Bosonic Path Integrals

1. Overview of effect of bose statistics
2. Permutation sampling considerations
3. Calculation of superfluid density and momentum distribution.
4. Applications of PIMC to liquid helium and helium droplets.
5. Momentum distribution calculations

Quantum statistics

- For quantum many-body problems, not all states are allowed: allowed are totally symmetric or antisymmetric. Statistics are the origin of BEC, superfluidity, lambda transition.
- Use permutation operator to project out the correct states:

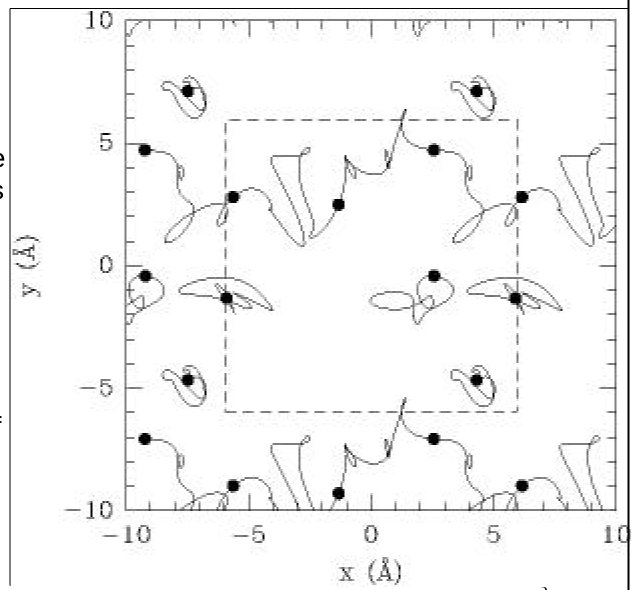
$$\widehat{P} f(R) = \sum_{p=1}^{N!} \tfrac{1}{N!} f(PR)$$

$$Z = \sum_{p=1}^{N!} \tfrac{1}{N!} \int dR_1 \ldots dR_M e^{-\sum_{i=1}^{M} S(R_i, R_{i+1})}$$

- Means the path closes on itself with a permutation. **$R_1 = PR_{M+1}$**
- Too many permutations to sum over; we must sample them.
- PIMC task: sample path { $R_1, R_2, \ldots R_M$ and P} with Metropolis Monte Carlo (MCMC) using "action", S, to accept/reject.

Exchange picture

- Average by sampling over all paths and over connections.
- Trial moves involve reconnecting paths differently.
- At the superfluid transition a “macroscopic” permutation appears.
- This is reflection of bose condensation within PIMC.



3 boson example

- Suppose the 2 particle action is exact.
- Make Jastrow approximation for spatial dependance (Feynman form)

$$\left\langle R \left| e^{-bH} \right| R' \right\rangle = e^{-\sum_i (r_i - r_i')^2} \prod_{i<j} f\left(r_{ij}, r_{ij}'\right) \qquad \text{units with } 4bl = 1$$

$$r_{bose}(R) = \sum_P \left\langle R \left| e^{-bH} \right| PR \right\rangle \sim \left[\sum_P \left\langle R \left| e^{-bH_0} \right| PR \right\rangle \right] \prod_{i<j} f\left(r_{ij}, r_{ij}\right)$$

$$r_{bose}(R) = \left|\Psi(R)\right|^2 \left[1 + e^{-r_{12}^2} + e^{-r_{13}^2} + e^{-r_{23}^2} + 2e^{-r_{12}^2 - r_{23}^2 - r_{13}^2} \right]$$

- Spatial distribution gives an effective attraction (bose condensation).
- For 3 particles we can calculate the “permanent” but larger system require us to sample it.
- Anyway permutations are more physical.

Permutation Sampling

For bosons we also have to move through permutation space. A “local” move is to take an existing permutation and multiply by a k-cycle

$$P_{trial} = \hat{p}(i_1, i_2, \ldots, i_k) P$$

- Sometimes need more than 2-particle exchanges- for fermions 3 particle exchanges are needed
- Need more than 1 time slice because of hard core.

Two alternative ways:

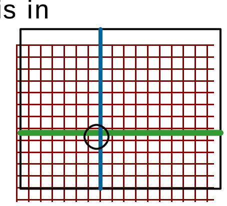
1. Make a table of possible exchanges and update the table. Good for up to 4 particle exchanges “SELECT”
2. Have a virtual table and sample permutation from that table. Good for longer exchanges (up to 10 body exchanges). “PERMUTE”

Heat Bath Method

Sample a neighborhood of a given point so that it is in local equilibrium.

$$T(s \to s') = \frac{p(s')}{C(s)}$$

$$C(s) = \sum_{s' \in N(s)} p(s'')$$



Then the acceptance probability will be: $A(s \to s') = \min\left(1, \frac{C(s)}{C(s')}\right)$

Can only be used if it is possible to quickly compute the normalization.

Acceptance ratio=1 if C(s) is independent of s.

For a given neighborhood, convergence is as fast as possible (it equilibrates in one step).

