TEL AVIV UNIVERSITY
אוניברסיטת תל אביב

Path Integral Molecular Dynamics for Indistinguishable Particles

Barak Hirshberg

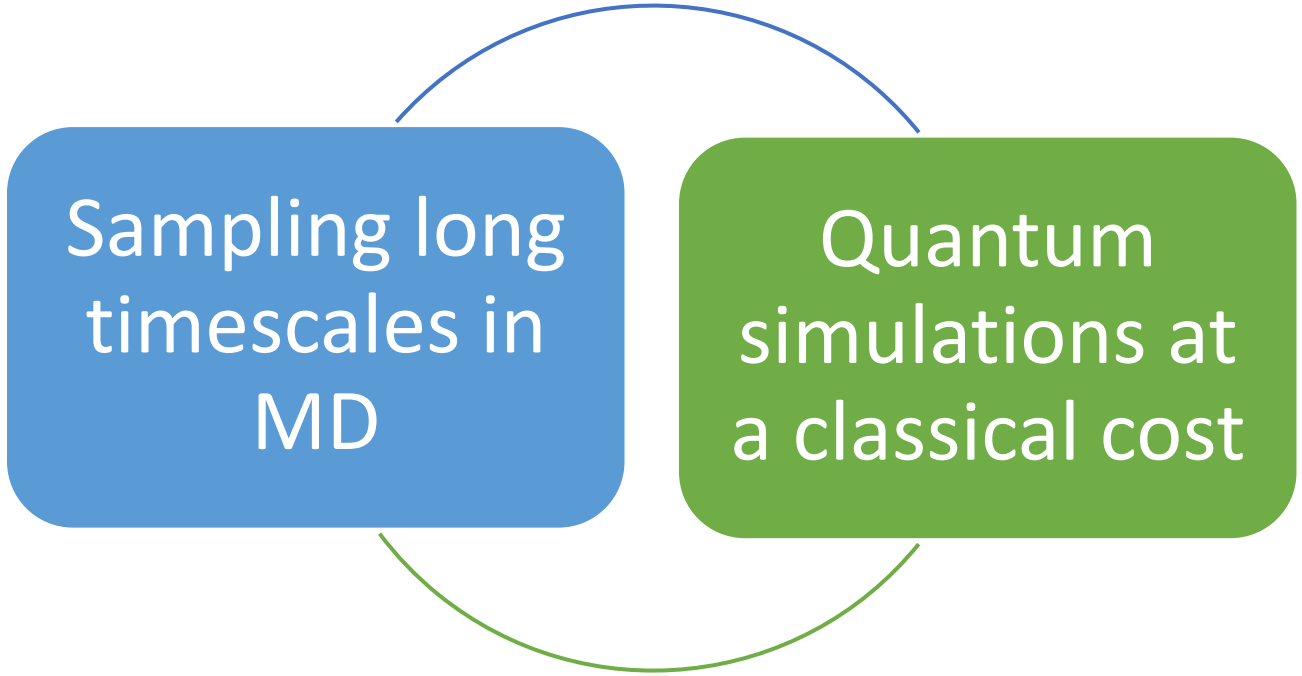
Hirshberg lab
Molecular simulations

The molecular dynamics (MD) group at TAU

One PD, three graduate students, three undergrad interns.

We are hiring!

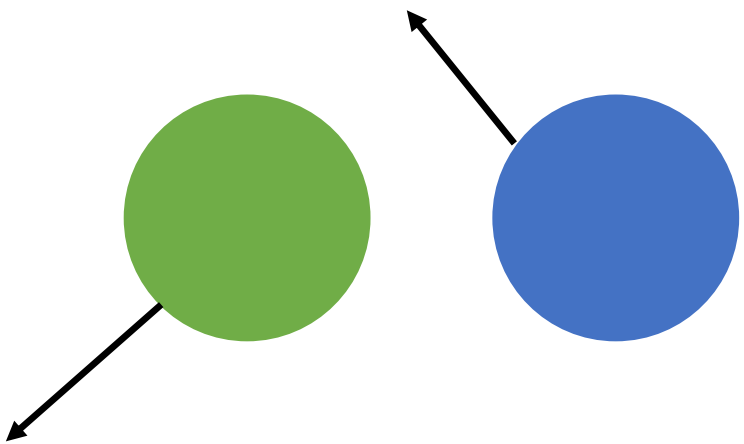
Looking for MSc, PhD students who are passionate about chemical physics, ML, MD simulations, and path integrals!



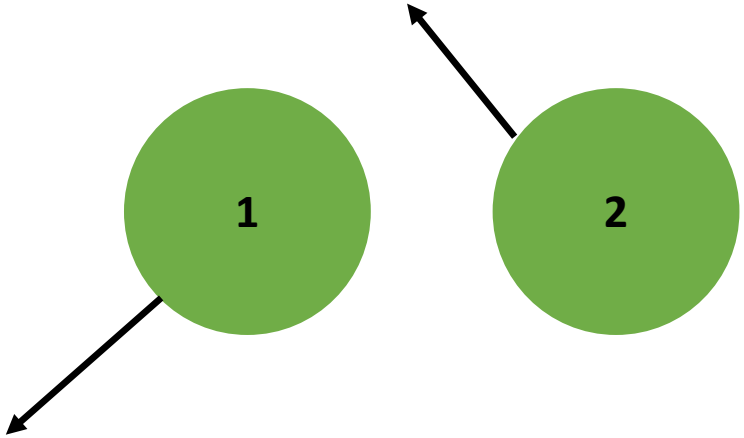
Outline

- **What are indistinguishable particles? What is PIMD?**
- **Exchange effects in PIMD – a great challenge!**
- **PIMD for bosons: reducing the scaling from $\sim N!$ to $\sim N^3$**
- **Fermions – alleviating the sign problem**
- **Applications (ultracold atoms, quantum dots and supersolids)**

Indistinguishable particles



Not identical



Identical
(but distinguishable in classical mechanics)

Because we cannot follow the trajectory of each particle in QM,

identical particles are indistinguishable!

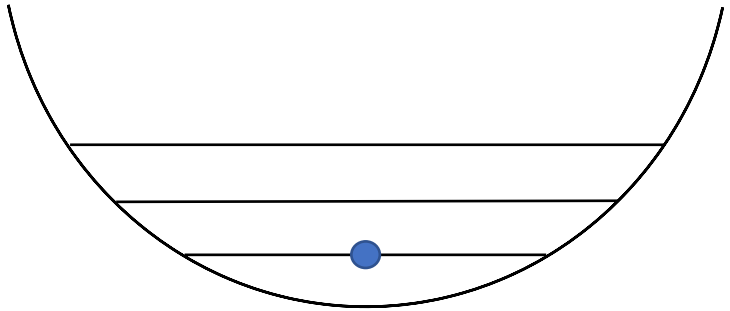
Symmetry repercussions

The permutation of two indistinguishable particles can only change the wavefunction by a phase factor

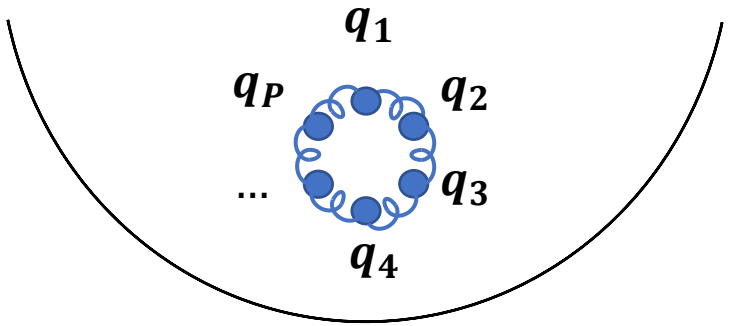
Bosons: $\hat{P}_{12}\psi(q_1, q_2) = \psi(q_1, q_2)$

Fermions: $\hat{P}_{12}\psi(q_1, q_2) = -\psi(q_1, q_2)$

PIMD for distinguishable particles



$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$



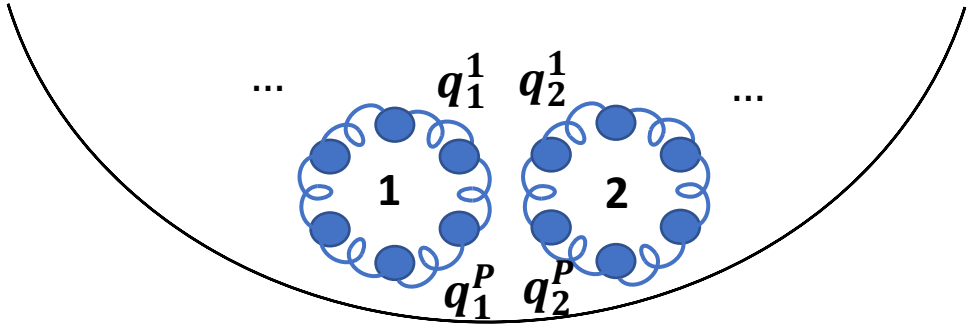
$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(q)$$

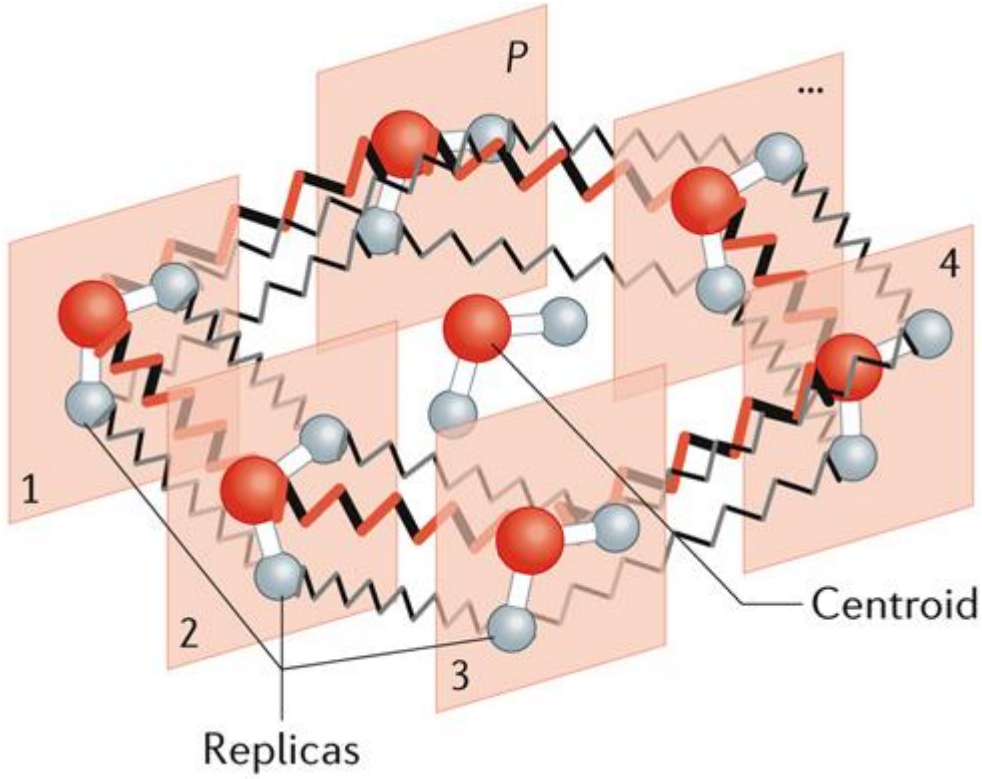
$$H(\boldsymbol{p},\boldsymbol{q}) = \sum_{j=1}^{P} \frac{p_j^2}{2m} + V_o + \frac{1}{P}\sum_{j=1}^{P} V(q_j)$$

$$Z = Tr\left(e^{-\beta\hat{H}}\right) \sim \int \langle q|e^{-\beta\hat{H}}|q\rangle dq$$

$$Z \sim \lim_{P\to\infty} \int e^{-\beta H(\boldsymbol{p},\boldsymbol{q})} d\boldsymbol{p}d\boldsymbol{q}$$

More than one particle





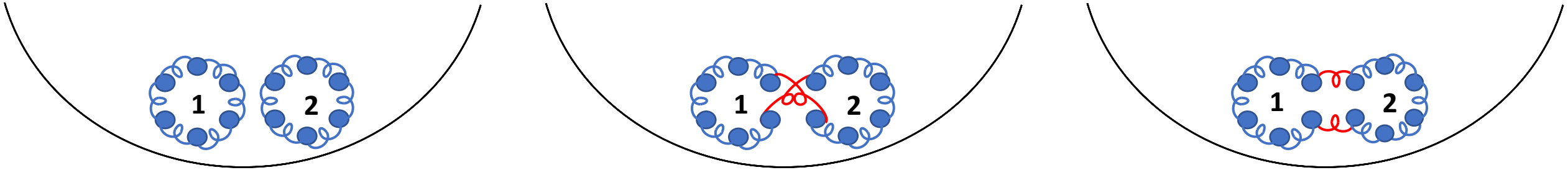
T.E. Markland and M. Ceriotti (2018) *Nat. Rev. Chem.*
DOI: 10.1038/s41570-017-0109

Part I: Bosons

Exchange symmetry in the PI formalism

The trace needs to be evaluated in a (anti-)symmetrized basis

$$Z = \int \left[\langle q_1 q_2 | e^{-\beta \hat{H}} | q_1 q_2 \rangle \pm \langle q_1 q_2 | e^{-\beta \hat{H}} | q_2 q_1 \rangle \right] dq_1 dq_2$$



$$Z \sim \int \left(e^{-\beta V_{oo}} \pm e^{-\beta V_O} \right) d\boldsymbol{q}_1 d\boldsymbol{q}_2 \equiv \int e^{-\beta V_B^{(2)}} d\boldsymbol{q}_1 d\boldsymbol{q}_2$$

Sampling Z in MD, a clear physical picture

$$Z \sim \int \left(e^{-\beta V_{oo}} + e^{-\beta V_O}\right) d\boldsymbol{q}_1 d\boldsymbol{q}_2 \equiv \int e^{-\beta V_B^{(2)}} d\boldsymbol{q}_1 d\boldsymbol{q}_2$$

$$V_B^{(2)} = -\frac{1}{\beta} \ln\left[e^{-\beta V_{oo}} + e^{-\beta V_O}\right]$$

$$\vec{F} = \frac{\vec{F}_{oo} e^{-\beta V_{oo}} + \vec{F}_O e^{-\beta V_O}}{e^{-\beta V_{oo}} + e^{-\beta V_O}}$$

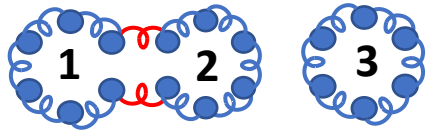
The force is the weighted average of contributions due to all ring polymer configurations!

