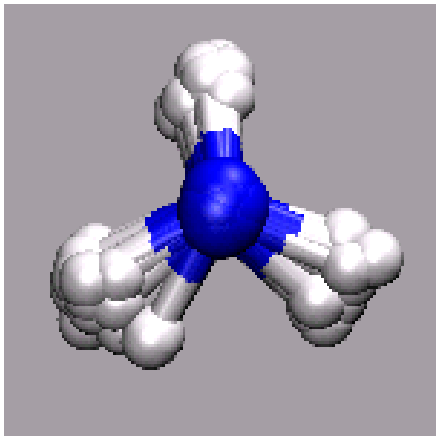
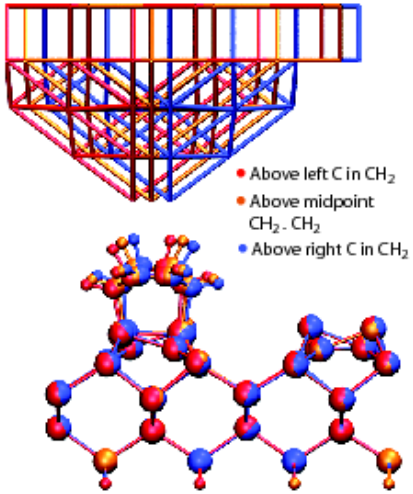
Two (unrelated) topics in quantum transport: Evaluating centroid and ring-polymer molecular dynamics and calculating STM images for molecules on semiconductor surfaces





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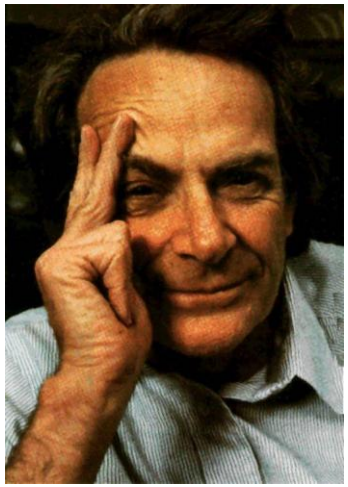


Quantum Statistical Mechanics á la Feynman

Energy eigenvalues:

$$\hat{\mathrm{H}}\left|E_k\right\rangle = E_k\left|E_k\right\rangle$$

Canonical partition function:

$$Q = \mathrm{Tr}\left[e^{-\beta\hat{\mathrm{H}}}\right] = \sum_k e^{-\beta E_k}$$

Ensemble average:

$$\left\langle \hat{\mathrm{A}} \right\rangle = \frac{1}{Q}\mathrm{Tr}\left[\hat{\mathrm{A}}e^{-\beta\hat{\mathrm{H}}}\right] = \frac{1}{Q}\sum_k e^{-\beta E_k}\left\langle E_k\left|\hat{\mathrm{A}}\right|E_k\right\rangle$$

"This law is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature *T* clarified"

-- *Statistical Mechanics: A Set of Lectures*

Path Integrals in Quantum Statistical Mechanics

Carry out trace in coordinate basis:

$$Q = \mathrm{Tr}\left[e^{-\beta \hat{\mathrm{H}}} \right] = \int dx \left\langle x \left| e^{-\beta(\hat{\mathrm{K}}+\hat{\mathrm{V}})} \right| x \right\rangle$$

Trotter theorem:

$$e^{-\beta(\hat{\mathrm{K}}+\hat{\mathrm{V}})} = \lim_{P\to\infty} \left[e^{-\beta \hat{\mathrm{V}}/P} e^{-\beta \hat{\mathrm{K}}/P} \right]^P \equiv \lim_{P\to\infty} \hat{\Omega}^P$$

Insert completeness of position eigenvectors:

$$Q = \lim_{P\to\infty} \int dx_1 \ \left\langle x_1 \left| \hat{\Omega}^P \right| x_1 \right\rangle$$

$$= \lim_{P\to\infty} \int dx_1 \ dx_2 \ dx_3 \cdots dx_P \ \left\langle x_1 \left| \hat{\Omega} \right| x_2 \right\rangle \left\langle x_2 \left| \hat{\Omega} \right| x_3 \right\rangle \left\langle x_3 \left| \hat{\Omega} \cdots \right| x_P \right\rangle \left\langle x_P \left| \hat{\Omega} \right| x_1 \right\rangle$$

Matrix elements:

$$\left\langle x_i \left| \hat{\Omega} \right| x_{i+1} \right\rangle = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{1/2} \exp\left[-\frac{mP}{2\beta\hbar^2} \left(x_i - x_{i+1} \right)^2 - \frac{\beta}{P} V(x_i) \right]$$

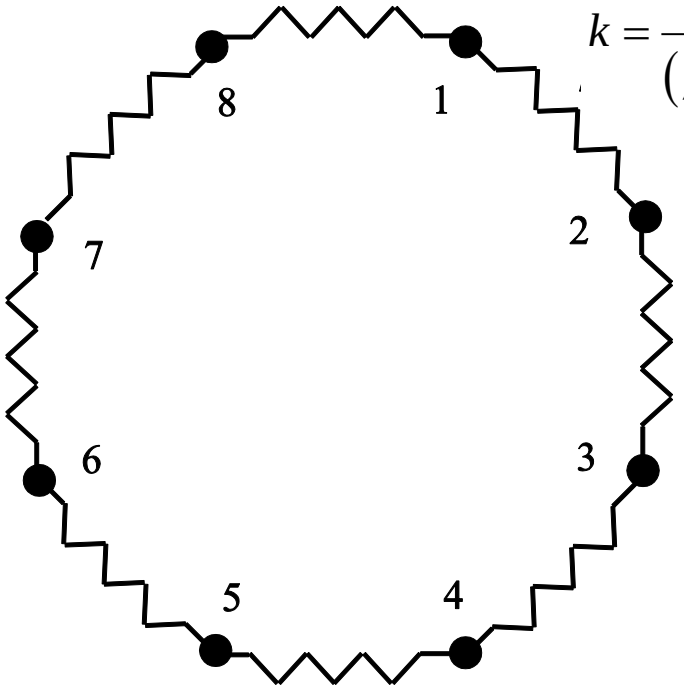
Discrete Path Integral

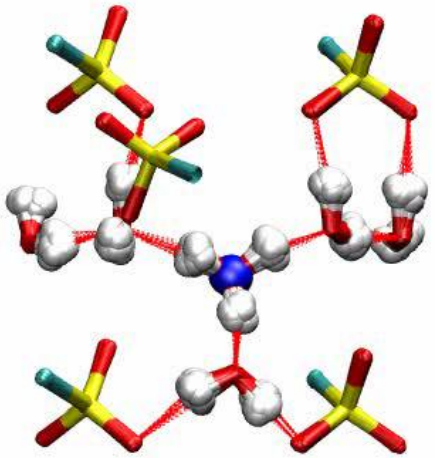
$$Q = \lim_{P\to\infty} Q_P$$

$$Q_P = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int dx_1 \cdots dx_P \exp\left\{-\beta \sum_{i=1}^{P}\left[\frac{mP}{2\beta^2\hbar^2}\left(x_i - x_{i+1}\right)^2 + \frac{1}{P}V(x_i)\right]\right\}\Bigg|_{x_{P+1}=x_1}$$

$$k = \frac{mP}{\left(\beta\hbar\right)^2}$$

Classical isomorphism:





D. Chandler and P. G. Wolynes *J. Chem. Phys*. **74**, 4078 (1981)

Path integral molecular dynamics

M. Parrinello and A. Rahman, *J. Chem. Phys*. **80**, 860 (1984); R. W. Hall and B. J. Berne, *J. Chem. Phys*. **81**, 3641 (1984).

