Superfluidity fingerprints in nanoscopic $^4$He droplets

M. Drabbels, E. Loginov, N. Brauer, S. Smolarek, W.J. Buma (experiments)
A. Hernando, A. Leal, D. Mateo, M. Pi, M. Barranco (dynamics)
F. Cargnoni, M. Mella (pair potentials)

IX Jornada de Recerca Dept. Física i Enginyeria Nuclear, UPC. February 6th, 2014
Let’s recall that ....

The liquefaction of helium from the gas below 5.2 K by Heike Kamerling Onnes on the 10th of July 1908 was a milestone in experimental physics, the conquest of the final “permanent” gas, that marked the end of an era and opened up a new world of low temperatures.

- **Two stable isotopes:**
  - $^3$He: (2p, 1n), 2 electrons: spin $\frac{1}{2}$: fermion.
  - $^4$He: (2p, 2n), 2 electrons: spin 0: boson.

- **Abundances:**
  - $^3$He/$^4$He: 14 atoms per 10 millions.
  - In commercial, “drugstore” $^3$He, $^4$He/$^3$He = 1/100
  - ... 3000 Tones /year disintegration of U, Th, ... (natural radiactivity)

A highly incompressible liquid whose density saturates.

$$\rho_0 = \begin{cases} 
0.0163 \, \text{Å}^{-3} & ^3\text{He} \\
0.0218 \, \text{Å}^{-3} & ^4\text{He} 
\end{cases}$$

$$\frac{E}{N} = \begin{cases} 
-2.49K & ^3\text{He} \\
-7.15K & ^4\text{He} 
\end{cases}$$
He dimers?

- $^4\text{He}_2$ does exist!
- Binding energy: $1.1+0.3/-0.2 \text{ mK}$ (recall that $1 \text{ eV} \approx 11604 \text{ K}$).
- Size: $52 \pm 4 \text{ Å}$ [Grissenti et al, PRL 85, 2284 (’00)]
  
  $\rightarrow$ droplets of any size appear in the experiments

$^3\text{He}_2$ does not

A minimum number of $^3\text{He}$ atoms needed for forming a droplet, $N_{\text{mín}} \sim 30$

[Barranco et al, PRL 78, 4729 (1997); Guardiola & Navarro, PRA 71, 035201 (2005); Sola et al, PRB 73, 092515 (2005)]
Some peculiar properties of Helium

- It’s a true liquid at $T=0$ K for pressures up to 25-30 bar ($^4\text{He}-^3\text{He}$) (Large zero point motion and weak He-He interaction)
- Superfluid: Below 2.17 K, $^4\text{He}$ flows without viscosity.
- $^3\text{He}$ becomes superfluid below 2.7 mK.
- Both properties are macroscopic manifestations of quantum effects: helium is the paradigm of a quantum liquid.

$^3\text{He}-^4\text{He}$ liquid mixtures:

- Below 0.87 K, limited solubility of $^3\text{He}$ into $^4\text{He}$
- At $T = 0$ K, the maximum solubility is $\approx 6.6 \%$ → phase segregation → In mixed droplets, $^3\text{He}$ goes to the droplet surface occupying the so-called Andreev states (again a zero point motion effect).
Why to study He droplets?

• Jan Northby wrote in a review paper [J.A. Northby, JCP 115, 10065 (2001)]: “let’s see what happens –it’s certain to be interesting and probably surprising” (human curiosity). I would add: It’s funny!

• He clusters are indeed “droplets” (recall, weak He-He interaction and large zero-point motion): “true” Fermi and Bose liquids (bulk liquid and droplets); interesting mixtures.

• They are able to capture any possible dopant. Key role played by doped droplets in this field some 35 years old.

• Due to its week interaction with any other substance, they can be used as a gentle matrix for atomic and molecular spectroscopy. Weak but not negligible (molecular complexes of different morphology than in gas phase).

• Dynamical evolution of an excited impurity in a He droplet, first step towards a better understanding of chemical reactions in this quantum environment.

• Superfluidity at the nanoscale?
Experimental setup: “Helium machine” (Cartoon version)

(20 bar, 10-20 K)

Where could vortices be nucleated?

Formation of droplet beam | Doping | Detection:
--- | --- | ---
PI | LIF | BD

1 ½ m apparatus!!!
Actual experimental setup

(by courtesy of Frank Stienkemeier, Freiburg)
What is the droplet temperature in a typical experiment?

Time-evolution of the temperature of a He$_{1000}$ droplet:


Predictions confirmed by experiments [Hartmann et al, PRL 75, 1566 (1995); Sartakov et al, JCP 138, 044321 (2013)]

Hence,

$^4$He droplets are superfluid (0.4 K)

$^3$He droplets are “normal” (0.1 K)
Another crucial question for doped droplets:

- Where are the impurities sitting?
  - The most attractive ones (the majority) in the bulk of the droplet.
  - The less attractive (alkali atoms), at the surface.
  - The alcaline-earth, it depends...

