

Fast path integral simulations using ring polymer contraction

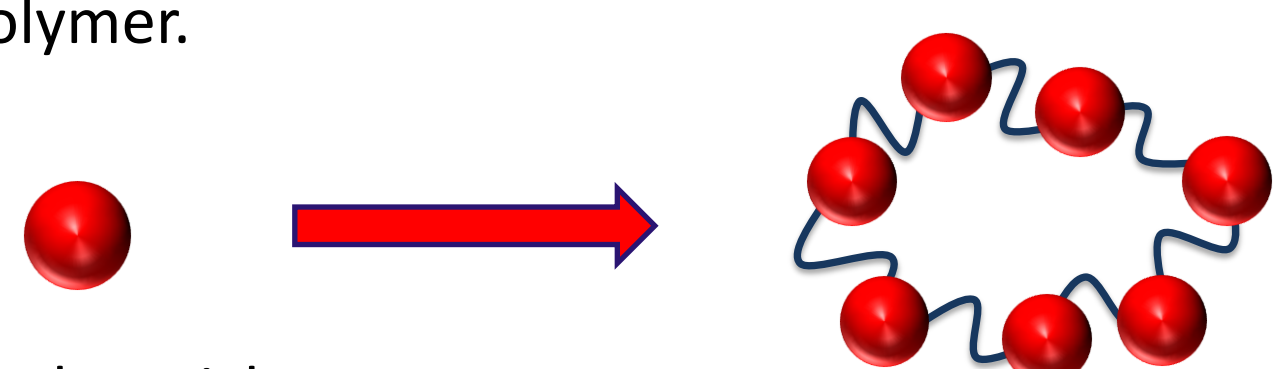
Thomas E. Markland and David E. Manolopoulos



Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK

Introduction

- When light particles are present or at low temperatures including quantum mechanical effects (zero-point energy and tunnelling) in simulations is desirable.
- Path Integral Monte Carlo (PIMC) and Path Integral Molecular Dynamics (PIMD) simulations allow these quantum mechanical effects to be included to calculate exact static equilibrium properties.
- These techniques exploit the isomorphism between the quantum mechanical partition function (Z) of a single particle and the classical partition function of a fictitious ring polymer.



Classical Particle

Ring Polymer (n beads)

$$Z = \text{tr} \left[e^{-\beta \hat{H}} \right] = \lim_{n \rightarrow \infty} \left[\frac{1}{2\pi\hbar} \int d\mathbf{p} \int d\mathbf{q} e^{-\beta_n H_n(\mathbf{p}, \mathbf{q})} \right]$$

$$H_n(\mathbf{p}, \mathbf{q}) = \sum_{k=1}^n \left(\frac{p_k^2}{2m} + V(q_k) + \frac{m}{2\beta_n^2 \hbar^2} (q_k - q_{k-1})^2 \right)$$

n beads ("copies" of classical system) Classical Hamiltonian for each bead Harmonic springs between each bead

- The Ring Polymer Molecular Dynamics (RPMD)⁵ and Centroid Molecular Dynamics (CMD)⁶ approaches also rely on this formalism to approximate quantum dynamics.
- Because n beads ("copies" of the classical system) are required path integral calculations are around n times more expensive than the corresponding classical simulation.

