approximation, for system only, we have

$$K(x_1, y_1; x_0, y_0) \approx \int \mathcal{D}[R, \xi] \exp\left\{-\frac{i}{\hbar}\int \xi(t) L_0(t) dt\right\}.$$

What is the effect of the bath?

$$K(x_1, y_1; x_0, y_0) \approx \int \mathcal{D}[R, \xi] \exp\left\{-\frac{i}{\hbar}\int \left(\xi(t) L_0(t) - \Phi(t)\right) dt\right\}$$

Expansion of the influence phase

Using $F(R,0)=1, \quad F(R,\xi)=F^*(R,-\xi)$, we expand Φ over ξ to 2nd order:

$$\Phi(R,\xi) = \Phi(R,0) - A(R;t,t')\xi(t) + \frac{i}{2}\xi(t')B(R;t,t')\xi(t) + \mathcal{O}(\xi^3)$$

Put this back to K:

$$K(x_1,y_1;x_0,y_0) \approx \int \mathcal{D}[R,\xi]\exp\left\{-\frac{i}{\hbar}\int \xi(t)(L_0(t)+A(t,t'))dt\right\} \times \exp\left\{-\frac{1}{2\hbar}\xi(t)B(t,t')\xi(t')\right\}$$

- Modifies the equation of motion of R
- Introduces a $\mathcal{O}(\xi^2)$ term

Expansion of the influence phase

Using $F(R,0)=1, \quad F(R,\xi)=F^*(R,-\xi)$, we expand Φ over ξ to 2nd order:

$$\Phi(R,\xi) = \Phi(R,0) - A(R;t,t')\xi(t) + \frac{i}{2}\xi(t')B(R;t,t')\xi(t) + \mathcal{O}(\xi^3)$$

Put this back to K:

$$K(x_1,y_1;x_0,y_0) \approx \int \mathcal{D}[R,\xi]\exp\left\{-\frac{i}{\hbar}\int \xi(t)(L_0(t)+A(t,t'))dt\right\} \times \exp\left\{-\frac{1}{2\hbar}\xi(t)B(t,t')\xi(t')\right\}$$

- Modifies the equation of motion of R
- Introduces a $\mathcal{O}(\xi^2)$ term

Probability interpretation

Using Gaussian integral:

$$\int d\xi e^{iL\xi} e^{-\frac{1}{2}a\xi^2} \rightarrow \int df \int d\xi e^{i(L+f)x} e^{-\frac{1}{2a}f^2} \rightarrow \int dk \delta(L+k) e^{-\frac{1}{2a}k^2},$$

we have

$$\begin{aligned} K(x_1, y_1; x_0, y_0) &\approx \int \mathcal{D}[R, \xi] \exp\left\{-\frac{i}{\hbar}\int \xi(t)(L_0(t) + A(t, t'))dt\right\} \\ &\times \exp\left\{-\frac{1}{2\hbar}\xi(t)B(t, t')\xi(t')\right\} \end{aligned}$$

Probability interpretation

Using Gaussian integral:

$$\int d\xi e^{iL\xi} e^{-\frac{1}{2}a\xi^2} \rightarrow \int df \int d\xi e^{i(L+f)x} e^{-\frac{1}{2a}f^2} \rightarrow \int dk \delta(L+k) e^{-\frac{1}{2a}k^2},$$

we have

$$\begin{aligned} K(x_1, y_1; x_0, y_0) &\approx \int \mathcal{D}[R, \xi, f] \exp\left\{-\frac{i}{\hbar}\int \xi(t)(L_0(t) + A(t,t') + f(t))dt\right\} \\ &\times \exp\left\{-\frac{1}{2\hbar} f(t) B^{-1}(t,t') f(t')\right\} \end{aligned}$$

Probability interpretation

Using Gaussian integral:

$$\int d\xi e^{iL\xi} e^{-\frac{1}{2}a\xi^2} \to \int df \int d\xi e^{i(L+f)x} e^{-\frac{1}{2a}f^2} \to \int dk \delta(L+k) e^{-\frac{1}{2a}k^2},$$

we have

$$\begin{aligned} K(x_1, y_1; x_0, y_0) &\approx \int \mathcal{D}[R, f] \Delta(L_0(t) + A(t, t') + f(t)) \\ &\times \exp\left\{ -\frac{1}{2\hbar} f(t) B^{-1}(t, t') f(t') \right\} \end{aligned}$$

