Path Integral Monte Carlo Studies of Hard Sphere Systems

William Dawkins & Alex Gezerlis

University of Guelph

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Overview of Path Integral Monte Carlo

- Used to calculate thermodynamic properties of systems
- Systems are at finite temperature
- Use Feynman path integral formalism to describe partition function as integrals over coordinate space
- Use Monte Carlo methods to calculate these integrals

Path Integral Form of Partition Function

- PIMC formalism begins with the thermal density matrix of the system:

$$\hat{\rho} = e^{-\beta \hat{H}} = \sum_i e^{-\beta E_i} |\psi_i><\psi_i|$$

- The partition function is the trace of the thermal density matrix:

$$Z = Tr(\hat{\rho})$$

- The trace can be performed in the position basis:

$$Z = \int dR < R|\hat{\rho}|R >$$

- Note: R = {$r_1, r_2, \ldots, r_i$}

Path Integral Form of Partition Function

- Take advantage of these two properties:

$$e^{-(\beta_1+\beta_2)\hat{H}} = e^{-\beta_1\hat{H}}e^{-\beta_2\hat{H}} \qquad \hat{1} = \int |R><R|dr$$

- With these it is possible to expand the matrix elements:

$$Z = \int dR < R|e^{\beta\hat{H}}|R >$$

$$Z = \int dRdR_2 < R|\, e^{-(\beta/2)\hat{H}}|R_2 >< R_2|e^{-(\beta/2)\hat{H}}|R >$$

$$Z = \int \ldots \int dRdR_1 \ldots dR_{M-1}\rho(R, R_1; \beta/M)\rho(R_1, R_2; \beta/M) \ldots \rho(R_{M-1}, R; \beta/M)$$

Evaluation of Intermediate Matrix Elements

- The intermediate matrix elements are referred to as propagators

$$\rho(R_N, R_{N+1}; \tau) = < R_N | \, e^{-\tau \hat{H}} | R_{N+1} >, \; {}^{\beta}/_{M} = \tau$$

- Use Trotter decomposition:

$$\rho(R_N, R_{N+1}; \tau) = < R_N | \, e^{-\tau \hat{K}} e^{-\tau \hat{V}} | R_{N+1} >$$

$$\rho(R_N, R_{N+1}; \tau) = \frac{1}{(4\pi\lambda\tau)^{3N/2}} \exp\left(-\frac{(R_N - R_{N+1})^2}{4\lambda\tau}\right) < R_N | e^{-\tau \hat{V}} | R_{N+1} >$$

- The first term is denoted as ρ_{free}

Evaluation of Intermediate Matrix Elements

- In many body simulations, the potential component of the propagator takes the form:

$$\rho(R_N, R_{N+1}; \tau) = \rho_{free} \prod_{i,j} \rho_{ij}(r_{ij}, r'_{ij})$$

- Where r_{ij} and r'_{ij} are the separation distances between particles at consecutive configurations

- The two body density matrix is often times difficult to evaluate exactly, often times approximations are used

- Results converge with increasing M, referred to as ‘time slices’

Hard Sphere Systems

- The hard sphere potential is infinite when the radii of the particles overlap, but zero otherwise
- Can add a hard cavity, infinite potential when the separation distance is greater than a specified distance
- Hard Sphere systems can model atoms or spherical molecules with minimal computational effort
- Previous work has been done deriving two body density matrices for the hard sphere problem

Hard Sphere Systems

- For the regular hard sphere problem:

$$\rho_{IA}(r_{ij}, r'_{ij}) = (1\text{-}e^{m/\hbar^2\tau(r-\sigma)(r'-\sigma)})$$

$$\rho_{CB}(r_{ij}, r'_{ij}) = (1\text{-}\frac{\sigma(r+r')-\sigma^2}{rr'} e^{m/2\hbar^2\tau(r-\sigma)(r'-\sigma)(1-cos\chi)})$$

- Current work in this project is to study comparative effectiveness of both propagators

Calculating Observables

- The full functional form of the partition function is now known

$$Z = \int d\boldsymbol{\mathcal{R}} \prod_{N=1}^{M} \rho_{free}(R_N, R_{N+1}) \prod_{i,j} \rho_{ij}(r_{ij}, r'_{ij}) \quad , \boldsymbol{\mathcal{R}} = \{R_N\}$$

$$Z = \int d\boldsymbol{\mathcal{R}}\, e^{-U_{eff}(\boldsymbol{\mathcal{R}})}$$

- Thermodynamic observables can be written as a function of $\boldsymbol{\mathcal{R}}$ by taking the appropriate derivatives of the partition function