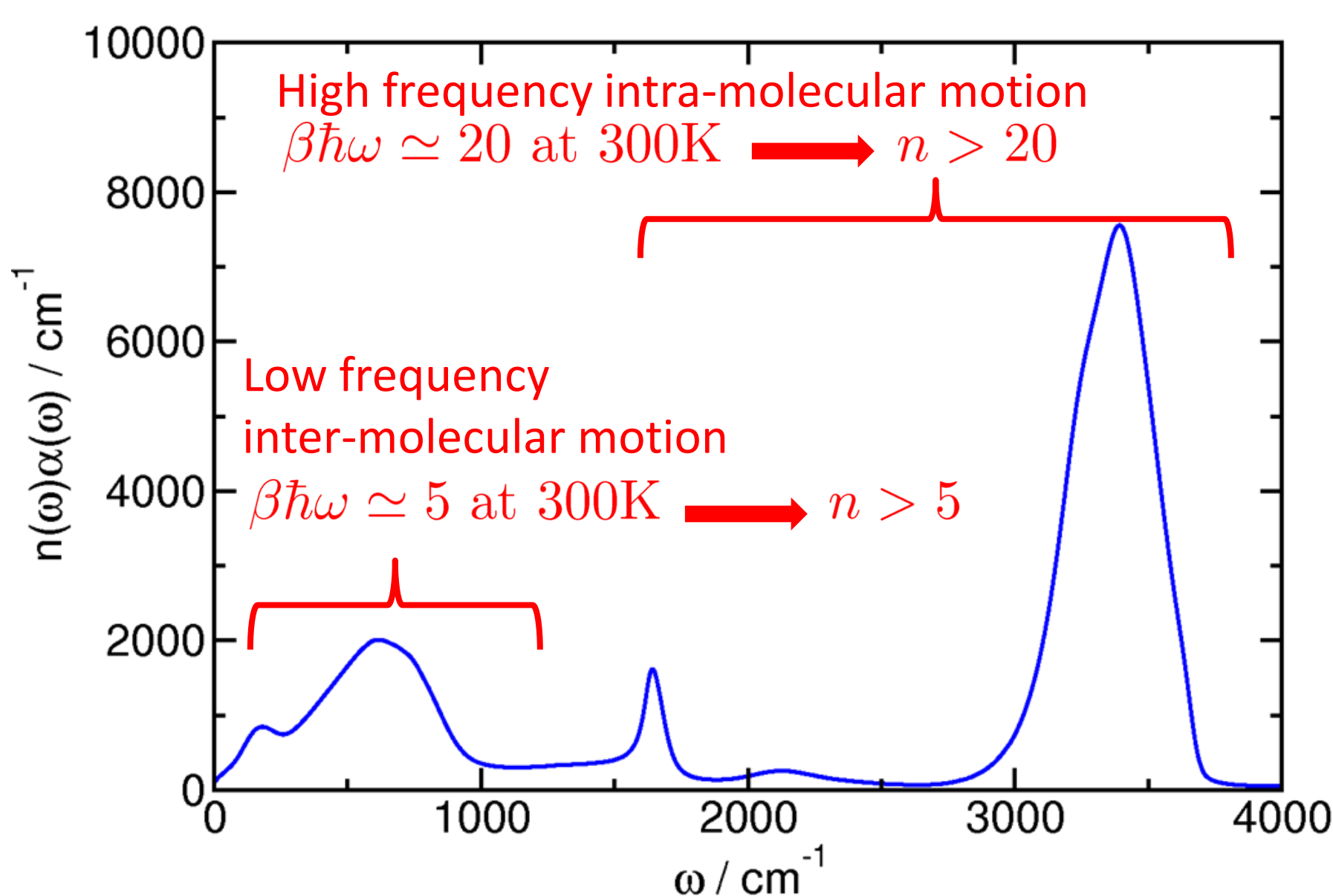
Can the computational cost be reduced?

- The number of beads required for convergence can be estimated by the condition:

$$n > \beta \hbar \omega_{max}$$

Where ω_{max} is the highest frequency present in the system.

- Below is infra-red dipole absorption spectrum of liquid water showing the different frequencies present.



- Due to the differing inter and intra-molecular frequencies rigid water simulations are typically only 6 times more expensive than a classical calculation whereas flexible water simulations are between 24 and 32 times more expensive.