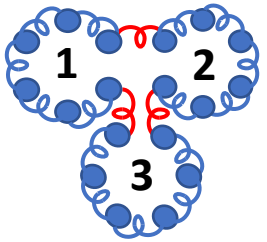
More than two particles

For N=3

$$Z \sim \frac{1}{6}\int \left(e^{-\beta V_{ooo}} \pm 3e^{-\beta V_{Oo}} + 2e^{-\beta V_{\Delta}}\right) d\boldsymbol{q}_1 d\boldsymbol{q}_2 d\boldsymbol{q}_3$$

V_{ooo} 

V_{Oo} 

V_{Δ} 

- **For N=4? N=40? N=400?**
- **How many configurations? How to generate them all?**
- **How does the number of configurations scale with N?**

Cycle notation of permutations

(1,2,3)

(1,2,3)

(1)(2)(3)

(1,2,3)

(1,3,2)

(1)(23)

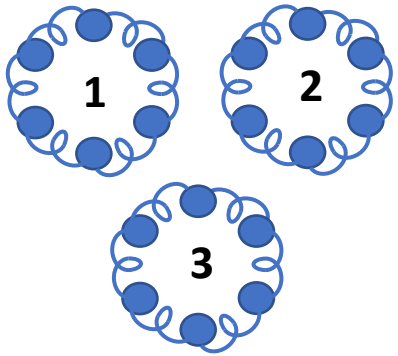
(1,2,3)

(2,3,1)

(123)

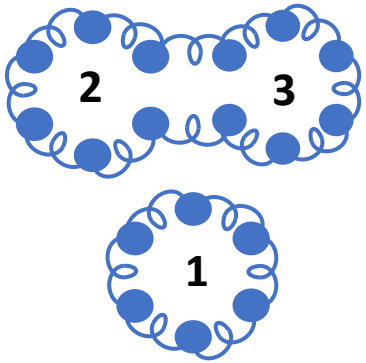
Ring-polymer configurations

V_{ooo}

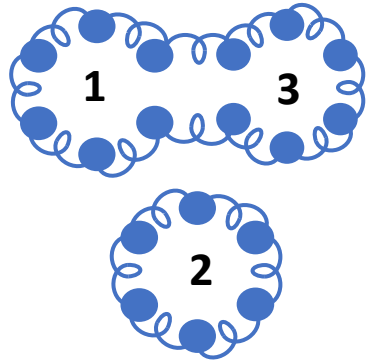


(1,2,3)
(1)(2)(3)

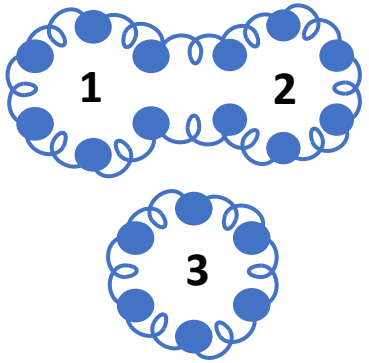
V_{Oo}



(1,3,2)
(1)(23)

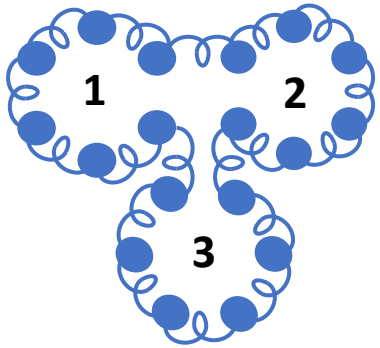


(3,2,1)
(13)(2)

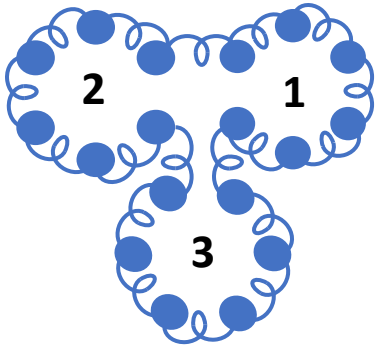


(2,1,3)
(12)(3)

V_{Δ}



(2,3,1)
(123)



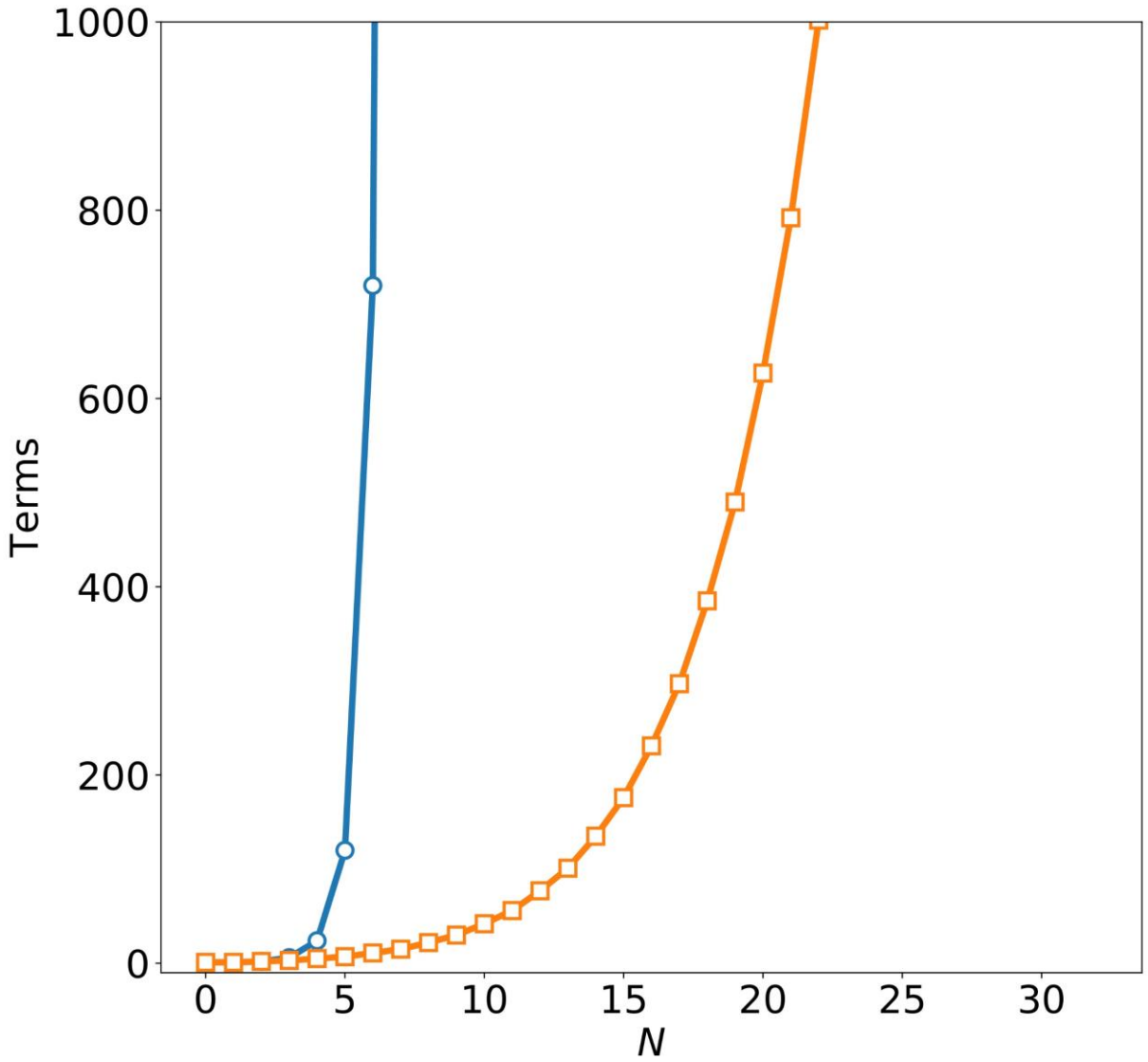
(3,1,2)
(132)

The Problem

- **# of permutations $\sim N!$**
- **# of diagrams $= p(N)$, still scales exponentially with N**

Not practical for large N,

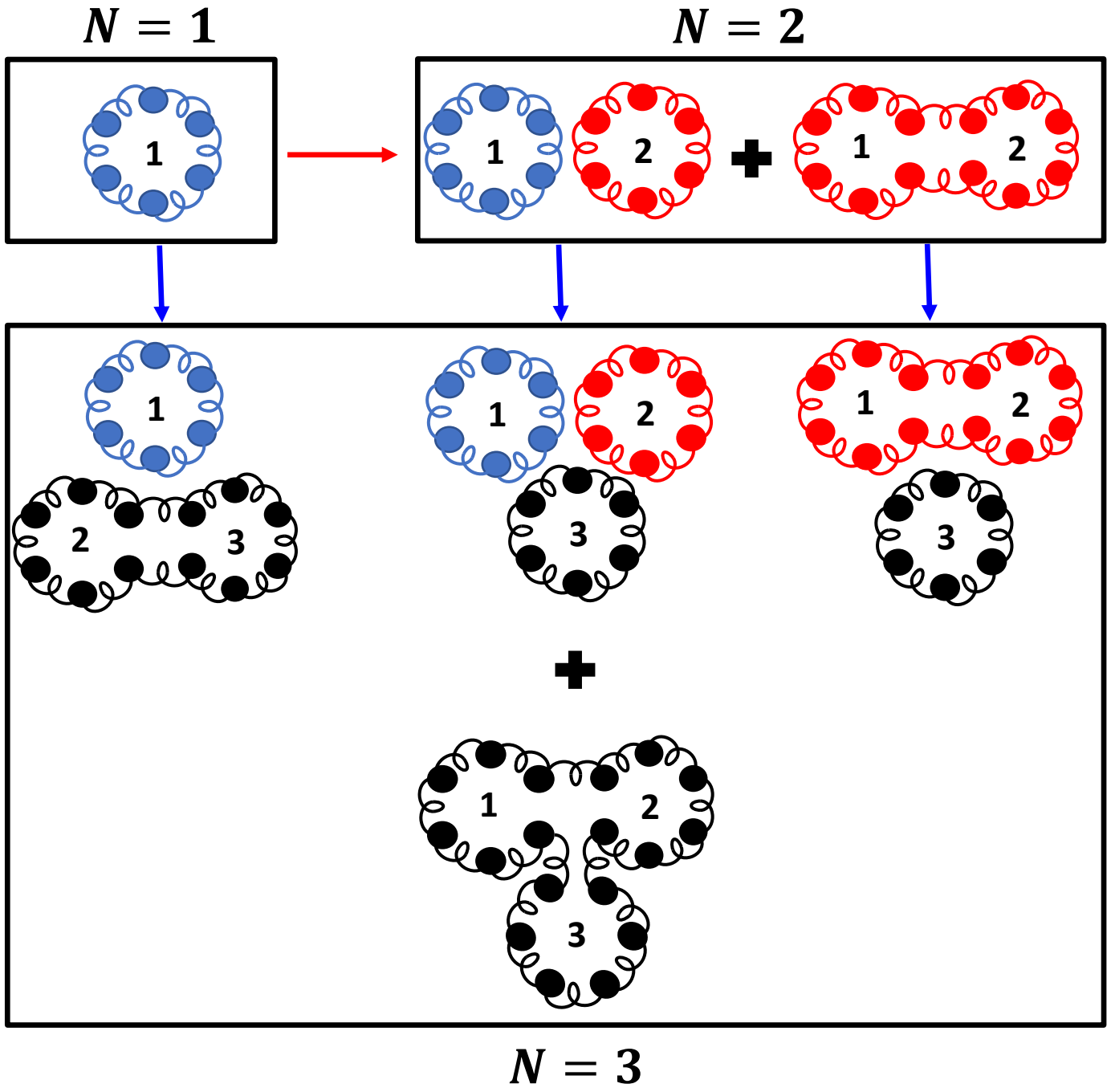
<u>Is there an alternative?</u>



Yes, there is!

