

Sampling Orientations of Diatomic Molecules: Application to Path Integral Monte Carlo Method Including Nuclear Quantum Effects to Compute Virial Coefficients

Ramachandran Subramanian, Andrew J. Schultz and David A. Kofke

Department of Chemical and Biological Engineering, State University of New York, Buffalo, New York, 14260, USA.

Objectives

- To implement Path Integral Monte Carlo (PIMC) method for explicitly capturing nuclear quantum effects in virial coefficient calculations at low temperatures
- To develop a mathematically simple and efficient algorithm for sampling orientations of diatomic molecules in a PIMC calculation
- To compute fully quantum virial coefficients of hydrogen (H_2) using methods stated above
- To compare the results with literature values and comment on the performance of the algorithm

Introduction

Virial coefficients ($B_n(T)$, given by eq. (1)) are important thermodynamic properties of a system as they not only lead to other properties but also serve as tools to test the accuracy of inter-molecular potential models.

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \dots \quad (1)$$

This is because they can be evaluated both experimentally and via numerical calculations for a given potential model. Potential Energy Surfaces (PESs) given as functions fitted to first-principles calculations and used as a basis for computing virial coefficients provide a route to connect *ab initio* calculations to thermodynamic bulk behavior. However, *ab initio* potential models do not capture the nuclear quantum effects that become important at low temperatures. PIMC methods can be used to account for the same in virial coefficient calculations.

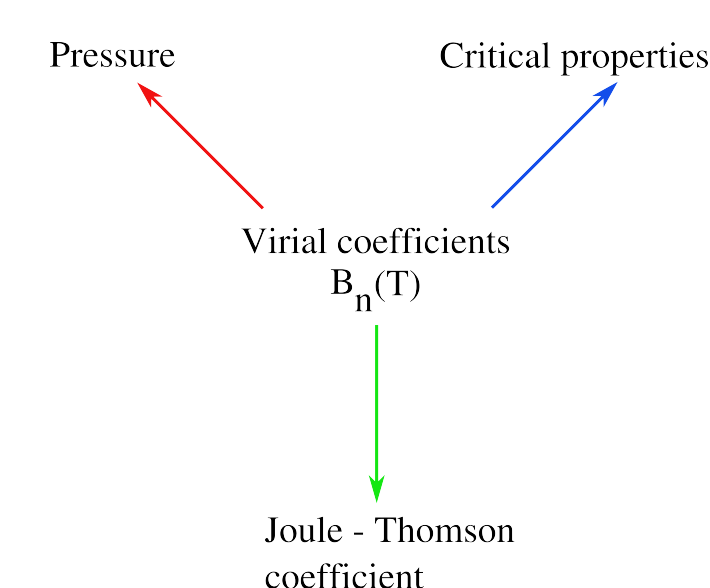


Figure: Some thermodynamic properties that can be computed from virial coefficients

PIMC represents the position of atoms at low temperatures as closed rings with a discrete number (P) of 'beads' that are connected by harmonic springs. The interaction energy is then computed as the average of the inter-molecular energy over corresponding beads of different rings. Using this interaction energy as input for methods like Mayer Sampling Monte Carlo (MSMC)¹ one can evaluate virial coefficients efficiently.

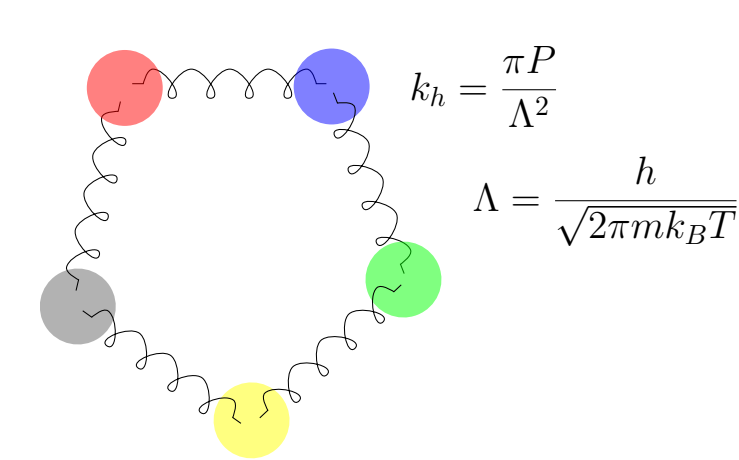


Figure: PIMC representation with $P = 5$ beads

Previously² we implemented PIMC for helium, wherein we generated configurations by regrowing the ring from scratch by translation of the beads. In the present work, we extend this approach to diatomics.

