Quantum Monte Carlo simulations of solid ^{4}He at zero temperature

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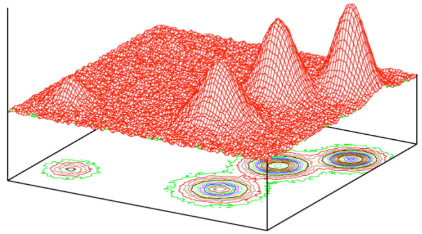
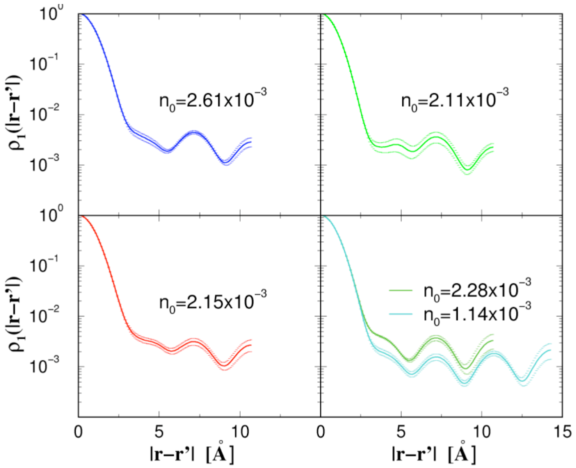
Sede centrale: facciata lungo largo Richini

Sede centrale: cortile del Richini





Coworkers:

L. Reatto

M. Rossi (PhD student)

Summary of my studies on solid ^{4}He:

- Full optimization of Shadow Wave Function (SWF)
  (Moroni, Galli, Fantoni, Reatto, Phys.Rev.B 58, 1998)
- Microscopic computation of BEC induced by a finite concentration of vacancies in solid ^{4}He (SWF)
  (Galli, Reatto, J. Low. Temp. Phys. 124, 2001)
- New exact projector Quantum Monte Carlo method:
  the Shadow Path Integral ground state (SPIGS)
  (Galli, Reatto, Mol. Phys. 101, 2003)
- Vacancy excitation spectrum in solid ^{4}He (SWF), longitudinal phonons (SWF), extra-vacancy formation energy (SPIGS)
  (Galli, Reatto, Phys. Rev. Lett. 90, 2003; J. Low. Temp. Phys. 124, 2004)

- BEC in commensurate solid ^{4}He (SWF)
  (Galli, Rossi, Reatto, Phys. Rev. B 71, 2005)
- Study of ^{4}He confined in a narrow pore (SWF)
  (Rossi, Galli, Reatto, Phys. Rev. B 72, 2005)
- Transverse phonons in bcc solid ^{4}He (SWF)
  (Mazzi, Galli, Reatto, proceedings LT24)
- Critical discussion on the nature of the ground state of solid ^{4}He (commensurate/incommensurate) and BEC in incommensurate solid ^{4}He (SPIGS) (Galli, Reatto, cond-mat/0602055)

Is the ground state of bulk solid ^{4}He commensurate or incommensurate?

- Early theoretical works were based on the assumption of zero-point vacancies (Andreev and Lifshitz, JETP 93 1969; Chester, Phys.Rev.A 2 1970)
- If ground state vacancies are present this will have significant effects on low T behavior of solid ^{4}He

(phenomenological theory by P.W. Anderson, W.F. Brinkman, D.A. Huse, Science 310 2005)

- Naive answer: it is commensurate because computation of $\langle \Psi_0 | \hat{H} | \Psi_0 \rangle$ in presence of a vacancy (n° of particles 100-500) gives an energy which is higher of energy of perfect solid

Vacancy formation energy Δe_v at melting density (fixed density)

Method	lattice	1 vacancy
SPIGS SWF	hcp	15.7±0.8 15.6±0.6

$$\Delta e_v = \left[\varepsilon(N-1, V\tfrac{N-1}{N}) - \varepsilon(N,V) \right](N-1)$$

- This argument is not conclusive: the small size of the system and the periodic boundary conditions do not allow to explore all relevant configurations allowed by $\Psi_0(\vec{r}_1,..,\vec{r}_N)$ in a real large system

Variational theory of a quantum solid

- In the framework of variational theory of quantum solids the wave functions fall in two categories:

1. translational invariant Ψ, one example:

$$\Psi_J(\vec{r}_1,..,\vec{r}_N) = \prod_{i<j}^{N} f\left(\left|\vec{r}_i - \vec{r}_j\right|\right) \quad \text{(Jastrow)}$$

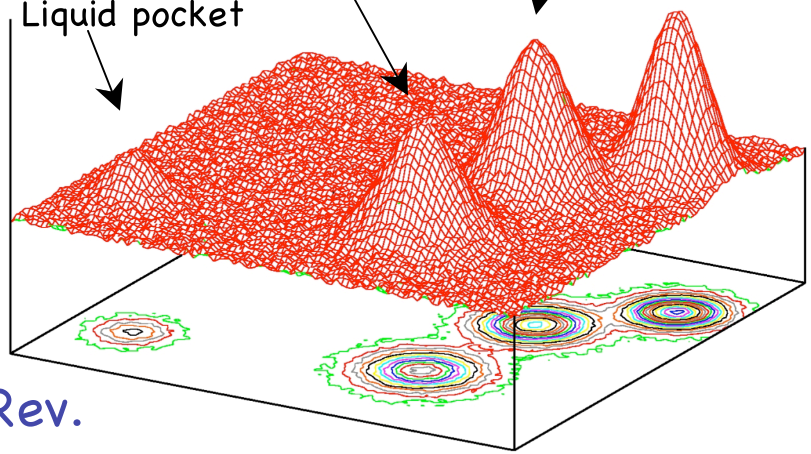
2. Ψ imposes the symmetry of the lattice localizing the atoms around the lattice sites $\{\vec{R}_i\}$

$$\Psi(\vec{r}_1,..,\vec{r}_N) = \Psi_J \times \prod_{i}^{N} e^{-C\left|\vec{r}_i - \vec{R}_i\right|^2}$$

(Jastrow+Nosanow)

- Example: Jastrow function: $\Psi_J(\vec{r}_1,...,\vec{r}_N) = \prod_{i<j}^{N} e^{-\frac{1}{2}u(r_{ij})} / Q_N^{1/2}$

Normalization constant $Q_N = \int d\vec{r}_1..d\vec{r}_N \prod_{i<j}^{N} e^{-u(r_{ij})}$



- Schematic landscape of probability distribution when density is large (similarity with probability in configuration space of suitable classical particles)
- Ψ_J has a finite BEC (Reatto, Phys.Rev. 183, 1969) and a finite concentration of vacancies
- For a Jastrow wf we know that overwhelming contribution to normalization Q_N comes from pockets with vacancies (finite concentration!): Hodgdon and Stillinger (1995) computed this vacancy concentration, unfortunately they used an unrealistic Ψ_J for solid ^{4}He
- Standard MC computation normalize Ψ_0 only in a single pocket, computed energy is biased by the choice of N and cell geometry

Our variational tool: Shadow Wave Function

Evolution of Vitiello, Runge and Kalos, Phys. Rev. Lett. 60, 1988

$$\Psi_{SWF}(R) = \phi_r(R) \times \int dS\, K(R,S) \times \phi_s(S)$$

Direct explicit Jastrow correlations (ϕ_r)

Indirect coupling via subsidiary (shadow) variables ($K(R,S)$, ϕ_s)

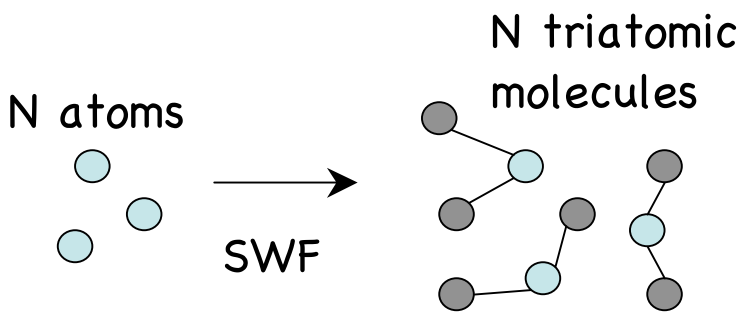
Particles coordinates: $R = \{\vec{r}_1,..,\vec{r}_N\}$

Shadow variables: $S = \{\vec{s}_1,..,\vec{s}_N\}$

Jastrow terms: $\phi_r(R), \quad \phi_s(S)$

$$K(R,S) = \prod_i^N e^{-C|\vec{r}_i - \vec{s}_i|^2}$$

Classical analogy of Ψ_{SWF}^2



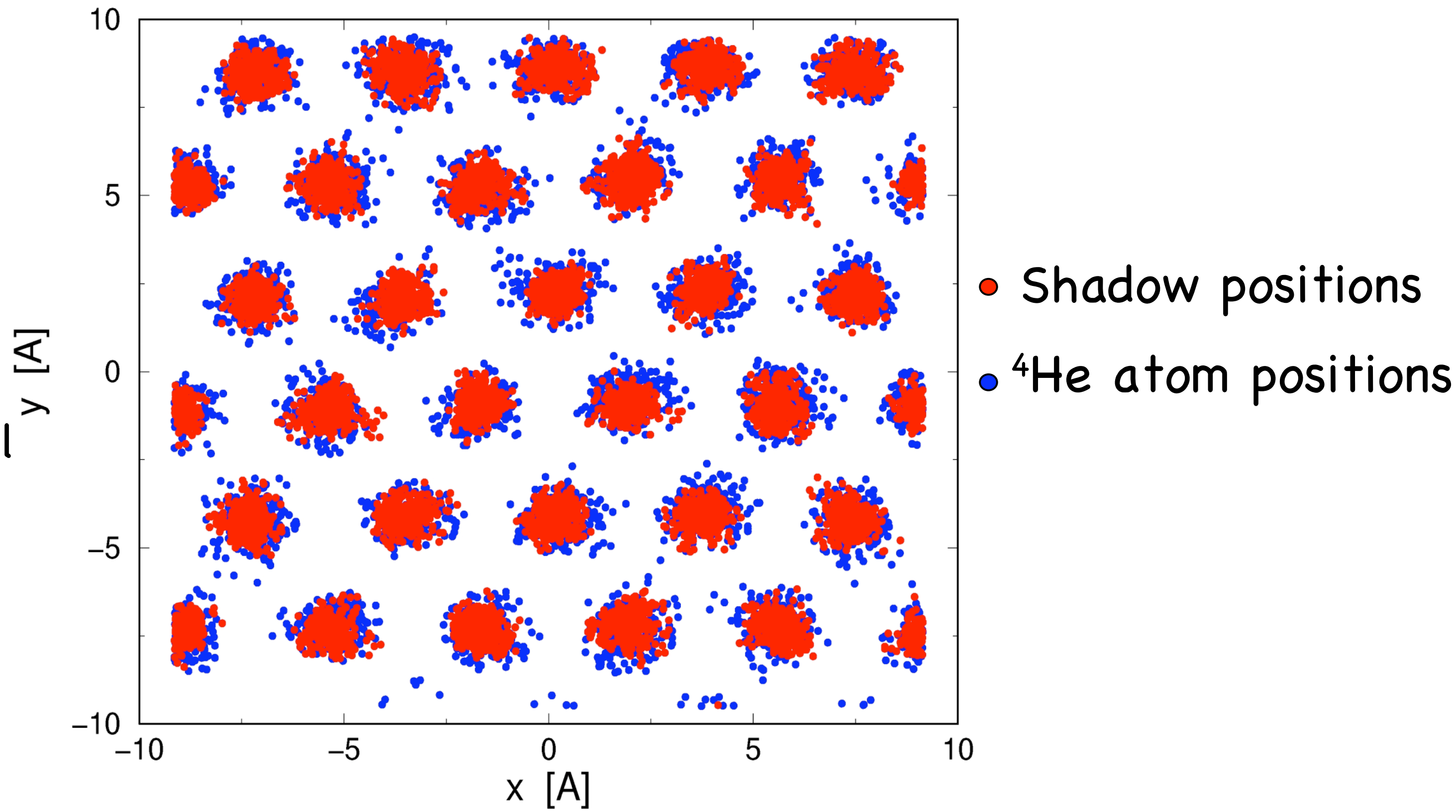
Shadow variables

- Shadow variables are strongly correlated

Spontaneous translational broken symmetry for $\rho > \rho_0$

Crystalline order of ^4He atoms induced by many-body correlations introduced by the shadow variables

