SUPERFLUID HELIUM DROPLETS: AN ULTRACOLD NANOLABORATORY

The unique environment in liquid helium droplets opens up new opportunities for molecular spectroscopy and for probing superfluid phenomena on the atomic scale.

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Superfluid phenomena in liquid helium-4 have fascinated both experimentalists and theoreticians since the discovery of superfluidity in 1938 simultaneously by Peter Kapitsa at the Soviet Academy of Sciences and by Jack Allen and Donald Misener at the Royal Society Laboratories in Cambridge, England. These phenomena include a vanishingly small viscosity, a very high heat conductivity (30 times greater than copper), and many other bizarre effects, such as the He fountain, film flow and creep, and quantized vortices (see the article by Russell Donnelly in PHYSICS TODAY, July 1995, page 30).

Compared to the extensive experimental and theoretical studies of macroscopic superfluid phenomena, experimental studies of the microscopic details have been sparse because of the lack of adequate probes. A major problem has been that liquid He has a natural ability to cleanse itself of impurities, which either aggregate in the bulk or condense on surfaces. In recent years, techniques have been developed[1] to laser ablate materials inside liquid or solid He. These experiments have been limited so far to metal atoms or ions, both of which interact strongly with the He environment following electronic excitation. These interactions lead to large line shifts and to broad features in the excitation spectrum of the embedded materials. It turns out, however, that nanoscopic droplets of He can readily be doped with various molecules—a technique that provides a powerful spectroscopic probe of the molecules and of the droplets themselves.

Droplet formation in gas expansions of He was reported by Heike Kamerling Onnes in 1908 during initial attempts at liquefying He at Leiden University, but was not subsequently pursued. In 1961, Erwin Becker and colleagues at the University of Karlsruhe reported formation of He droplet beams in experiments using cryogenic free-jet gas expansions. Research at Karlsruhe continued in the 1970s and early 1980s with scattering and deflection studies led by Jürgen Gspann. In the late 1980s, experiments in the laboratory of one of us (Toennies) in Göttingen showed that He droplets could be readily doped by one or more gas atoms and molecules. Then, in 1992, Giacinto Scoles and his colleagues at Princeton University combined their pickup technique (illustrated in figure 1) with spectroscopic interrogation by laser-induced evaporation and were thereby able to detect the infrared absorption of embedded sulfur hexafluoride (SF_6) molecules. In 1994, two of us (Vilesov and Toennies) and colleagues in Göttingen performed high-resolution measurements that revealed that the SF_6 spectral lines were unusually sharp and presented evidence of rotational fine structure, indicating that the embedded molecules can rotate freely inside the ^{4}He droplets. Box 1 describes the method of droplet formation in these experiments.

The very narrow spectral features render these molecular probes an ideal tool to address a number of long-standing, intriguing questions. How is it possible to detect superfluidity in droplets? What does it even mean for a droplet to be superfluid, when most of the known characteristic phenomena are macroscopic and not obviously applicable to nanoscale droplets? How many atoms are needed for a fluid to become a superfluid? Can molecule-sized objects move without friction inside a superfluid?

Spectroscopic evidence for superfluidity

A typical apparatus for detecting spectroscopic transitions of embedded molecules is illustrated in figure 1. This technique uses the so-called depletion method, in which photon absorption in the doped droplets leads to the evaporation of atoms from the droplet and a consequent decrease in the signal from a mass spectrometer monitoring the droplet beam. The depletion method is especially sensitive for He droplets because of their very low heat of vaporization (7.2 K per atom for ^{4}He, 2.7 K per atom for ^{3}He). This simple apparatus, together with modifications in different research groups, has proven to be quite universal for spectroscopic investigations of a wide range of substances.[2]

The first experimental evidence that the ^{4}He droplets are superfluid came in 1996 from electronic excitation spectra of an embedded glyoxal ($C_2H_2O_2$) molecule, measured in Göttingen and summarized in figure 2. The spectrum has a sharp feature, termed the zero phonon line (ZPL), that is split into several lines corresponding to partially resolved rotational transitions in the molecule, and a phonon wing (PW) at higher frequencies that derives from simultaneous excitation of the He collective modes.[3] PWs are well known for species trapped in low-temperature

