

Nuclear Quantum Effects and Introduction to Imaginary-Time Path Integrals

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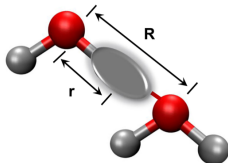
Dec 30, 2019

1 Introduction

2 Basics of Imaginary-time Path Integrals

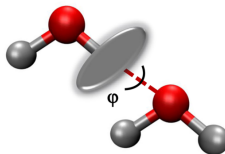
Isotope Effects in Water

Proton sharing and delocalization

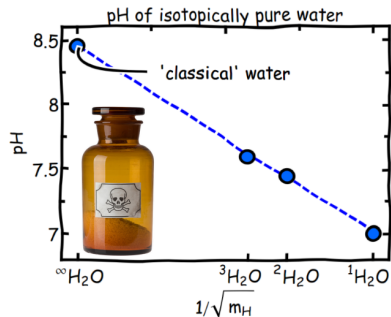
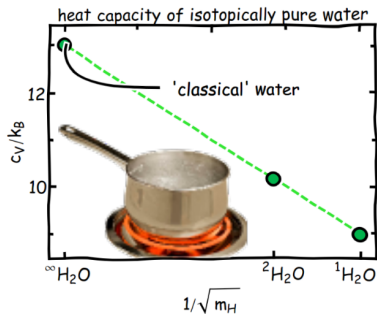


Strengthens hydrogen bonding, increases structure and slows the dynamics.

Hydrogen bond bending and distortion



Weakens hydrogen bonding, de-structures the liquid and speeds up dynamics

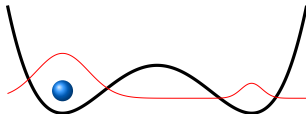


- The *thermal* de Broglie wavelength of a particle:

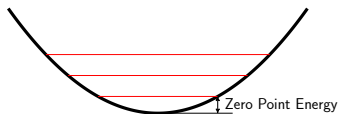
$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

for a hydrogen atom at 300 K, $\Lambda \approx 1.0 \text{ \AA}$.

- NQEs are important for any vibrational mode for which $\hbar\omega/k_B T > 1$. If $T = 300 \text{ K}$, $\omega \approx 208 \text{ cm}^{-1}$.
- NQEs include tunneling and zero-point motion.



Quantum Tunneling



Zero Point Motion

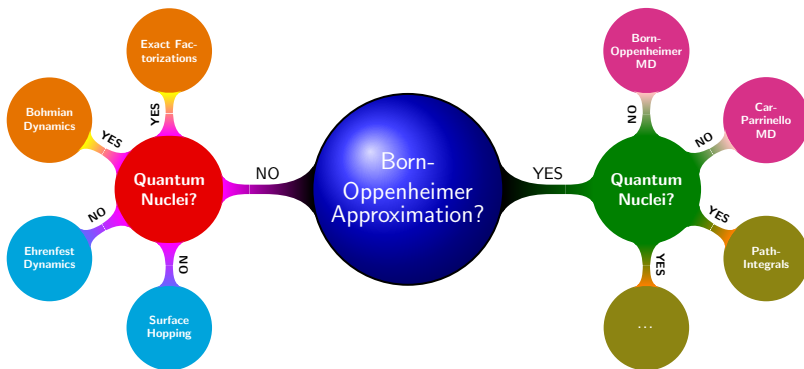
other nuclear quantum effects: exchange effects, quantum coherence. . .

How to model the dynamics of electrons and nuclei from *ab initio*?

