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Research Workshop on Condensed Matter Physics
30 June - 22 August 1997
MINIWORKSHOP ON
QUANTUM MONTE CARLO SIMULATIONS OF LIQUIDS AND SOLIDS
30 JUNE - 11 JULY 1997
and
CONFERENCE ON
QUANTUM SOLIDS AND POLARIZED SYSTEMS
3 - 5 JULY 1997

**"Theory of disorder phenomena in solid 4He:
vacancies and liquid-solid interfaces"**

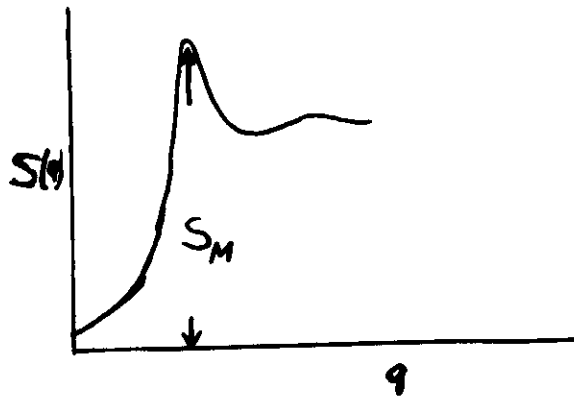
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These are preliminary lecture notes, intended only for distribution to participants.

THEORY OF DISORDER PHENOMENA IN SOLID ^4He : VACANCIES AND LIQUID-SOLID INTERFACES

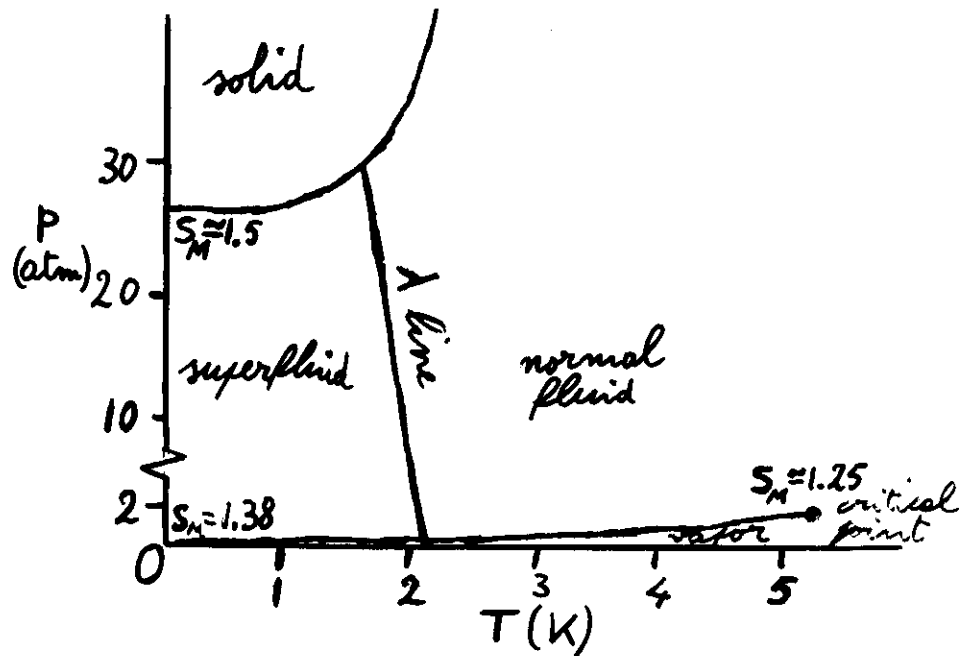
- motivation
- microscopic theory of a perfect quantum solid
the shadow wave function technique
- a crystal with one vacancy
formation energy
relaxation and mobility
~~crystal with a vacancy and one ^3He impurity~~
- the liquid-solid interface
local density shadow w.f.
local density and order parameter in the interfacial region
interfacial energy
 ^3He and the interface
- conclusion

SHORT RANGE ORDER AND PHASE DIAGRAM



uniform quantum fluid becomes unstable toward solidification in presence of remarkably small amount of short range order

${}^4\text{He}$



S_M has similar values in liquid ${}^3\text{He}$
 $\Rightarrow$ statistics is not too important

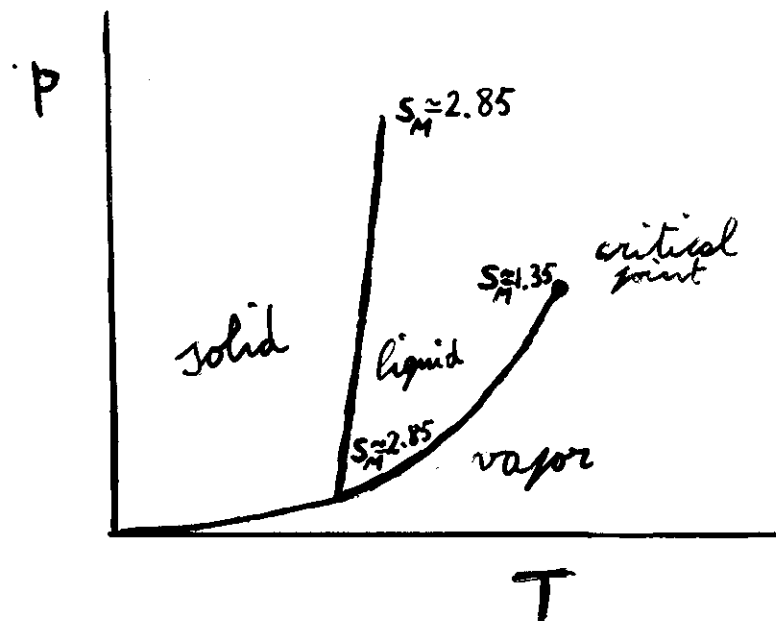
COMMON SIMPLE

SUBSTANCE
 (CLASSICAL)

INDEMANN RATIO AT MELTING

$$\gamma = \sqrt{K |\bar{r}_i - \bar{r}_{eq}|^2} / a$$

HE	NORMAL SOLID
$\gamma \approx 0.25-0.30$	$\gamma = 0.12-0.15$



QUANTUM SOLID (low density solid ^4He)

similarities with usual solids:

- crystalline order: Bragg peaks
- collective modes: phonon modes (longit. and trans)

differences:

- large local motion
- exchange of particles
- very different shape of phonon peaks in $S(q, \omega)$ at equivalent points in q -space

disorder phenomena in a quantum solid

vacancies:

- low energy of creation
- are vacancies present in the ground state? (supersolid phase?)
- vacancy bands

liquid-solid interfaces

- collective modes: melting-freezing waves

what has to tell the microscopic theory on these issues?

GROUND STATE OF N BODY SYSTEM $\mathcal{H} = T + \sum_{i,j} v(r_{ij})$

$$\Psi_0(\vec{r}_1 \dots \vec{r}_N)$$

VARIATIONAL APPROACH : LIQUID PHASE

$$\Psi_0(\vec{r}_1 \dots \vec{r}_N) = \exp \left\{ -\frac{1}{2} \sum_{i,j} u(r_{ij}) - \frac{1}{2} \sum_{i,j,k} u^{(3)}(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots \right\}$$

Jastrow
Jastrow + triplet
...

