Ergodicity in Path Integral Simulations

Matthew Schmidt

Group Meeting Seminar

November 11, 2016

What is Ergodicity?

- **Ergodic**: A system's statistical properties can be deduced from a single, sufficiently long, random sample of the process
  - Monte Carlo, statistics/econometrics
- **Ergodic ("dynamics")**: The time average of a system is equal to the phase space average
  - During the course of a long simulation, the system explores all of it's accessible states with the correct statistical probabilities

Outline

- Path Integral Methods (Molecular Dynamics)
  - Finite Temperature PIMD
  - Zero Temperature LePIGS
- LePIGS vs Low Temperature PIMD
  - H_2-H_2O
- "Quantifying Ergodicity"
  - LePIGS on pure hydrogen clusters (and isotopologues)
  - What can we infer from a system lacking ergodicity?
- Discrepancy stemming from lack of ergodicity
  - Chemical Potential of hydrogen clusters
- Possible solution to more effective sampling
  - WORM Algorithm

Path Integral Formulation
Finite Temperature

- Partition function Z
- In canonical ensemble $Z = Tr(e^{-\beta\hat{H}}) = \int dR \langle R | e^{-\beta(\hat{K}+\hat{V})} | R \rangle$

$$Z = \int dR_1 ... dR_P \, \langle R_1 | \, \Omega \, | R_2 \rangle \, ... \, \langle R_P | \, \Omega \, | R_1 \rangle$$

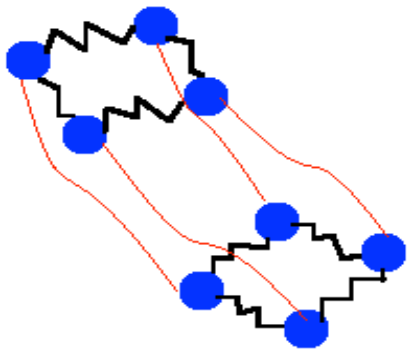
$$\Omega = e^{-\frac{\tau}{2}\hat{V}} e^{-\tau\hat{K}} e^{-\frac{\tau}{2}\hat{V}}$$

$$\beta = \frac{1}{k_B T}$$

$$\tau = \frac{\beta}{P}$$

- Particles represented by quantum beads (P) connected by harmonic springs

$$Z = \lim_{P\to\infty} \left(\frac{m}{2\pi\tau\hbar^2}\right)^{\frac{P}{2}} \int dR_1 ... dR_P \times \exp\left\{-\sum_{i=1}^{P}\left[\frac{m}{2\tau\hbar^2}(R_{i+1}-R_i)^2 + \tau V(R_i)\right]\right\}$$



Feynman, R. P., 1953, Phys. Rev. 90, 1116

Path Integral Ground State
Zero Temperature Limit

- Ground state partition function

$$Z_0 = \lim_{\beta \to \infty} \langle \psi_T | \exp(-\beta \hat{H}) | \psi_T \rangle$$

- ψ_T is a 'guess' of the exact ground state wavefunction
- β relaxes ψ_T to the ground state
- In position representation:

$$Z_0 = \lim_{P \to \infty} \int dR_1 \ldots \int dR_P \exp\left\{ - \left[\sum_{i=1}^{P-1} \left[-\frac{m}{2\tau\hbar^2} (R_i - R_{i+1})^2 \right] + \sum_{i=1}^{P} \left[\tau V_i'(R_i) \right] \right] \right\}$$

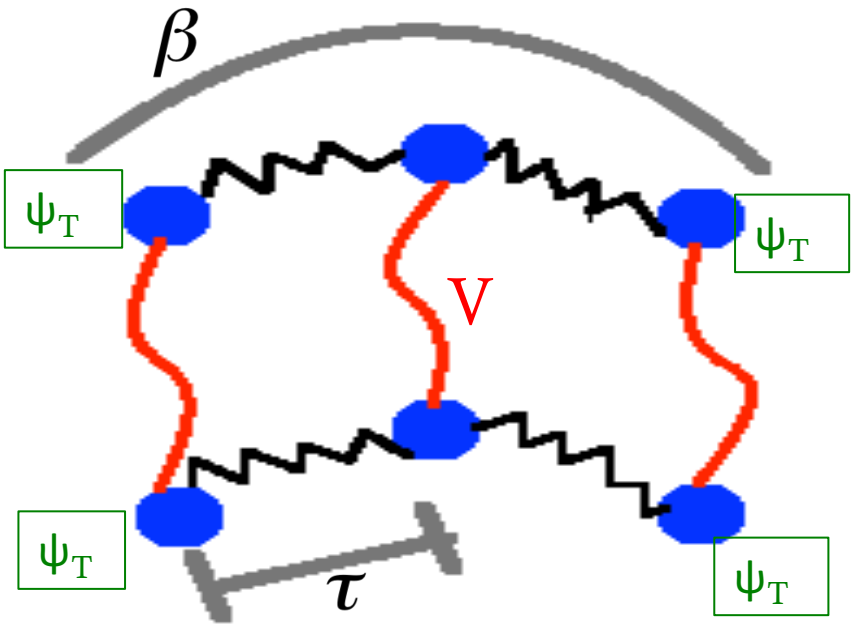
$$V_i' = \begin{cases} \frac{1}{2} V(R_i) - \frac{1}{\tau} \ln\left[\psi_T(R_i)\right] & \text{if } i = 1 \text{ or } i = P \\ V(R_i) & \text{otherwise.} \end{cases}$$

$$\tau = \frac{\beta}{P-1}$$

S. Constable, M. Schmidt, C. Ing, T. Zeng, and P.-N. Roy, J. Phys. Chem. A 117, 7461 (2013)

Path Integral Ground State

Zero Temperature Limit



$$Z_0 = \lim_{P\to\infty} \int dR_1 \ldots \int dR_P \exp\left\{ - \left[\sum_{i=1}^{P-1} \left[-\frac{m}{2\tau\hbar^2} \left(R_i - R_{i+1}\right)^2 \right] + \sum_{i=1}^{P} \left[\tau V_i' \left(R_i\right) \right] \right] \right\}$$

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S. Constable, M. Schmidt, et al. J. Phys. Chem. A 117, 7461 (2013)

Path Integral Methods

- Monte Carlo (PIMC)[1]
  - Randomly sample path configuration
  - Maintain the canonical ensemble detailed balance
- Molecular Dynamics (PIMD)[2]
  - Path configurations determined by equations of motion
  - More general – no need to design MC moves
    - Only a few simulation parameters required!
  - Can approximate real-time dynamics
  - Similar efficiency[3]
  - Our code: Cartesian co-ordinates only

Fig: http://www.coinsandcanada.com/news-archives.php?month=12&year=2009

[1] D. M. Ceperley, Rev. Mod. Phys. 67, 279 (1995)

[2] M. Parrinello and A. Rahman, J. Chem. Phys. 80, 860 (1984)

[3] C. Ing, K. Hinsen, J. Yang, T. Zeng, H. Li, and P.-N. Roy, J. Chem. Phys. 136, 224309 (2012).

Quantum Methods to obtain Ground State Properties

Monte Carlo	Molecular Dynamics
Low Temperature Path Integrals (PIMC)	Low Temperature Path Integrals (PIMD)
Path Integral Ground State (PIGS-MC)	Langevin equation Path Integral Ground State (LePIGS)
Diffusion Monte Carlo (DMC)[1]	

[1] J. B. Anderson, *J. Chem. Phys.* **63**, 1499–1503 (1975)

