Negative Pressures and Cavitation in Liquid Helium

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NEGATIVE PRESSURES AND CAVITATION IN LIQUID HELIUM

When subjected to intense sound waves, liquids can be stretched until they break and gas bubbles appear.

Humphrey Maris and Sebastien Balibar

Cavitation—the formation of bubbles—is a familiar phenomenon. Whenever a liquid is agitated violently, there is a possibility that cavitation will occur (see, for example, figure 1). In the case of boat propellers or hydraulic machines, cavitation is a problem that engineers try to avoid. In other contexts, however, cavitation can be useful—as, for example, in ultrasonic cleaning devices.

Desirable or not, cavitation is a complex phenomenon because inhomogeneities in the liquid—such as walls, dissolved gases, vortices, and impurities—usually play a major role in the nucleation of bubbles. As a consequence, our understanding of cavitation is incomplete. To make some progress, our research groups have examined cavitation in superfluid helium, a simple and pure liquid. It is the coldest liquid in nature and exists only at temperatures near absolute zero, where every other liquid is frozen. It can therefore be filtered very efficiently and prepared without impurities. Furthermore, it has been predicted that, at very low temperatures, the nucleation of bubbles will occur by means of quantum tunneling—a process we believe has now been observed.

How does a liquid break?

Measuring the tensile strength of a solid involves applying an increasing stress until the solid breaks. The study of cavitation in liquids follows a similar path.

Suppose that some water is put into a cylinder that is sealed with a piston. If the piston is above the water and has a weight placed on top of it, the water will be under a positive pressure. The pressure will be equal to the weight divided by the cross-sectional area of the cylinder. But if the apparatus is turned upside down and a weight hung from the piston, what happens? The correct answer depends critically on some details of the situation that we have not yet specified. If there is an air bubble in the water above the piston, then when the weight pulls on the piston, the bubble will grow and the piston will fall. If there is no air bubble and the weight is small, the piston will move down a short distance but soon come to rest. In that equilibrium position, the force exerted by the weight is balanced by a force that the water exerts. The water is thus under negative pressure—that is, under positive stress. If there is no air bubble and the weight is heavy enough, then the piston will move down, the water will be stretched, and eventually a bubble will spontaneously appear within the liquid or possibly on the wall of the container.

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Why do such things happen? At low pressure P, the equation of state for air (or any other gas) is the well-known ideal-gas law. As P decreases toward zero, the volume V varies as the inverse of the pressure. Consequently, when an air bubble is present in the water, the size of the bubble grows without limit as soon as the weight pulls on the piston. But what happens when there is no bubble and the water is able to stay in a state of tension? This state is only metastable: If a bubble forms, the piston will be able to move, and that movement will clearly lower the potential energy of the system. Before a large bubble can be formed, however, the system has to overcome an energy barrier.

The existence of an energy barrier against nucleation is very general. The barrier arises because the liquid–gas transition is discontinuous, or "first order." Such a barrier exists for any first order transition because the interface between the two phases has a finite energy per unit area. In our example, this energy is nothing but the surface tension α of water. Since α is nonzero, the formation of a bubble with radius R has an energy cost of $4\pi R^2\alpha$. When such a bubble forms, the energy of the whole system also contains the work of the negative pressure over the bubble volume, so that the total energy cost of forming the bubble is

$$\Delta E = 4\pi R^2\alpha + \frac{4\pi}{3}R^3P. \tag{1}$$

At negative pressures, this energy has a maximum for a critical radius $R_c = 2\alpha/|P|$. The energy at this radius establishes the energy barrier (see figure 2) at

$$\Delta E = \frac{16\pi\alpha^3}{3P^2}. \tag{2}$$

A thermal fluctuation may enable the system to pass over the energy barrier. The probability of such an occurrence is proportional to the factor

$$\exp\,(-\Delta E/kT), \tag{3}$$

where T is the absolute temperature and k is Boltzmann's constant. In this simplified model, it is clear that cavitation should be a random process that depends on temperature.