- **PIMC – sample permutations (D.M. Ceperley)**
- **PIMD – forces can be evaluated recursively without enumerating permutations!**

B. Hirshberg, V. Rizzi and M. Parrinello, *PNAS* (2019) 116, 21445-21449


N = 1
N = 2
1
1
2
1
2
1
2
3
1
2
3
1
2
3
N = 3

Generalization: a recurrence Relation

$$e^{-\beta V_B^{(N)}(R_1,\ldots,R_N)} = \frac{1}{N}\sum_{k=1}^{N} e^{-\beta\left[E_N^{(k)}(R_{N-k+1},\ldots,R_N)+V_B^{(N-k)}(R_1,\ldots,R_{N-k})\right]}$$

$$V_B^{(N)}(R_1,\ldots,R_N) = -\frac{1}{\beta}\ln\left[\frac{1}{N}\sum_{k=1}^{N} e^{-\beta\left[E_N^{(k)}+V_B^{(N-k)}\right]}\right];\ V_B^{(0)} = 0$$

- **$E_N^{(k)}$ is the spring energy of a ring connecting atoms $R_{N-k+1},\ldots,R_N$ sequentially.**

The problem

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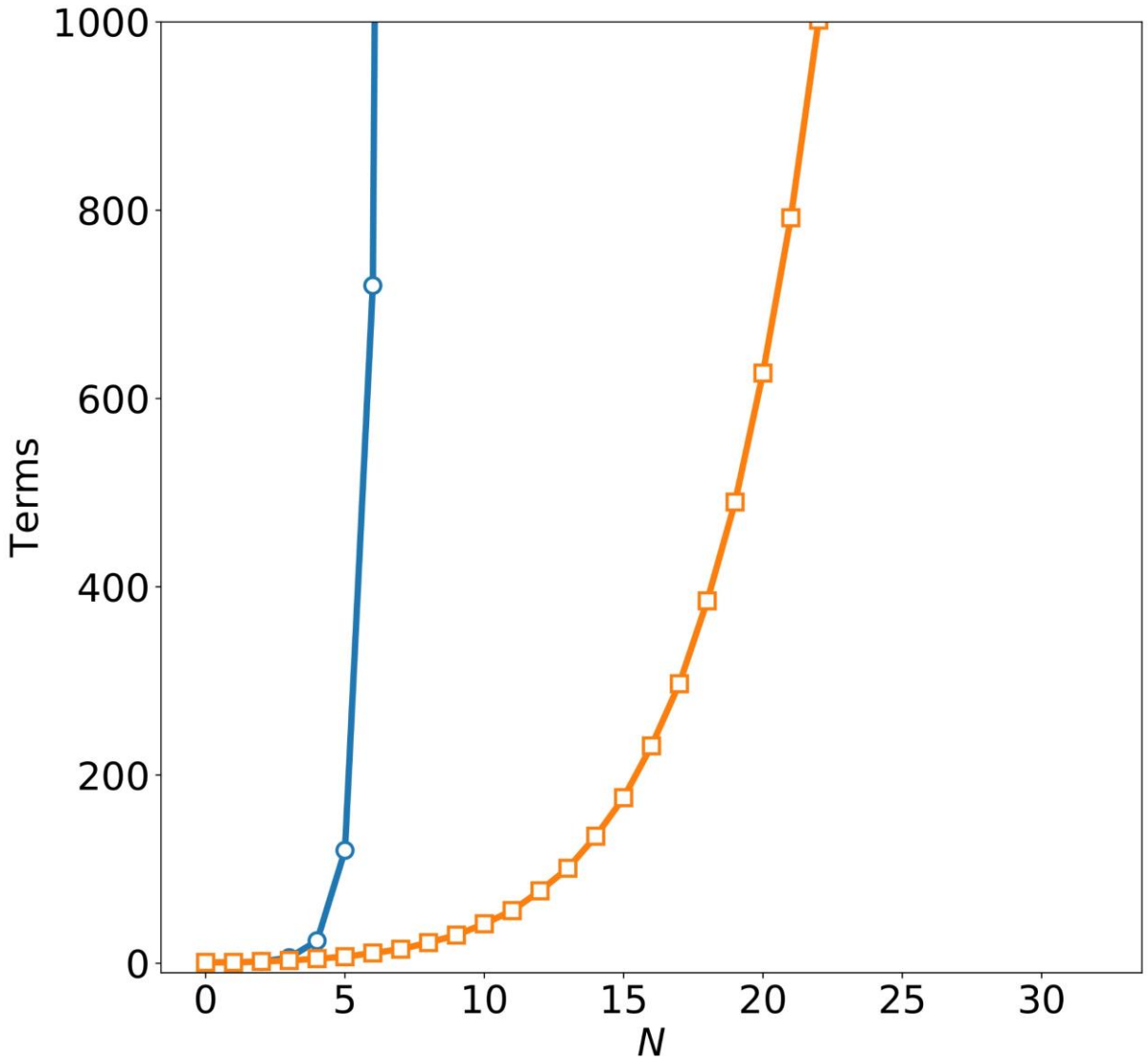
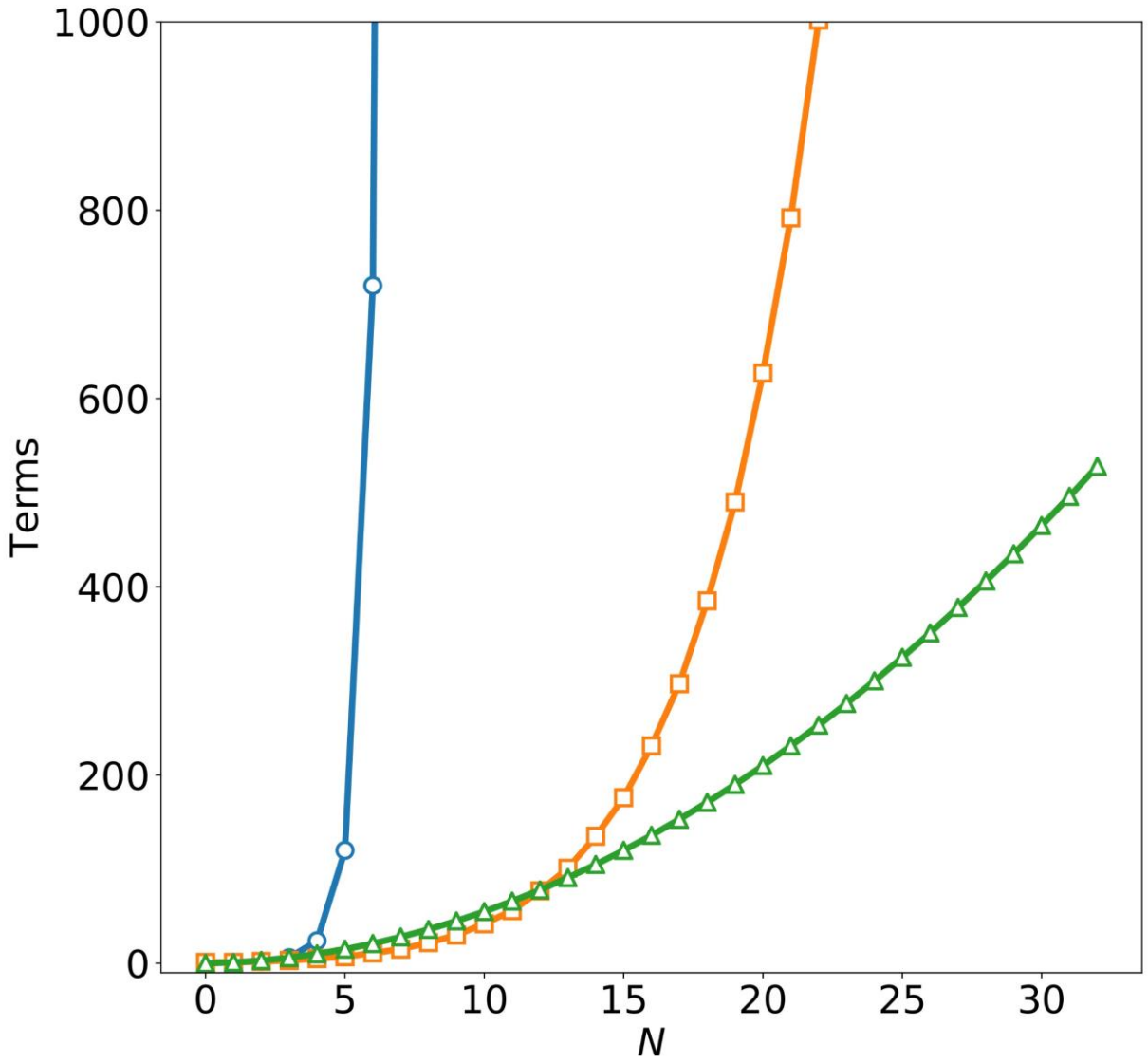
Not practical for large N,

<u>Is there an alternative?</u>



The solution

- **Using the recurrence relation, only $\sim N^2$ energies are needed!**
- **The algorithm scales as $\mathcal{O}(PN^3)$**



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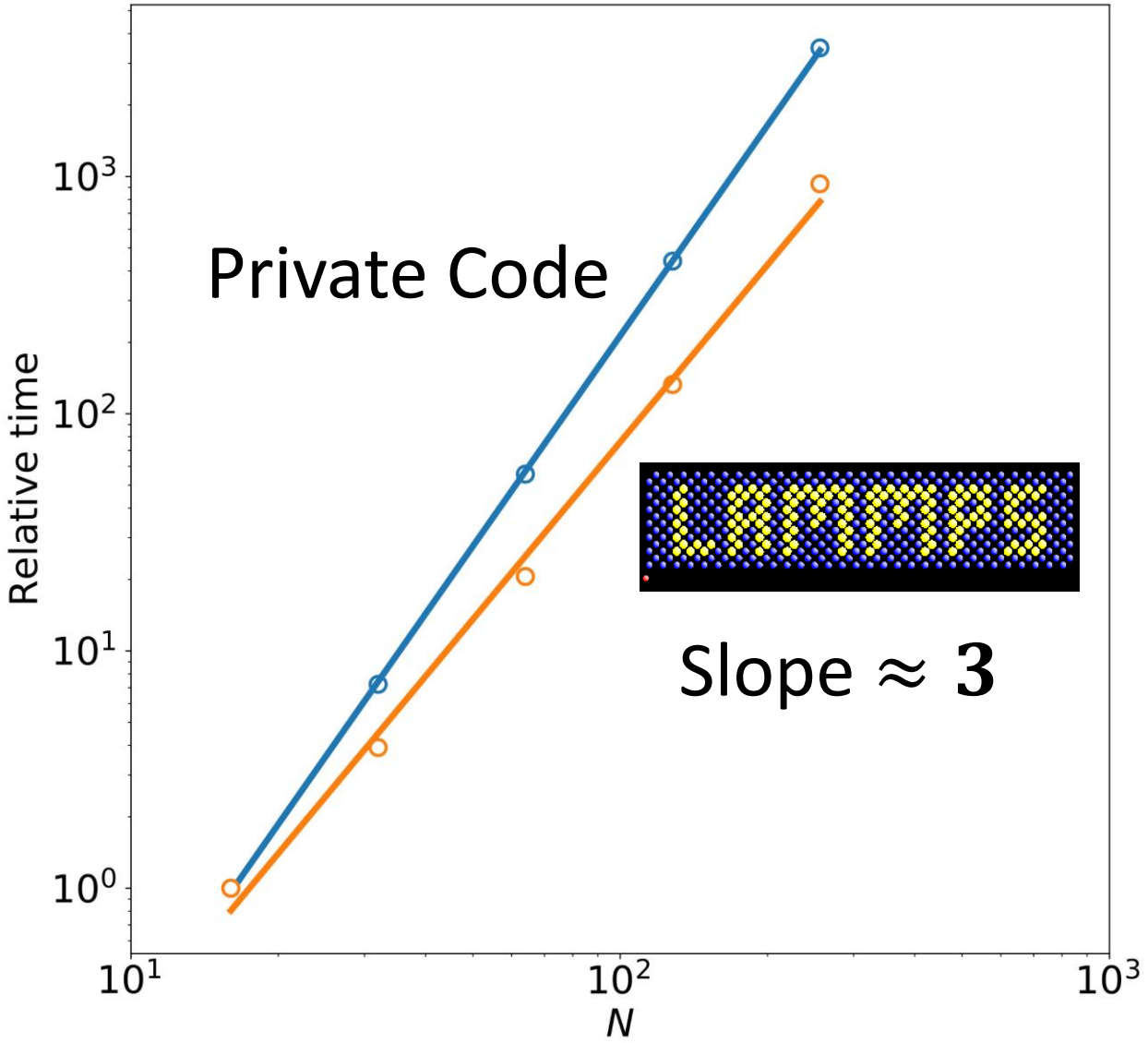
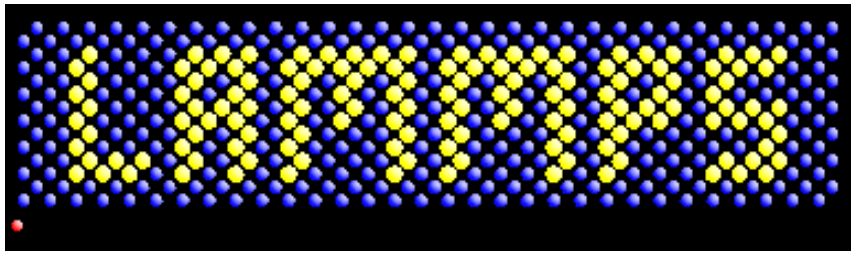


