

Quantum Virial Coefficients via Path Integral Monte Carlo: Theory and Development of Novel Algorithms

PhD dissertation defense by: Ramachandran Subramanian

Committee: Prof. David A. Kofke (Chair),
Prof. Jeffrey R. Errington, Prof. Johannes Hachmann, Dr.
Andrew J. Schultz

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Overview

- 1 Introduction
 - Virial coefficients
 - *Ab initio* potentials
- 2 Objectives
- 3 Methods
 - Mayer Sampling Monte Carlo
 - Path Integral Monte Carlo
 - Novel algorithms
- 4 Results
 - Hydrogen
 - Nitrogen
 - Oxygen
- 5 Summary

Virial equation of state (VEOS)

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

- B_n - n^{th} order virial coefficient represents the effect of interaction of n molecules.
- Second and third order virial coefficients are given by:

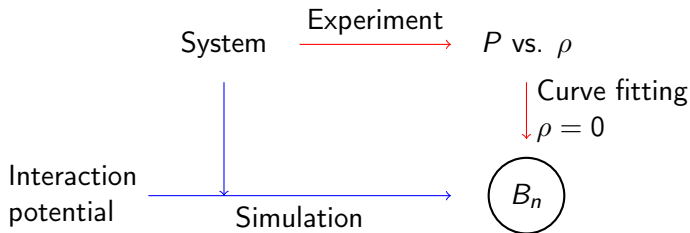
$$B_2(T) = -\frac{1}{2} \int d1 \, f(0, 1)$$

$$B_3(T) = -\frac{1}{3} \int \int d1 \, d2 \, f(0, 1) \, f(0, 2) \, f(1, 2)$$

where $f(0, 1) = \left(\exp \left[-\beta U_2(\mathbf{r}) \right] - 1 \right)$ and indices '1' and '2' denote the position and orientational degrees of freedom of molecules 1 and 2, respectively, with respect to molecule '0' at the origin.

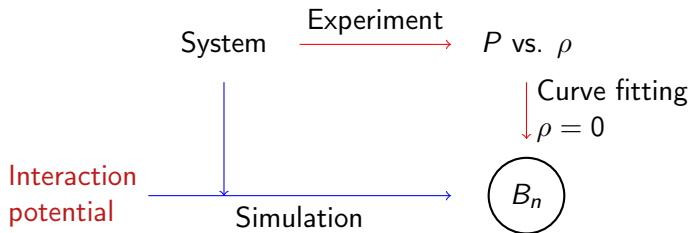
Main uses:

- To compute other thermodynamic properties like the Joule-Thomson coefficient, critical point etc.
- To rank different potential models by comparing their virial coefficients to experimental results



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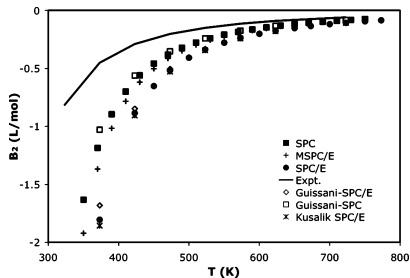
- To systematically tune and improve potentials as a result.

Empirical potential models

- Usually functions fitted to experimental data of bulk property measurement.
- Represent the net effect of a variety of phenomena taking place including 2 body interactions, multi-body interactions, nuclear quantum effects etc.
- As a result, fail to accurately represent interaction potential.
- Interaction potentials that better represent condensed (high density) phase fail to predict accurate virial coefficients for the gas (low density) phase.

Example - different empirical models of water

- Importance of the accuracy of interaction potential¹:



¹ K. M. Benjamin et al., J. Phys. Chem. B (2007).