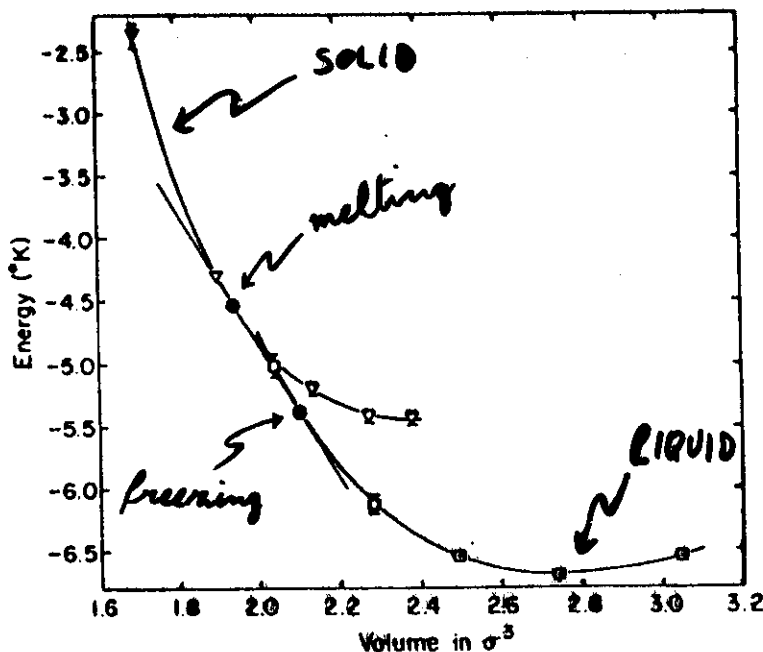
SOLID PHASE

$$\Psi_0(\vec{r}_1 \dots \vec{r}_N) = \prod_i e^{-K|\vec{r}_i - \vec{R}_i^0|^2} \exp \left\{ -\frac{1}{2} \sum_{i,j} u(r_{ij}) - \frac{1}{2} \sum_{i,j,k} u^{(3)}(\vec{r}_i, \vec{r}_j, \vec{r}_k) \right\}$$

$\vec{R}_i^0$ equilibrium positions of atoms

Jastrow-Noromon w_i

w.f. with explicit broken symmetry



difficulties with the interface
- how do we choose $\vec{R}_i^0$
- difficult to guarantee
box symmetry

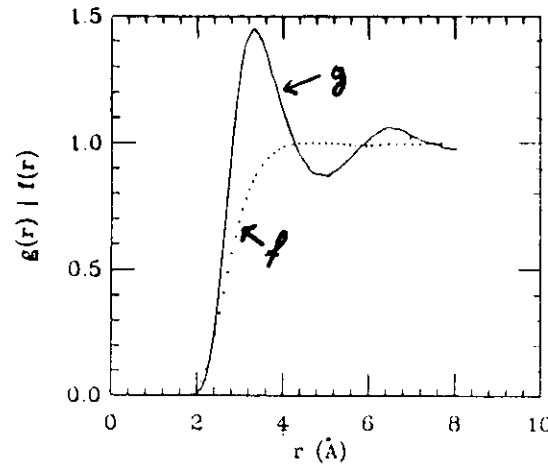
FIG. 24. Double tangent construction which locates the freezing and melting volumes. The upper curve is for the crystal phase, the lower for the fluid phase. The two points of common slope are shown as solid circles (●).

variational result from
stochastic optimized
repulsion, Aziz
potential

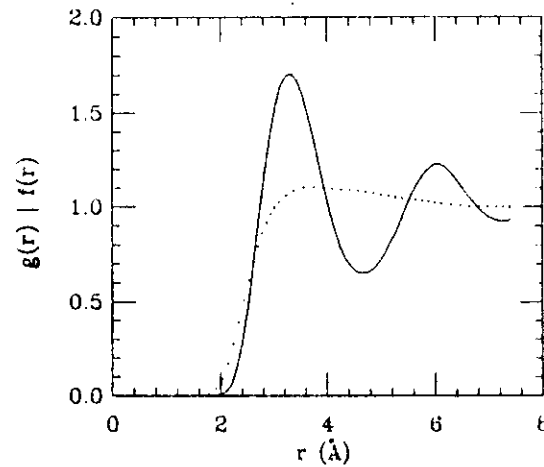
$$Z_{\text{liquid}}^{\text{trial}} = \prod_{i,j} f(r_{ij}) \prod_{i,j,k,l} f^{(3)}(r_{ijkl})$$

$$Z_{\text{solid}}^{\text{trial}} = \prod_i e^{-K|\vec{r}_i - \vec{r}_j|^2} \times$$

$$\times \prod_{i,j} f(r_{ij}) \prod_{i,j,k,l} f^{(3)}(r_{ijkl})$$



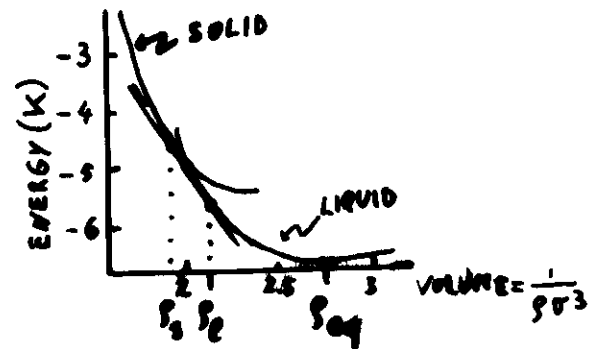
LIQUID AT
FREEZING
 $\rho\sigma^3 = 0.438$



SOLID: $\rho\sigma^3 = 0.56$ ($\rho\sigma^3 = 0.45$ melt)
ANGLE AVERAGED n.d.f.
 $g(r) = \langle g(\vec{r}) \rangle_{\Omega}$

at short distance the local order in the liquid and
in the solid is very similar

we know how to compute
the liquid-solid transition



WHY THE SYSTEM HAS LONG RANGE ORDER
(CONFIGURATIONAL) WHEN THERE IS SUCH
LARGE LOCAL DISORDER?

IN CLASSICAL SYSTEMS FREEZING IS USUALLY
DIRECTLY RELATED TO STERIC HINDRANCE DUE
TO CONDITION OF NO CORE OVERLAP

THE SHADOW WAVE FUNCTION

$$\Psi(R) = \varphi(R) \int dS K(R, S) \varphi_S(S)$$

$$R = \{\vec{r}_1 \dots \vec{r}_N\} \quad \text{particles}$$

$$S = \{\vec{s}_1 \dots \vec{s}_N\} \quad \text{shadows}$$

$\varphi(R)$ and $\varphi_S(S)$ are functions of the Jastrow form. The kernel $K(R, S)$ is a gaussian:

$$K(R, S) = \prod_{i=1}^N e^{-C(\vec{r}_i - \vec{s}_i)^2}$$

MAIN PROPERTIES:

- Gives a realistic description of the equation of state over a wide range of densities;
- The solid phase is obtained without a factor localizing the particles: the wave function is always translationally invariant;
- Introduces implicitly correlations between particles at any order (not only second or third...);
- Optimal parameters in $\varphi(R), \varphi_S(S)$ and $K(R, S)$ depend on density.



**NOT POSSIBLE TO OBTAIN
A REALISTIC COEXISTENCE**

EXPECTATION VALUE OF THE HAMILTONIAN

$$\hat{\mathcal{H}} = \hat{T} + \sum_{i,j} v(r_{ij})$$

$$E_0 = \frac{1}{N} \left\langle \frac{\hat{\mathcal{H}} \psi_r(R) K(R,S)}{\psi_r(R) K(R,S)} \right\rangle_{RSS'}$$

$$\Psi_0(R) = \psi_r(R) \int dS K(R,S) \psi_s(S)$$

$$\left\langle \dots \right\rangle_{RSS'} = \frac{\int dR dS dS' \dots \psi_r^2(R) K(R,S) K(R,S') \psi_s(S) \psi_s(S')}{\text{normalization}}$$

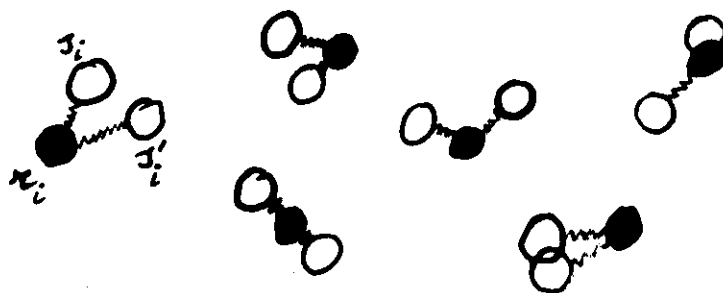
$$R \equiv (\vec{r}_1, \dots, \vec{r}_N)$$