The time-dependent Schrödinger equation:

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

In practice, *approximations* have to be made! ¹



¹ "Ab initio molecular dynamics", Mariana Rossi, DFT Workshop 2017

1 Introduction

2 Basics of Imaginary-time Path Integrals

For a single particle moving in one spatial dimension potential ²

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

The quantum partition function

$$\begin{aligned} Z &= \text{tr} \left[e^{-\beta \hat{\mathcal{H}}} \right] = \text{tr} \left[(e^{-\frac{\beta}{P} \hat{\mathcal{H}}})^P \right] = \text{tr} \left[(e^{-\beta_P \hat{\mathcal{H}}})^P \right] \\ &= \int dx_1 \langle x_1 | (e^{-\beta_P \hat{\mathcal{H}}})^P | x_1 \rangle \\ &= \int dx_1 \dots \int dx_P \langle x_1 | e^{-\beta_P \hat{\mathcal{H}}} | x_2 \rangle \dots \langle x_P | e^{-\beta_P \hat{\mathcal{H}}} | x_1 \rangle \end{aligned}$$

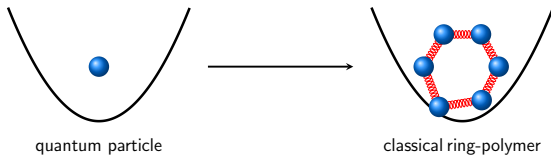
Note the connection between the quantum propagator and the density matrix,

$$\langle x' | e^{-i\hat{\mathcal{H}}t/\hbar} | x \rangle \quad \Rightarrow \quad \langle x' | e^{-\beta \hat{\mathcal{H}}} | x \rangle; \quad t = -i\beta\hbar$$

Hence the name *imaginary-time path integral*. By using the Trotter splitting³

$$\begin{aligned} e^{-\beta_P \hat{\mathcal{H}}} &= e^{-\beta_P \hat{V}/2} e^{-\beta_P \hat{T}} e^{-\beta_P \hat{V}/2} + \mathcal{O}(\beta_P^3) \\ \Rightarrow \quad \langle x_i | e^{-\beta_P \hat{\mathcal{H}}} | x_j \rangle &\approx \left(\frac{m}{2\pi\beta_P \hbar^2} \right)^{1/2} e^{-\beta_P \left[\frac{m}{2(\beta_P \hbar)^2} (x_i - x_j)^2 + \frac{1}{2} (V(x_i) + V(x_j)) \right]} \end{aligned}$$

$$\begin{aligned}
 Z &= \text{tr} \left[e^{-\beta \hat{\mathcal{H}}} \right] \\
 &= \lim_{P \rightarrow \infty} \int dx_1 \dots \int dx_P \left(\frac{m}{2\pi\beta_P \hbar^2} \right)^{P/2} \exp \left\{ -\beta_P \underbrace{\sum_{i=1}^P \left[\frac{m}{2(\beta_P \hbar)^2} (x_{i+1} - x_i)^2 + V(x_i) \right]}_{V_{\text{eff}}(x_1, \dots, x_P)} \right\} \Big|_{x_{P+1}=x_1}
 \end{aligned}$$



- Maps the *quantum partition function* to the *configuration integral* of classical ring-polymers.
- **EXACT** when $P \rightarrow \infty$. Reduce to classical partition function when $P = 1$.
- The integral can be sampled with Monte Carlo method (PIMC, not covered in this talk), but for MD we need *momenta*!

² "Statistical Mechanics: Theory and Molecular Simulation", Mark E. Tuckerman

³ There are higher-order splitting techniques.

Expectation Values from Path Integral

For a Hermitian operator \hat{A} , the expectation value follows,

$$\langle \hat{A} \rangle = \frac{1}{Z} \text{tr} [\hat{A} e^{-\beta \hat{\mathcal{H}}}] = \frac{1}{Z} \text{tr} [\hat{A} (e^{-\beta_P \hat{\mathcal{H}}})^P]$$

if \hat{A} is purely a function of **position operator** \hat{x} , i.e. $\hat{A}(\hat{x}) |x\rangle = a(x) |x\rangle$, then ⁴

$$\langle \hat{A} \rangle = \frac{1}{Z} \lim_{P \rightarrow \infty} \int dx_1 \dots \int dx_P \left(\frac{m}{2\pi\beta_P \hbar^2} \right)^{P/2} \left(\frac{1}{P} \sum_{i=1}^P a(x_i) \right) \exp \left\{ -\beta_P \sum_{i=1}^P \left[\frac{m}{2(\beta_P \hbar)^2} (x_{i+1} - x_i)^2 + V(x_i) \right] \right\} \Bigg|_{x_{P+1}=x_1}$$