Calculating Observables

- The expectation values of the operators can be calculated as:

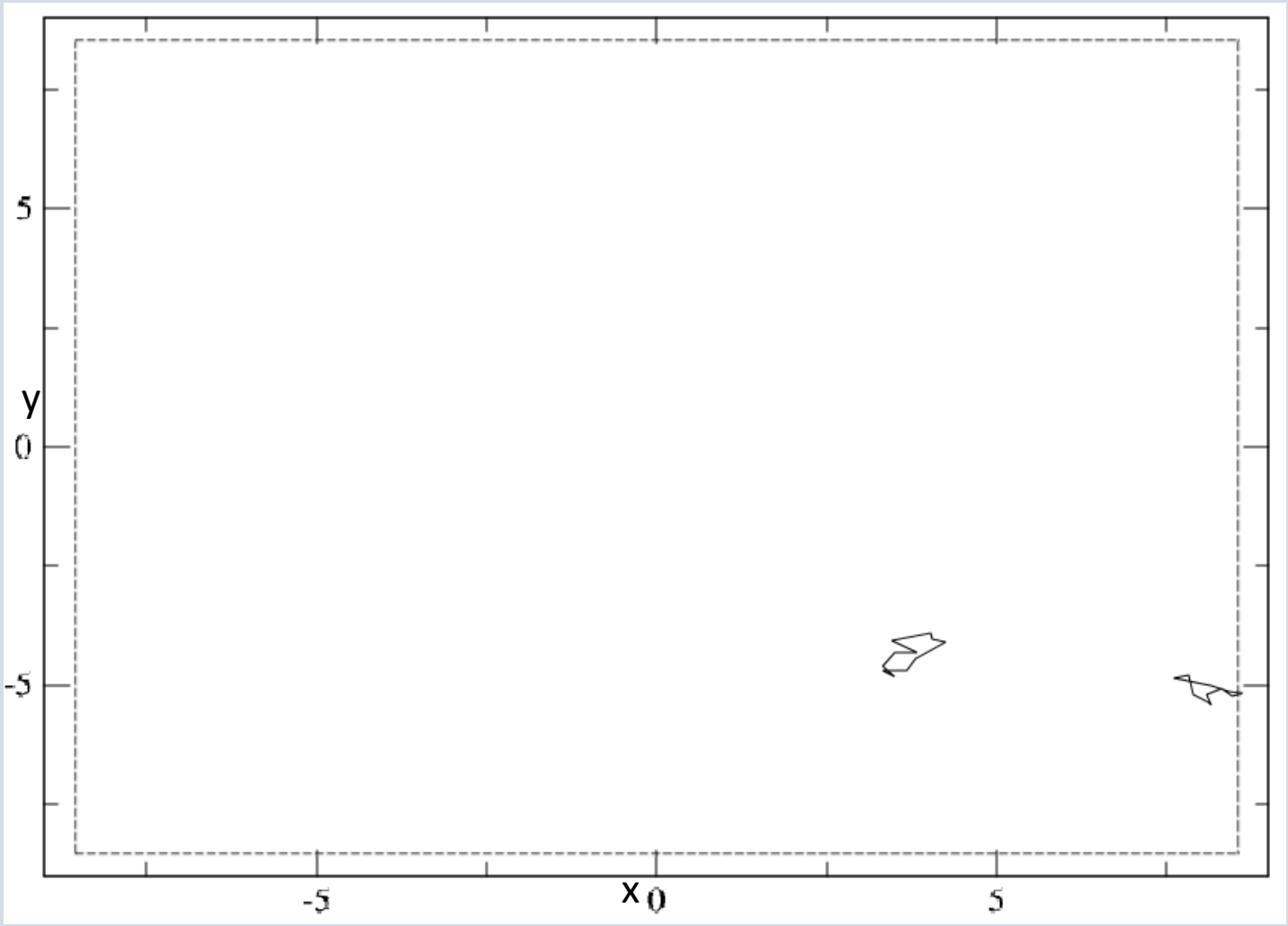
$$< O > = Z^{-1} \int d\boldsymbol{\mathcal{R}} O(\boldsymbol{\mathcal{R}}) e^{-U_{eff}(\boldsymbol{\mathcal{R}})}$$