Probability interpretation

Using Gaussian integral:

$$\int d\xi e^{iL\xi} e^{-\frac{1}{2}a\xi^2} \to \int df \int d\xi e^{i(L+f)x} e^{-\frac{1}{2a}f^2} \to \int dk \delta(L+k) e^{-\frac{1}{2a}k^2},$$

we have

$$\begin{aligned} K(x_1, y_1; x_0, y_0) &\approx \int \mathcal{D}[R, f] \Delta(L_0(t) + A(t, t') + f(t)) \\ &\times \exp\left\{-\frac{1}{2\hbar} f(t) B^{-1}(t, t') f(t')\right\} \end{aligned}$$

$f(t')$ plays a role of a stochastic force acting on the equation of motion, with a Gaussian correlation.

Generalised Langevin equation

Langevin equation:

$$\frac{\partial^2}{\partial t^2} R(t) + V'(R) = -\int^t dt' A(t,t') R(t') - f(t).$$

with the noise correlation

$$\langle f(t) f(t') \rangle = \hbar B(t,t').$$

Example: Harmonic oscillators

For a harmonic oscillator coupling linearly (in displacement) with harmonic oscillator bath, the semi-classical approximation is exact:

$$A(t-t') = \sum_k \frac{C_k^2}{2m\omega_k} \sin \omega_k (t-t'),$$

$$B(t-t') = \sum_k \frac{C_k^2}{2m\omega_k} \coth \frac{\hbar\omega_k}{2k_B T} \cos \omega_k (t-t').$$

Feynman&Vernon, Caldeira&Leggett,$\cdots$

Outline

Outline

Adiabatic expansion

We have the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(r,R(t)) \quad = \quad \hat{H}_{BO}(r,R(t))\Psi(r,R(t))$$

Within the adiabatic (Born-Oppenheimer) basis:

$$\hat{H}_{BO}(r,R)\phi_n(r,R) = \varepsilon_n(R)\phi_n(r,R),$$

Expand $\Psi(r,R(t))$:

$$\Psi(r,R(t)) = \sum_n a_n(R(t))\phi_n(r,R(t)).$$

Including correction $\mathcal{O}(V^2)$

$$V = i\langle\phi_m|\dot{\phi}_n\rangle \quad \rightarrow \mathcal{O}(\xi^2).$$

Adiabatic expansion

We have the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(r,R(t)) \quad = \quad \hat{H}_{BO}(r,R(t))\Psi(r,R(t))$$

Within the adiabatic (Born-Oppenheimer) basis:

$$\hat{H}_{BO}(r,R)\phi_n(r,R) = \varepsilon_n(R)\phi_n(r,R),$$

Expand $\Psi(r,R(t))$:

$$\Psi(r,R(t)) = \sum_n a_n(R(t))\phi_n(r,R(t)).$$

Including correction $\mathcal{O}(V^2)$

$$V = i\langle\phi_m|\dot{\phi}_n\rangle \quad \rightarrow \mathcal{O}(\xi^2).$$

Adiabatic expansion

We have the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(r,R(t)) \quad = \quad \hat{H}_{BO}(r,R(t))\Psi(r,R(t))$$

Within the adiabatic (Born-Oppenheimer) basis:

$$\hat{H}_{BO}(r,R)\phi_n(r,R) = \varepsilon_n(R)\phi_n(r,R),$$

Expand $\Psi(r,R(t))$:

$$\Psi(r,R(t)) = \sum_n a_n(R(t))\phi_n(r,R(t)).$$

Including correction $\mathcal{O}(V^2)$

$$V = i\langle\phi_m|\dot{\phi}_n\rangle \quad \rightarrow \mathcal{O}(\xi^2).$$

Influence functional

Influence functional from electron bath:

$$
\begin{aligned}
F_e &= \mathrm{Det}\left[[G^0]^{-1} + V\right] \\
&\approx \exp\left\{\mathrm{Tr}\left[\ln G_0^{-1}\right]\right\} \exp\left\{\mathrm{Tr}\left[G_0 V\right]\right\} \exp\left\{-\frac{1}{2}\mathrm{Tr}\left[G_0 V G_0 V\right]\right\}
\end{aligned}
$$