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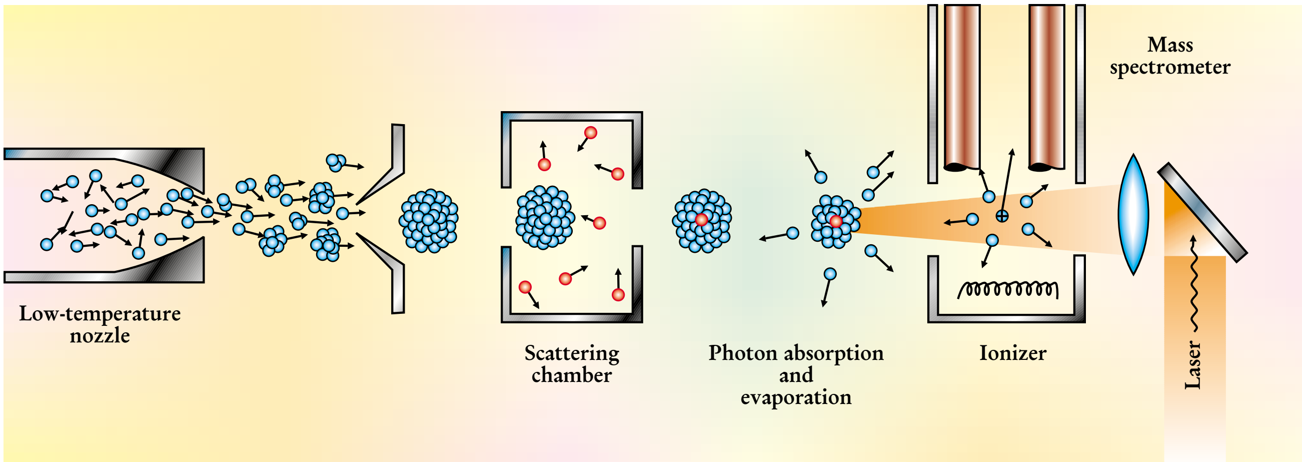


FIGURE 1. DROPLET SPECTROSCOPY APPARATUS used in Göttingen. The droplets are formed by adiabatic expansion of helium gas, at a temperature of 10–20 K and a pressure of typically 20 bar (2 MPa), through a 5-μm-diameter orifice into vacuum. Individual molecules (red) are captured by the droplets as they pass through a pickup scattering chamber. The energy imparted to a droplet by an absorbed molecule is rapidly converted to the evaporation of several hundred He atoms, and the droplet quickly returns to its ambient temperature (0.38 K for ^{4}He, 0.15 K for ^{3}He). The doped clusters then interact with an antiparallel laser beam. Photon absorption by the doped droplets is detected by monitoring the ion signal from a mass spectrometer used to detect the droplets. The energy of an absorbed photon is quickly dissipated, producing extensive evaporation of He atoms and a decrease in droplet size. This decrease causes a significant reduction in the cross section for droplet ionization and a 2–10% decrease in ion signal.

condensed media—so-called matrices. However, the PW in ^{4}He is unusual: It rises sharply and is separated from the ZPL by a distinct gap of about 6 cm^{-1}. The intensity of the PW is essentially proportional to the density of the available phonon states in the droplet. For superfluid He, the phonon–roton dispersion curve of elementary excitations (see box 2) leads to a density of states with two pronounced maxima. Detailed analysis of the coupling to the electronic excitation using this density of states yields good agreement with experiment. Furthermore, the sharp rise of the PW indicates that the width of the roton energy levels is much less than the roton gap. Since a well-defined roton gap is characteristic of superfluid He, these experiments produced the first evidence that the ^{4}He droplets are indeed superfluid.

Rotations of molecules in helium droplets

Additional insights into the nature of He droplets come from examining the rotations of embedded molecules. The first high-resolution spectrum in ^{4}He droplets in the infrared, where rotational transitions occur, was measured in Göttingen[4] for SF_6 and is shown in figure 3. The lines are nearly as narrow as those measured for free molecules. By contrast, rotational lines in classical liquids are rarely resolved. For the octahedral SF_6 molecule, the rotational lines in the droplet are about a factor of three closer together than in the free molecules. Since the rotational energies for this molecule are approximately given by $E_{\rm rot} = (\hbar^2/2I)\, j(j+1)$, where I is the moment of inertia of the molecule and j is its rotational quantum number, the narrower spacing indicates a considerably larger effective moment of inertia of the molecule in ^{4}He. In virtually all other respects, the embedded molecule can be described by the same Hamiltonian as that of the free molecule. From the ratios of the intensities of the lines, an ambient temperature of 0.38 K in the ^{4}He droplet can be deduced.

More than 14 different molecular species, with various geometries, have now been studied, mostly in Göttingen, in Princeton, or in Roger Miller's group at the University of North Carolina at Chapel Hill. In all cases, sharp rotational lines are found. The increase in the effective moment of inertia varies, however, from factors of

Box 1. Cluster and Droplet Formation in Supersonic Jets

Clusters of most substances can be readily produced by passing a gas or vapor of the substance at a high pressure through a narrow orifice into vacuum.[17] This adiabatic expansion is accompanied by a very rapid cooling of the flowing gas, which can approach a rate of 10^{11} K/s. As the temperature becomes very low, condensation of even helium, the most weakly bound system, becomes favorable. In many cases, mixtures of an inert buffer gas and molecules of interest are coexpanded. These so-called seeded beams, which have proven to be an extremely versatile tool to cool molecules and to produce various clusters, are now readily available in many areas of molecular physics and chemistry. However, they cannot be applied to He droplet experiments because the nozzle must generally be cooled down to temperatures below 25 K to obtain condensation. At these temperatures, any foreign species will freeze and clog the nozzle. Therefore the pickup technique, introduced by Giacinto Scoles at Princeton University in 1985 for the study of doped argon clusters, provides the best opportunity to embed or attach molecules.