This discussion of the energy required to form a bubble is inadequate in one very important respect. Equation

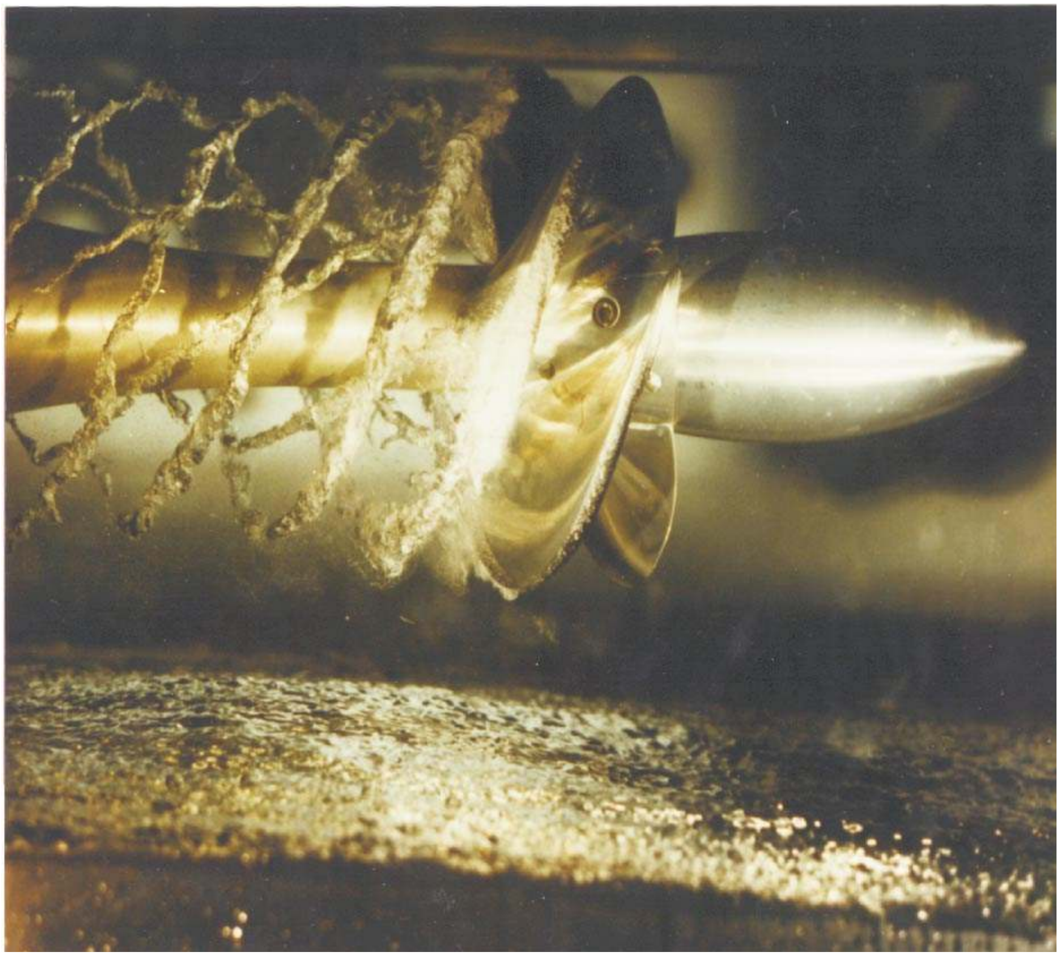

FIGURE 1. VORTEX lines are generated at the edge of boat propellers in motion. Toward the core of the vortices, the liquid velocity increases and the pressure decreases. The lower pressure triggers cavitation, and the resulting bubbles produce noise, vibrations, and erosion of the propellers. (Photo courtesy of DGA–DCE, Bassin des Carenes, Paris, France.)

3 says that to maintain a given probability that nucleation will take place, the ratio of the energy barrier ΔE to kT must have a particular value; this requirement would lead to the conclusion that as the temperature decreases, the pressure at which nucleation occurs should diverge as $T^{-1/2}$. But such reasoning ignores the obvious fact that there is an upper limit to the force one molecule in a liquid can exert on another, so that for some negative pressure of finite magnitude, the liquid will stretch without limit (that is, the compressibility will become infinite). The pressure at which that happens is called the spinodal limit. When it is reached, the sound velocity becomes zero and the barrier to nucleation vanishes.

