Quantum Symmetry from Enhanced Sampling

A First Exploration

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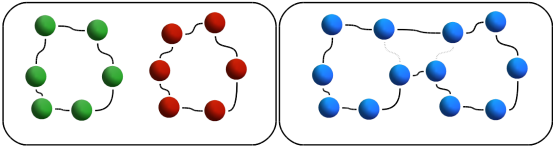


Outline of the talk

- Contextualization: Fermions at finite Temperature
- Path Integral Molecular Dynamics
- Reweighted Sampling
- Enhanced Sampling with Metadynamics
- Results for non-interacting systems and hard spheres
- Application to Quantum Dots
- Perspectives and Conclusions

Simulating Fermions at Finite Temperature (and continuous coordinates)

- Use the Feynman Path Integral formulation of Statistical Mechanics

$$\mathcal{Z} = \int \mathcal{D}[x(t)] \mathrm{e}^{i \int_0^{\hbar\beta} dt \frac{L(x,\dot{x})}{\hbar}}$$

  - Sample closed paths in imaginary time.
  - Distribution of the paths from a product of density matrices.
- Fermi symmetry: $\Psi\left(\ldots,\vec{r}_i,\ldots\vec{r}_j,\ldots\right) = -\Psi\left(\ldots,\vec{r}_j,\ldots\vec{r}_i,\ldots\right)$
- Inherited by the density matrix: nontrivial nodal surface
- Sign problem: cancellation errors from $+$ and $-$ subdomains:
  $\rightarrow$ signal-to-noise ratio decays exponentially with degrees of freedom.

Way around: go to $T = 0K$

- If quantum symmetry is important we are likely deep in the quantum regime:
  $\rightarrow$ assume the ground state is largely the most populated.
- Easier to deal with the sign problem:
  - Use a trial wave function and assume nodal surface: fixed node approximation
  - Allow the nodes of the trial wave function to relax: release node methods
  - Diffusion on other basis representations
  - Use imaginary-time correlation functions
  - ...

Another way around: Hamiltonian diagonalization

- Represent the Hamiltonian on a finite basis set
  - Coupled Cluster: Slater Determinants
  - System dependent
- Diagonalize and use eigenstates/eigenenergies to make the density matrix
- Limited to very small systems and still approximate

Remaining at finite Temperature

- Using Path Integral Monte Carlo:
  - Antisymmetrize (and truncate) permutation sampling
  - Antisymmetrize propagator (and use importance sampling)
  - Restricted path approximation of the nodes
- Weighted sampling: simulate distinguishable particles and consider the effect of quantum symmetry through a weight factor W.
  - Exact in principle, easy in implementation
  - W very hard to deal with, even for two particles
  - Not easy to obtain non-local estimators
  - Can be implemented in Path Integral Molecular Dynamics

Feynman's Path Integral

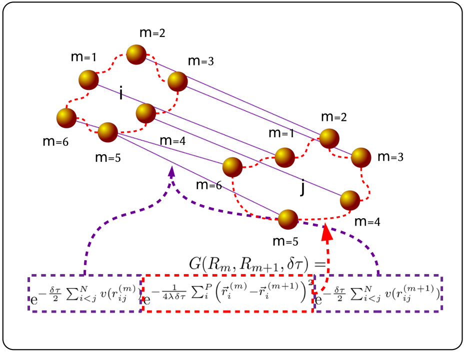
Thermal average of a property at $\beta = \frac{1}{k_B T}$:
$< \hat{O} >= \frac{1}{\mathcal{Z}} \mathrm{Tr}[\hat{\rho}\hat{O}]$, with the density matrix $\hat{\rho} = e^{-\beta \hat{H}}$.