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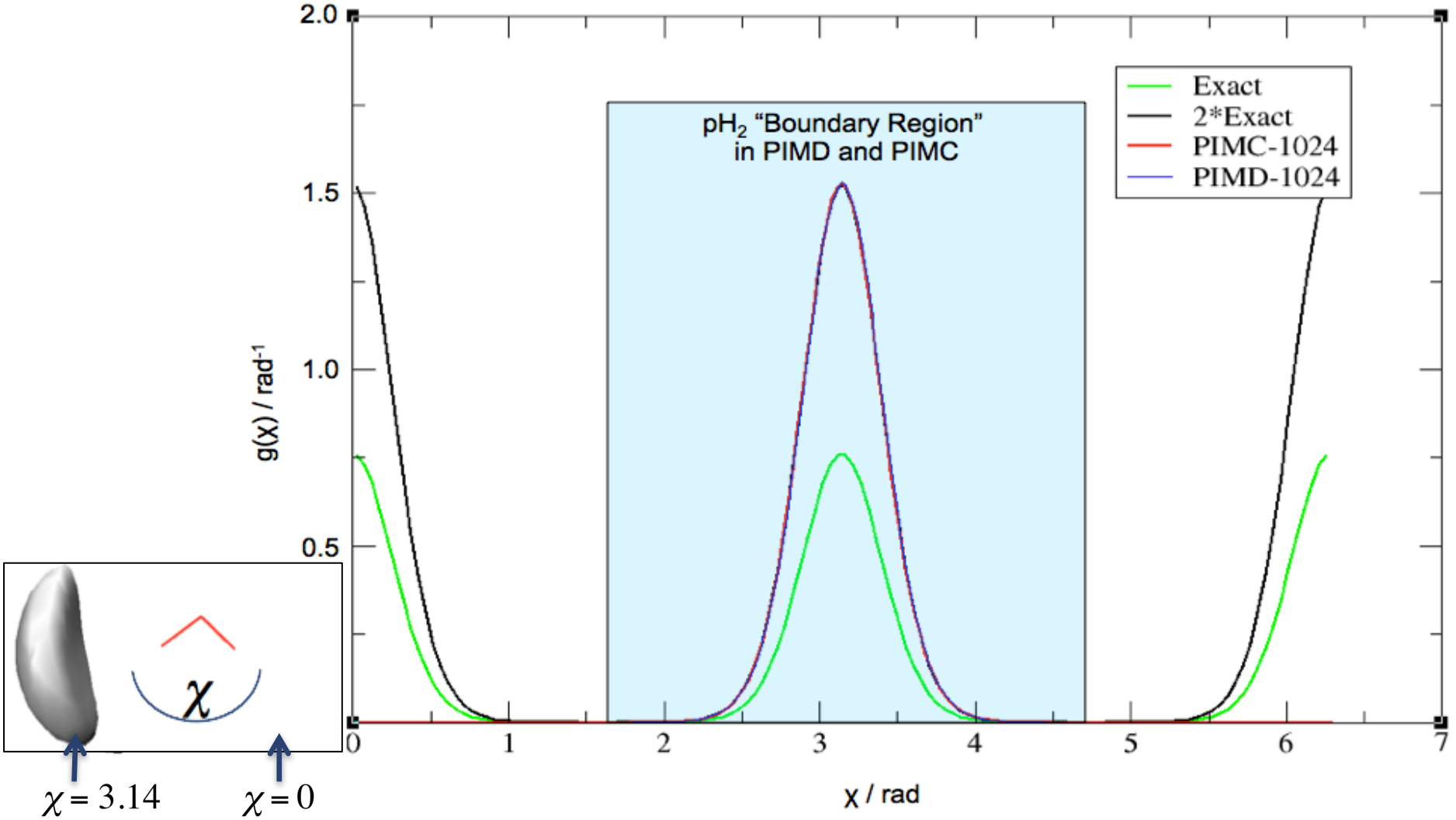
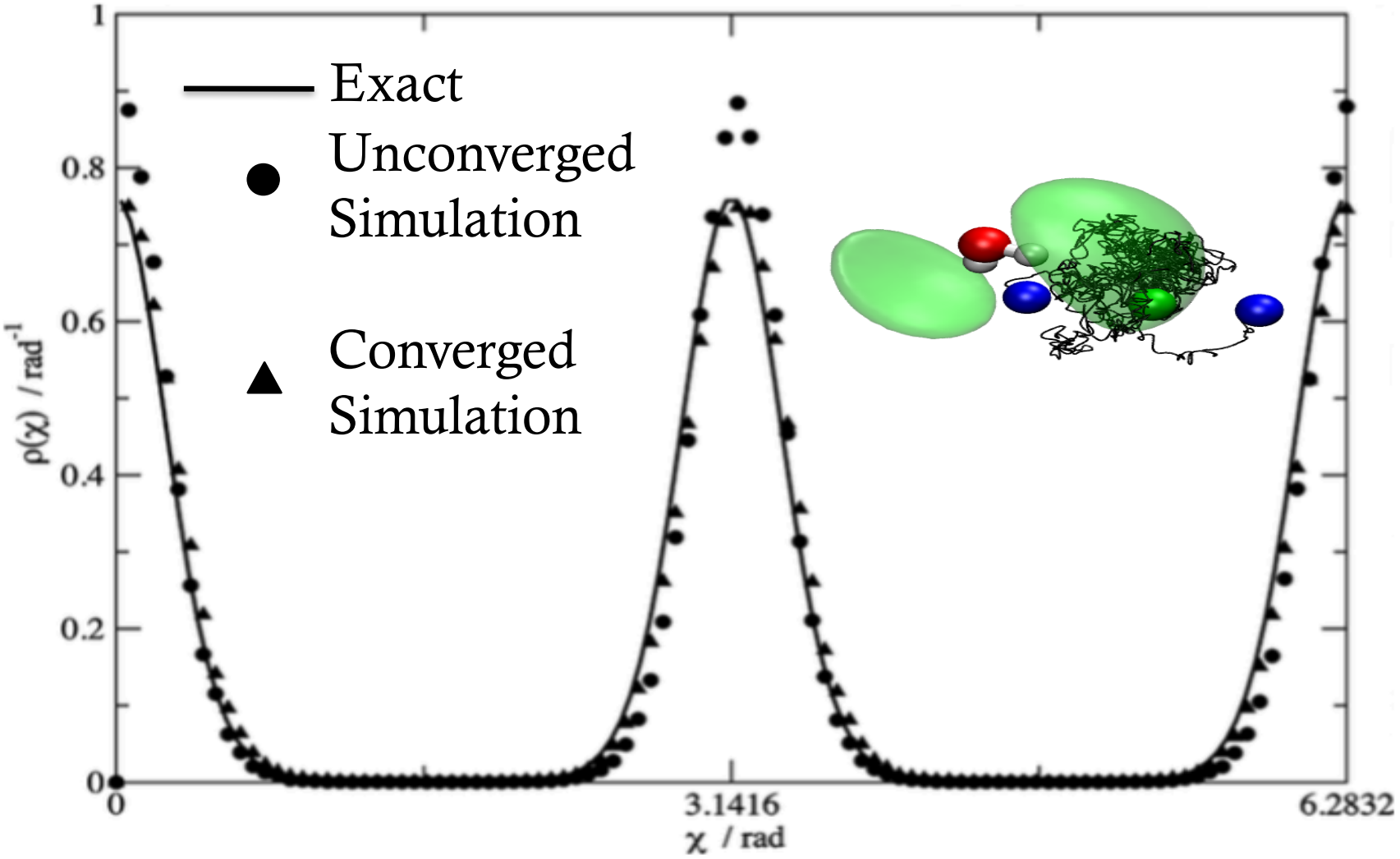
[1] J. B. Anderson, *J. Chem. Phys.* **63**, 1499–1503 (1975)

PIMD: (Fixed H_2O)-pH_2

T = 0.37K



LePIGS: (Fixed H_2O)-pH_2



Accelerated nuclear quantum effects sampling with open path integrals

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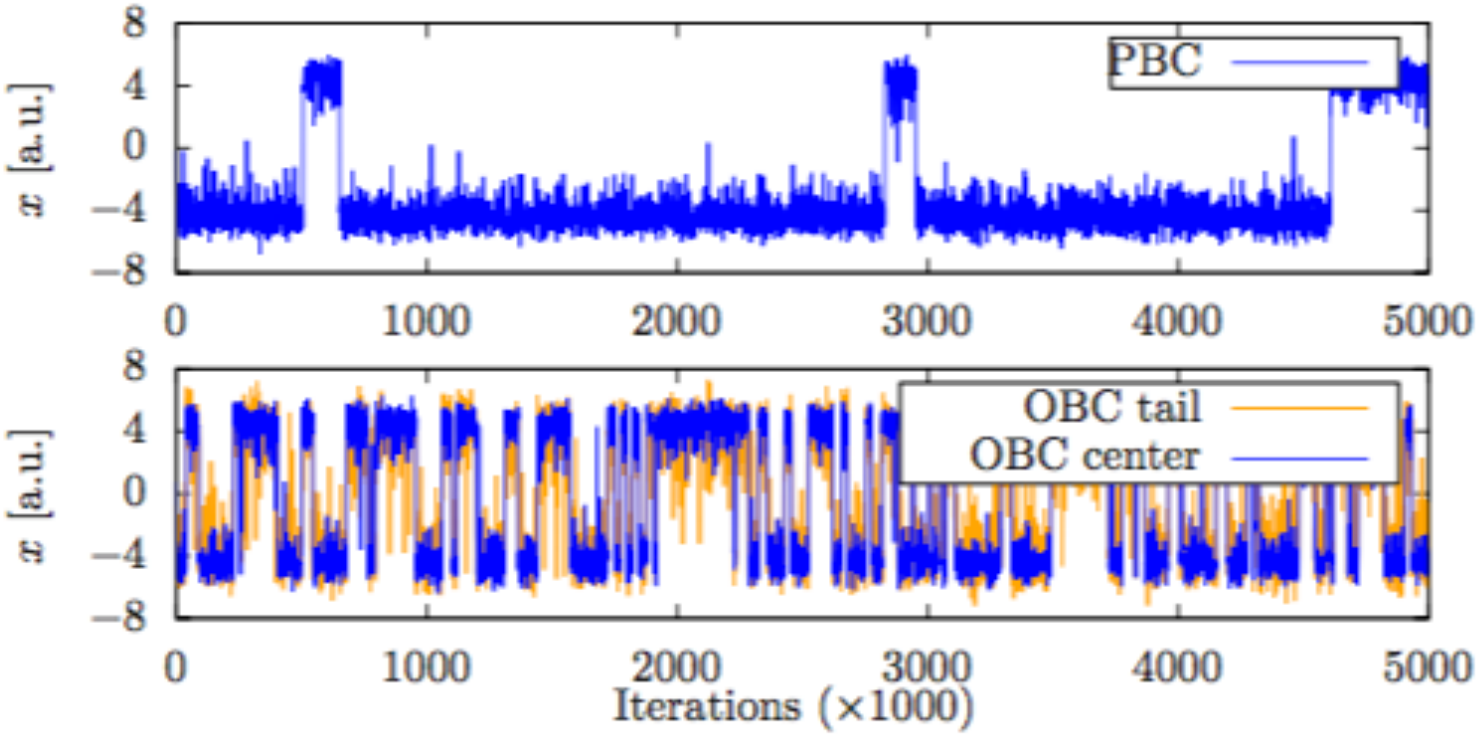
Theoretische Physik, ETH Zurich, 8093 Zurich, Switzerland
Matthias Troyer
Theoretische Physik, ETH Zurich, 8093 Zurich, Switzerland and
Quantum Architectures and Computation Group, Microsoft Research, Redmond, WA 98052, USA

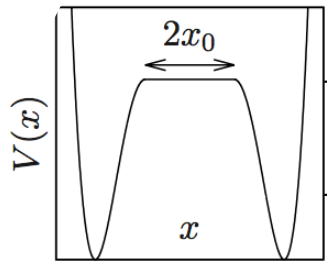
(Dated: 4 August 2016)

We numericaly demonstrate that, in double well models, the autocorrelation time of open path integral Monte Carlo simulations can be much smaller compared to standard ones using ring polymers. We also provide an intuitive explanation based on the role of *instantons* as transition states of the path integral pseudodynamics. Therefore we propose that, in all cases when the ground state approximation to the finite temperature partition function holds, open path integral simulations can be used to accelerate the sampling in realistic simulations aimed to explore nuclear quantum effects.



Closed Path

Open Path



Pure Hydrogen Clusters

- Numerous groups have looked at pure pH_2 and oD_2 clusters[1-3]
- For us: Benchmark for LePIGS
  - Energetic and structural properties
  - The effect of trial wavefunctions
- Investigated the ergodicity of these systems
  - Solid-like or liquid-like behaviour
  - Attempts to quantify ergodicity?

[1] J. E. Cuervo and P.-N. Roy
[2] Guardiola and Navarro
[3] Mezzacapo and Boninsegni

Lindemann Criterion

[1]

$$\delta_L = \frac{2}{N(N-1)} \sum_{i<j} \frac{\left(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2\right)^{1/2}}{\langle r_{ij} \rangle}$$

[2]

$$\delta_{LG} = \frac{\left(\langle r^2 \rangle - \langle r \rangle^2\right)^{1/2}}{\langle r \rangle}$$

Limit of long simulation, $\delta_L = \delta_L{}^G$

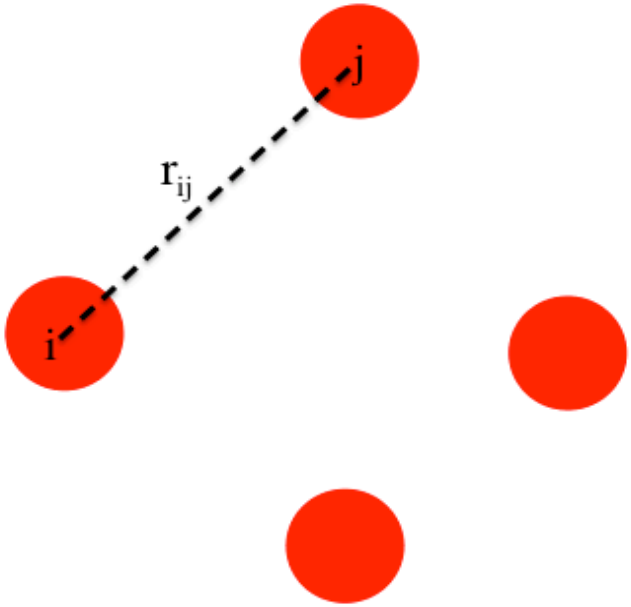
Deviation between δ_L and $\delta_L{}^G$ – enhanced rigidity