SWF simulation of hcp solid ^4He: projection of the coordinates of the real and shadow particles in a basal plane for 100 MC steps



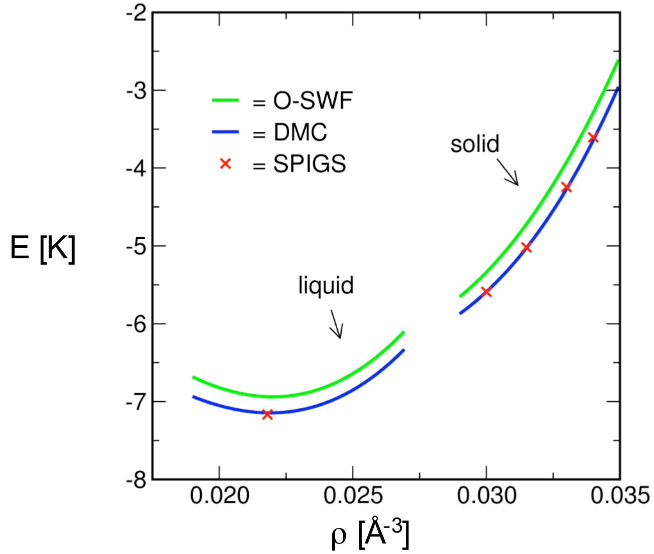
SWF: the solid phase

- Presently (a fully optimized) SWF provides the most accurate variational description of ^{4}He in the liquid and in the solid phase

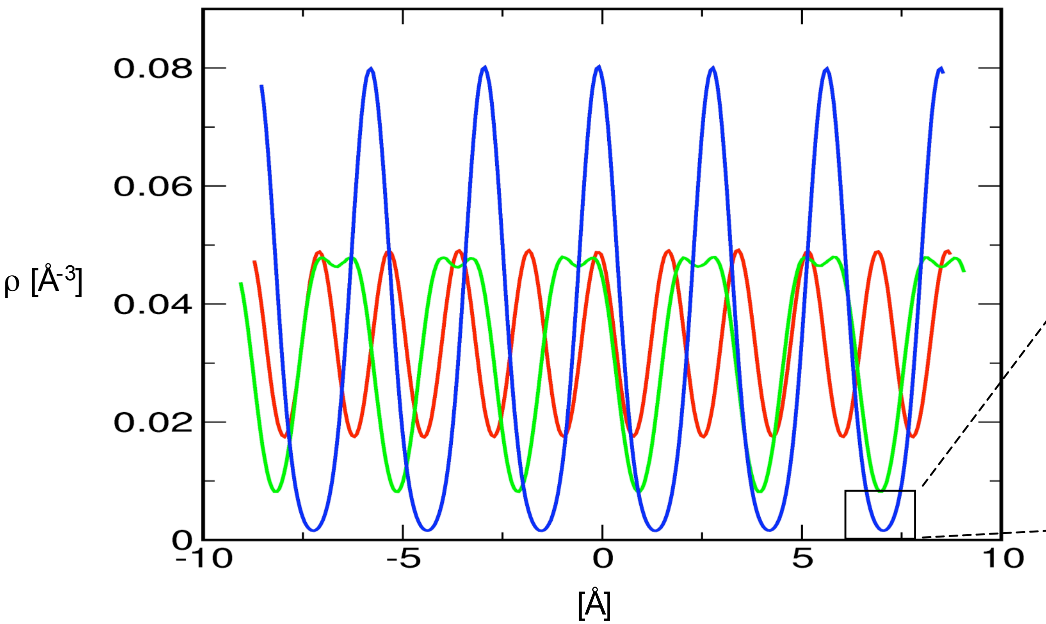
Moroni, Galli, Fantoni, Reatto, Phys.Rev.B58, 1998

- Accurate freezing and melting densities
- Solid phase: spontaneously broken translational symmetry

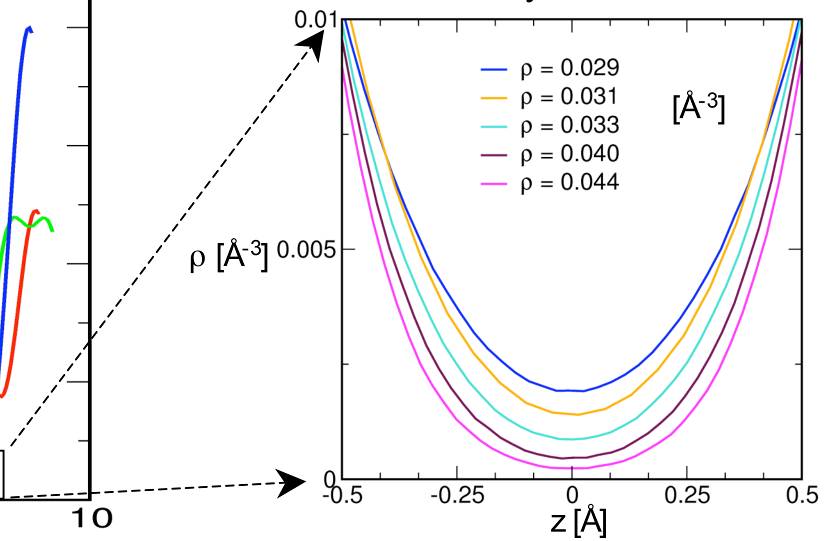
Equation of state (Aziz potential, 1979)



Local density hcp lattice ρ=0.029 Å^{-3}



Local density: direction ⊥ basal plane



- <u>Classical interpretation</u>: normalization of Ψ_{SWF} coincides with the configurational partition function of a classical system of suitable flexible triatomic molecules

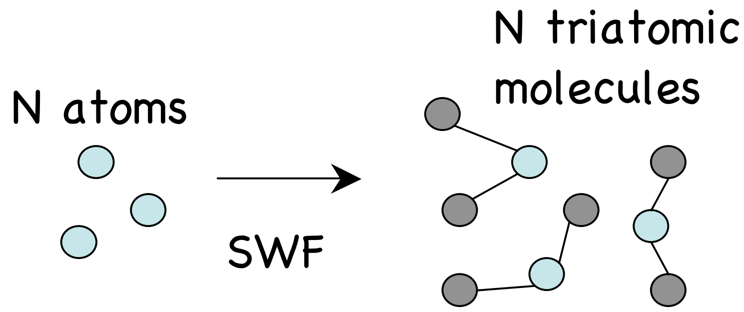
$\Rightarrow$ Ψ_{SWF} describes a quantum solid with vacancies and BEC

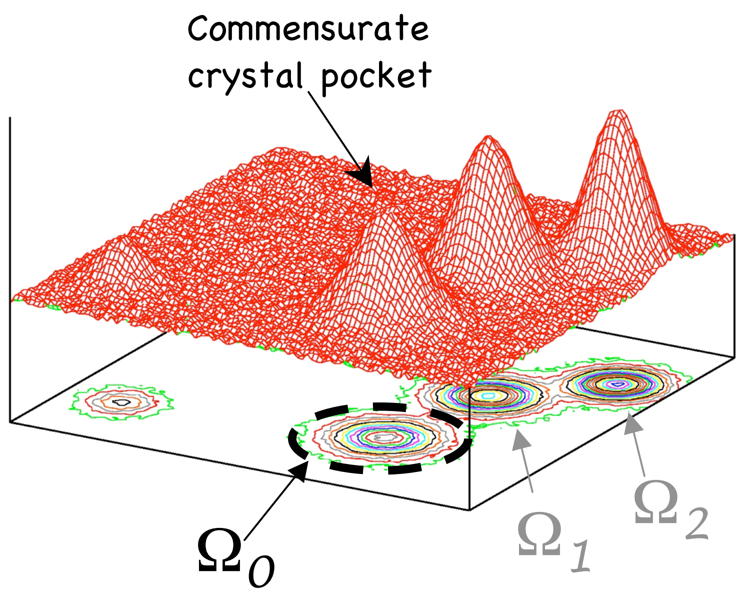
(Reatto, Masserini, Phys.Rev.B <u>38</u>, 1988)

- $\Psi_{SWF} \times \Gamma_{\Omega o}$ where $\Gamma_{\Omega o} \neq 0$ only in the commensurate solid pocket, $\Gamma_{\Omega o}$ increase the kinetic energy

$\Rightarrow$ only a direct calculation can discriminate commensurate or incommensurate ground state

Classical analogy





- Ground state energy per particle of a truly macroscopic system: $e_G=E_G/N$
- Energy per particle from the simulation of a commensurate state: $e_0=E_0/N$
- Total energy from the simulation of an incommensurate state with one vacancy: $E_1=E_0+\Delta e_v$

$$e_G=e_0+X_v\Delta e_v$$

where X_v is the average concentration of vacancies

- At melting the best energy of a wave function with localizing factors is 0.056 K per atom above SWF

$\Rightarrow$ allowing for $X_v\Delta e_v$, SWF are still the best for any $X_v<0.8\%$ ($\Delta e_v \approx 7$K at fixed lattice parameter)

- Calculation of X_v for Ψ_{SWF} is a priority computation for the future.