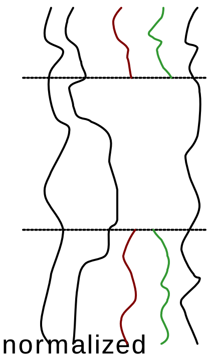
How to select permutation

- Heat bath probability of move being accepted is:

$$T(p) \propto \left\langle p R \left| e^{-nt H} \right| R' \right\rangle \approx \exp\left[-\frac{\sum_j \left(r_j - r_{pj}' \right)^2}{4nl\, t} \right] = \prod_j h_{jPj}$$

$$h_{i,j} = \exp\left[-\frac{\left(r_j - r_i' \right)^2}{4nl\, t} \right] = \text{distance table}$$

Example: $T(1,2) \propto h_{1,2} h_{2,1}$

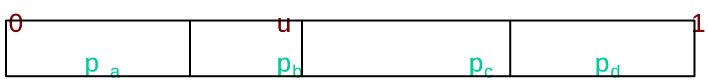


- – Set up “h” matrix
- – Loop over all pairs and find all T(i,j)’s
- – Loop over triplets and find T(I,j,k)’s …
- – In acceptance probability we need the normalized probability: $\hat{T} = \frac{T}{C} \text{ where } C = \sum_p T(p)$
- – This gives an addition rejection rate.

Discrete Distributions

$$c_k = \sum_{i=1}^{k} p_i$$

Any discrete distribution p_k can be sampled by constructing the cumulant.



- Sample 0<u<1.
- Find which region it is in. i.e. find k: $c_{k-1} < u < c_k$
- Return label “k”.

- The search operation can be done by bisection in $\log_2(N)$ steps.

Bisection method

1. Select time slices

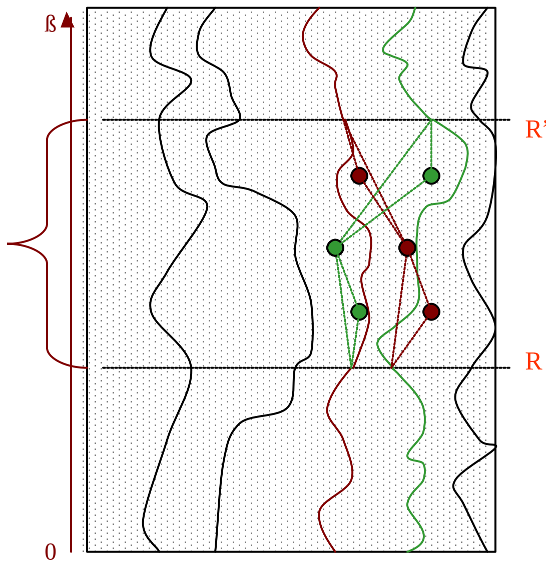
2. Select permutation from possible pairs, triplets, from:

   $r(R,PR';4t)$

3. Sample midpoints

4. Bisect again, until lowest level

5. Accept or reject entire move



Helium phase diagram

•Because interaction is so weak helium does not crystallize at low temperatures. Quantum exchange effects are important

•Both isotopes are quantum fluids and become superfluids below a critical temperature.

•One of the goals of computer simulation is to understand these states, and see how they differ from classical liquids starting from non-relativistic Hamiltonian:

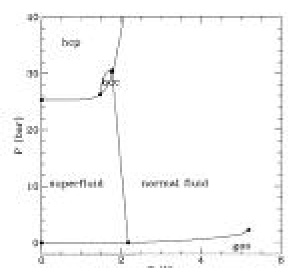


FIG. 3. The phase diagram of ^{4}He.

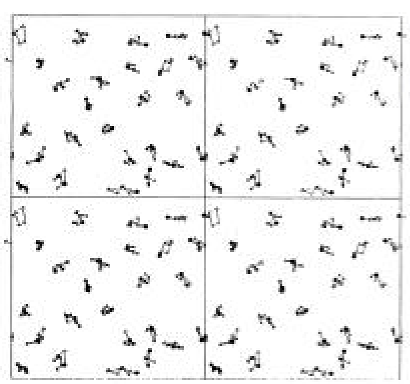
$$\widehat{H} = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + V(R)$$

$$l \equiv \frac{\hbar^2}{2m_i}$$

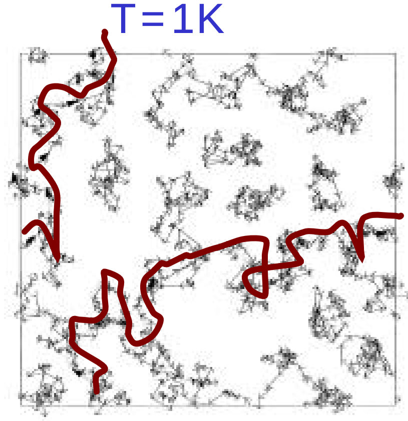
Path Integral explanation of Boson superfluidity

- Exchange can occur when thermal wavelength is greater than interparticle spacing $k_B T \le h^2 r^{2/d}/m$
- Localization in a solid or glass can prevent exchange.
- Macroscopic exchange (long permutation cycles) is the underlying phenomena leading to:
  - Phase transition: bump in specific heat: entropy of long cycles
  - Superfluidity winding paths
  - Offdiagonal long range order--momentum condensation separation of cut ends
  - Absence of excitations (gaps)
- Some systems exhibit some but not all of these features.
- Helium is not the only superfluid. (2001 Nobel Prize for BEC)