- $\mathcal{Z} = \int dR \ < R|e^{-\beta \hat{H}}|R >$
- $< \hat{O} >= \frac{1}{\mathcal{Z}} \int dR \ O(R) < R|e^{-\beta \hat{H}}|R >$ ($\hat{O}$ diagonal on R for simplicity)
- $\rightarrow < \hat{O} >= \int dR \ p(R) O(R)$, p is a multi-dimensional probability density.
- Monte carlo: $< \hat{O} >= \lim_{M \rightarrow +\infty} \frac{1}{M} \sum_i^M O(R_i)$, R_i sampled from $p(R)$.
- We use the Primitive Approximation: $e^{-\beta \hat{H}} = e^{-\beta \hat{T}} \cdot e^{-\beta \hat{V}} + O(\beta^2)$
- Small β approx.:
  $G(R_1, R_2, \beta) \simeq \frac{1}{\Gamma} e^{-\frac{\beta}{2} \sum_{i<j} v(r_{ij}^{(1)})} e^{-\sum_i \frac{1}{4\lambda_i \beta} \left(\vec{r}_i^{(1)} - \vec{r}_i^{(2)}\right)^2} e^{-\frac{\beta}{2} \sum_{i<j} v(r_{ij}^{(2)})}$

Quantum-Classical isomorphism

How do we express a large β Green's function?

- Convolution property: $G(R_1, R_2, \beta_1 + \beta_2) = \int dR_m\, G(R_1, R_m, \beta_1) G(R_m, R_2, \beta_2)$
- $p(R_1) = \frac{1}{\mathcal{Z}} \int \prod_{m=2}^{P} dR_m\, G(R_1, R_2, \delta\tau = \frac{\beta}{P}) \cdots G(R_m, R_{m+1}, \delta\tau) \cdots G(R_P, R_1, \delta\tau)$



$\prod_{m=1}^{P} G(R_m, R_{m+1}, \delta\tau), \quad R_{P+1} \equiv R_1$

is the probability distribution of a system of special interacting closed polymers composed of P beads.

The classical Lagrangian used for sampling

$$\mathcal{Z} = \int \prod_{m=1}^{P} dR_m \; G(R_1, R_2, \delta\tau) \cdots G(R_m, R_{m+1}, \delta\tau) \cdots G(R_P, R_1, \delta\tau)$$

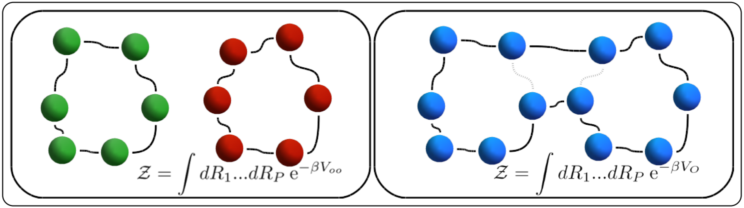
PIMD: $\mathcal{Z}$ is also the configurational part of the partition function of the *classical* system of polymers: to sample $p(R_m)$, PIMD uses Molecular Dynamics in the canonical ensemble at inverse temperature β.

$$\mathcal{Z} = \int dR_1 ... dR_P \; e^{-\beta\left[\cdots \frac{1}{2P}\sum_{i<j} v\left(r_{ij}^{(m)}\right) + \sum_{i=1}^{N} \frac{P}{4\lambda\beta^2}\left(\vec{r}_i^{(m)} - \vec{r}_i^{(m+1)}\right)^2 + \frac{1}{2P}\sum_{i<j} v\left(r_{ij}^{(m+1)}\right)\cdots\right]}$$

Equipping each bead with a fictitous mass M_i and momenta $\vec{p}_i^{(m)}$ one gets the classical Lagrangian for the beads

$$\mathcal{L} = \sum_{i,m}\left\{\frac{\left(\vec{p}_i^{(m)}\right)^2}{2M_i} - \frac{1}{2P}\sum_{j\neq i} v(r_{ij}^{(m)}) - \frac{P}{4\lambda_i\beta^2}\left(\vec{r}_i^{(m)} - \vec{r}_i^{(m+1)}\right)^2\right\}$$