Projector QMC methods: Path Integral Ground State

Sarsa, Schmidt, Magro, J.Chem.Phys., 113, 2001

- Projector QMC: Ground state as imaginary time evolution of a trial variational state

$$\Psi_0(R) = \lim_{\tau \to \infty} \int dR' \left\langle R \middle| e^{-\tau \hat{H}} \middle| R' \right\rangle \Psi_T(R') \qquad R \equiv \{\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N\}$$

- Path Integral representation of the propagator:

$$\Psi_0(R) = \lim_{\tau \to \infty} \int dR_1 \cdots dR_M \left\langle R \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_1 \right\rangle \times \cdots \times \left\langle R_{P-1} \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_P \right\rangle \Psi_T(R_P)$$

- Approximation: finite imaginary time propagation

$$\Psi_0(R) \cong \int dR_1 \cdots dR_N \left\langle R \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_1 \right\rangle \times \cdots \times \left\langle R_{P-1} \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_P \right\rangle \Psi_T(R_P)$$

Accurate approximation for the short-time propagator, es: Pair-Product (Ceperely, Rev.Mod.Phys. 67, 1995)

Our "exact" tool: Projector QMC: from SWF to SPIGS

- SWF: single (variationally optimized) projection step of a Jastrow wave function

Vitiello, Runge, Kalos, Phys.Rev.Lett. 60, 1988

$$\Psi_T^{SWF}(R) = \int dS\; F(R,S)\; \Psi_T(S)$$

  - Implicit correlations (all orders)
  - Bose symmetry preserved

- SPIGS: "exact" T=0 projector method which starts from a SWF

Galli, Reatto, Mol. Phys. 101, 2003

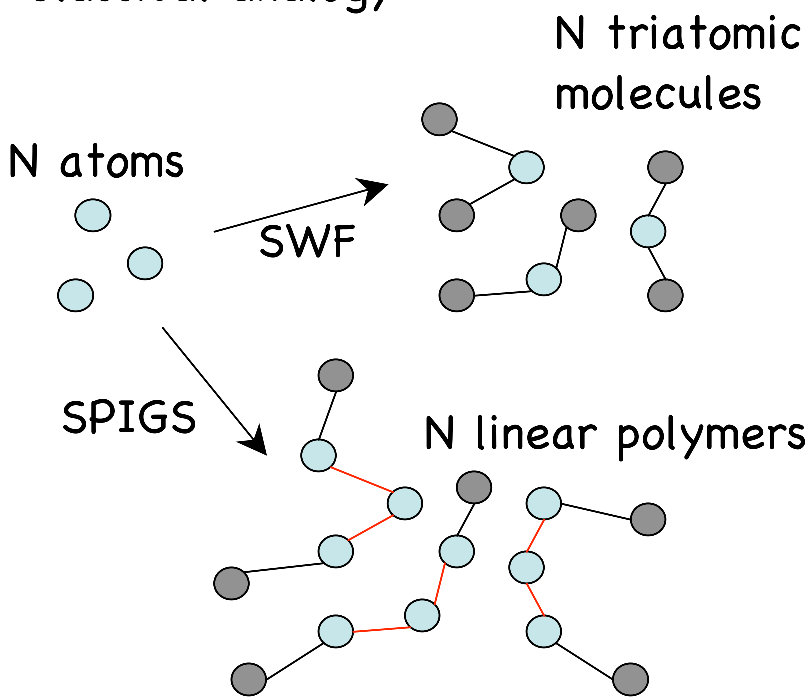
$$\Psi_0(R) = \int dR_1..dR_P dS \left\langle R \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_1 \right\rangle \times \ldots$$

$$\cdots \times \left\langle R_{P-1} \middle| e^{-\frac{\tau}{P}\hat{H}} \middle| R_P \right\rangle F(R_P,S) \Psi_T(S)$$

  - Notice: unlike PIMC at finite T here no summation over permutation is necessary, this $\Psi_0(R)$ is Bose symmetric if Ψ_T is symmetric

Calculation of $\left\langle \Psi_0 \middle| \hat{O} \middle| \Psi_0 \right\rangle$

Classical analogy



The whole imaginary time evolution is sampled at each MC step

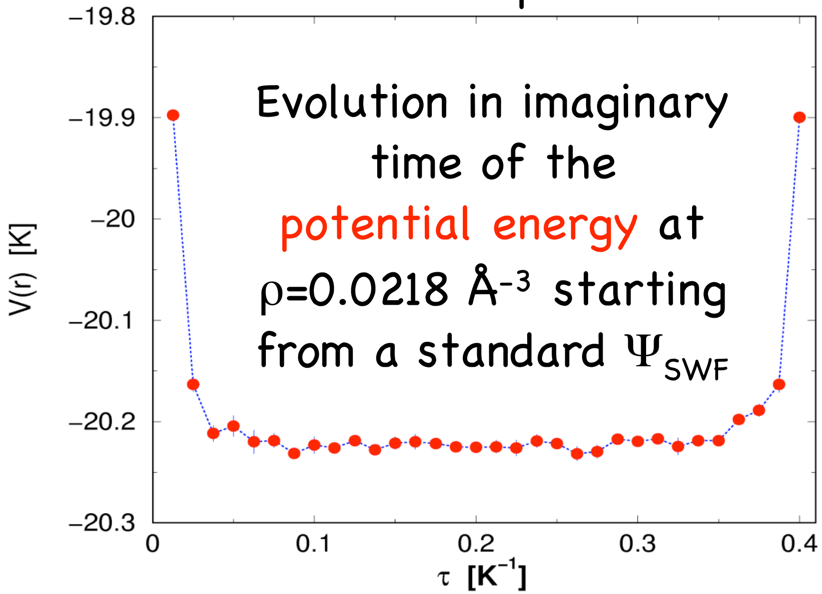
SPIGS

In principle the method is exact,

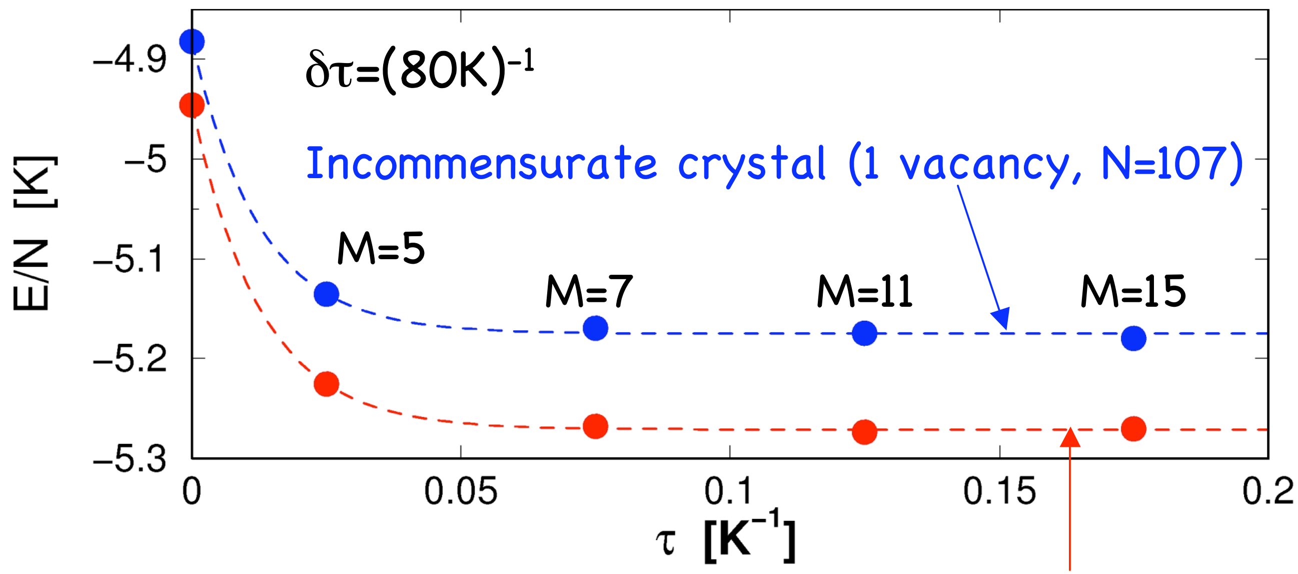
two parameters control convergence:

- Evolution in imaginary time τ (number of projections P, number of monomers [time slices] M=2P+1)
- $\delta\tau=\tau/P$ → accuracy of the short time propagator (pair-product approximation: Ceperley, Rev.Mod.Phys., 67 1995)

example



Evolution in imaginary time of the potential energy at ρ=0.0218 Å^{-3} starting from a standard Ψ_{SWF}



Commensurate crystal, N=108, ρ=0.031 Å^{-3}

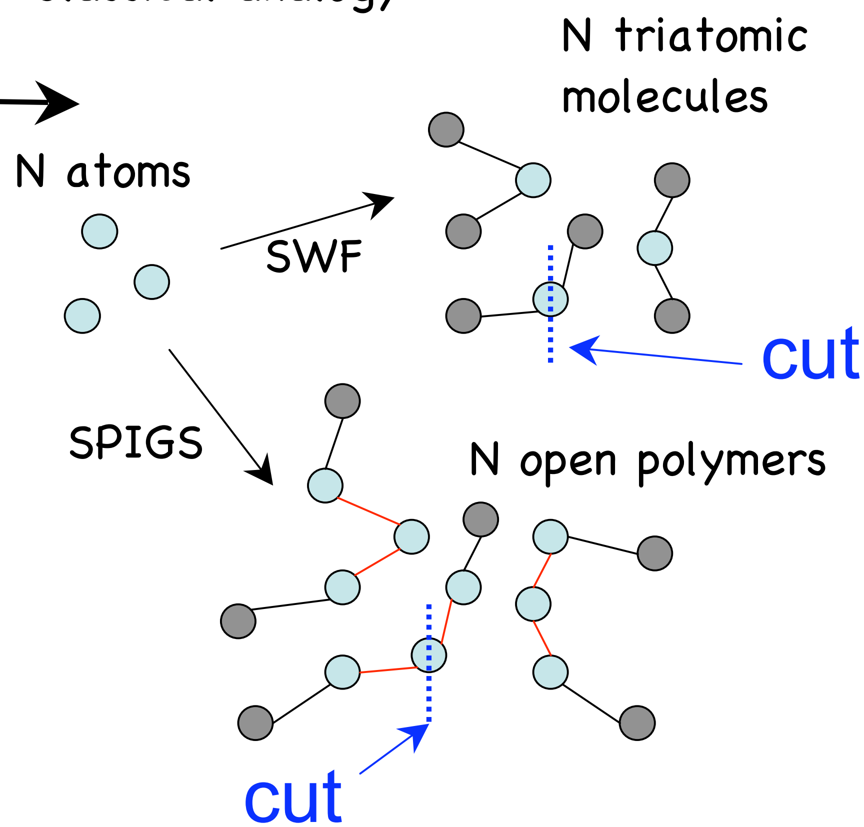
Convergence of the energy per particle as function of τ in a simulation of solid ^{4}He starting from a fully optimized SWF. Exponential convergence: $\approx e^{-(80K)\tau}$

QMC: calculation of the one-body density matrix

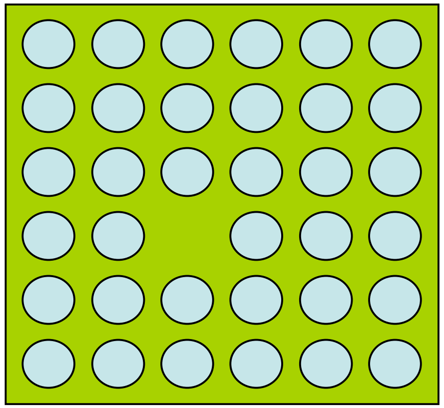
$$\rho_1(\vec{r},\vec{r}\,') = N \int dr_2 \cdots dr_N \Psi^*(r,r_2,\cdots,r_N)\Psi(r',r_2,\cdots,r_N)$$

- One of the open polymers is cut and the histogram of the relative distance of the two cut ends is computed
- We have studied incommensurate and commensurate solid ^{4}He: the periodic boundary conditions forces the structure of the solid.