Ab initio potential models

- Fundamentally different from empirical models as they focus only on two or three molecules at a time
- Solve for the interaction energies starting with the Schrödinger equation and involve many approximations:

$$\mathcal{H} \Psi = E \Psi,$$

$$\mathcal{H} = \mathcal{T}_e + \mathcal{T}_N + \mathcal{V}_{ee} + \mathcal{V}_{eN} + \mathcal{V}_{NN}$$

- Account for electronic structure using different levels of theory and different basis sets
- We use potentials fitted to *ab initio* data rather than compute it on-the-fly (expensive)

Nuclear quantum effects

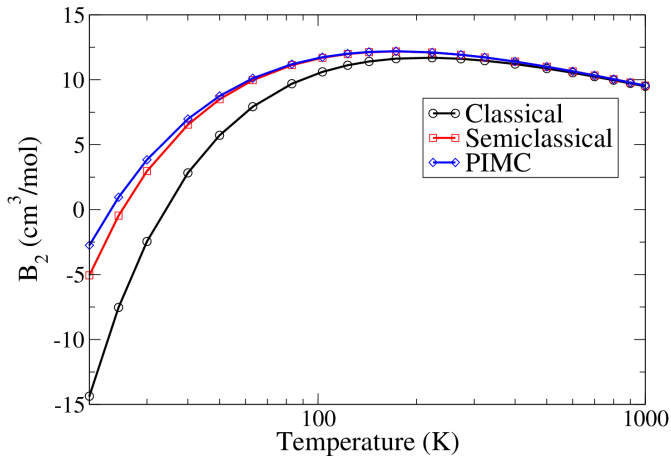
- Can be explained by the zero-point vibrational energy and result in uncertainty in the positions of atoms at low temperatures.
- Have to be explicitly included in virial coefficient calculations as they are ignored in the development of *ab initio* potentials.
- Semi-classical routes to include quantum effects:
 1. Computing first order quantum corrections.
 2. Using an effective potential like the Quadratic Feynman-Hibbs (QFH)² or Takahashi-Imada (TI)³.
- Quantum route: path integral Monte Carlo (PIMC) (will be explained in detail later).

² R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (1965).

³ G. K. Schenter, J. Chem. Phys. (2002); M. Takahashi and M. Imada, J. Phys. Soc. Jpn. (1984).

Nuclear quantum effects

- Importance of nuclear quantum effects⁴ for helium-4.



⁴ K. R. S. Shaul, A. J. Schultz, and D. A. Kofke, J. Chem. Phys. (2012).

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Objective

Previous work

Monatomic molecules (helium-4 by Kate)

Current challenges

Diatomic molecules: compute accurate virial coefficients using state-of-the-art *ab initio* potentials and PIMC method.

Future goals

Multiatomic molecules: compute accurate virial coefficients using state-of-the-art *ab initio* potentials and PIMC method.

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Mayer Sampling Monte Carlo

- Quick recap of the VEOS:

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

- The number of integrals to be summed⁵ is: 3 for B_4 , 10 for B_5 , 56 for B_6 , 468 for B_7 .
- MSMC⁶ is a free energy perturbation technique to evaluate the integrals in the above equations efficiently.

$$\Gamma(T) = \Gamma_o \frac{\langle \gamma/\pi \rangle_\pi / \langle \gamma_{os}/\pi \rangle_\pi}{\langle \gamma_o/\pi_o \rangle_{\pi_o} / \langle \gamma_{os}/\pi_o \rangle_{\pi_o}}$$

$$\gamma_{os} = \frac{|\gamma_o||\gamma|}{\alpha|\gamma_o| + |\gamma|}$$

⁵ J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (2006).

⁶ J. K. Singh and D. A. Kofke, Phys. Rev. Lett. (2004).

PIMC - thermal density matrix

- From statistical mechanics: the partition function is given as:

$$P(x) = \frac{1}{Z} \rho(x, x),$$
$$Z = \int \rho(x, x) dx \equiv \text{trace}\{\rho\}.$$

- For the more general case: the probability of going from a state x to x' is proportional to $\rho(x, x'; \beta)$.
- Richard Feynman⁷ was able to connect it with quantum mechanics:

$$\rho(R, R'; \beta) = \langle R | e^{-\beta \mathcal{H}} | R' \rangle$$

where $R = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n\}$

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Important equations

- Product of two or more density matrices is also a density matrix⁸:

$$\rho(R_0, R_P; \beta) = \int \cdots \int dR_1 dR_2 \cdots dR_{P-1} \rho(R_0, R_1; \beta/P) \\ \rho(R_1, R_2; \beta/P) \cdots \rho(R_{P-1}, R_P; \beta/P)$$

⁸ D. M. Ceperley, Rev. Mod. Phys. (1995).

⁹ T. Cui et al., Phys. Rev. B (1997).