Quantum Symmetry for two particles

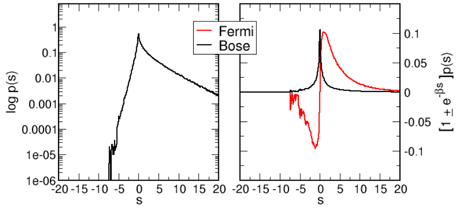


- Two possible permutations at each bead
- Reconnect two kinetic springs
- For fermions V_O configurations carry a minus sign
- (anti)symmetrized propagator: $\mathcal{Z} = \Gamma \int dR_1 ... dR_P \, \left(e^{-\beta V_{oo}} \pm e^{-\beta V_O}\right)$

- Factorize out $e^{-\beta V_{oo}}$: $\mathcal{Z} = \Gamma \int dR_1 ... dR_P e^{-\beta V_{oo}} W$
- Simulation of distinguishable particles, W contains the effect of the exchanges
- $W = 1 \pm e^{-s} \qquad s = \frac{P^2}{2\lambda\delta\tau} \left(\vec{r}_{1,j} - \vec{r}_{2,j}\right) \left(\vec{r}_{1,j+1} - \vec{r}_{2,j+1}\right)$

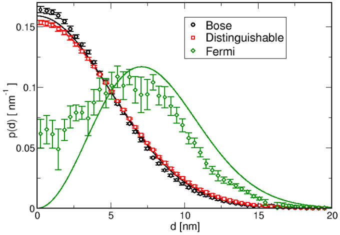
Two ideal 1D particles in a harmonic potential ($T = 1$K)

- The negative domain is poorly sampled.
- Energy difference is also poorly sampled.
- For Bosons results affected only marginally: most of the statistical weight is elsewhere.
- Fermions: negative tail of $p(s)$ is important.



Pair distribution function

- Slightly inaccurate for Bosons
- Extreme noise for Fermions



Metadynamics

- Hamiltonian becomes "time" dependent: $H \to H + V_b(s(t), t)$
- V_b increases the energy of the visited configurations ...
- ... these configurations are identified with one (or more) collective variable s

Algorithm in a nutshell

While the simulation is running...

→ Compute the instantaneous value of s, say $s = s_i$

→ Add a gaussian to V_b: $V_b \to V_b + w_t e^{-\frac{(s-s_i)^2}{2\sigma^2}}$

→ After some simulation time τ_g repeat.

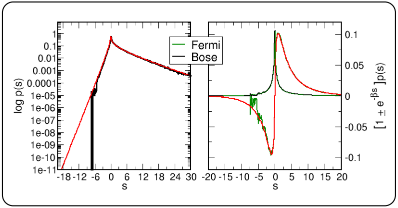
(Credit: Giovanni Bussi)

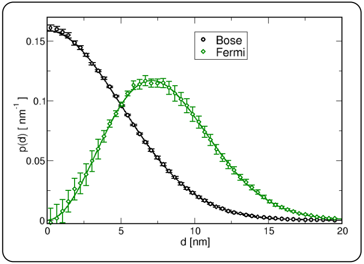
In Well-Tempered Metadynamics w_t is monotonically decreasing and history dependent: V_b converges asymptotically [PRL 112, 240602 (2014)]

V_b is accounted for through reweighting [J. Phys. Chem. B 119, 736 (2015)]

Two ideal 1D particles again...

- Now sampling a broader region
- Cancellation errors under control

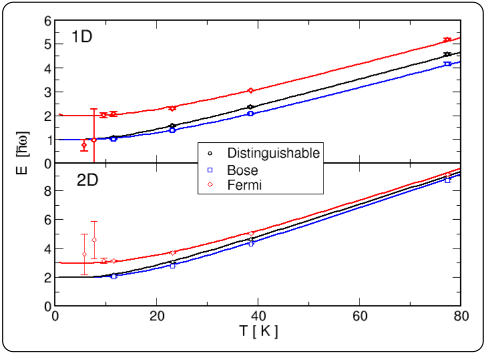


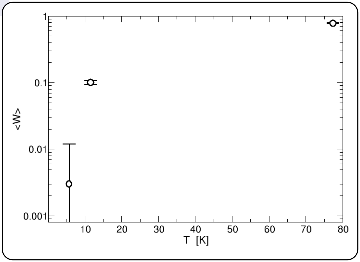


- Pauli "repulsion" for Fermions
- Bosons: it's the $T = 0$ distribution: reminiscent of condensation

The energies...