$$S \equiv (\vec{s}_1, \dots, \vec{s}_N)$$

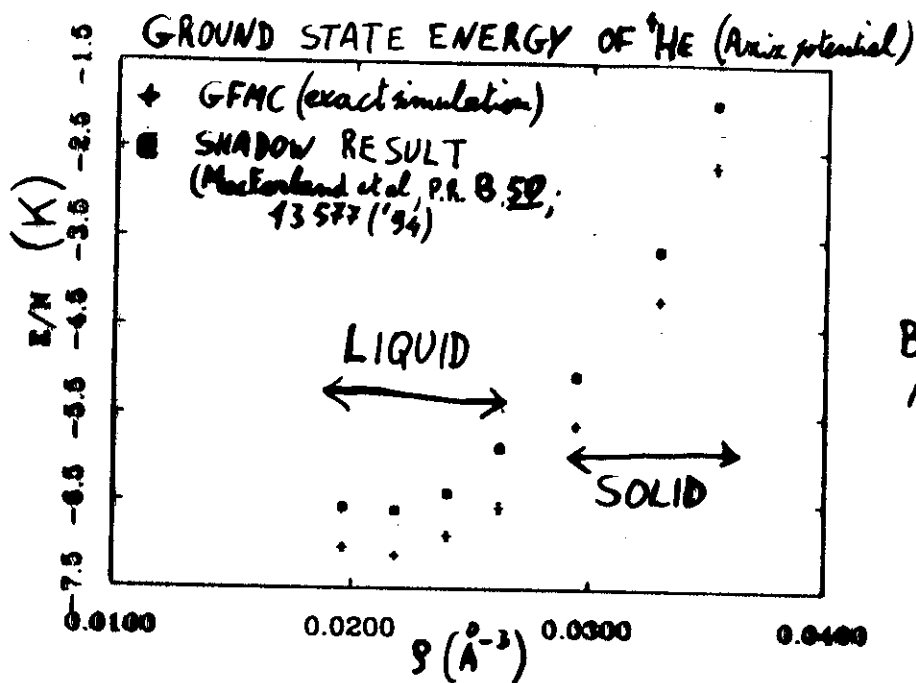
$$S' \equiv (\vec{s}'_1, \dots, \vec{s}'_N)$$

AVERAGE COMPUTED WITH METROPOLIS MONTE CARLO

N atoms $\Rightarrow 3N$ variables



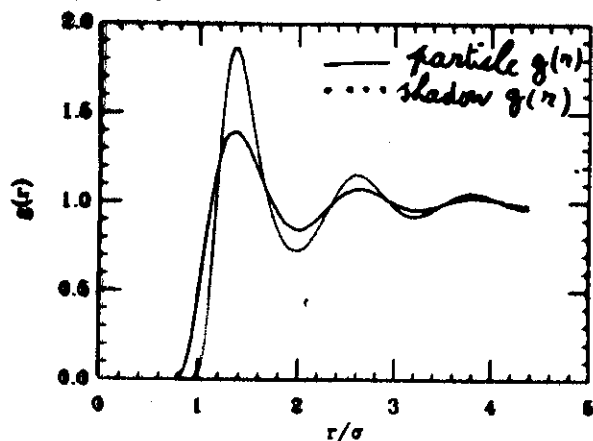
equivalent to a canonical average
for a chemical system of flexible
triatomic molecules



SHADOW WF: unique form describes either a liquid or a solid, depending on density

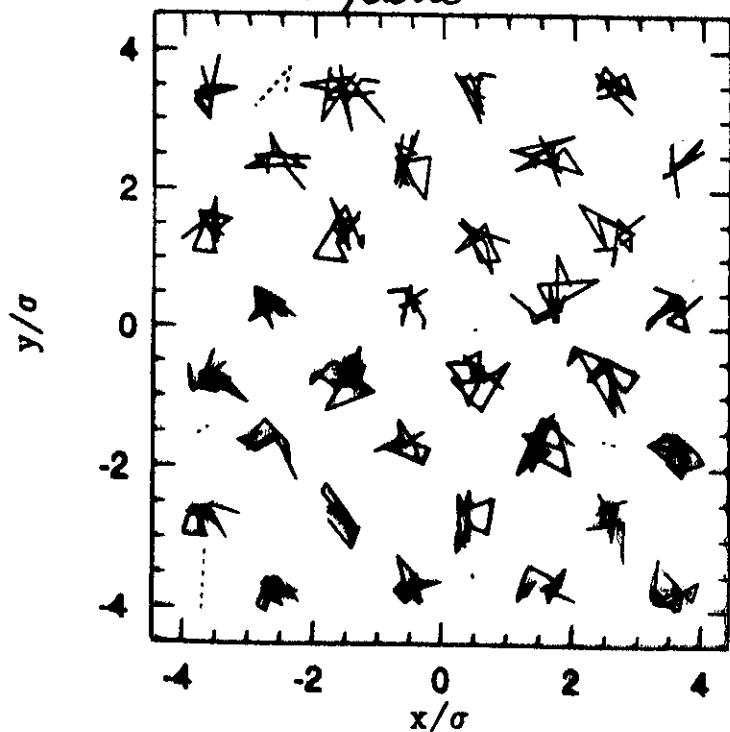
BROKEN SYMMETRY DUE TO MANY BODY CORRELATIONS

LIQUID PHASE



Shadow variables are much more localized than particles and induce strong many body coupling between the particles

SOLID PHASE: projection of particle positions on a plane



LINDEMANN RATIO $\gamma = \frac{\sqrt{\langle (x - \bar{x})^2 \rangle}}{d}$

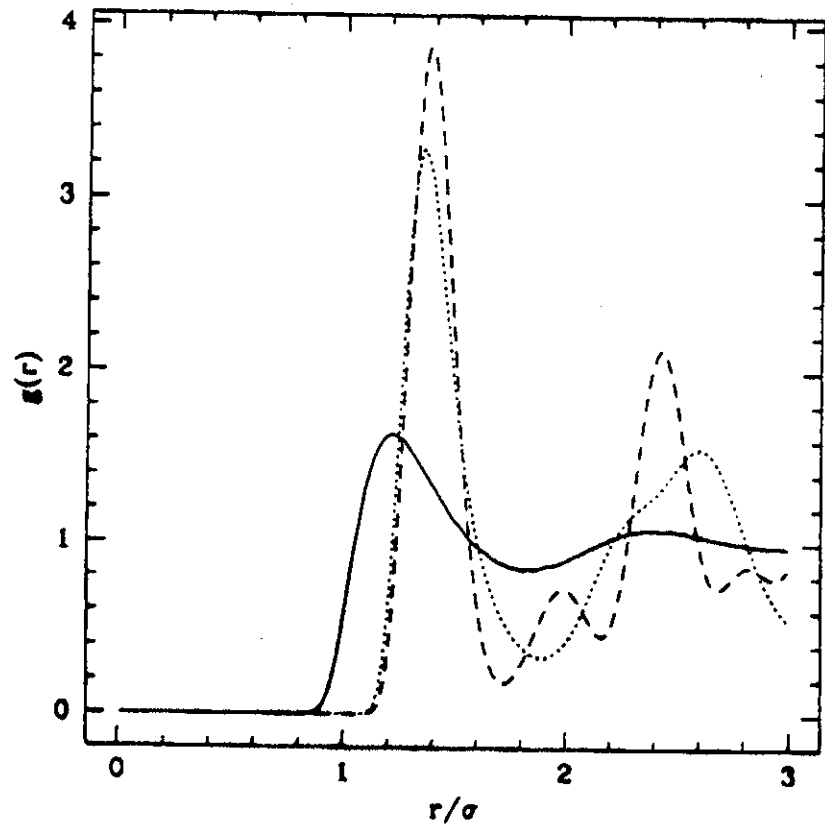
$\gamma = 0.27$ particles

$\gamma = 0.20$ shadow

$$N=108$$

$$\rho V = 0.5$$

— initial condition (compressed liquid)
... after 10^5 Monte Carlo steps
--- after 2×10^5 MCS



