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

May 9, 2016

Overview

Virial equation of state (VEOS)

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

- B_n - n^{th} order virial coefficient represents the effect of interaction of n molecules.
- Depends only on temperature.
- Works well for systems with low density (typically gases).

Expressions for the virial coefficients

- 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 $f(0,1) = \left(\exp\left[-\beta U_2(\boldsymbol{r}) \right] - 1 \right)$ 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.

- The number of such integrals to be summed[1] is: 3 for B_4, 10 for B_5, 56 for B_6, 468 for B_7.

---

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

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
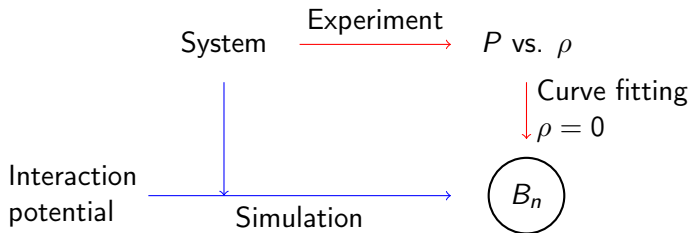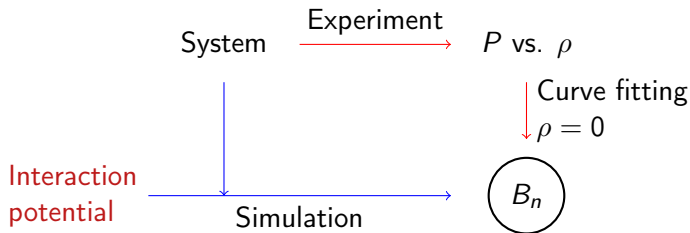
Main uses:

- 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


- 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 potential[2]:

---
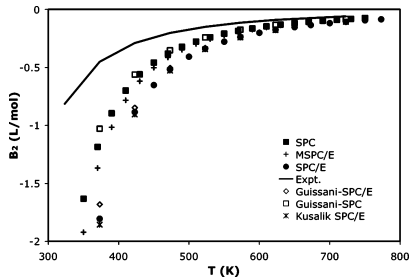
[2] K. M. Benjamin et al., J. Phys. Chem. B (2007).

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

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

---

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

Nuclear quantum effects

- Importance of nuclear quantum effects[4] for ^{4}He.

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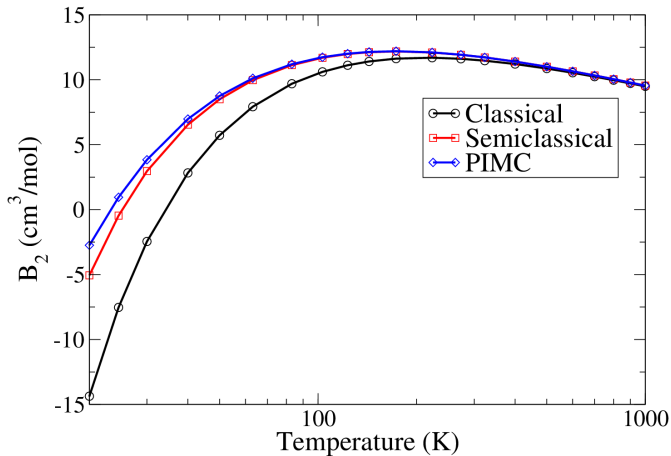
[4] K. R. S. Shaul, A. J. Schultz, and D. A. Kofke, J. Chem. Phys. (2012).

Overview

Objective

Previous work

Monatomic molecules (helium-4 by Kate)

Curent 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.

Objective

Previous work
Monatomic molecules (helium-4 by Kate)

Curent 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.