T=2.5K



T=1K

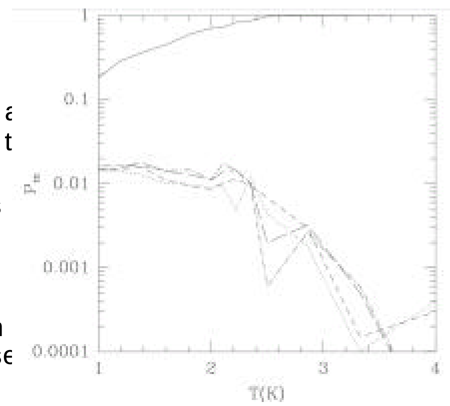


Normal "atomic" state

"entangled" liquid

Permutation Distribution

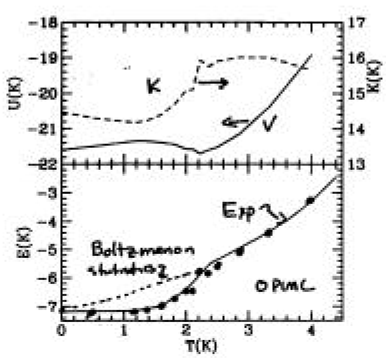
- As paths get longer probability of permutation gets significant.
- Shown is the probability of a given atom attaching itself to a permutation of length n.
- Superfluid transition occurs when there is a non-zero probability of cycle length N=size of system
- Permutations are favored in the polymer system because of entropy. In the quantum system because of kinetic energy.
- Impurities can be used to “measure” the permutations.



ENERGY

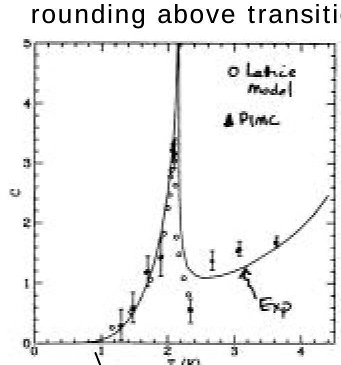
Bose statistics have a small effect on the energy

Below 1.5K ^{4}He is in the ground state.



SPECIFIC HEAT

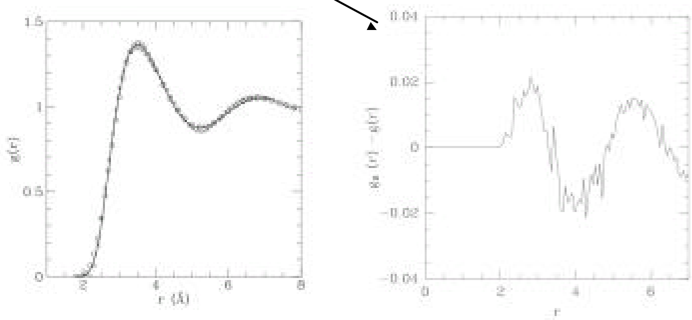
- Characteristic λ shape when permutations become macroscopic
- Finite size effects cause rounding above transition



$$E = \left\langle V + \frac{3N_{cycles}}{2b} + \frac{1}{2}(r_i - c_i)\cdot\nabla_i V \right\rangle$$

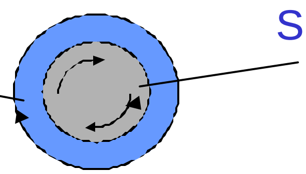
Kinetic term becomes smaller because N_{cycke}<N. Springs stretched more.

- Transition is not in the static distribution functions like S(k) or g(r). They do not change much at the transition. NON-CLASSICAL TRANSITION
- Effect of turning off bose statistics at the transition:



- Transition is in the imaginary-time connections of the paths-the formation of the macroscopic exchange.

Superfluidity and PIMC



rotating disks:

Andronikashvili's expt (1946)

$$(\rho_s + \rho_N \equiv \rho)$$

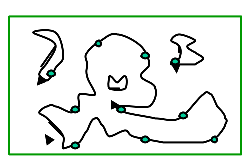
- We define superfluidity as a linear response to a velocity perturbation (the energy needed to rotate the system) "NCRI=nonclassical rotational inertia"

$$\frac{\rho_s}{\rho} = 1 - \frac{I}{I_c} = \left.\frac{dF}{d\omega^2}\right|_{\omega=0}$$

- To evaluate with Path Integrals, we use the Hamiltonian in rotating frame:

$$\hat{H}_\omega = \hat{H}_0 - \omega \hat{L}_z$$

$$\frac{\rho_s}{\rho} = 1 - \frac{1}{I_c}\left\langle \int_0^\beta dt\, \hat{L}_z\, e^{-(\beta-t)\hat{H}_0}\, \hat{L}_z\, e^{-t\hat{H}_0} \right\rangle$$

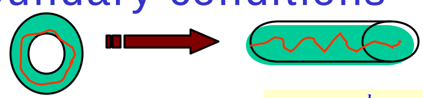


$$\frac{r_s}{r} = \frac{2m}{b\; l}\,\frac{\langle A_z^2 \rangle}{I_c}$$

A = signed area of imaginary-time paths

Winding numbers in periodic boundary conditions

- Distort annulus



- The area becomes the **winding** (average center of mass velocity)

$$W = \sum_{i=1}^{N} \int_0^{\beta} dt \, \frac{dr_i(t)}{dt}$$

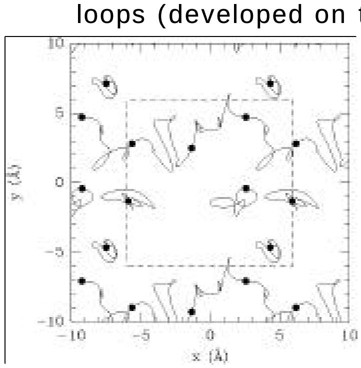
- The superfluid density is now estimated as:

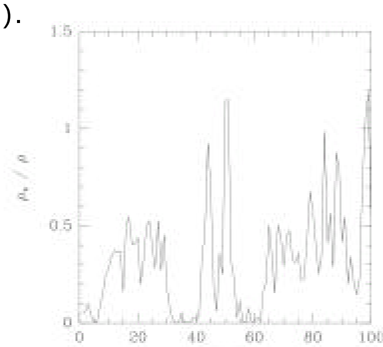
$$\frac{\rho_s}{\rho} = \frac{\langle W^2 \rangle}{2 \lambda \beta N}$$

- Exact linear response formula. (analogous to relation between $\chi \sim \langle M^2 \rangle$ for Ising model.
- Relates **topological** property of paths to dynamical response. Explains why superfluid is "protected."
- Imaginary time dynamics is related to real time response.
- How the paths are connected is more important than static correlations.