PROBABILITY IN CONFIGURATION SPACE

CLASSICAL PARTICLES

$$P(R) \propto e^{-\beta \sum_{i < j} v(r_{ij})}$$

solidification due to
pair terms only $\Rightarrow$ strong steric
constraints

QUANTUM PARTICLES

$T=0K$

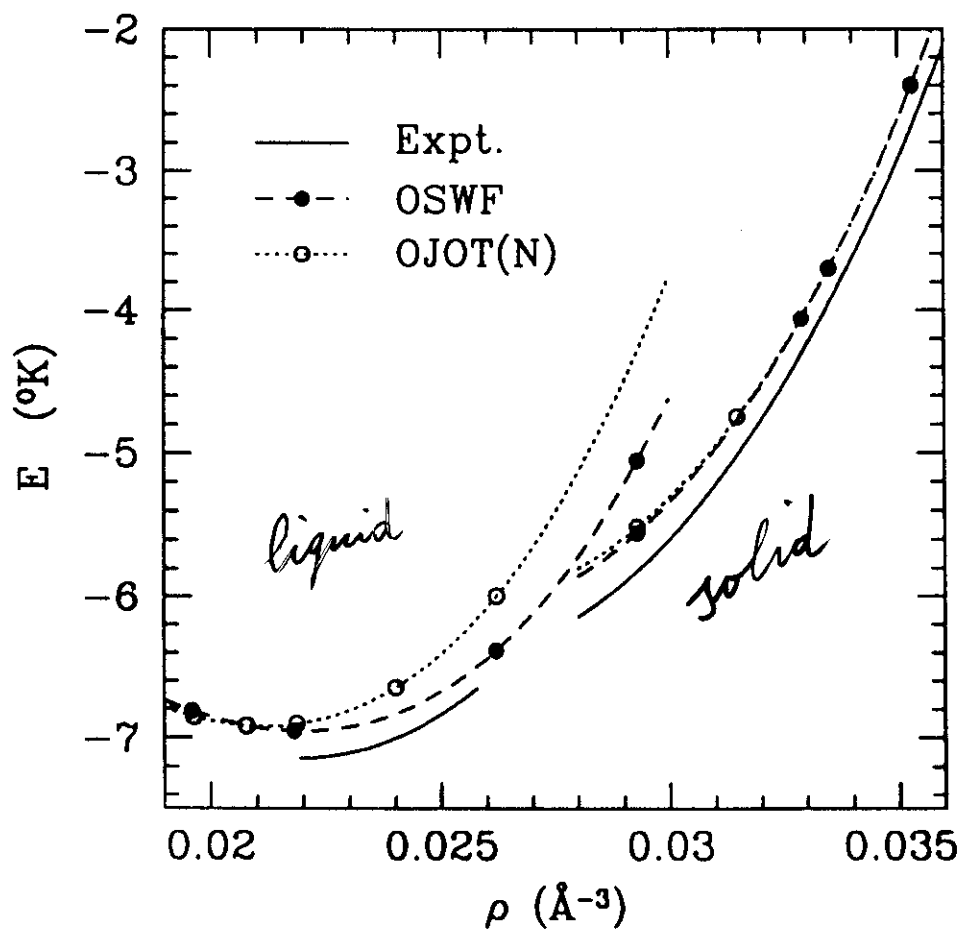
$$P(R) = |\psi_0(R)|^2$$

essential role of terms
beyond the pair and
triplet terms } effect of
quantum hole
of delocalization

GROUND STATE ENERGY OF ⁴He

fully optimized shadow vs optimized (Jastrow+triplet)
and experiment

VMC calcs. with HFDHE2 vs. Expt.



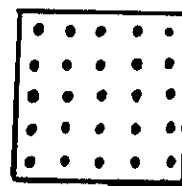
	density ($\text{\AA}^{-3}$)		
	equilibrium	freezing	melting
fully opt. shadow	0.0220	0.0253	0.0232
experiment	0.0218	0.0258	0.0280

ONE VACANCY IN SOLID ^4He

ground state : shadow w/f for N atoms
in volume V which fits
the crystalline order

$$\text{density } \rho = N/V$$

$$\text{energy } E(V, N)$$



initial
state

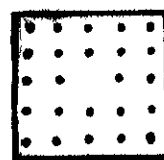
1-vacancy state : same w/f for $N-1$ atoms
in volume V'

$$V' = V \frac{N-1}{N}$$

so the average density
is the same

$$\rho = \frac{N-1}{V'} = \frac{N}{V}$$

$$\text{energy } E(V', N-1)$$



initial
state

energy of formation of a vacancy

$$\Delta E_{\text{vac}} = E(V', N-1) - \frac{N-1}{N} E(V, N)$$

energy of formation for a static vacancy

$$\Delta_{\text{vac}}^{\text{stat}} = - \frac{\langle \text{potential en.} \rangle}{N} - v \frac{\partial E(v)}{\partial v}$$

$$v = \frac{V}{N}$$

$$E = E/V$$

computational details: 1979 Aziz pair interaction pot. $v_A(r)$

$$\Psi(R) = e^{-\frac{1}{2} \sum_{i,j} u_{pp}(r_{ij})} \int dS e^{-\sum_i u_{ps}(\vec{r}_i - \vec{s})} e^{-\sum_{i,j} u_{ss}(r_{ij})}$$

$$u_{pp}(r) = (b/r)^5$$

b, c, δ, d : variational parameters

$$u_{ps}(r) = C r^2$$

MC sampling: collective

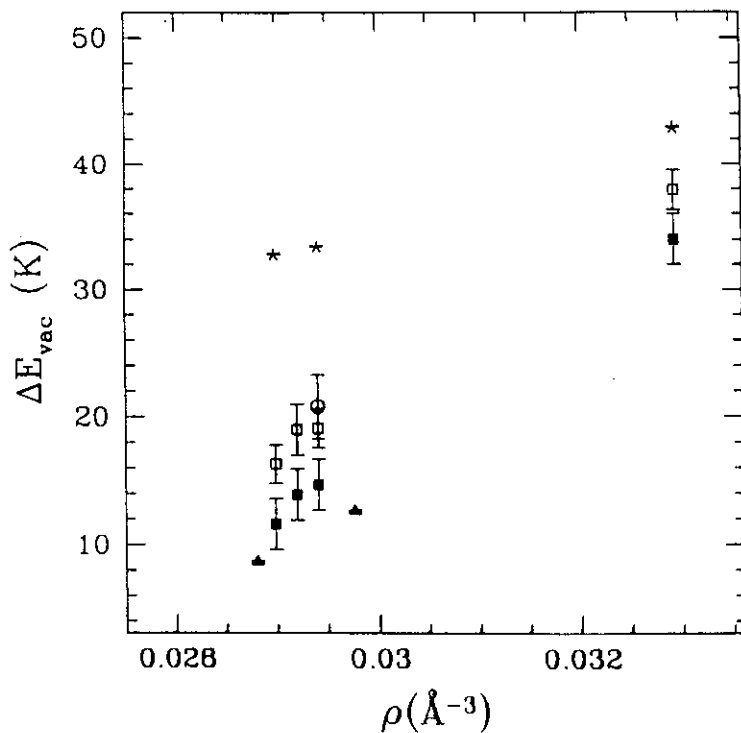
$$u_{ss}(r) = \delta v_A(r)$$

"trimer" moves by smart MC

computations for fcc ($N=108, 256$) crystal

hcp ($N=180$)

bcc ($N=54$)

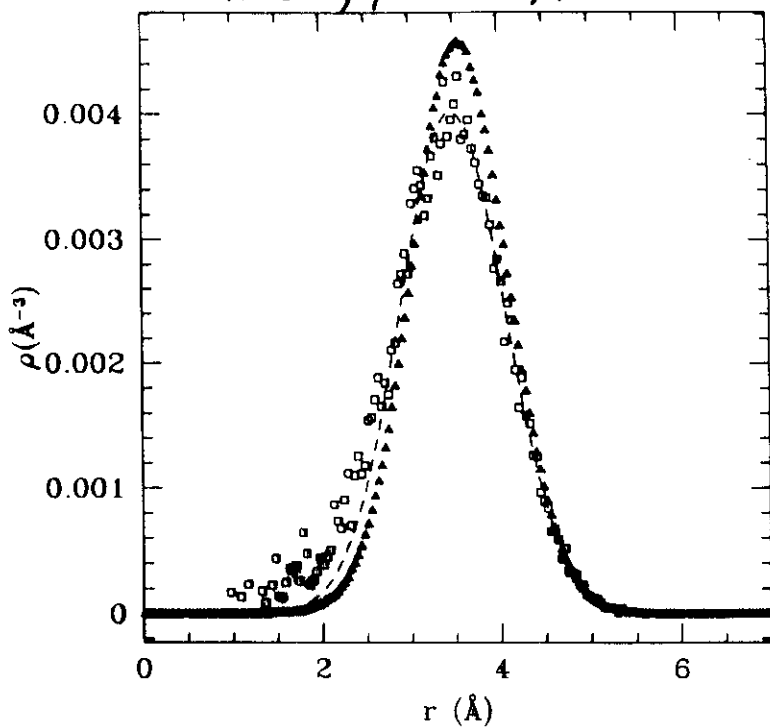


- hcp
- fcc
- bcc
- * energy for a static vacancy
- ▲ experiment
(Fress, Granfors, Simons '89)