Given these considerations, one can see that if the applied pressure is only slightly negative, the energy barrier is very large and the chance that a bubble will form is very small. Then the liquid can exist in a state of negative pressure for a long time—but only if the liquid is very clean. If the liquid contains dirt or dissolved gas, the formation of bubbles is usually much likelier. Bubbles also tend to form preferentially on the walls of a container. Bubble production associated with walls or impurities is called heterogeneous nucleation—as distinguished from homogeneous nucleation, which takes place within the volume of an ideal bulk liquid and is an intrinsic property of the liquid.

Everyday negative pressures

Before entering further into our subject, let us mention some everyday situations in which negative pressures occur. In a tree, water passes from the roots up to the leaves through the xylem and evaporates from the leaf surfaces (figure 3). Consider now the variation in the water pressure within the trunk of the tree. The pressure must decrease with height so as to balance the force of gravity acting on the water and drive the water through the xylem at the necessary rate. The pressure, which is 1 bar (10^5 pascals, or about 1 atmosphere) at ground level, must decrease by 1 bar for each 10 meters going up the tree. At the top of a California redwood tree—which may be 100 m above the ground—the pressure must therefore be about –9 bars. One might therefore think that a terrible accident would happen if a bird made a little hole in the trunk near the top: Air might rush into the hole and cause all the water to flow back to the ground, leaving a dried-out tree. In fact, the tree is protected against such a disaster, thanks to the presence of very small constrictions in the xylem channels, safety hatches that can hold water through capillarity.

The water pressure can also become negative in vortices generated by a propeller at the rear of a boat. The pressure decreases because the local velocity increases towards the vortex core, in accordance with a general law of hydrodynamics established by Daniel Bernoulli in the 18th century. But the spinodal limit of water is far from being reached in such vortices. In a complex medium such as seawater, bubbles grow from seeds that are already present, such as microbubbles of dissolved air or various particles floating around.

Achieving large negative pressures in water has actually been a challenge to scientists for more than a century. Marcellin Berthelot claimed in 1850 that he had reached –50 bars in a glass ampoule completely filled with pure water.[1] In 1967, Edwin Roedder at the US Geological Survey reached –1000 bars with water inclusions in natural rocks.[2] The world's record now belongs to Austen Angell and his collaborators at Arizona State University, who in 1991 reported achieving –1400 bars with a similar technique but synthetic materials.[3] Such very large negative pressures are comparable to theoretical predictions

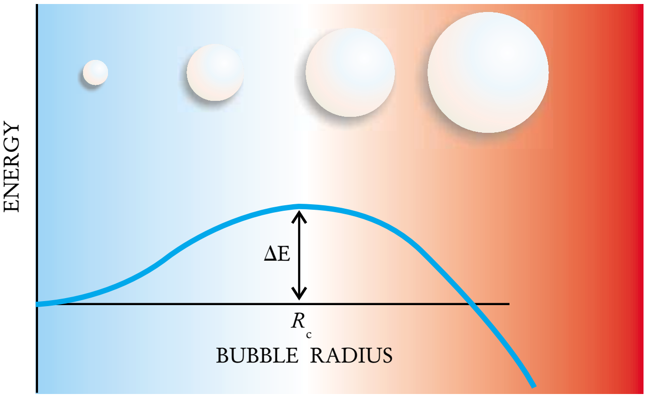

FIGURE 2. ENERGY OF A SMALL BUBBLE in a liquid under negative pressure, as a function of bubble radius. For small bubbles, the energy increases with radius because the surface energy makes the largest contribution to the energy. Above a critical radius R_c, the energy begins to decrease because of the negative energy associated with the work done by the applied negative pressure. When its radius reaches R_c, a bubble can grow without limit. Thus, the liquid "breaks."

by Robin Speedy of the University of Wellington (in New Zealand) for the maximum negative pressure in water.[4]

Helium at negative pressures

Helium remains a liquid at absolute zero because the interatomic forces are extremely weak and the small helium mass results in a large zero-point energy. At 2.17 K, the so-called lambda point, the liquid becomes superfluid (see the helium-4 phase diagram in figure 4). Although the phase diagram and other properties of helium for positive pressures have been studied in great detail for many years, the properties for negative pressure have not yet been measured.