Add Gaussian integrals to partition function:

$$Q_P = \int dp_1 \cdots dp_P dx_1 \cdots dx_P \exp\left\{ -\beta \sum_{i=1}^{P} \left[\frac{p_i^2}{2m'} + \frac{1}{2} m\omega_P^2 \left(x_i - x_{i+1} \right)^2 + \frac{1}{P} V(x_i) \right] \right\} \Bigg|_{x_{P+1}=x_1}$$

$$\omega_P = \frac{\sqrt{P}}{\beta\hbar}$$

Partition function can be sampled using the Hamiltonian:

$$H = \sum_{i=1}^{P} \left[\frac{p_i^2}{2m'} + \frac{1}{2} m\omega_P^2 \left(x_i - x_{i+1} \right)^2 + \frac{1}{P} V(x_i) \right]_{x_{P+1}=x_1}$$

"Primitive" equations of motion:

$$\dot{x}_i = \frac{p_i}{m'}, \qquad \dot{p}_i = -m\omega_P^2 \left(2x_i - x_{i+1} - x_{i-1} \right) - \frac{1}{P} \frac{\partial V}{\partial x_i} + \text{Heat bath}$$

Variable Transformations in path integrals

MET, G. J. Martyna, M. L. Klein and B. J. Berne *J. Chem. Phys*. **99**, 2796 (1993)

Staging transformation:

$$u_1 = x_1$$

$$u_k = x_k - \frac{(k-1)x_{k+1} + x_1}{k}, \qquad k = 2,\ldots,P$$

Normal mode transformation:

$$x_k = \sum_{l=1}^{P} a_l e^{2\pi i(k-1)(l-1)/P}$$

$$u_1 = a_1, \qquad u_P = a_{(P+2)/2}, \qquad u_{2k-2} = \mathrm{Re}(a_k), \qquad u_{2k-1} = \mathrm{Im}(a_k)$$

Diagonalization of quantum kinetic energy:

$$\sum_{k=1}^{P}\left(x_k - x_{k+1}\right)^2 = \sum_{k=2}^{P}\lambda_k u_k^2$$

Staging: $\lambda_k = \dfrac{k}{k-1}$ Normal modes: $\lambda_{2k-1} = \lambda_{2k-2} = 2\left[1-\cos\left(\dfrac{2\pi(k-1)}{P}\right)\right]$

Path integral molecular dynamics

MET, G. J. Martyna, M. L. Klein and B. J. Berne *J. Chem. Phys.* **99**, 2796 (1993)

Transformed Hamiltonian:

$$H = \sum_{i=1}^{P} \left[\frac{p_i^2}{2m_i'} + \frac{1}{2} m\omega_P^2 \lambda_i u_i^2 + \frac{1}{P} V(x_i(u)) \right]_{x_{P+1}=x_1}$$

Fictitious masses:

$$m_1' = m, \qquad m_i' = \lambda_i m, \qquad i = 2, \ldots, P$$

Equations of motion:

$$\dot{u}_i = \frac{p_i}{m_i'}$$

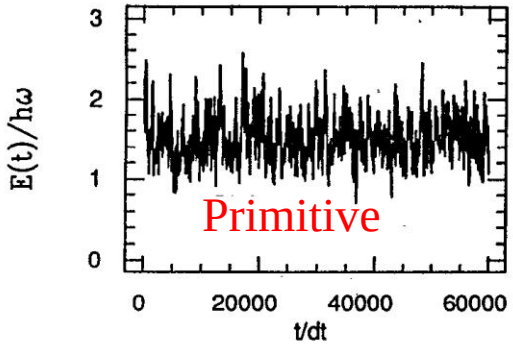
$$\dot{p}_i = -m\omega_P^2 \lambda_i u_i - \frac{1}{P} \sum_{j=1}^{P} \frac{\partial V}{\partial x_j} \frac{\partial x_j}{\partial u_i} + \text{Heat bath}(i)$$

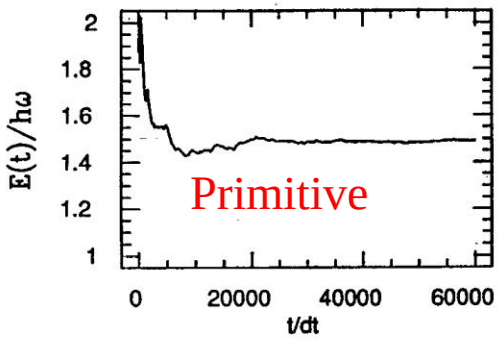
Results for harmonic oscillator

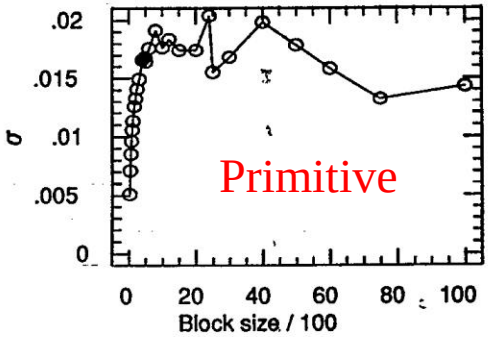
$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \ , \qquad \beta\hbar\omega = 15.8, \qquad \frac{m\omega}{\hbar} = 0.03, \qquad P = 400$$

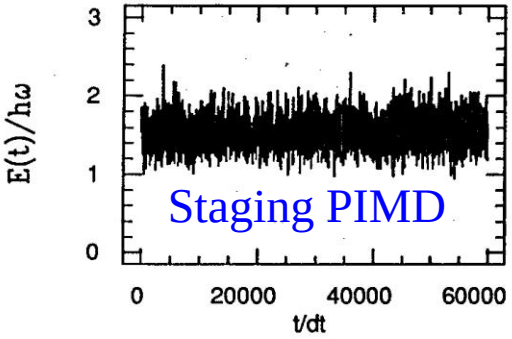
$$E_{\text{vir}} = \frac{1}{P}\sum_{i=1}^{P}\left[V(x_i) + \frac{1}{2} x_i \frac{\partial V}{\partial x_i} \right]$$

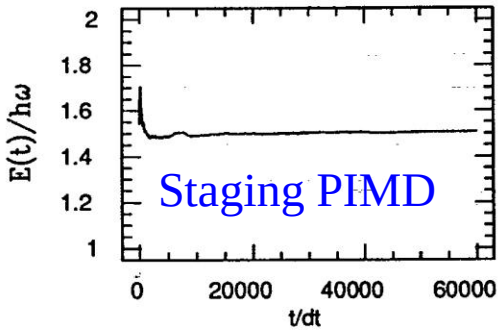
M. F. Herman, E. J. Bruskin and B. J. Berne
J. Chem. Phys. **76**, 5150 (1982).