F. Pedernini, G.V. Chester, S. Fantoni and L.R. (Phys. Rev. B 1997)

nearest neighbor density
around a lattice site

$N=255$, fcc lattice, $\rho=0.0294 \text{ \AA}^{-3}$



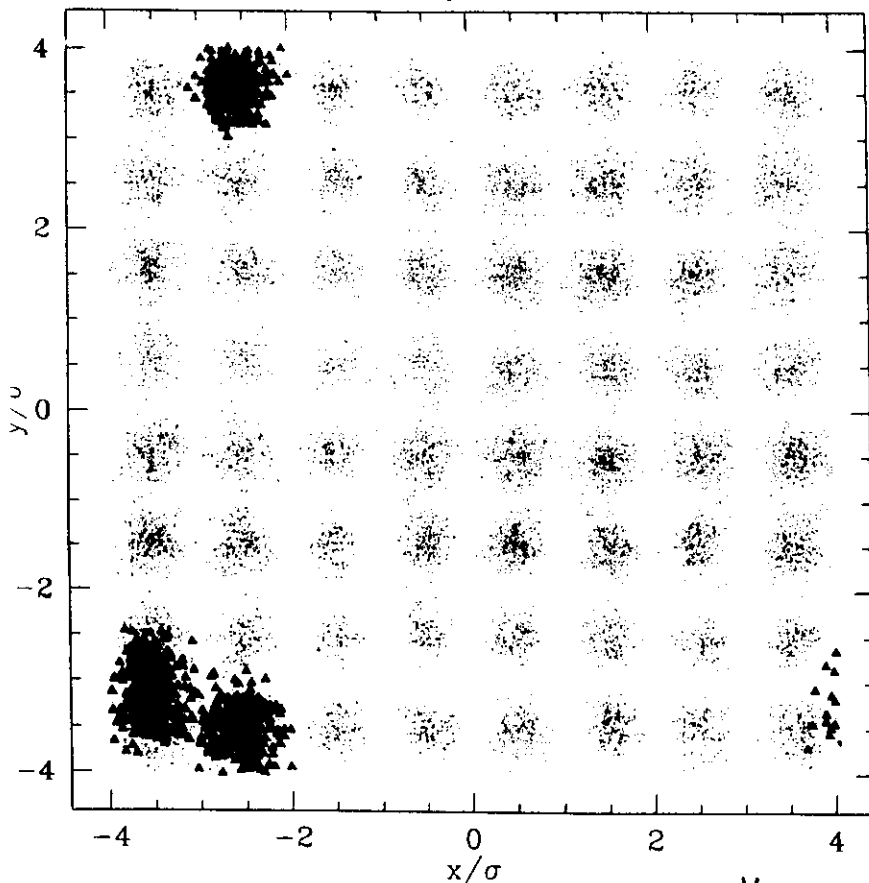
• perfect crystal

□ density around an empty site in the crystal with one vacancy

-- gaussian fit of the outer part of the density around an empty site

measure of relaxation and asymmetry around a vacancy

projection on x-y plane of position of atoms
for a number of configuration along the MC run ($N=255$, fcc lattice, $\rho=0.0294 \text{ \AA}^{-3}$)



• positions of generic atoms

▲ positions of one specific atom

particles jump from one crystal position to another

no such jumps are seen in the perfect crystal

LOCAL DENSITY SHADOW WAVE FUNCTION

In order to be able to describe a two-phase coexistence we need to describe both the phases with the same wave function. Shadow Wave Function alone does not match this requirement.

Problem

Can we describe the solid and the liquid with a unique set of parameters (i.e. with the same wave function?)

Solution

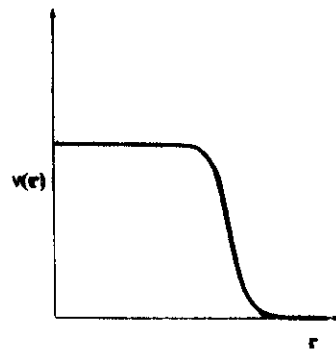
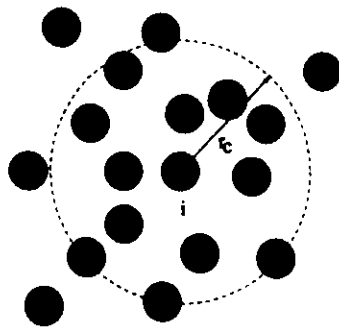
Promote the variational parameters to operators dependent on some local property of the system, as the local density.

$$\alpha \longrightarrow \alpha(\hat{\rho}_i)$$

The local density operator $\hat{\rho}_i$ is defined as:

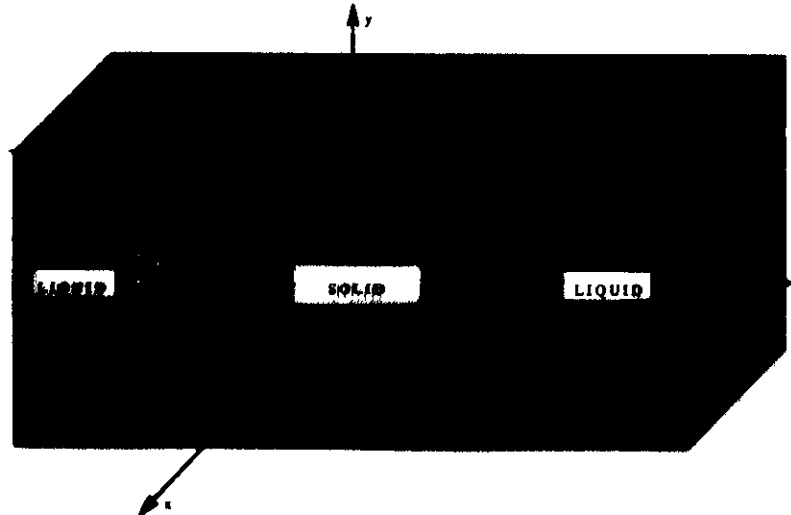
$$\hat{\rho}_i = \frac{1}{A} \sum_{j=1}^N \nu(r_{ij}) \quad \nu(r) = \frac{1}{1 + e^{-\mu(r-r_c)}}$$

and it measures the density within a radius r_c around the particle of coordinates $\vec{r}_i$



THE SIMULATIONS

Initial Configuration



Periodic boundary conditions are imposed in all directions.

- The number of particles employed is very high (1900–4000)
- Simulations require very long CPU time
- Simulation of $\{111\}$ and $\{100\}$ interfaces of a fcc crystal

as interatomic interaction the '79 Aziz pair potential is used

From the analysis of the results obtained in the homogeneous phases we can infer that most of the properties of the phase transition are driven by the shadows. In particular it is enough to make only the parameters in $\varphi_S(S)$ dependent on the local density in order to stabilize the coexistence. The explicit forms of the functions $\varphi(R)$ and $\varphi_S(S)$ are:

$$\varphi(R) = \prod_{i < j} \exp(-b/r_{ij})^5$$

$$\varphi = \prod_{i < j} e^{-\left(b_s/s_{ij}\right)^9}$$

$$\varphi_S(S) = \prod_{i < j} \exp\left(-\frac{b_0 + b_1 \frac{\rho_i + \rho_j}{2}}{s_{ij}}\right)^9$$

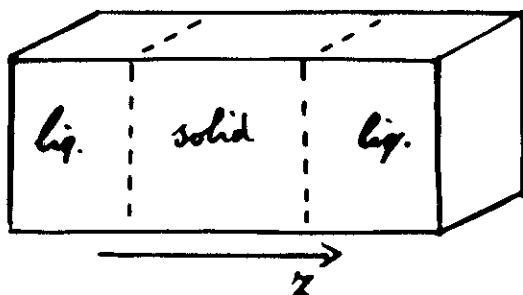
b, b_0, b_1 are variational parameters.

Computations have been performed for the solid-liquid coexistence and interface in ^4He .

See:

F.Pederiva, A. Ferrante, S. Fantoni and L. Reatto,
Phys. Rev. Lett. **72**, 2589, (1994).

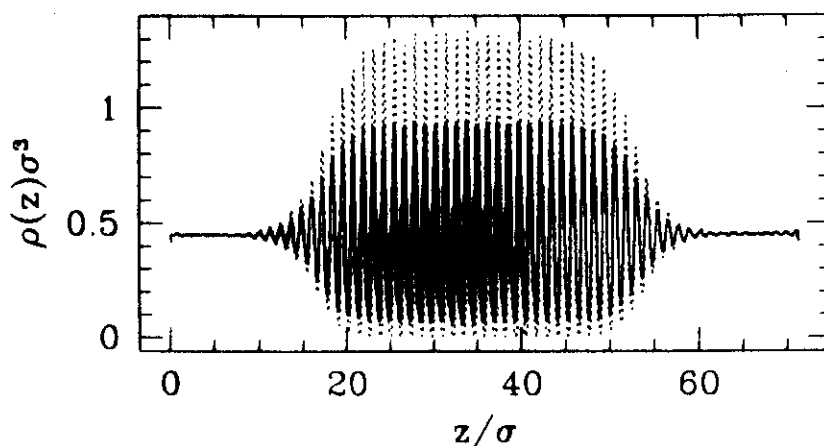
- When the average density ρ falls in a certain range, the coexistence of liquid and solid is stable, outside the system melts or freezes.
- The interface is mobile, but the fraction of liquid and of solid reaches a stationary value which depends on ρ but not on initial conditions.