- $a(x_1, \dots, x_P) = \frac{1}{P} \sum_{i=1}^P a(x_i)$ is referred to as the *estimator* of $\langle \hat{A} \rangle$.
- If \hat{A} is a function of **momentum operator** \hat{p} , then the **cyclic-path** condition $x_{P+1} = x_1$ is released, in which case one should resort to the so-called **open-path** path integral method.
- The thermodynamic functions, which may depend on both \hat{x} and \hat{p} , are exceptional because thermodynamic relations can be used. For example

$$E = \langle \hat{\mathcal{H}} \rangle = \left\langle \frac{\hat{p}^2}{2m} + V(\hat{x}) \right\rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

⁴ "Statistical Mechanics: Theory and Molecular Simulation", Mark E. Tuckerman

- The **primitive** energy estimator $\varepsilon_{\text{prim}}(x_1, \dots, x_P)$

$$\begin{aligned}\varepsilon_{\text{prim}}(x_1, \dots, x_P) &= \frac{P}{2\beta} - \sum_{i=1}^P \frac{mP}{2\beta^2 \hbar^2} (x_{i+1} - x_i)^2 + \frac{1}{P} \sum_{i=1}^P V(x_i) \\ &= \mathcal{K}_{\text{prim}} + \frac{1}{P} \sum_{i=1}^P V(x_i)\end{aligned}$$

- $\mathcal{K}_{\text{prim}}$ is the estimator for the quantum kinetic energy, which scale linearly with the number of beads P .
- The virial theorem:

$$\frac{P}{2\beta} - \left\langle \sum_{i=1}^P \frac{mP}{2\beta^2 \hbar^2} (x_{i+1} - x_i)^2 \right\rangle = \left\langle \frac{1}{2P} \sum_{i=1}^P x_i \frac{\partial V}{\partial x_i} \right\rangle$$

- The **virial** energy estimator $\varepsilon_{\text{vir}}(x_1, \dots, x_P)$ and virial kinetic energy estimator \mathcal{K}_{vir} ⁵

$$\begin{aligned}\varepsilon_{\text{vir}}(x_1, \dots, x_P) &= \frac{1}{P} \sum_{i=1}^P \frac{1}{2} x_i \frac{\partial V}{\partial x_i} + \frac{1}{P} \sum_{i=1}^P V(x_i) \\ &= \frac{1}{2\beta} + \frac{1}{P} \sum_{i=1}^P \frac{1}{2} (x_i - x_c) \frac{\partial V}{\partial x_i} + \frac{1}{P} \sum_{i=1}^P V(x_i)\end{aligned}$$

⁵ "Statistical Mechanics: Theory and Molecular Simulation", Mark E. Tuckerman

Insert P Gaussian integral into Z : $\left(\frac{\beta}{2\pi\tilde{m}}\right)^{1/2} \int d\mathbf{p} e^{-\beta p^2/2\tilde{m}} = 1$

$$Z = \left(\frac{1}{2\pi\hbar}\right)^P \prod_{i=1}^P \sqrt{\frac{m}{\tilde{m}_i}} \lim_{P \rightarrow \infty} \int dx_1 \dots \int dx_P \int d\mathbf{p}_1 \dots \int d\mathbf{p}_P$$

More general: $\prod_i \tilde{m}_i \Rightarrow \det[\mathbf{M}]$

$$\exp \left\{ -\beta_P \sum_{i=1}^P \left[\frac{p_i^2}{2\tilde{m}_i} + \frac{m}{2(\beta_P \hbar)^2} (x_{i+1} - x_i)^2 + V(x_i) \right] \right\}$$

real physical mass

$$= C \lim_{P \rightarrow \infty} \int d\mathbf{x}^P \int d\mathbf{p}^P \exp[-\beta_P H_P(\mathbf{x}, \mathbf{p})]$$

\tilde{m}_i need **not** be physical. More general form: $\frac{1}{2} \mathbf{p}^T \mathbf{M}^{-1} \mathbf{p}$, where \mathbf{M} is the mass matrix, and $\mathbf{p} = (p_1, \dots, p_P)$.