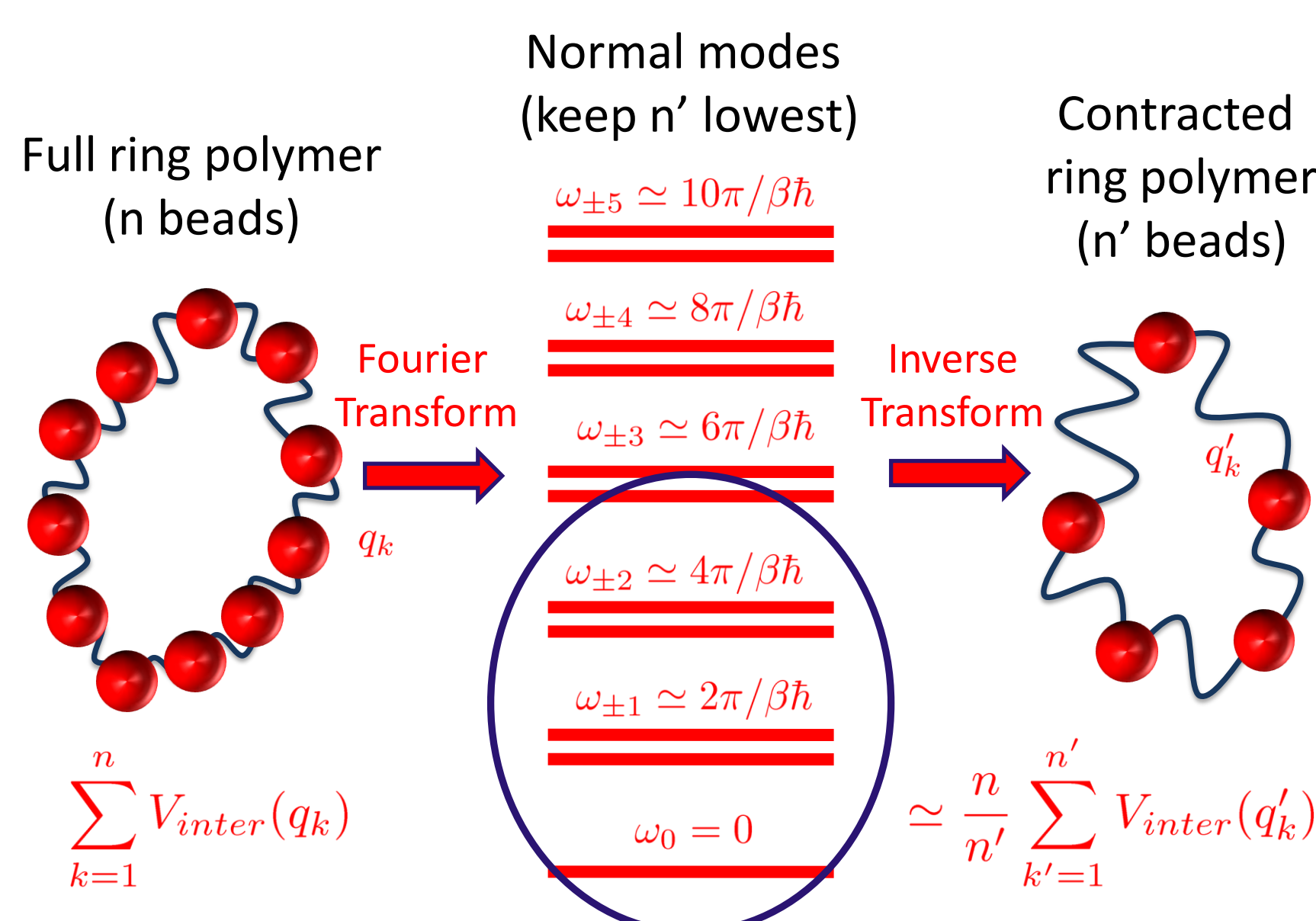
- But it seems wasteful to calculate the computationally costly but lower frequency inter-molecular interactions 32 times since if we were to simulate them alone we would only be required to calculate them 6 times.