Ergodicity of Winding Number

- Because winding number is topological, it can only be changed by a move stretching all the way across the box.
- For cubic boundary conditions we need $m \geq N^{1/3}$
- Problem to study finite size scaling: we get stuck in a given winding number sector.
- Advanced algorithms needed such as worm or directed loops (developed on the lattice).





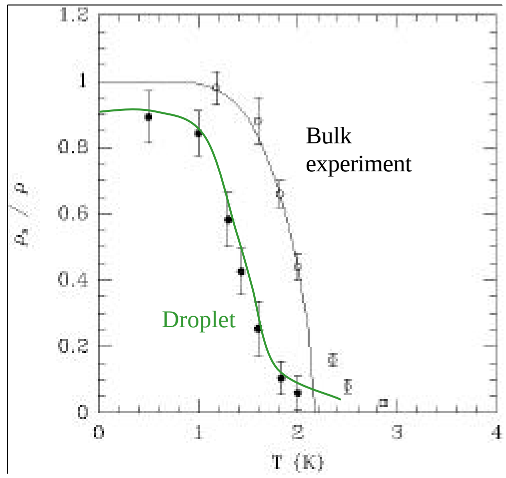
Superfluidity in pure Droplets

$$\frac{r_s}{r} = \frac{2m}{b\ \ l}\frac{\langle A_z^2 \rangle}{I_c}$$

- 64 atom droplet goes into the superfluid state in temperature range 1K <T <2K.

  NOT A PHASE TRANSITION!
- But almost completely superfluid at 0.4K (according to response criteria.)
- Superfluidity of small droplets recently verified.

Sindzingre et al 1990



Determination of T_c

Runge and Pollock PRB.

At long wavelength, the free energy is given by the functional:

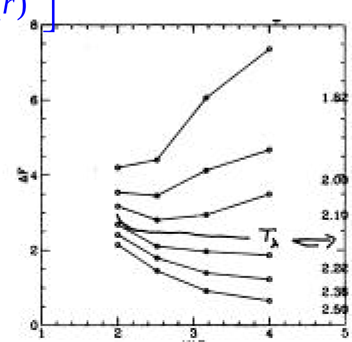
$$F = \int dr \left[l \left|\nabla f(r)\right|^2 + m\left|f(r)\right|^2 + V f(r)^4 \right]$$

The energy to go from PBC to ABC is given by:

$$F = \frac{m\, l\, p^2 L^{d-2}}{V} = -k_B T \left\langle e^{iWp/L} \right\rangle$$

We determine T_c by where F is constant with respect to number of atoms N.

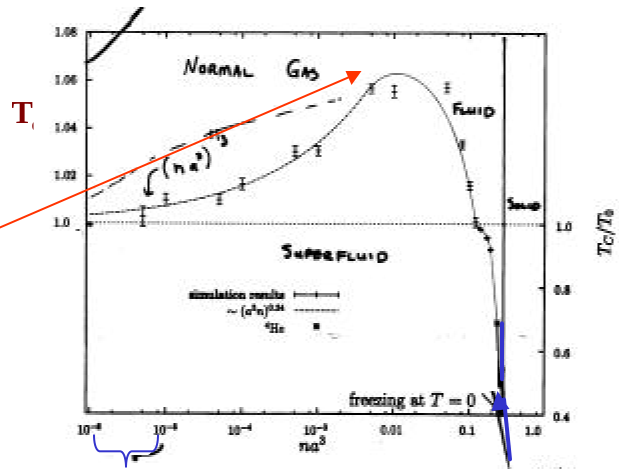
For N~100 , T_c correct to ~1%.



Phase Diagram of Hard Sphere Bosons

- Atomic traps are at low density
- With PIMC we mapped out range of densities
- There is an enhancement of T_c by 6% because of density homogenization.

Gruter et al PRL 99.



$T_c / T_{c0} \sim 1 + n^{1/3} a$

Density of atom traps

Liquid ^{4}He

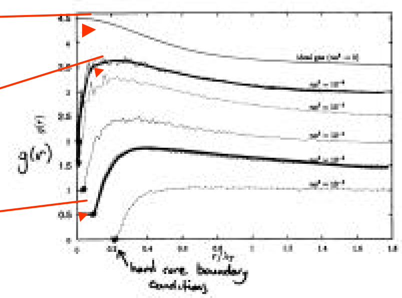
Ceperley PIMC for bosons 23

Pair correlations at low density

Free boson pair correlation.

Peak caused by attraction of bosonic exchange.

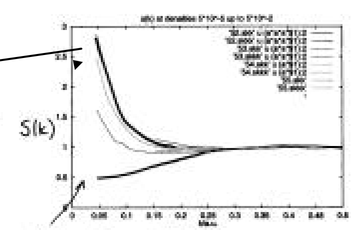
Zero is hard core interaction.