Open-source implementations

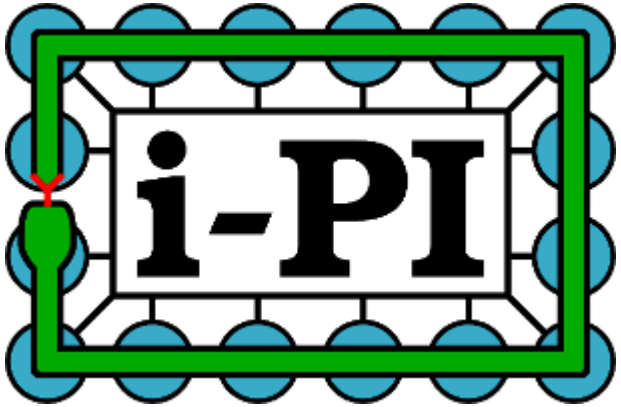
- **Development version of LAMMPS (infrastructure by Voth Group)**

https://github.com/BarakHirshberg



- **Recently implemented in i-PI (Ceriotti, Rossi, Marsalek, Kapil,…)**

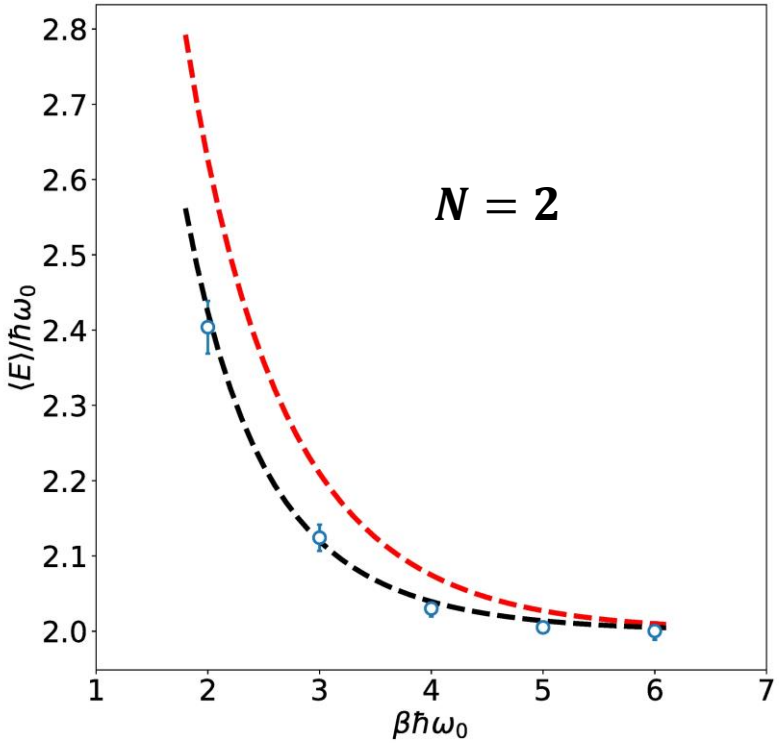
http://ipi-code.org

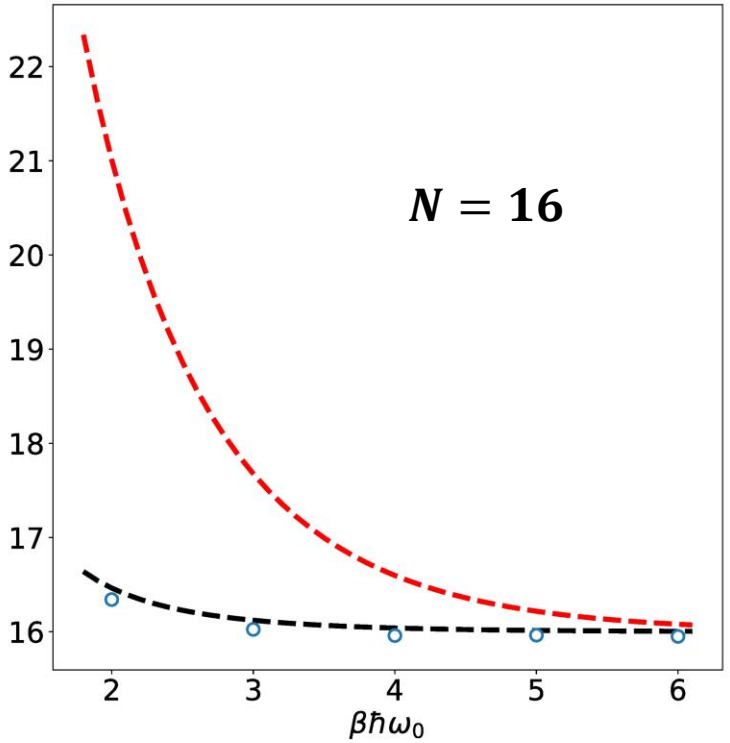


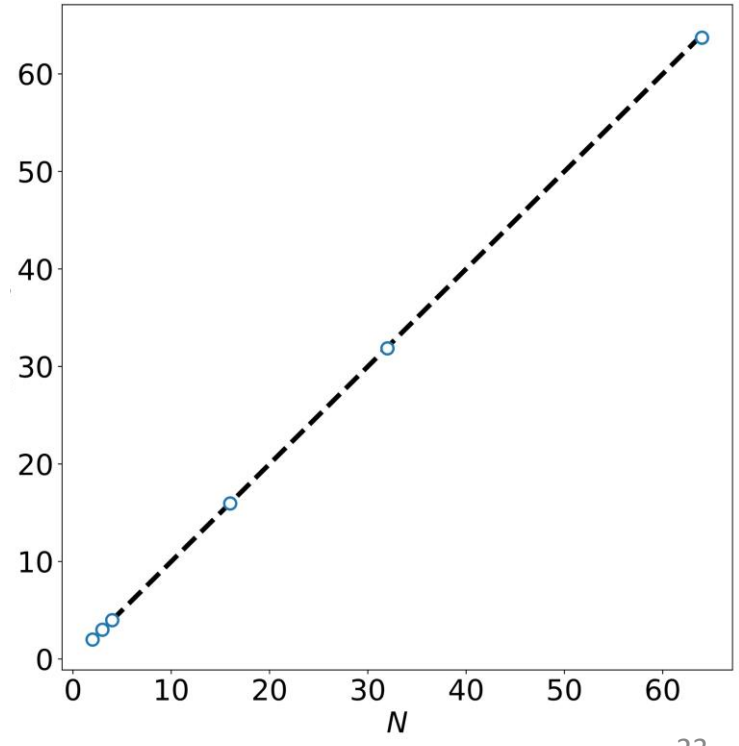
S. Plimpton, J. Comp. Phys. (1995) 117, 1-19
V. Kapil *et. al,* Comput. Phys. Commun. (2019) 236, 214-223

Benchmarking: noninteracting particles in 2D trap

- **Correct statistics as a function of temperature**
- **Correct ground-state energy up to $\mathbf{N = 64}$**







Benchmarking: interacting particles in 2D trap

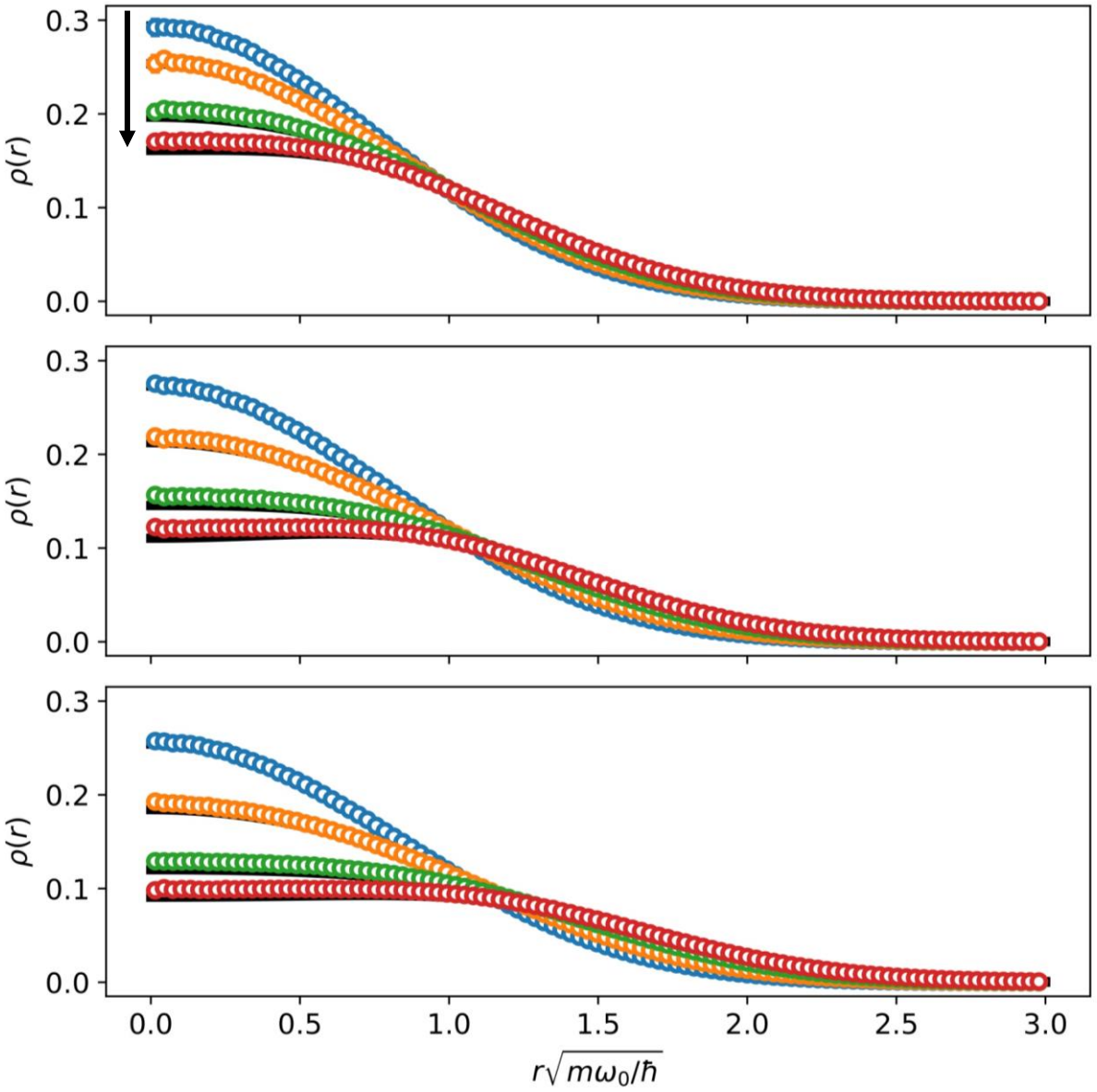
- **Comparison to exact diagonalization by P. Mujal *et al.* Phys. Rev. A 96, 043614 (2017)**
- **Interacting Bosons in a 2D trap, repulsive Gaussian potential**

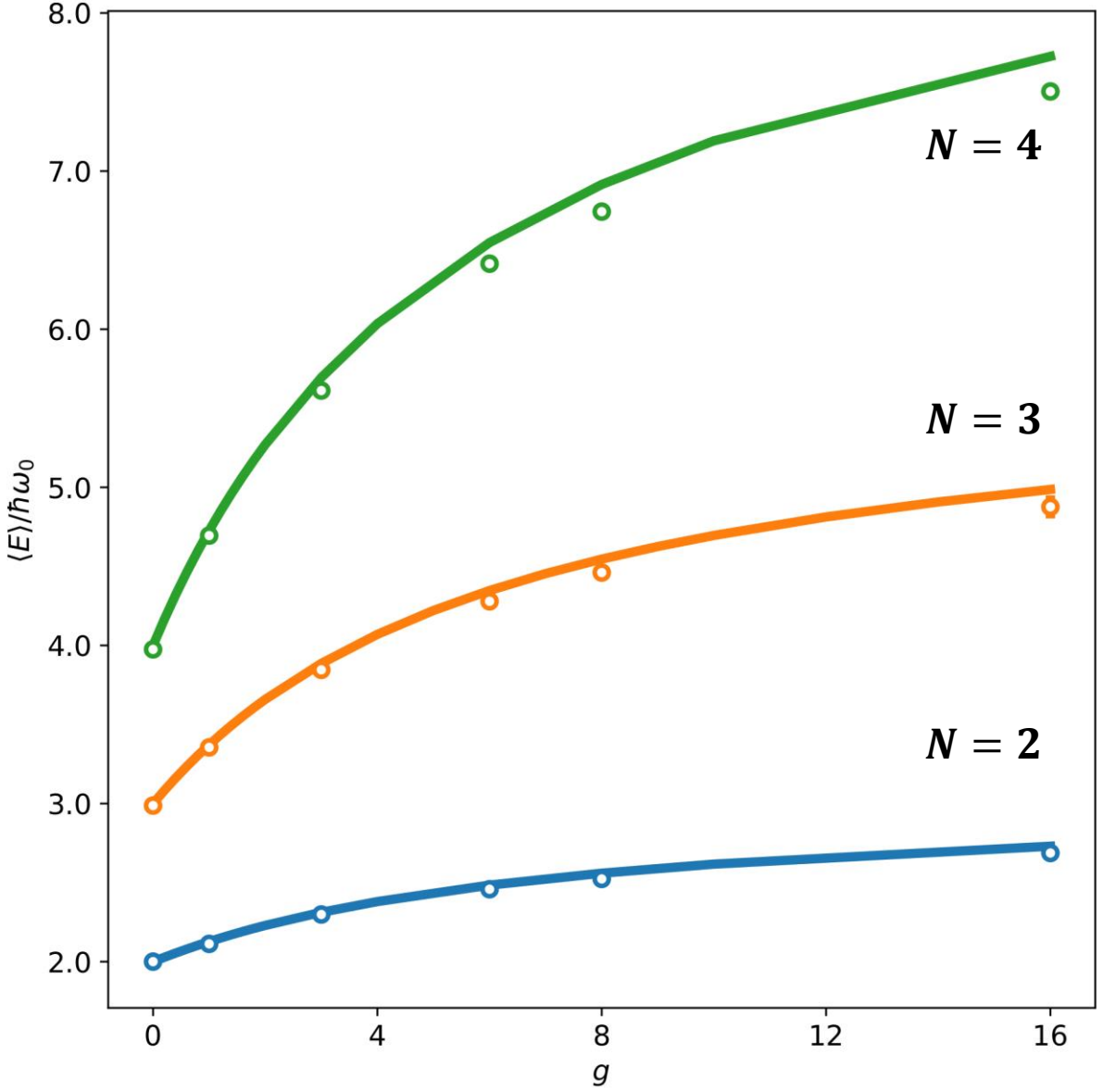
$$U\left(\left|\vec{r}_i - \vec{r}_j\right|\right) = \frac{g}{\pi s^2} e^{-\frac{\left(\vec{r}_i - \vec{r}_j\right)^2}{s^2}}$$