One important question concerns the determination of the pressure at the spinodal. One method of estimating the location of the spinodal relies on an extrapolation of the sound velocity into the negative pressure range—the spinodal is the pressure at which the sound velocity reaches zero. This approach requires making some assumption about the way in which the sound velocity goes to zero at the spinodal, an interesting problem of statistical physics that has not yet been completely solved. Estimates based on this approach[5] give a spinodal pressure of between –9 and –10 bars at $T = 0$ K. At the University of Trento (in Italy), Franco Dalfovo and his coworkers[6] have used a density functional theory to describe liquid helium-4 and have obtained about –9.5 bars for the zero-temperature spinodal pressure. The Spanish group of Jordi Boronat at the Polytechnic University of Catalonia in Barcelona found –9.3 bars using a Monte Carlo numerical method.[7] Thus, it now seems well established that the extreme limit of metastability of liquid ^{4}He is around –9.5 bars. (For ^{3}He, the corresponding result is approximately –3 bars.) At higher temperatures, the spinodal pressure becomes less negative. Indeed, the spinodal line has to reach the liquid–gas critical point (5.2 K and +2.2 bars in ^{4}He), because there the difference between liquid and gas vanishes.

The location of the superfluid transition—the "lambda line"—at negative pressures is even more difficult to estimate; the curve shown in figure 4 is based only on a guess. The lambda line is expected to reach the spinodal at some finite temperature, but again, essentially nothing is known about the behavior of the spinodal or the lambda line in the vicinity of where they meet.

In the phase diagram of helium, there is thus a new world at negative pressure that has not yet been very much explored and is not shown in textbooks. It extends from the liquid–gas equilibrium curve at small positive pressures down to the spinodal line a few bars below zero. This regime has been our playground in recent years.

To study the liquid in this pressure regime, it is important to use very clean liquid. Robert Finch and his coworkers[8] made several studies of cavitation in helium in the 1960s and 1970s using liquid from the main bath of a helium dewar. In those early experiments, cavitation was detected even at very small negative pressures of only a few millibars, presumably because of some form of contamination of the helium. A sample of clean liquid helium can easily be prepared by filling a cell through a fine capillary. This procedure removes any particles of solid air that might be present in a helium dewar.

It is also important that the negative pressure be produced in the interior of the liquid, far from any wall at which heterogeneous nucleation could occur. We use a sound wave with a frequency of around 1 MHz generated by a hemispherical ultrasonic transducer (figure 5). The sound comes to a focus in the interior of the liquid. This method readily produces a pressure oscillation with an amplitude of several bars at the focal point. The volume throughout which the pressure swing is produced is determined by the sound wavelength and is typically on the order of 10^{-6} cm^3. To determine whether a cavitation bubble has been produced, we shine a laser beam through the acoustic focus. Bubbles will scatter the light, which is detected by a photomultiplier.[9]

Landmarks in a quantum sea

In our experiments, determining the pressure that has been reached is a challenging problem that requires calibrating the sound transducer, estimating the efficiency of the focusing, and so forth. Landmarks along the road to the spinodal are consequently of great value. Fortunately, there is one such landmark, and a remarkable one indeed. When an electron is injected into helium, it forms a spherical cavity—an "electron bubble"—from which helium atoms are excluded. The bubble forms because the electron is strongly repelled by helium; the electron therefore tends to be localized in an empty cavity rather than propagated through the liquid.

FIGURE 3. INSIDE A GIANT redwood tree, the pressure of the water is 1 bar at ground level, but it decreases to –10 bars near the top of the tree. If a woodpecker (not shown to scale) were to make a small hole in the trunk near the top of the tree, why wouldn't air rush in to replace the water that is at negative pressure? See the text for the explanation.