[3]

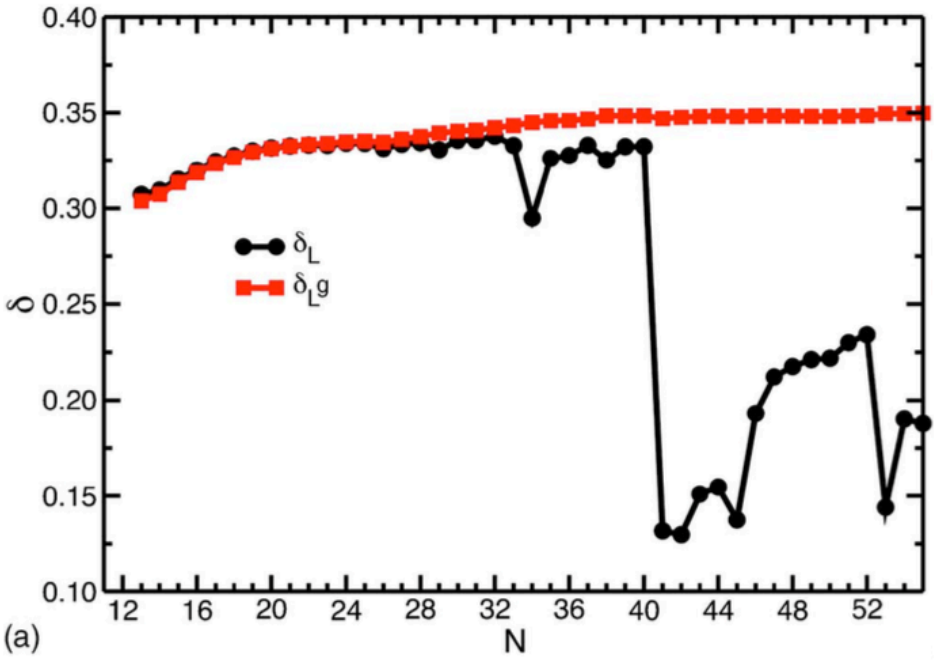
$$\delta_Q = \sqrt{N-1} \frac{\sqrt{\langle \left[\sum_{i<j} r_{ij}^2\right]^2 \rangle - \langle \sum_{i<j} r_{ij}^2 \rangle^2}}{\langle \sum_{i<j} r_{ij}^2 \rangle}$$

Our Work[4]

$$\delta_F = \frac{\sqrt{\langle \left[\sum_{i<j} r_{ij}\right]^2 \rangle - \langle \sum_{i<j} r_{ij} \rangle^2}}{\langle \sum_{i<j} r_{ij} \rangle}$$

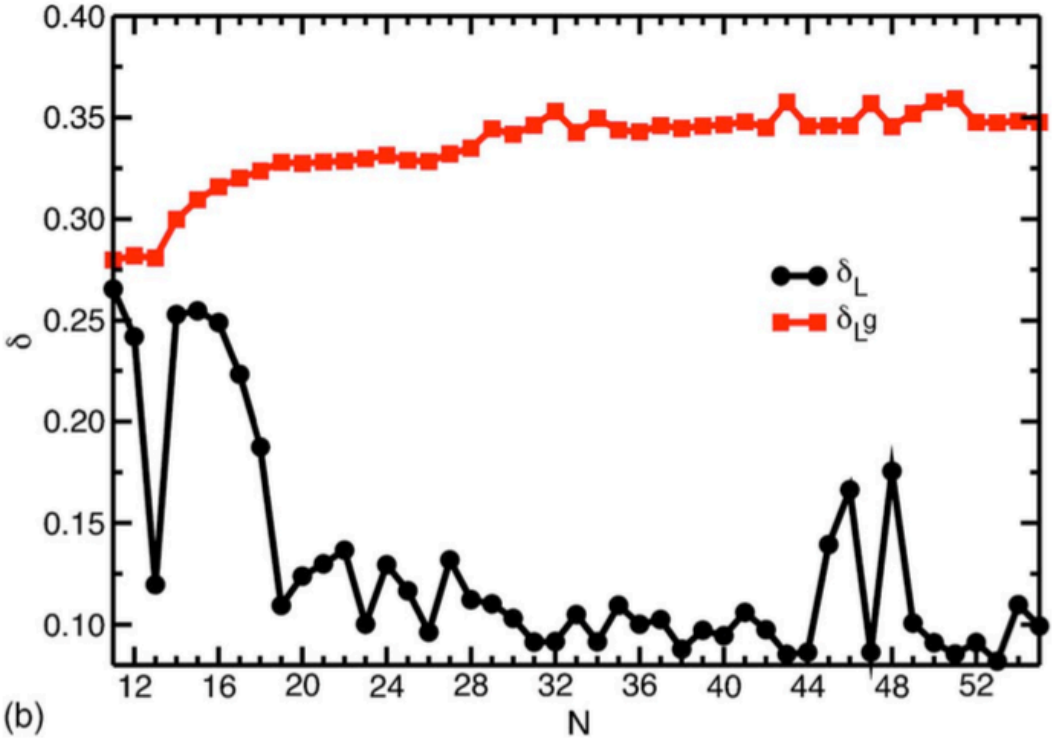


[1] F. Lindemann, Physik. Z. 11, 609 (1910)
[2] J. E. Cuervo and P.-N. Roy, J. Chem. Phys. 128, 224509 (2008)
[3] R. Guardiola and J. Navarro, J. Phys. Chem. A 115, 6843 (2011)
[4] M. Schmidt et al, J. Chem. Phys, **140**, 234101 (2014)



$(pH_2)_N$

$(oD_2)_N$



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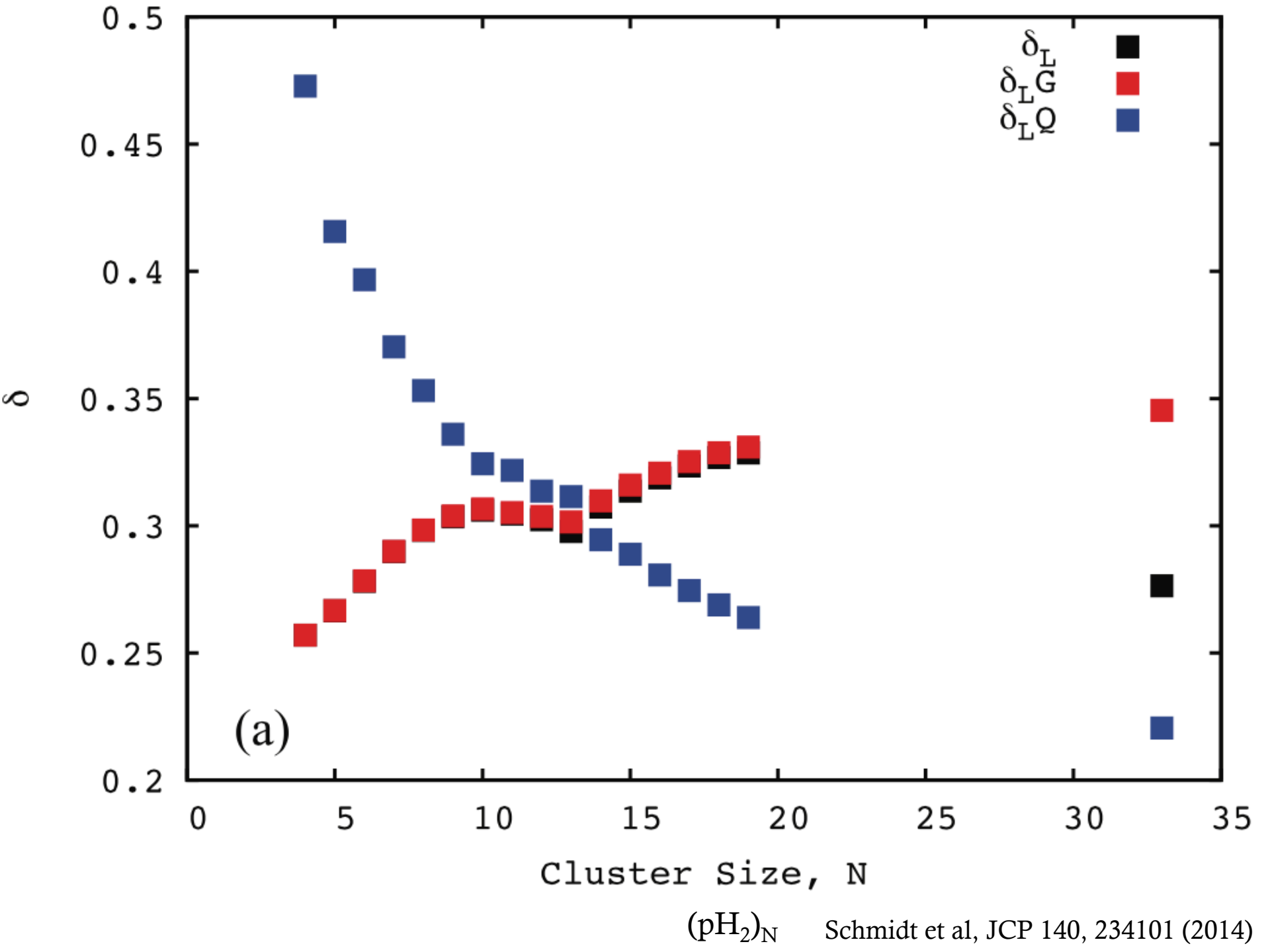
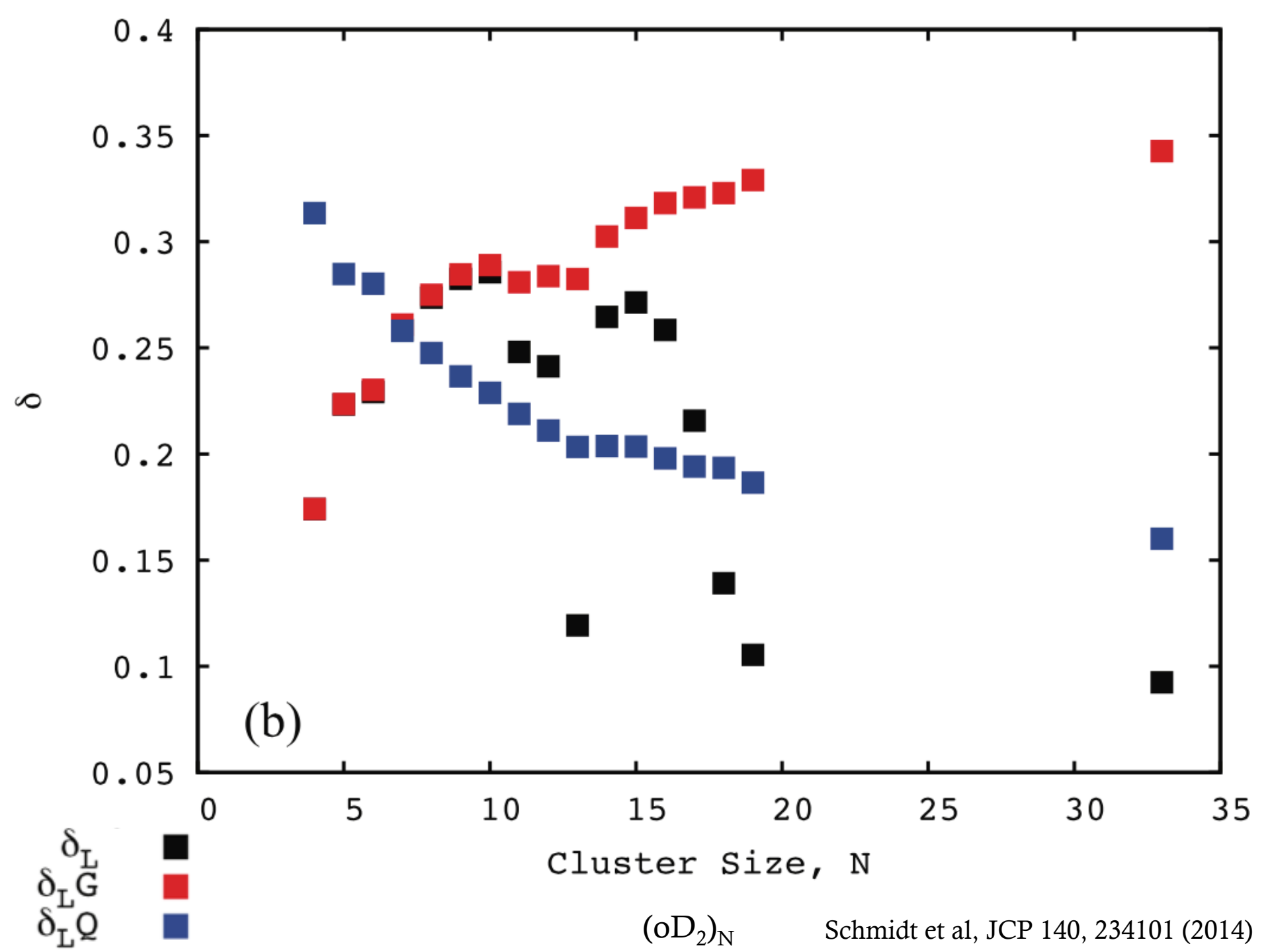