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

Influence functional

Influence functional from electron bath:

$$\begin{aligned} F_e &= \mathrm{Det}\left[[G^0]^{-1} + V\right] \\ &\approx \exp\left\{\mathrm{Tr}\left[\ln G_0^{-1}\right]\right\} \exp\left\{\mathrm{Tr}\left[G_0 V\right]\right\} \exp\left\{-\frac{1}{2}\mathrm{Tr}\left[G_0 V G_0 V\right]\right\} \end{aligned}$$

The adiabatic Green's function:

$$\left(i\frac{\partial}{\partial t} - \varepsilon_n(R)\right) G^0_{nn}(t,t') = \delta(t-t')$$

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

Influence functional

Influence functional from electron bath:

$$\begin{aligned} F_e &= \mathrm{Det}\left[[G^0]^{-1} + V\right] \\ &\approx \exp\left\{\mathrm{Tr}\left[\ln G_0^{-1}\right]\right\} \exp\left\{\mathrm{Tr}\left[G_0 V\right]\right\} \exp\left\{-\frac{1}{2}\mathrm{Tr}\left[G_0 V G_0 V\right]\right\} \end{aligned}$$

The adiabatic Green's function:

$$\left(i\frac{\partial}{\partial t} - \varepsilon_n(R)\right) G^0_{nn}(t,t') = \delta(t-t')$$

Adiabatic correction:

$$V_{mn} = i\langle\phi_m|\dot{\phi}_n\rangle$$

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

Outline

Langevin equation (Equilibrium electrons)

$$\frac{\partial^2}{\partial t^2} R(t) = -V' - \gamma_{eh}(t)\dot{R}(t) + f(t)$$

Langevin equation (Equilibrium electrons)

$$\frac{\partial^2}{\partial t^2} R(t) = -V' - \gamma_{eh}(t)\dot{R}(t) + f(t)$$

The adiabatic(Born-Oppenheimer) force

$$V' = \sum_j n_F(\varepsilon_j) \frac{\partial}{\partial R} \varepsilon_j(t, R(t))$$

Langevin equation (Equilibrium electrons)

$$\frac{\partial^2}{\partial t^2} R(t) = -V' - \gamma_{eh}(t)\dot{R}(t) + f(t)$$

The electronic friction

$$\begin{aligned} \gamma_{eh}(\omega) &\approx -\sum_{k,j} \frac{1}{\omega} \langle \phi_j | \nabla_R V_{ep} | \phi_k \rangle \langle \phi_k | \nabla_R V_{ep} | \phi_j \rangle \\ &\times \left(n_F(\varepsilon_k - \mu) - n_F(\varepsilon_j - \mu) \right) \delta(\omega - (\varepsilon_k - \varepsilon_j)) \end{aligned}$$

- Generally friction not local in time! But very short memory for electrons.
- Excitation of electron-hole pairs!

Langevin equation (Equilibrium electrons)

$$\frac{\partial^2}{\partial t^2} R(t) = -V' - \gamma_{eh}(t)\dot{R}(t) + f(t)$$

The equilibrium noise correlation

$$\langle ff \rangle(\omega) = 2\omega\gamma_{eh}\left(n_B(\omega, T) + \frac{1}{2}\right) \leftarrow \text{colored noise}$$

Fluctuations around the classical path:

- zero T, zero point motion, $\sim \omega\gamma_{eh}$
- high T, thermal fluctuation, $\sim 2\gamma_{eh}k_B T$

Langevin equation (Equilibrium electrons)

$$\frac{\partial^2}{\partial t^2} R(t) = -V' - \gamma_{eh}(t)\dot{R}(t) + f(t)$$

The equilibrium noise correlation

$$\langle ff \rangle(\omega) = 2\omega\gamma_{eh}\left(n_B(\omega, T) + \frac{1}{2}\right) \leftarrow \text{colored noise}$$

Fluctuations around the classical path:

- zero T, zero point motion, $\sim \omega\gamma_{eh}$
- high T, thermal fluctuation, $\sim 2\gamma_{eh}k_B T$

$\rightarrow$ Ignoring $f(t)$, phonons keep losing energy to electrons! (Ehrenfest)

Energy of harmonic phonons

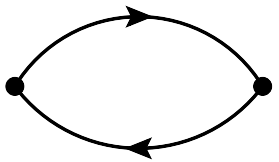
For a harmonic oscillator coupling weakly with an equilibrium electron bath at T_e, we can calculate the energy of the phonons from the Langevin equations