- $g = 0 \rightarrow$ ***non-interacting,*** $g = 16 \rightarrow$ ***strong repulsion***

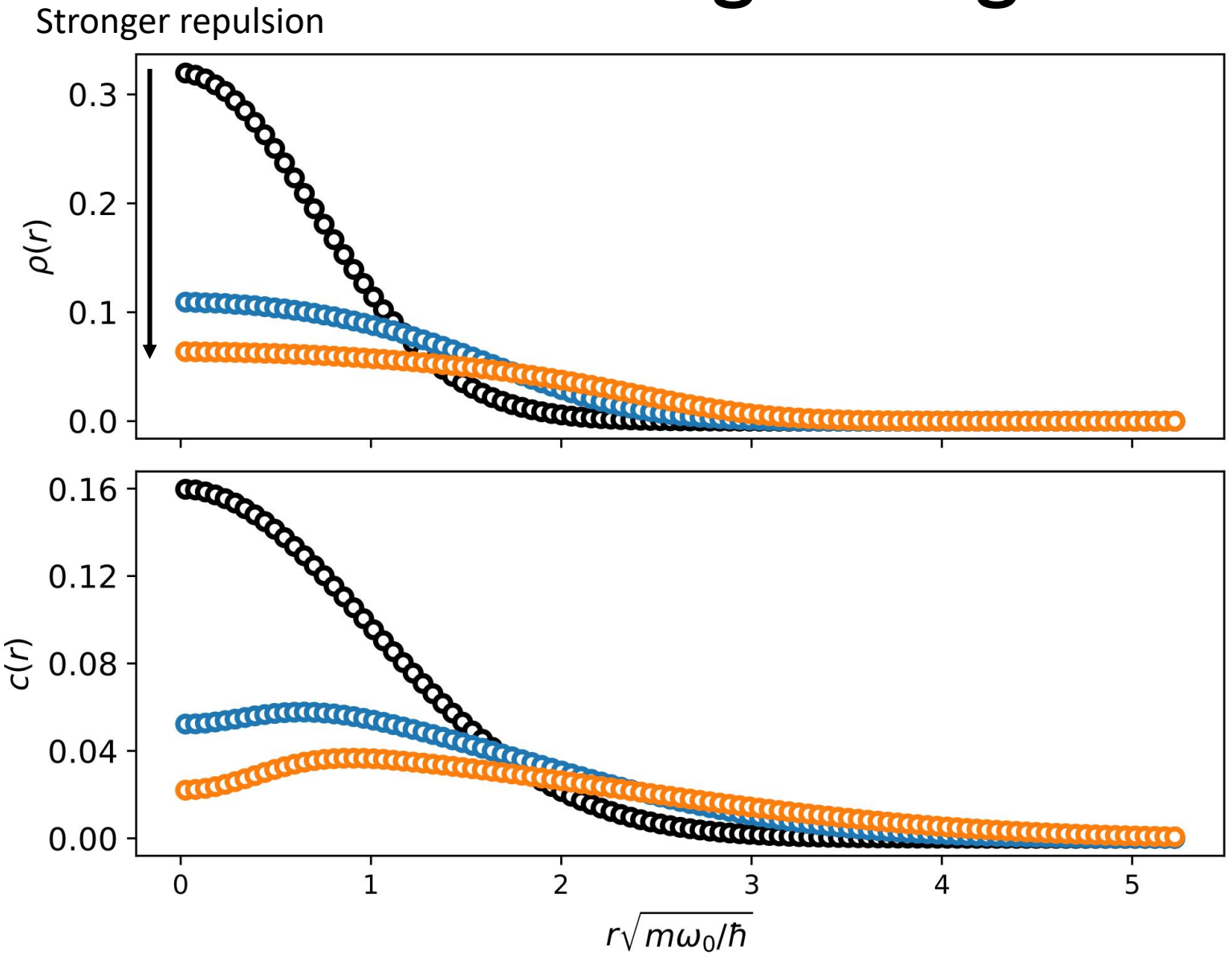
Density and energy $N = 2 - 4$

Stronger repulsion





Interacting Bose gas in 2D, $N = 32$

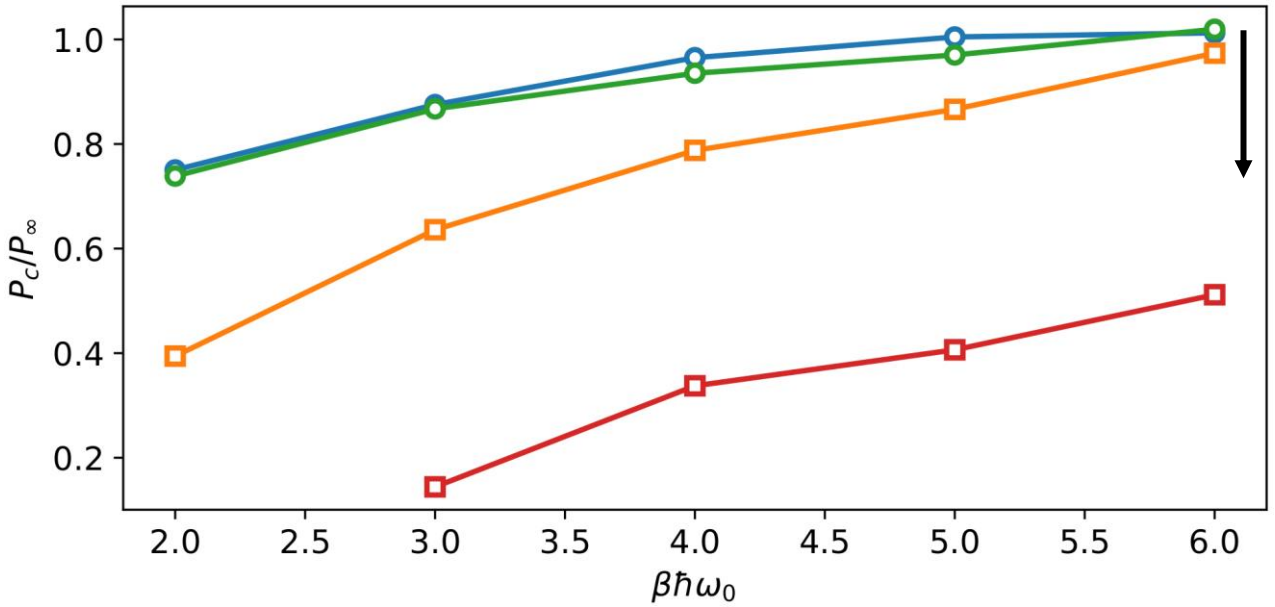


- As g is increased, the density drops at the center of the trap.
- The probability to find two Bosons at zero separation drops as well

Importance of exchange effects

- **The probability for long rings indicates the importance of exchange effects**
- **The asymptotic value P_∞ for the longest ring is $1/N$**
- **For a given T, repulsion interactions lower the probability for long rings**

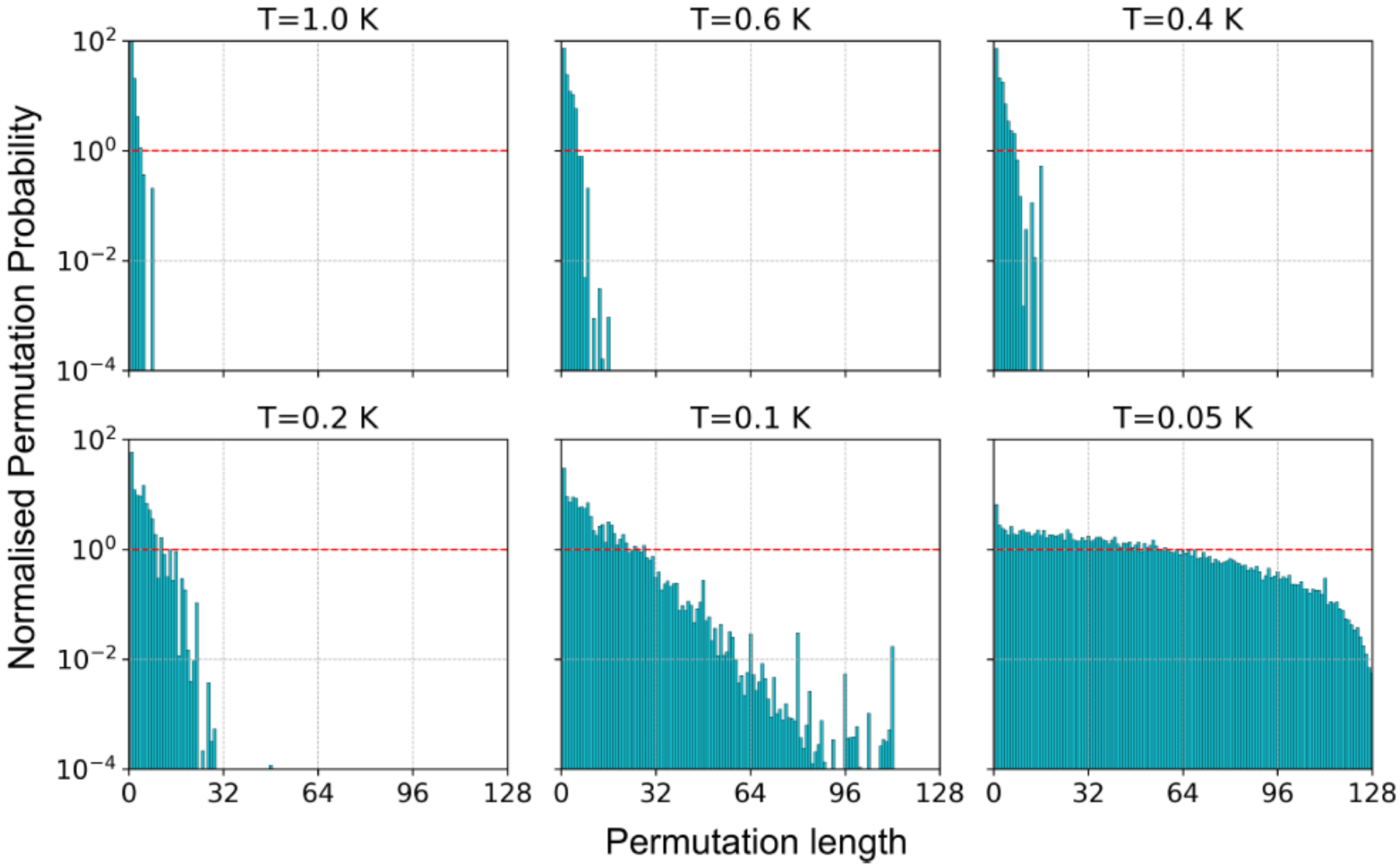
Stronger repulsion

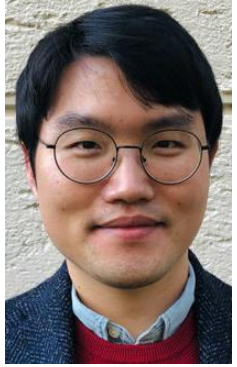


$$P_C = \frac{w_c \cdot e^{-\beta E_C}}{\frac{1}{N}\sum_{k=1}^{N} e^{-\beta\left[E_N^{(k)} + V_B^{(N-k)}\right]}}$$

Deuterium goes supersolid!

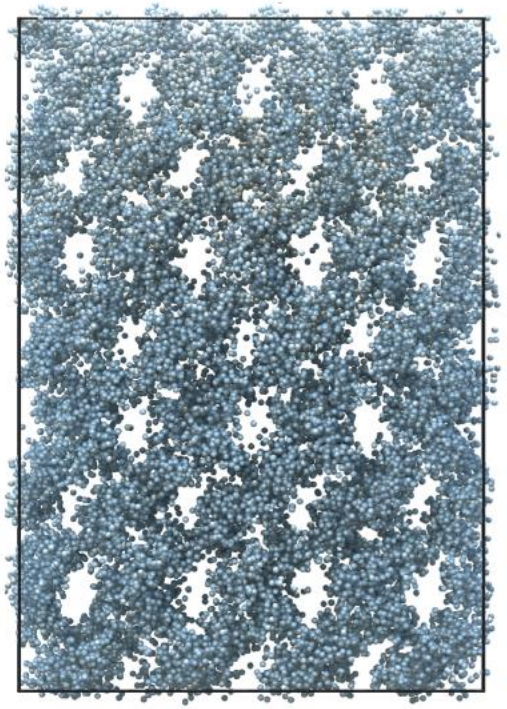
C.W. Myung, B. Hirshberg and M. Parrinello PRL (2022) 128, 045301.