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- The “primitive approximation” is given by⁹:

$$e^{-\frac{\beta}{P}(\mathcal{T}+\mathcal{V})} \approx e^{-\frac{\beta}{P}\mathcal{T}} e^{-\frac{\beta}{P}\mathcal{V}}$$

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- The Trotter formula¹⁰:

$$e^{-\beta(\mathcal{T}+\mathcal{V})} = \lim_{P \rightarrow \infty} \left[e^{-\frac{\beta}{P}\mathcal{T}} e^{-\frac{\beta}{P}\mathcal{V}} \right]^P$$

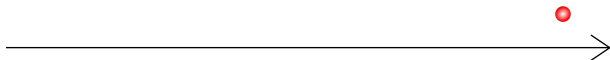
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PIMC

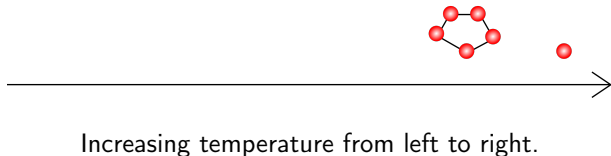
- More the P , the finer the mapping of the quantum mechanical partition function onto the classical ring polymer.



Increasing temperature from left to right.

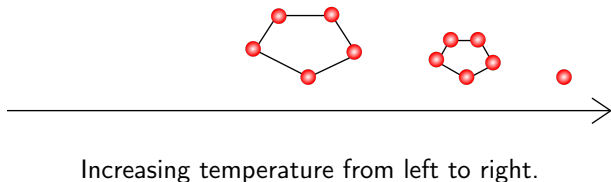
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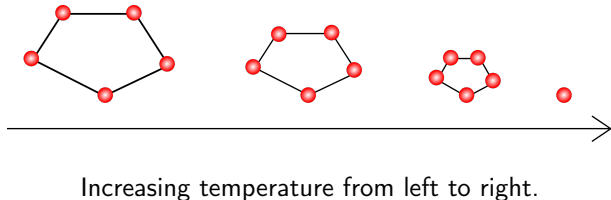
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PIMC

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Diatomic molecule - rigid rotor¹¹

- Let m and I denote the mass of the atom and moment of inertia of the rigid rotor respectively. Its Hamiltonian is given by:

$$\hat{h}_2 = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{\hat{\mathbf{J}}_1^2}{2I} + \frac{\hat{\mathbf{J}}_2^2}{2I} + \hat{U}(r, \Omega_1, \Omega_2)$$

Matrix elements

$$\begin{aligned}\mathcal{T}_{\text{tra}}^{i,i+1} &= \left\langle \mathbf{x}^i \left| \exp \left(-\frac{\beta \hat{\mathbf{p}}^2}{2mP} \right) \right| \mathbf{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp \left(-\frac{\pi P (\mathbf{x}^i - \mathbf{x}^{i+1})^2}{\Lambda_m^2} \right) \\ \mathcal{T}_{\text{rot}}^{i,i+1} &= \left\langle \Omega^i \left| \exp \left(-\frac{\beta \hat{\mathbf{J}}^2}{2IP} \right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1})) \\ &\quad \times \exp[-\beta j(j+1)\Upsilon/P]\end{aligned}$$

¹¹ K. Patkowski et al., J. Chem. Phys. (2008).

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Diatomic molecule - rigid rotor¹²

- Defining $\mathbf{r} \equiv \mathbf{x}^{(1)}$, $\Delta^{(i)} \equiv \mathbf{x}^{(i+1)} - \mathbf{x}^{(i)}$,

$$\exp[-\beta \bar{U}(|\mathbf{r}|)] = \left\langle \exp \left[-\frac{\beta}{P} \sum_{i=1}^P U(|\mathbf{x}^i|, \Omega_1^i, \Omega_2^i) \right] \right\rangle_{F, \varrho}$$