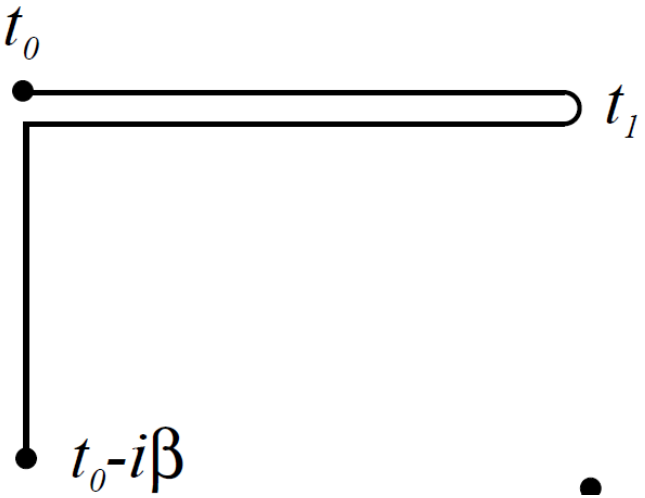
$$E = \hbar\omega_0 \left(n_B(\omega, T_e) + \frac{1}{2} \right)$$

Nonequilibrium electrons

Nonequilibrium Green's function method:

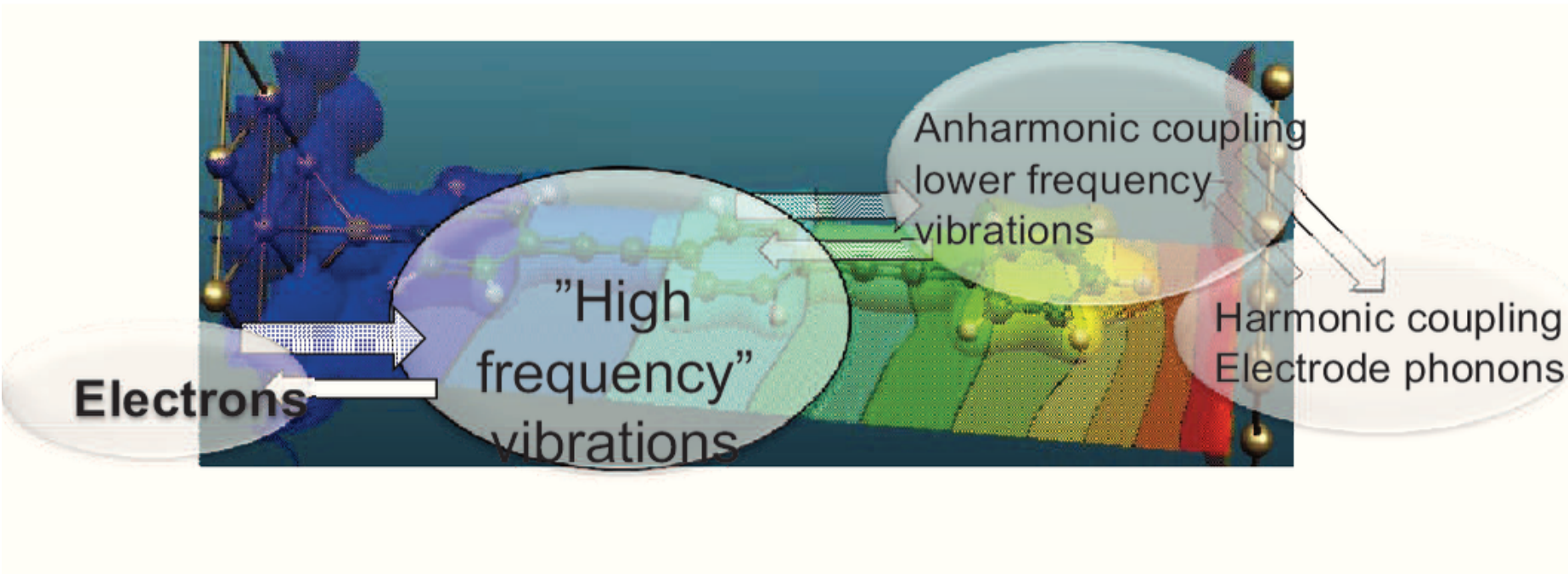
$$B(t-t') = \frac{i}{2}\left(\Pi^{>} + \Pi^{<}\right),$$
$$A(t-t') = \Pi^{>}(t-t') - \Pi^{<}(t-t')$$





Outline

Joule heating, Current-induced forces



Molecular dynamics in the presence of current!