Structure Factor S(K)

(FT of density)

Large compressiblity near T_c (clustering)



Ceperley PIMC for bosons 24

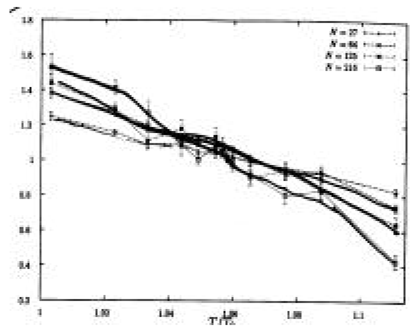
Determination of T_c using superfluid density. Finite size scaling.

$$r_s = \frac{1}{L} Q\left(\frac{L}{z}\right)$$

z = bulk correlation length

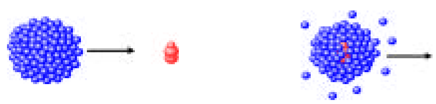
$$z \to \left(\frac{T - T_c}{T_c}\right)^{-n}$$

- Near T_c a single length enters into the order parameter.
- Write superfluid density in terms of the available length.
- Determine when the curves cross to get T_c and exponent.
- Exponent is known or can be computed.

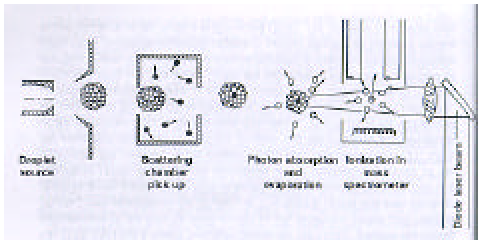


Droplets and PIMC

E. Draeger (LLNL) D. Ceperley(UIUC)



- Provide precise microscopic probes for phenomenon such as superfluidity and vortices.
- Provide a nearly ideal “spectroscopic matrix” for studying molecular species which may be unstable or weakly interacting in the gas phase.
- PIMC can be used to simulate ^{4}He droplets of up to 1000 atoms, at finite temperatures containing impurities, calculating the density distributions, shape deformations and superfluid density.
- Droplets are well-suited to take advantage of the strengths of PIMC:
  - Finite temperature (T=0.38 K)
  - Bose statistics (no sign problem)
  - Finite size effects are interesting.



Experimental Setup for He droplets

Toennies and Vilesov,
Ann. Rev. Phys. Chem. 49, 1 (1998)

- Adiabatic expansion cools helium to below the critical point, forming droplets.
- Droplets then cool by evaporation to:

  T=0.38 K, $N \approx 10^4$ (^{4}He)
  T=0.15 K, $N \approx 10^3$ (^{3}He)

- The droplets are sent through a scattering chamber to pick up impurities, and are detected either with a mass spectrometer with electron-impact ionizer or a bolometer.
- Spectroscopy yields the rotational-vibrational spectrum for the impurity to accuracy of 0.01/cm. Almost free rotation in superfluid helium but increase of MOI of rotating impurities.

Demonstration of droplet superfluidity

Grebenev, Toennies, Vilesov: *Science 279, 2083 (1998)*

- An OCS molecule in a ^{4}He droplet shows rotational bands corresponding to free rotation, with an increased moment of inertia (2.7 times higher)

  → ^{4}He are “coat” the impurity allowing it to freely rotate in the superfluid

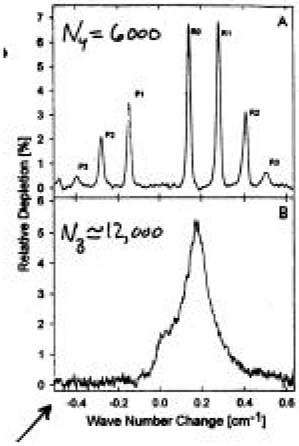
- They replaced boson ^{4}He with fermion ^{3}He. If Bose statistics are important, then rotational bands should disappear. → they didn’t!
- However, commercial ^{3}He has ^{4}He impurities, which would be more strongly attracted to an impurity.

  → How much ^{4}He does it take to “coat” the impurity and get free rotation?

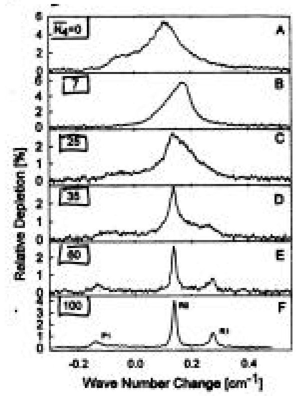
- They found that it takes around 60 ^{4}He atoms.

^4He

^3He



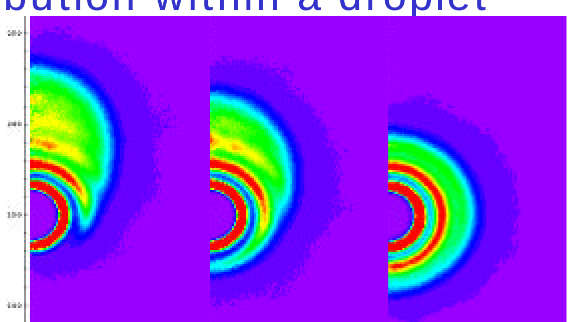
Small impurities of ^4He in ^3He



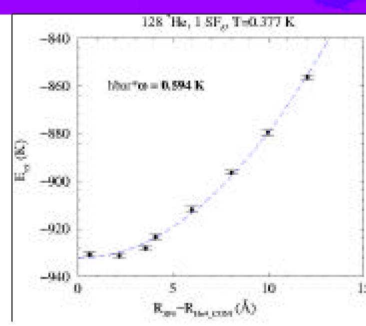
^4He is more strongly attracted to impurity because of zero point effects, so it coats the impurity, insulating it from the ^3He.

