Speeding up path integral simulations

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Outline

- I. Ring polymer molecular dynamics
- 2. Ring polymer contraction
- 3. Conclusions and future work

I. Ring polymer molecular dynamics



$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j-1})^2 + V(q_j) \right] \text{ with } \beta_n = \beta/n \text{ and } \omega_n = 1/\beta_n \hbar.$$

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$$Z = \operatorname{tr} \left[e^{-\beta H} \right] = \operatorname{tr} \left[\left(e^{-\beta_n H} \right)^n \right] \text{ where } \beta_n = \beta/n.$$

So

$$Z = \int dq_1 \cdots \int dq_n \langle q_1 | e^{-\beta_n H} | q_2 \rangle \cdots \langle q_n | e^{-\beta_n H} | q_1 \rangle,$$

$$\langle q_{j-1} | e^{-\beta_n H} | q_j \rangle \simeq \langle q_{j-1} | e^{-\beta_n T} e^{-\beta_n V} | q_j \rangle$$

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$$\begin{aligned} \langle q_{j-1} | e^{-\beta_n H} | q_j \rangle &\simeq \langle q_{j-1} | e^{-\beta_n T} e^{-\beta_n V} | q_j \rangle \\ &= \frac{1}{2\pi\hbar} \int dp \, e^{-\beta_n p^2 / 2m - ip(q_j - q_{j-1})/\hbar - \beta_n V(q_j)} \\ &= \frac{1}{2\pi\hbar} \left(\frac{2\pi m}{\beta_n} \right)^{1/2} e^{-\beta_n \left[m\omega_n^2 (q_j - q_{j-1})^2 / 2 + V(q_j) \right]} \end{aligned}$$

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Path Integral Molecular Dynamics:

PIMD uses the ring polymer trajectories

$$\dot{\mathbf{q}} = + \frac{\partial H_n(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}} \qquad \dot{\mathbf{p}} = - \frac{\partial H_n(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}}$$

as a sampling tool to calculate *exact* values of static equilibrium properties such as

$$\langle A \rangle = \frac{1}{Z} \operatorname{tr} \left[e^{-\beta H} A \right].$$

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Ring Polymer Molecular Dynamics:

RPMD uses the same trajectories to calculate *approximate* Kubo-transformed correlation functions of the form

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \operatorname{tr} \left[e^{-(\beta - \lambda)H} A(0) e^{-\lambda H} B(t) \right].$$

Ring Polymer Molecular Dynamics

The RPMD approximation to

$$\tilde{c}_{AB}(t) = \frac{1}{\beta Z} \int_0^\beta d\lambda \operatorname{tr} \left[e^{-(\beta - \lambda)H} A(0) e^{-\lambda H} B(t) \right]$$

is simply

$$\tilde{c}_{AB}(t) \simeq \frac{1}{(2\pi\hbar)^n Z} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \, e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} A_n(\mathbf{q}_0) B_n(\mathbf{q}_t),$$

where

$$A_n(\mathbf{q}) = \frac{1}{n} \sum_{j=1}^n A(q_j) \text{ and } B_n(\mathbf{q}) = \frac{1}{n} \sum_{j=1}^n B(q_j).$$

Classical molecular dynamics in an extended phase space!

Properties of RPMD:

- 1. Exact in the limit as $t \to 0$.
- 2. Exact in the classical (high temperature) limit.
- 3. Exact in the harmonic limit (for linear A and/or B).
- 4. Exact when A = 1 (for all B).
- 5. Correct time-reversal, time-translation, and detailed balance symmetries.

tunneling

(exact QM rate coefficient for a parabolic barrier)



zero point energy



(exact QM rate coefficient for a parabolic barrier) (exact QM $Z = e^{-\beta E_0}$ in the low T limit)



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But it neglects QM interference effects in the real-time dynamics (no $e^{\pm iHt/\hbar}$).

Applications of RPMD:

- 1. Quantum diffusion in liquid para-hydrogen (2005).
- 2. Quantum diffusion in liquid water (2005).
- 3. Neutron scattering from liquid para-hydrogen (2006).
- 4. Proton transfer in a polar solvent (2008).
- 5. Diffusion of H isotopes in water and ice (2008).
- 6. Gas phase chemical reaction rates (2009).
- 7. Dynamics of the solvated electron (2009).
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Quantum diffusion in liquid $p-H_2$:





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$$S_{\rm inc}(\kappa,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} F_s(\kappa,t) dt;$$
$$F_s(\kappa,t) \simeq e^{-\kappa^2 \gamma(t)}; \qquad \gamma(t) = -i\frac{\hbar t}{2m} + \frac{1}{3} \int_0^t (t-t') c_{\mathbf{v}\cdot\mathbf{v}}(t') dt'.$$

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Gas phase chemical reaction rates:



Quantum versus classical rates for the $H+H_2$ reaction on the LSTH potential between 200 and 2000 K.

$$k(T) = \frac{1}{Q_r(T)} \int_0^\infty \tilde{c}_{f \cdot f}(t) dt$$

2. Ring polymer contraction

(a) A RPMD simulation requires around n times the computational effort of a classical MD simulation:

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{j=1}^n \left[\frac{p_j^2}{2m} + \frac{1}{2} m \omega_n^2 (q_j - q_{j-1})^2 + V(q_j) \right]$$

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(b) And a converged calculation requires $n > \beta \hbar \omega_{\text{max}}$, where ω_{max} is the highest frequency present in the problem:





Ring polymer contraction:

Ring polymer contraction:

$$\omega_{\pm 4} \simeq 8\pi/\beta\hbar$$

(etc.)