Overview

Mayer Sampling Monte Carlo

- Second and third order virial coefficients are given by:

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

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

- MSMC[5] is a free energy perturbation technique to evaluate the integrals in the above equations indirectly.

$$\Gamma(T) = \Gamma_o \frac{<\gamma/\pi>_\pi / <\gamma_{os}/\pi>_\pi}{<\gamma_o/\pi_o>_{\pi_o} / <\gamma_{os}/\pi_o>_{\pi_o}}$$

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

[5] J. K. Singh and D. A. Kofke, Phys. Rev. Lett. (2004).

PIMC - thermal density matrix

- The probability of starting at a state x' and reaching state x is proportional to $\rho(x', x; \beta)$, the statistical thermal density matrix. The partition function is given as:

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

- Richard Feynman[6] was able to connect it with quantum mechanics:

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

---

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

Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution[7]:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1)\rho(R_2, R_3; \beta_2)$$

---

[7] D. M. Ceperley, Rev. Mod. Phys. (1995).

[8] T. Cui et al., Phys. Rev. B (1997).

Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution[7]:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1) \rho(R_2, R_3; \beta_2)$$

- As $\frac{\beta}{P} \to 0$ or equivalently as $PT \to \infty$, the "primitive approximation" is given by[8]:

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

---

[7] D. M. Ceperley, Rev. Mod. Phys. (1995).

[8] T. Cui et al., Phys. Rev. B (1997).

Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution[7]:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1) \rho(R_2, R_3; \beta_2)$$

- As $\frac{\beta}{P} \to 0$ or equivalently as $PT \to \infty$, the "primitive approximation" is given by[8]:

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

- The Trotter formula proves that this approximation does converge to the right result in the $P \to \infty$ limit and is given by:

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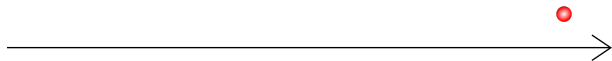
---

[7] D. M. Ceperley, Rev. Mod. Phys. (1995).

[8] T. Cui et al., Phys. Rev. B (1997).

Brilliance of PIMC

- What does the convolution mean?

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

Increasing temperature from left to right.

Brilliance of PIMC

- What does the convolution mean?

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

Increasing temperature from left to right.

Brilliance of PIMC

- What does the convolution mean?

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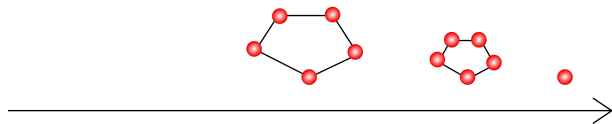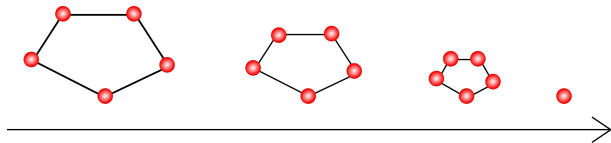$$\rho(R_1, R_2; \beta/P) \ldots \rho(R_{P-1}, R_P; \beta/P)$$

Increasing temperature from left to right.

Brilliance of PIMC

- What does the convolution mean?

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

Increasing temperature from left to right.

Diatomic molecule - rigid rotor[9]

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

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

Matrix elements

$$\mathcal{T}_{\text{tra}}^{i,i+1} = \left\langle \boldsymbol{x}^i \left| \exp\left(-\frac{\beta \hat{\boldsymbol{p}}^2}{2mP}\right) \right| \boldsymbol{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp\left(-\frac{\pi P(\boldsymbol{x}^i - \boldsymbol{x}^{i+1})^2}{\Lambda_m^2}\right)$$

$$\mathcal{T}_{\text{rot}}^{i,i+1} = \left\langle \Omega^i \left| \exp\left(-\frac{\beta \hat{\boldsymbol{J}}^2}{2IP}\right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1}))$$

$$\times \exp\left[-\beta j(j+1)\Upsilon/P\right]$$

---

[9] K. Patkowski et al., J. Chem. Phys. (2008).