Density distribution within a droplet

- Helium forms shells around impurity (SF_6)
- During addition of molecule, it travels from the surface to the interior boiling off 10-20 atoms.



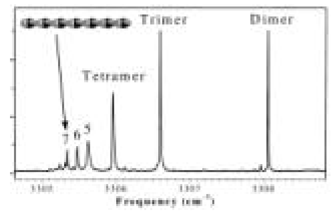
- How localized is it at the center?
- We get good agreement with experiment using the energy vs. separation from center of mass.



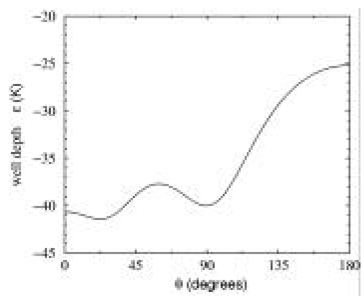
$(HCN)_x$: Self-Assembled Linear Isomers

Nauta and Miller: HCN molecules in ^{4}He droplets self-assemble into linear chains

- They measured the rotational constants for $(HCN)_1$, $(HCN)_2$, and $(HCN)_3$.
- Adiabatic following holds for $(HCN)_3$, allowing us to compare both models to experiment.
- Line vortices are unstable in pure helium droplets. Linear impurity chains may stablize and pin them.

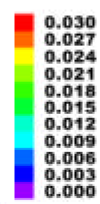


K. Nauta, R. E. Miller, Science **238**, 1895 (1999).

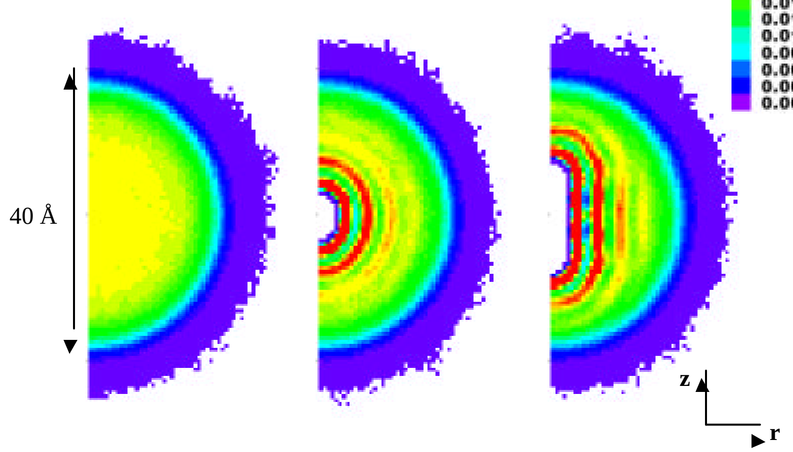


Atkins and Hutson: Calculated the anisotropic ^{4}He-HCN pair potential from experimental scattering data. This fit can be reproduced within error bars by a sum of three spherical Lennard-Jones potentials and a small anisotropic term.

Density Distribution of ^{4}He+$(HCN)_x$ Droplets



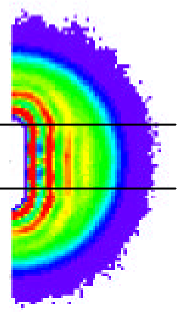
T=0.38 K, N=500



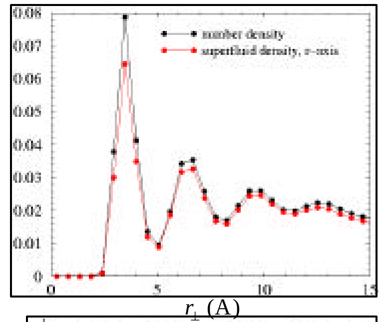
pure 1 HCN 3 HCN

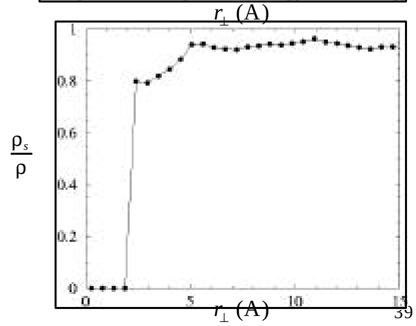
Local Superfluid Reduction

Average over region with cylindrical symmetry



T=0.38 K, N=500 $(HCN)_3$





The local superfluid estimator shows a decrease in the superfluid response throughout the first solvation layer.

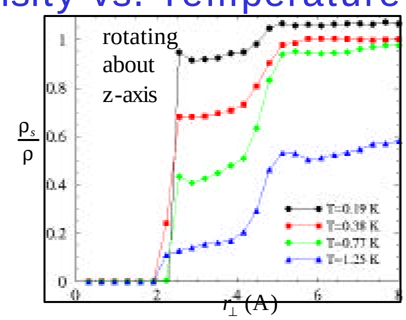
Local Superfluid Density vs. Temperature

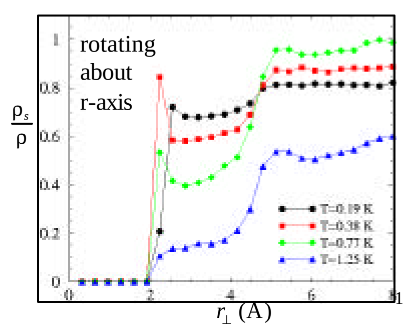
We calculated the superfluid density distribution of N=128 ^{4}He droplets with an $(HCN)_3$ isomer at several temperatures

The superfluid density in the first layer is temperature dependent!