- Can be obtained from s as $E_{b(f)} - E_d$
- Follow the theoretical curves but...
- ... become hard to compute in the $T = 0$K regime.

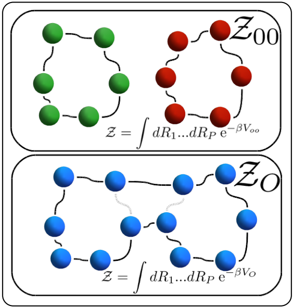




$$\langle \hat{O} \rangle = \frac{\langle W \hat{O} \rangle}{\langle W \rangle}$$

- Energy at low T can be obtained with the Bennett's method
- From the free energy difference (FED) of two systems:

$$\frac{\mathcal{Z}_{O}}{\mathcal{Z}_{OO}} = \frac{\left\langle f_w e^{-V_{OO}} \right\rangle_{O}}{\left\langle f_w e^{-V_{O}} \right\rangle_{OO}}$$



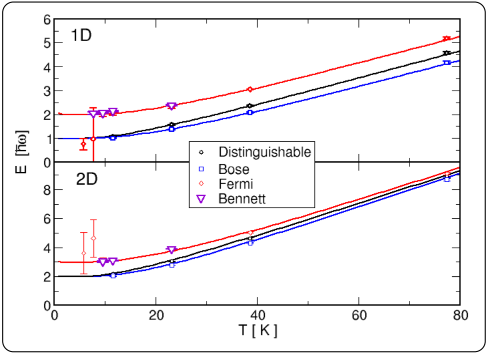
- Fermi partition function $\mathcal{Z}_F$: $\frac{\mathcal{Z}_F}{\mathcal{Z}_B} = \frac{\left(1 - \frac{\mathcal{Z}_O}{\mathcal{Z}_{OO}}\right)}{\left(1 + \frac{\mathcal{Z}_O}{\mathcal{Z}_{OO}}\right)}$

  (because $\mathcal{Z}_{B(F)} = \frac{\mathcal{Z}_{OO} \pm \mathcal{Z}_O}{2}$)

- FED between Fermi and Bose systems $-\frac{1}{\beta} \log \frac{\mathcal{Z}_F}{\mathcal{Z}_B}$
- Assumption: at low T, FED $\simeq$ ED

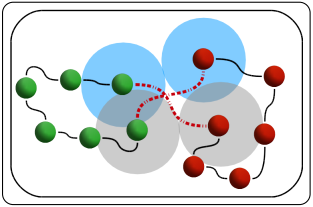
Energy vs Temperature for two ideal particles

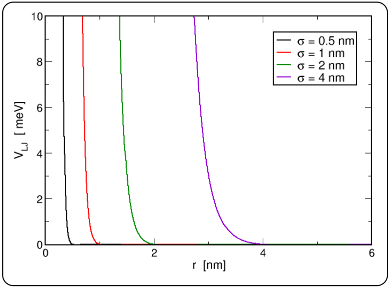
- Can get the FED between Fermi and Distinguishable (or Bose) states
- At low T is also good approximation for the energy difference



The interparticle interaction

- With interaction: $< W >$ further away from 0
- Core repulsion suppresses exchanges
- Connecting springs are more stretched
  $\rightarrow$ correspond to higher energy differences



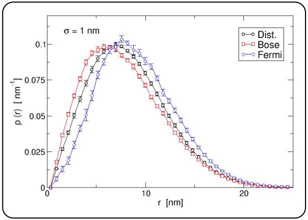


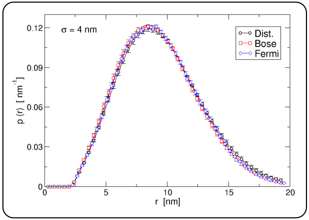
Example...