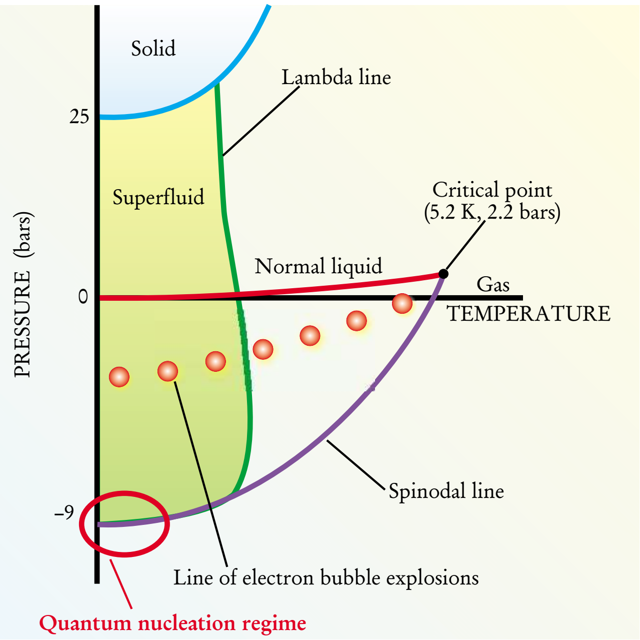

Figure 4. Liquid helium-4 phase diagram, including the negative-pressure regime. (The diagram is not to scale.) The positive-pressure region of the phase diagram, including the equilibrium liquid–gas transition (red line), has been studied extensively in many experiments. The spinodal line indicates the pressure at which the liquid's sound velocity becomes zero and the liquid becomes unstable against long-wavelength fluctuations. The lambda line for negative pressures is based largely on guesswork. Bubbles formed around free electrons will explode if the pressure reaches the line of red circles.

The radius R of electron bubbles is determined by minimizing the total energy, given by the sum of the ground state energy of the electron ($h^2/8m_eR^2$, with m_e being the electron mass), the surface energy of the bubble ($4\pi R^2\alpha$), and the work done against the liquid's pressure in forming the bubble ($4\pi R^3P/3$). If the pressure is zero, a bubble will have a radius of around 19 Å. When the pressure is made negative, the bubble grows, and at a critical pressure of around –2 bars, the electron bubble explodes—it becomes unstable and grows without limit. The critical pressure can be calculated in a reliable way in terms of known quantities; therefore, it provides a milepost in the negative-pressure regime. Lying approximately 20% of the way to the spinodal, this milepost offers a good calibration of our system for the production of negative pressure.[10]

To study the explosions of electron bubbles, we use a radioactive β source to inject electrons into the liquid. Electrons from the β source enter the liquid with high velocity, lose energy, and then form stable bubbles that wander around in the liquid. If such a bubble wanders into the region of the sound focus, it will expand on the negative part of the pressure oscillation, become unstable, and explode (see figure 6).

These explosions are distinct from the processes that occur in a conventional helium bubble chamber. In a bubble chamber, an energetic charged particle passes through a liquid that is already at a negative pressure. In fact, there has been some uncertainty about the mechanism of bubble formation in bubble chambers. The traditional view has been that the bubble is formed as a result of the energy that is deposited by one of the secondary electrons produced along the track of the fast particle.[11] Our studies of electron explosions have revealed another possibility (for liquids in which electrons form bubbles).[12] When a secondary electron is produced, it quickly comes to rest in the liquid. It then pushes liquid away to open up a cavity. The inertia of the liquid surrounding the bubble causes the radius of the cavity to increase beyond the radius corresponding to the minimum energy configuration. For example, in liquid helium at a pressure of –0.3 bars, the cavity will reach a maximum radius of about 28 Å and then oscillate for a while before finally settling down into a state with a radius of 20 Å. But if the pressure is more negative, the inertia of the liquid around the bubble may be sufficient to make the bubble reach a size beyond the critical radius for bubble nucleation. Then the bubble will grow without limit. The critical pressure that can be calculated for this process is in very good agreement with the old measurements for the threshold pressure for operation of helium and hydrogen bubble chambers.