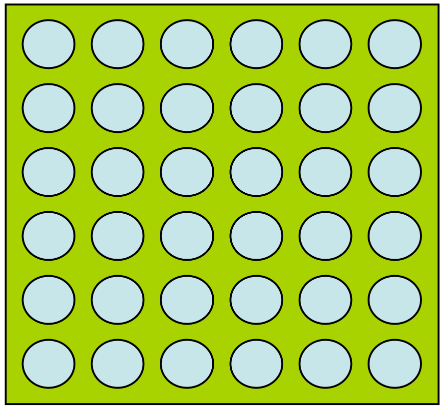
Classical analogy



Finite concentration of vacancies



Commensurate solid

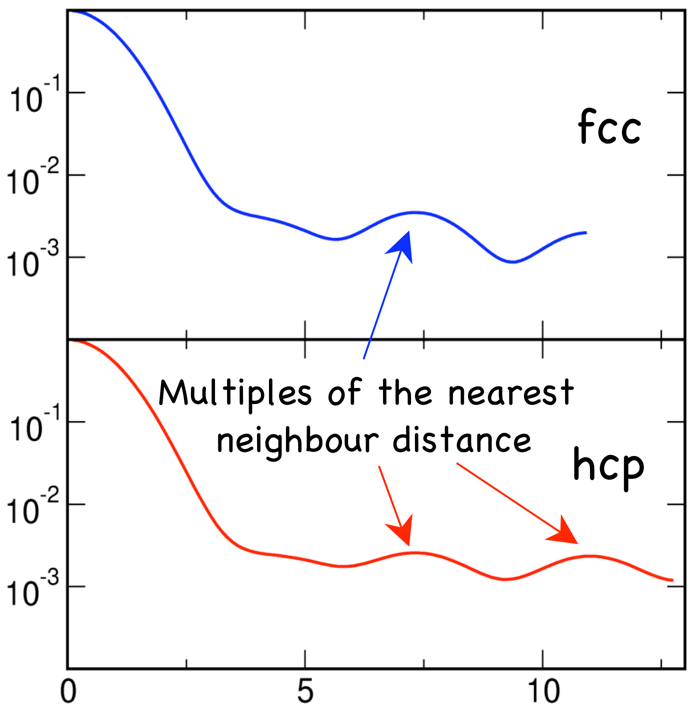


Incommensurate solid, SWF results: ODLRO in solid ^{4}He with vacancies

(Galli, Reatto, J. Low. Temp. Phys. 124, 2001)

- ODLRO is present in the low density defected solid
- $\rho_1(\vec{r}-\vec{r}\,')$ is Gaussian like only for small distances

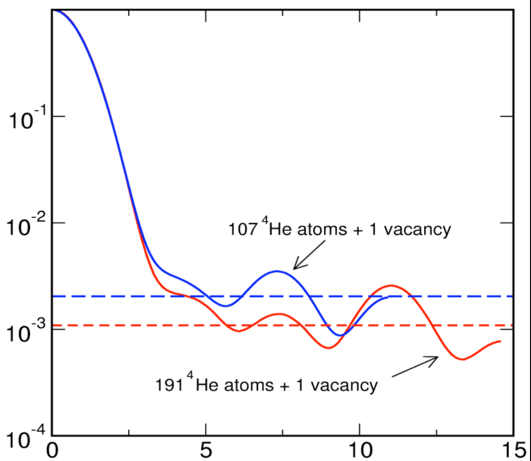
$\rho_1(\vec{r}-\vec{r}\,')$



$\vec{r}-\vec{r}\,'$ [Å]

along nearest neighbours distance

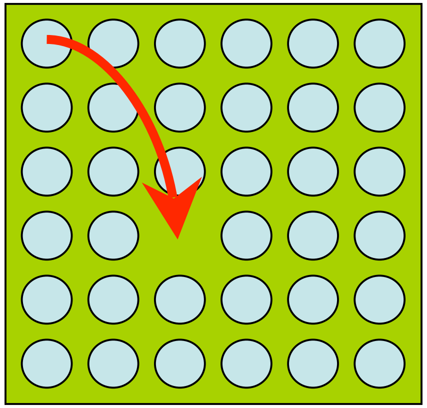
melting density $\rho=0.029$ Å^{-3}



$\vec{r}-\vec{r}\,'$ [Å]

ODLRO: microscopic origin

$$\rho_1(\vec{r},\vec{r}\,') = \left\langle 0 \middle| \hat{\Psi}^+(\vec{r})\hat{\Psi}(\vec{r}\,') \middle| 0 \right\rangle$$



Condensate fraction proportional to the concentration of vacancies

$n_0 = 0.22\, X_v$

at melting density

BEC in presence of a finite concentration of vacancies

(Galli, Reatto, J. Low. Temp. Phys. 124, 2001)

- Using a Shadow Wave Function for fcc and for hcp crystal with one or two vacancies a BEC was found:

At melting density (ρ=0.02898 Å^{-3})

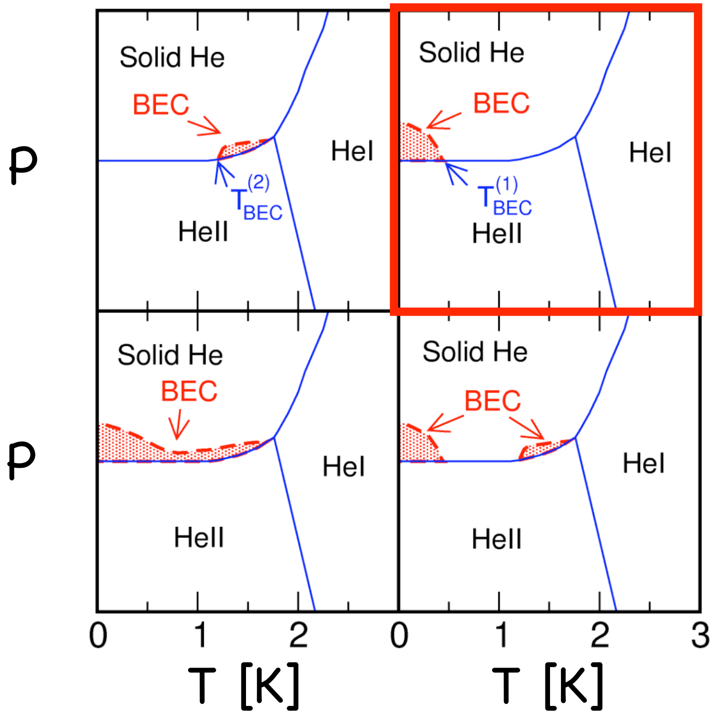
condensate per vacancy: $n_0^v = 0.22$ (fcc)

$n_0^v = 0.21$ (hcp)

i.e. for a sample with 1% vacancies, the condensate fraction per atom is $n_0 = 2.2 \times 10^{-3}$

We did not answer the question if vacancies are present in the ground state

Speculation on the phase diagram: ($T^{(2)}_{BEC} \approx 1.32 \Delta e_v$)

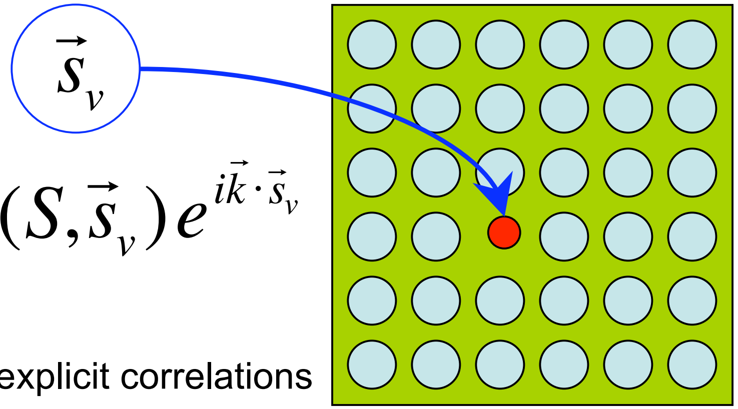


Vacancy excitation spectrum

- We have found a way to extend the excited state SWF technique to study the vacancy excitation spectrum:
  - We have associated one extra-shadow which localizes in the void of the vacancy in order to study the excitation at finite quasi-momentum

$$\Psi_{\vec{k}}^{SWF}(R) = \int dS\, d\vec{s}_v F(R,S)\Psi_T(S)L(S,\vec{s}_v)e^{i\vec{k}\cdot\vec{s}_v}$$

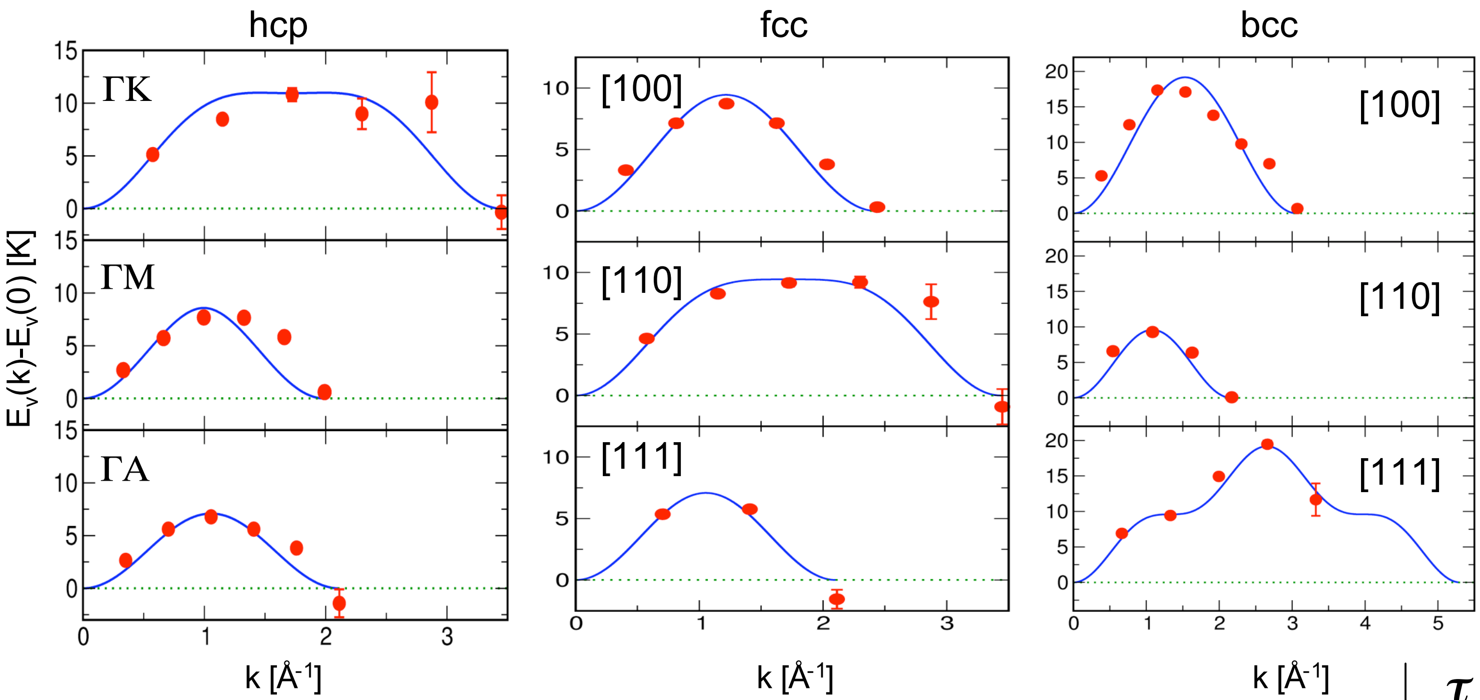
Shadow-extashadow explicit correlations



  - The inclusion of the extra-shadow improves the variational energy
  - Integration over extra-shadow is a way to change locally the effective many-body correlations around the vacancy