Methods

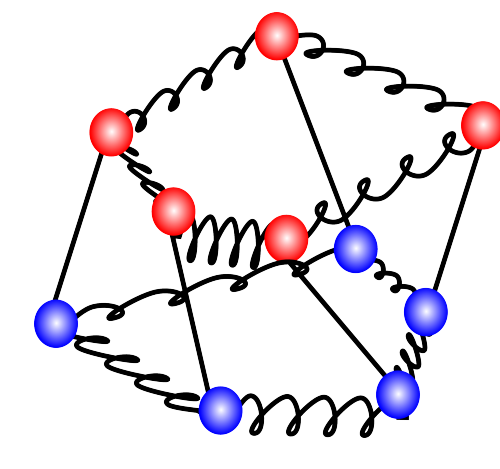


Figure: Diatomic molecule with orientational degrees of freedom and $P = 5$ images. The term 'image' is used to denote the set of two atoms (one red, one blue) that make up a molecule

- Garberoglio et al.³ used quantum rigid rotors and hybrid-PIMC⁴ algorithm to sample orientations of H_2 images
- Our approach: Instead of a quantum rigid rotor, consider diatomic molecule as two independent atoms with a fixed bond length
- Probability distribution of the orientation of images is affected by only the harmonic spring energy; its unnormalized form is:

$$P_{act} = \exp[-U_h] \quad (2)$$

$$U_h = \sum_{i=0}^{P-1} k_h \Delta x_{i,i+1}^2$$

where $\Delta x_{i,i+1}^2$ denotes the distance between images $i, i+1$.

- Using geometric and trigonometric relations, we can express $\Delta x_{i,i+1}^2$ in terms of angles ($\alpha_n, \beta_n, \psi_n$) defined below. This unnormalized probability distribution for image n between two given images i_1 and i_2 is:

$$P_{an}(\alpha_n) = 2\pi r \sin(\alpha_n) \times \exp[-8k_h r^2 (1 - \cos(\psi_n/2) \cos(\alpha_n))] \quad (3)$$

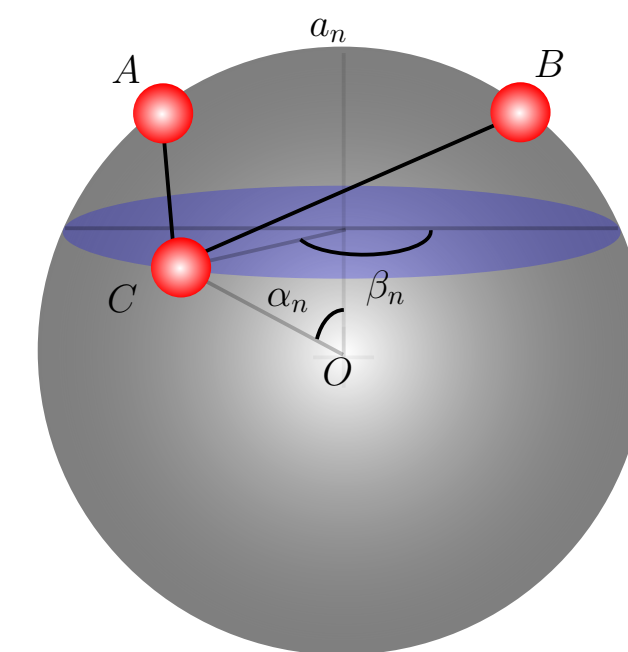


Figure: Simplified picture where the harmonic springs and the second ring of image atoms have been omitted for clarity. Here, images i_1 and i_2 are at A and B respectively with $\angle AOA_n = \angle a_n OB = \psi_n/2$ and $r = (\text{bond length})/2$ is the radius of the sphere.