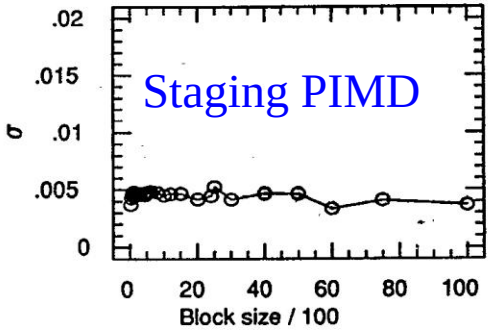


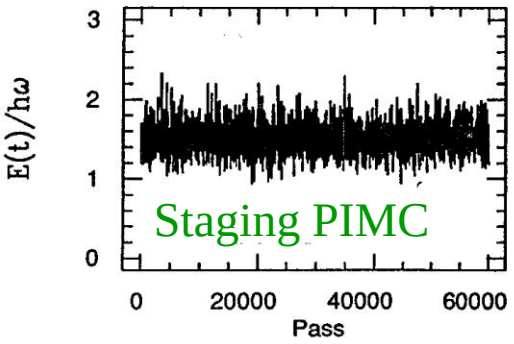


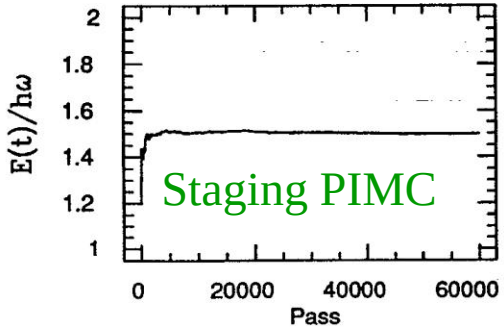


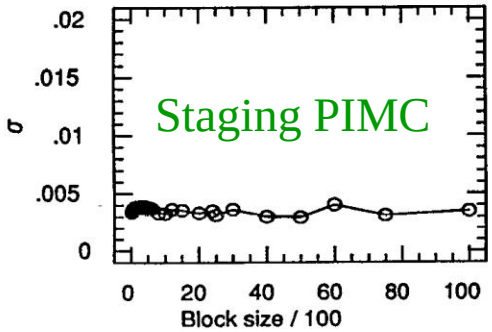








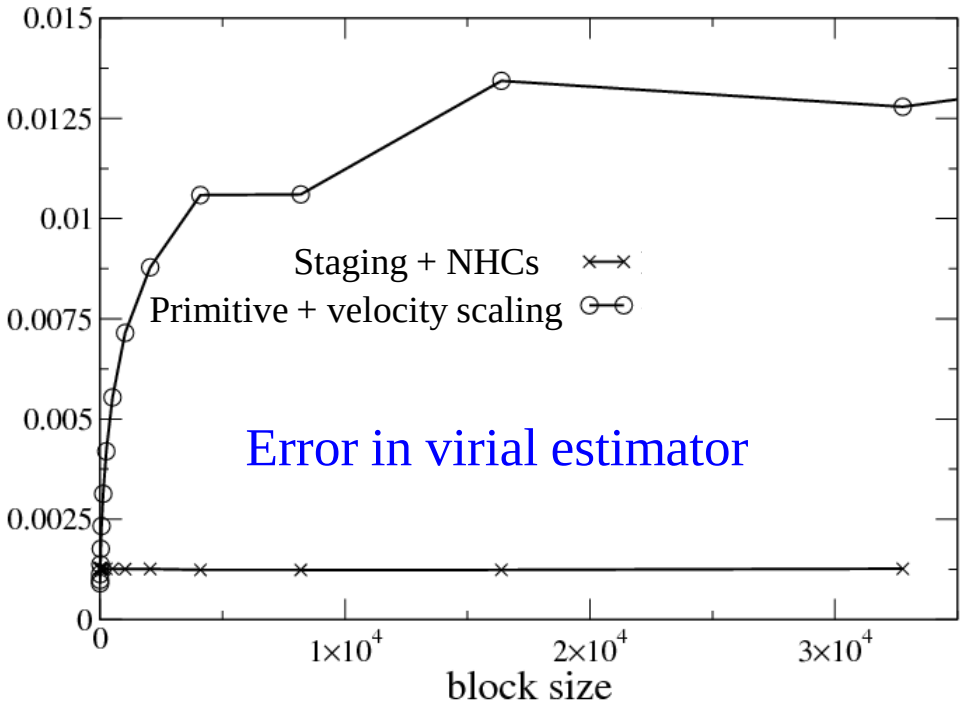




A. Pérez, M. Müser, MET
J. Chem. Phys. **130**, 184105 (2009)

$$V(x) = \frac{x^4}{4}$$

$$\beta = 8, \quad P = 32$$



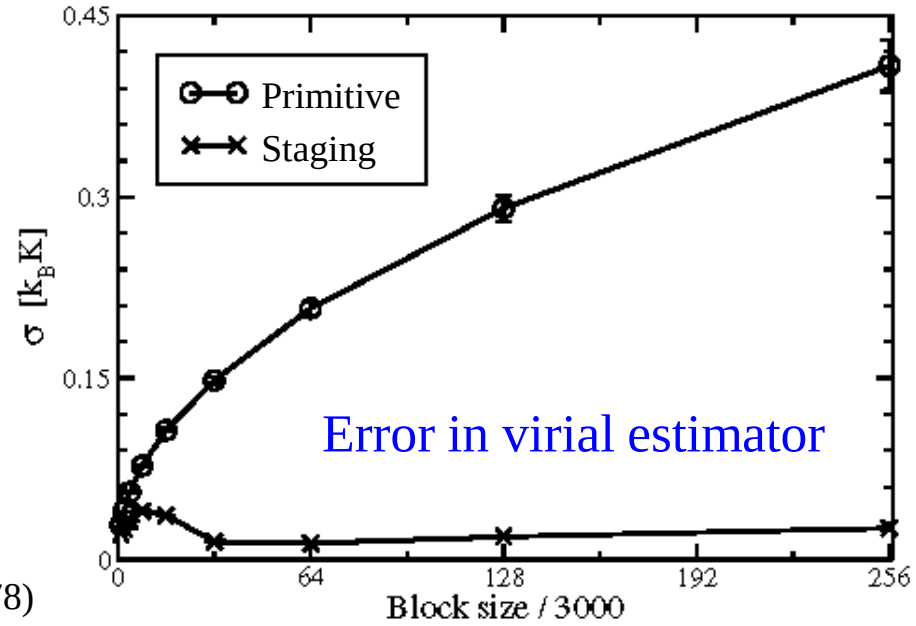
Liquid *para*-Hydrogen

Silvera-Goldman potential

$T = 14$ K , $\rho = 0.0235$ A^{-3}

$N = 256, \quad P = 64$

Time = 6 ps



I. F. Silvera and V. V. Goldman, *JCP* **69**, 4209 (1978)

Quantum time correlation functions

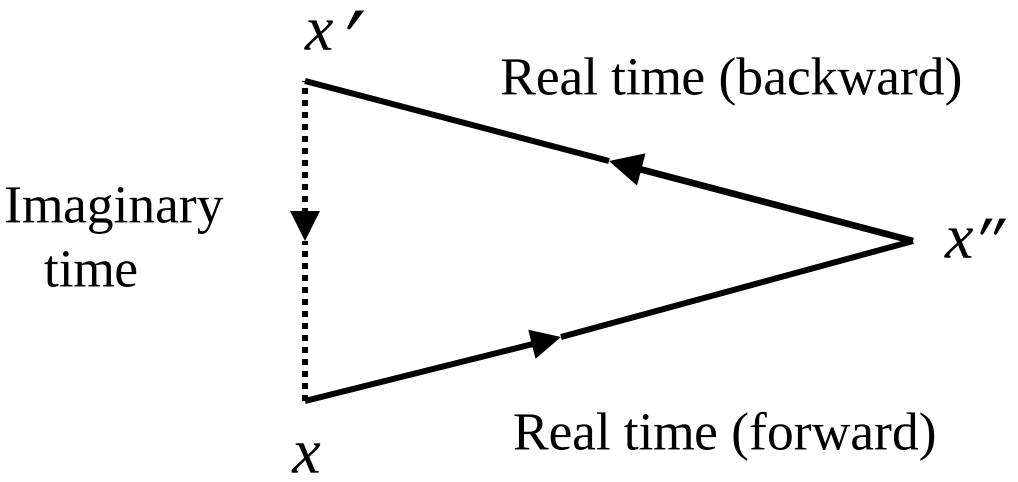
G. Krilov, E. Sim and B. J. Berne *J. Chem. Phys.* **114**, 1075 (2001)

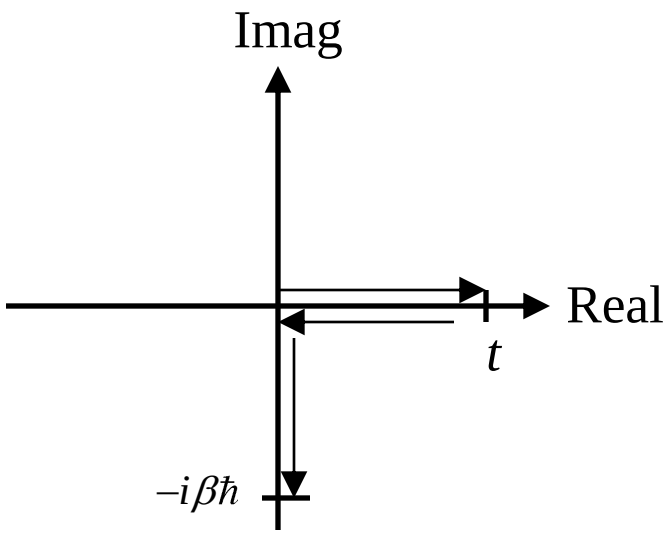
Non-symmetric correlation function:

$$C_{AB}(t) = \left\langle \hat{A}(0)\hat{B}(t) \right\rangle = \frac{1}{Q}\mathrm{Tr}\left[e^{-\beta\hat{H}} A e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right]$$

Assume $\hat{A} = \hat{A}(\hat{x}),\ \hat{B} = \hat{B}(\hat{x}),$ trace in coordinate basis

$$C_{AB}(t) = \frac{1}{Q}\int dx\, dx'dx'' \left\langle x \middle| e^{-\beta\hat{H}} \middle| x' \right\rangle a(x') \left\langle x' \middle| e^{i\hat{H}t/\hbar} \middle| x'' \right\rangle b(x'') \left\langle x'' \middle| e^{-i\hat{H}t/\hbar} \middle| x \right\rangle$$