Diatomic molecule - rigid rotor[9]

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

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

Matrix elements

$$\mathcal{T}_{\text{tra}}^{i,i+1} = \left\langle \boldsymbol{x}^i \left| \exp\left(-\frac{\beta \hat{\boldsymbol{p}}^2}{2mP}\right) \right| \boldsymbol{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp\left(-\frac{\pi P(\boldsymbol{x}^i - \boldsymbol{x}^{i+1})^2}{\Lambda_m^2}\right)$$

$$\mathcal{T}_{\text{rot}}^{i,i+1} = \left\langle \Omega^i \left| \exp\left(-\frac{\beta \hat{\boldsymbol{J}}^2}{2IP}\right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1}))$$

$$\times \exp\left[-\beta j(j+1)\Upsilon/P\right]$$

[9] K. Patkowski et al., J. Chem. Phys. (2008).

Diatomic molecule - rigid rotor[9]

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

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

Matrix elements

$$\mathcal{T}_{\text{tra}}^{i,i+1} = \left\langle \boldsymbol{x}^i \left| \exp\left(-\frac{\beta\hat{\boldsymbol{p}}^2}{2mP}\right) \right| \boldsymbol{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp\left(-\frac{\pi P(\boldsymbol{x}^i - \boldsymbol{x}^{i+1})^2}{\Lambda_m^2}\right)$$

$$\mathcal{T}_{\text{rot}}^{i,i+1} = \left\langle \Omega^i \left| \exp\left(-\frac{\beta\hat{\boldsymbol{J}}^2}{2IP}\right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(cos(\theta_{i,i+1}))$$

$$\times \exp\left[-\beta j(j+1)\Upsilon/P\right]$$

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

Diatomic molecule - rigid rotor[10]

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

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

- Probability distributions:

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

$$q_{rot} = \sum_{j'} (2j' + 1) \exp\left[-\beta \Upsilon j'(j' + 1) \right]$$
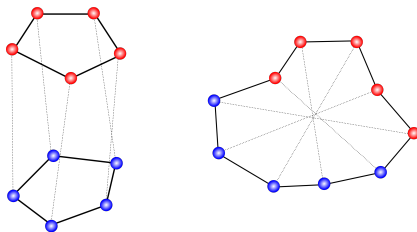
Fully quantum second virial coefficient

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

---

[10] K. Patkowski et al., J. Chem. Phys. (2008).

Diatomic molecule - rigid rotor[11]

- A closer look at the effective potential:

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

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

---

[11] 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.[12]: two independent atoms (vs. one rigid rotor previously).
- Leads to possibility of avoiding quantum mechanical calculations.
- Sampling problem can be analyzed more mathematically, without having to worry about the physics of the rigid rotor.
- A more viable path to study multiatomic systems.

---

[12] G. Garberoglio et al., J. Chem. Phys. (2014).

Orientation sampling

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

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

- Define π to be the $\boldsymbol{b}$-dependent terms of the probability distribution F.

- We generate a trial configuration with probability $\tau(o \to n)$, based on an approximation for π denoted as $\tilde{\pi}$, and accept or reject based on:

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

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

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

Orientation sampling - bisection algorithm

- The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images $\boldsymbol{b}_i, \boldsymbol{b}_k$ 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 $= 8$

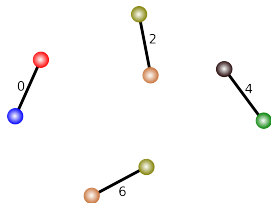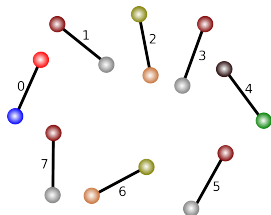# Orientation sampling - bisection algorithm

- The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images $\boldsymbol{b}_i, \boldsymbol{b}_k$ 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

- The choice of orientation of image 0 is arbitrary

- At every stage, we are given two images $\boldsymbol{b}_i, \boldsymbol{b}_k$ 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

- The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images $\boldsymbol{b}_i, \boldsymbol{b}_k$ 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