Langevin equation (Nonequilibrium electrons)

$$\frac{\partial^2}{\partial t^2}R(t) = -V' - (\gamma_{eh}(eV) + \Delta\gamma(t))\dot{R}(t) + f(t)$$
$$-\mathcal{B}(eV)\dot{R}(t) + \mathcal{A}(eV)R(t)$$

Nonequilibrium corrections:

- Joule heating: $\langle ff\rangle(\omega) = \omega(\gamma_{eh} + \Delta\gamma)\coth\frac{\omega}{2k_BT} + \Delta\Pi(\omega)$
- Nonequilibrium correction to the friction coefficient
- Berry-phase induced effective magnetic field - $\mathcal{B}$ anti-symmetric
- Non-conservative current-induced forces - $\mathcal{A}$ anti-symmetric

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

JTL, P. Hedegård, M. Brandbyge, PRL, 107, 046801 (2010)

Langevin equation (Nonequilibrium electrons)

$$\frac{\partial^2}{\partial t^2}R(t) = -V' - (\gamma_{eh}(eV) + \Delta\gamma(t))\dot{R}(t) + f(t)$$
$$-\mathcal{B}(eV)\dot{R}(t) + \mathcal{A}(eV)R(t)$$

Nonequilibrium corrections:

- Joule heating: $\langle ff\rangle(\omega) = \omega(\gamma_{eh} + \Delta\gamma)\coth\frac{\omega}{2k_BT} + \Delta\Pi(\omega)$
- Nonequilibrium correction to the friction coefficient
- Berry-phase induced effective magnetic field - $\mathcal{B}$ anti-symmetric
- Non-conservative current-induced forces - $\mathcal{A}$ anti-symmetric

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

JTL, P. Hedegård, M. Brandbyge, PRL, 107, 046801 (2010)

Langevin equation (Nonequilibrium electrons)

$$\frac{\partial^2}{\partial t^2}R(t) = -V' - (\gamma_{eh}(eV) + \Delta\gamma(t))\dot{R}(t) + f(t)$$
$$-\mathcal{B}(eV)\dot{R}(t) + \mathcal{A}(eV)R(t)$$

Nonequilibrium corrections:

- Joule heating: $\langle ff\rangle(\omega) = \omega(\gamma_{eh} + \Delta\gamma)\coth\frac{\omega}{2k_BT} + \Delta\Pi(\omega)$
- Nonequilibrium correction to the friction coefficient
- Berry-phase induced effective magnetic field - $\mathcal{B}$ anti-symmetric
- Non-conservative current-induced forces - $\mathcal{A}$ anti-symmetric

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

JTL, P. Hedegård, M. Brandbyge, PRL, 107, 046801 (2010)

Langevin equation (Nonequilibrium electrons)

$$\frac{\partial^2}{\partial t^2}R(t) = -V' - (\gamma_{eh}(eV) + \Delta\gamma(t))\dot{R}(t) + f(t)$$
$$-\mathcal{B}(eV)\dot{R}(t) + \mathcal{A}(eV)R(t)$$

Nonequilibrium corrections:

- Joule heating: $\langle ff\rangle(\omega) = \omega(\gamma_{eh} + \Delta\gamma)\coth\frac{\omega}{2k_BT} + \Delta\Pi(\omega)$
- Nonequilibrium correction to the friction coefficient
- Berry-phase induced effective magnetic field - $\mathcal{B}$ anti-symmetric
- Non-conservative current-induced forces - $\mathcal{A}$ anti-symmetric

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010)

JTL, P. Hedegård, M. Brandbyge, PRL, 107, 046801 (2010)

Computational tools

- SIESTA for electronic structure calculation

  J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys. Condens. Matter 14, 2745 (2002)

- TranSIESTA for electronic transport

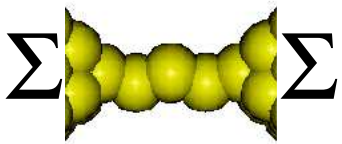
  M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B 65, 165401 (2002)

