School of Chemistry
The Raymond and Beverly Sackler
Faculty of Exact Sciences
Tel Aviv University

בית הספר לכימיה
הפקולטה למדעים מדויקים
ע"ש ריימונד ובברלי סאקלר
אוניברסיטת תל אביב

Path Integral Molecular Dynamics for Indistinguishable Particles

Virtual International Seminar on Theoretical Advancements (VISTA)

Barak Hirshberg

Hirshberg lab
Molecular simulations

We are hiring!

- **Looking for PhD students and postdocs who are passionate about physical chemistry, MD simulations, and Path Integrals!**

Prestigious Fellowships for suitable candidates

THE RAYMOND AND BEVERLY
SACKLER CENTER
FOR COMPUTATIONAL MOLECULAR
AND MATERIALS SCIENCE

POSTDOCTORAL FELLOWS PROGRAM

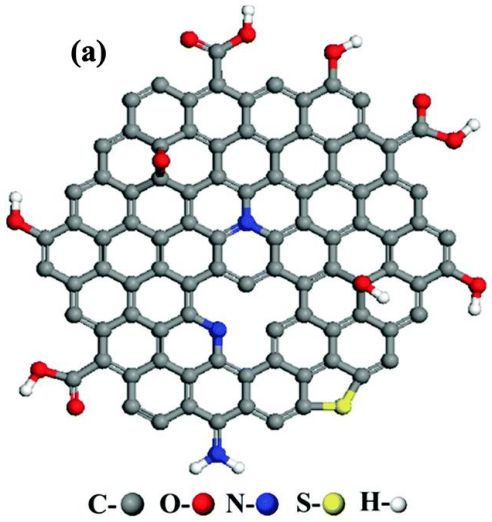
The Sackler Center for Computational Molecular and Materials Science at Tel Aviv University is now receiving applications for two prestigious postdoctoral positions. Postdoctoral fellows are expected to perform leading-edge computational research focusing on the chemistry and physics of complex systems and to interact with at least one, but preferably more of the research groups associated with the center. Applicants should have recently completed their PhD thesis in a relevant field, in an academic institute outside Israel, or expect to complete it by March 2022. Candidates already at Tel Aviv University or who have performed research at Tel Aviv University may not be considered. Postdoctoral fellows joining the center are expected to start after October 2021. They will enjoy a two-year appointment with Tel Aviv University's highest fellowship, plus relocation expenses (including arrival flights and if needed, temporary housing). A personal allowance of 2000 USD/year will be given for travel expenses to conferences.

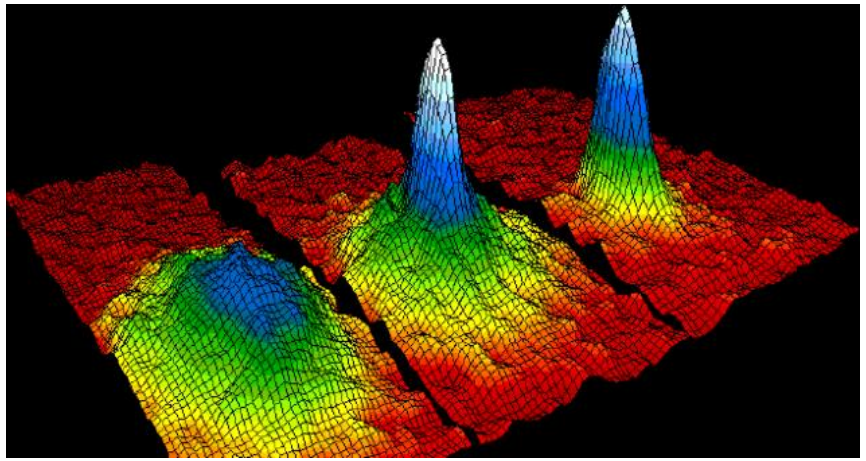
Outline

- **Motivation**
- **Path integral molecular dynamics for distinguishable particles**
- **Exchange effects in PIMD – a great challenge!**
- **PIMD for bosons at $\sim N^3$ cost (ultracold atoms, supersolids)**
- **Fermions – alleviating the sign problem (2D quantum dots)**

Motivation

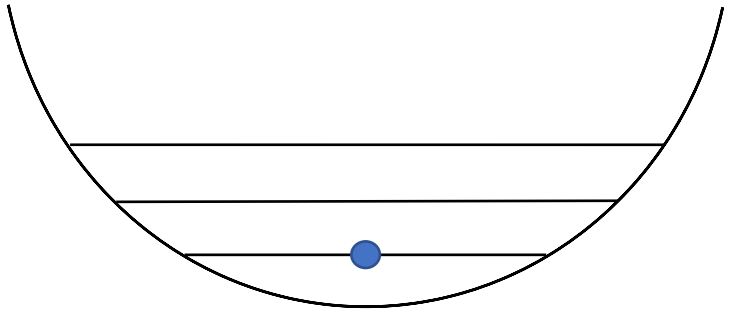
- **Quantum symmetry is the most fundamental properties of quantum particles**
- **Exchange effects at finite T are important for many systems:**



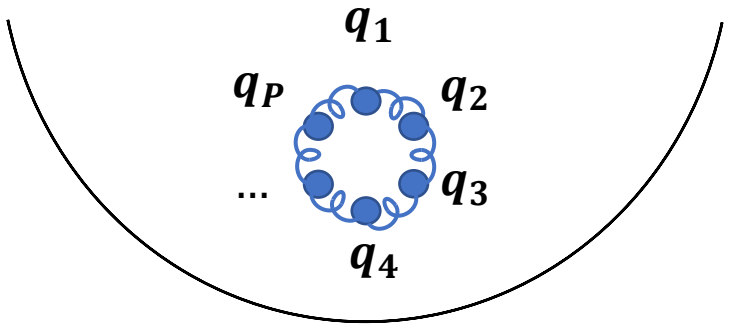


- **Why PIMD? A dynamical method, approximate quantum time correlation functions using ring polymer molecular dynamics**

PIMD for distinguishable particles



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



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

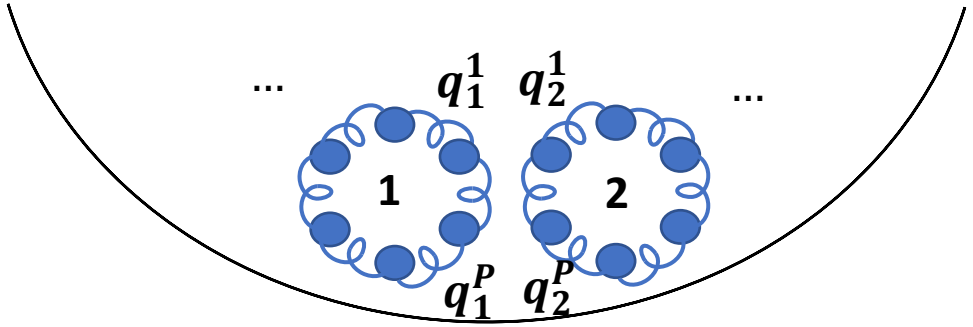
$$Z = Tr\left(e^{-\beta\hat{H}}\right) \sim \int \langle q|e^{-\beta\hat{H}}|q\rangle dq$$

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

$$V_o = \frac{1}{2}m\omega_P^2\sum_{j}^{P}\left(q_{j+1} - q_j\right)^2 ; q_{P+1} = q_1$$

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

More than one particle



$$H(\boldsymbol{p},\boldsymbol{q}) = \sum_{l=1,2}\sum_{i=j}^{P}\frac{{p_l^j}^2}{2m} + V_{oo} + \frac{1}{P}\sum_{j=1}^{P} V(q_1^j, q_2^j)$$

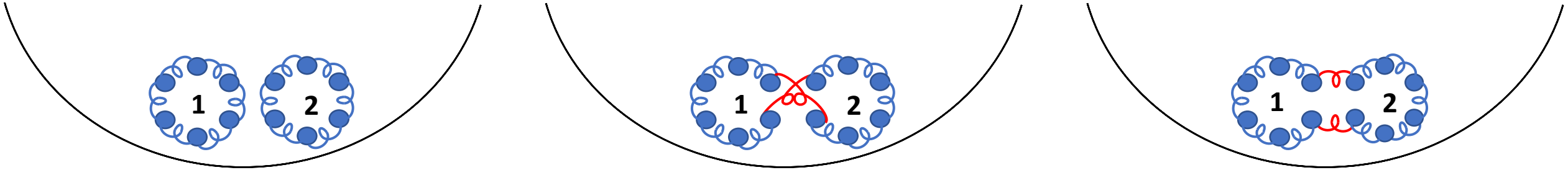
$$V_{oo} = \frac{1}{2}m\omega_P^2 \sum_{l=1,2}\sum_{j=1}^{P}\left(q_l^{j+1} - q_l^j\right)^2 \;\; ; \;\; q_l^{P+1} = q_l^1$$

$$Z \sim \lim_{P\to\infty}\int e^{-\beta H(\boldsymbol{p},\boldsymbol{q})} d\boldsymbol{p_1} d\boldsymbol{p_2} d\boldsymbol{q_1} d\boldsymbol{q_2}$$

Exchange Symmetry in the PI formalism

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

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



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

$$V_O = \frac{1}{2} m\omega_P^2 \sum_{l=1,2} \sum_{j=1}^{P} \left(q_l^{j+1} - q_l^j\right)^2 \;\; ; \;\; q_1^{P+1} = q_2^1, q_2^{P+1} = q_1^1$$

Part I: Bosons

Sampling Z, a clear physical picture

$$Z \sim \int e^{-\beta V_B^{(2)}} d\boldsymbol{q}_1 d\boldsymbol{q}_2$$

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

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

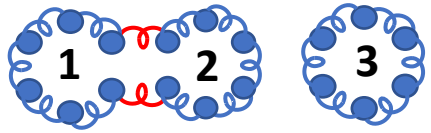
The force is the weighted average of contributions due to all ring polymer configurations!