- Adjacent image probability distribution:

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

Simplified picture

- The angle α can be calculated by choosing C at random, uniformly on $[0, 1]$.
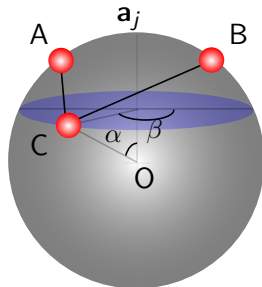
$$\alpha = \cos^{-1}\left[1 + (1/\kappa)\right.$$
$$\left. \times \ln\left(1 - C(1 - \exp[-2\kappa])\right)\right],$$
$$\kappa = 4\cos(\psi_{i,k}/2)k_h\ b^2$$

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 ($<r>_T$)[13].

- Average the entire intermolecular potential ($<U>_T$) over internal degrees of freedom of each monomer, weighted by the appropriate wave function[14].

- 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 flexibility[15].

---

[13] G. Garberoglio et al., J. Chem. Phys. (2012).

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

[15] G. Garberoglio et al., J. Chem. Phys. (2014).

Bond-length sampling

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

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

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

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:-

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

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

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

- 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:

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

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

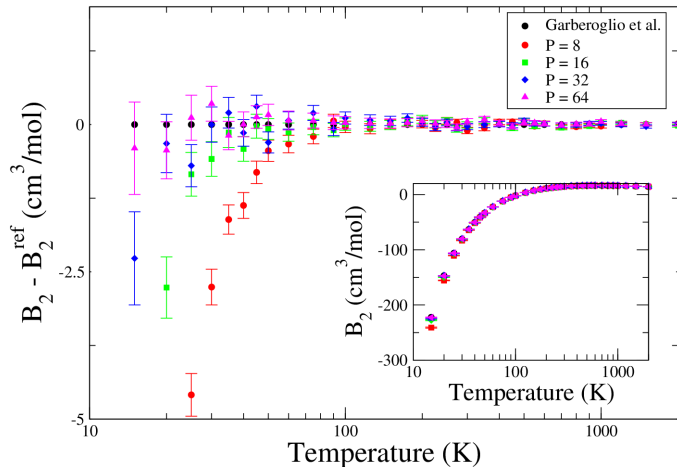# B_2 values for Hydrogen compared with Garberoglio et al.[16].

Bond length: $< r >_0$, total configuration samples: 10^7.
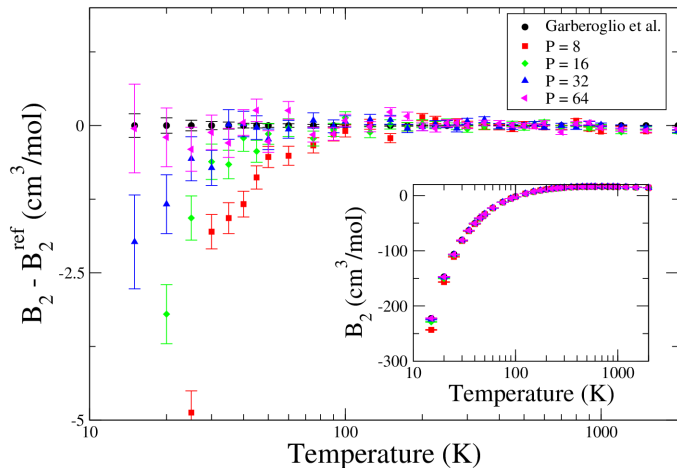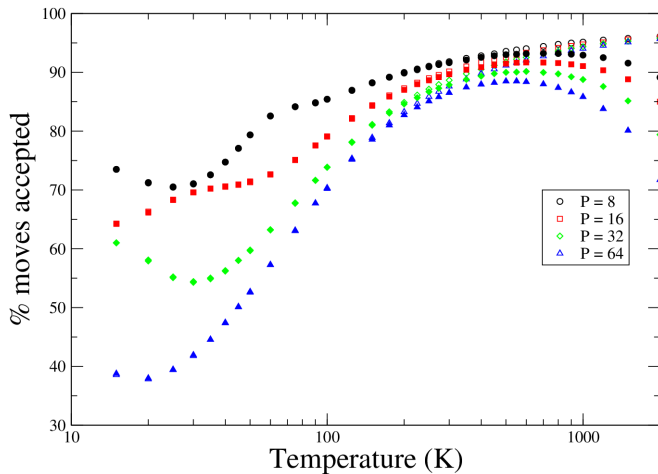
[16] G. Garberoglio et al., J. Chem. Phys. (2014).