- PIMD trajectories are obtained by integrating Hamilton's classical equation of motion

$$\frac{dp_i}{dt} = + \frac{\partial H_P(\mathbf{x}, \mathbf{p})}{\partial x_i}; \quad \frac{dx_i}{dt} = - \frac{\partial H_P(\mathbf{x}, \mathbf{p})}{\partial p_i}$$

- $\beta_P H_P(\mathbf{x}, \mathbf{p}) \Rightarrow \beta (H_P(\mathbf{x}, \mathbf{p})/P)$, which affects the dynamics but not the statistics.
- Different mass matrices give the same static average, only dynamics will be changed.
- Mathematically, the main difference between PIMD, PACMD and RPMD is the choice of the mass matrix. Physically, they differ dramatically!

Multiparticle Generalization

For a system of N *distinguishable* nuclei,⁶

$$\hat{\mathcal{H}}_P = \sum_I^N \frac{\mathbf{p}_I^2}{2m_I} + \hat{V}(\mathbf{x}_1, \dots, \mathbf{x}_N),$$

Potential energy: could be from empirical potential or from *ab initio* calculations. *Born-Oppenheimer approximation* implicitly implied.

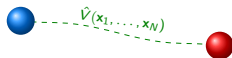
The PIMD Hamiltonian is

$$H_P(\{\mathbf{x}\}, \{\mathbf{p}\}) = \sum_{I=1}^N \sum_{i=1}^P \left[\frac{(\mathbf{p}_I^i)^2}{2\tilde{m}_I^i} + \frac{1}{2} m_I \omega_P^2 (\mathbf{x}_I^{i+1} - \mathbf{x}_I^i)^2 \right] + \sum_{i=1}^P \hat{V}(\mathbf{x}_1^i, \dots, \mathbf{x}_N^i)$$

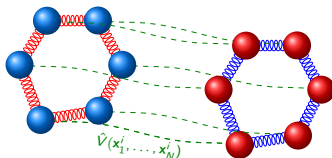
sum over nuclei index

sum over bead index

$$\omega_P = P k_B T / \hbar$$



quantum particle



classical ring-polymers

⁶We are neglecting the exchange effect, which is generally fine for nuclei (unless treating 4 K Helium) but not for electrons.

Terminologies and Properties of the Ring-Polymer

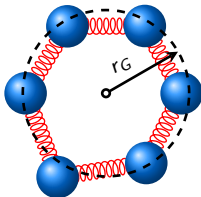
- **Radius of Gyration** – the spread in imaginary time. For a free particle the root mean square radius of gyration is:

$$\langle r_G^2(T) \rangle^{1/2} = \frac{\Lambda(T)}{\sqrt{8\pi}} \quad \Lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

- **Bead to bead distance** –
For a free particle the average is:

$$\sqrt{\frac{\beta \hbar^2}{Pm}}$$

Note the distance decreases as P increases.



- **Centroid** – the center of the Ring-Polymer.

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

- **Bead spring constants**⁷ – determined by $m\omega_P^2$

$$\omega_P = \frac{1}{\beta_P \hbar} = P k_B T / \hbar$$

The overall object is referred to as an *Imaginary Time Path* or a *Ring-Polymer*.