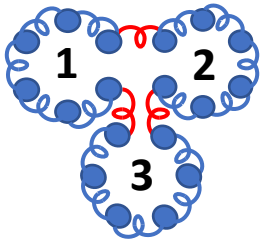
More than two particles

- **For N=3**

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

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)

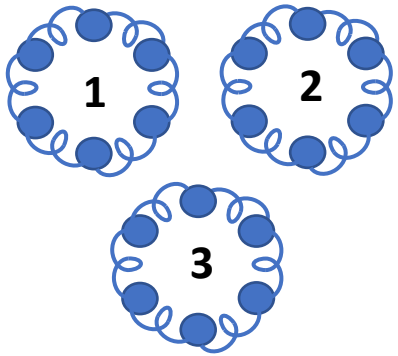
(1,2,3)

(2,3,1)

(123)

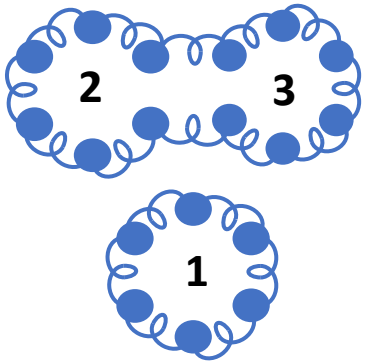
Ring-polymer configurations

V_{ooo}

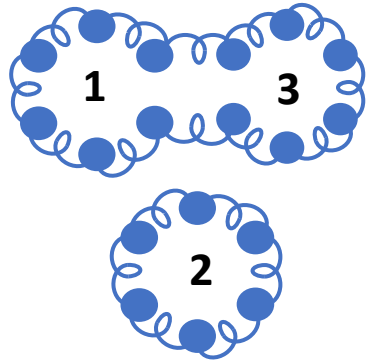


(1,2,3)
(1)(2)(3)

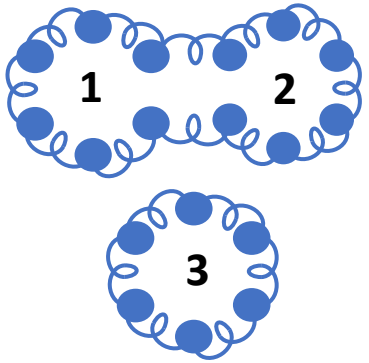
V_{Oo}



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

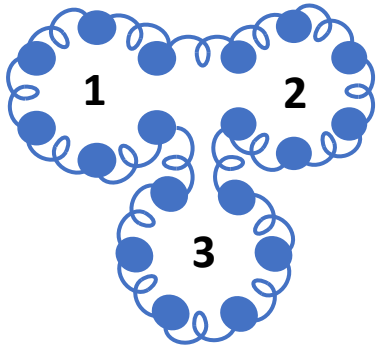


(3,2,1)
(13)(2)

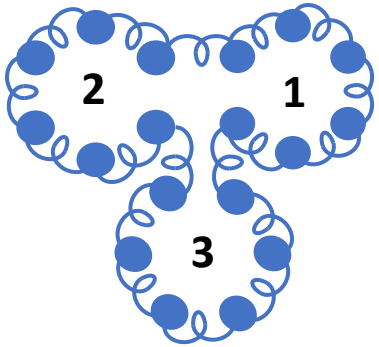


(2,1,3)
(12)(3)

V_{Δ}



(2,3,1)
(123)



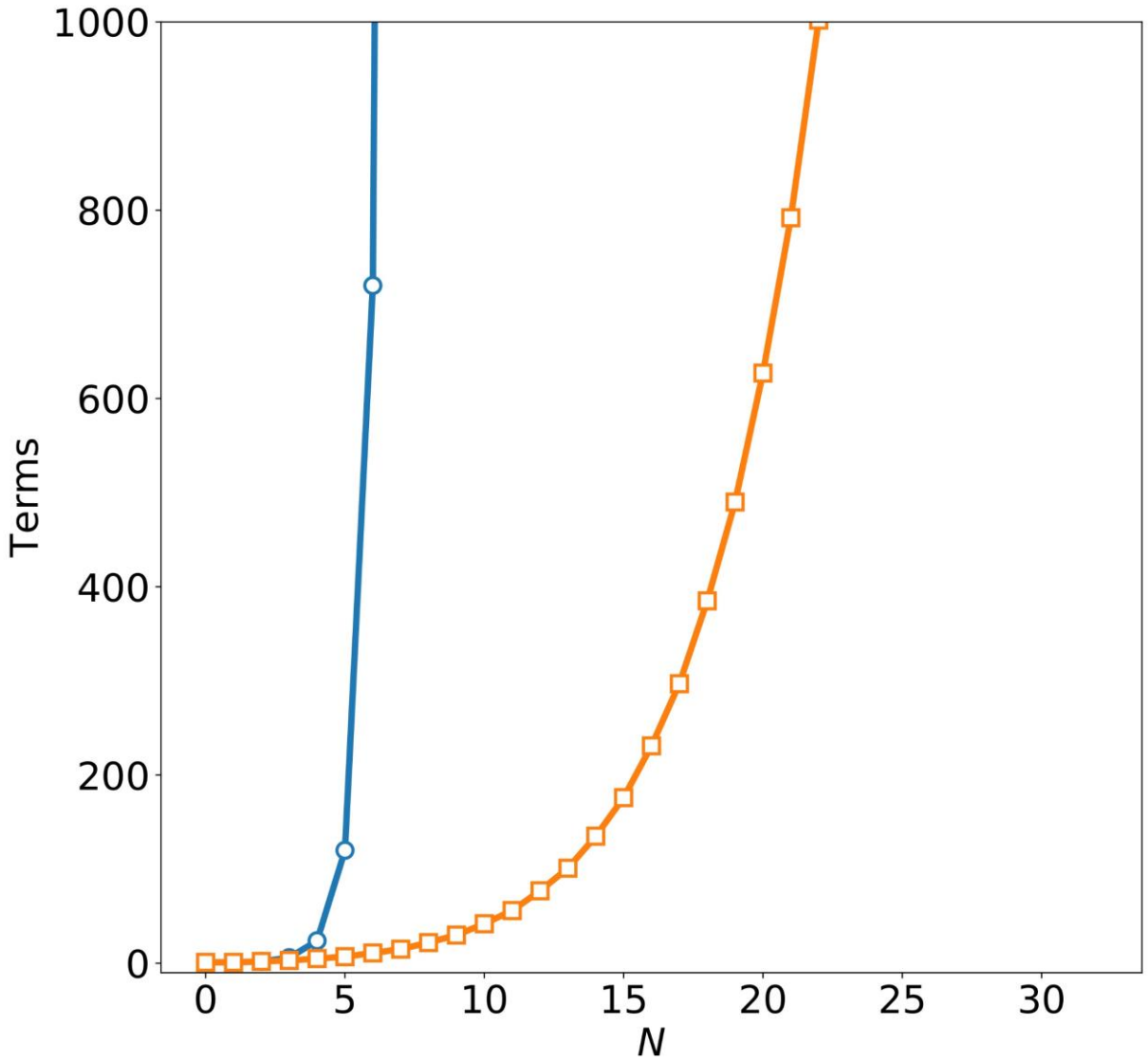
(3,1,2)
(132)