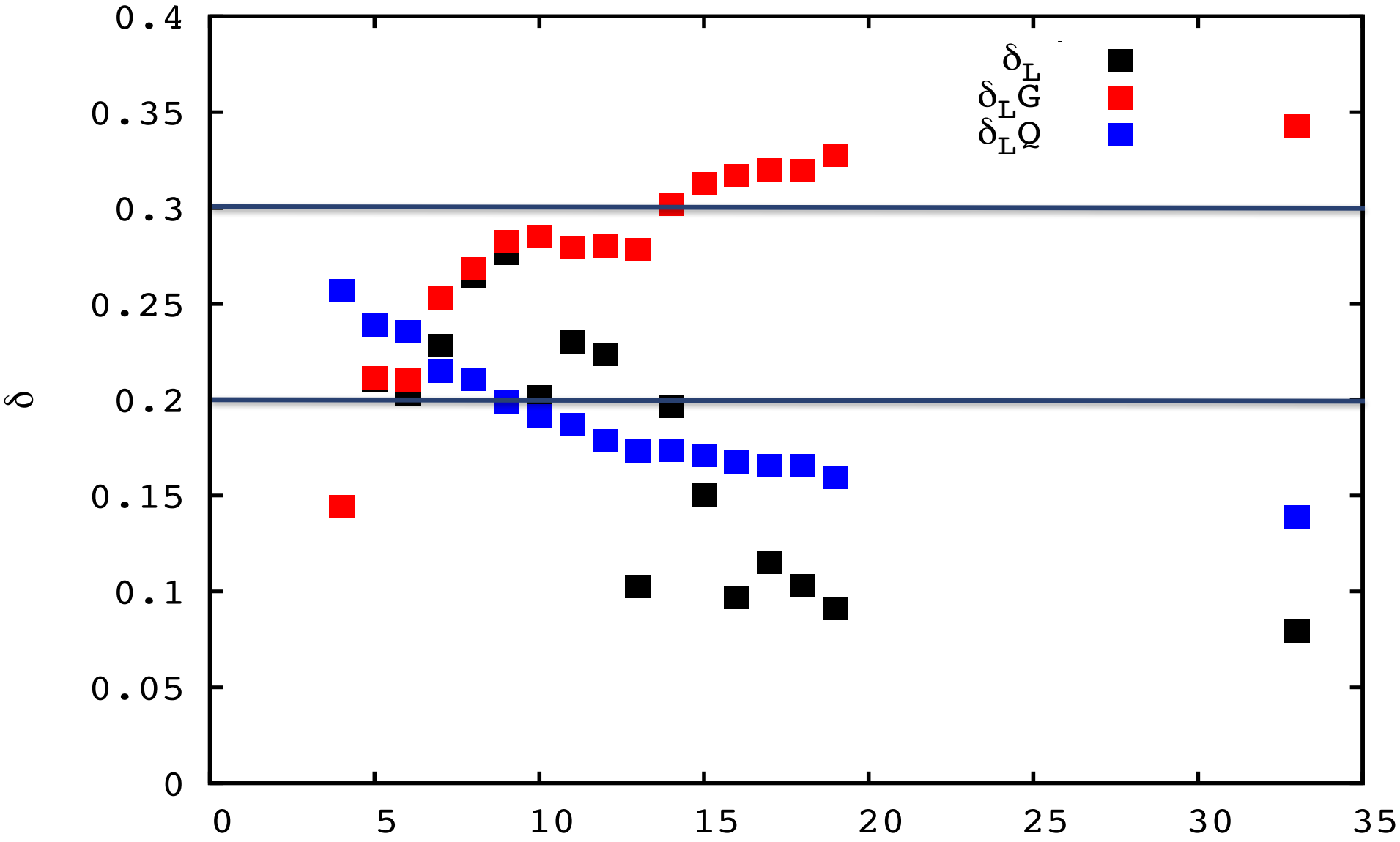
$(pH_2)_N$ Schmidt et al, JCP 140, 234101 (2014)



$(oD_2)_N$

Schmidt et al, JCP 140, 234101 (2014)

Lindemann – $(pT_2)_N$



Schmidt et al, JCP 140, 234101 (2014)

Trial Wavefunctions

- Unity: $\psi_T = 1$
  - Contains no information about system
  - Ensures overlap with the ground state wavefunction
- Jastrow: $\psi_T = \exp\left[-\frac{1}{2}\sum_{i<j}\left(\frac{b}{r_{ij}}\right)^5\right]$
  - Liquid-like trial wavefunction
  - 'b' represents hard-core repulsion between pair distance (r_{ij})
- Normal Mode: $\psi_T = \exp\left[-\frac{1}{2\mathrm{h}}\sum_{k=1}^{3N-6}\omega_k Q_k^2\right]$
  - Solid-like trial wavefunction (harmonic)
  - ω_k – vibrational frequencies, Q_k – normal modes

Energy convergence with τ for "Stable" System

Normal Modes Wavefunction

Jastrow Wavefunction

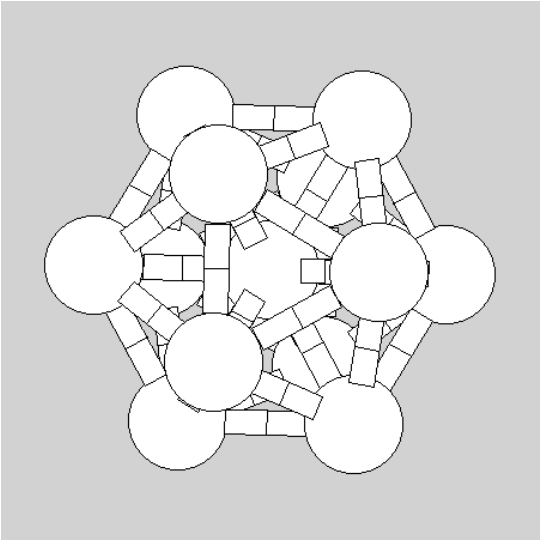
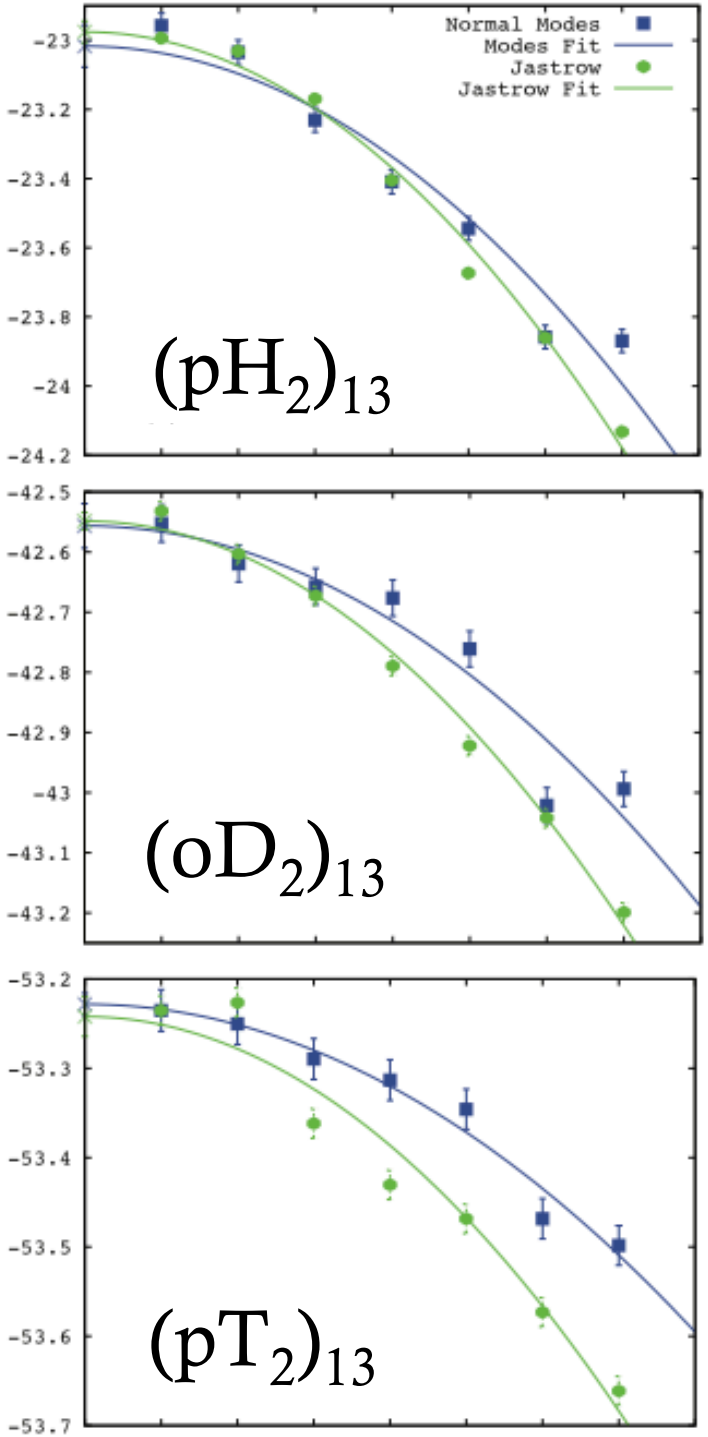