After the droplets are formed, they continue on into a collision-free region of high vacuum where they undergo very rapid evaporative cooling. Due to the low heat of evaporation for He, the final temperatures are very low: 0.38 K for ^{4}He droplets and 0.15 K for mixed ^{3}He/^{4}He and ^{3}He droplets.

The mean number and the distribution in the number of atoms in He droplets have been measured in Göttingen by deflecting the droplets using a directed secondary beam. ^{4}He droplets with 3×10^3–10^4 atoms, used in the spectroscopic experiments described in this article, are conveniently produced with a source pressure of 20 bar (2 MPa) and a temperature of 12–15 K. Larger droplets, with up to 10^7 atoms, can be produced by expanding liquid He at lower temperatures.

about 3–5 for heavy or extended molecules, such as SF_6 and substituted acetylenic derivatives, to zero increase for H_2O, HF, and other small, light molecules.[2]

A microscopic rotating bucket

Initially, it was unclear whether the sharp rotational lines might merely be a consequence of the extremely weak van der Waals interactions of He atoms with molecules, or are somehow related to the superfluidity of the medium. One way to differentiate between these possibilities would be to heat the droplets above the superfluid transition temperature to see whether the free rotations persisted, in analogy to the famous 1946 rotating bucket experiment of Élevter Andronikashvili at the Soviet Academy of Sciences (see box 2). This has not proven feasible yet, because of the very rapid evaporative cooling. Alternatively, the effect has been probed by measuring the spectra inside ^{3}He droplets, which are not superfluid at the inferred ^{3}He droplet temperature of 0.15 K. In these experiments, the SF_6 molecule was replaced by the linear carbonyl sulfide (OCS) molecule, whose spectrum is simpler.[5] The OCS infrared spectrum measured in pure ^{4}He droplets (figure 4a) shows a sequence of sharp rotational lines, indicating coherent rotation, with a full width at half maximum as small as 150 MHz (5×10^{-3} cm^{-1}). In pure ^{3}He droplets (figure 4b), the rotational lines merge into a broad single band, very similar to what would be expected in a classical liquid. If the sharp rotational lines were merely a consequence of the weak van der Waals potential, then in ^{3}He, the lines should be even sharper because of the larger zero-point energy and lower temperature. Thus, the ability of the embedded molecule to rotate coherently over many periods is a *microscopic* manifestation of superfluidity.

This experiment also yields insight into the size dependence of superfluid behavior in ^{4}He clusters. Passing ^{3}He droplets containing a single OCS molecule through a second scattering chamber filled to different pressures with ^{4}He gas allowed a variable number of ^{4}He atoms to be added to each droplet. These ^{4}He atoms diffused inside the ^{3}He liquid droplet, where, because of their heavier mass and hence lower zero-point energy and stronger binding, they replaced the ^{3}He atoms adjacent to the OCS molecule. Figures 4c to 4f show how the measured spectra change with increasing numbers of added ^{4}He atoms. Rotational lines begin to reappear with about 35 ^{4}He atoms, and are well established after the addition of about 60 ^{4}He atoms.

The density of He atoms immediately around the molecule is highly modulated, characterized by a first, highly structured layer containing about 17 atoms and having peak density considerably higher than the bulk, surrounded by a second, more weakly modulated layer.[6] These layered structures, known as quantum solvation shells, result from the interplay between the molecule–He and He–He interactions.[7] The approximately 60 ^{4}He atoms that suffice to restore the conditions for free rotation in the mixed droplets constitute about two solvation shells. Recent density functional calculations by Manuel Barranco and his colleagues at the University of Barcelona for such mixed droplets indicate that about 30% of the outermost of the two ^{4}He solvation layers may actually be composed of ^{3}He. The extent to which the ^{3}He atoms influence the superfluidity near the molecule is unclear at present.

These experiments illustrate some of the new opportunities for studying phase transitions in finite-sized quantum systems, and other phenomena, by using mixed droplets to modify either the environment of the molecule or the droplet temperature. At 0.15 K, the droplets are at temperatures that are otherwise only accessible inside unwieldy and expensive dilution refrigerator cryostats.