- We can easily sample the angle α_n by obtaining a cumulative distribution function of $P(\alpha_n)$ and inverting it:

$$\alpha_n = \cos^{-1} \left[\frac{-k_n + \ln(\exp[2k_n] - C \times (\exp[2k_n] - 1))}{k_n} \right], \quad (4)$$

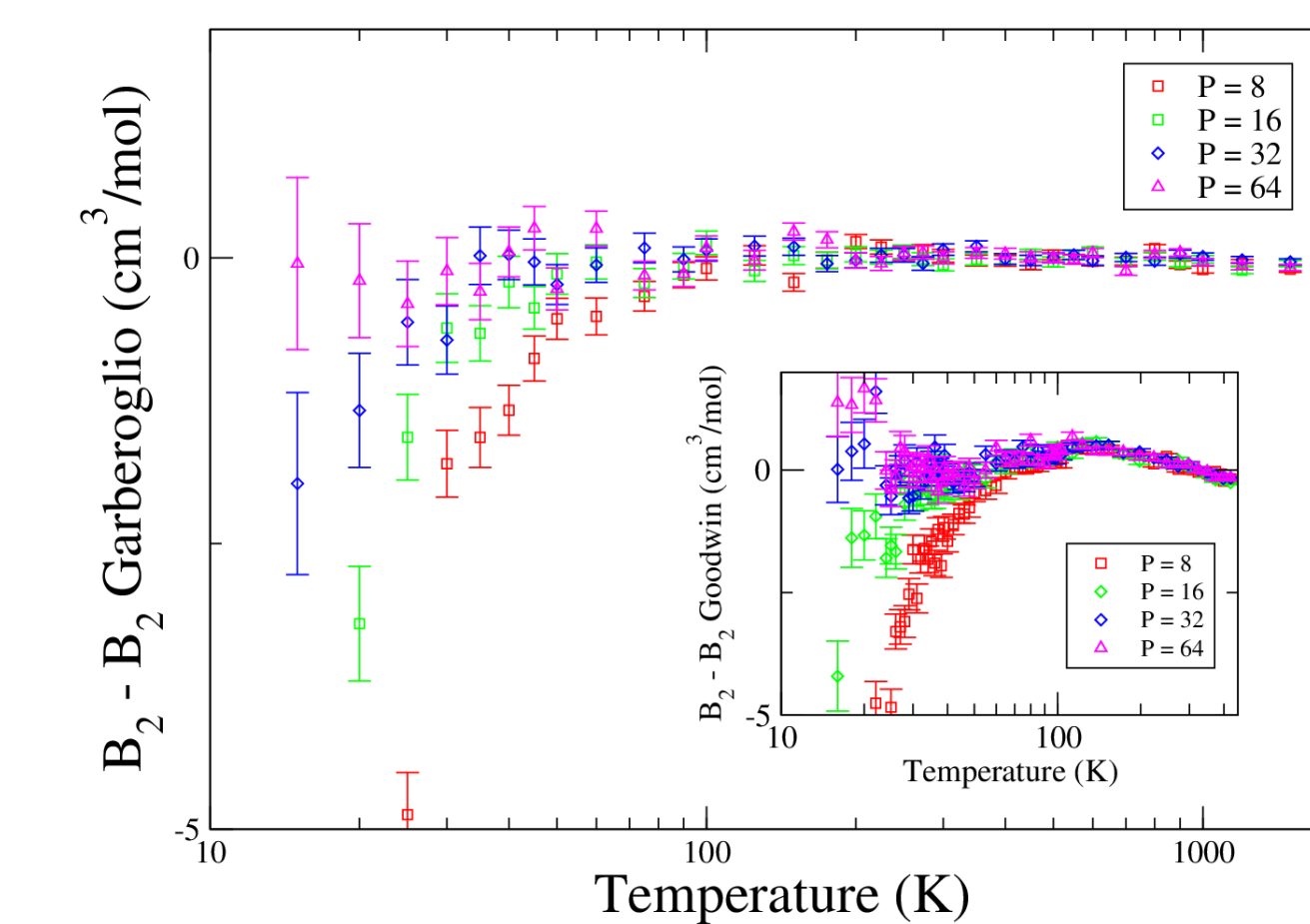
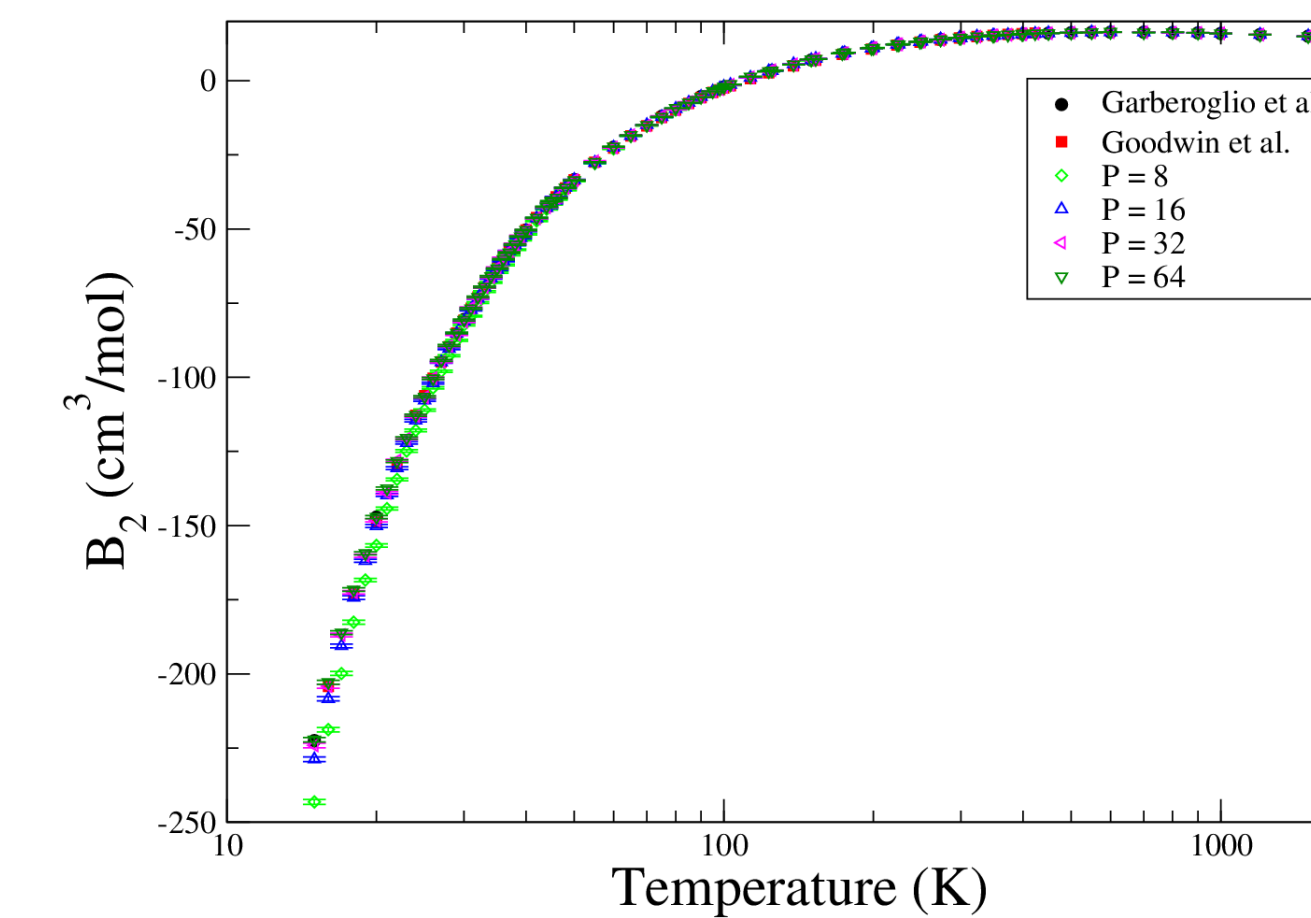
$$k_n = 8r^2 \cos(\psi_n/2) k_h$$