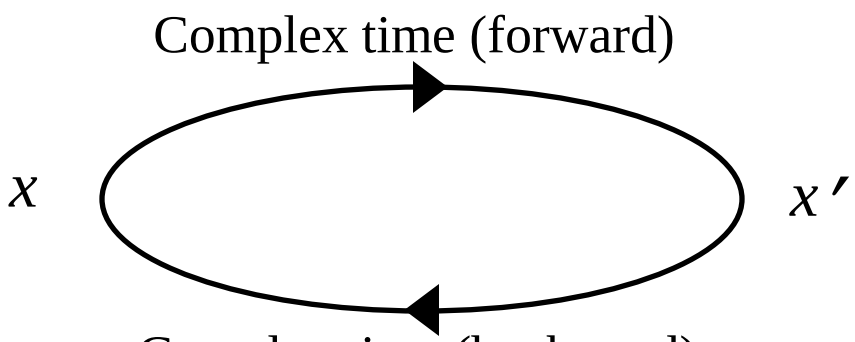
Quantum time correlation functions

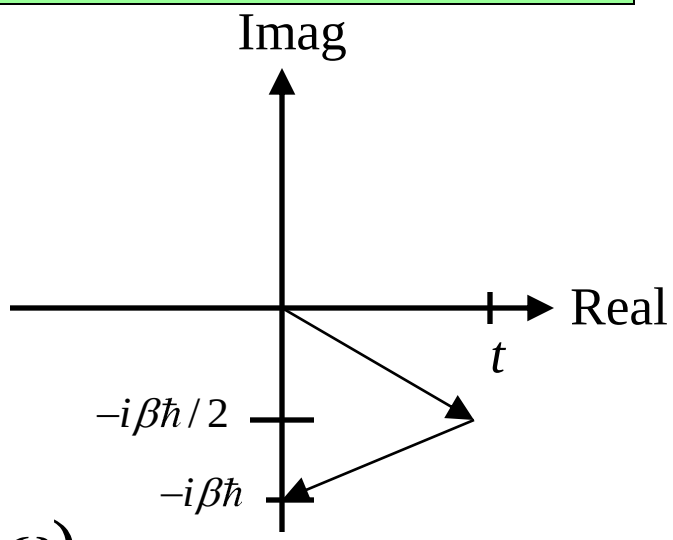
Symmetric complex-time correlation function:

$$G_{\mathrm{AB}}(t) = \frac{1}{Q}\mathrm{Tr}\left[\mathrm{A}e^{i\hat{\mathrm{H}}\tau^*/\hbar}\hat{\mathrm{B}}e^{-i\hat{\mathrm{H}}\tau/\hbar}\right], \qquad \tau = t - \frac{i\beta\hbar}{2}$$

Assume $\hat{\mathrm{A}} = \hat{\mathrm{A}}(\hat{x}),\ \hat{\mathrm{B}} = \hat{\mathrm{B}}(\hat{x}),$ trace in coordinate basis

$$G_{\mathrm{AB}}(t) = \frac{1}{Q}\int dx\, dx'\, a(x)\left\langle x\middle|e^{i\hat{\mathrm{H}}\tau^*/\hbar}\middle|x'\right\rangle b(x')\left\langle x'\middle|e^{-i\hat{\mathrm{H}}\tau/\hbar}\middle|x\right\rangle$$





Fourier transforms: $\tilde{C}_{\mathrm{AB}}(\omega) = e^{\beta\hbar\omega}\tilde{G}_{\mathrm{AB}}(\omega)$

Quantum time correlation functions

Kubo-transformed correlation function:

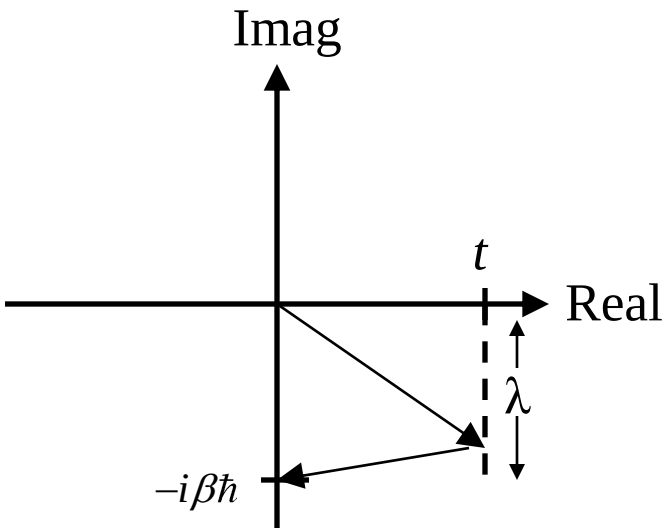
$$K_{AB}(t) = \frac{1}{\beta Q}\int_0^\beta d\lambda \; \mathrm{Tr}\left[\mathrm{A} e^{i\hat{\mathrm{H}}\tau_\lambda^{*}/\hbar} \hat{\mathrm{B}} e^{-i\hat{\mathrm{H}}\tau_{\beta-\lambda}/\hbar} \right], \qquad \tau_\lambda = t - i\lambda\hbar$$

Assume $\hat{\mathrm{A}} = \hat{\mathrm{A}}(\hat{x}),\ \hat{\mathrm{B}} = \hat{\mathrm{B}}(\hat{x}),$ trace in coordinate basis

$$K_{AB}(t) = \frac{1}{\beta Q}\int_0^\beta d\lambda \int dx\, dx'\, a(x) \left\langle x \middle| e^{i\hat{\mathrm{H}}\tau_\lambda^{*}/\hbar} \middle| x' \right\rangle b(x') \left\langle x' \middle| e^{-i\hat{\mathrm{H}}\tau_{\beta-\lambda}/\hbar} \middle| x \right\rangle$$

Fourier transforms:

$$\tilde{C}_{AB}(\omega) = \left[\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} \right] \tilde{K}_{AB}(\omega)$$



Centroid molecular dynamics

J. Cao and G. A. Voth *J. Chem. Phys*. **99**, 10070 (1993)
J. Cao and G. A. Voth *J. Chem. Phys*. **100**, 5106 (1994)
J. Cao and G. A. Voth *J. Chem. Phys*. **101**, 6168 (1994)

Path Centroid

$$x_c = \frac{1}{P}\sum_{i=1}^{P} x_i$$

x_c is the unbound mode u_1 in a normal-mode transformation.

Centroid potential of mean force:

(Feynman and Kleinert *Phys. Rev. A* **34**, 5080 (1986))

$$W(x_c) = W(u_1) = -kT \ln\left\{\int du_2 \cdots du_P \exp\left[-\beta\sum_{k=2}^{P}\frac{1}{2}m\omega_P^2\lambda_k u_k^2 - \frac{\beta}{P}\sum_{k=1}^{P}V(x_k(u))\right]\right\}$$

Discrete partitionfunction:

$$Q_P = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_c e^{-\beta W(x_c)}$$

Centroid molecular dynamics

Approximate quantum dynamics as dynamics on the centroid PMF

$$\dot{x}_c = \frac{p_c}{m}, \qquad \dot{p}_c = -\frac{dW}{dx_c}$$

Approximation to Kubo-transformed time correlation function:

$$K_{AB}(t) \approx \frac{1}{Q}\int dp_c dx_c a(x_c(0)) b(x_c(t)) \exp\left[-\beta\left(\frac{p_c^2}{2m} + W(x_c)\right)\right]$$

Generate centroid PMF "on the fly" by performing imaginary-time PIMD with

$$m_1' = m, \qquad m_k' = \gamma m_k, \qquad \gamma < 1$$

called "partially adiabatic CMD". (J. Cao and G. J. Martyna, *J. Chem. Phys.* **104**, 2028 (1996))

Short-time accuracy (B . J. Braams and D. E. Manolopoulos *J. Chem. Phys.* **127**, 174108 (2007))

$$K_{xx}(t) = \langle x_c(0) x_c(t) \rangle + O(t^6), \quad K_{vv}(t) = \langle v_c(0) v_c(t) \rangle + O(t^4)$$

Exact in harmonic and classical limits.