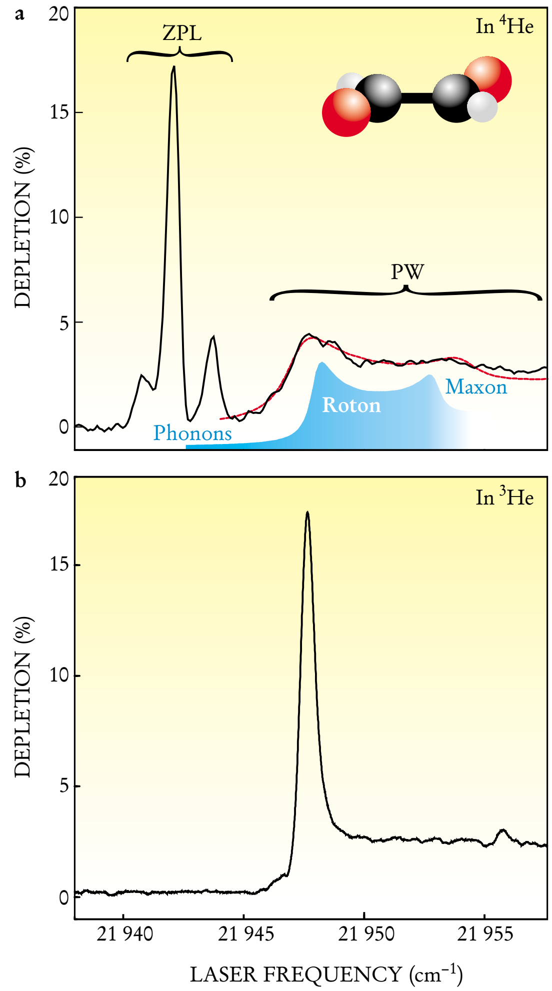


Figure 2. Electronic excitation spectrum reveals superfluidity of helium-4 droplets. **(a)** The spectrum (black) of a glyoxal ($C_2H_2O_2$) molecule inside a ^{4}He droplet with 5500 atoms, measured using the depletion method of figure 1. The gap between the zero phonon line (ZPL) and phonon wing (PW) features, as well as the structure in the PW, can be attributed to the shape of the density of states of excitations within superfluid ^{4}He, sketched beneath the spectrum, and indicates that the droplet is indeed superfluid. The red curve shows a theoretical fit to the PW using the superfluid excitation spectrum. **(b)** The conclusion that ^{4}He droplets are superfluid is strengthened by complementary measurements of the glyoxal spectrum inside a nonsuperfluid ^{3}He droplet with 50 000 atoms, where no gap is observed—only a broad, continuous PW band extending to higher frequencies. (Adapted from ref. 3.)

Theoretical understanding

Experimental investigations of He droplets have been accompanied by theoretical insights from a range of simple models and from microscopic calculations.[7] Early variational calculations by Vijay Pandharipande and colleagues at the University of Illinois showed that significant Bose–Einstein condensate fractions exist inside small ^{4}He clusters. In analogy to Andronikashvili's rotating bucket

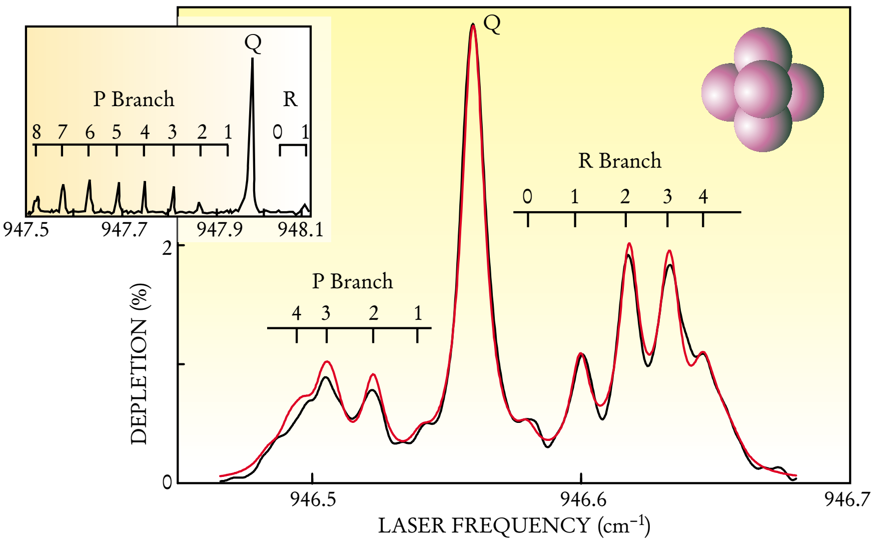


FIGURE 3. RESOLVED ROTATIONAL TRANSITIONS can be seen in the infrared spectrum (black) of a single sulfur hexafluoride (SF_6) molecule in a helium-4 droplet consisting of 2700 atoms. The various lines correspond to different transitions in the rotational quantum number j accompanying the $\nu = 0 \rightarrow 1$ transition of the asymmetric vibration of the sulfur atom inside its octahedral fluorine cage. The P branch corresponds to $j \rightarrow j - 1$; the Q branch, to $j \rightarrow j$; the R branch, to $j \rightarrow j + 1$. The P and R lines are labeled by initial j value. The spectrum closely resembles that for a freely rotating molecule (red), as calculated by Boris Sartakov. The inset shows the analogous spectrum of SF_6 in the gas phase (Gerhard Schweizer, PhD dissertation, Bonn University, 1983). Note the reduced spacing of the lines in the He droplet, due to a larger effective moment of inertia. This spacing also decreases with j, indicating a large centrifugal distortion constant.[4]