where C is chosen at random uniformly on 0 to 1.

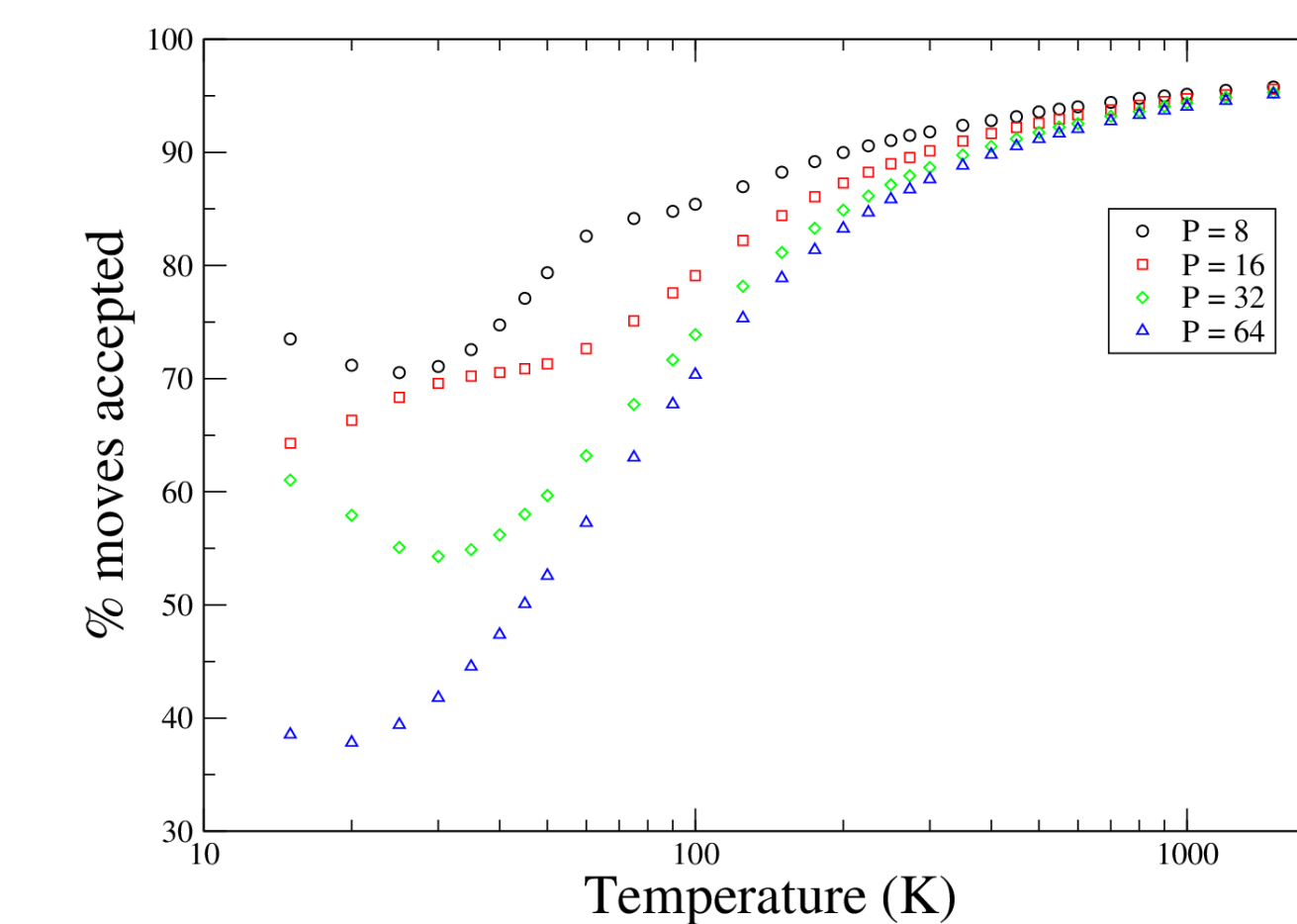
- We regrow the ring by bisection, progressively inserting 1 image between 2 previously positioned images until desired P has been reached. Eq. (4) is exact for α_n iff n is to be the only image between i_1 and i_2 , so its use for all stages but the last represents an approximation.
- The bias introduced by this approximation is removed via the Monte Carlo sampling process
- Eq. (3) is independent of β_n and so we choose it uniformly