SWF results: vacancy excitation spectrum

Galli, Reatto, Phys.Rev.Lett. 90, 2003;
Galli, Reatto, J.Low Temp.Phys. 134, 2004



$m^*=0.31m_4$
$m^*=0.39m_4$ (ΓA)

$m^*=0.39m_4$

$m^*=0.3m_4$

Near melting density

$\rho=0.029$ Å^{-3}

residence time (hcp)

$$\tau = \frac{h}{\Delta} \cong 0.6 \times 10^{-11} \sec$$

only 4 time larger than the period of high frequancy phonon in the crystal

- Vacancy very mobile, in agreement with recent experiments

Andreeva et al., J.Low Temp.Phys. 110, 1998

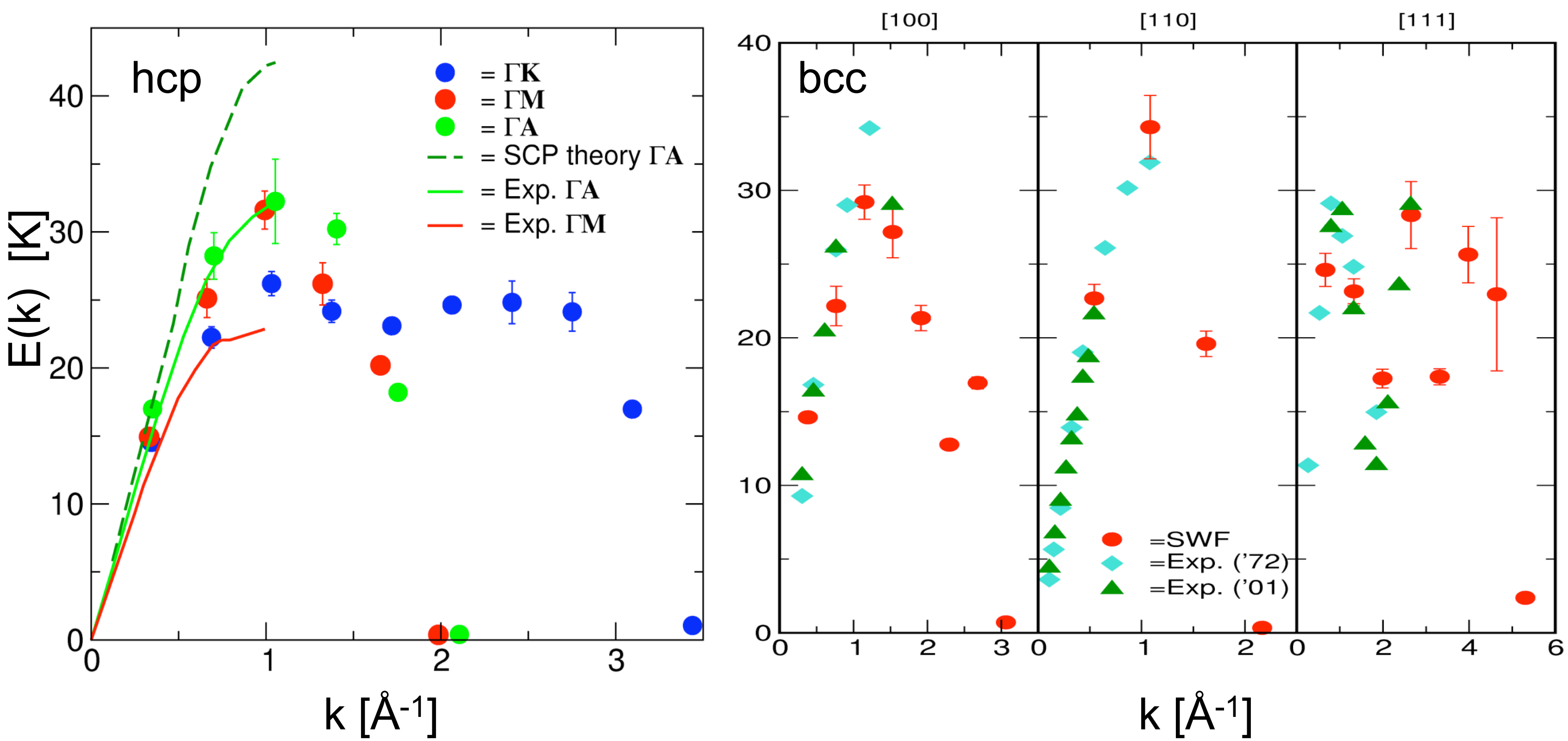
- Band width decreases at larger density

SWF: longitudinal phonons

Galli, Reatto, Phys.Rev.Lett. 90, 2003 and J.Low Temp.Phys. 134, 2004

- We have computed longitudinal phonons in hcp and bcc solid ^{4}He finding good agreement with experiments
- Also transverse phonon in bcc solid ^{4}He (Mazzi, Galli, Reatto, Proceedings LT24)

Near melting density ρ=0.029 Å^{-3}



Incommensurate solid, SPIGS results: ODLRO in solid ^{4}He with vacancies

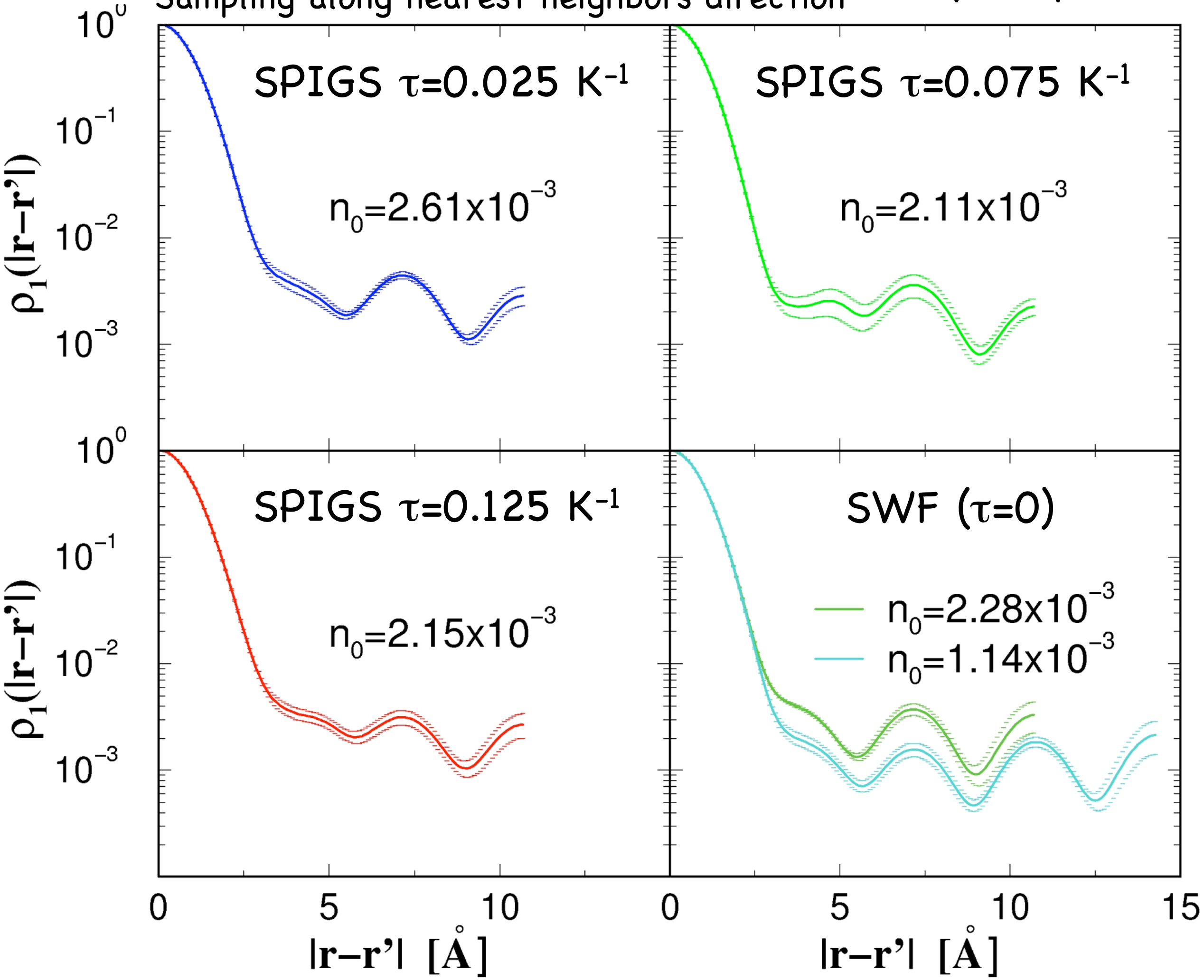
(Galli, Reatto, cond-mat/0602055)

- ODLRO is still present with SPIGS

fcc ρ=0.031 Å^{-3} P=54 bars

pair-product approximation $\delta\tau=(40\ K)^{-1}$

Sampling along nearest neighbors direction



Condensate fraction proportional to the concentration of vacancies?

If yes $n_0 = 0.23X_v$

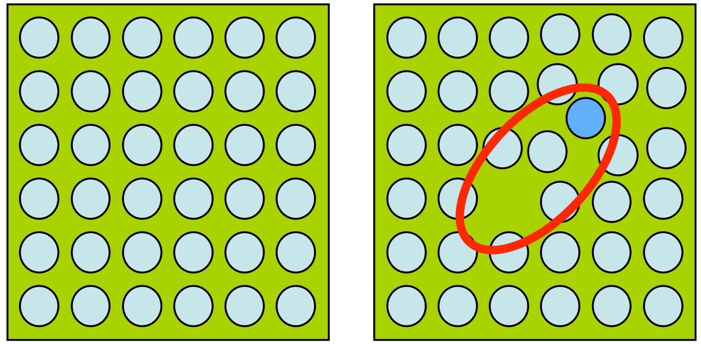
Vacancies are very efficient in inducing BEC: Ideal gas of vacancies with effective mass $m^*=0.35m_{4He}$

$T_{BEC} \approx 10.8 X_v^{2/3} = 0.2$ K

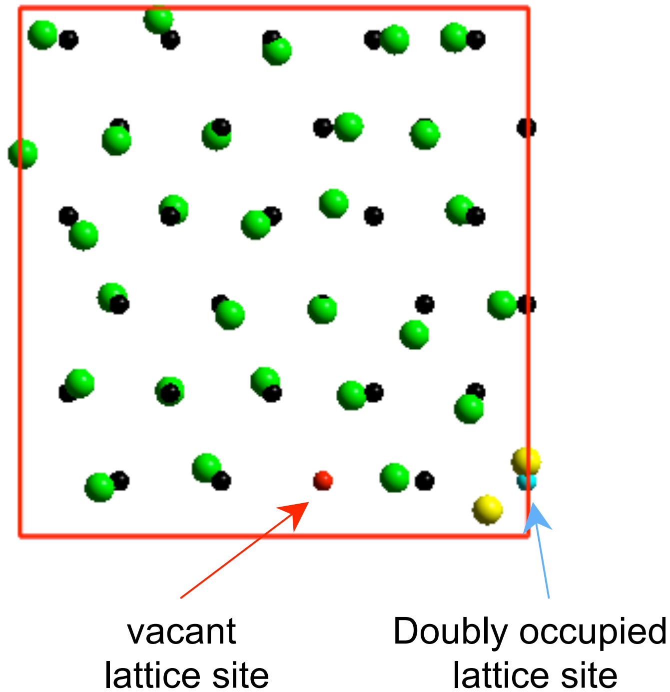
If $X_v = 2.5\text{x}10^{-3}$

Vacancy-interstitial pairs (VIPs)

- Even by forcing the solid to be commensurate one finds the presence of vacancy-interstitial pairs (VIPs)
- These VIPs are not excitations but simply fluctuations of the lattice; they are part of the large zero-point in the ground state of the solid
- The term "pairs" is used to underline the origin of these zero-point processes.
- Are VIPs unbound?