DENSITY PROFILES ($\{111\}$ INTERFACE)

Fine scale density profile

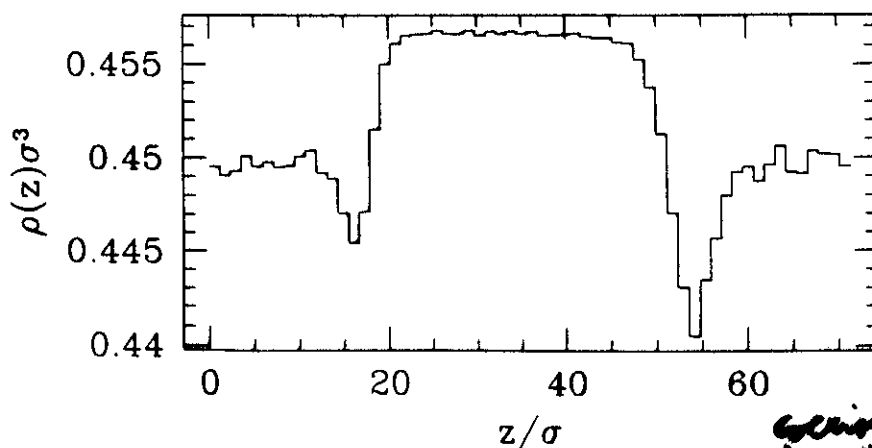
$$\rho(z) = \left\langle \frac{N_i}{\Delta z A} \right\rangle \quad A = x-y \text{ area}, \quad \Delta z \sim 0.2 \text{ \AA}$$



$$\sigma = 2.556 \text{ \AA}$$

Layer-based density profile

$$\rho(z) = \left\langle \frac{N_i}{\Delta z A} \right\rangle \quad A = x-y \text{ area}, \quad \Delta z \sim 3 \text{ \AA}$$



$$-\rho_{\text{sl}} \sigma^3 \approx 0.458$$

$$-\rho_{\text{li}} \sigma^3 \approx 0.450$$

$$\frac{\Delta \rho}{\rho} = 1.8\%$$

Experiment
 $\rho_{\text{melting}} \sigma^3 = 0.468$
 $\rho_{\text{li}} \sigma^3 = 0.430$

$$\frac{\Delta \rho}{\rho} = 8.5\%$$

existence in the correct density range
 jump in density much smaller than experiment

previous computation was based not on the best form of shadow wave function

we have extended the previous computation by using a more accurate form of shadow wave function

$$\Psi(R) = \varphi(R) \int dS K(R, S) \varphi(S) \quad \begin{array}{l} R = \{\vec{r}_1, \dots, \vec{r}_N\} \\ S = \{\vec{s}_1, \dots, \vec{s}_N\} \end{array}$$

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

$$\varphi(R) = \prod_{i < j} e^{-(b/r_{ij})^5}$$

$$\varphi(S) = \prod_{i < j} e^{-\delta v(\alpha s_{ij})}$$

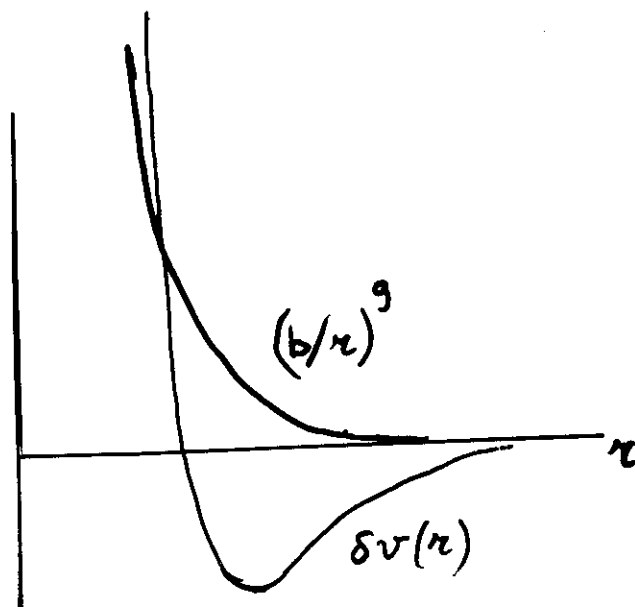
δ, α variational parameters
 $v(r)$ interatomic potential
 (79 Aziz form)

at equilibrium density this wf gives $E_0 = -6.6$ K/atom (exp. -7.14,

LOCAL DENSITY W.F.

$$\alpha \rightarrow \alpha(\hat{\rho}) = \alpha_0 + \alpha_1 \hat{\rho}$$

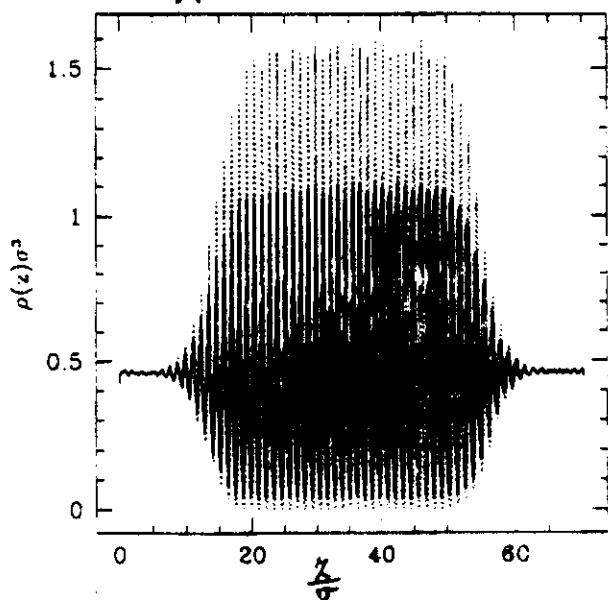
results from
 F. Raderiva, S. Fantoni and L.R.
 (Israel J. Phys. 46 (1996) 277)