Ring-polymer molecular dynamics

I. R. Craig and D. E. Manolopoulos *J. Chem. Phys*. **121**, 3368 (2004)

Classical ring-polymer Hamiltonian:

$$H_{\mathrm{cl}}(x,p)=\sum_{i=1}^{P}\left[\frac{p_i^2}{2m}+\frac{1}{2}m\omega_P^2P\left(x_i-x_{i+1}\right)^2+V(x_i)\right]_{x_{P+1}=x_1}$$

(Can also be written in terms of normal-mode and staging variables)

Equations of motion:

$$\dot{x}_i=\frac{p_i}{m},\qquad \dot{p}_i=-m\omega_P^2P(2x_i-x_{i+1}-x_{i-1})-\frac{\partial V}{\partial x_i}$$

Approximate correlation function:

$$K_{AB}(t)\approx\frac{1}{Q}\int d^Pp\,d^Px\;a_P(0)b_P(t)\exp\left[-\beta H_{\mathrm{cl}}(x,p)/P\right]$$

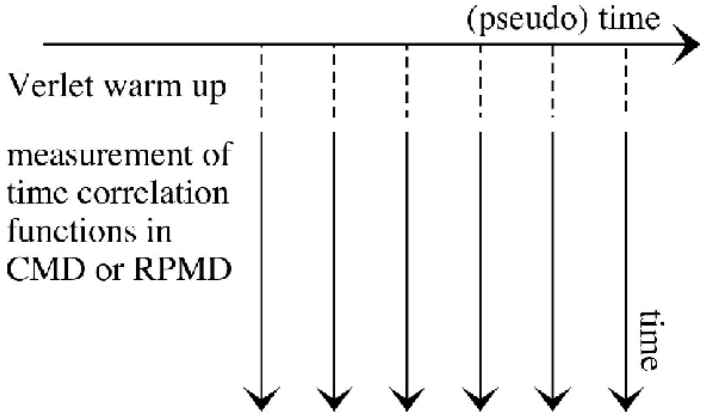
$$a_P(t)=\frac{1}{P}\sum_{i=1}^{P}a(x_i(t)),\qquad b_P(t)=\frac{1}{P}\sum_{i=1}^{P}b(x_i(t))$$

Short-time accuracy: (B . J. Braams and D. E. Manolopoulos *J. Chem. Phys*. **127**, 174108 (2007))

$$K_{xx}(t)=\left\langle x_P(0)x_P(t)\right\rangle+O(t^8),\qquad K_{vv}(t)=\left\langle v_P(0)v_P(t)\right\rangle+O(t^6)$$

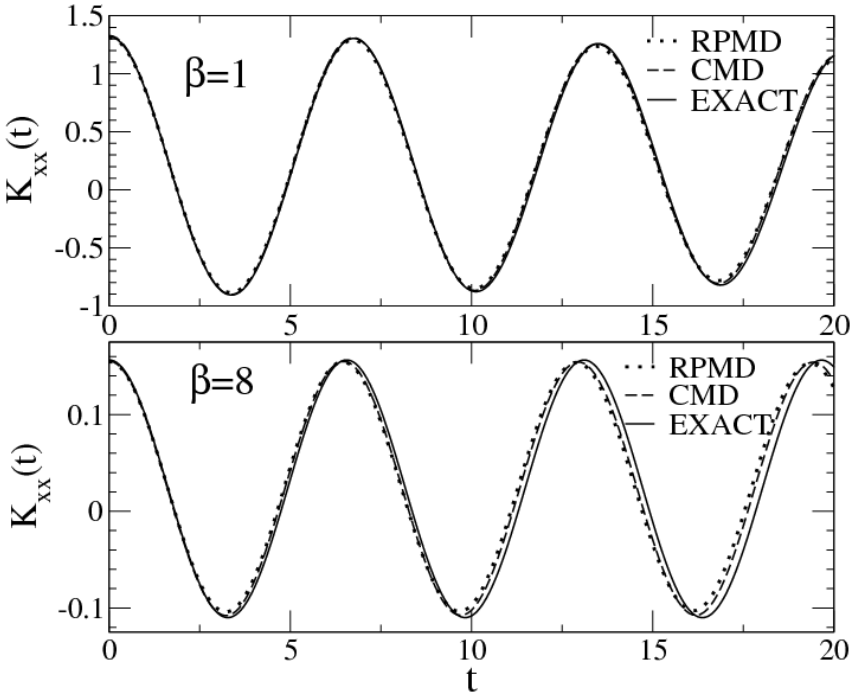
Some numerical examples

Recommended algorithm:



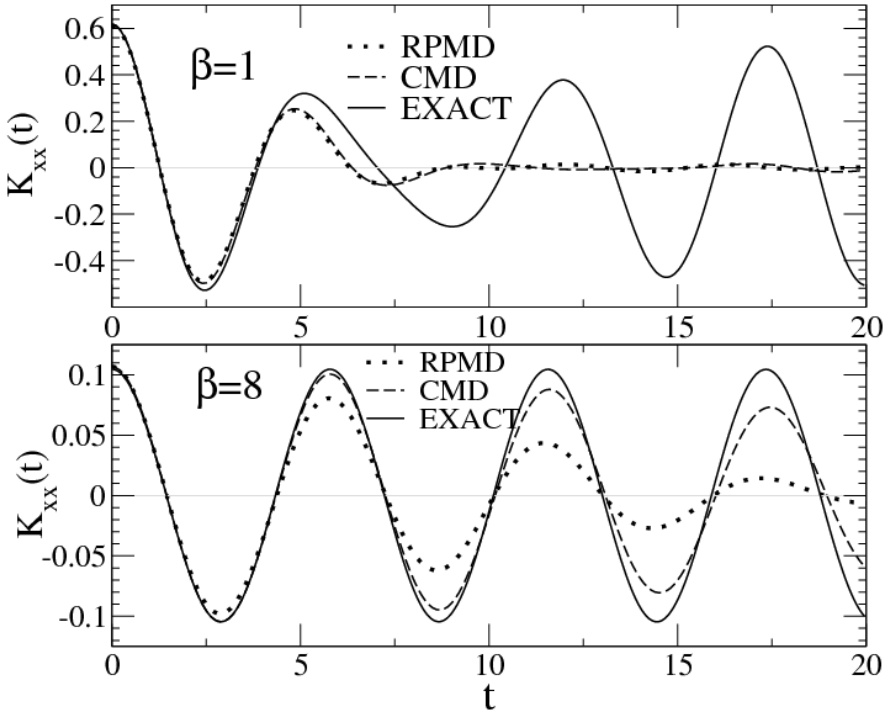
$$V(x) = \frac{x^2}{2} + 0.1x^3 + 0.01x^4$$