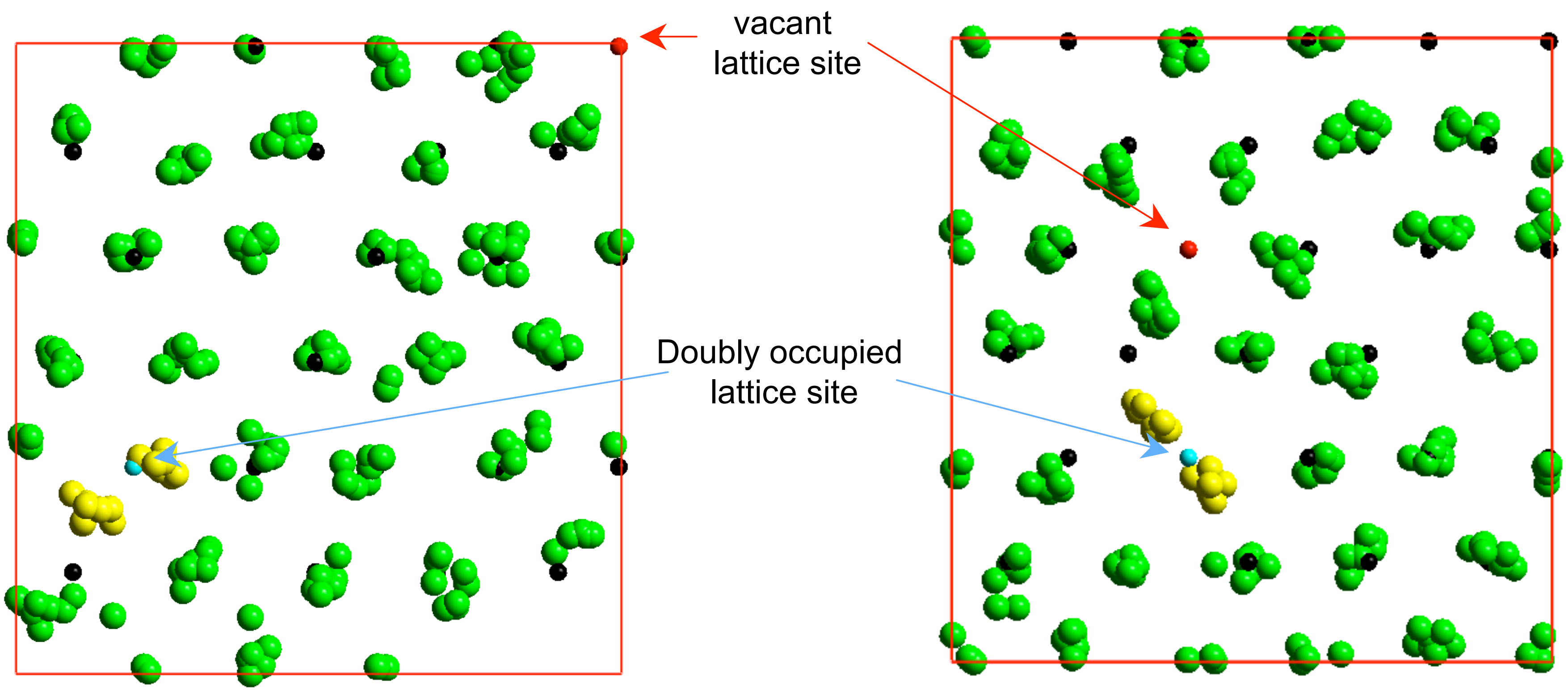


hcp basal plane $\rho=0.029$ Å^{-3}



SPIGS: Vacancy-interstitial pairs

- These VIPs are present also in the "exact" sampling of $|\Psi_0|^2$ (SPIGS method); in the examples only the internal atoms of the polymers are shown
- VIP-frequency: ≈1 every 2-3x10^3 MC steps with 180 ^{4}He atoms $\Rightarrow X_{vip} \approx 2 \times 10^{-6}$
- New excitations? Correlations with ^{3}He atoms?



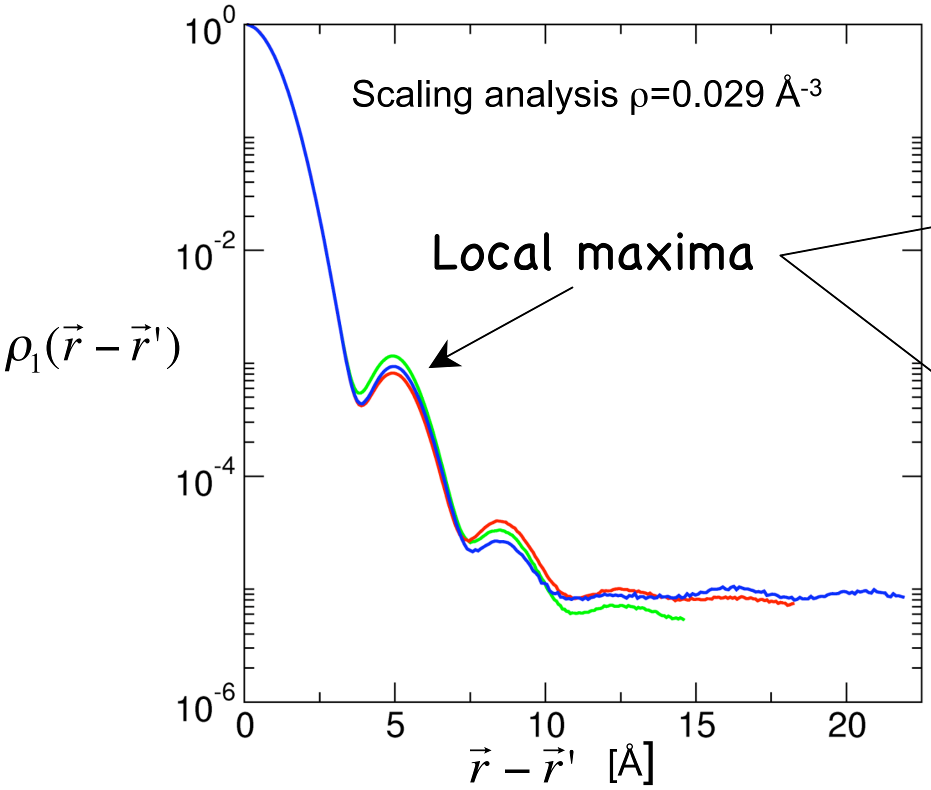
SWF results: ODLRO in commensurate solid ^{4}He

Galli, Rossi, Reatto, Phys.Rev. B 71, 2005

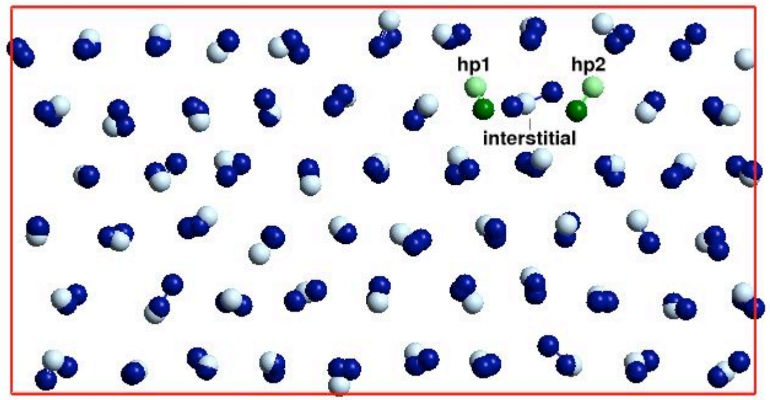
- ODLRO is present: $n_0 \approx 5 \pm 2 \times 10^{-6}$ at melting and for a finite range of densities (up to 54 bars)
- Local maxima: signature of distorted lattice
- No finite-size effects
- Key process is the presence of VIPs

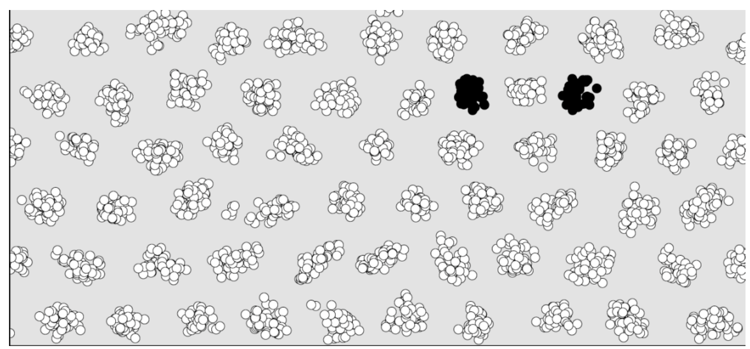
ODLRO:
microscopic origin

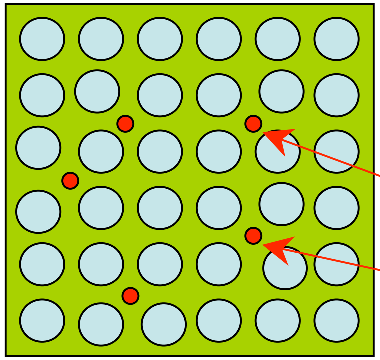
$$\rho_1(\vec{r},\vec{r}\,') = \left\langle 0 \middle| \hat{\Psi}^+(\vec{r})\hat{\Psi}(\vec{r}\,') \middle| 0 \right\rangle$$