The Problem

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

Not practical for large N,

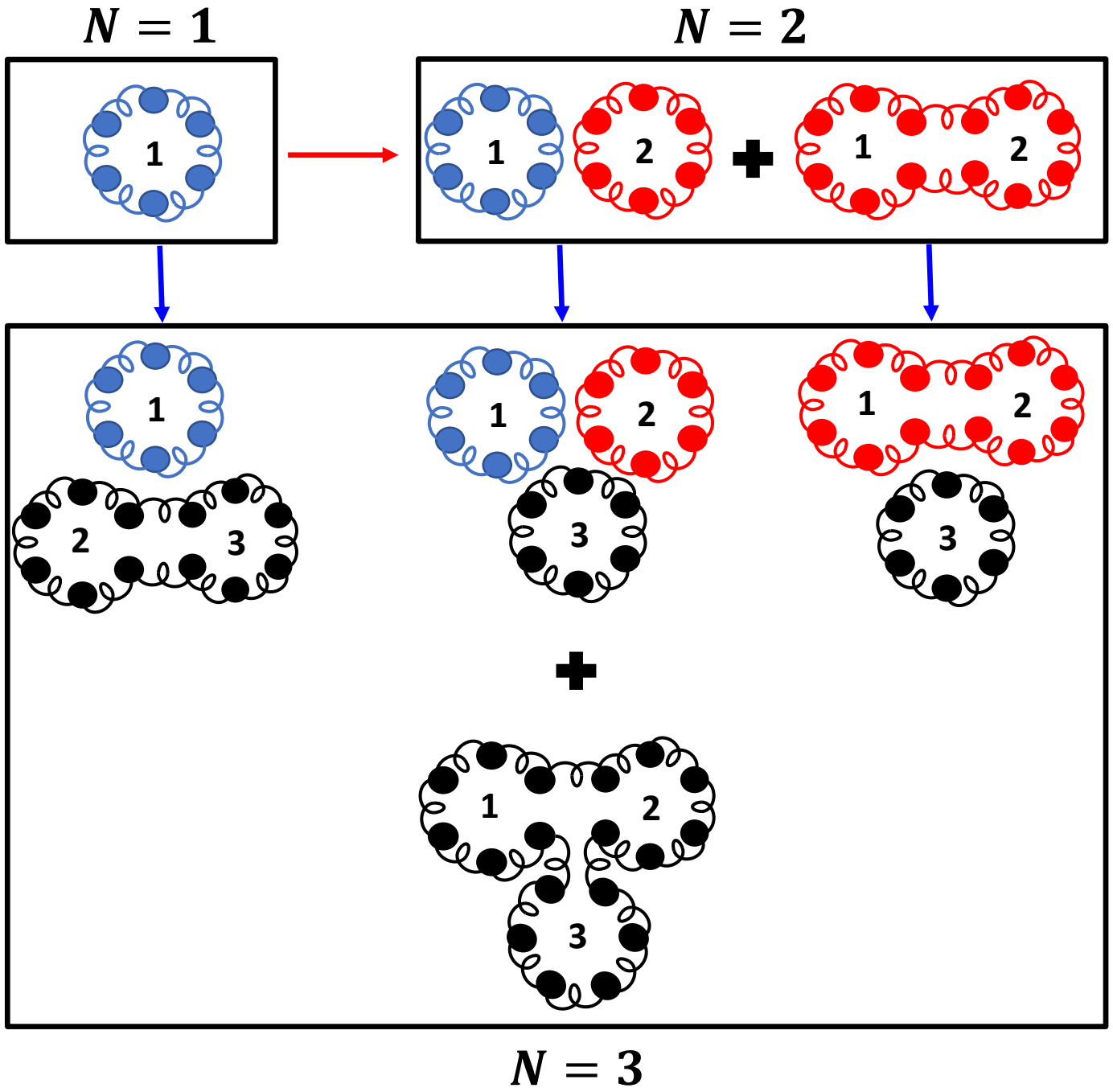
<u>Is there an alternative?</u>



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

- **# of permutations $\sim N!$**
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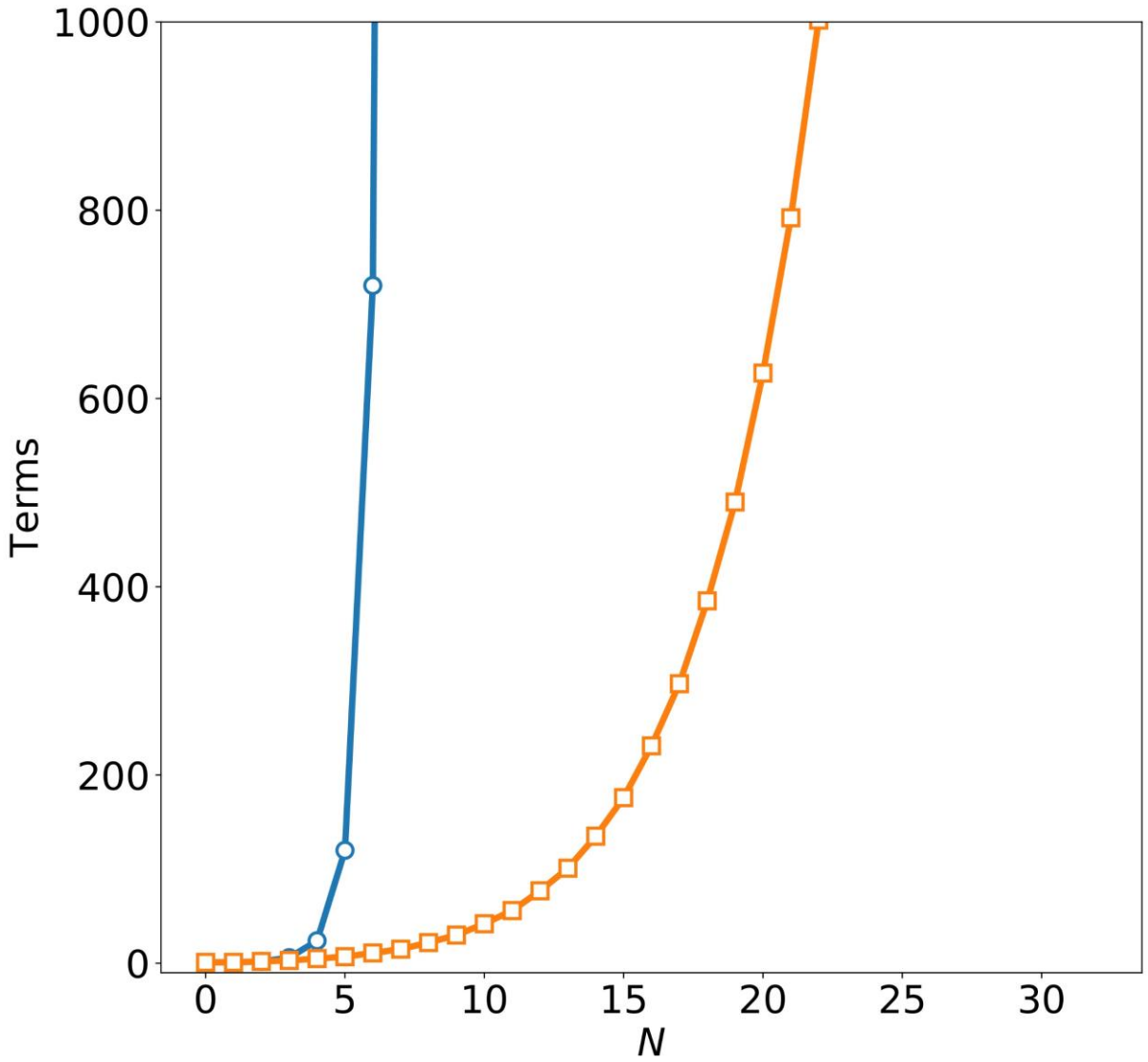
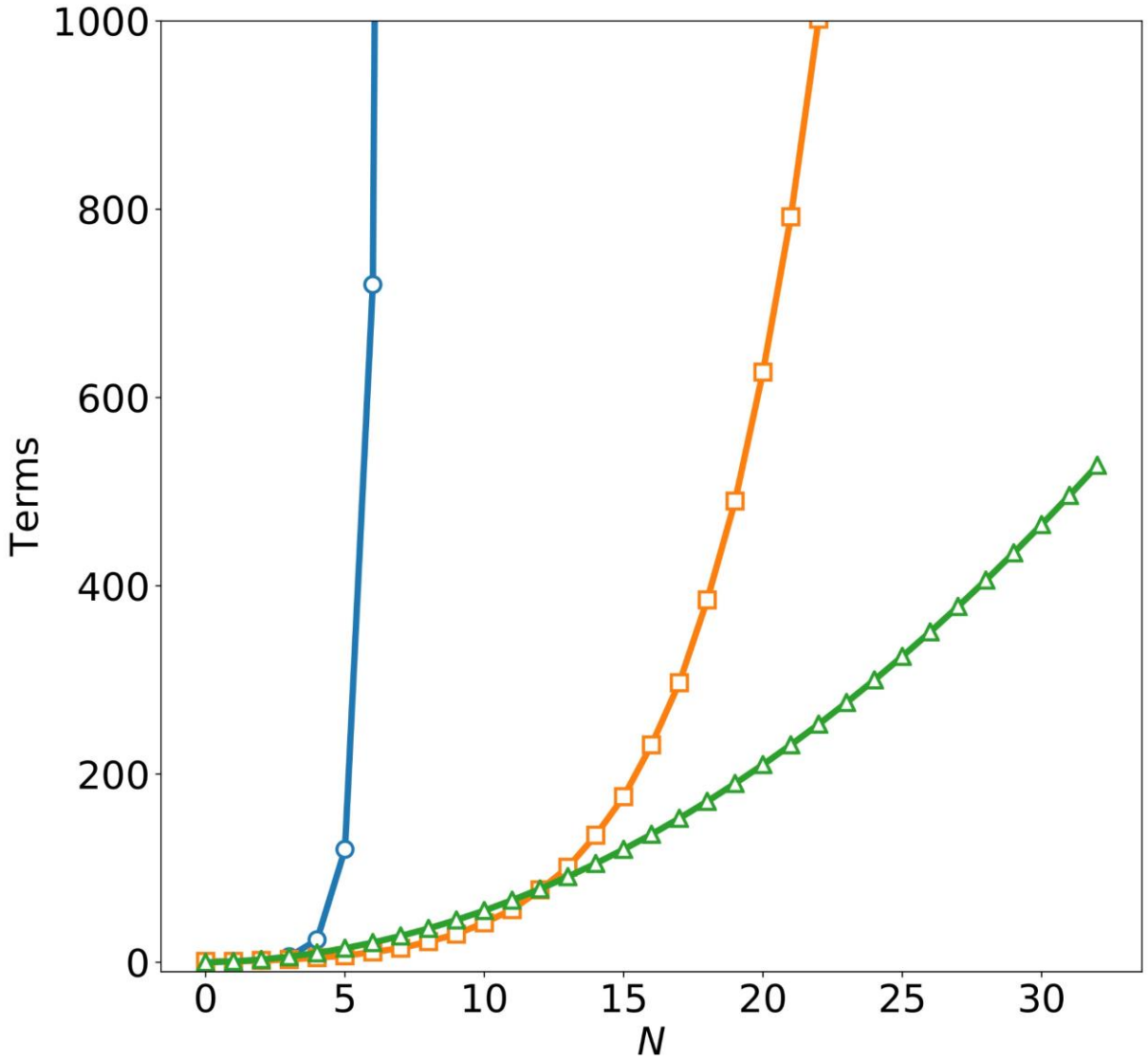
Not practical for large N,

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



The Solution

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



The Solution

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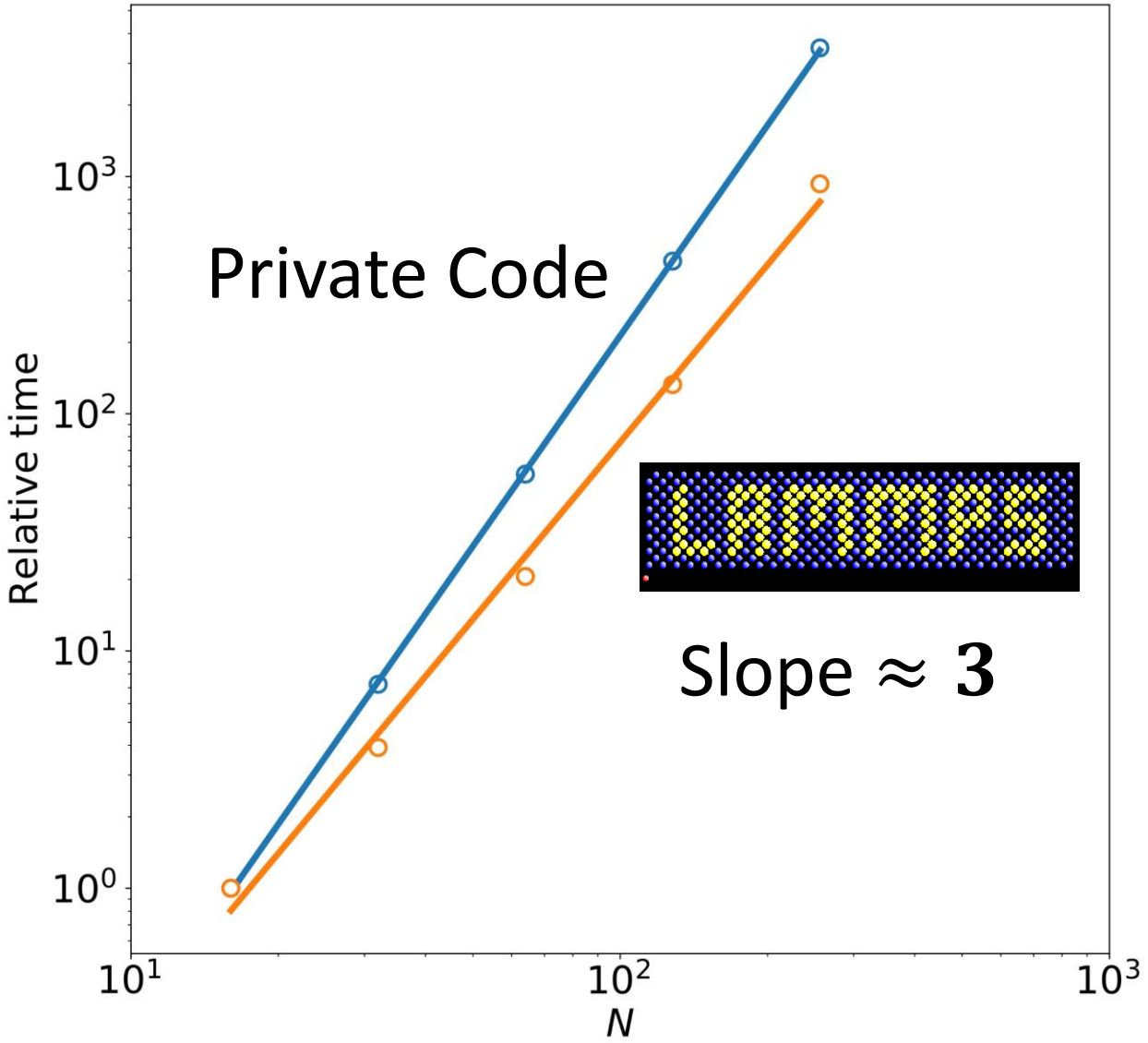
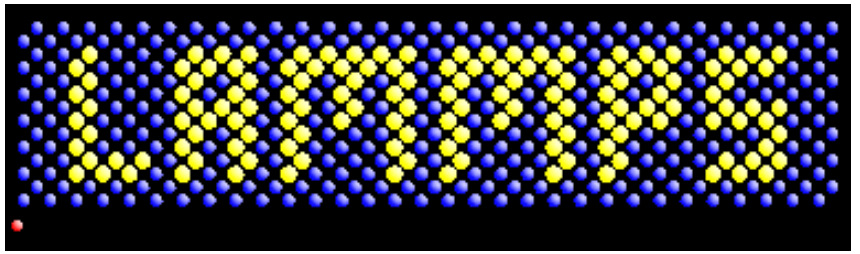