- Integrate using Metropolis algorithm to sample configurations $\boldsymbol{\mathcal{R}}$ from the probability distribution:

$$\mathrm{P}(\boldsymbol{\mathcal{R}}) = Z^{-1} e^{-U_{eff}(\boldsymbol{\mathcal{R}})}$$

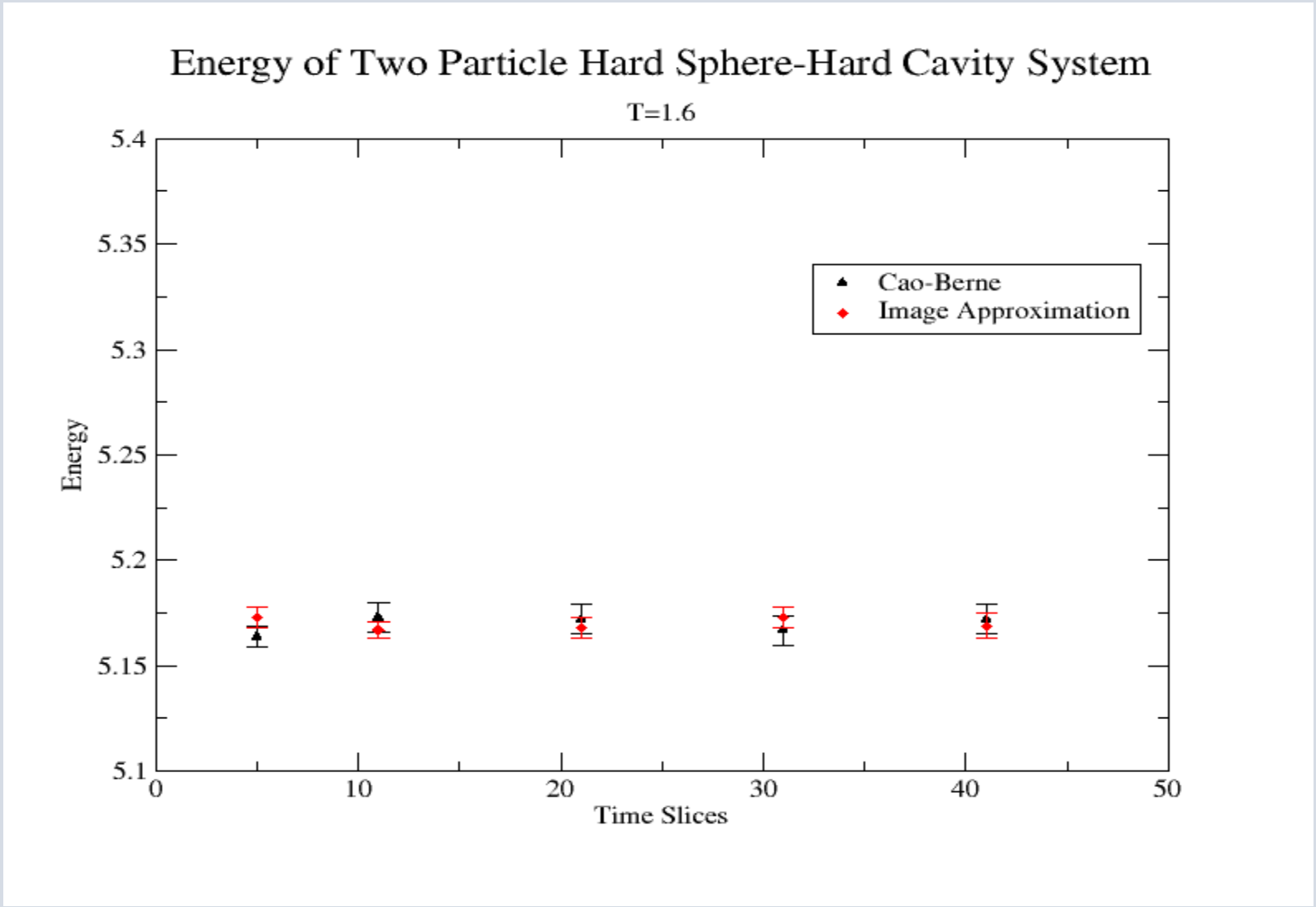
Calculating Observables

- PIMC simulation of two particles at a given Monte Carlo Step
- Particles are represented as ring polymers