Fig: Cambridge Cluster Database



Schmidt et al, JCP 140, 234101 (2014)

Energy convergence with τ for "Floppy" System

Normal Modes Wavefunction

Jastrow Wavefunction

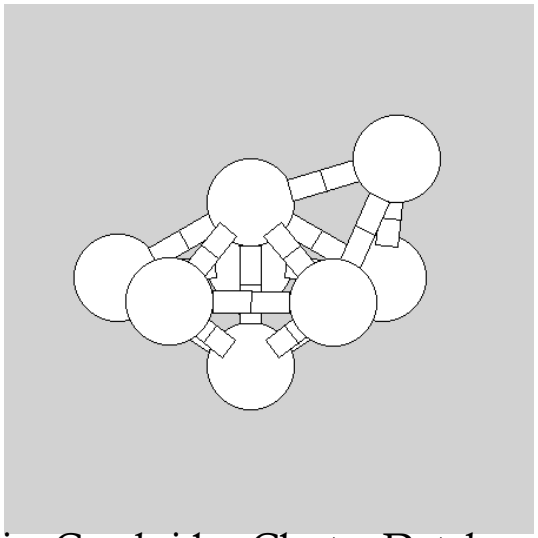
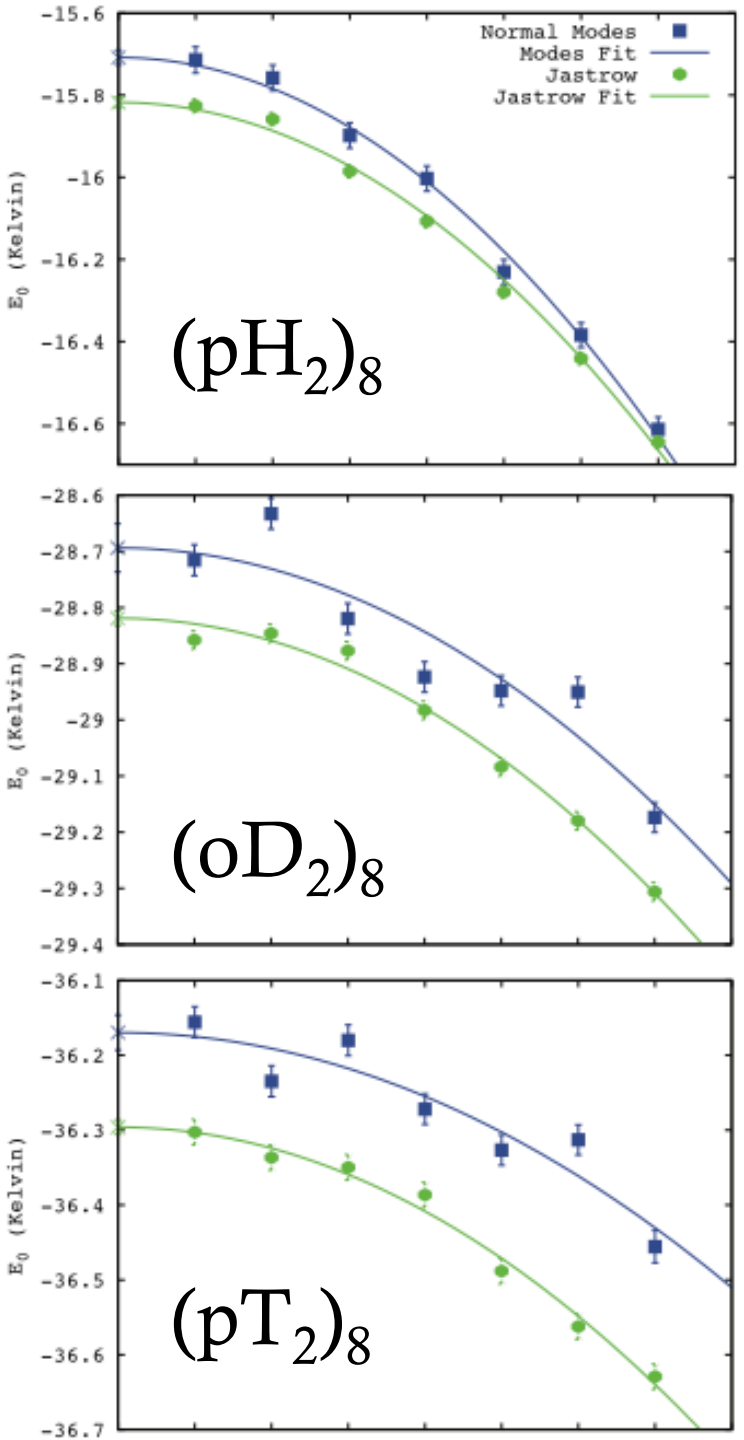
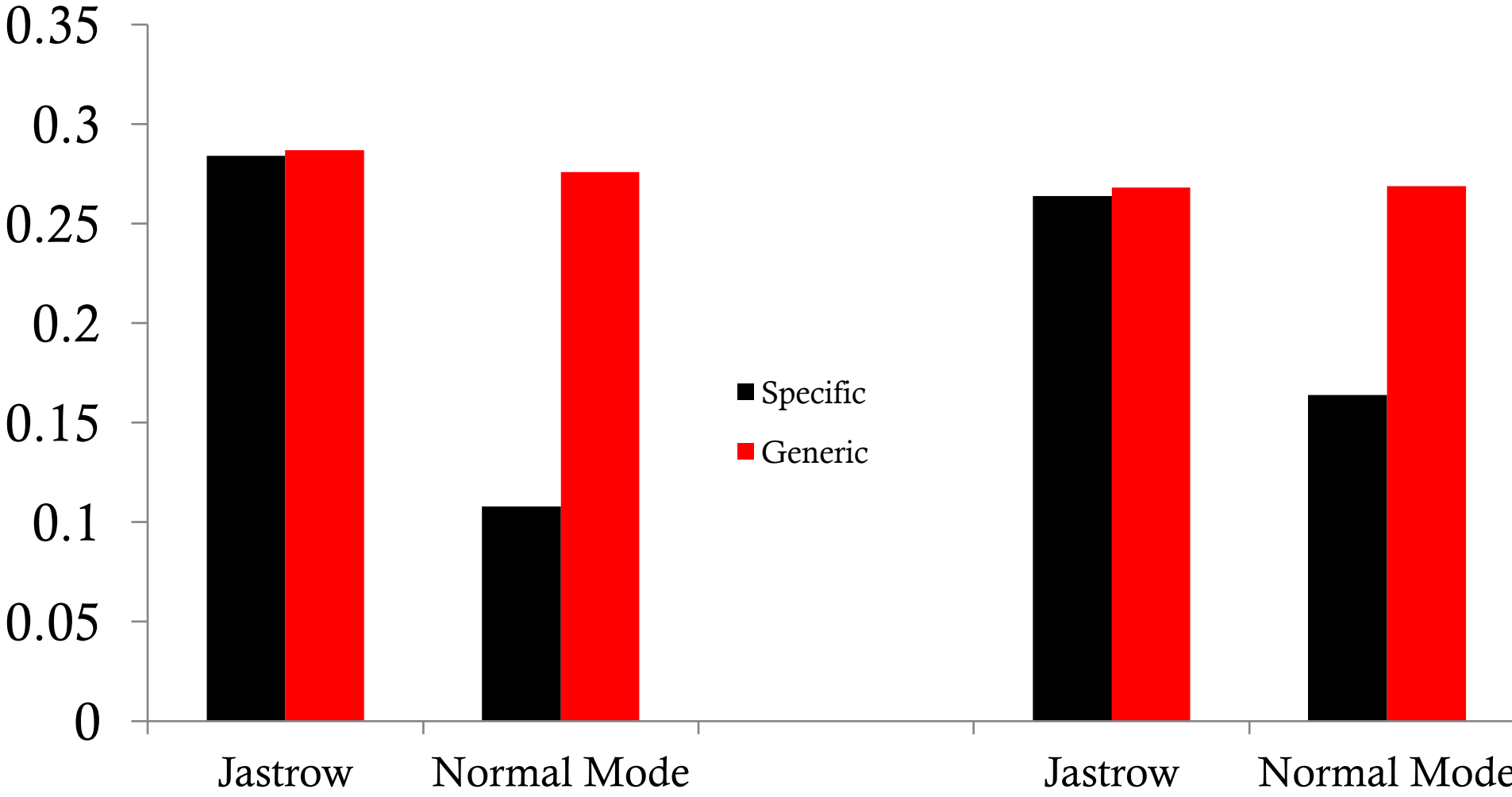


Fig: Cambridge Cluster Database



Schmidt et al, JCP 140, 234101 (2014)

Lindemann: $(pT_2)_8$

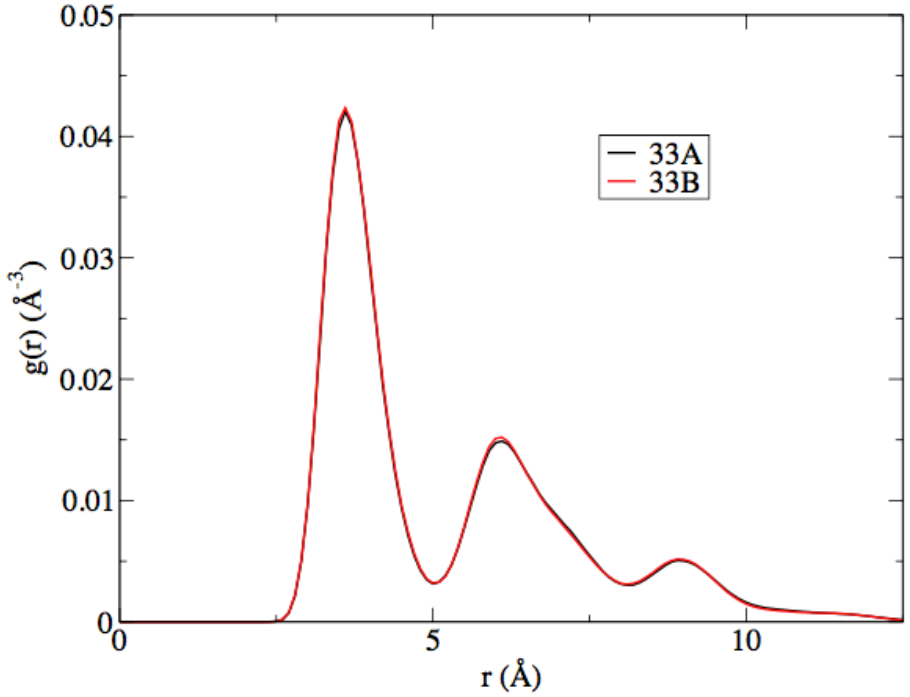


End Bead

(Prediction of Middle Bead Distribution)