Open-source implementations

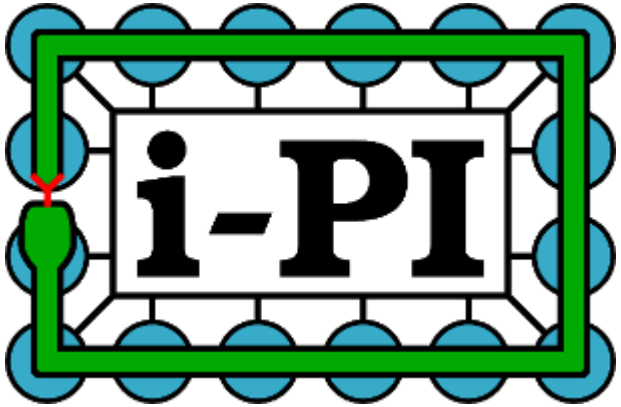
- **Development version of LAMMPS (infrastructure by Voth Group)**

https://github.com/BarakHirshberg



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

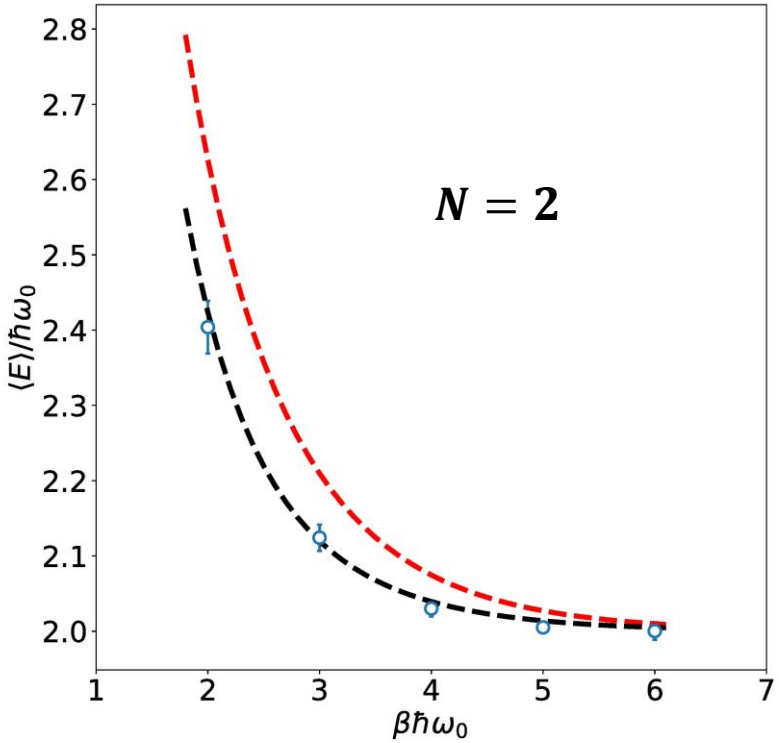
http://ipi-code.org

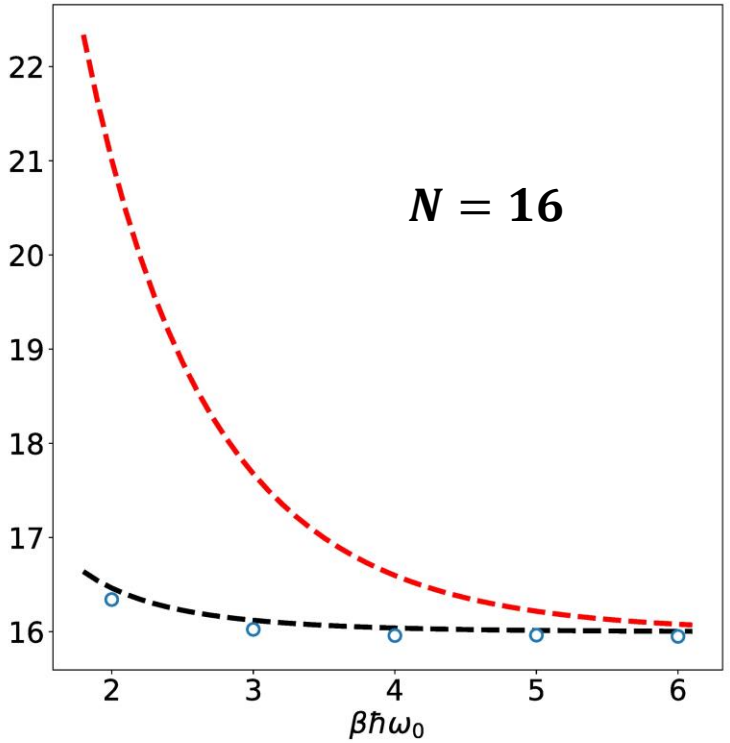


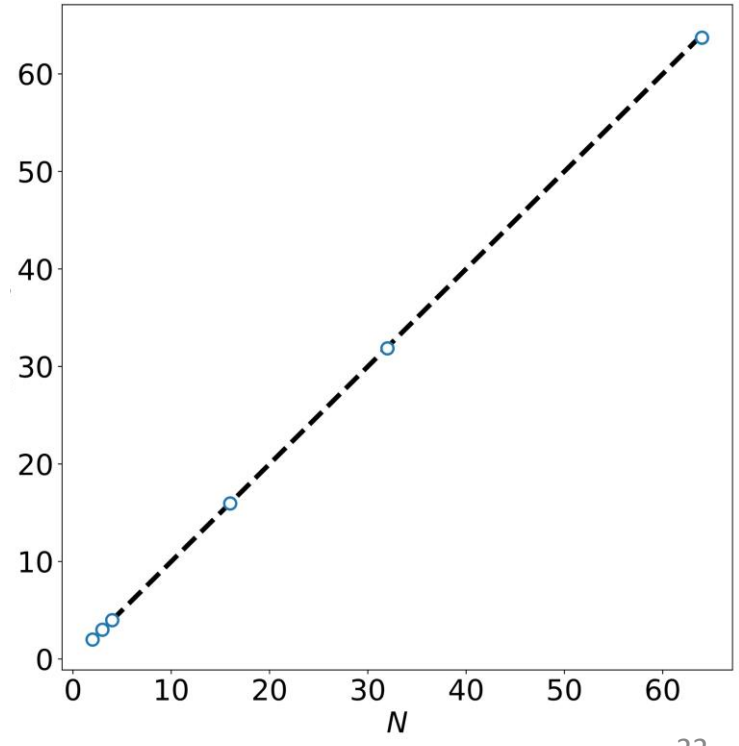
S. Plimpton, J. Comp. Phys. (1995) 117, 1-19
V. Kapil *et. al,* Comput. Phys. Commun. (2019) 236, 214-223