- Therefore we have developed a method to allow less beads to be used for the more slow-varying interactions (such as the inter-molecular interactions) while still using the full number for the rapidly varying ones.

Ring Polymer Contraction

- If it is possible to split the Hamiltonian into rapidly-varying and slowly-varying parts then ring polymer contraction can be used to dramatically reduce the cost of the path integral simulation. To perform this splitting many of the ideas developed for use in multiple time stepping of simulations can be exploited.
- The ring polymer contraction method generates a reduced set of points on which the energy and forces of the low frequency (slowly varying) part of the potential can be evaluated.

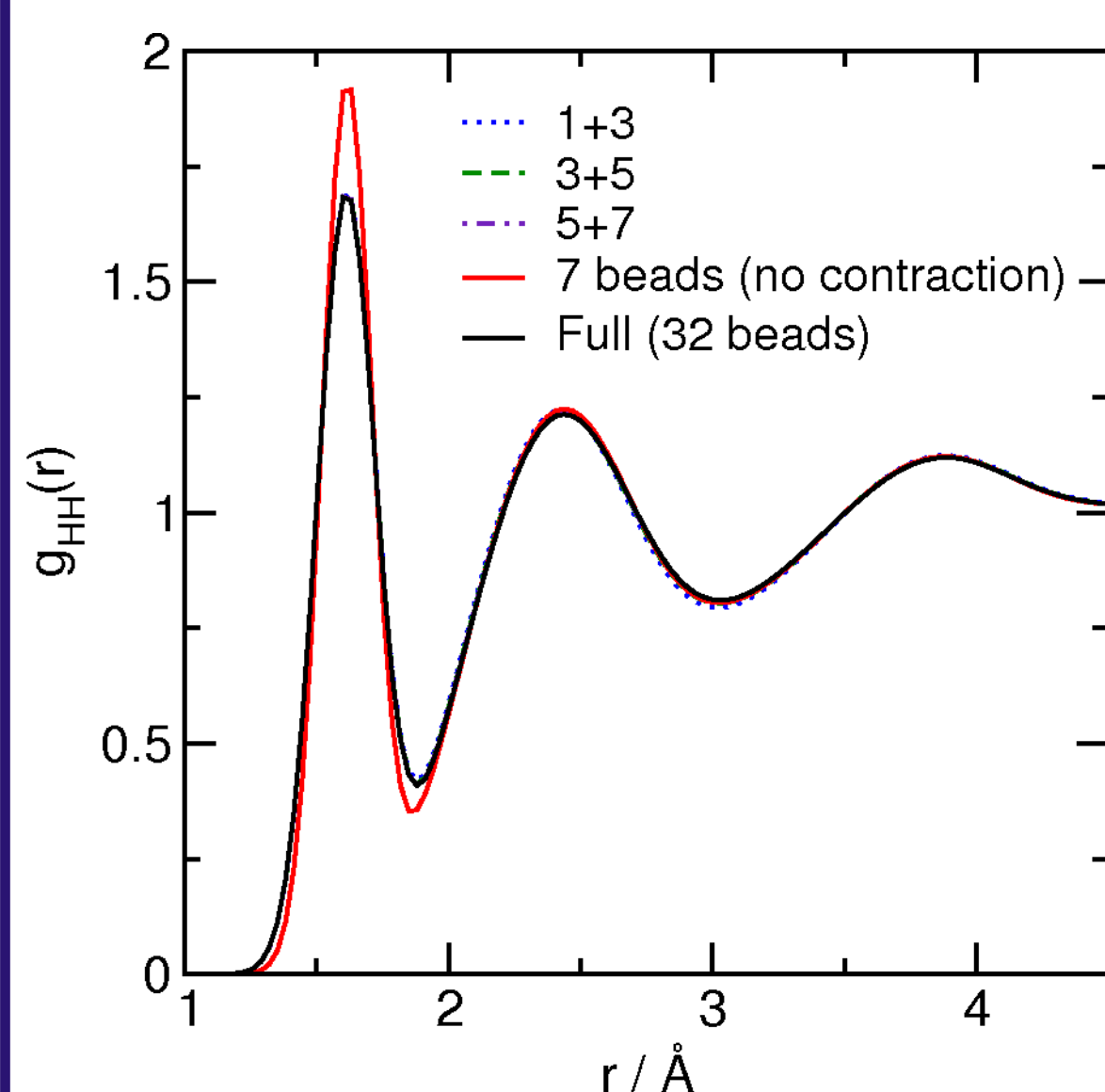
The Ring Polymer Contraction Method