Middle Bead

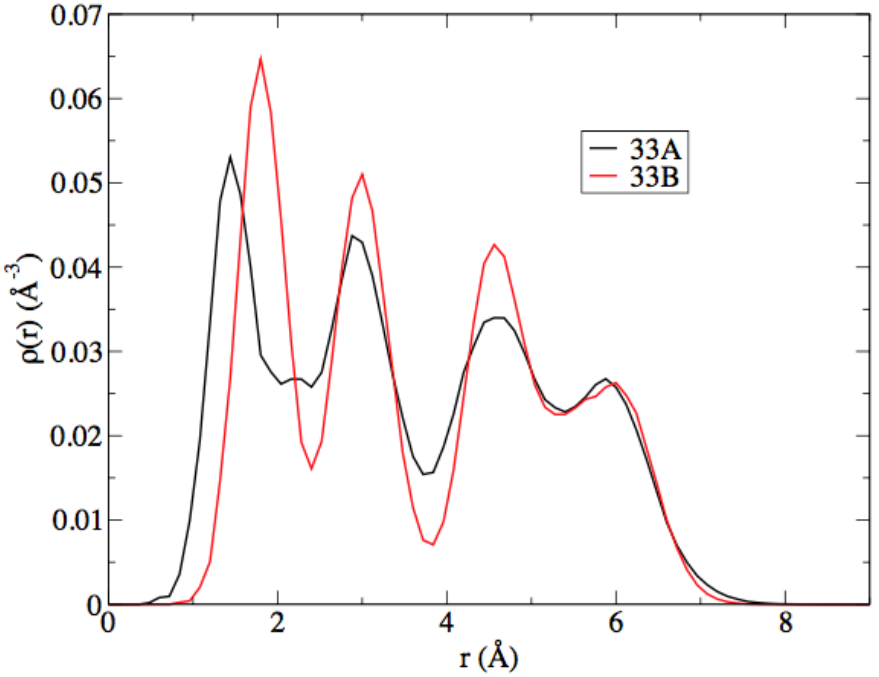
Different Conformers of $(pT_2)_{33}$



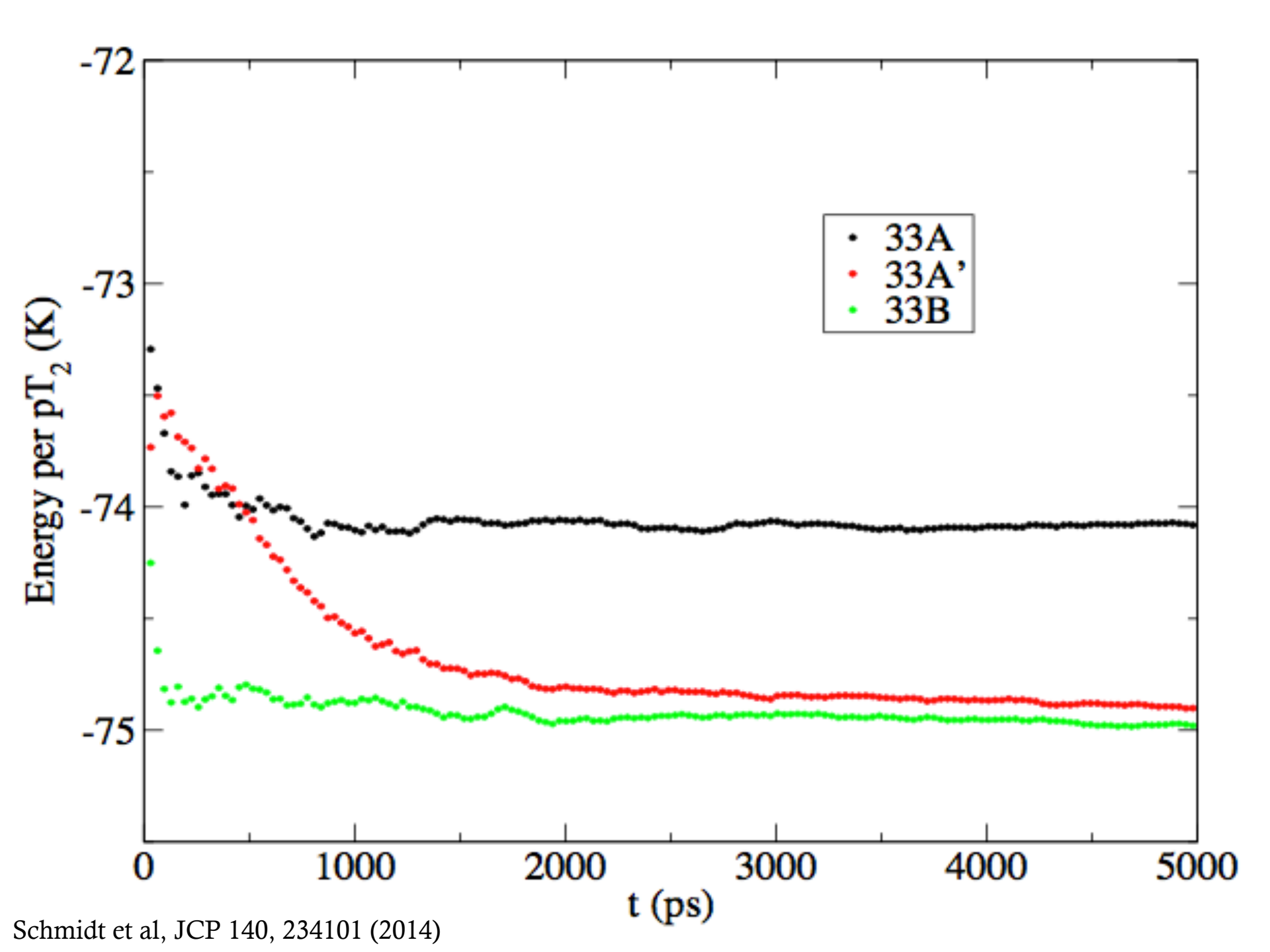
33A – Mackay
33B – AntiMackay

Distribution of interparticle distance

Density Profile:
Distribution of particles to center of mass



Schmidt et al, JCP 140, 234101 (2014)



Schmidt et al, JCP 140, 234101 (2014)

So Far…

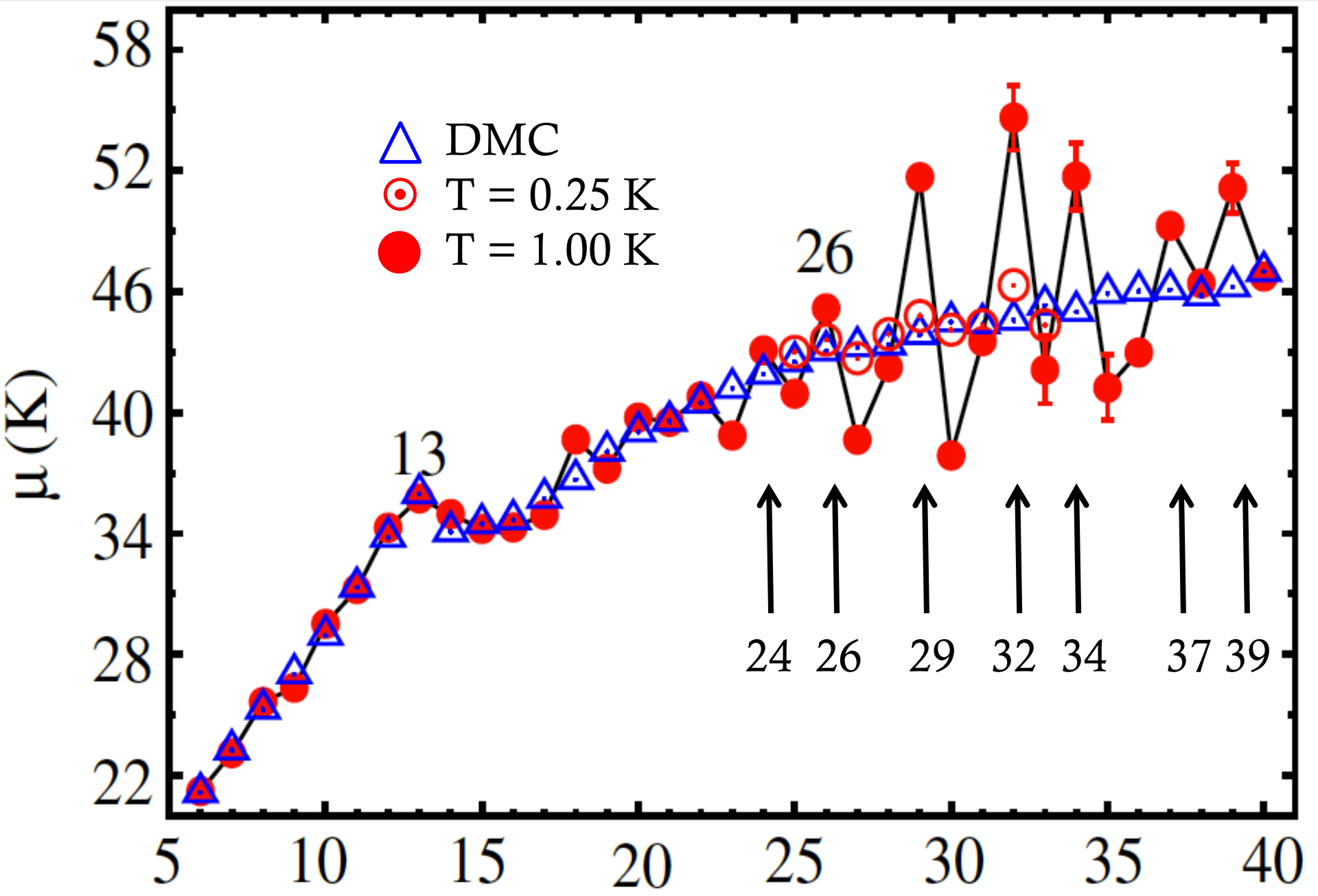
- Ergodicity issues arise from:
  - Method – Low Temperature PIMD/PIMC vs PIGS
  - Trial wavefunctions can introduce additional ergodicity problems
  - Solid-like behaviour of the system
- Effect of ergodicity problems?
  - Wrong energies!
- This could lead to the wrong chemical potential