experiment (see box 2), Philippe Sindzingre and Michael Klein at the University of Pennsylvania, together with David Ceperley at the University of Illinois, calculated the quantum response of a liquid droplet undergoing hypothetical rotation, to obtain a direct measure of the normal fluid fraction. For clusters as small as 64 atoms, substantial superfluid fractions were found to arise below a broadened, size-dependent transition temperature that is somewhat depressed below the bulk superfluid transition at 2.17 K. Mushti Rama Krishna, then at Berkeley, and one of us (Whaley) calculated the collective excitation spectrum in ^{4}He clusters and found that the roton excitations characteristic of the bulk superfluid state already appear at about 70 atoms. Calculations for doped clusters predict that strongly bound atoms and molecules are located in the interior, while very weakly bound species may be located at the droplet surface. Other properties of He droplets, such as their very low temperatures resulting from evaporative cooling, have been explored by Sandro Stringari and colleagues at the University of Trento, using the liquid drop model from nuclear physics. These studies imply that the interior of the droplets, where the embedded molecules are located, are expected to be largely devoid of thermal excitations at these low temperatures.

Over the past two years, several theoretical groups have investigated the phenomenon of molecular rotations in He droplets.[6] The Princeton group has advocated the use of hydrodynamics to describe the superfluid response to molecular rotation, and Carlo Callegari and Kevin Lehmann at Princeton have obtained agreement with measured molecular moments of inertia for some linear polyatomic molecules. In contrast, Vladimir Babichenko and Yuri Kagan at the Kurchatov Institute in Moscow have pointed out that the difference between the line widths in the molecular spectra found in pure ^{4}He and ^{3}He droplets (compare panels a and b in figure 4) can be explained in terms of the different elementary excitations in these two quantum fluids (see box 2), and argued that the hydrodynamic manifestations of superfluidity are not relevant on this molecular length scale.

To address these questions at the microscopic level, one of us (Whaley), with Yongkyung Kwon from Konkuk University in Korea, and with colleagues at Berkeley, has carried out a variety of quantum Monte Carlo investigations into the rotational dynamics of embedded molecules.[6] Explicit calculations of ground and low-lying excited states of ^{4}He clusters containing an embedded rotating molecule show that, for the heavier molecules, a relatively small number of ^{4}He atoms are effectively responsible for the increased moment of inertia. Related finite-temperature path-integral calculations have analyzed the perturbing effect of an embedded molecule on the Feynman paths of He atoms that result from the Bose permutation exchange symmetry.[8] According to Richard Feynman's 1953 theory, these paths become macroscopically long in the bulk superfluid state.[9] Calculations for strongly bound molecules such as SF_6 show that the attractive molecular interaction removes ^{4}He atoms from long permutation cycles close to the molecule, resulting in a local accumulation of density that is characterized by short permutations. Consequently, there is a molecule-induced nonsuperfluid component in the first solvation layer (figure 5). The path-integral analysis has been used to construct a microscopic two-fluid model for the He response,[6] which yields predicted moments of inertia in excellent agreement with experimental values for the heavier molecules such as SF_6 and OCS. This analysis of the local He solvation is consistent with numerous low-temperature studies of thin films of superfluid ^{4}He on substrates such as graphite, where the superfluid fraction in the layer closest to the substrate is depleted as a result of the relatively strong van der Waals interactions with the substrate.

A critical concept emerging from these quantum calculations is that of "adiabatic following," the notion that some of the He density in the first solvation shell may adiabatically follow the molecular rotation. Detailed quantum Monte Carlo analysis of this phenomenon shows that, for heavier molecules, a fraction of the density in the first solvation shell can indeed follow the molecular rotation adiabatically, while for lighter molecules such as HCN, the extent of adiabatic following is very much reduced.[6]

The ultimate spectroscopic matrix

The unusually small line shifts and the narrow spectral lines demonstrate that these He droplets are the gentlest and coldest of all matrices used for molecular spectroscopy. Up to now, about 50 different molecules have been studied in the infrared, visible, or near ultraviolet,[2] including amino acids and porphyrin derivatives, which