Results and discussion

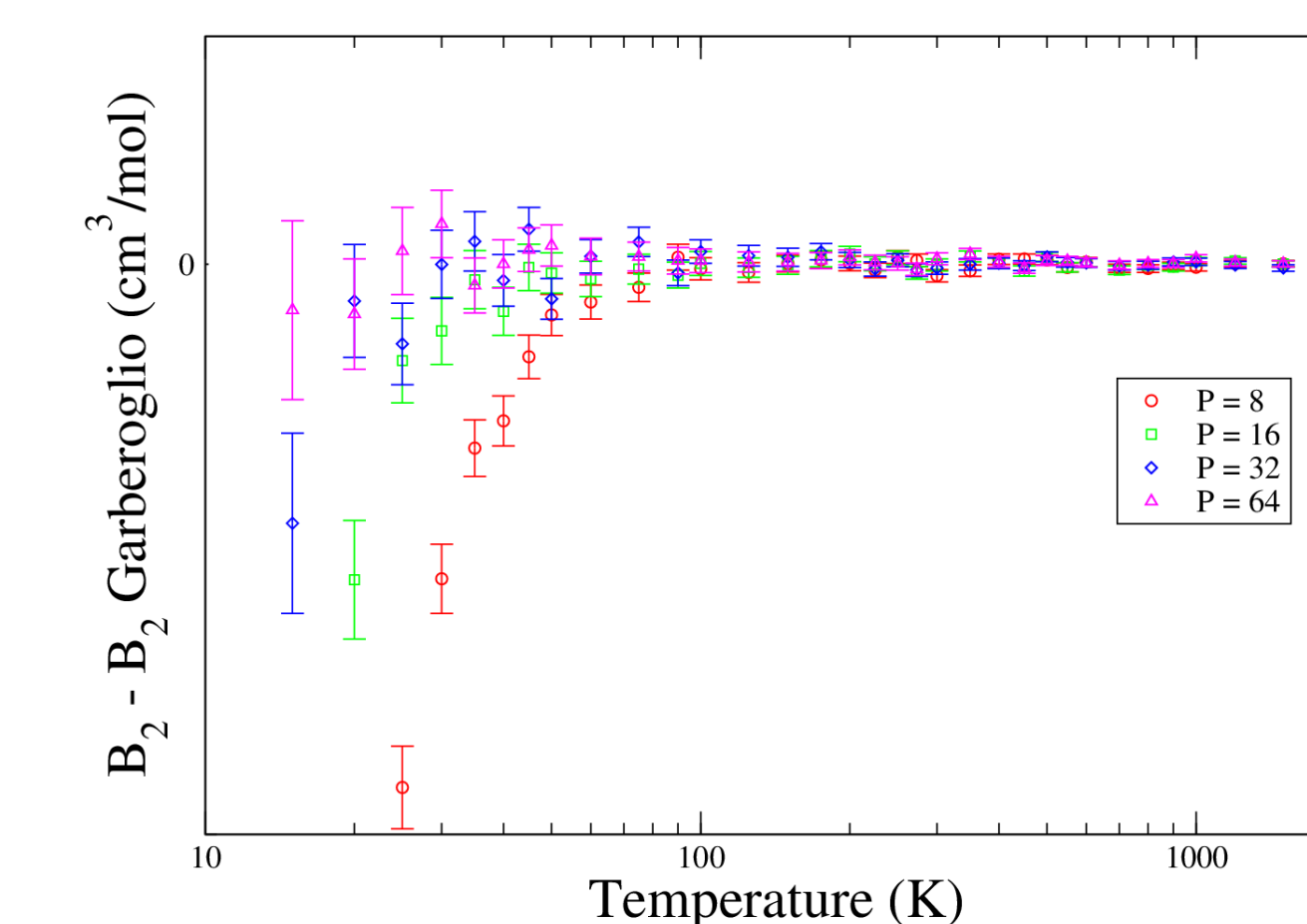
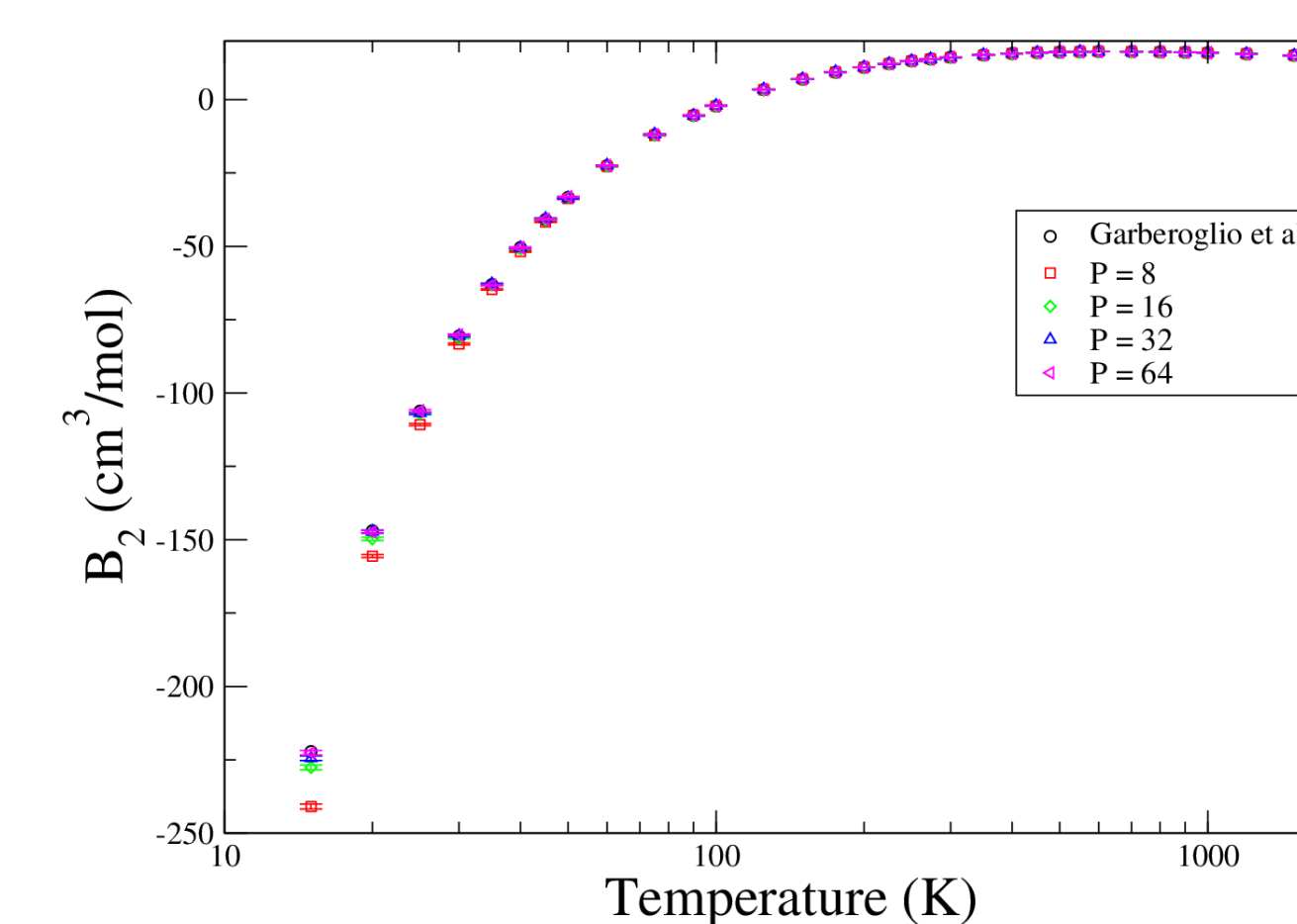
- B_2 results using rigid *ab initio* potential⁵ and ground state bond length values compared against literature values³ and experimental results⁶:



- Performance of the algorithm in terms of the % of moves accepted:

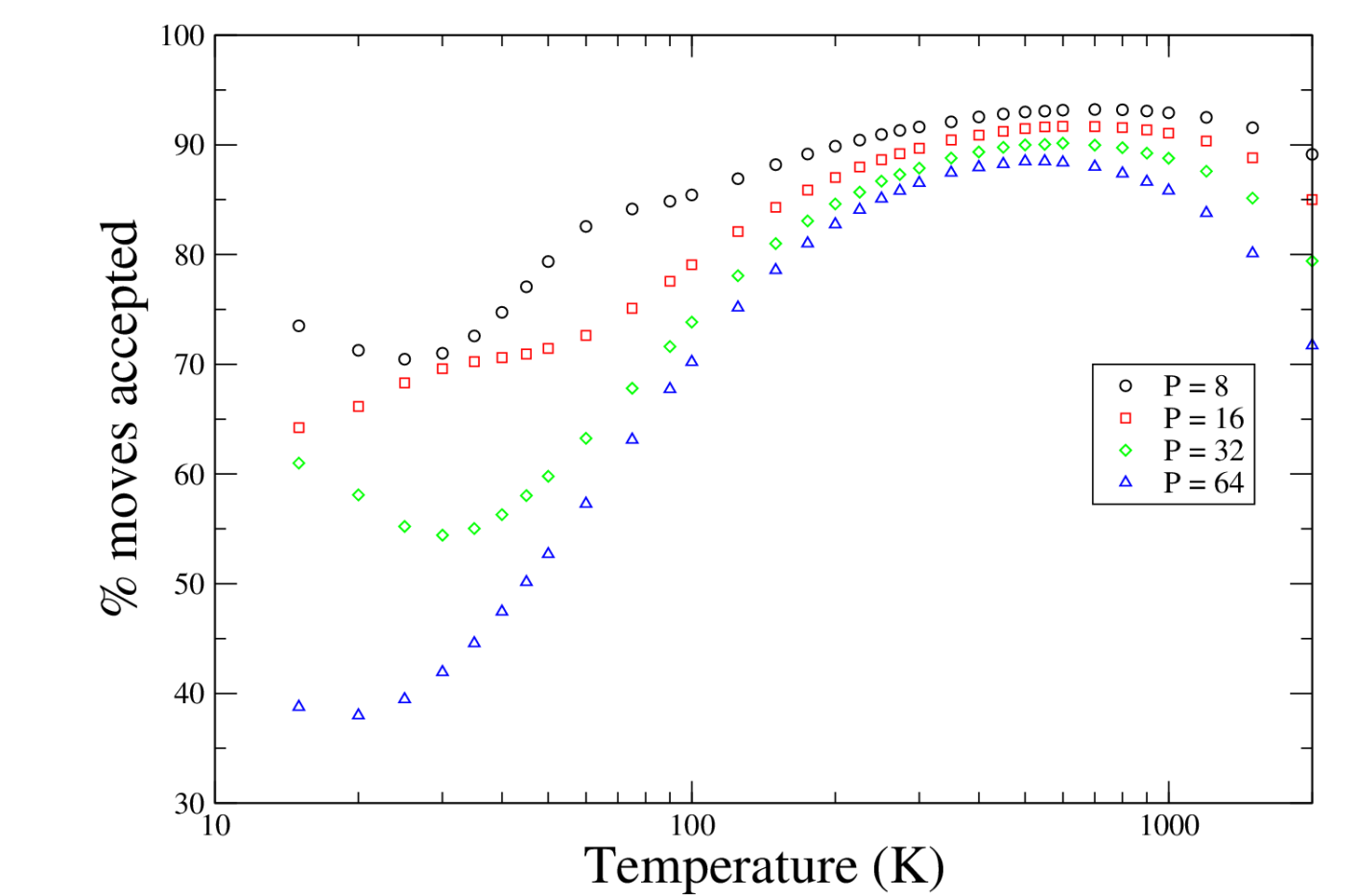


- B_2 results using flexible *ab initio* potential⁷ and temperature averaged bond length values compared against literature values³:



Results and discussion

- Performance of the algorithm in terms of the % of moves accepted:



- The overall approximate nature of α_n for all the images that are not placed in the last step becomes better with increasing temperature. For low temperatures however, the algorithm performance is affected significantly. This approximation also has the effect that if P increases, then efficiency of the algorithm decreases

Conclusions and future work

- We have successfully developed a new orientation sampling algorithm for diatomic molecules and applied it for H_2 as a test case using two *ab initio* potentials and PIMC method
- We observed good agreement with both literature values as well as experimental results over the whole range of temperatures considered for $P = 64$ and increasing disagreements at low temperatures for $P = 32, 16$ and 8
- Performance of the algorithm in terms of % of moves accepted has also been found to be satisfactory even for the highest P and lowest temperature considered
- Future work: Study other systems like N_2, O_2 etc. and extend it to multiatomic molecules like H_2O . Compute higher order virial coefficients.

References

- Singh and Kofke Phys. Rev. Lett. **92**, 220601 (2004)
- Shaul, Schultz, and Kofke J. Chem. Phys. **137**, 184101 (2012)
- Garberoglio et al. J. Chem. Phys. **141**, 044119 (2014)
- Garberoglio and Johnson ACS Nano **4**, 1703–1715 (2010)
- Patkowski et al. J. Chem. Phys. **129**, 094304 (2008)
- Goodwin et al. J. Res. Natl. Bur. Stds. - A. Phys. and Chem. **68A**, 121–126 (1963)
- Garberoglio et al. J. Chem. Phys. **137**, 154308 (2012)

Acknowledgments

We would like to thank Dr. Giovanni Garberoglio for helping us identify sources of error in our implementation of both the *ab initio* potentials considered and also Dr. Allan H. Harvey for insightful discussions.