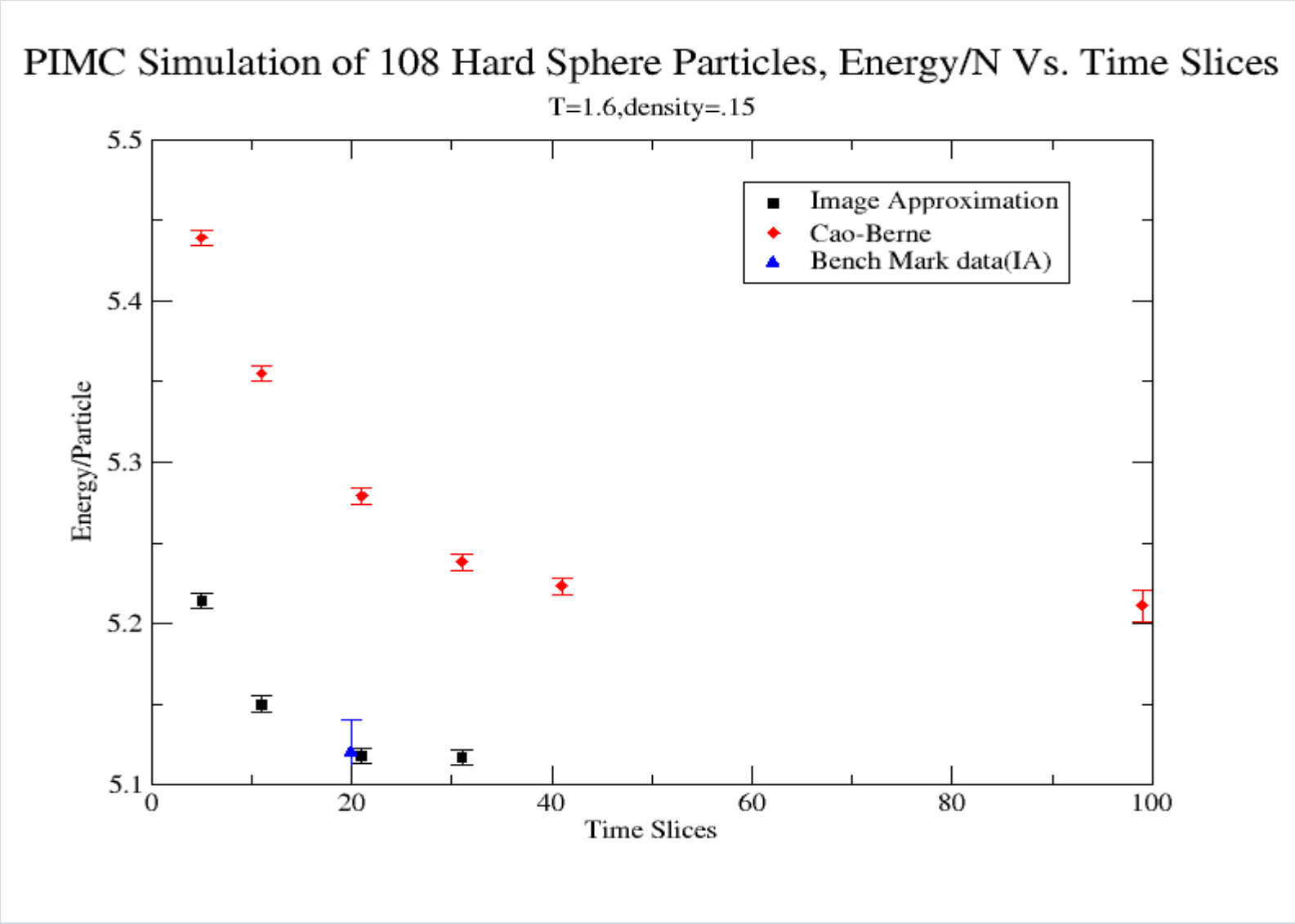
Convergence in Energy of Two Hard Sphere Particles Inside Hard Cavity

- V is an infinite spherical well in separation distance
- Calculation performed with both propagators
- Convergence seems to be similar between propagators