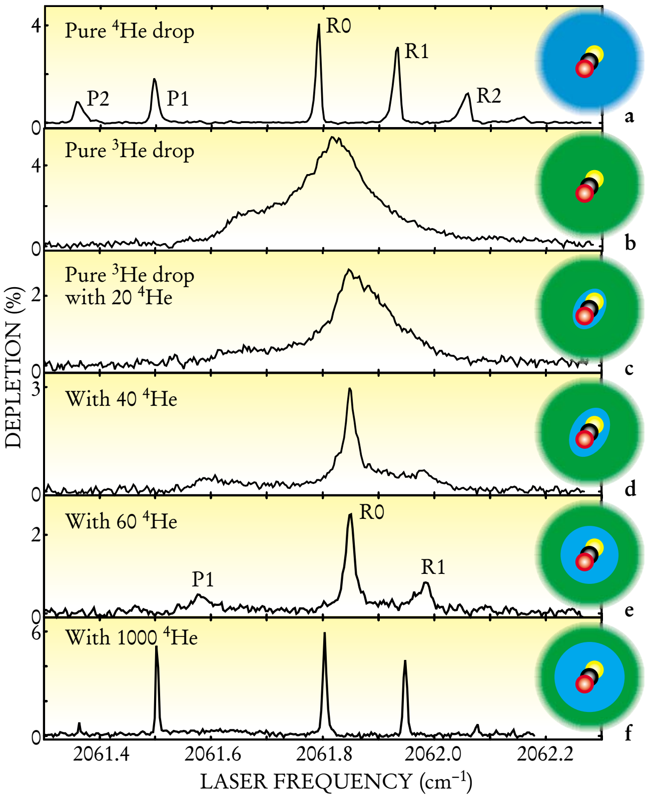


FIGURE 4. INFRARED SPECTRA of single carbonyl sulfide (OCS) molecules. **(a)** Rotational transitions accompanying the vibrational transitions of the asymmetric stretch vibrational mode of a single OCS molecule in a helium-4 droplet consisting of 6000 atoms. Several P- and R-branch lines are seen. **(b)** The same spectrum but for OCS in a ^{3}He droplet consisting of 12 000 atoms. The smearing in **b** indicates that the sharp lines in **a** are unique to the superfluid ^{4}He droplets. **(c–f)** As increasing numbers of ^{4}He atoms are added to ^{3}He droplets, the OCS spectrum sharpens. The ^{4}He atoms form layered, shell-like structures around the OCS molecule, as shown in the insets. (Adapted from ref. 5.)

play important roles in many biological processes.

Another striking advantage of He droplets for spectroscopy derives from their large capture cross sections. These facilitate the pickup of foreign atoms and molecules, so that only very low vapor pressures of about 10^{-5} mbar (1 mPa) are required. Consequently, samples can be kept well below their decomposition temperatures, an important factor for biological molecules. The alkali and alkaline earth metals have been investigated in the visible by the Princeton group and by Frank Stienkemeier at the University of Bielefeld in Germany.[10] These atoms appear to be located at the droplet surface. High-resolution spectral studies of alkali dimers and trimers in Princeton have shown a surprising enhancement of the weakest bound triplet and quartet states, which are not easily accessible in the gas phase (figure 6). Experiments carried out in Göttingen show that other metal atoms, such as europium and silver, are located in the interior, and that large clusters—for silver, up to Ag_{65}—not only can be grown and detected inside He droplets, but also show sharp spectral features.[11] Helium droplets also offer a route to the creation and analysis of novel multicomponent aggregates constituted from mixtures of metals or semiconductors.

There is now evidence that weakly bound van der Waals and hydrogen-bonded complexes may self-assemble inside He droplets to different structures than those produced in seeded beams. This has been vividly demonstrated recently by Klaas Nauta and Miller.[12] Free HCN clusters containing four or more HCN molecules show nonpolar, cyclic structures. In He droplets, however, predominantly linear chains of up to eight HCN molecules are found; the chain length seems to be limited only by the radius of the droplet. This abundance of chains is attributed to the very low temperatures, which enable the long-range dipole forces to line the molecules up over large distances. These results suggest strategies for growing nanoscale oligomers with novel structures.

In addition, chemical reactions at ultralow temperatures may be studied in He droplets, as recently demonstrated[13] with the bimolecular reaction $Ba + N_2O \rightarrow BaO + N_2$. The unusual features associated with solvation in He droplets may provide interesting new opportunities for control of reaction pathways.