local density, fine scale

{111} interface

$\sigma = 2.556 \text{ \AA}$



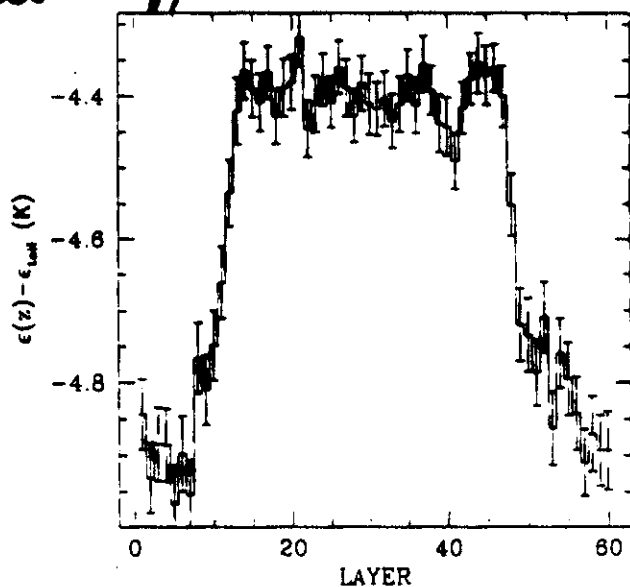
average density $\rho \sigma^3 = 0.471$

$\rho_{\text{sol}} \sigma^3 = 0.479$

$\rho_{\text{liq}} \sigma^3 = 0.462$

$$\frac{\Delta \rho}{\bar{\rho}} = 3.6\%$$

local energy

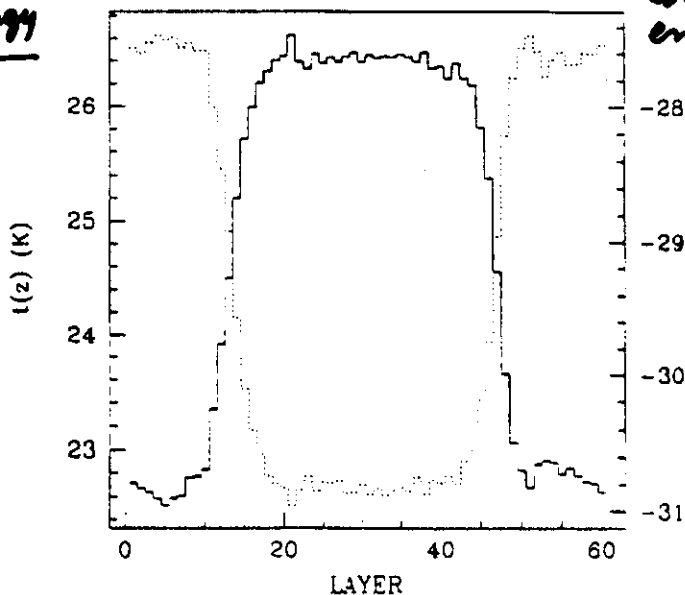


$$\Delta E_{\text{liq-solid}} = -0.5 \text{ K/atom}$$

from experiment

$$\Delta E_{\text{liq-solid}} = -0.82 \text{ K/atom}$$

local kinetic energy



local potential energy -----

$$\Delta \text{kinetic ener.} \approx 3.8 \text{ K/atom}$$

$$\Delta \text{potential ener.} \approx 3.2 \text{ K/atom}$$

INTERFACIAL ENERGY

$$\epsilon(v) = \epsilon(v_m) \cos^2 \theta + \epsilon(v_f) \sin^2 \theta + \frac{2S}{N} \sigma_{\text{int}}$$

We can fit σ_{int} from the calculated total energies For the $\{100\}$ interface :

$$\sigma_{\text{int}} = 0.18 \pm 0.07 \text{K}/\text{\AA}^2$$

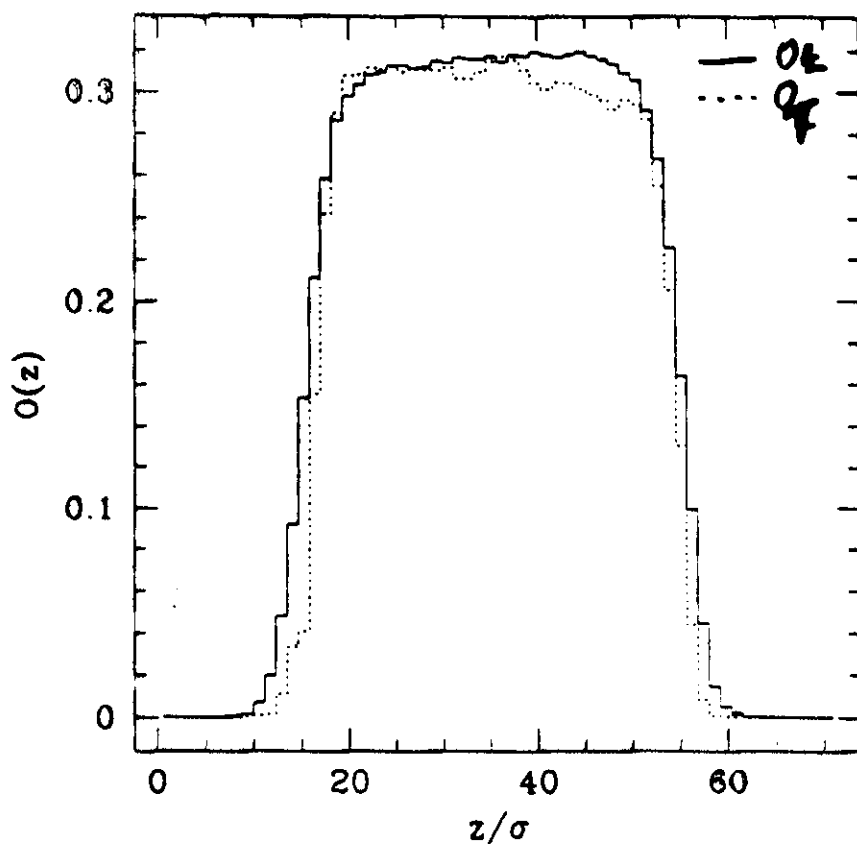
For the $\{111\}$ interface :

$$\sigma_{\text{int}} = 0.16 \pm 0.09 \text{K}/\text{\AA}^2$$

Error is mostly due to the uncertainty on the values of the freezing and of the melting densities.

- CONSISTENT WITH EXPERIMENTAL VALUES
- INDEPENDENT ON THE PARAMETRIZATION

Experiments refer to basal plane of a hcp crystal and to a finite temperature



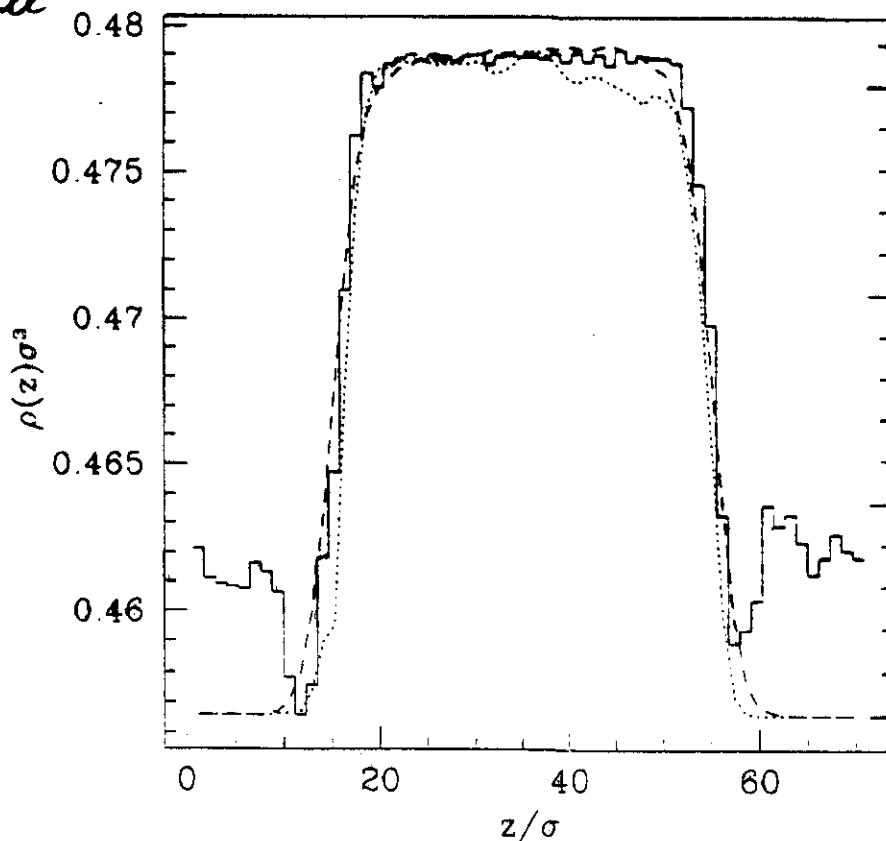
--- transverse O.P.: O_T
 — longitudinal O.P.: O_L

$$O_G(z) = \left| \left\langle \frac{1}{N_s} \sum_{\vec{k} \in k\text{-th layer}} e^{i\vec{G} \cdot \vec{r}_i} \right\rangle \right|^2$$

$\vec{G}$: reciprocal lattice vector

interfacial width $\approx 24 \text{ \AA}$
 the transverse order parameter
 decays somewhat faster than
 the longitudinal one