Ground State Chemical Potential

$(pH_2)_N$

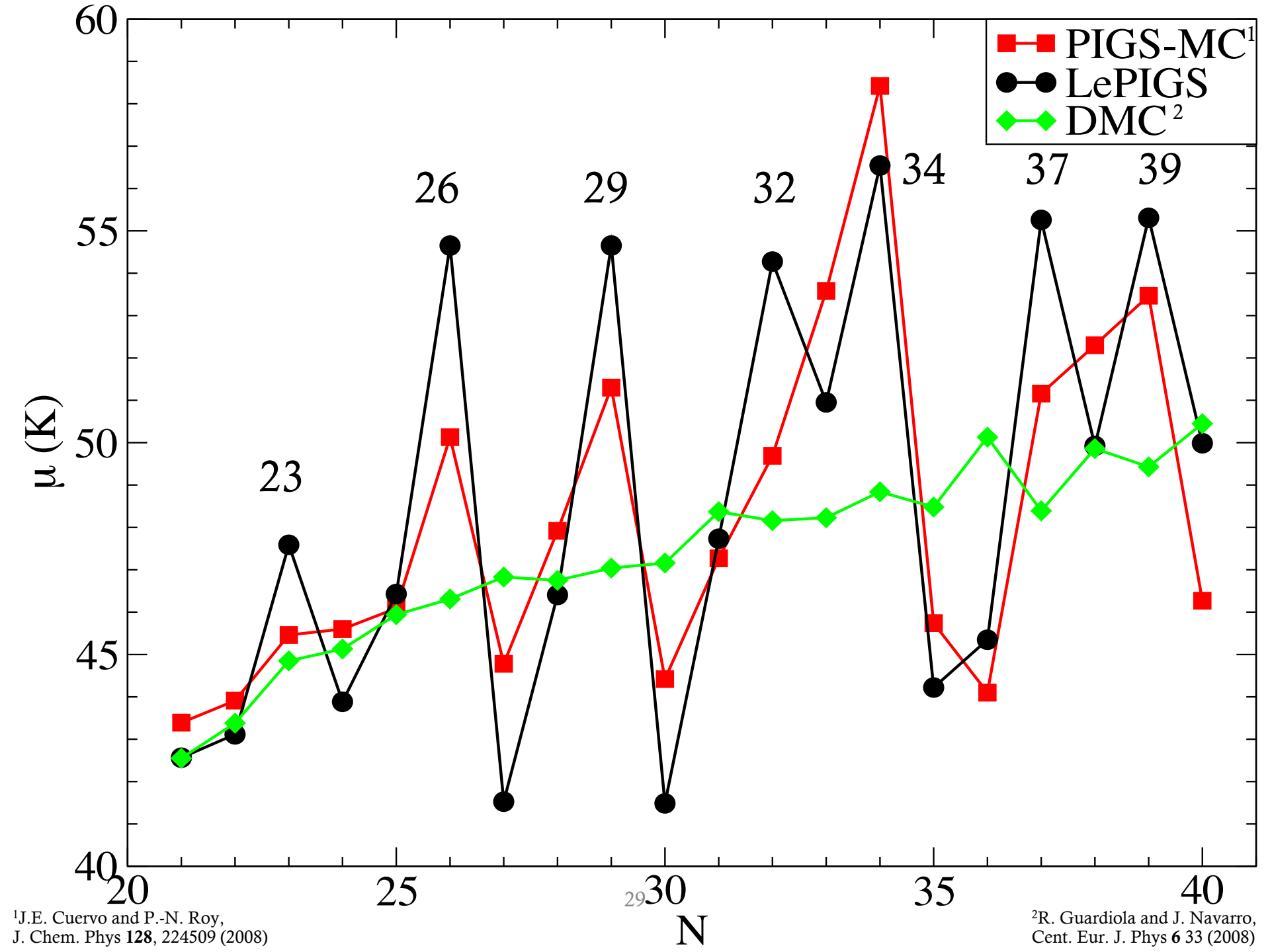
- Subject of much research: conflicting results between N=20-40
- Some methods show subtle oscillations
  - PIMC[1] : T = 0.25 K
  - DMC[2] : Ground state method
- Some methods show large oscillations
  - PIMC[3] : $T \geq 0.50$ K
  - PIGS-MC[4] : Ground state method
- Consequences
  - "Super-solid" (superfluid with solid order)
  - Quantum melting

[1]F. Mezzacapo and M. Boninsegni, J. Phys.: Condens. Matter **21** 164205 (2009)
[2]R. Guardiola and J. Navarro, Cent. Eur. J. Phys **6** 33 (2008)
[3]S.A Khairallah, M.B. Sevryuk, D.M. Ceperley, J.P. Toennies, PRL **98** 183401 (2007)
[4]J. E. Cuervo and P.-N. Roy, J. Chem. Phys. **128** 224509 (2008)



$$\mu(N) = E(N-1) - E(N)$$

Fig: F. Mezzacapo and M. Boninsegni, J. Phys.: Condens. Matt. **21** (2009), 164205



[1]J.E. Cuervo and P.-N. Roy,
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[2]R. Guardiola and J. Navarro,
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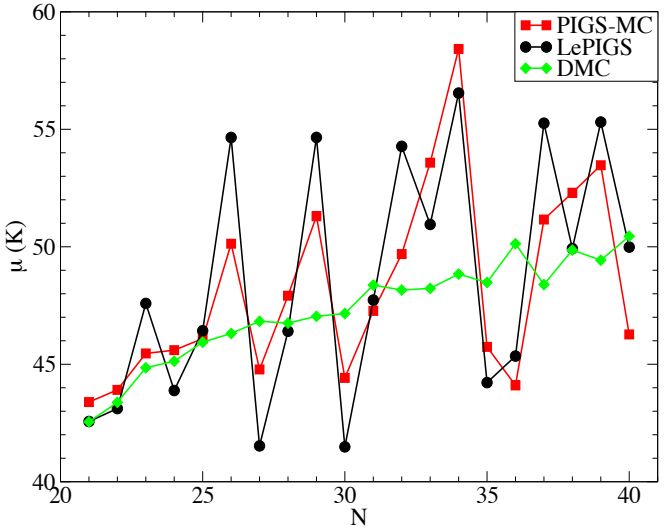
Consensus?

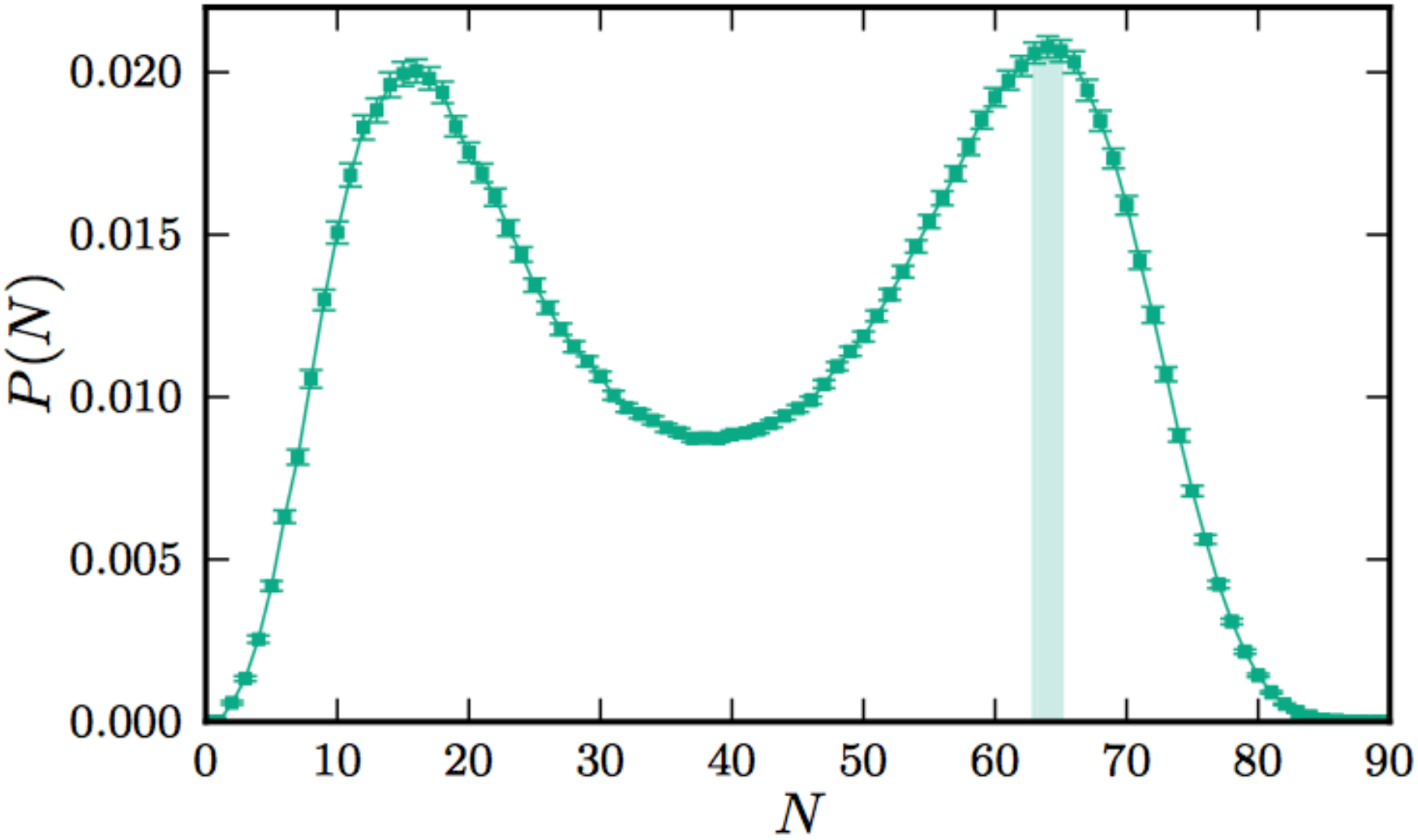
- LePIGS gives similar results to PIGS-MC
- PIGS disagrees with DMC
  - Both ground state methods
  - DMC – population size bias
  - PIGS – ergodicity problem?
- Look to finite temperature
  - Changes between 0.50K and 0.25K
  - Quantum melting?