$$P = 32, \quad \gamma_{\mathrm{CMD}} = 0.005$$

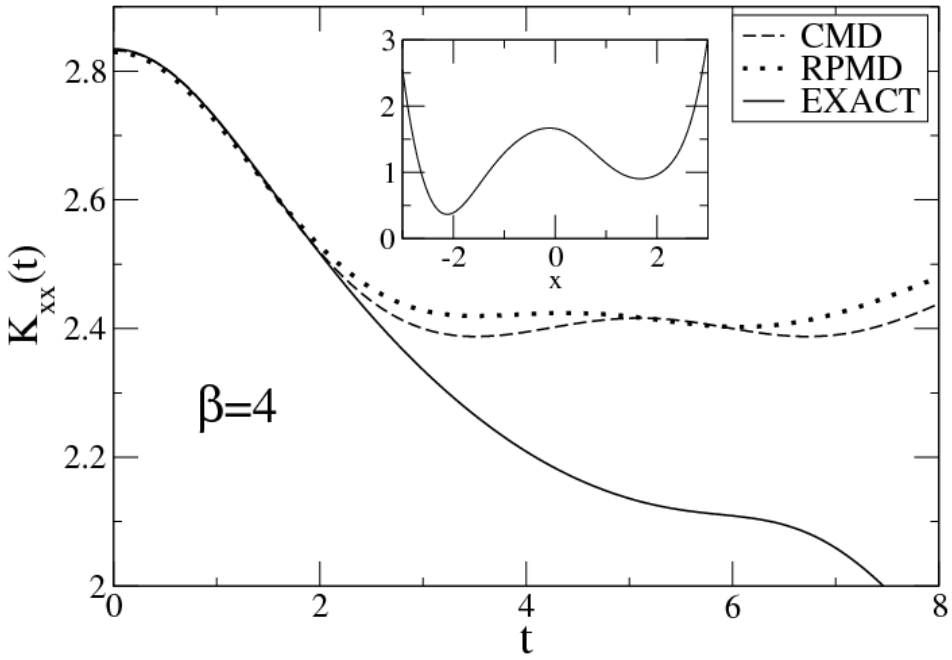


$$V(x) = \frac{x^4}{4}$$

$$P = 32, \quad \gamma_{\mathrm{CMD}} = 0.005$$



Some numerical examples



$$V(x) = 0.1\left(x^2 - 4\right)^2 + e^{-(x-2.2)^2} + 0.5e^{-(x+1.5)^2}$$

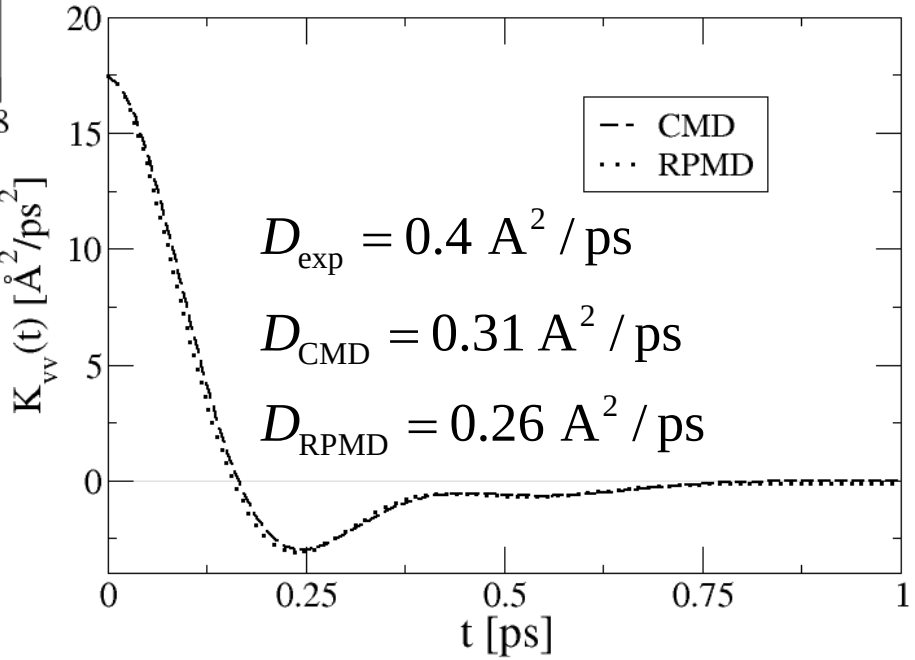
$$P = 32, \qquad \gamma_{\mathrm{CMD}} = 0.005$$

Liquid *para*-Hydrogen

$$T = 14 \text{ K}, \quad \rho = 0.0235 \text{ A}^{-3}$$

$$N = 256, \quad P = 64, \quad \gamma_{\mathrm{CMD}} = 0.005$$

Time = 6 ps



$$D_{\mathrm{exp}} = 0.4 \text{ A}^2/\text{ps}$$

$$D_{\mathrm{CMD}} = 0.31 \text{ A}^2/\text{ps}$$

$$D_{\mathrm{RPMD}} = 0.26 \text{ A}^2/\text{ps}$$

Diffusion constants agree with Hone et al. *JCP* **124**, 154103 (2006) and Miller and Manolopoulos *JCP* **122**, 184503 (2005)

Self-consistent quality measure of CMD and RPMD correlation functions

Imaginary-time mean-square displacement:

$$G(\tau) = \left\langle \left(\hat{x}(0) - \hat{x}(\tau) \right)^2 \right\rangle \xrightarrow[\text{free particle}]{} \frac{1}{2m\beta} \tau(\beta\hbar - \tau)$$

$$G(\tau) = \frac{1}{N} \sum_{i=1}^{N} \left\langle \left(\hat{\mathbf{r}}_i(0) - \hat{\mathbf{r}}_i(\tau) \right)^2 \right\rangle \xrightarrow[\text{free particles}]{} \frac{\pi}{m\beta} \tau(\beta\hbar - \tau)$$

Relation to real-time position and velocity correlation functions:

$$G(\tau) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega e^{-\beta\hbar\omega} \tilde{K}_{xx}(\omega) \left\{ \cosh\left[\omega \left(\frac{\beta\hbar}{2} - \tau \right) \right] - \cosh\left(\frac{\beta\hbar\omega}{2} \right) \right\}$$

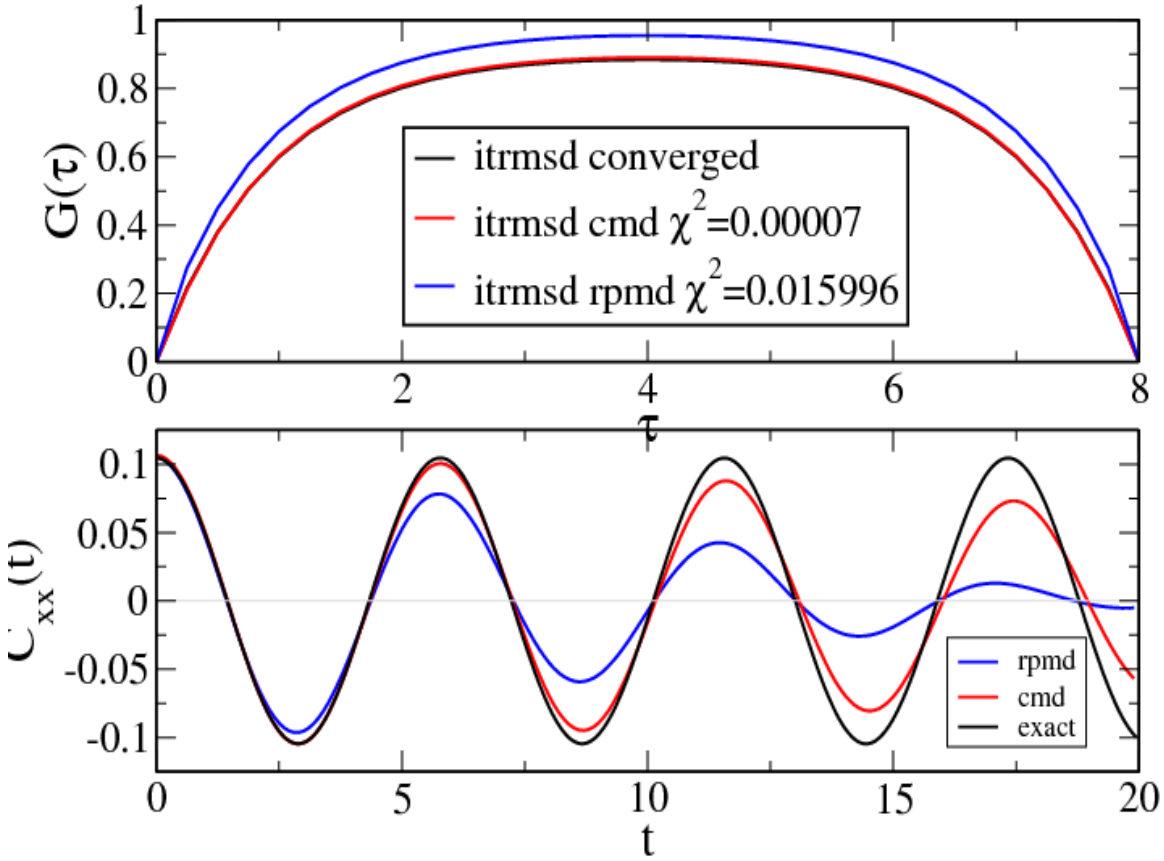
$$= \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega e^{-\beta\hbar\omega} \frac{\tilde{K}_{vv}(\omega)}{\omega^2} \left\{ \cosh\left[\omega \left(\frac{\beta\hbar}{2} - \tau \right) \right] - \cosh\left(\frac{\beta\hbar\omega}{2} \right) \right\}$$

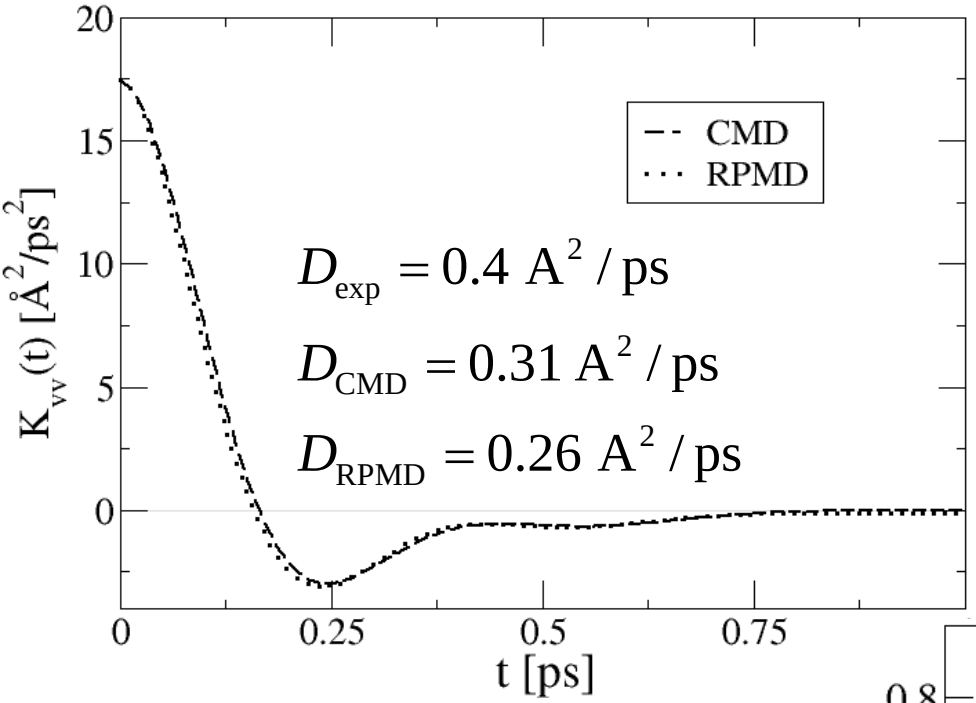
χ^2 Error Measure

A. Pérez, M. Müser, MET *J. Chem. Phys*. **130**, 184105 (2009)

$$\chi^2 = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} d\tau \left[\frac{G^{(\mathrm{est})}(\tau) - G(\tau)}{G(\tau)}\right]^2$$