- Probability distributions:

$$\varrho(\Omega) = \frac{1}{q_{\text{rot}}} \prod_{i=1}^P \mathcal{T}_{\text{rot}}^{i,i+1}, \quad F(\Delta) = \Lambda_m^3 \prod_{i=1}^P \mathcal{T}_{\text{tra}}^{i,i+1}$$

$$q_{\text{rot}} = \sum_{j'} (2j' + 1) \exp[-\beta \Upsilon j'(j' + 1)]$$

Fully quantum second virial coefficient

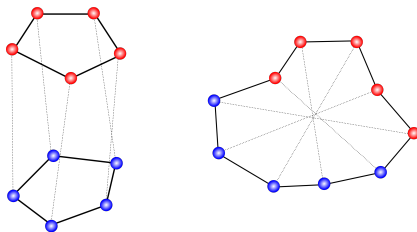
$$B_2(T) = -2\pi \int dr \, r^2 (e^{-\beta \bar{U}(r)} - 1)$$

¹² K. Patkowski et al., J. Chem. Phys. (2008).

Diatomic molecule - rigid rotor¹³

- A closer look at the effective potential:

$$\exp[-\beta \bar{U}(|\mathbf{r}|)] = \left\langle \exp \left[-\frac{\beta}{P} \sum_{i=1}^P U(|\mathbf{x}^i|, \Omega_1^i, \Omega_2^i) \right] \right\rangle_{F, \varrho}$$



Boltzmann- and exchange-type conformations shown on the left and right respectively.

¹³ K. Patkowski et al., J. Chem. Phys. (2008).

Objectives

Diatomic molecules

Compute accurate virial coefficients using state-of-the-art *ab initio* potentials, MSMC and PIMC methods for the rigid case.

Challenges

Lack of efficient an sampling algorithm for orientations.

Orientation sampling

- Idea proposed by Garberoglio et al.¹⁴: two independent atoms (vs. one rigid rotor previously).
- Leads to possibility of avoiding quantum mechanical calculations.
- Sampling problem can be reduced to choosing a ring of beads on the surface of a sphere.
- A more viable path to study multiatomic systems.

¹⁴ G. Garberoglio et al., J. Chem. Phys. (2014).

Orientation sampling

- Probability associated with a configuration $\mathbf{Z} \equiv (\mathbf{R}, \mathbf{b})$ is given as:

$$P_{\sigma}(\mathbf{Z}) = \frac{1}{Q_1^{(\sigma)}} F(\mathbf{R}; 2m) F(\mathbf{b}^{(\sigma)}; m/2) e^{-\beta \bar{u}(\mathbf{b})}$$

- Define π to be the \mathbf{b} -dependent terms of the path integral weight F .
- We generate a trial configuration with probability $\tau(o \rightarrow n)$, based on an approximation for π denoted as $\tilde{\pi}$, and accept or reject based on:

$$P_{\text{acc}} = \text{Min} \left[1, \frac{\pi(n)/\pi(o)}{\tau(o \rightarrow n)/\tau(n \rightarrow o)} \right]$$

where 'o' and 'n' denote the old and new configurations respectively.

- We derive a simple and analytic expression for $\tau(o \rightarrow n)$

Orientation sampling - bisection algorithm

- The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images $\mathbf{b}_i, \mathbf{b}_k$ and we choose the orientation of image $j = (i + k)/2$.
- We note that $\tilde{\pi}$ is exact for the last step of the algorithm.



Schematic for $P = 8$

Orientation sampling - bisection algorithm

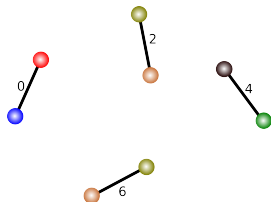
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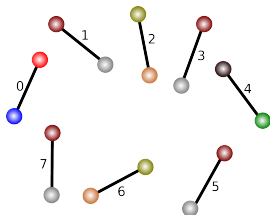
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Schematic for $P = 8$

Orientation sampling

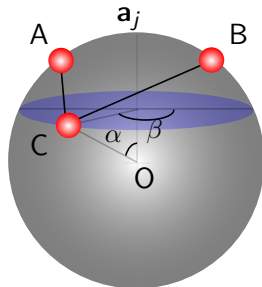
- Adjacent image probability distribution:

$$\begin{aligned}
 \tilde{\pi}(\mathbf{b}_j(\alpha, \beta) : \mathbf{a}_j, \psi_{i,k}) \\
 &= \pi(\mathbf{b}_i, \mathbf{b}_j) \pi(\mathbf{b}_j, \mathbf{b}_k) \\
 &= \exp(-k_h [d_{AC}^2 + d_{BC}^2]) \\
 &= \exp(-4k_h b^2 [1 - \cos(\psi_{i,k}/2) \cos(\alpha)])
 \end{aligned}$$