Experimentally determined from the absorption spectrum of the impurity
Some examples:

[Hernando et al, PRB 77, 0245513 ('08)]
\(N=300, 500, 1000, 2000, 3000, 5000\)

(notice that the particle density saturates)

[Hernando et al, JPC A 111, 7303 (2007)]
[F. Stienkemeir et al., PRB 70, 214509 ('04)]

(N=1000)

N~5000

(Experiment)

N=2000

[O. Bünermann et al., JPC A 111, 12684 ('07)]
Some studies aiming at determining the superfluid character of $^4$He droplets

Size (atom) dependence: how many are enough?

In search of ‘relics’ of bulk superfluid behavior:

- Spectrum of elementary excitations
- Lambda point transition
- “Free” molecular rotations
- Critical Landau velocity (somewhat related to the previous item)
- Quantized vortex appearance

Hard to carry out theoretically, some impossible to check experimentally!
The excitation spectra of compressional modes of $^4$He$_N$, $N = 20$, 70, and 240, clusters at 0 K are calculated by treating the cluster as a quantum liquid drop. The spectrum of $N = 240$ strongly resembles that of liquid helium with a visible roton structure, while for $N = 20$ no roton minimum is seen and $N = 70$ shows a weak minimum. Implications of these findings for superfluidity in helium clusters are discussed.

**Critical Landau velocity for the appearance of excitations:**

$$v_L = \left( \frac{\omega}{q} \right)_{\text{min}}$$
Lambda transition

Path-Integral Monte Carlo Study of Low-Temperature $^4$He Clusters

Philippe Sindzingre and Michael L. Klein
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

David M. Ceperley
National Center for Supercomputer Applications, Department of Physics, University of Illinois, Champaign, Illinois 61820
(Received 12 July 1989)

Path-integral Monte Carlo calculations have been used to study $^4$He clusters at low temperatures. We develop a fluctuation formula for the superfluid fraction in terms of a projected area swept out by a path. Manifestations of superfluid behavior are shown to exist in a cluster of 64 atoms and a remnant of the $\lambda$ transition persists in a cluster of 128 atoms. The temperature dependence of the superfluid fraction is similar to that observed in the liquid.

FIG. 1. Path-integral results for the (a) energy and (b) heat capacity of $^4$He clusters with $N=64$ (open circles) and 128 (solid circles). The $T=0$ K energy values were taken from Green's-function Monte Carlo calculations (Ref. 2). The solid line refers to the bulk heat capacity (Ref. 11) and other lines are drawn as a guide to the eye.
Quasi free molecular rotations

[Grebennev et al, Science 279, 2083 (1998)]

(Long vs short rotational lifetimes)

\[ N_4 = 6000 \]

\[ N_3 = 12000 \]

RJ: \( J \rightarrow J+1 \)

PJ: \( J \rightarrow J-1 \)
[A. Leal et al, JCP 139, 17430 (2013)]

[D. Mateo et al, PRB 83, 174505 (2011)]
Critical Landau Velocity in Helium Nanodroplets

Nils B. Brauer,1 Szymon Smolarek,2,* Evgeniy Loginov,1,‡ David Mateo,3 Alberto Hernando,3,‡ Marti Pi,3 Manuel Barranco,3 Wybren J. Buma,2 and Marcel Drabbeeks1,‡

1Laboratoire de Chimie Physique Moléculaire, Ecole polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
2Faculty of Science, Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, Netherlands
3Departament ECM, Facultat de Fisica, and IN2UB, Universitat de Barcelona, 08028 Barcelona, Spain

(Received 6 May 2013; published 8 October 2013)

The best-known property of superfluid helium is the vanishing viscosity that objects experience while moving through the liquid with speeds below the so-called critical Landau velocity. This critical velocity is generally considered a macroscopic property as it is related to the collective excitations of the helium atoms in the liquid. In the present work we determine to what extent this concept can still be applied to nanometer-scale, finite size helium systems. To this end, atoms and molecules embedded in helium nanodroplets of various sizes are accelerated out of the droplets by means of optical excitation, and the speed distributions of the ejected particles are determined. The measurements reveal the existence of a critical velocity in these systems, even for nanodroplets consisting of only a thousand helium atoms. Accompanying theoretical simulations based on a time-dependent density functional description of the helium confirm and further elucidate this experimental finding.

Ag: Experimental observation

\[ ^2S_{1/2} \rightarrow (^2P_{1/2}, ^2P_{3/2}) \]

Excitation \(^^2P_{1/2} : \) 100% ejection of Ag \(^^2P_{1/2} , \) speed distribution peaks at \( \sim 55 \text{ m/s} \).