B_2 values for Hydrogen compared with Garberoglio et al.[17].

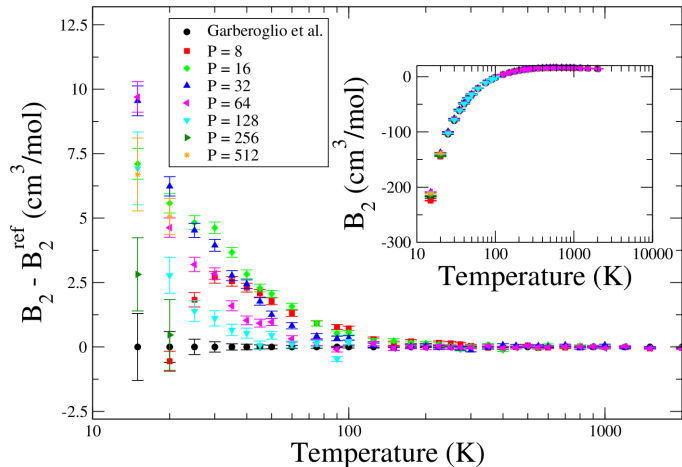Bond length: $<r>_T$, total configuration samples: 10^7.

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

Performance of the orientation move.

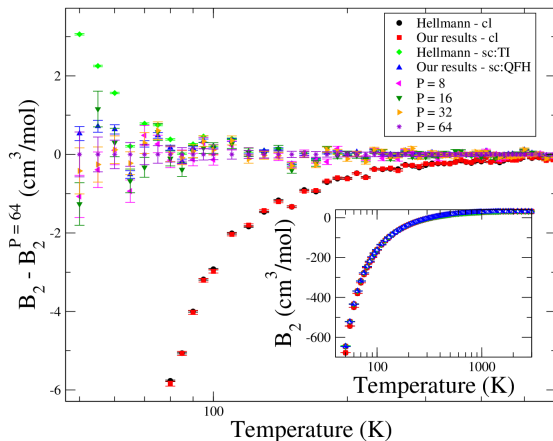# B_2 values for Hydrogen compared with Garberoglio et al.[18].

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

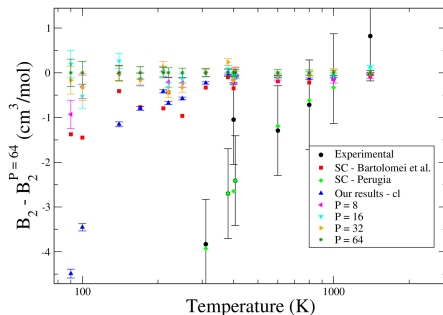[18] G. Garberoglio et al., J. Chem. Phys. (2014).

B_2 values for Nitrogen compared with Hellmann[19].

Bond length: $< r >_0$, total configuration samples: 10^9 for cl, sc and 10^8 for all PI cases.

19 R. Hellmann, Mol. Phys. (2013).

B_2 values for Oxygen compared with Bartolomei et al.[22].

Bond length: $< r >_0$, total configuration samples: 10^8 for cl and 10^7 for all PI cases. Experimental[20], SC - Perugia[21].

---

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

[21] V. Aquilanti et al., J. Am. Chem. Soc. (1999).

[22] 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