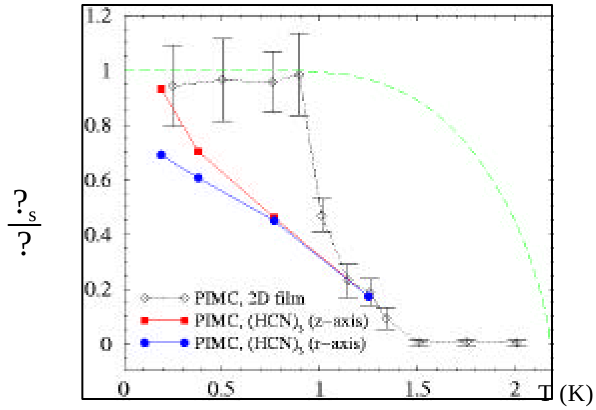
Bulk ^{4}He is 100% superfluid below 1.0 K. Both experimental measurements on helium films and PIMC studies of 2D helium show transition temperatures T_c which are significantly lower than bulk helium.

The first layer is a two-dimensional system with important thermal excitations at 0.4K: “vortex-antivortex excitations”.





First Layer Superfluid Density vs. T



M. C. Gordillo and D. M. Ceperley, Phys. Rev. B **58**, 6447 (1998)

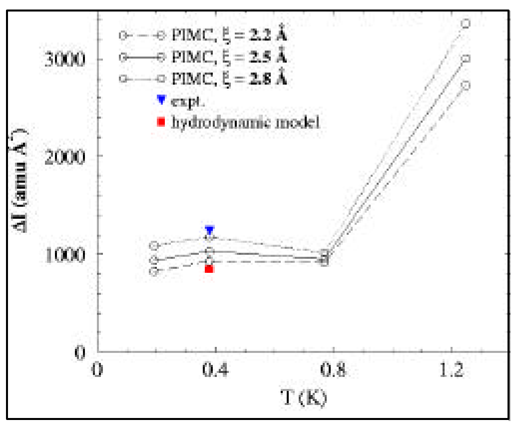
- Very broad transition, due to the small number of atoms in first layer (around 30)
- How will this affect the moment of inertia?

Moment of Inertia

The moment of inertia due to the normal helium does not depend on temperature below 1.0 K.

This is in agreement with experimental results, which found that the moment of inertia of an OCS molecule was the same at T=0.15 K and T=0.38 K.

We only looked at the superfluid density in the cylindrically-symmetric region of the first layer, not the entire first layer.



$$\Delta I = \int_{v(?)} d\vec{r}\, m_4 r_\perp^2 \left(?(\vec{r}) - ?_s(\vec{r})\right)$$

Bose condensation

- BEC is the macroscopic occupation of a single quantum state (e.g. momentum distribution in the bulk liquid).

$$n_k = \int \frac{d^3r d^3s}{(2p)^3 V} \exp(-ik(r-s)) n(r,s)$$

- The one particle density matrix is defined in terms of open paths:

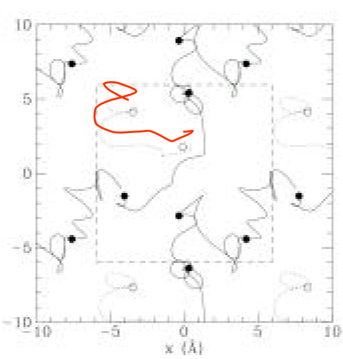
$$n(r,s) = \frac{V}{Q} \int dr_2 ... dr_N \left\langle r, r_2 .. r_N \left| e^{-bH} \right| s, r_2 ... r_N \right\rangle$$

- We cannot calculate n(r,s) on the diagonal. We need one open path, which can then exchange with others.
- Condensate fraction is probability of the ends being widely separated versus localized. **ODLRO** (off-diagonal long range order) (*The FT of a constant is a delta function.)*
- The condensate fraction gives the linear response of the system to another superfluid.

How to calculate n(r)

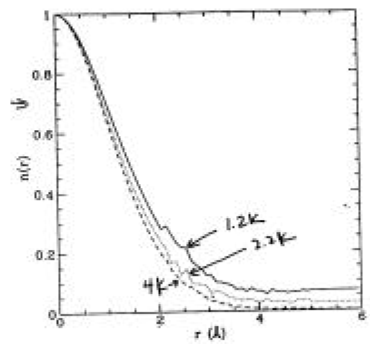
1. Take diagonal paths and find probability of displacing one end.
- advantage:
  - simultaneous with other averages,
  - all time slices and particle contribute.
- disadvantage: unreliable for r>Λ.

2. Do simulation off the diagonal and measure end-end distribution. Will get condensate when free end hooks onto a long exchange.
- advantage: works for any r
- Disadvantage:
  - Offdiagonal simulation not good for other properties
  - Normalization problem.

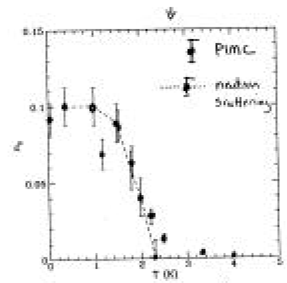


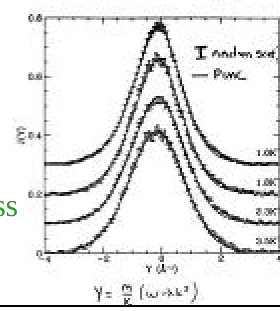
Comparison with experiment

Single particle density matrix



Condensate fraction





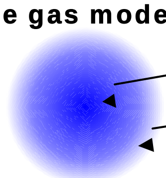
Neutron scattering cross section

Surface of Liquid Helium

2 possible pictures of the surface

- **Dilute Bose gas model:** Griffin and Stringari, PRL 76, 259 (1996).