![Experimental Ag speed distribution](image)

FIG. 5 (color online). Energy of \(^^2P_{1/2} \) excited Ag as a function of position with respect to the center of a \( \text{He}_{1000} \) droplet and calculated speed of Ag following excitation to the \(^^2P_{1/2} \) state. The shaded area indicates the helium density profile of a pure \( \text{He}_{1000} \) droplet.
Implementation of the Ag dynamics

Due to its large mass, the Ag atom is treated classically.

It is suddenly excited to the 6-dimensional $^2P$ manifold, where it is allowed to evolve without restrictions.

Spin-orbit interaction taken into account. We work in cartesian coordinates $i=x,y,z$ and consider the two spin states $s=\uparrow$ and $\downarrow$.

\[ |Ag\rangle = \sum \lambda_{i,s} |i, s\rangle \]

Total energy:

\[ E_T = E_{He} + \int d\mathbf{r} \rho(\mathbf{r}) \lambda^*_{i,s} V^{ij}(\mathbf{r}-\mathbf{r}_{Ag}) \delta_{ss'} \lambda_{j,s'} + \frac{p^2_{Ag}}{2m_{Ag}} + \lambda^*_{i,s} V^{ij}_{SO} \lambda_{j,s'} \]
Starting $^2$P configuration

- We start from one of the “internal $\lambda$-states” obtained diagonalizing

$$V^{ijss'} = \int dr \rho_0(r) V^{ij}(r - r_{Ag}) \delta_{ss'} + V_{SO}^{ijss'}$$

Ag-He pair potentials: Cargnoni, Mella et al, JCP 129, 204307 (2008), and JPCA 115, 7141 (2011).

**Dynamical variables:**

$\Psi(r)$: He complex effective wavefunction, with $\rho(r)=|\Psi(r)|^2$

$r_{Ag}$: Vector position of Ag

$\lambda$: 6-D complex vector describing the internal state of Ag
Some dynamical evolutions from the $^{2}P_{1/2}$ state:

$^{109}$Ag excited while at rest at a distance $R$ from the center of the droplet, time evolutions for about 50-60 ps

$R = 10 \text{ Å}, \quad ^{2}P_{1/2}$

Tsunamies …

$R = 14 \text{ Å}, \quad ^{2}P_{1/2}$
... and Puffballs!

“Pet de llop”
Quantized vortices in $^4\text{He}$

“Any container of superfluid $^4\text{He}$, treated in conventional fashion, will be permeated ab initio by numerous quantized vortices by surface pinning”


- Whirpools, as in viscous liquids. Difference: circulation of the velocity is quantized

- Plausible existence in droplets, in view of the low working temperatures.

- Especially for doped droplets because of the doping process

Girona, Temps de flors (2005)

$$2\pi R v = \frac{n\hbar}{m_4}, \quad n = 1, 2, 3, \ldots$$

$$r_c \sim 1 - 2 \text{ Å}$$

$$d(\text{He} - \text{He}) \sim 2.5 \text{ Å}$$
Vortices in small droplets

[DFT: F. Dalfovo et al, PRL 85, 1028 (2000); R. Mayol et al, PRL 87, 145301 (2001)]

[QMC: Sola et al, PRB 76 052507 (2007)]
Search of vortices in small He droplets: a very frustrating activity
A plausible scenario for efficient vortex ring nucleation in $^4$He droplets:

The solvation of Ba$^+$ ions created by photoionization of neutral Ba at the surface of a droplet

- A quite general and very efficient process under standard experimental conditions:

- The process is initiated from a well-defined, experimentally reproducible condition, namely the equilibrium of Ba atoms at a surface “dimple”
Equations of motion for the He and Ba$^+$

\[
i\hbar \frac{\partial}{\partial t} \Psi_{\text{He}} = \left[ -\frac{\hbar^2}{2m_{\text{He}}} \nabla^2 + \frac{\delta \mathcal{E}_{\text{He}}}{\delta \rho(r)} + V_{6s}^+(\mathbf{r} - \mathbf{r}_{\text{Ba}^+}) \right] \Psi_{\text{He}}
\]

\[
m_{\text{Ba}^+} \ddot{\mathbf{r}}_{\text{Ba}^+} = -\nabla_{\mathbf{r}_{\text{Ba}^+}} \left[ \int d\mathbf{r} \rho(\mathbf{r}) V_{6s}^+(\mathbf{r} - \mathbf{r}_{\text{Ba}^+}) \right]
\]
Visualization of the sinking of Ba$^+$

[Mateo et, submitted to PRL (2014)]
Velocity circulation analysis:

Circulation around
(0Å–10Å)x(2Å–8Å) path

$C = 40 \text{ ps}$

$C = 50 \text{ ps}$

$C = 60 \text{ ps}$
The quantum panettone: $\text{Ba}^+@^4\text{He}_{1000}$
Some Review References


El Periódico de Catalunya (ed. català), 5-12-2012 p. 32: “L’heli s’esgotarà en 30 anys si segueix el consum actual”

Thanks for your attention!