Benchmarking: noninteracting particles in 2D trap

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







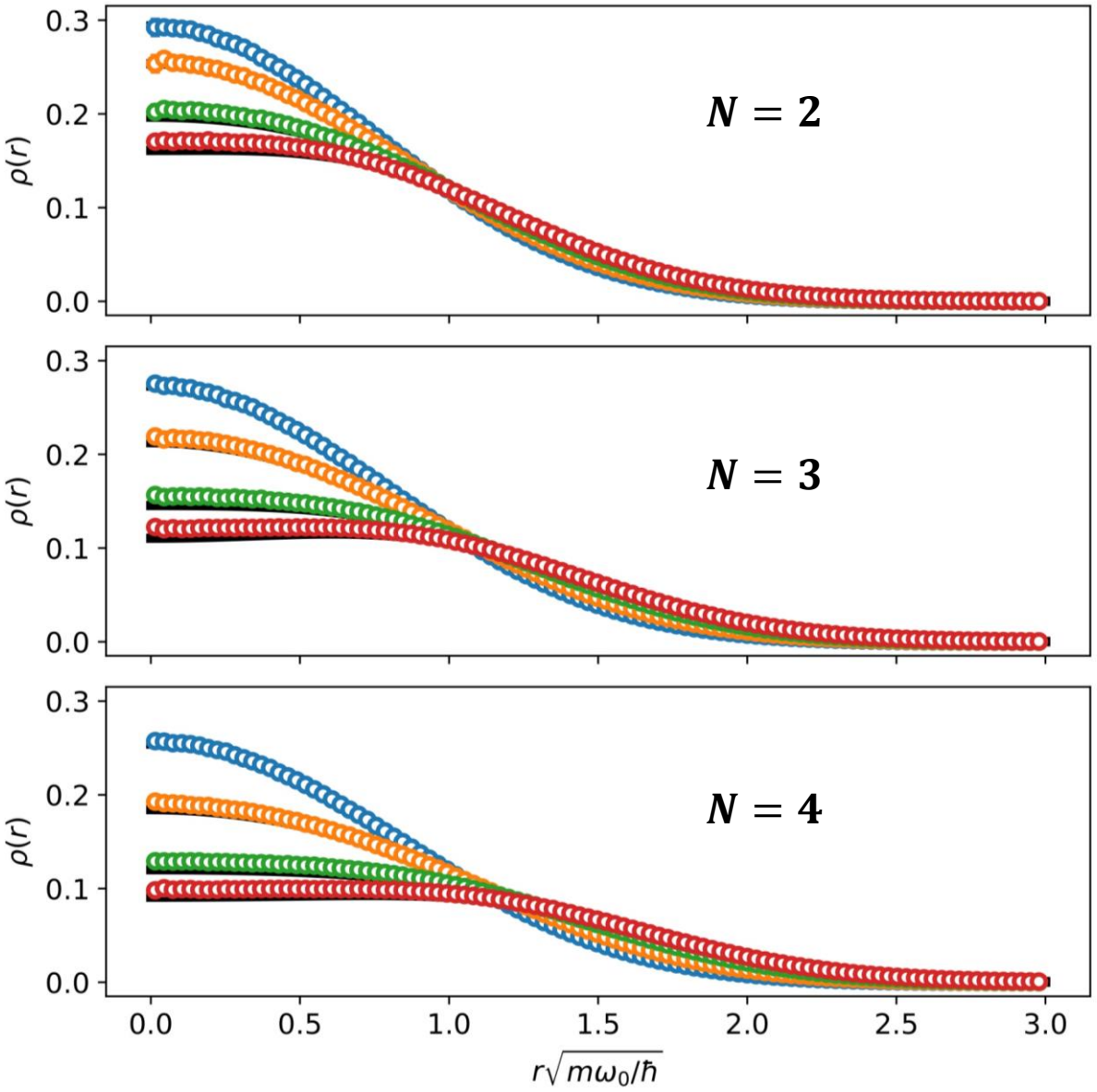
Benchmarking: Interacting particles in 2D trap

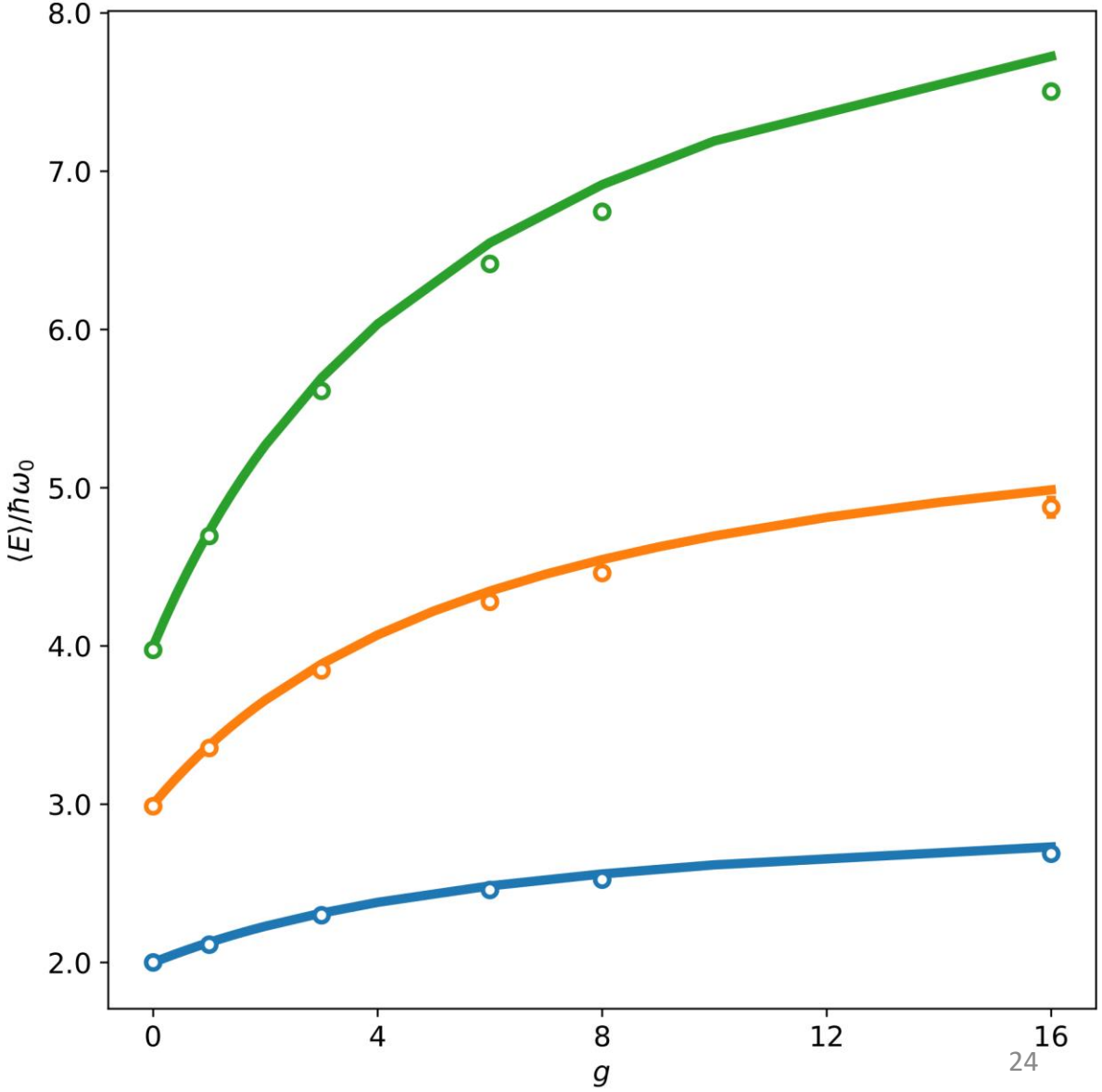
- **Comparison to exact diagonalization by P. Mujal *et al.* Phys. Rev. A 96, 043614 (2017)**
- **Interacting Bosons in a 2D trap, repulsive Gaussian potential**

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

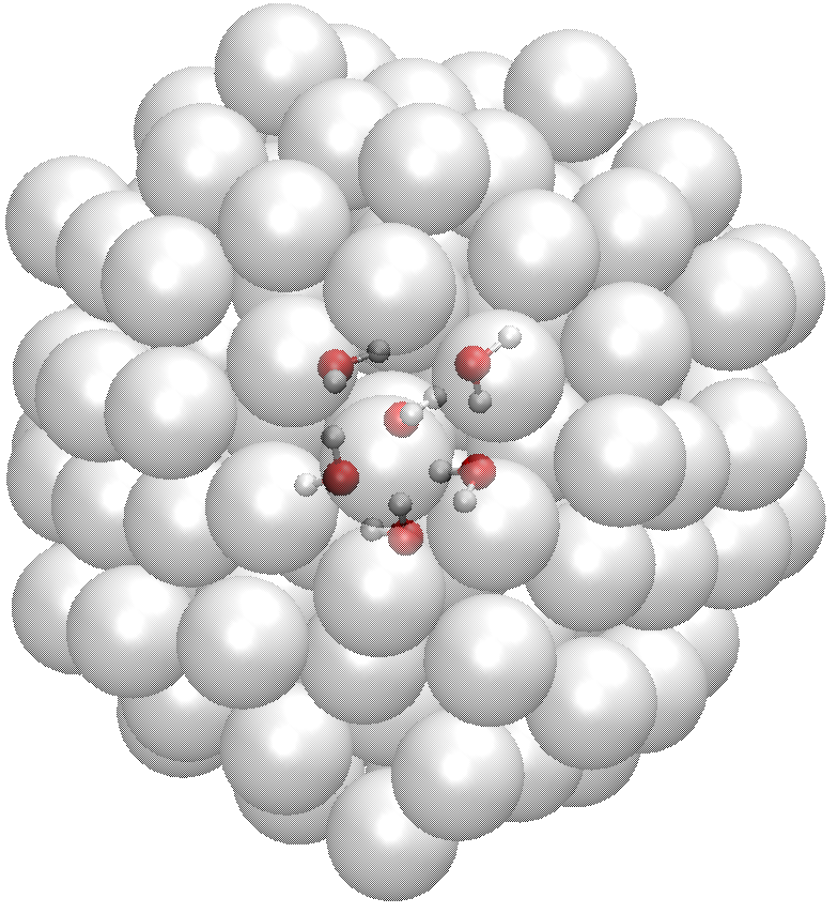
- $g = 0 \rightarrow$ ***non-interacting,*** $g = 16 \rightarrow$ ***strong repulsion***