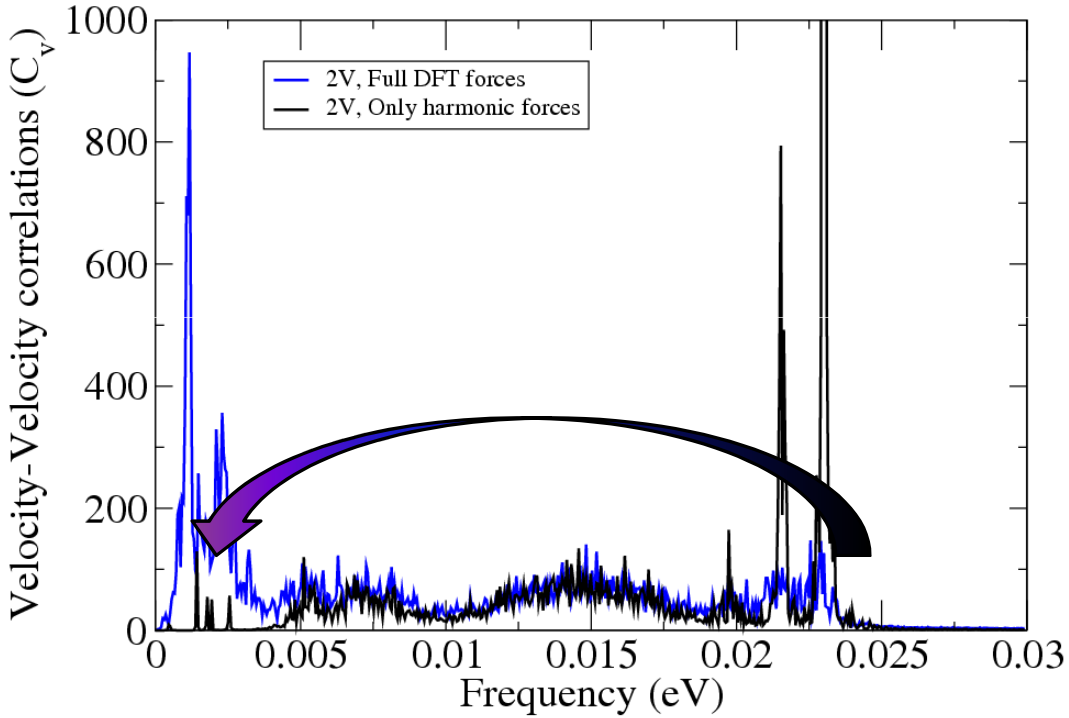
- Inelastica for phonons and e-ph coupling

  T. Frederiksen, M. Paulsson, M. Brandbyge, A.-P. Jauho, Phys. Rev. B 75, 205413 (2007)

Harmonic vs. Anharmonic

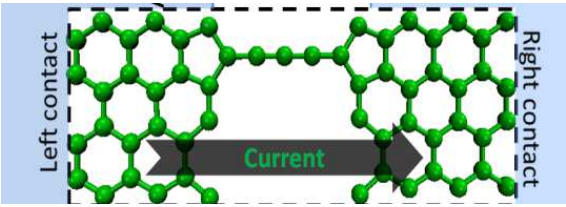
$$\ddot{Q}_I + \nabla_I V(Q) + \sum_J \gamma_{IJ}\,\dot{Q}_J + \mathcal{N}_{IJ}\,Q_J \;=\; f_I$$