⁷In some textbooks, $\omega_P = \sqrt{P} k_B T / \hbar$ if the Hamiltonian is $H_P(\mathbf{x}, \mathbf{p})/P$

Ring-Polymer Normal Modes

- Normal Modes:** – the ring-polymer potential can be diagonalized

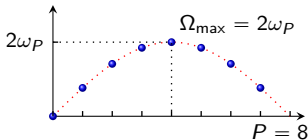
$$\sum_{i=1}^P \frac{1}{2} m \omega_P^2 (x_{i+1} - x_i)^2 \iff \begin{aligned} \tilde{\mathbf{x}} &= \mathbf{U} \cdot \mathbf{x} \\ \mathbf{x} &= \mathbf{U}^T \cdot \tilde{\mathbf{x}} \end{aligned} \iff \sum_{j=1}^P \frac{1}{2} m \Omega_j^2 \tilde{x}_j^2;$$

where \mathbf{x} is the bead **Cartesian coordinate** and $\tilde{\mathbf{x}}$ is the **normal mode** coordinate.

- \tilde{x}_1 corresponds to the centroid motion and $\Omega_1 = 0$.
- The transformation $\tilde{\mathbf{x}} \Leftrightarrow \mathbf{x}$ can be done with FFT.⁸
- The normal mode frequencies⁹

$$\Omega_j = 2\omega_P \sin\left(\frac{(j-1)\pi}{P}\right)$$

e.g. $P = 8$



- The matrix element U_{kj} of the unitary transformation matrix \mathbf{U} for even P

$$\begin{cases} \sqrt{1/P}, & k = 1 \\ \sqrt{2/P} \cos\left(\frac{2\pi}{P}(j-1)(k-1)\right), & 2 \leq k \leq P/2 \\ \sqrt{1/P}(-1)^j, & k = P/2 + 1 \\ \sqrt{2/P} \sin\left(\frac{2\pi}{P}(j-1)(k-1)\right), & P/2 + 2 \leq k \leq P \end{cases}$$

$$\text{and } \tilde{x}_k = \sum_{j=1}^P U_{kj} x_j.$$

- Note if we choose $\beta_P H_P \Rightarrow \beta(H_P/P)$, then

$$\begin{aligned} \tilde{\mathbf{x}} &= \frac{1}{\sqrt{P}} \mathbf{U} \cdot \mathbf{x} \\ \mathbf{x} &= \sqrt{P} \mathbf{U}^T \cdot \tilde{\mathbf{x}} \end{aligned}$$

⁸J. Chem. Phys., **104**, 2828(1996).

⁹This reminds me of the phonon dispersion of 1-D atomic chain
Q.J. Zheng (D.P. USTC)

Initializing PIMD — Positions and Momenta

$$H_P(\{\mathbf{x}\}, \{\mathbf{p}\}) = \sum_{I=1}^N \sum_{i=1}^P \left[\frac{(\mathbf{p}_I^i)^2}{2\tilde{m}_I^i} + \frac{1}{2} m_I \omega_P^2 (\mathbf{x}_I^{i+1} - \mathbf{x}_I^i)^2 \right] + \sum_{i=1}^P \hat{V}(\mathbf{x}_1^i, \dots, \mathbf{x}_N^i)$$

- To initialize PIMD requires specification of $3NP$ positions and $3NP$ momenta.

MOMENTA

- We inserted P Gaussians when introducing momenta

$$\left(\frac{\beta}{2\pi\tilde{m}} \right)^{1/2} \int d\mathbf{p} e^{-\beta \mathbf{p}^2 / 2\tilde{m}}$$

- We can then sample the momentum of each bead from a Gaussian distribution with

$$\bar{\mathbf{p}} = 0$$
$$\sigma_P = \sqrt{\frac{\tilde{m}}{\beta_P}} = \sqrt{\tilde{m} k_B P T}$$

POSITIONS

- 1 Start all beads at the same positions and equilibrate.
 - RP will expand under NVE, T will drop.
 - Strong Thermostatting is need!
- 2 Sample from the **free** ring-polymer distribution.
 - The only potential is the harmonic springs.
 - In normal mode coordinates

$$\sum_{j=1}^P \frac{1}{2} m \Omega_j^2 \tilde{x}_j^2 \Rightarrow \int d\tilde{x}_j e^{-\beta_P \left(\frac{1}{2} m \Omega_j^2 \tilde{x}_j^2 \right)}$$

- $\bar{\tilde{x}}_j = 0$ and $\sigma_{\tilde{x}_j} = \sqrt{\frac{1}{\beta_P m \Omega_j^2}}$.
- In practice, RP slightly too extended.