Snapshot of SWF trimers in a basal plane



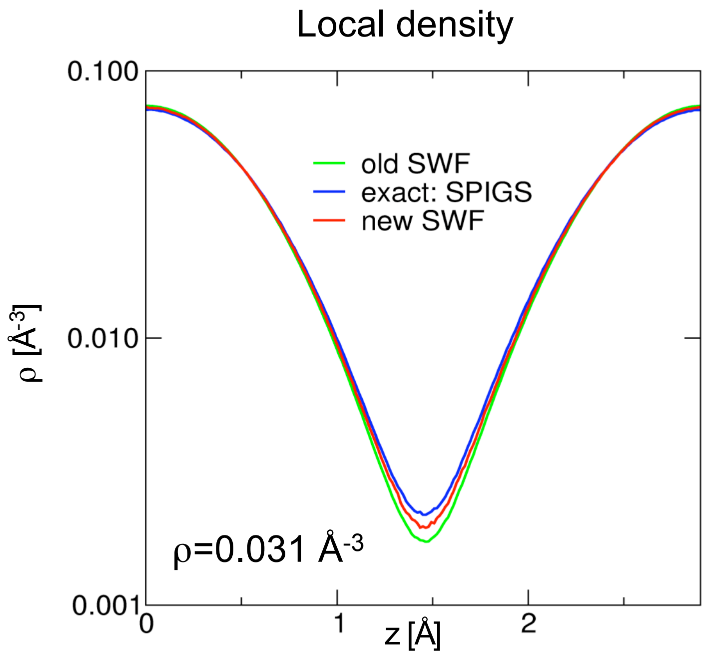


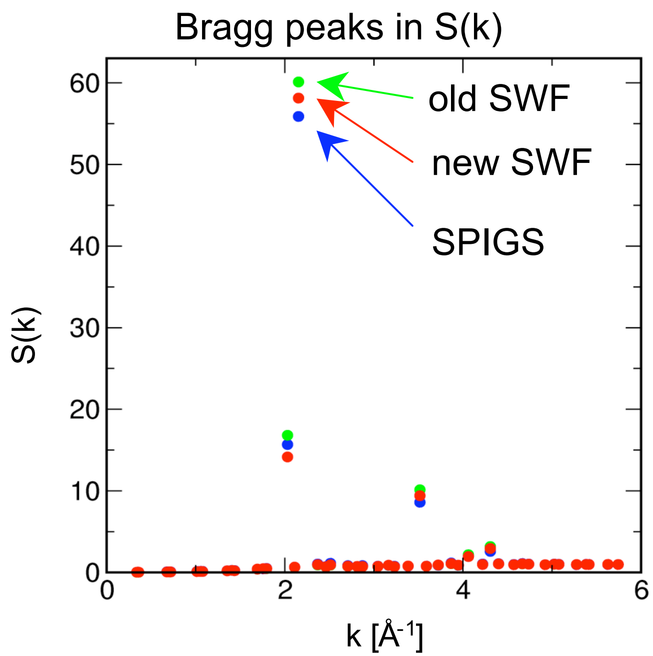


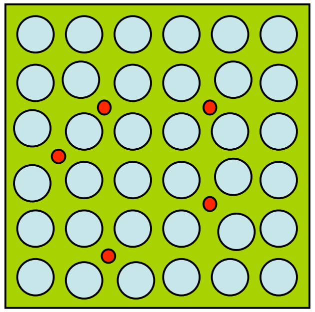
New SWF

$$\Psi_{new}^{SWF}(R) = \int dS\, dS_v\, F(R,S)\,\Psi_T(S)\,L(S,S_v)$$

- We have obtained a more accurate description of the structure of solid ^{4}He by means of a new SWF
- As in the calculations of the excitations spectrum of a vacancy, we have included some extra-shadow variables in the commensurate solid; these extra variables interfere with the structure of the solid leaving the lattice less structured
- Variational energy improves (2%)
- Optimal size of extra-shadows depends on their number.

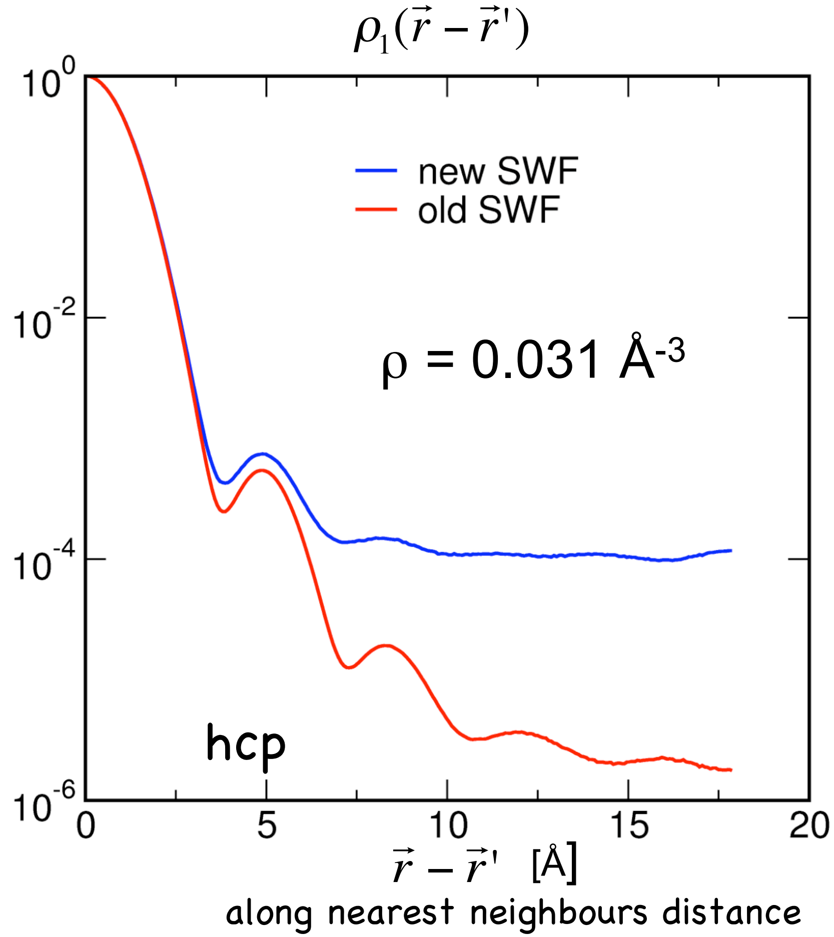






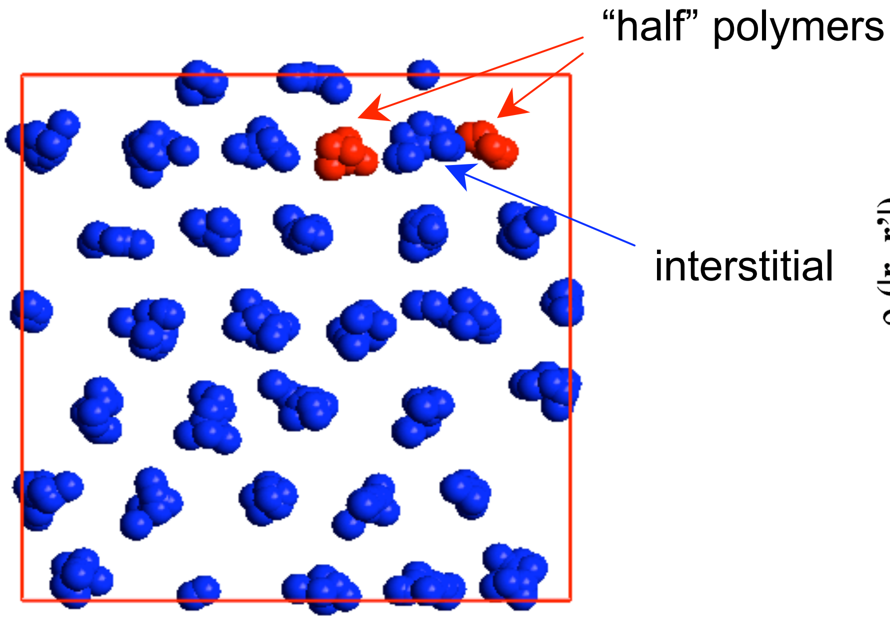
New SWF: ODLRO results

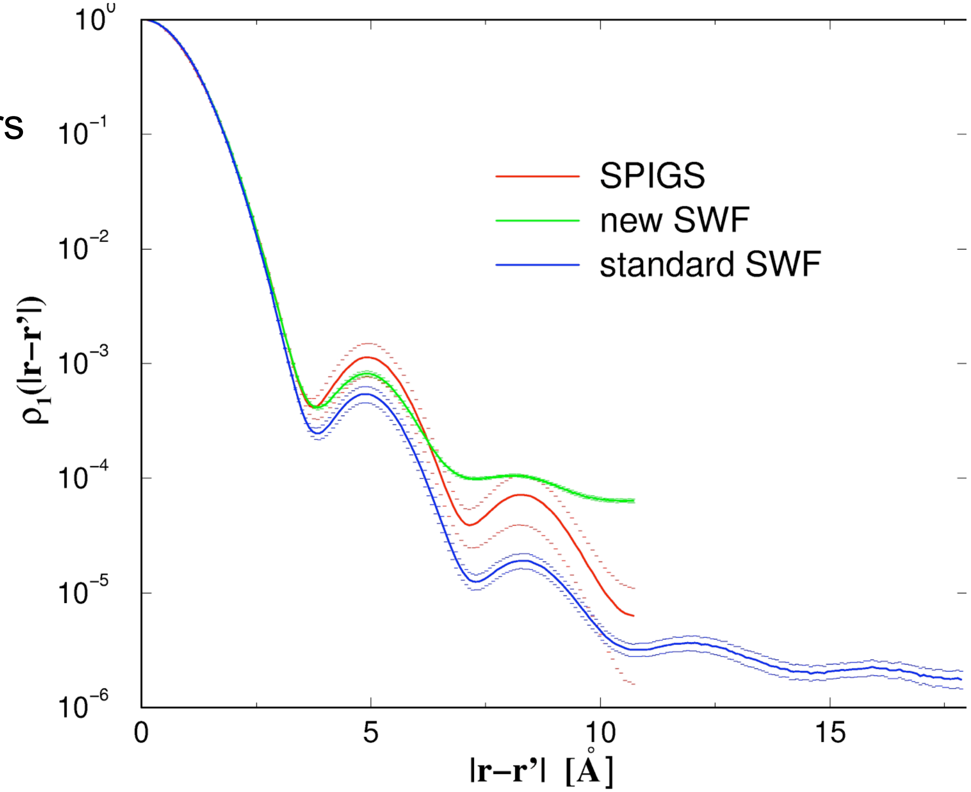
- ODLRO: in the less structured solid the condensate fraction is greater: about 40 times higher
- With this new SWF the density range, where ODLRO is present, will probably be larger
- More damped oscillations at large distance: the plateau is reached at shorter distances



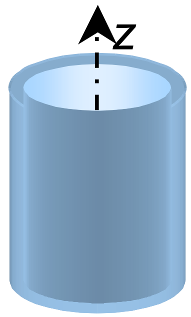
One-body density matrix: SPIGS results

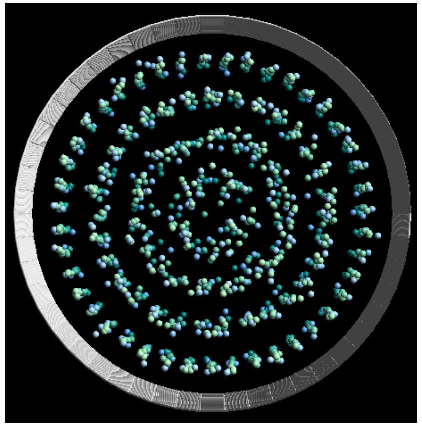
- Calculations of the one-body density matrix in fcc solid ^{4}He at ρ=0.031 Å^{-3} with SPIGS
- Oscillations in the tail region are still present (VIPs) but the "projected" ρ_1 tends to return on the standard SWF results
- Pair-product approximation: $\delta\tau$=(40 K)$^{-1}$; τ=0.075 K^{-1}
- Calculation only at short range: ODLRO ?