Dr. C.W. Myung

Indistinguishable quantum particle



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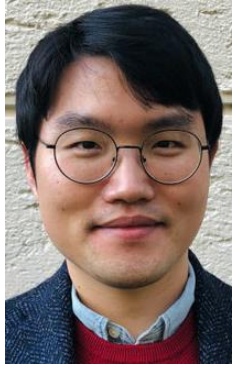
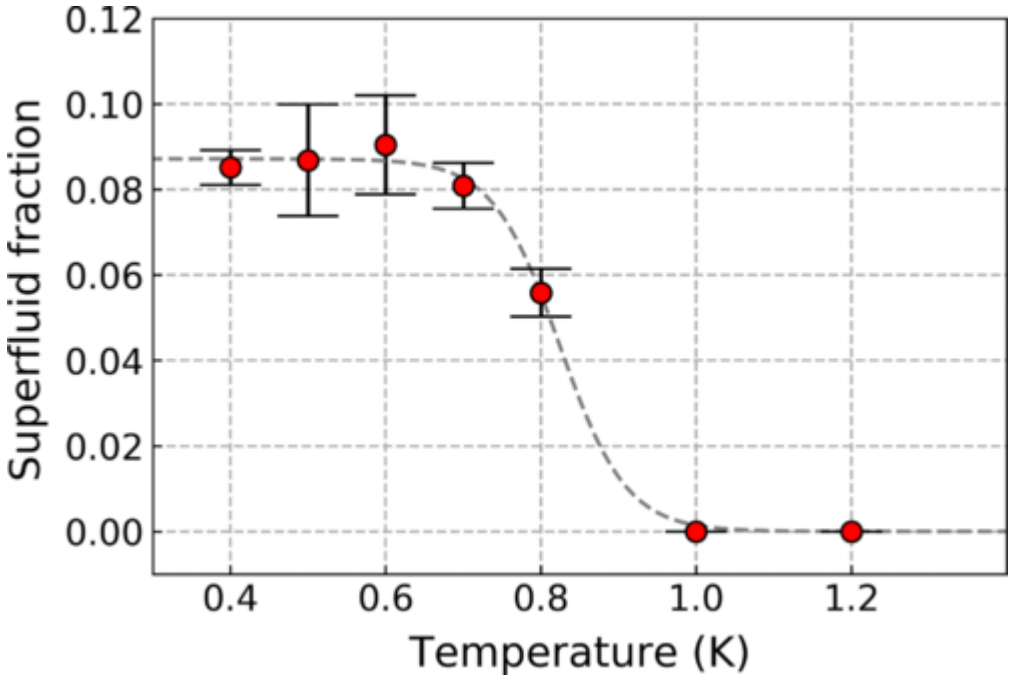
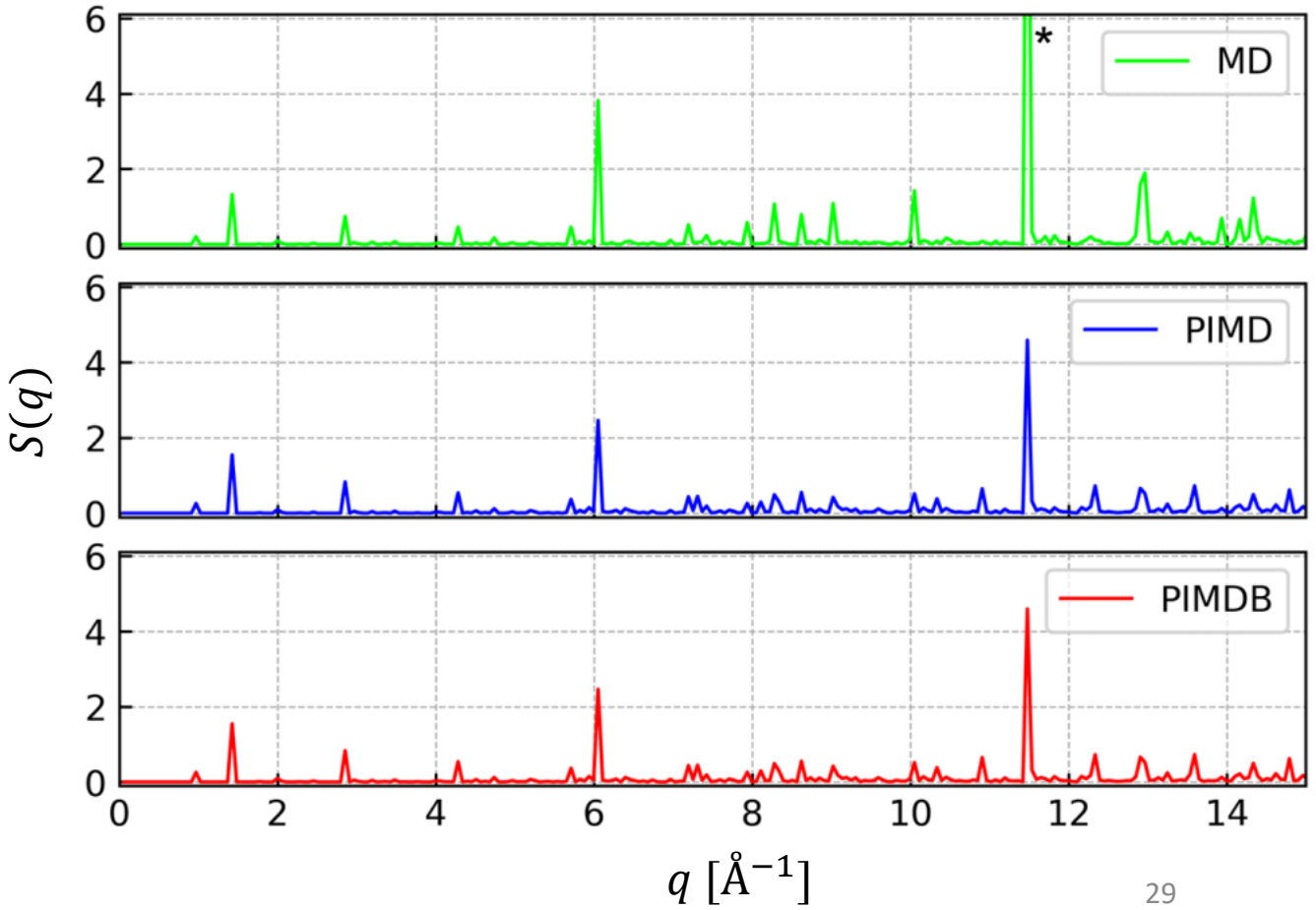


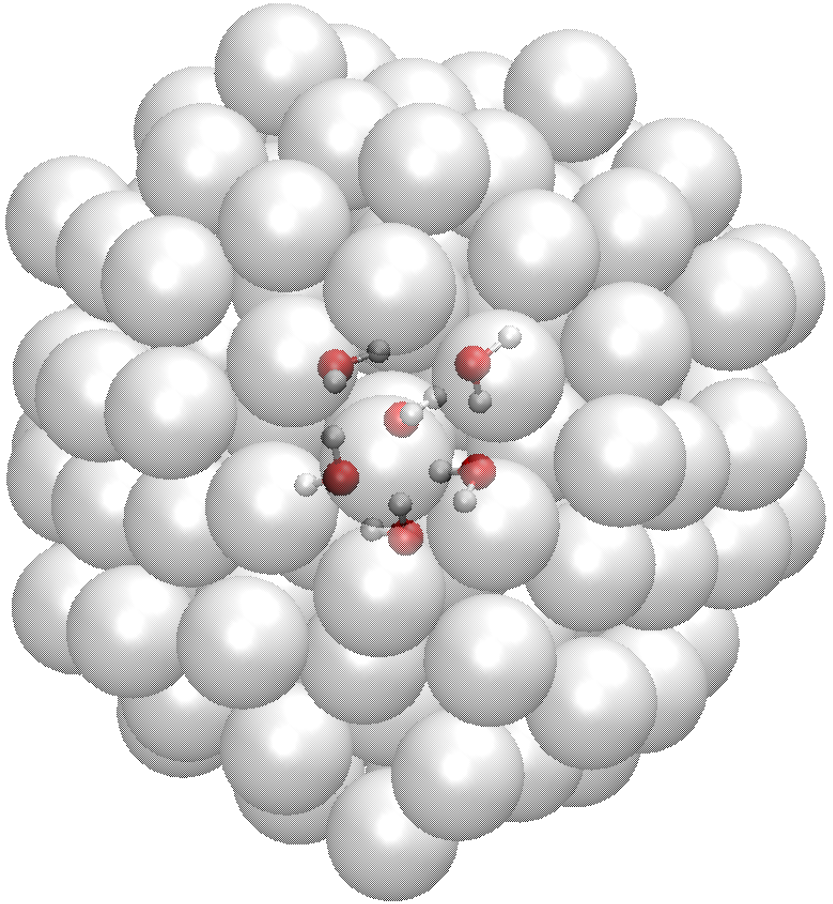
Dr. C.W. Myung

$$P = 800\ GPa$$





Largest system (so far) – superfluid He droplets



256 atoms, CC level PES, collaboration with Paesani group UCSD

Why do we need PIMD for bosons?

Dynamics!

PIMD can also provide approximate time correlation functions

$$C_{AB}(t) = \langle \hat{A}(0)\hat{B}(t) \rangle = \frac{1}{Z} Tr \left\{ e^{-\beta \hat{H}} \hat{A}(0) e^{\frac{i}{\hbar}\hat{H}t} \hat{B}(0) e^{-\frac{i}{\hbar}\hat{H}t} \right\}$$

Ring Polymer MD uses the fictitious polymer trajectories:

$$C_{AB}(t) = \frac{1}{Z_{cl}} \int d\boldsymbol{q}_0 e^{-\beta V(\boldsymbol{q}_0)} A(\boldsymbol{q}_0) B(\boldsymbol{q}_t);\ \boldsymbol{q}_0 = q_1(0), \ldots, q_P(0)$$

$$A(\boldsymbol{q}) = \frac{1}{P} \sum_{j=1}^{P} A(q_j)$$

Habershon, Manolopoulos et al. Annu. Rev. Phys. Chem. (2013) 64, 387–413; Althorpe Eur. Phys. J. B (2021) 94, 155 .

Part II: Fermions

Direct sampling of fermions is not feasible

$$e^{-\beta V_F^{(N)}(R_1,\ldots,R_N)} = \frac{1}{N}\sum_{k=1}^{N}(-1)^{k-1} e^{-\beta\left[E_N^{(k)}(R_{N-k+1},\ldots,R_N)+V_F^{(N-k)}(R_1,\ldots,R_{N-k})\right]}$$

$$V_F^{(N)}(R_1,\ldots,R_N) = -\frac{1}{\beta}\ln\left[\frac{1}{N}\sum_{k=1}^{N}(-1)^{k-1} e^{-\beta\left[E_N^{(k)}+V_B^{(N-k)}\right]}\right];\ V_F^{(0)} = 0$$

$$Z \sim \int e^{-\beta V_F^{(N)}} dR_1 \ldots dR_N$$

Problem: **The argument can be negative, $V_F^{(N)}$ becomes complex!**

The solution: sample bosons and reweight

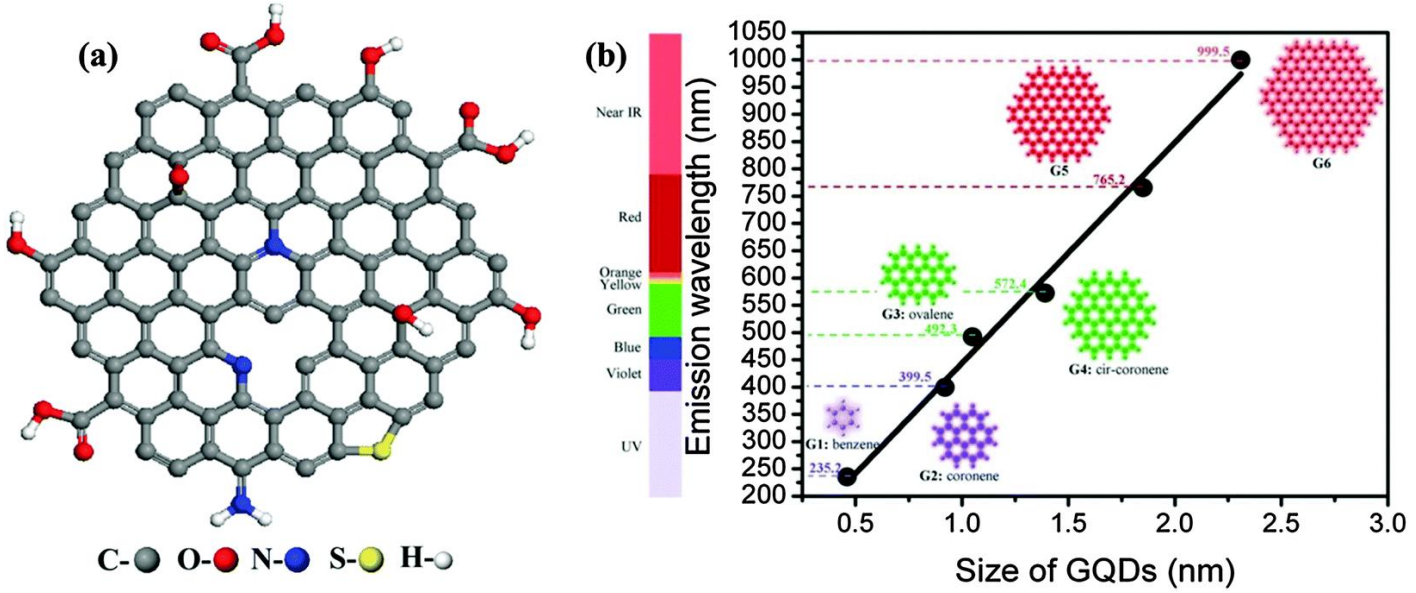
$$\langle O \rangle_F = \frac{\left\langle \varepsilon_O e^{-\beta\left[V_F^{(N)} - V_B^{(N)}\right]} \right\rangle_B}{\left\langle e^{-\beta\left[V_F^{(N)} - V_B^{(N)}\right]} \right\rangle_B} \equiv \frac{\langle \varepsilon_O S \rangle_B}{\langle S \rangle_B}$$