•

$\omega_{\pm 3} \simeq 6\pi/\beta\hbar$
$\omega_{\pm 2} \simeq 4\pi / \beta \hbar$
$\omega_{\pm 1} \simeq 2\pi/\beta\hbar$
$\omega_0 = 0$

 $\sum_{j=1}^{n} V_{\text{inter}}(q_j)$

Ring polymer contraction:

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Some results for the SPC/F water model:

$$\begin{split} V_{\text{intra}} &= \sum_{I=1}^{N} V_{\text{intra}}^{I} \\ V_{\text{intra}}^{I} &= \frac{a}{2} \left(\delta r_{OH}^{2} + \delta r_{OH'}^{2} \right) + \frac{b}{2} \delta r_{HH'}^{2} + c \left(\delta r_{OH} + \delta r_{OH'} \right) \delta r_{HH'} + d \delta r_{OH} \delta r_{OH'}. \end{split}$$

$$V_{\text{inter}} = \sum_{I=1}^{N} \sum_{J>I}^{N} V_{\text{inter}}^{IJ}$$

$$V_{\text{inter}}^{IJ} = 4\epsilon \left[\left(\frac{\sigma}{r_{IJ}} \right)^{12} - \left(\frac{\sigma}{r_{IJ}} \right)^6 \right] + \sum_{i \in I}^3 \sum_{j \in J}^3 \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

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$$V_{\text{inter}}^{IJ} = 4\epsilon \left[\left(\frac{\sigma}{r_{IJ}} \right)^{12} - \left(\frac{\sigma}{r_{IJ}} \right)^{6} \right] \left(+ \sum_{i\in I}^{3} \sum_{j\in J}^{3} \frac{q_{i}q_{j}}{4\pi\epsilon_{0}r_{ij}} \right)^{6} \right]$$

Electrostatic interactions dominate the calculation *(Ewald sum)*.

O-O radial distribution function (*PIMD*):

Velocity autocorrelation function (RPMD):

$n_{ES} + n_{LJ}$	$D (\text{\AA}^2 \text{ ps}^{-1})$	
1+3	0.364(3)	
3+5	0.395(3)	
5+7	0.397(3)	
Full	0.400(3)	

A refinement:

- (a) Contracting V_{inter} is a bit naive: Coulomb and Lennard-Jones potentials also contain some "hard" short-range components.
- (b) If we could remove these components, perhaps we could contract the ring polymer all the way to its centroid, and evaluate the remaining long-range interactions with purely classical effort:

$$V_{\text{inter}}(q) = V_S(q) + V_L(q)$$
$$\sum_{j=1}^n V_L(q_j) \simeq n V_L(q_c)$$
$$q_c = \frac{1}{n} \sum_{j=1}^n q_j$$

Fractional error in the centroid approximation to the Coulomb interaction between two $\mathcal{H}^{\delta+}$ ring polymers at 298 K as a function of $r_{ij}^{(c)}$, compared with the asymptotic result

$$\Delta V(r_{ij}^{(c)})/nV(r_{ij}^{(c)}) \sim \frac{1}{\sqrt{15}} (r_{ij}^G/r_{ij}^{(c)})^2$$

The centroid approximation is indeed fine for the longrange part of the Coulomb potential, but it is no good at short range.

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So let's split the Coulomb potential into short- and long-range parts:

$$V(r_{ij}) = V_S(r_{ij}) + V_L(r_{ij})$$
$$V_S(r_{ij}) = [1 - f(r_{ij})] V(r_{ij})$$
$$V_L(r_{ij}) = f(r_{ij}) V(r_{ij})$$
$$f(r_{ij}) \simeq \operatorname{erf}(\sqrt{\pi}r_{ij}/\sigma)$$

And only apply the centroid approximation to the long-range part:

Now the error can be systematically reduced for all $r_{ij}^{(c)}$ simply by increasing the cutoff radius σ .

σ (Å)	D (Å ² ps ⁻¹)
3	0.402(3)
4	0.397(3)
5	0.399(3)
∞	0.400(3)

And since all electrostatic interactions beyond $r_{ij} = \sigma$ are evaluated on the ring polymer centroid it gives a method with purely classical computational effort in the limit of infinite system size:

3. Conclusions and future work

- 1. We can now obtain well-converged path-integral results for simple point charge water models with little more than classical computational effort in the limit of large system size.
- 2. We have also recently developed a ring polymer contraction scheme for *polarizable* water models, so that we can look beyond the homogeneous liquid.
- 3. Lots of interesting applications should now be possible (to the surfaces of water and ice and other interfaces, the water phase diagram, aqueous solvation dynamics, and so on). Eg:

A melting point simulation:

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References

- An efficient ring polymer contraction scheme for imaginary time path integral simulations. T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. 129, 024105 (2008).
- A refined ring polymer contraction scheme for systems with electrostatic interactions. T. E. Markland and D. E. Manolopoulos, *Chem. Phys. Lett.* 464, 256 (2008).
- A fast path integral method for polarizable force fields. G. S. Fanourgakis, T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. 131, 094102 (2009).