The future

Given that the first spectroscopic evidence for sharp spectral lines was found only in 1994, the progress since has been quite impressive. A significant recent technical advance is the use of double resonance techniques by the groups at Princeton, Göttingen, and the University of Bochum in Germany led by Martina Havenith, which reveal additional fine structure in the spectra having only 100 MHz spacings.[14] The next generation of experiments is now poised to explore more subtle issues, such as the effect of the finite size of the droplets on spectroscopic features. Of particular interest is the interplay between

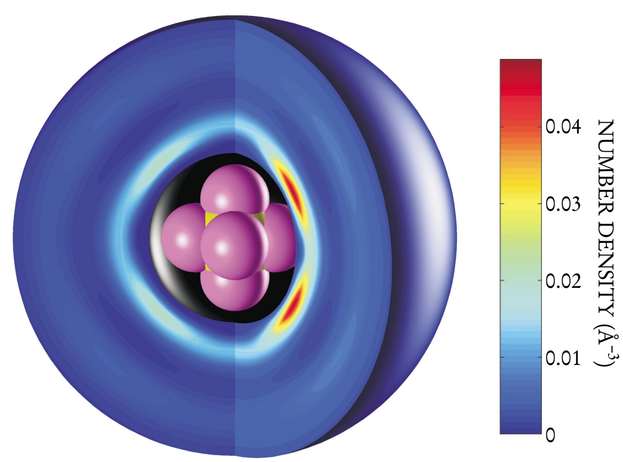


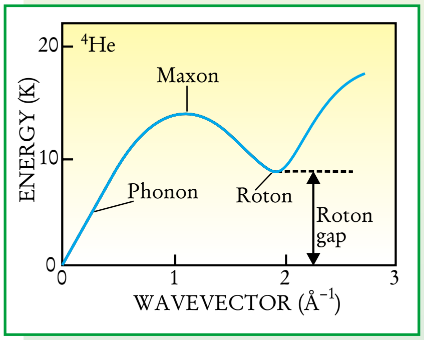
FIGURE 5. LOCAL PERTURBATION of the superfluid density. The nonsuperfluid density, calculated from a path-integral analysis for a helium-4 droplet at 0.3 K, is shown here with cuts along different symmetry axes of the embedded octahedral sulfur hexafluoride (SF_6) molecule. The strong interaction between SF_6 and the surrounding He atoms removes some density from the superfluid component and increases the nonsuperfluid density in the layer of He atoms closest to the molecule. The angular structure reflects the anisotropy of the interaction. Outside this layer, there is little effect on the superfluid density. (Adapted from ref. 6, courtesy of Patrick Huang.)

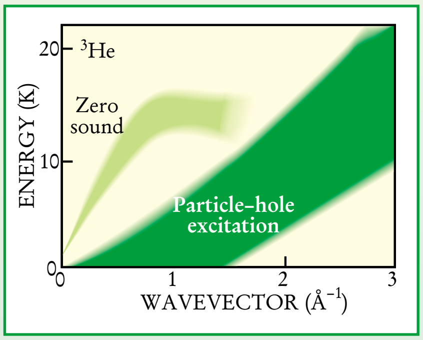
Box 2. Landau's Legacy

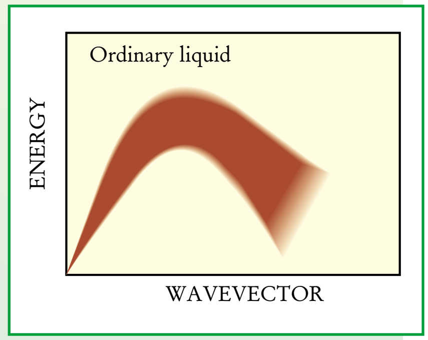
In 1941, Lev Landau at the Soviet Academy of Sciences derived a complete set of macroscopic hydrodynamic equations for superfluid helium, described as a two-fluid mixture (originally suggested by Laszlo Tisza at the Collège de France in 1938), and showed how these may be related to the sharp dispersion curve for elementary excitations in the superfluid.[18]

The figure shows the dispersion curves for the bulk quantum fluids ^{4}He (left) and ^{3}He (middle) and for an ordinary liquid (right). The sharpness of the superfluid ^{4}He curve reflects the long lifetime of collective excitations, which are characterized by a phonon branch and rotons, with a maximum in between called a maxon. This sharpness contrasts with the broad widths seen in ordinary liquids and in ^{3}He's "zero sound" collective excitations. ^{3}He also possesses particle–hole excitations similar to electronic excitations in metals. In the interior of large He droplets, the dispersion curves are expected to be similar to those in the bulk.