- Forces can be easily calculated from the contracted ring polymer potential leading to a conserved approximate Hamiltonian and therefore formally perfect energy conservation¹.
- When $n'=1$ the ring polymer contraction method is just equivalent to evaluating all interactions at the ring polymer centroid (centre of mass). As $n' \rightarrow n$ the exact path integral result is obtained.
- Consider as an example the SPC/F model of liquid water. We split the potential into intra and inter-molecular components

$$V = V_{intra} + V_{inter}$$

and evaluate V_{inter} on the contracted polymer while V_{intra} is still evaluated on all 32 beads.



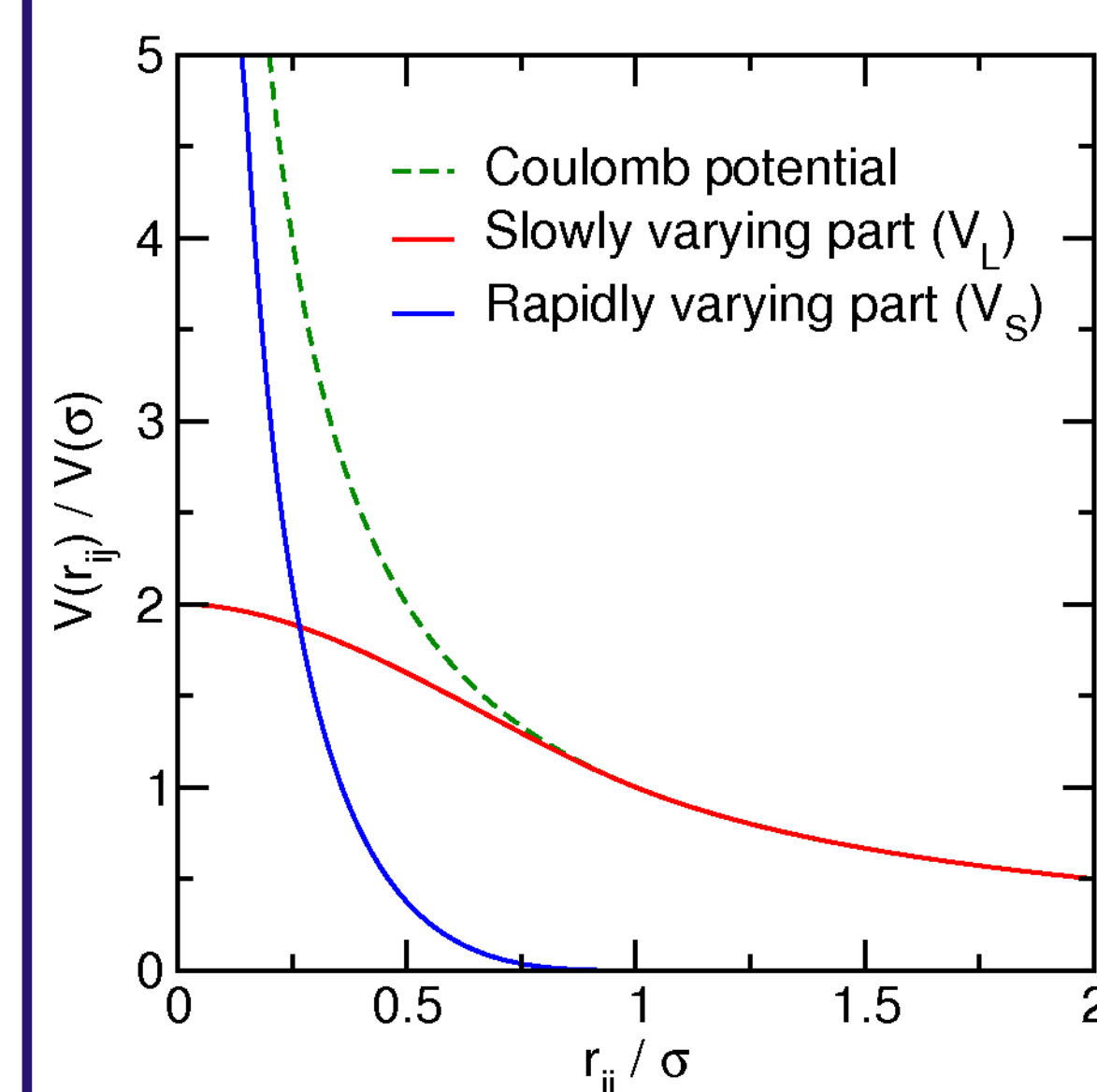
Method	$\Delta V_{intra} / \%$	$\Delta V_{inter} / \%$	$\Delta T / \%$	$\Delta D / \%$
1+3	0.03	1.7	1.5	9.0
3+5	0.03	0.6	0.6	1.2
5+7	0.00	0.3	0.3	0.8
7 bead	31	0.3	7.6	1.3