Density and Energy $N = 2 - 4$





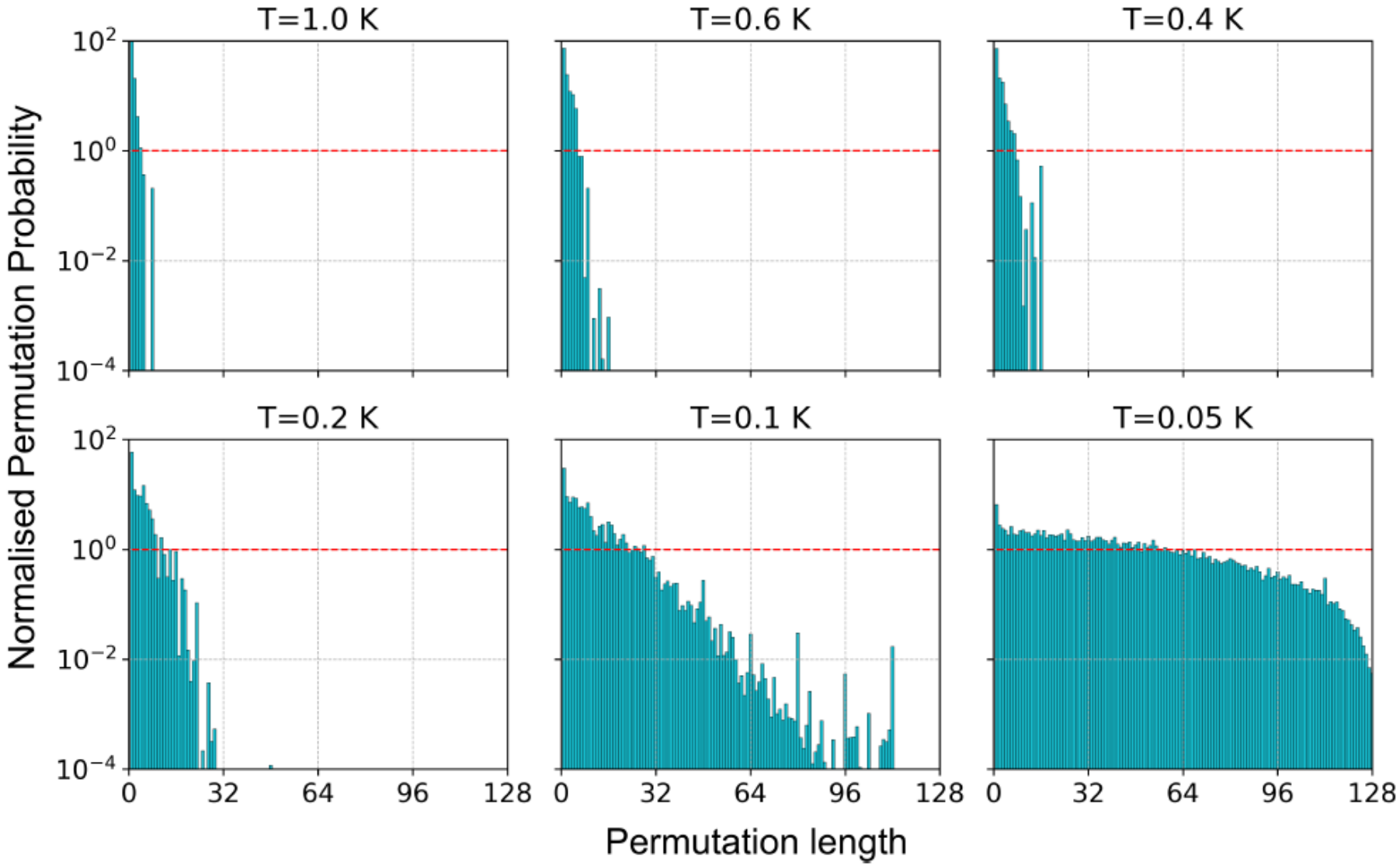
Larger systems – superfluid He droplets

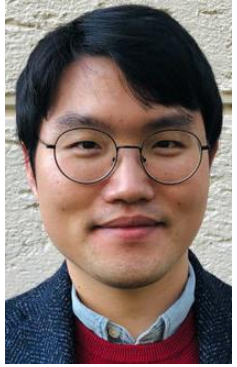


256 atoms, CC level PES, collaboration with Paesani group UCSD

Evidence of superfluidity in solid D!

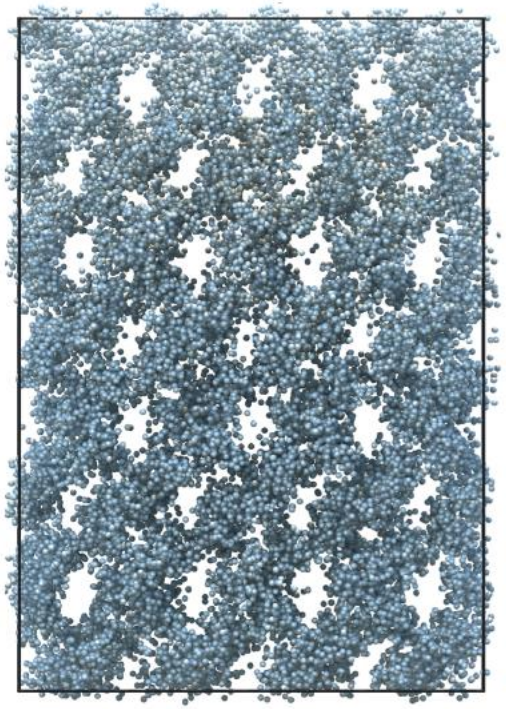
C.W. Myung, B. Hirshberg and M. Parrinello (2021) arXiv:2103.13974





Dr. C.W. Myung

Indistinguishable quantum particle



Part II: Fermions

Direct Sampling of Fermions is not feasible

$$W_F^{(N)}(R_1,\dots,R_N)=\frac{1}{N}\sum_{k=1}^{N}(-1)^{k-1}e^{-\beta E_N^{(k)}(R_{N-k+1},\dots,R_N)}W_F^{(N-k)}(R_1,\dots,R_{N-k})$$

$$V_F^{(N)}(R_1,\dots,R_N)=-\frac{1}{\beta}\ln W_F^{(N)}(R_1,\dots,R_N);\ \ V_F^{(0)}=0$$

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

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

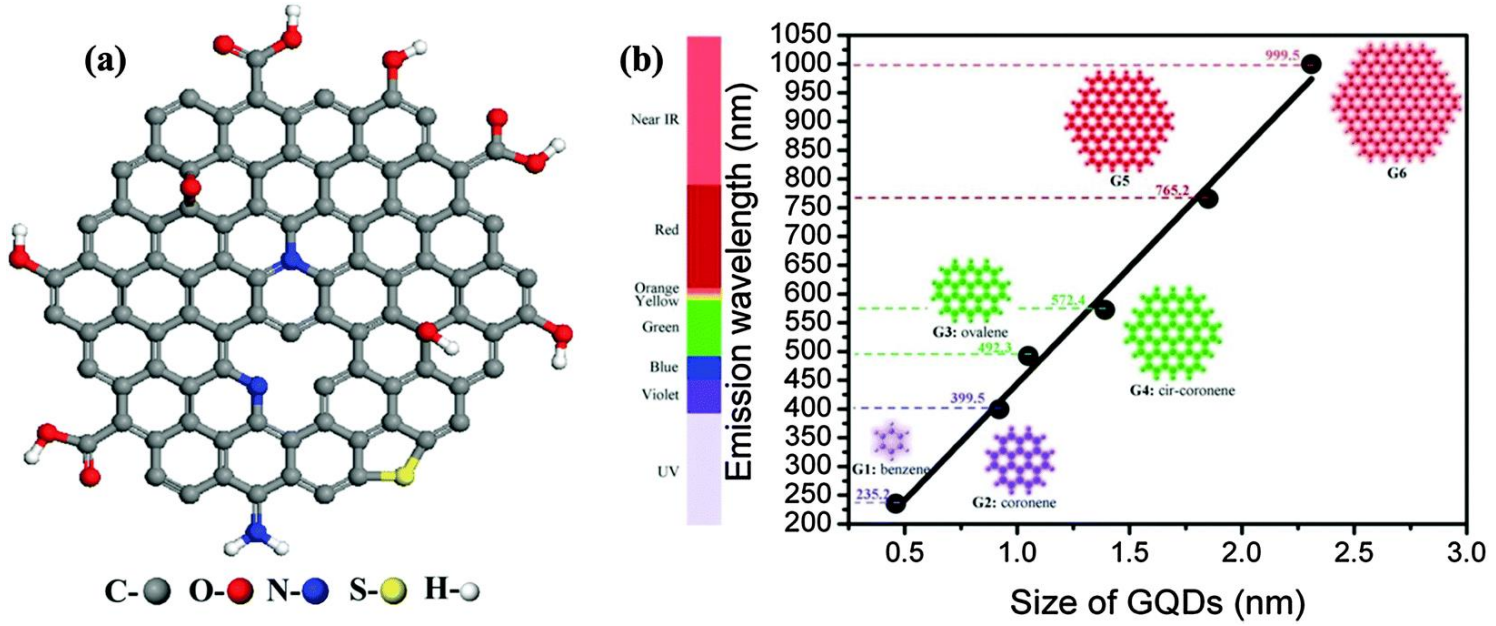
Sample Bosons and Reweight

$$\langle O \rangle_F = \frac{\left\langle O W_F^{(N)} e^{\beta V_B^{(N)}} \right\rangle_B}{\left\langle W_F^{(N)} e^{\beta V_B^{(N)}} \right\rangle_B}$$

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

Applications

- **Electrons in 2D quantum dots (P. Chen *et al.* Chem. Soc. Rev., 2016)**



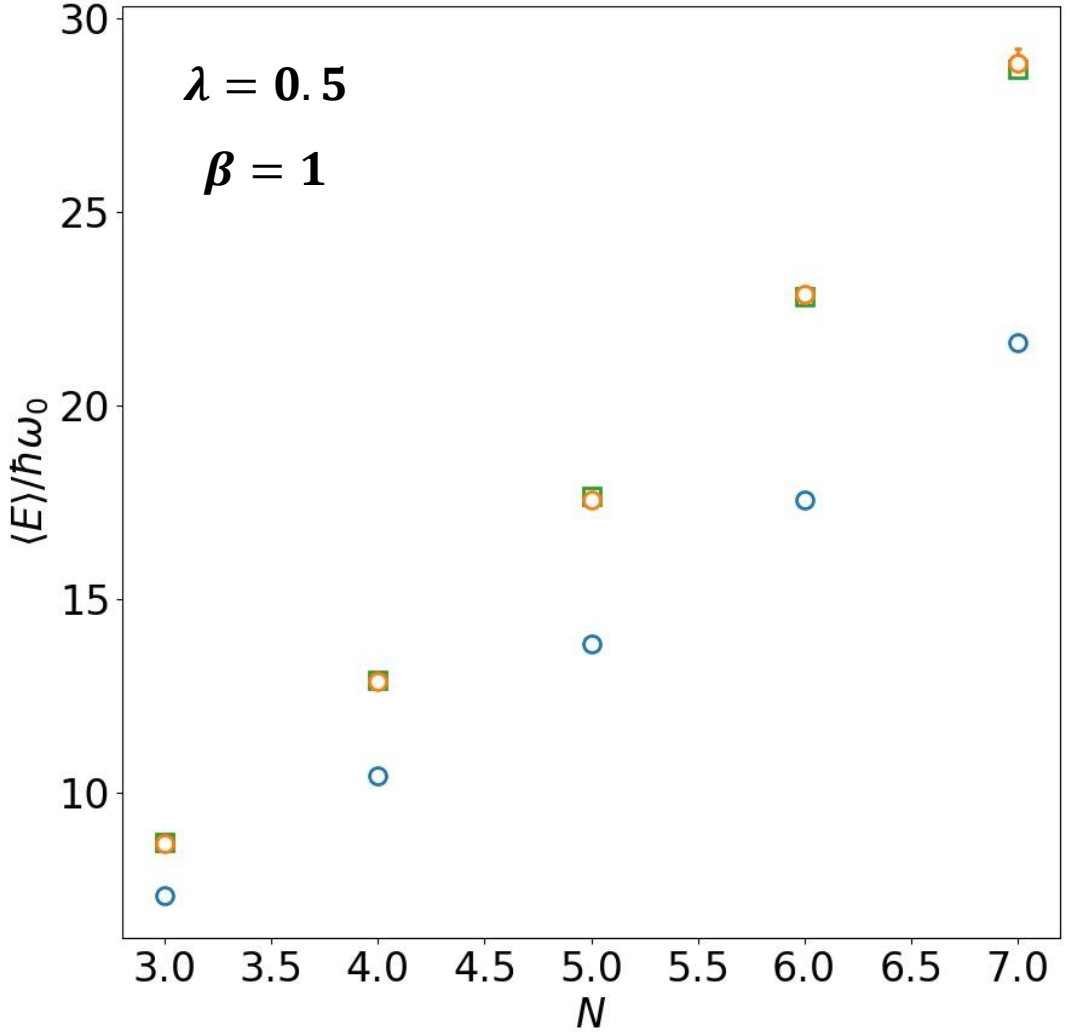
$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{i=1}^{N}\boldsymbol{r}_i^2 + \sum_{i,j>i}^{N}\frac{\lambda}{|\boldsymbol{r}_i - \boldsymbol{r}_j|};\quad \lambda \equiv \frac{e^2}{k l_0 \hbar\omega_0};\quad l_0 \equiv \sqrt{\frac{\hbar}{m\omega_0}}$$