ITRMSD of $0.25X^4$ with P=32 and β=8





Liquid *para*-Hydrogen

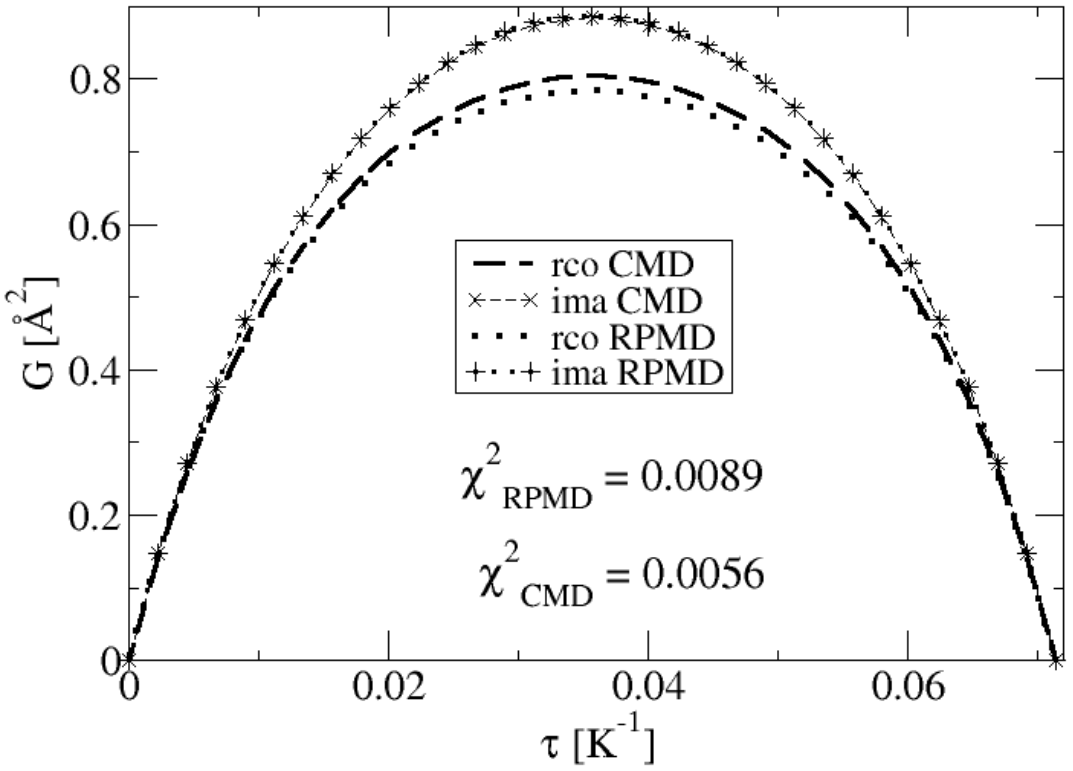
$T = 14\ \mathrm{K}, \quad \rho = 0.0235\ \mathrm{A}^{-3}$

$N = 256, \quad P = 64, \quad \gamma_{\mathrm{CMD}} = 0.005$

Time = 6 ps

Considerations of CMD and RPMD in calculating vibrational spectra:

A. Witt *et al*. *JCP* **130,** 194501 (2009)
S. D. Ivanov *et al*. *JCP* **132**, 031101 (2010)

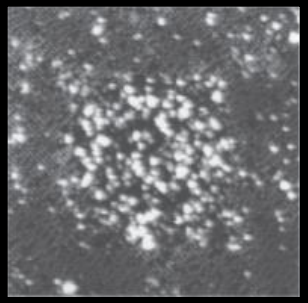


Organic-Semiconductor Interfaces

Organic chem.

Surface physics

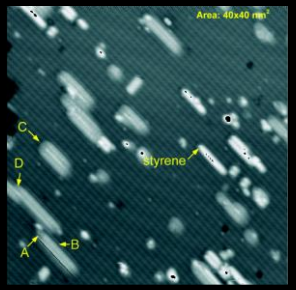
Chemo-/bio-sensors



Nano-lithography

Example: - Passivate Si(100) surface with benzene
- Create 2 nm wide patterns with STM tip
- React with vinyl ferrocene

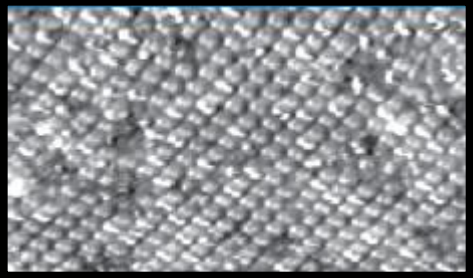
Kruse and Wolkow *Appl. Phys. Lett*. **81** (2002) 4422.



Self-assembled nanowires and other nanostructures

Example: - styrene forms lines on H-Si(100)
- precursor to molecular electronics

DiLabio, Piva, Kruse, and Wolkow JACS **126** (2004) 16048.



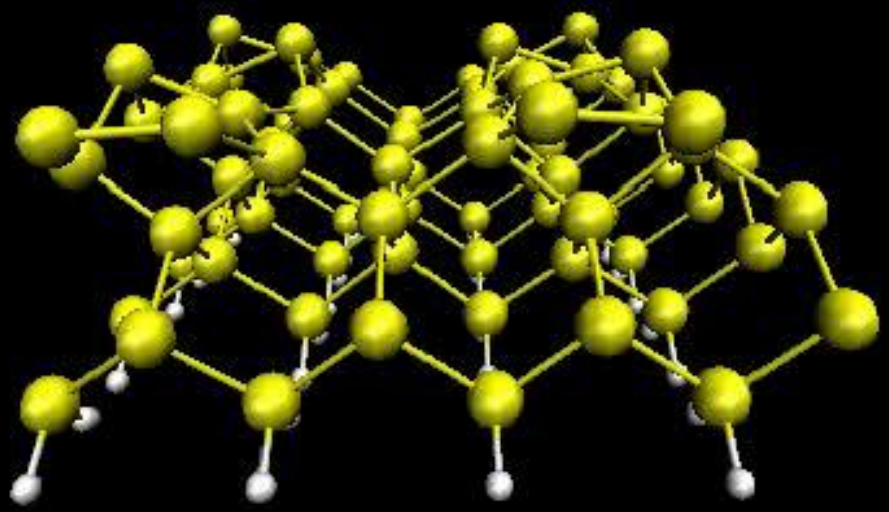
Monolayers

Example: - monolayer of 1,5-cyclooctadiene absorbed on Si(100)
- π-bond on surface available for further rxns
- precursor to molecular sensor

DiLabio, Piva, Kruse, and Wolkow JACS **126** (2004) 16048.