^{4}He



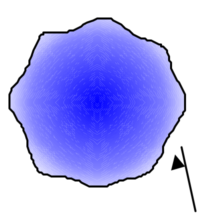
bulk: n_0 = 9%

surface: n_0 = 100%

- **Ripplon model:** Galli and Reatto, J. Phys. CM 12,6009 (2000).

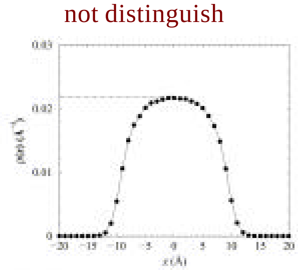
Can smeared density profile be caused by ripplons alone?

^{4}He

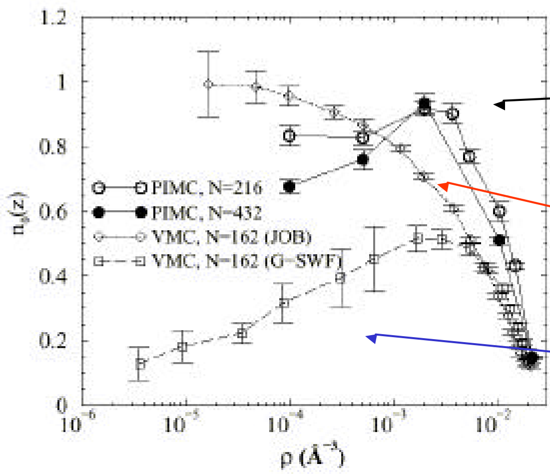


surface: n_0 = 50%

Density profile does not distinguish



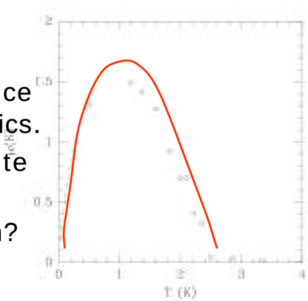
Condensate Fraction at the Surface of ^{4}He



- PIMC supports dilute gas model.
- Jastrow wavefunction
- Shadow wavefunction

Exchange energy

- Let's calculate the chemical potential of a ^{3}He atom in superfluid ^{4}He.
- First suppose that we neglect the difference in mass but only consider effect of statistics.
- The "tagged particle" is should not permute with the other atoms.
- How does this effect the partition function?
- We do not need to do a new calculation



$$e^{-b\mu_3} = \frac{Z_{N-1,1}}{Z_N} = \Pr(\text{atom 1 does not exchange})$$

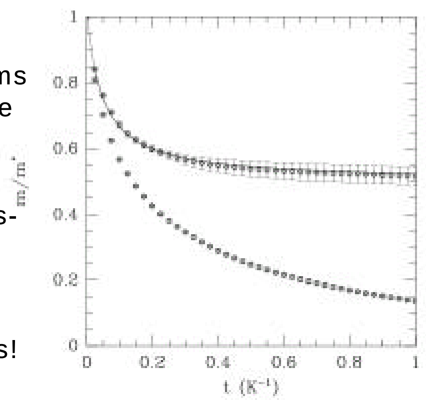
$$\mu_3 = \mu_4 - kT\ln\left(P_1\right) + \int_{\ln(3)}^{\ln(4)} d\ln(m) K(m)$$

- Cycle length distribution is measurable, not just a theoretical artifact.

Effective mass

$$\frac{m}{m^*} = \frac{\left\langle \left[r(t) - r(0) \right]^2 \right\rangle}{6\lambda t}$$

- Effective mass is gotten from the diffusion constant at low temperature
- At short time KE dominates and $m = m^*$
- At large times, neighboring atoms block the diffusion increasing the mass by a factor of 2.
- Same formula applies to DMC!
- Lower curve is for Boltzmannons- they have to return to start position so they move less.
- Diffusion in imaginary time has something to do with excitations!



Dictionary of the Quantum-Classical Isomorphism

Properties of a quantum system are mapped into properties of the fictitious polymer system

Attention: *some words have opposite meanings.*

Quantum	**Classical**
Bose condensation	Delocalization of ends
Boson statistics	Joining of polymers
Exchange frequency	Free energy to link polymers
Free energy	Free energy
Imaginary velocity	Bond vector
Kinetic energy	Negative spring energy
Momentum distribution	FT of end-end distribution
Particle	Ring polymer
Potential energy	Iso-time potential
Superfluid state	Macroscopic polymer
Temperature	Polymer length

Introduction to the UPI code

- Does an arbitrary collection of classical or quantum (bolzmannons,bosons and fermions) at finite temperature (restricted path for fermions)
- 2 or 3 dimensions in periodic boundary conditions
- Only pair potentials, and long-ranged charged interactions. Uses pair density matrix.
- Point, line or plane “particles”
- Calculates energy, pressure, density pair correlation, structure factor, superfluid density, ...
- Various analysis codes, such as MAXENT.
- F77 code freely available. Extension to order(N) parallel version.
- Basic code written by D. Ceperley + others 1990-94. Few updates since then.