The sign

- **Applicable to N particles (in principle)**
- **Commonly done in PIMC**

Application – electrons in 2D quantum dots

P. Chen *et al.* Chem. Soc. Rev., 2016

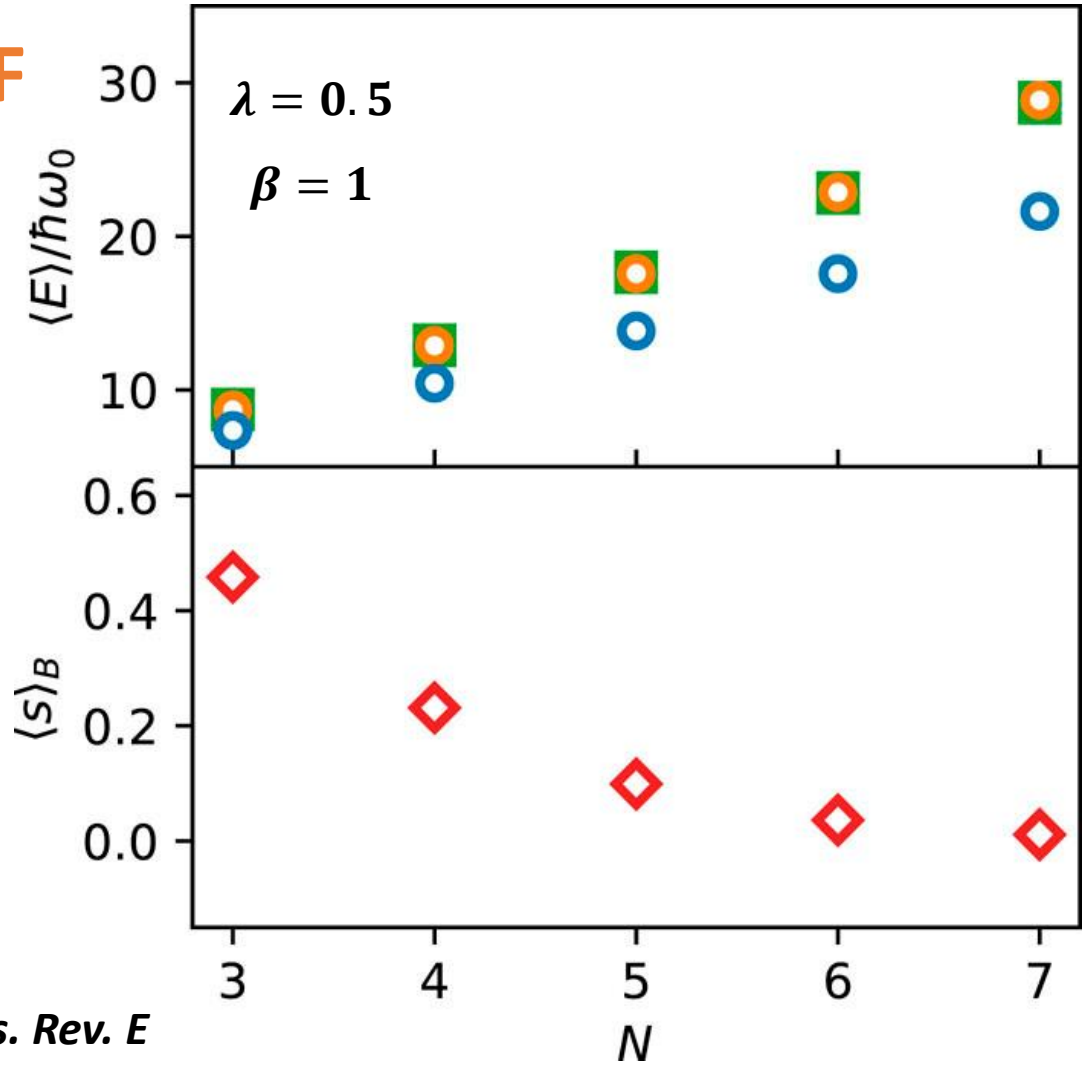


$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{i=1}^{N}\boldsymbol{r}_i^2 + \sum_{i,j>i}^{N}\frac{\lambda}{|\boldsymbol{r}_i - \boldsymbol{r}_j|};\quad \lambda \equiv \frac{e^2}{k l_0 \hbar\omega_0};\quad l_0 \equiv \sqrt{\frac{\hbar}{m\omega_0}}$$

- $\lambda < 1$ – Exchange dominates; $\lambda > 1$ – Repulsion dominates

N=3-7 electrons in QD

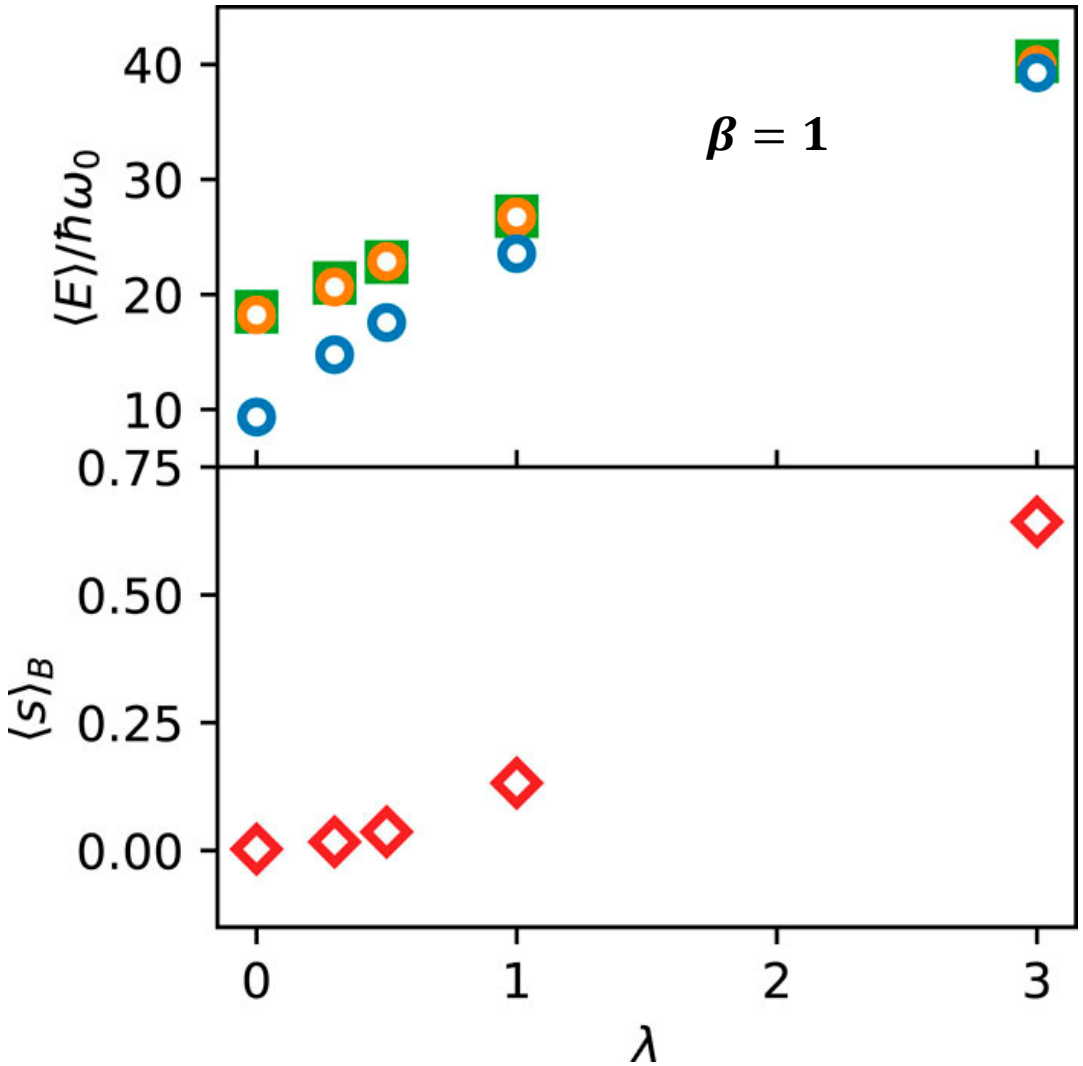
- **Blue: PIMD-B**
- **Orange: PIMD-F**
- **Green: PIMC**