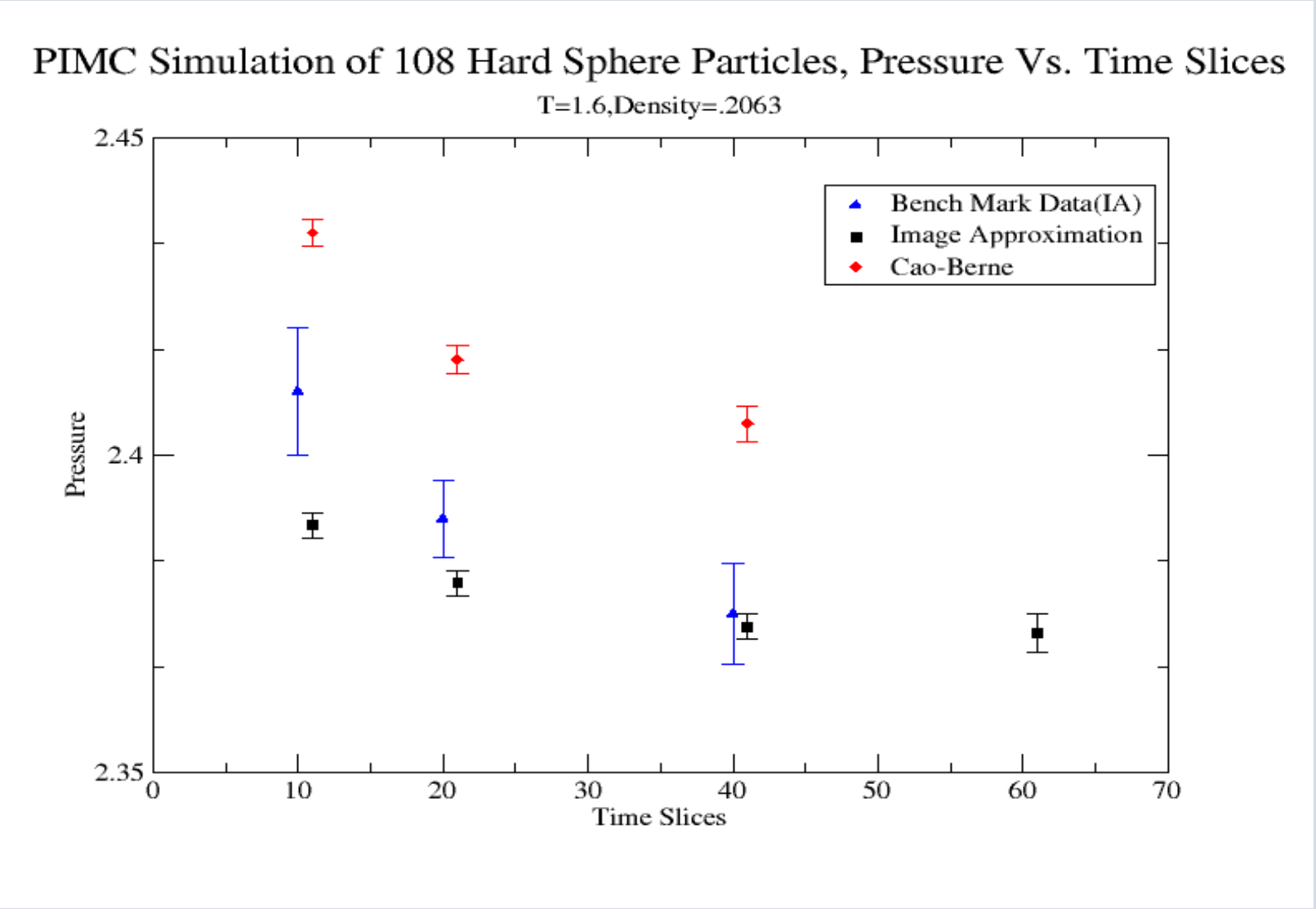
Convergence in Energy of ‘N’ Hard Sphere System

- 108 Hard sphere particles
- Convergence in E/N occurs faster with image approximation propagator



Convergence in Pressure of ‘N’ Hard Sphere System

- 108 Hard sphere particles
- Convergence in pressure appears to be equal between propagators



Conclusions

- Path integral Monte Carlo is a technique used to calculate thermodynamic averages on finite temperature systems
- Hard Sphere systems are a popular choice due to being a realistic model that is computationally straight forward
- Varying propagators yield varying convergence/accuracy