- $\lambda \ll 1$ **– Exchange dominates**
- **Large λ – Coulomb repulsion dominates**

N=3-7 electrons in QD

PIMC: Dornheim, T. *Phys. Rev. E*, (2019) 100, 023307

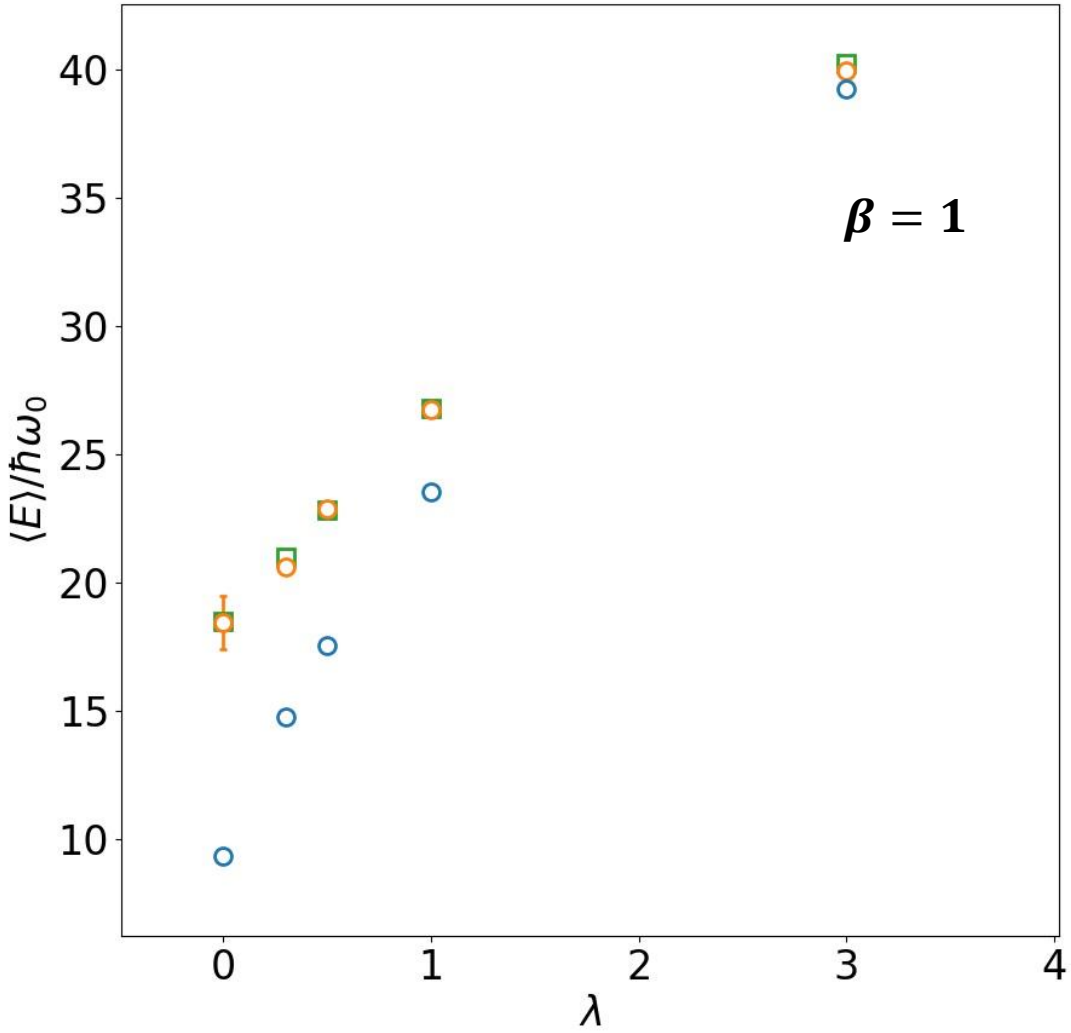
- **Green: PIMC; Orange: PIMD-F; Blue: PIMD-B**