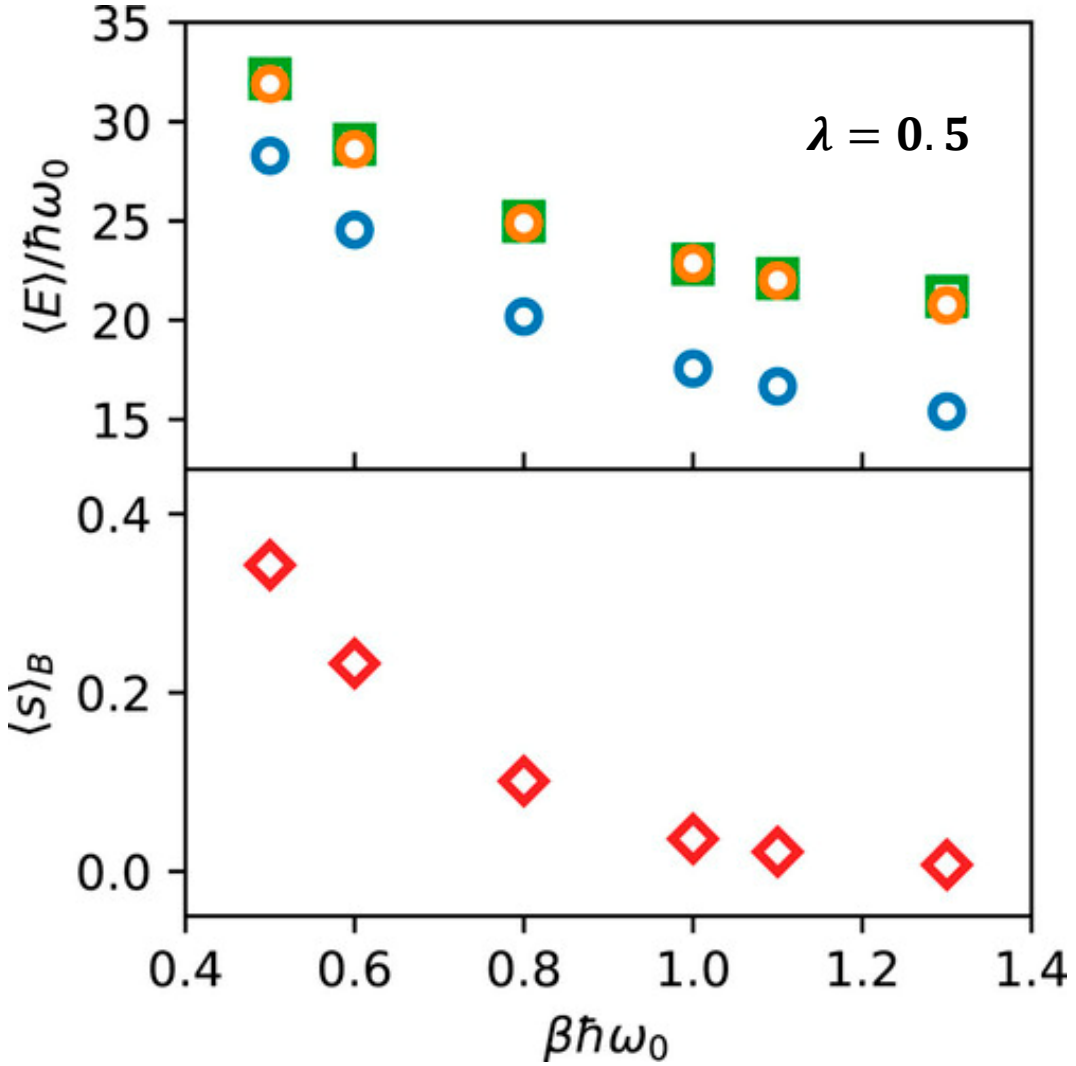


PIMC: T. Dornheim (2019) *Phys. Rev. E*

N=6 electrons in QD

- **Green: PIMC; Orange: PIMD-F; Blue: PIMD-B**



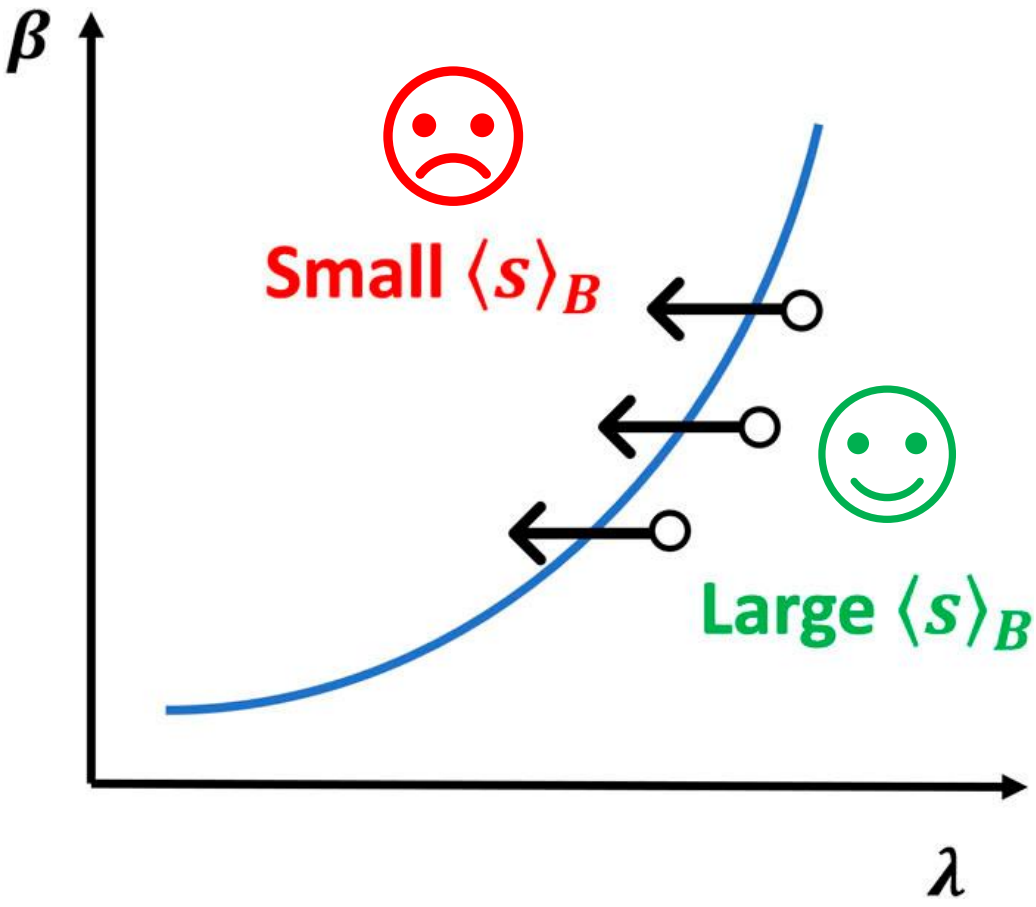


The fermion sign problem

$$\langle O \rangle_F = \frac{\langle \varepsilon_O S \rangle_B}{\langle S \rangle_B}; \quad \langle S \rangle_B \sim e^{-\beta N \Delta F}$$

- As $\beta \to \infty$ calculations become exponentially harder (Ceperley).
- Most probably no general solution exists (Troyer).
- Can we push the boundaries for fixed N?

The fermion sign problem



- **Simulate systems with added fictitious repulsion.**

$$\hat{H}(\lambda) = \hat{H}_0 + \eta\hat{U}$$

- **Correct using a variational principle**

$$F_{\hat{H}_0} \leq F_{\hat{H}} - \eta\langle\hat{U}\rangle_{\hat{H}}$$

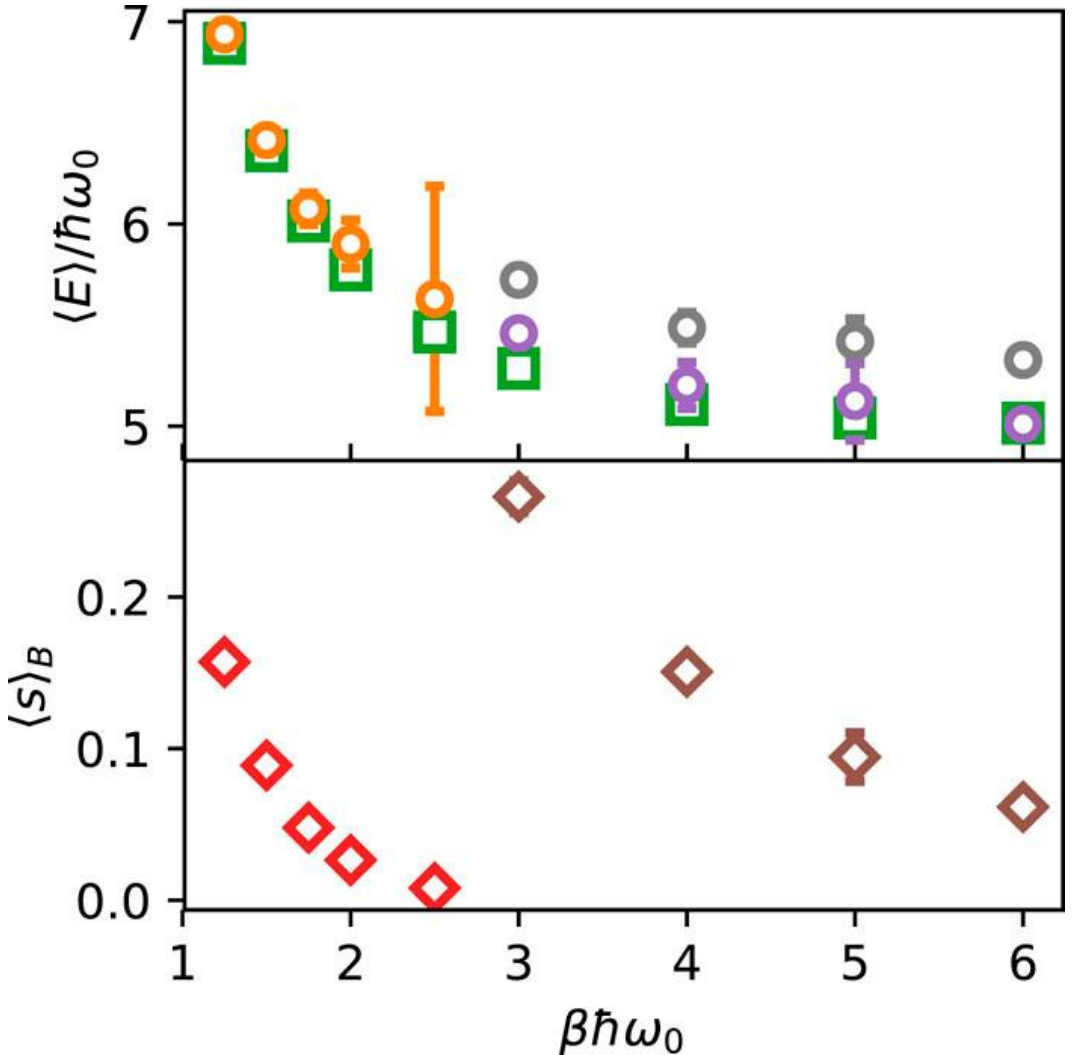
- **Or using thermodynamic integration**

$$F_{H_0} = F_H - \int_0^\eta \mathrm{d}\eta' \langle\hat{U}\rangle_H$$

JCP (2020) 152, 171102, JCP (2020) 153, 234104.

Bogoliubov inequality: noninteracting electrons

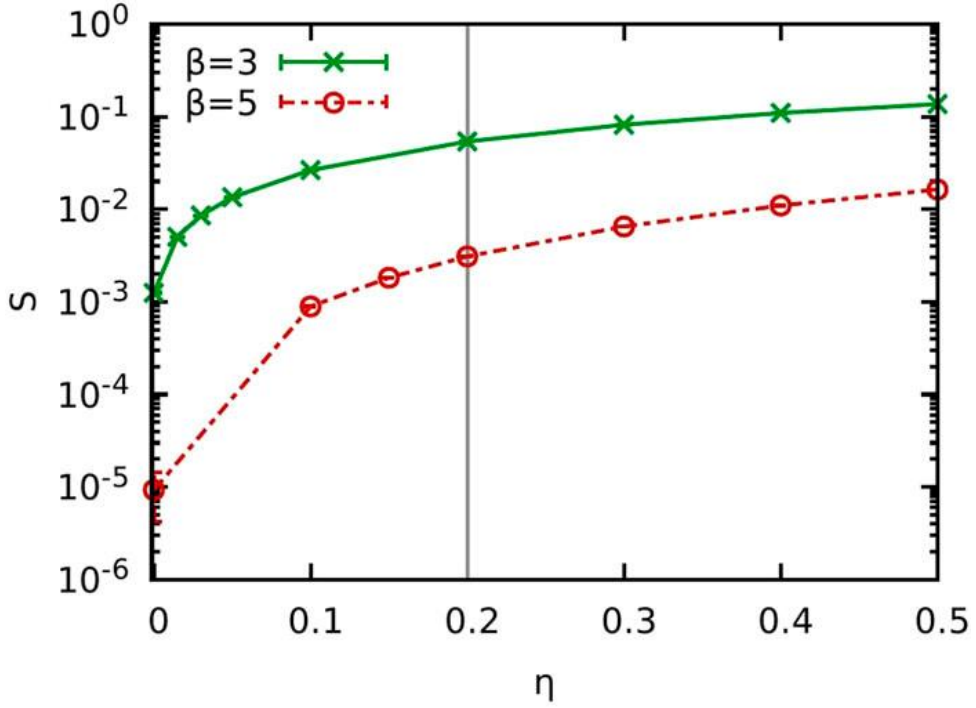
Added Gaussian repulsion interaction allow 3x lower T

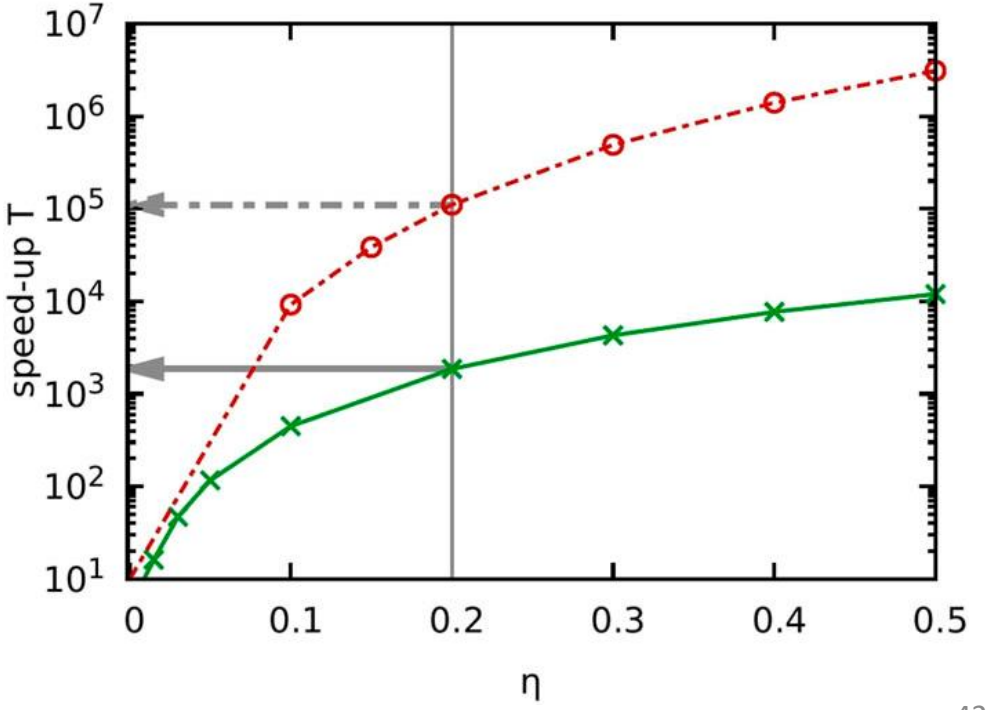


Thermodynamic integration

Speedup T gained by adding fictitious repulsion is 10^3-10^5

$$T(\eta) = \frac{\langle s \rangle_H}{\langle s \rangle_{H_0}}$$





Conclusions - bosons

PNAS (2019) 116, 21445-21449, PRL (2022) 128, 045301.

- **A new method for simulating Bosonic systems.**
- **Evaluation of forces can be done without enumerating or sampling permutations.**
- **The resulting algorithm reduced the scaling from $\sim N!$ to $\sim N^3$.**
- **First application of PIMD to large bosonic systems.**
- **Prediction of supersolid deuterium at P>800 GPa and T<1 K.**

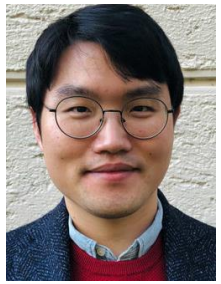
Conclusions - fermions

JCP (2020) 152, 171102; JCP (2020) 153, 234104.

- **We can apply PIMD-B to evaluate fermionic observables.**
- **Very good agreement with PIMC (if sign ≥ 0.01).**
- **Using the Bogoliubov inequality, ~3x lower temperatures can be sampled.**
- **Using thermodynamic integration, 3-5 orders of magnitude speedups are obtained.**

Thank you!

M. Parrinello



C.W. Myung

V. Rizzi

M. Invernizzi

ETH zürich

Università della Svizzera italiana

יד הנדיב
يادِ هَنَديف
Yad Hanadiv