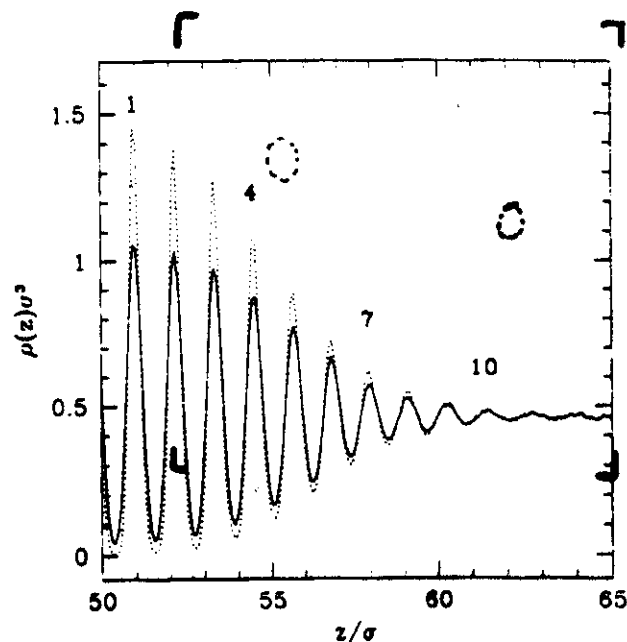
density
 profile



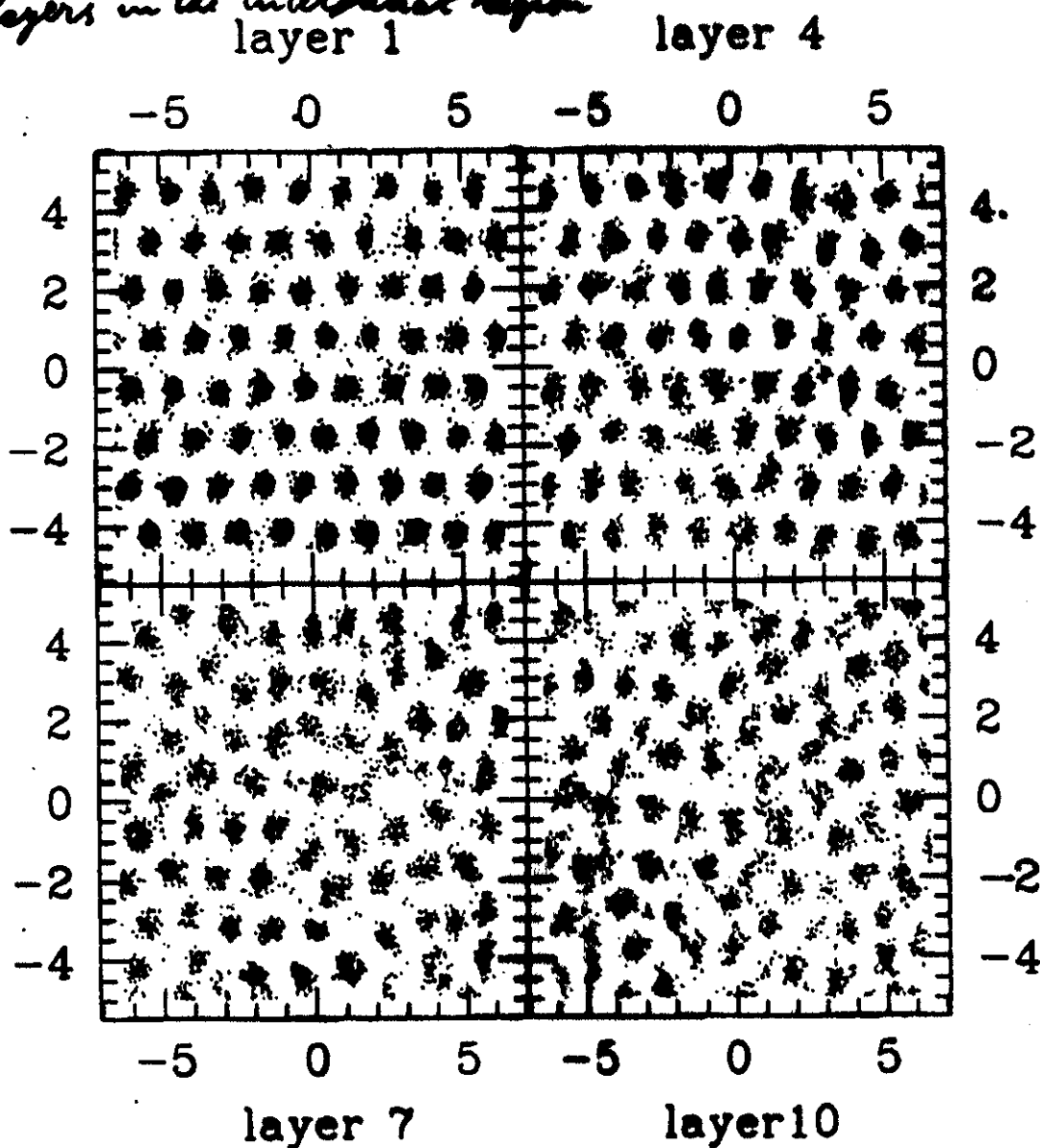
order
 parameters --- O_L
 O_T

the local density has
 a dip at the interface
 in layers in which
 $O_L \neq 0$ and $O_T \approx 0$

up



projections on the X-Y plane of the
He positions of atoms belonging
to some layers in the interfacial region



He impurity and the liquid-solid interface of ^4He : there is experimental evidence for a bound state (Carmichael '89) (Rolley et al. '95)

first attempt of a microscopic theory:

Lehner-Feynman theory
1 impurity, $N-1$ ^4He atoms

$$\Psi(R) = f(\vec{r}_1) \Psi_0(R) \quad \Psi_0: \text{ground state of } N \text{ } ^4\text{He atoms}$$

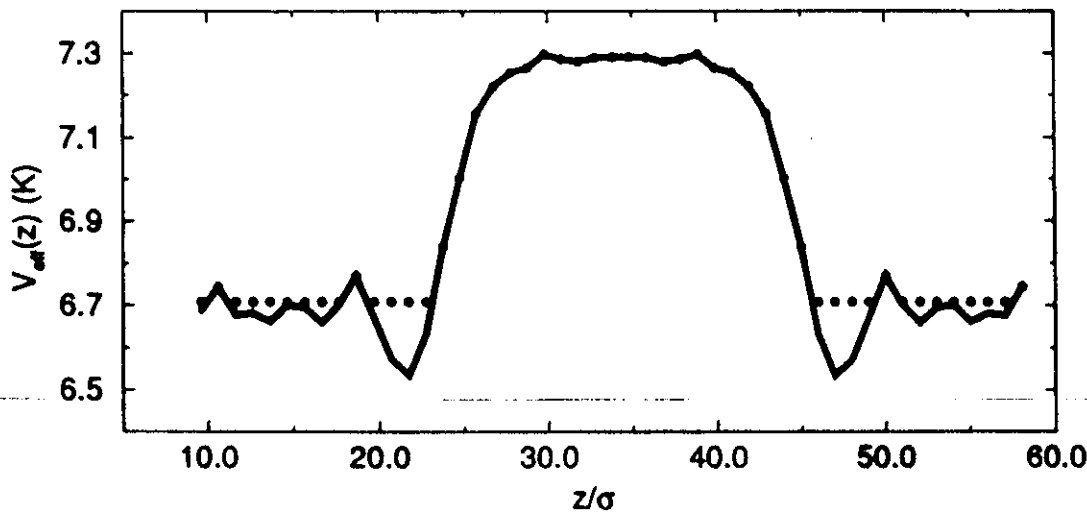
$$f(\vec{r}_1) \text{ solution of } -\frac{\hbar^2}{2m_I} \nabla^2 \varphi(\vec{r}_1) + V_{\text{eff}}(\vec{r}_1) \varphi(\vec{r}_1) = \mu_I \varphi(\vec{r}_1)$$

$$\varphi(\vec{r}) = \sqrt{\rho(\vec{r})} f(\vec{r})$$

μ_I : chemical potential of impurity

V_{eff} : function of $\rho(\vec{r})$, $g(r)$ and local kinetic energy

V_{eff} computed from the results of the previous computation



We find $\mu_I = 6.7 \text{ K} \approx$ chemical potential of ^3He in bulk ^4He : no bound state

(F. Pedersen, F. Dalfovo, S. Stringari, S. Fantoni and L.R., Phys. Rev. B 55, 3122 (1997))

within this approximation only the average density profile enters the computation, the density dip is not enough to trap an ^3He atom

non-uniformity of interface is important: vacancies in the interface act as trapping sites?

CONCLUSION

disorder phenomena is within reach of microscopic theory,
the shadow wave function technique is very useful

- VACANCY

- we allow for a mobile vacancy with relaxation around it
- formation energy is strongly density dependent
- evidence for bound state vacancy - ^3He impurity

- LIQUID-SOLID INTERFACE

- full Born symmetry is preserved and disorder phenomena at the interface are automatically taken into account
- interfacial width $\approx 24\text{\AA}$
- the transverse order parameter decays faster in the liquid than the longitudinal one
- the local density has a dip at the interface below the density of the liquid ($\sim 1\%$)
- some evidence that the interface can be described by crystal planes with very mobile vacancy
- interfacial energy $0.1 \div 0.2 \text{ K/\AA}^2$
- binding of an ^3He atom to the interface is still an open problem