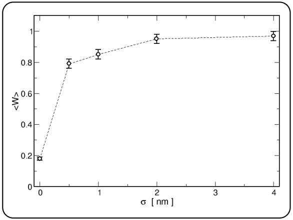
- Two Lennard-Jones particles in a well
- Different core "sizes" σ

The interparticle interaction

- High σ: distinguishable limit.







- Average weight rapidly deviates from the noninteracting limit ($\sigma = 0$)
- $< W >= 1$: no quantum symmetry effects in any sampled configuration.
- For $\sigma = 4$ nm, $\langle W \rangle = 0.97$

The model

- Two electrons in a 2D harmonic potential

$$\hat{H} = \hat{T} + \hat{V}_{coul} + \hat{U}$$

- External potential $\hat{U}$: elongation $\frac{\omega_x}{\omega_y}$ depends on the nature of the confinement

$$\hat{U} = \frac{1}{2} m^\star \left(\omega_x^2 x^2 + \omega_y^2 y^2\right)$$

- Coulomb potential $\hat{V}_{coul} = \frac{\gamma e^2}{k r_{12}}$
  - k and m^* are the dielectric constant and the effective mass
  - γ: correction parameter for finite size of z direction

- Wigner parameter R_W: ratio of typical Coulomb interaction strength and single-particle energy level splitting
  $\rightarrow$ at high R_W: interaction dominated

- Experimental and theoretical data available in literature

The two electrons are in...

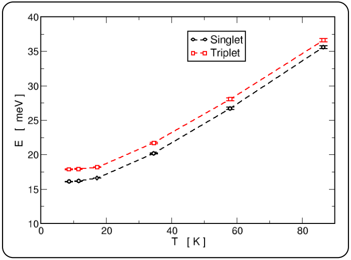
- Singlet: $\Psi_s(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\phi_B(\vec{r}_1,\vec{r}_2)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$
- Triplets: $\Psi_t(\vec{r}_1,\vec{r}_2) = \phi_F(\vec{r}_1,\vec{r}_2)\begin{pmatrix} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \end{pmatrix}$

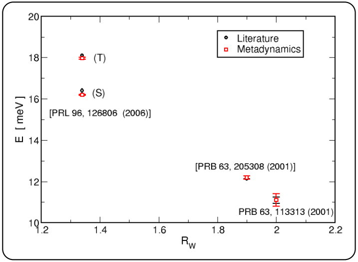
- ϕ_B and ϕ_F are symmetric and antisymmetric wavefunctions of "bosonic" and "fermionic" particles.
- Access to:
  - Structural properties of the triplet and singlet states.
  - Energy and Free energy differences between those states.

Results for the Quantum Dot

- R_W and $\frac{\omega_x}{\omega_y}$: different temperatures for transition to zero-temperature behavior

- Compare with literature: T in the zero T regime.

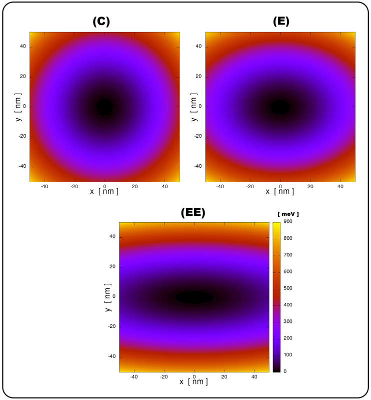




- Comparison with experiments and exact diagonalization

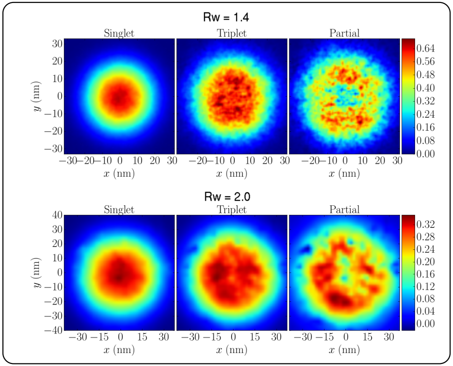
Results for the Quantum Dot

- Three confinements:
  - Circular (C): $r_W = 1.4$ and $\hbar\omega = 5.1 meV$
  - Elliptic (E): $r_W = 1.34$ and $\frac{\omega_x}{\omega_y} = 1.38$
  - More Elliptic (EE): $r_W = 1.4$ and $\frac{\omega_x}{\omega_y} = 3.0$