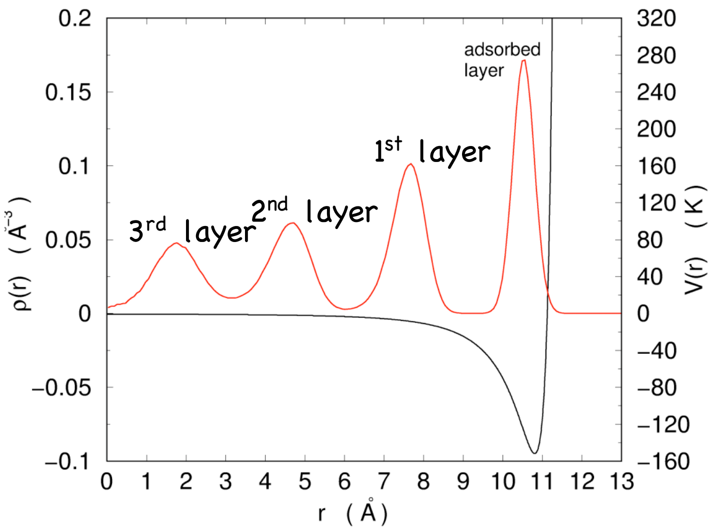
Within the SWF technique we have studied the properties of ^{4}He adsorbed in porous materials
(Rossi, Galli and Reatto, Phys. Rev. B **72**, 064516 (2005))



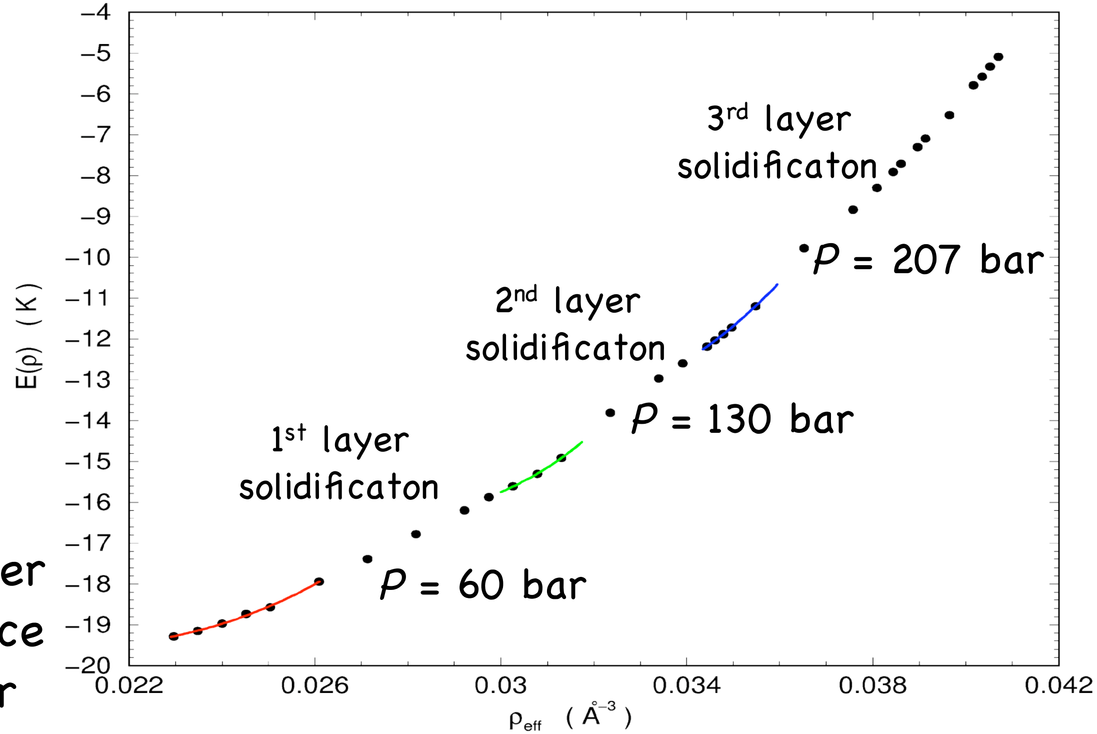


- confining media modeled with a cylindrical smooth pore
- potential ^{4}He-cylinder: model potential for Si-^{4}He
  (Vidali, Ihm, Kim, Cole, Surf.Sci.Rep. 12, 133 (1991))
- R = 13 Å comparable with Gelsil nominal pore size

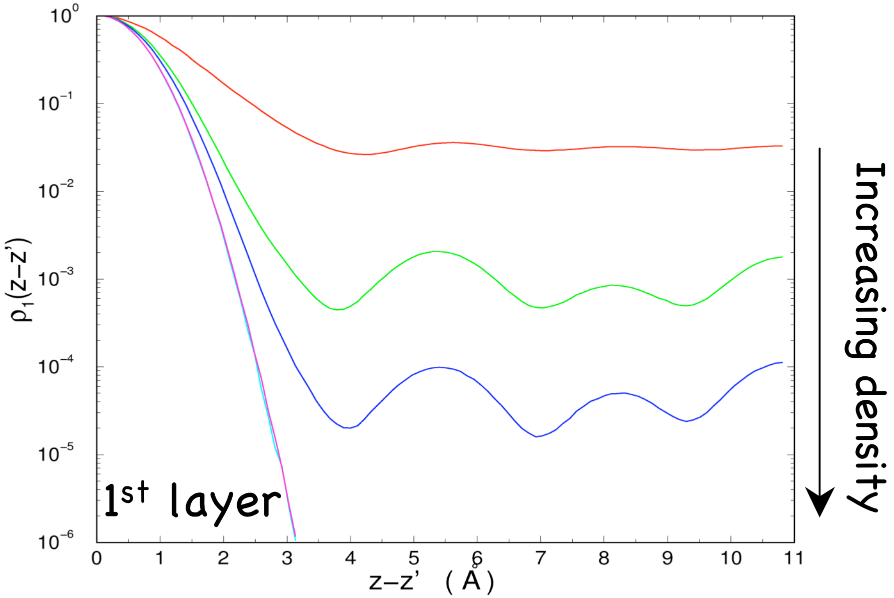
Results:
- ^{4}He atoms form a distinct layered structure
- at all the considered fillings the adsorbed layer is solid and insensitive of the total density

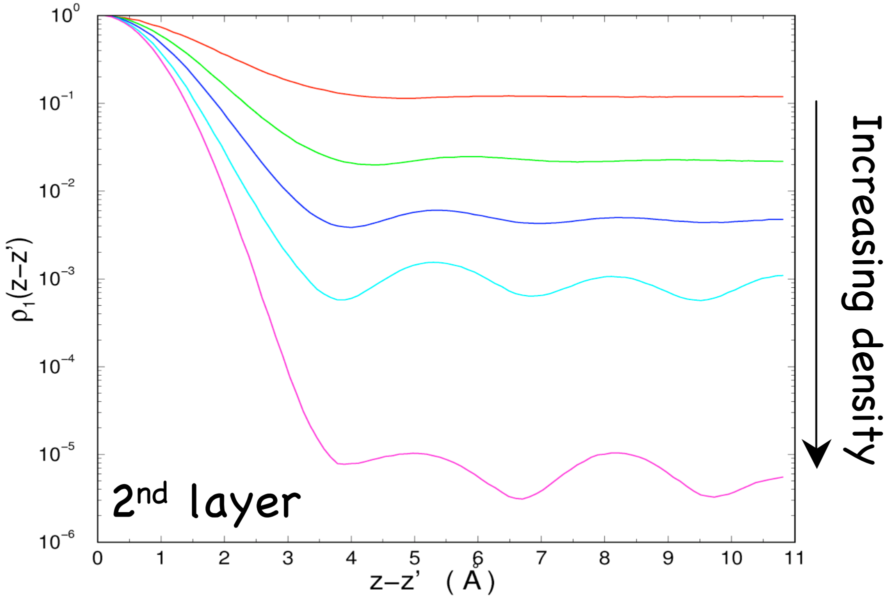


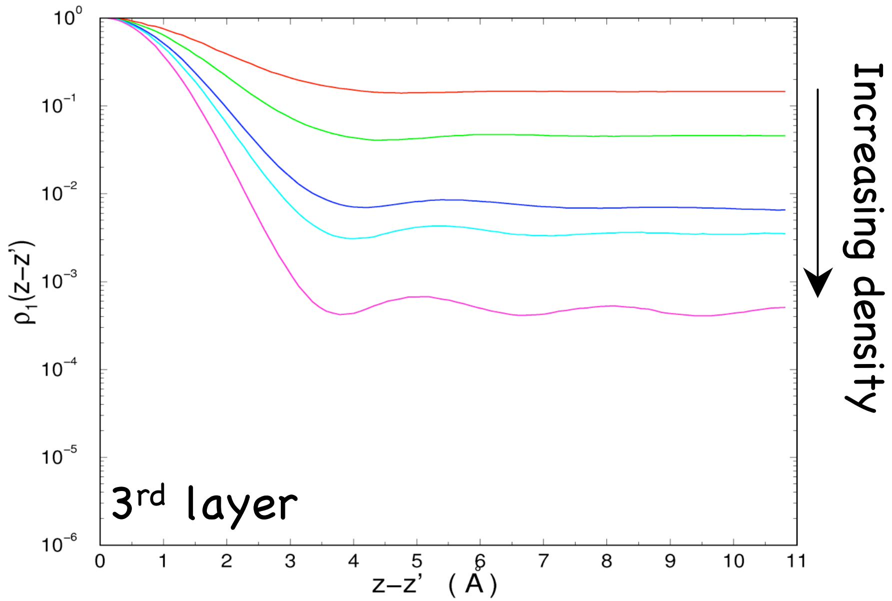
increasing the ^{4}He density a layer by layer solidification takes place starting from the outermost layer



single layer contributions to ρ_1 along the *z* direction







<u>Results</u>:

- non-zero plateau (BEC) for a wide range of pressures
- in the central region of the pore there is BEC even if the system is in the solid phase
- the oscillations in the ρ_1 tails are registered with the crystalline lattice therefore the major contribution to BEC comes from defects such as mobile vacancies

Conclusions and open questions

I have discussed the microscopic theoretical evidence on the simultaneous presence of diagonal and off diagonal long range order in solid ^{4}He by zero temperature QMC methods

- If vacancies are present as an equilibrium or a non equilibrium effect we conclude that there is ODLRO both from variational (SWF) and from exact projection method (SPIGS): condensate of $0.23X_v$ at 54 bar
- Non homogeneous X_v could explain the smoothed transition.
- The question commensurate (no vacancies) - incommensurate (yes vacancies) ground state of solid ^{4}He is still an open question, SWF has ground state vacancies but we do not know how many, for SPIGS we do not know
- evidence for VIPs also from the exact projection method (SPIGS); ODLRO at zero (very low) temperature?
- Vacancies are efficient for BEC; more disorder?
- Effect of small concentrations of ^{3}He on vacancies or VIPs?
- We have studied ^{4}He in a cylindrical narrow pore (ϕ=26Å) mimicking Gelsil, with SWF. We find evidence for layer by layer solidification and ODLRO also in the (defected) solid phase.
- If it is not an equilibrium effect of vacancies, by improving the quality of the sample, NCRI should disappear only in the bulk, not in the confined system.