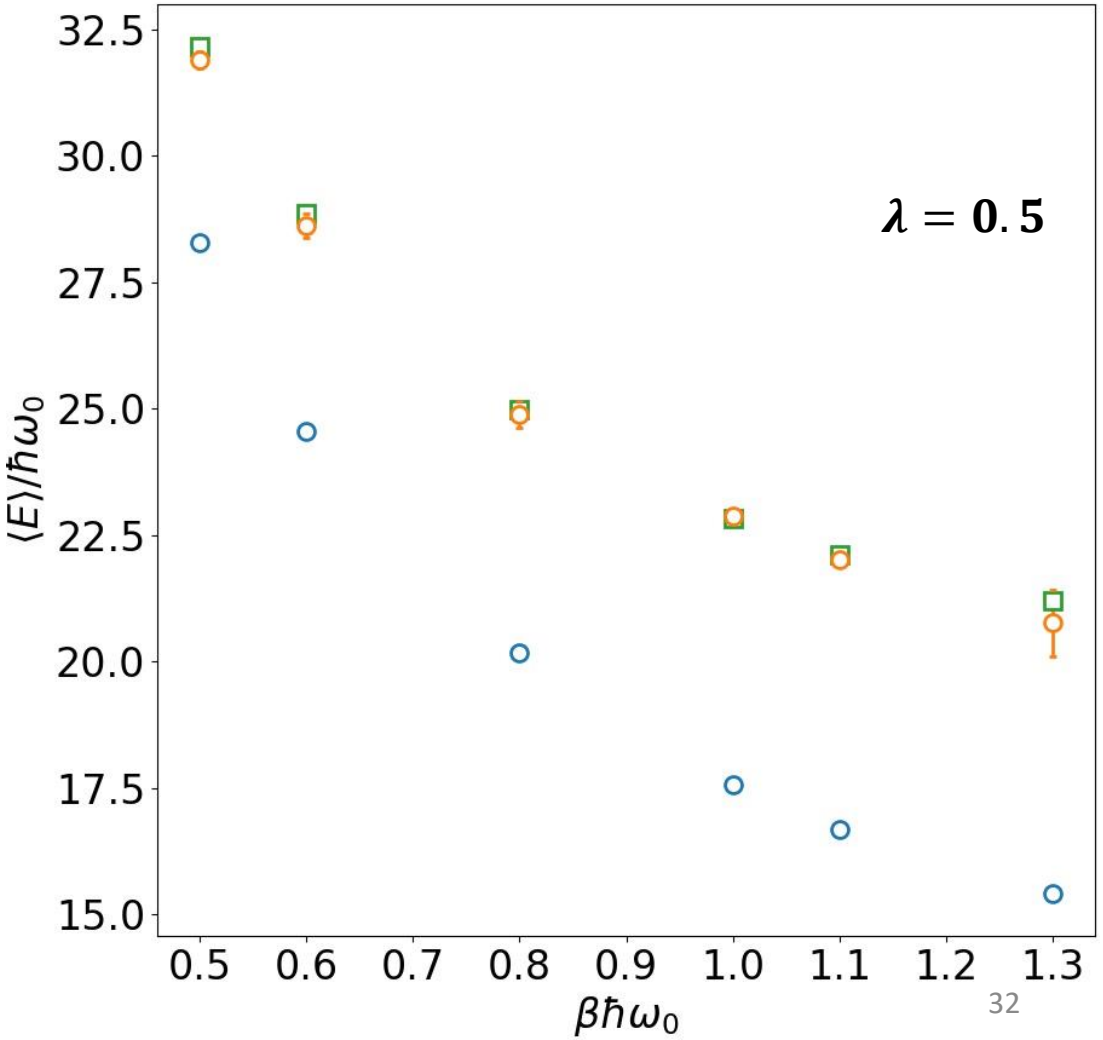


N=6 electrons in QD

PIMC: Dornheim, T. *Phys. Rev. E*, (2019) 100, 023307

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





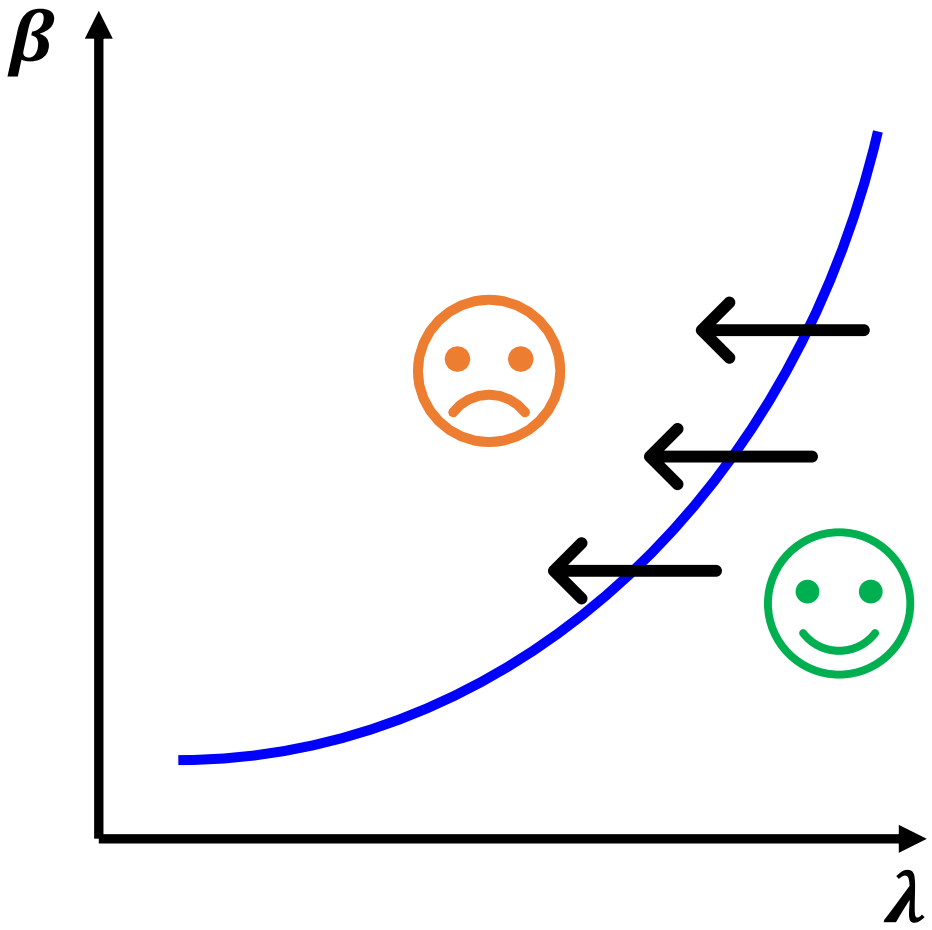
The fermion sign problem

$$\langle O \rangle_F = \frac{\left\langle O W_F^{(N)} e^{\beta V_B^{(N)}} \right\rangle_B}{\left\langle W_F^{(N)} e^{\beta V_B^{(N)}} \right\rangle_B}; \quad \left\langle W_F^{(N)} e^{\beta V_B^{(N)}} \right\rangle_B \sim e^{-\beta N \Delta F}$$

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

Alleviating the fermion sign problem

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



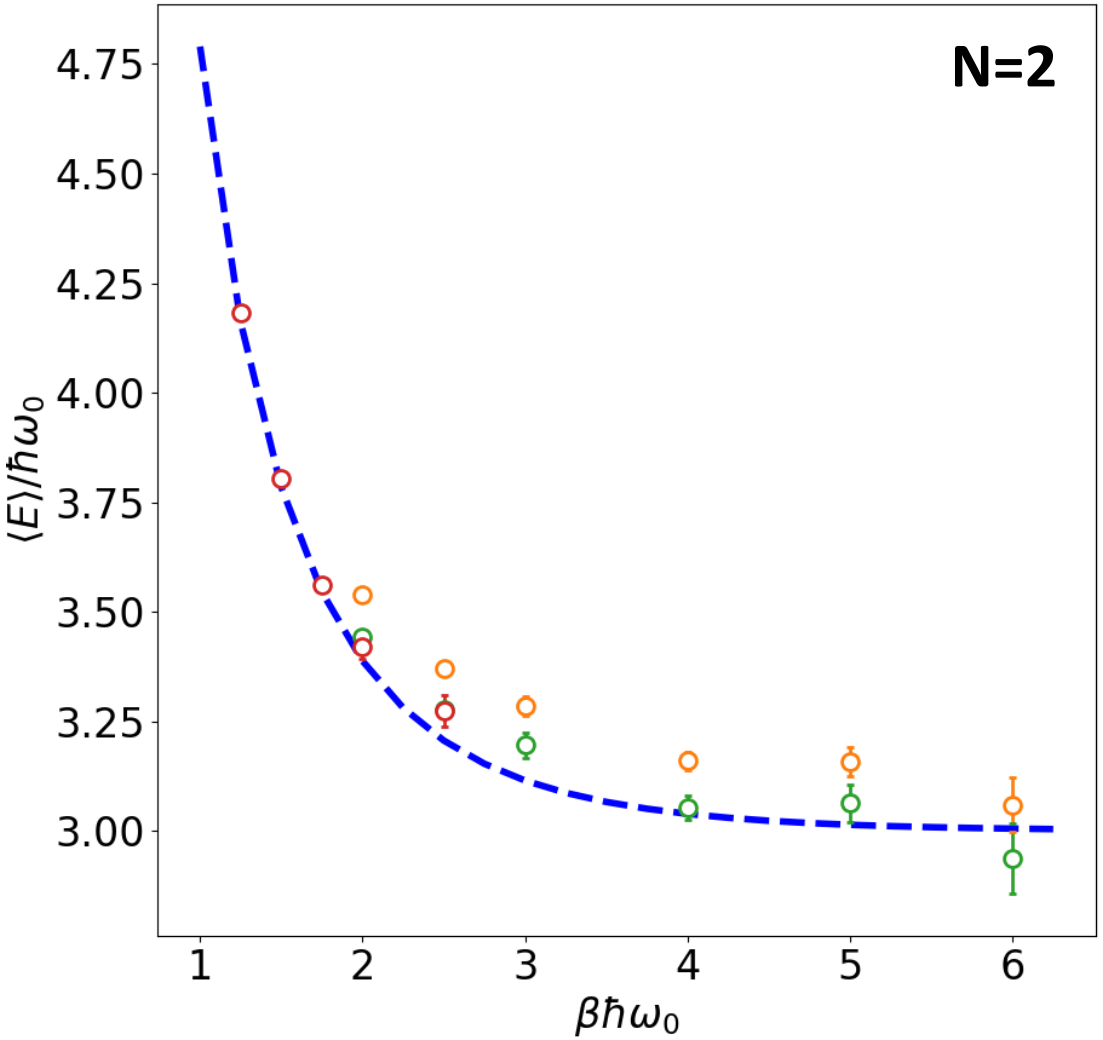
- Simulate systems with stronger repulsion
- Correct the results using a variational principle for the free energy

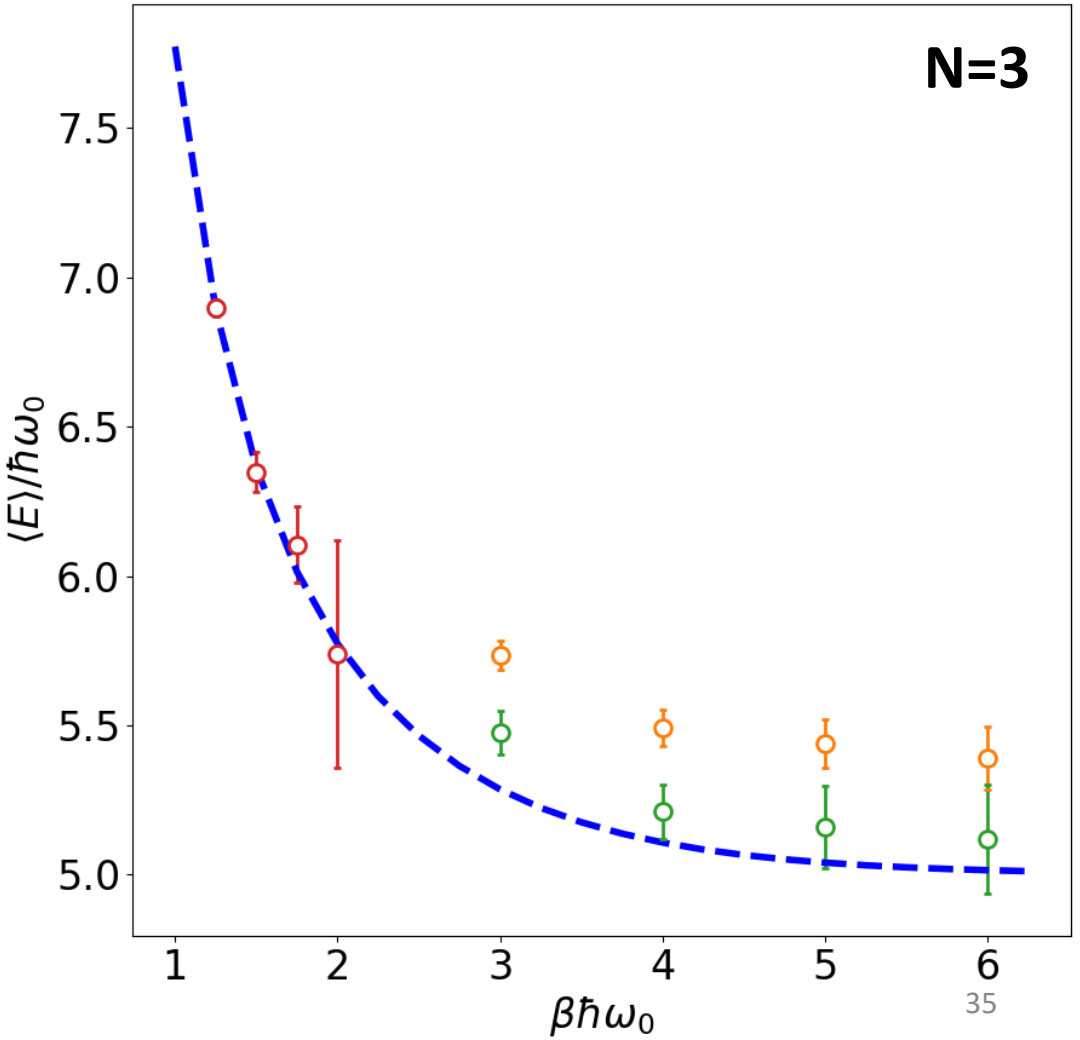
$$F_{H_0} \leq F_H + \langle H_0 - H \rangle_H$$

- More recently: thermodynamic integration (w/ T. Dornheim)

Non-interacting Fermions

- **Gaussian repulsion with $g = 16$ and $\sigma = 0.5$**





Conclusions

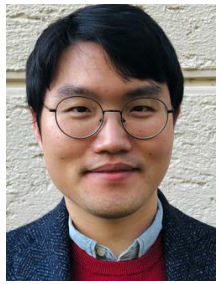
PNAS (2019) 116, 21445-21449, JCP (2020) 152, 171102, JCP (2020) 153, 234104

- **A new PIMD method for indistinguishable particles**
- **Recursive evaluation of forces without enumerating permutations**
- **Reduced computational cost from exponential to $\sim N^3$**
- **We can apply PIMD-B to obtain results for fermions**
- **Alleviating the sign problem using enhanced sampling**

J. Runeson, M. Nava, and M. Parrinello, PRL (2018) 121, 140602

Thank you!

M. Parrinello



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