Above: Table showing the percentage error in the intra and inter-molecular potential (V) energy, the virial kinetic (T) energy and the diffusion constant (D) calculated using the RPMD method relative to a full 32 bead path integral simulation of SPC/F water at 300K. A seven bead calculation without ring polymer contraction is shown for comparison.

- By splitting of the potential into inter and intra-molecular parts path integral simulations of flexible water can be performed at the same computational cost as rigid water simulations¹.

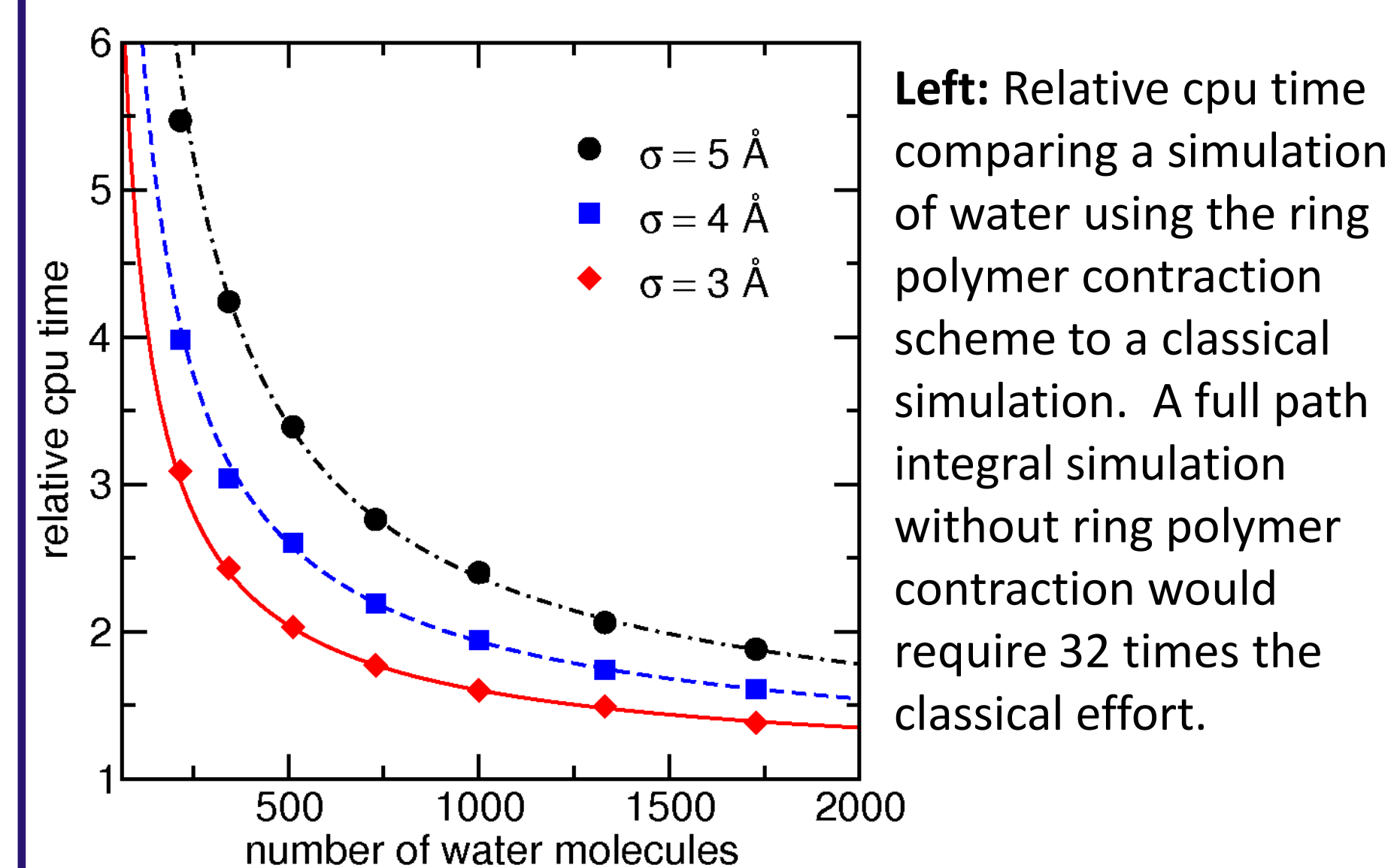
Splitting the electrostatic potential

- We can improve the efficiency of path integral simulations even more by also splitting the inter-molecular coulomb interactions into rapidly and slowly varying parts².



$\sigma / \text{\AA}$	$\Delta V_{intra} / \%$	$\Delta V_{inter} / \%$	$\Delta T / \%$	$\Delta D / \%$
3	0	0.4	0.5	0.5
4	0	0.02	0.1	0.8
5	0	0.05	0.05	0.3

Above: Results with V_S evaluated on the ring polymer centroid only and V_L evaluated on all beads.



Conclusions

- The ring polymer contraction method allows path integral simulations of systems where the potential can be split into rapidly and slowly varying parts to be performed with near classical effort while still obtaining the exact result^{1,2}.
- We have recently extended the method to allow systems with many-body (polarisable) potentials to be treated and have shown that the exact result can be obtained with near classical computation cost even for ice at 100K³.
- The ring polymer contraction method has also recently been used to study the quantum effects in the water-ice phase transition using a new water model developed for use in path integral simulations⁴.

References

- T. E. Markland and D. E. Manolopoulos, *J. Chem. Phys.* **129**, 024105 (2008)
- T. E. Markland and D. E. Manolopoulos, *Chem. Phys. Lett.* **464**, 256-261 (2008)
- G. S. Fanourgakis, T. E. Markland and D. E. Manolopoulos, *In preparation*
- S. Habershon, T. E. Markland and D. E. Manolopoulos, *Submitted*
- J. Cao and G. A. Voth, *J. Chem. Phys.* **100**, 5106 (1994)
- I. R. Craig and D. E. Manolopoulos, *J. Chem. Phys.* **121**, 3368 (2004)

Acknowledgements

Oxford University Chemistry Department, the EPSRC and Balliol College for funding.