- The angle α can be calculated by choosing C at random, uniformly on $[0, 1]$.

$$\begin{aligned}
 \alpha = \cos^{-1} \big[&1 + (1/\kappa) \\
 &\times \ln(1 - C(1 - \exp[-2\kappa])) \big],
 \end{aligned}$$

$$\kappa = 4 \cos(\psi_{i,k}/2) k_h b^2$$



Simplified picture

Objectives

Diatomic molecules

Compute accurate virial coefficients using state-of-the-art *ab initio* potentials, MSMC and PIMC methods for the flexible case.

Challenges

To include vibrational degrees of freedom.

Methods to handle flexibility

- Instead of using ground state bond length (r_0) use average bond length at each temperature ($\langle r \rangle_T$)¹⁵.
- Average the entire intermolecular potential ($\langle U \rangle_T$) over internal degrees of freedom of each monomer, weighted by the appropriate wave function¹⁶.
- Average the intermolecular potential over all four ring polymer configurations and two types of conformations to get an expression for the quantum virial coefficient including monomer flexibility¹⁷.

¹⁵ G. Garberoglio et al., J. Chem. Phys. (2012).

¹⁶ G. Garberoglio et al., J. Chem. Phys. (2014).

¹⁷ G. Garberoglio et al., J. Chem. Phys. (2014).

Bond-length sampling

- Define π in a similar fashion to the orientation sampling algorithm:

$$\pi(\mathbf{b}) = \prod_{i=0}^{P-1} b_i^2 e^{-\beta u(b_i)/P} \pi(b_i, b_{i+1}, \theta_{i,i+1})$$

$$\pi(b_i, b_j, \theta_{i,j}) = \exp\left(-\frac{1}{2}k_h (b_i^2 + b_j^2 - 2b_i b_j \cos(\theta_{i,j}))\right)$$

where $\theta_{i,j}$ is the angle between orientations of images i and j .

Bond-length sampling

- Let $\pi(\mathbf{b}) = \exp(-y)$, where y can be defined as follows:-

$$y = \sum_{i=0}^{P-1} \left\{ k_h \left(b_i^2 - b_i b_j \cos(\theta_{ij}) \right) - 2 \log b_i + \frac{\beta u(b_i)}{P} \right\}$$

- We define $\tilde{y} \approx y$ such that:

$$\tilde{y} = \sum_{i=0}^{P-1} \left\{ k_h \left(b_i^2 - b_i b_j \right) - \frac{2 \log b_i}{P} + \frac{\beta u(b_i)}{P} \right\}$$

- We solve for the nominal $\cos(\hat{\theta})$ value by:

$$\frac{\partial y}{\partial b_i} = \frac{\partial \tilde{y}}{\partial b_i} \Rightarrow \cos(\hat{\theta}) = 1 - \frac{P-1}{P k_h b_i^2}$$

- Using this nominal value in the expression for y , we find b_m such that:

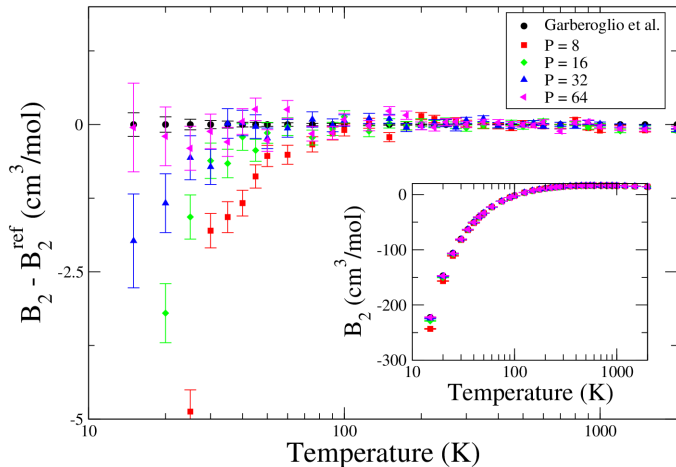
$$\left. \frac{\partial y}{\partial b_i} \right|_{b_i=b_m} = 0 \quad \forall i$$

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B_2 values for Hydrogen compared with Garberoglio et al.¹⁸.