MD: Follow how energy is redistributed by anharmonic couplings

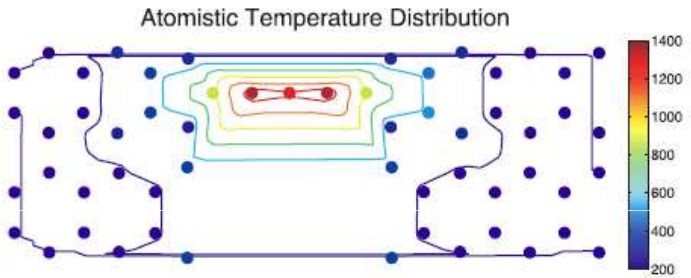
Carbon chain MD simulations

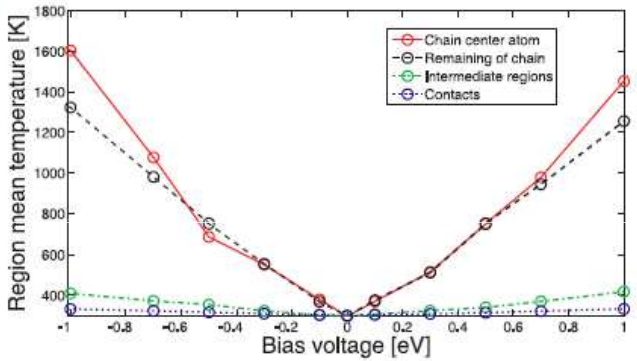


Tight-binding + Brenner potential

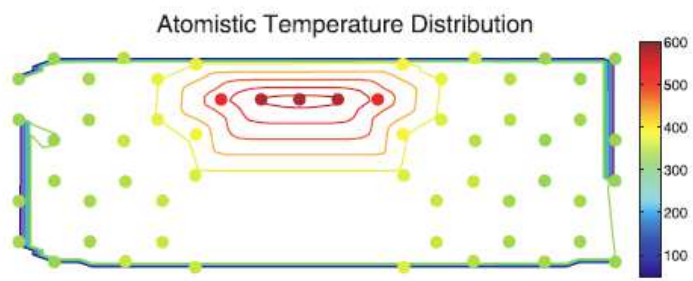
Importance of anharmonic couplings in energy redistribution

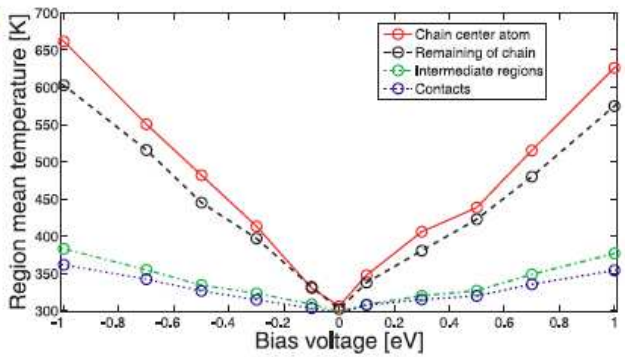
Harmonic





Anharmonic





Tue Gunst, M.Sc. Thesis, DTU

Take home message

- General first-principles way of deriving Langevin equation for system+bath model
- Applied to ions coupling with nonequilibrium, time-dependent (in the adiabatic sense) electron baths
- Non-adiabatic effect enters as friction and noise. The noise is crucial for the energy transfer.
- Application to radiation damage???

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010),
M. Brandbyge, P. Hedegård, PRL, 72, 2919 (1994),

M. Brandbyge, P. Hedegård, T. F. Heinz, J. A. Misewich, and D. M. Newns, PRB, 52, 6042 (1995).

Take home message

- General first-principles way of deriving Langevin equation for system+bath model
- Applied to ions coupling with nonequilibrium, time-dependent (in the adiabatic sense) electron baths
- Non-adiabatic effect enters as friction and noise. The noise is crucial for the energy transfer.
- Application to radiation damage???

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010),
M. Brandbyge, P. Hedegård, PRL, 72, 2919 (1994),

M. Brandbyge, P. Hedegård, T. F. Heinz, J. A. Misewich, and D. M. Newns, PRB, 52,

6042 (1995).

Take home message

- General first-principles way of deriving Langevin equation for system+bath model
- Applied to ions coupling with nonequilibrium, time-dependent (in the adiabatic sense) electron baths
- Non-adiabatic effect enters as friction and noise. The noise is crucial for the energy transfer.
- Application to radiation damage???

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010),
M. Brandbyge, P. Hedegård, PRL, 72, 2919 (1994),

M. Brandbyge, P. Hedegård, T. F. Heinz, J. A. Misewich, and D. M. Newns, PRB, 52,

6042 (1995).

Take home message

- General first-principles way of deriving Langevin equation for system+bath model
- Applied to ions coupling with nonequilibrium, time-dependent (in the adiabatic sense) electron baths
- Non-adiabatic effect enters as friction and noise. The noise is crucial for the energy transfer.
- Application to radiation damage???

JTL, M. Brandbyge, P. Hedegård, Nano. Letters, 10, 1657 (2010),
M. Brandbyge, P. Hedegård, PRL, 72, 2919 (1994),

M. Brandbyge, P. Hedegård, T. F. Heinz, J. A. Misewich, and D. M. Newns, PRB, 52,

6042 (1995).