Convergence of Standard Path Integral MD

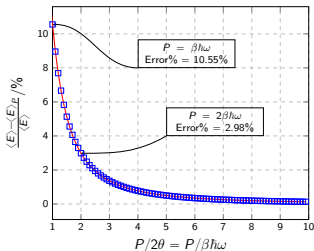
For the 1D harmonic oscillator: $V(x) = \frac{1}{2}m\omega x^2$, the RP potential in the normal-mode coordinates

$$\sum_{i=1}^P \left[\frac{m}{2(\beta_P \hbar)^2} (x_{i+1} - x_i)^2 + V(x_i) \right] \Rightarrow \sum_{i=1}^P \frac{1}{2} m (\Omega_i^2 + \omega^2) \tilde{x}_i^2$$

then $\langle \tilde{x}_i^2 \rangle = 1/\beta_P m (\Omega_i^2 + \omega^2)$, the energy of the harmonic oscillator $\langle E \rangle_P$

$$\begin{aligned} \langle E \rangle_P &= \langle T \rangle_P + \langle V \rangle_P = 2 \langle V \rangle_P = 2 \cdot \frac{1}{2} m \omega^2 \langle x^2 \rangle = \frac{m \omega^2}{P} \sum_{i=1}^P \langle x_i^2 \rangle = \frac{m \omega^2}{P} \sum_{i=1}^P \langle \tilde{x}_i^2 \rangle \\ &= \frac{\theta}{\beta} \sum_{i=1}^P \frac{\theta}{P^2 \sin^2 \left(\frac{(i-1)\pi}{P} \right) + \theta^2} \quad (\theta = \beta \hbar \omega / 2) \end{aligned}$$

the exact solution is $\langle E \rangle = \frac{\theta}{\beta} \coth(\theta)$



- Commonly used convergence criteria:
 $P > \hbar \omega_{\max} / k_B T$
- Standard PIMD converges as $1/P^2$.
- Some properties converges faster, e.g. RDF converges fast but heat capacity very slowly.
- Methods exist to accelerate the convergence, e.g. PI + GLE.

For the 1D harmonic oscillator: $V(x) = \frac{1}{2}m\omega x^2$, the normal mode frequencies

$$\tilde{\Omega}_i = \sqrt{\Omega_i^2 + \omega^2}; \quad \Omega_i = 2\omega_P \sin\left(\frac{(i-1)\pi}{P}\right)$$

Hence the highest frequency is

$$\tilde{\Omega}_{\max} = \sqrt{\Omega_{\max}^2 + \omega^2} = \sqrt{4\omega_P^2 + \omega^2}$$

If we use the typical convergence criteria: $P = \alpha\hbar\omega/k_B T$, where $\alpha > 1$ determines how accurate the calculation is.

$$\tilde{\Omega}_{\max} = (4\alpha^2 + 1)^{\frac{1}{2}}\omega$$

-
- For $\alpha = 1$, the highest frequency in PIMD is $\sqrt{5}$ times larger than classical MD.
 - For a *naive* implementation of PIMD, the time step should be $\sqrt{5}$ times smaller than classical MD.
 - Methods to allow bigger time-steps:
 - 1 Scale the normal mode masses so they all oscillate at the same frequency.
 - 2 Multiple time-scale molecular dynamics: use smaller time-steps for bead forces.
 - 3 Use an integrator where the free ring polymer is evolved exactly.