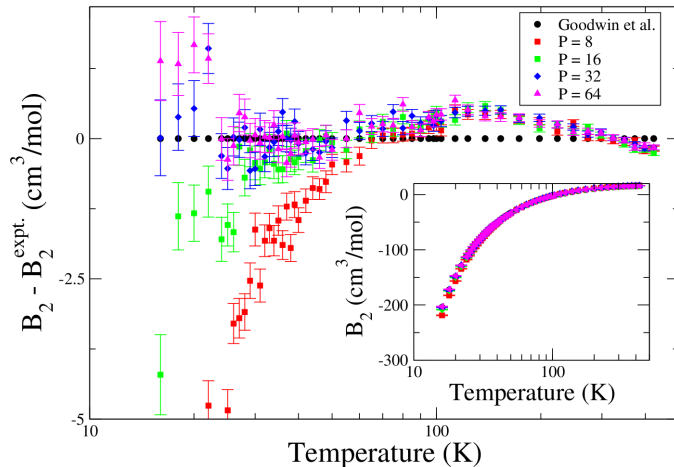
Bond length: $\langle r \rangle_0$, total configuration samples: 10^7 .



¹⁸ G. Garberoglio et al., J. Chem. Phys. (2014).

B_2 values for Hydrogen compared with Goodwin et al.¹⁹.

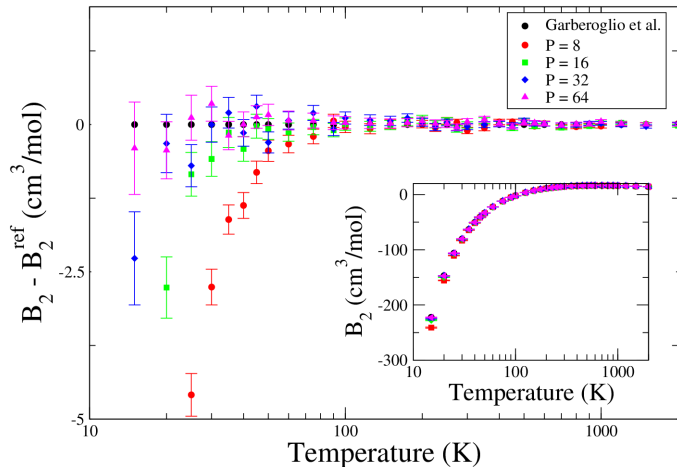
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¹⁹ R. D. Goodwin et al., J. Res. Natl. Bur. Stds. - A. Phys. and Chem. (1963).

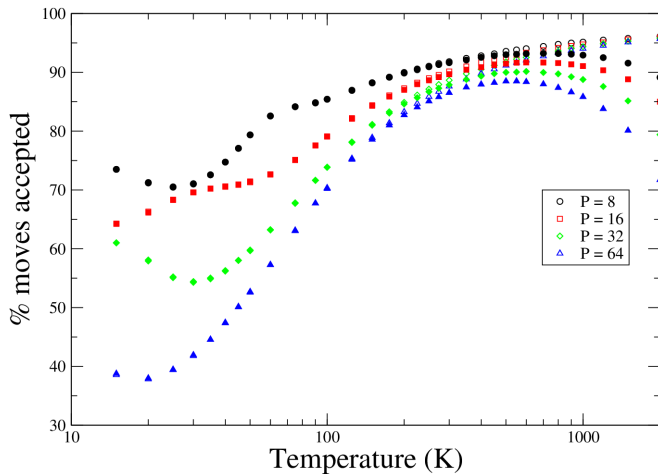
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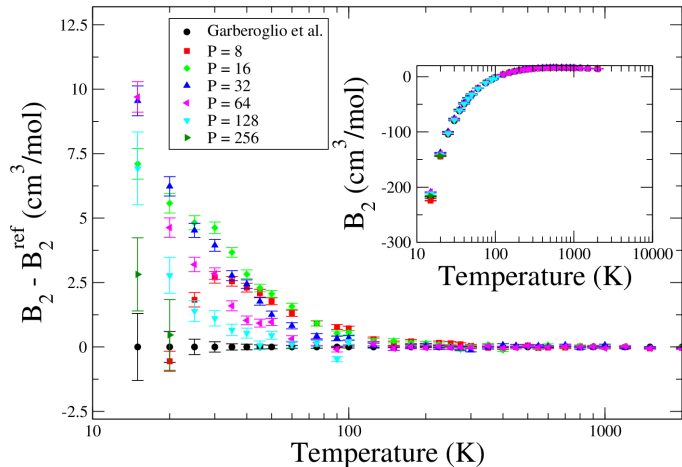
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Performance of the orientation move.