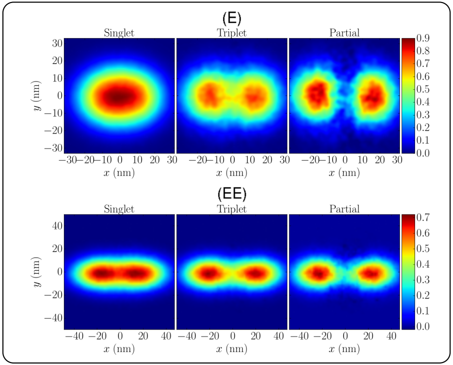
- Electron density $\rho(\vec{r})$
  - Singlet: $|\phi_1(\vec{r})|^2$
  - Triplet: $|\phi_1(\vec{r})|^2 + |\phi_2(\vec{r})|^2$
  - Partial contribution to triplet $\rho(\vec{r})$: $|\phi_2(\vec{r})|^2$
- Pair densities
- Breaking degeneracy of states:
  - Symmetry breaking in the density
  - Interplay between T and energy splitting between x and y levels

Results for the Quantum Dot



- Higher r_W: broader distributions due to larger repulsion
- $|\phi_1(\vec{r})|^2$ depletion at $(0,0)$ ("p-like" orbital)
- The circular symmetry of ϕ_1 is challenging

Results for the Quantum Dot



- Singlet state on (EE): peaked density, "solid" like
- ϕ_1 circular symmetry broken discontinously (but can be different if T is higher)

Add an external magnetic field H ?

- Primitive approx. for non-interacting particles in a magnetic field:

$$G(R_1, R_2; H_z) = \Gamma e^{-\gamma_1 Z_{12}^2} e^{-\gamma_2 R_{12}^2} e^{\frac{im\omega}{\hbar}(y_1+y_2)(x_1-x_2)}$$

- Hard to treat imaginary phase
- Can apply the same weighted sampling approach but...
  - s acquires an imaginary part $\propto (x_{2,j} - x_{1,j})(y_{1,j+1} - y_{2,j+1}) + (x_{1,j+1} - x_{2,j+1})(y_{1,j} - y_{2,j})$
  - An additional sign function in the reweighting for the imaginary phase
- Metadynamics on a complex CV ?
- Steered sampling on the real axis ?

Beyond two particles...

- The Singlet/Triplet approach can be extended only in part:
  - i.e. "maximal" spin projection states are totally antisymmetryc
  - Generally for N, spins states may have not defined symmetry
- Generalization: method for spinless Bose/Fermi particles
- Considering all the permutation families:

  for $N = 3$: $e^{-\beta V_{ooo}} \left(1 \pm 3e^{-\beta \frac{V_{Oo}}{V_{ooo}}} + e^{-\beta \frac{V_{O}}{V_{ooo}}}\right)$
- Enhancing the sampling becomes increasingly harder...

- For $N = 3$ particles there are different choices for the CV s:
  - Consider only the problematic $-$ term: $s = \beta(E_{\mathbf{O}\mathbf{o}} - E_{\mathbf{ooo}})$
  - Use the log of everything with a regularization term:
    $s = \log\left(\left|1 \pm 3e^{-\beta(E_{\mathbf{O}\mathbf{o}} - E_{\mathbf{ooo}})} + e^{-\beta(E_{\mathbf{O}} - E_{\mathbf{ooo}})}\right| + \eta\right)$
- For higher N: approximate by neglecting infrequent exchange patterns
- Resort to Replica Exchange methods

- A proof of principle:
  - Non-interacting: where the exchanges are "worse"
  - Hard-spheres: a test for the handling of the interaction
  - Quantum Dot: a comparison with other methods/experiments
- Explore the idea: can we use free energy methods to get the effects of quantum exchanges?
- Free energy difference between Bosonic and Fermionic states