CMD

- Approximate quantum **dynamics**
- Path centroid idea

$$m\ddot{x}_c = \left\langle \delta(x_0 - x_c) \frac{-1}{P} \sum_{i=1}^P \frac{\partial V(x_i)}{\partial x_i} \right\rangle$$

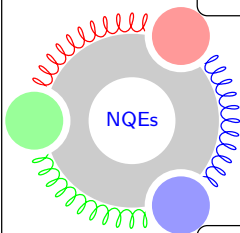
- Sample the whole configuration space available to the non-centroid modes at each given position of centroid x_0 .

(PA)CMD

- PIMD with **adiabatic decoupling** of centroid and non-centroid motions.
- **No** thermostat for the centroid mode.
- Thermostatting for noncentroid mode as in PIMD.
- Must sample initial conditions.

PIMD

- Static **equilibrium** properties.
- Need to efficiently and ergodically sample the phase surface.
 - Thermostatting
 - Coordinate transformation and bead masses scaling



RPMD


- Approximate quantum **dynamics**
- PIMD with **physical** bead masses.
- Thermostats should **not** be used.
- Must sample initial conditions.

¹⁰ *J. Chem. Phys.*, **130**, 194510(2009);
J. Chem. Phys., **129**, 074501(2008);

The RP Hamiltonian in the normal-mode coordinates

$$\begin{aligned}
 H_P(\{\tilde{\mathbf{x}}\}, \{\tilde{\mathbf{p}}\}) &= \sum_{i=1}^P \left[\frac{\tilde{p}_i^2}{2\tilde{m}_i} + \frac{1}{2} m \Omega_i^2 \tilde{x}_i^2 \right] + \sum_{i=1}^P V(x_i(\tilde{x}_1, \dots, \tilde{x}_P)) \\
 \Rightarrow \quad \tilde{m}_i \ddot{\tilde{x}}_i &= -m \Omega_i^2 \tilde{x}_i - \sum_{j=1}^P \frac{\partial V(x_j(\tilde{x}_1, \dots, \tilde{x}_P))}{\partial \tilde{x}_i} \\
 \Rightarrow \quad \tilde{m}_1 \ddot{\tilde{x}}_1 &= -\frac{1}{\sqrt{P}} \sum_{j=1}^P \frac{\partial V(x_j)}{\partial x_j}
 \end{aligned}$$

$= \sum_{j=1}^P \frac{\partial V(x_j)}{\partial x_j} U_{ji}^T$



- **PIMD** — scale the mass to bring all the frequencies to the same value ω_P .

$$\tilde{m}_1 = m, \quad \tilde{m}_i = 4 \sin^2 \left(\frac{(i-1)\pi}{P} \right) m \quad (2 \leq i \leq P)$$

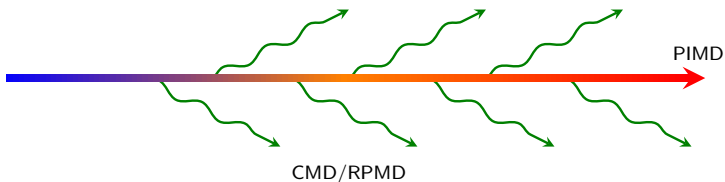
- **(PA)CMD** — adiabatic parameter $\gamma > 1$, shifting the noncentroid frequencies $\gamma\omega_P$ off the physical spectra ω_{\max} .

$$\tilde{m}_1 = m, \quad \tilde{m}_i = 4 \sin^2 \left(\frac{(i-1)\pi}{P} \right) m / \gamma^2 \quad (2 \leq i \leq P)$$

- **RPMD** — Use real masses for all the beads.

$$\tilde{m}_i = m, \quad (1 \leq i \leq P)$$

- CMD and RPMD are intended to provide approximations to quantum dynamics and not to efficiently sample the quantum phase space.
- The ergodicity problem can be circumvented by launching trajectories from many different choice of configurations and momenta.



- 1 Run a PIMD trajectory using an efficient thermostat scheme.
- 2 Pick configurations and momenta from the thermostatted trajectory and launch RPMD or CMD trajectories from them.
- 3 Ideally the separation in time between each should be determined by the correlation time of the properties in the system.

Thank you!