- Next steps:
  - Formulate grand canonical PIGS (with WORM algorithm)[1]
  - Allows for calculation of μ as a function of N

[1]C. Herdman, A. Rommal, and A. Del Maestro, Phys Rev B **89** 224502 (2014)

Grand Canonical (μVT) Ensemble



[1]C. Herdman, A. Rommal, and A. Del Maestro, Phys Rev B **89** 224502 (2014)

Implementing WORM in MMTK

- WORM algorithm[1] allows sampling of nuclear exchange
- Will be first to implement in molecular dynamics framework
- Operations include:
  - OPEN/CLOSE – switching between Z- and G-sectors
  - ADVANCE/RECEDE– changing path length
  - SWAP – permutation sampling
- Currently implemented canonically
  - Without INSERT/REMOVE
  - We use an infinite universe, no volume
- Systems can be compared vs PIMC (ex. MoRiBS[2])

[1] M. Boninsegni, N.V. Prokof'ev, and B.V. Svistunov, Phys. Rev. E **74**, 036701 (2006)
[2] T. Zeng, N. Blinov, K. Bishop, G. Guillon, H. Li, and P.-N. Roy, Comp. Phys. Comm, **204**, 170 (2016)

```
if (self.wormExists==False):
    p_updates[0]=0.70    #remain (do nothing)
    p_updates[1]=0.30    #open
    p_updates[2]=0.0    #close
    p_updates[3]=0.0    #advance
    p_updates[4]=0.0    #recede
    p_updates[5]=0.0    #swap

else:
    p_updates[0]=0.50    #remain
    p_updates[1]=0.0    #open
    p_updates[2]=0.30    #close
    p_updates[3]=0.05    #advance
    p_updates[4]=0.05    #recede
    p_updates[5]=0.10    #swap

xval=arange(6)
## CHOOSE UPDATE ###
chosen_update=choice(xval,p=p_updates)

if(chosen_update==1):
    accept=self.openWORM(x)
elif(chosen_update==2):
    accept=self.closeWORM(x,v)
elif(chosen_update==3):
    accept=self.advanceWORM(x,v)
elif(chosen_update==4):
    accept=self.recedeWORM(x)
elif(chosen_update==5):
    accept=self.swapWORM(x,v)
```


Progress:

- Utilizes Dmitri's MMTK modifications allowing dynamic changing of path configurations and potential scaling

- "Dummy beads" (set of non-interacting beads) allow for advance/recede moves

- The "Area Estimator" analysis script has been coded to calculate the superfluid fraction

- Currently testing on hydrogen cluster

PIMD : $(pH_2)_5$ at T=0.5K

```
Step 992500 [0.0498430865793 0.316595901791] 0.0148148148148 0.00174927113703 [0.157467232786 0.159313273029] 0.372801875733 0.384704519119 [0.316780505815] 0.03962703962
Step 993000 [0.0498154981555 0.316605166052] 0.0148148148148 0.00174825174825 [0.157564575646 0.159225092251] 0.373536299766 0.384704519119 [0.316789667897] 0.039603960396
Step 993500 [0.0497879402545 0.316614420063] 0.0148148148148 0.00174723354688 [0.157477411027 0.159321408814] 0.373536299766 0.384259259259 [0.316798819841] 0.03958090803
Step 994000 [0.0497604128271 0.316623663841] 0.0148148148148 0.00174621653085 [0.157574640619 0.159233210147] 0.373099415205 0.384259259259 [0.316807961666] 0.03955788248
Step 994500 [0.0497329158224 0.316632897403] 0.0148148148148 0.00174520069808 [0.157671762756 0.159145330632] 0.372663551402 0.384259259259 [0.316817093387] 0.03953488372
Step 995000 [0.04970544919 0.316642120766] 0.0148148148148 0.00174418604651 [0.157584683358 0.159241531664] 0.372663551402 0.384971098266 [0.316826215022] 0.0395119116793
Step 995500 [0.0496780128795 0.316651333947] 0.0148148148148 0.00174317257408 [0.157681692732 0.159153633855] 0.372228704784 0.384971098266 [0.316835326587] 0.03948896631
Step 996000 [0.0496506068408 0.316660536962] 0.0148148148148 0.00174216027875 [0.157594703935 0.159249724163] 0.372228704784 0.385681293303 [0.316844428099] 0.03946604759
Step 996500 [0.0496232310237 0.316669729829] 0.0148148148148 0.00174114915844 [0.157507811064 0.159345708509] 0.372228704784 0.386389850058 [0.316853519574] 0.03944315545
Step 997000 [0.0495958853784 0.316678912564] 0.0148148148148 0.00174013921114 [0.15742101396 0.159441587068] 0.372228704784 0.385944700461 [0.316862601029] 0.039420289855
Step 997500 [0.0495685698555 0.316688085185] 0.0148148148148 0.00173913043478 [0.157517899761 0.159353772719] 0.37296037296 0.385944700461 [0.31687167248] 0.0393974507532
Step 998000 [0.0495412844037 0.316697247706] 0.0148148148148 0.00173812282735 [0.157431192661 0.159449541284] 0.37296037296 0.385500575374 [0.316880733945] 0.039374638100
Step 998500 [0.0495140289749 0.316706400147] 0.0148148148148 0.0017371163868 [0.157527966257 0.159361819182] 0.373690337602 0.385500575374 [0.316889785439] 0.039351851851
Step 999000 [0.0494868035191 0.316715542522] 0.0148148148148 0.00173611111111 [0.157441348974 0.159457478006] 0.373690337602 0.385057471264 [0.316898826979] 0.03932909196
Step 999500 [0.0494596079868 0.316724674849] 0.0148148148148 0.00173510699826 [0.157538010625 0.159369847958] 0.373255813953 0.385057471264 [0.316907858582] 0.03930635838
Step 1000000 [0.0494324423288 0.316733797144] 0.0148148148148 0.00173410404624 [0.157634566093 0.159282314171] 0.373983739837 0.385057471264 [0.316916880264] 0.0392836510
```

MoRiBS: $(pH_2)_5$ at T=0.5K

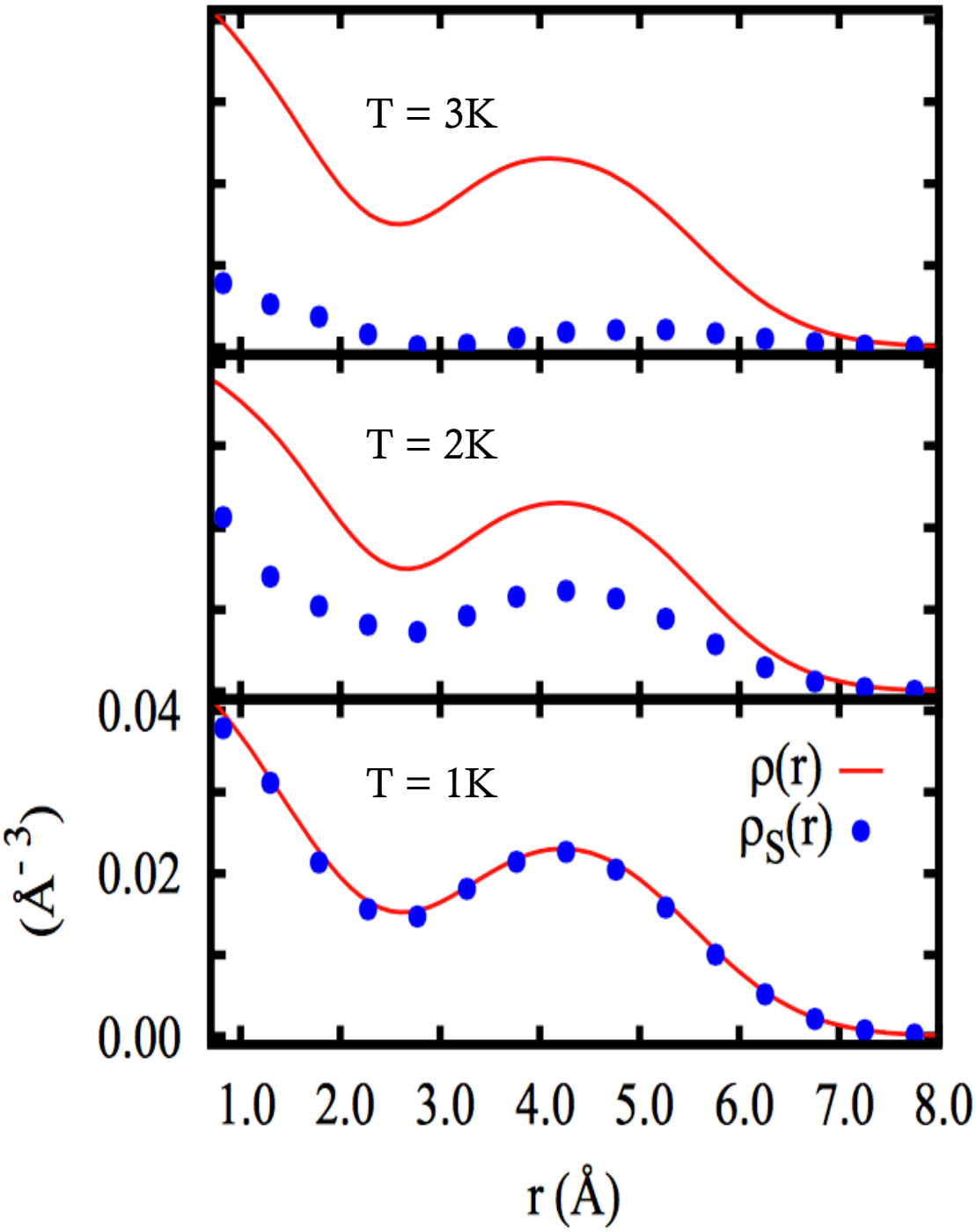
```
STEP: 2470000   open/close [ 0.0048507-0.3301 ]    0.0214257   0.000314843   advance/recede [ 0.164998-0.165101 ]    0.989489   0.988991      swap [ 0.3301 ]    0.00018815
STEP: 2480000   open/close [ 0.00483105-0.330113 ]    0.0214257   0.000313555   advance/recede [ 0.165003-0.16511 ]    0.989498   0.988981      swap [ 0.330113 ]    0.00018738
STEP: 2490000   open/close [ 0.00481164-0.330126 ]    0.0214309   0.000312359   advance/recede [ 0.165016-0.165109 ]    0.989489   0.989019      swap [ 0.330126 ]    0.000186617

STEP: 2500000   open/close [ 0.00482011-0.33012 ]    0.0214357   0.000312984   advance/recede [ 0.165015-0.165105 ]    0.989493   0.989044      swap [ 0.33012 ]    0.000185875
STEP: 2510000   open/close [ 0.00481645-0.330122 ]    0.021444   0.000312946   advance/recede [ 0.165017-0.165105 ]    0.989494   0.989071      swap [ 0.330122 ]    0.000185132
STEP: 2520000   open/close [ 0.00489186-0.330072 ]    0.021466   0.000318138   advance/recede [ 0.164992-0.16508 ]    0.989403   0.988971      swap [ 0.330072 ]    0.000195232
STEP: 2530000   open/close [ 0.00491729-0.330055 ]    0.0214811   0.000320034   advance/recede [ 0.164986-0.165069 ]    0.989289   0.988925      swap [ 0.330055 ]    0.000200091

STEP: 2540000   open/close [ 0.0048986-0.330068 ]    0.0214831   0.000318836   advance/recede [ 0.164989-0.165079 ]    0.989318   0.988911      swap [ 0.330068 ]    0.000199292
STEP: 2550000   open/close [ 0.0048793-0.33008 ]    0.0214831   0.000317567   advance/recede [ 0.164988-0.165092 ]    0.989355   0.98888      swap [ 0.33008 ]    0.000198499
STEP: 2560000   open/close [ 0.00486015-0.330093 ]    0.0214831   0.000316308   advance/recede [ 0.164997-0.165096 ]    0.989362   0.988882      swap [ 0.330093 ]    0.000197713
```

Radial distribution of density and superfluid density of $(pH_2)_{18}$

Density = g(r)

Superfluid density computed from:

$$\frac{\rho_S(r)}{\rho(r)} = \frac{4m^2\langle AA(r)\rangle}{\beta\hbar^2 I_C(r)}$$



Mezzacapo F and Boninsegni M, *Phys.Rev.Lett,* **100**, 145301 (2008)

To Do List

- Continue to test the WORM algorithm
  - Currently small clusters of hydrogen
- Implement Grand Canonical scheme
  - Will further help with ergodicity
  - For PIMD and LePIGS
- Recalculate hydrogen chemical potential
  - See if peaks diminish

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- Pierre-Nicholas Roy
- Whole theory group!