Non-concerted mechanism of Diels-Alder adduct from *ab initio* MD

P. Minary and MET *J. Am. Chem. Soc*. **126**, 13920 (2004)
P. Minary and MET *J. Am. Chem. Soc*. **127**, 1110 (2005)
R. L. Hayes and MET *J. Am. Chem. Soc*. **129**, 12172 (2007)
R. Iftimie, P. Minary, MET *Proc. Natl. Acad. Sci*. **102**, 6654 (2005)

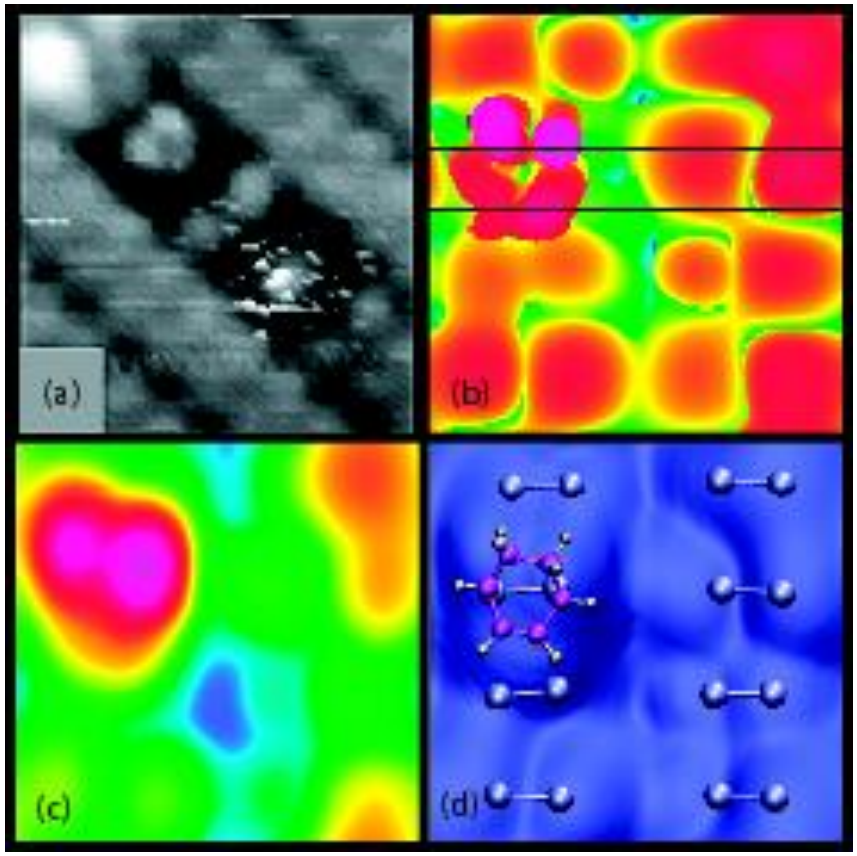


1,3-cyclohexadiene
on Si(100)-2x1

Calculation of Empty-State STM Images

R. L. Hayes and MET (to be submitted)

L. C. Teague and J. J. Boland
JPCB **107**, 3820 (2003)



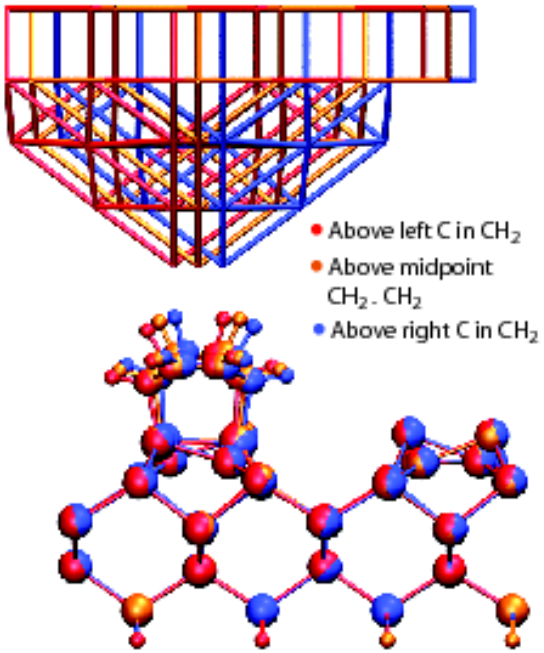
Tersoff-Hamann

Bardeen

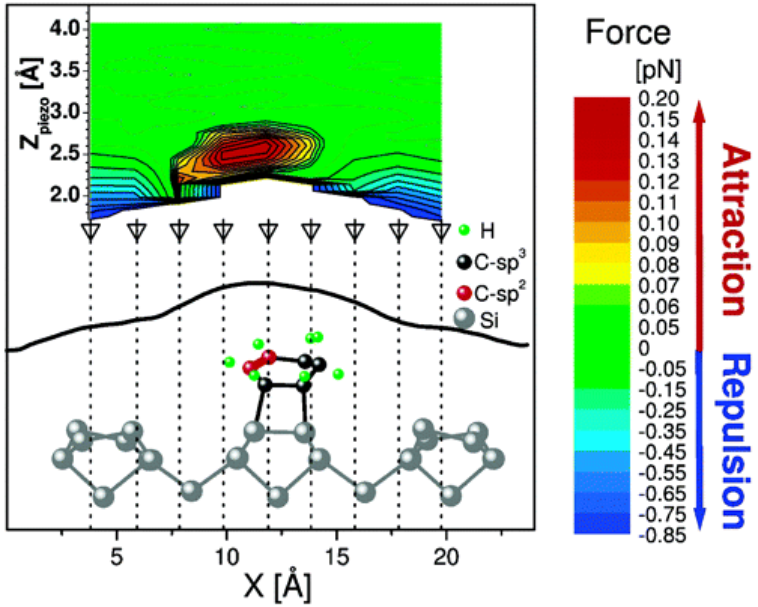
Tersoff-Hamann: $$I \propto \sum_{\nu} \left|\psi_{\nu}(\mathbf{r}_{\text{tip}})\right|^2 \delta\left(E_{\nu} - E_F\right)$$

Bardeen: $$I \propto \sum_{\mu,\nu} f(E_{\mu})\left[1 - f(E_{\nu} + eV)\right]\left|M_{\mu\nu}\right|^2 \delta\left(E_{\mu} - E_{\nu}\right)$$

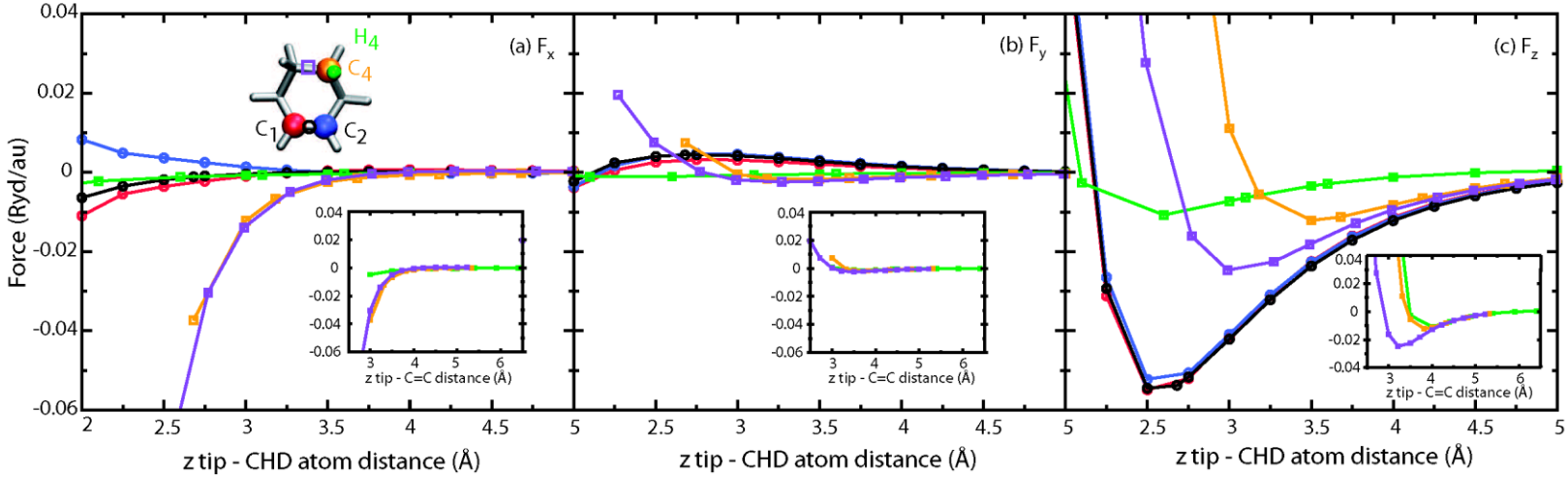
Calculation of STM Images



Naydenov *et al*. *Nano Lett*. **6**, 1752 (2006)



Need to perform self-consistent conductance calculations (NEGF) on a full grid!



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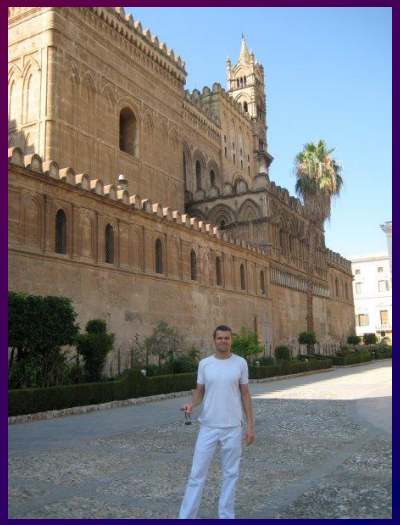
- Alejandro Pérez
- Yanli Zhang



Postdocs

- Robin Hayes (now AAAS Fellow)

External

- Martin Müser (Saarbrücken)