B_2 values for Hydrogen compared with Garberoglio et al.²¹.

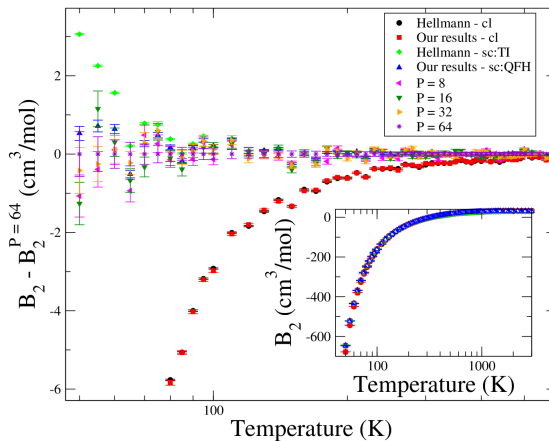
Bond length: variable, total configuration samples: 10^7 .



²¹ G. Garberoglio et al., J. Chem. Phys. (2014).

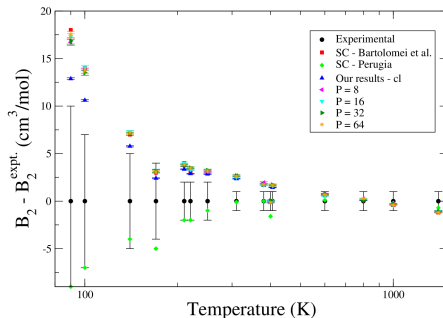
B_2 values for Nitrogen compared with Hellmann²².

Total configuration samples: 10^9 for cl, sc and 10^8 for all PI cases.



B_2 values for Oxygen compared with Bartolomei et al.²⁵.

PES: PT2, Total configuration samples: 10^8 for cl and 10^7 for all PI cases.
Experimental²³, SC - Perugia²⁴.



²³ J. H. Dymond and E. B. Smith, *The Second Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*. (1979).

²⁴ V. Aquilanti et al., *J. Am. Chem. Soc.* (1999); M. Bartolomei et al., *J. Chem. Phys.* (2010).

²⁵ M. Bartolomei et al., *J. Chem. Phys.* (2010).

Overview

- 1 Introduction
 - Virial coefficients
 - *Ab initio* potentials
- 2 Objectives
- 3 Methods
 - Mayer Sampling Monte Carlo
 - Path Integral Monte Carlo
 - Novel algorithms
- 4 Results
 - Hydrogen
 - Nitrogen
 - Oxygen
- 5 Summary

Conclusion



THE BEST THESIS DEFENSE IS A GOOD THESIS OFFENSE.

<https://xkcd.com/1403/>

Summary

- We have developed two direct sampling algorithms for orientations and bond-lengths of diatomic molecules.
- Fundamental to both these algorithms is the idea of treating the two atoms independently as opposed to a rigid rotor.
- Owing to the simple nature of the probability distributions, our algorithms are efficient.
- We have tested these algorithms by computing quantum virial coefficients using PIMC method for three different diatomic systems.
- We observed overall good agreement with literature values for the temperatures considered.
- For nitrogen and oxygen, lower temperatures need to be considered for quantum effects to be significant.

Future direction of work

Analysis

- More detailed analysis to identify sources of inefficiency.
- A rigorous comparison of computational performance with existing algorithms could provide useful insight, or at the very least, lead to quantification of the effort saved.

Application

- Isotopes of hydrogen - D_2 , T_2 , HD and HT.
- Mixtures of diatomic molecules - $O_2 + N_2$, $O_2 + H_2$.

Development

- Extension of these algorithms to multiatomic systems. Linear multiatomics ,e.g., CO_2 could be a first step.