In Landau's theory, below the superfluid transition temperature, liquid He consists of a mixture of a normal fluid, attributed to thermally excited phonons and rotons, and a superfluid that is characterized as an inviscid fluid having zero entropy. The two-fluid model has been remarkably successful in explaining many of the macroscopic properties of superfluid He. Landau also proposed the famous rotating bucket experiment to measure the superfluid fraction as a function of temperature, carried out in 1946 by his colleague Élevter Andronikashvili: A torsional pendulum consisting of thinly spaced disks suspended in liquid He couples only to the normal component, not to the superfluid component. Measuring the pendulum's resonant frequency as a function of temperature yields the superfluid and normal fractions. These concepts and experiments are described at greater length in the article by Moses Chan, Norbert Mulders, and John Reppy in PHYSICS TODAY, August 1996, page 30.







confinement and superfluid solvation. Several groups have addressed the intrinsic delocalization of embedded molecules in quantum droplets with microscopic calculations or particle-in-a-box models.[7] Lehmann has predicted that the confining surface provides both symmetry breaking, which can introduce a splitting of spectral lines, and a potential source of line broadening.[15] Some evidence for frictionless, delocalized motion within ^{4}He droplets has already been obtained in recent studies of electron bubble lifetimes performed in Göttingen.[16]

The rich multiplicity of phenomena associated with the bulk superfluid state of He suggests a number of

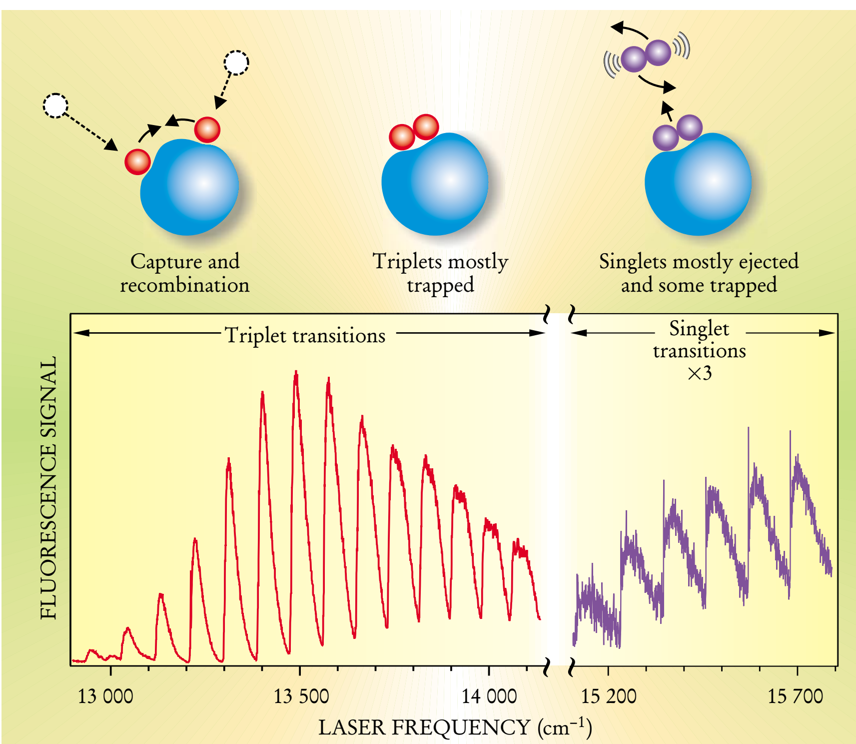


FIGURE 6. ALKALI DIMERS created by recombination at the surface of liquid helium droplets are formed in both their triplet (spin-1) and singlet (spin-0) electronic states, resulting in distinct electronic spectra, shown here for sodium dimers on droplets of about 10 000 helium-4 atoms. Formation of the strongly bound singlet dimer releases a large amount of energy, which results in extensive evaporation and significant probability for desorption of the alkali molecule. In contrast, triplet dimers are very weakly bound by van der Waals interactions, and are therefore preferentially trapped on the surface. Their higher spectral intensity confirms the enrichment of the high-spin species above their statistical weight. The excitation spectra for both species show a progression of vibrational bands. The singlet bands show zero phonon lines and phonon wings analogous to those seen in figure 2. (Adapted from ref. 10.)

additional topics in which these spectroscopic probes can offer new, microscopic insight into the local superfluid dynamics. Vortices, while energetically unfavorable in finite clusters, can potentially be stabilized by long, chain-like molecules. They should give rise to additional dynamical modes of the molecule, while the associated spectral features may reveal details of the He flow on a molecular length scale. Large planar organic molecules offer the possibility of studying the solvation behavior of the superfluid state on a "nanosubstrate," whose size and symmetry may be systematically varied. This would allow probing the transition from superfluid liquid to a localized adsorbed layer. Combining doped He nanodroplets with molecular spectroscopy, therefore, allows the vast gap between isolated atomic impurities and miniature solid surfaces to be probed, opening up for the first time the microscopic behavior of liquid He and its interfacial dynamics over many length scales.

Complementary to the next generation of cluster experiments, it is now imperative to revisit the significant experimental challenge of introducing single molecules into the bulk liquid. This could open up novel opportunities for using liquid He as a special medium for assembling or manipulating molecules, using laser tweezers or three-dimensional scanning microscope probes for example, while simultaneously monitoring what is going on with high-resolution spectroscopy. The cluster spectroscopy experiments to date have demonstrated the capability of molecular dopants to probe quantum liquid phenomena. We can expect many more exciting and rewarding results in the future.

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