It may be possible to find other landmarks along the path to the spinodal. One possibility is to use light to raise an electron bubble to an excited state; the bubble should then explode at a negative pressure of smaller magnitude that can also be calculated accurately. A second possibility is to introduce quantized vortices into the liquid. When a vortex is present, each helium atom in the liquid near it will have one unit of angular momentum. Consequently, the liquid will circulate around the vortex with a tangential velocity of h/m_4r, where r is the distance from the vortex core and m_4 is the mass of a helium atom. This circulation will result in a pressure at the vortex that is more negative than the pressure in the bulk of the liquid. Thus, the vortex core should explode before the spinodal is reached, thereby providing another way in which bubbles can form.[13]

Thermal versus quantum cavitation

How close can experiments come to the spinodal of helium? As the pressure is made more negative, the energy barrier preventing the nucleation of a bubble becomes smaller and smaller. At some distance from the spinodal, the barrier is small enough that there becomes a chance that, with the aid of a thermal fluctuation, a bubble larger than the critical size will be created. Such a bubble will

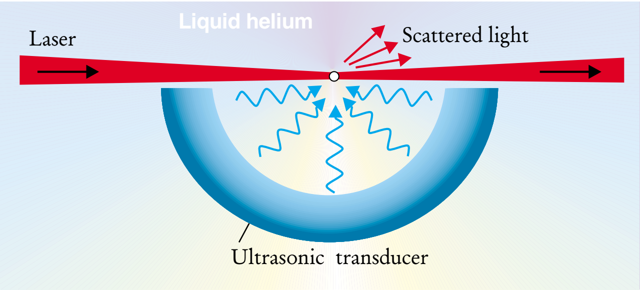

Figure 5. Apparatus for detecting cavitation. A hemispherical ultrasonic transducer immersed in liquid helium is driven by an RF pulse to emit a burst of sound. At the acoustic focus, a large oscillating pressure is produced. If the amplitude of the sound is large enough, bubbles (like the white dot shown here) may form during the negative pressure swing. The bubbles will scatter part of the laser light passing through the focus.

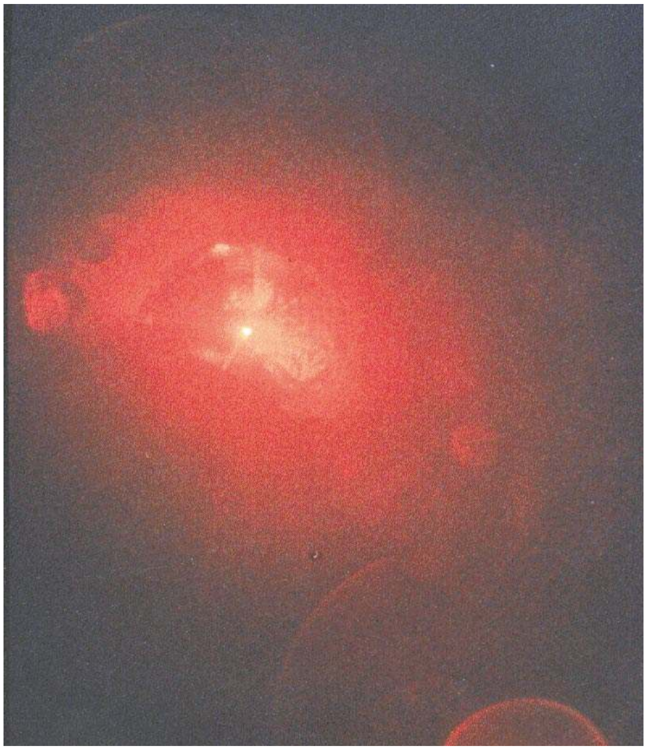

FIGURE 6. LIGHT SCATTERED from the explosion of an electron bubble. The white dot in the center of the picture is a small bubble containing a single electron that has wandered into the region of the acoustic focus and exploded during the negative pressure swing of the sound field. This photograph was taken after the bubble had reached a diameter of approximately 200 μm. (Photo by Claire Cramer.)

then grow to a macroscopic size. As the temperature is lowered, the thermal fluctuations become weaker, and the probability of bubble nucleation remains small until the pressure is very close to the spinodal. Below a critical temperature T_c, thermally activated passage over the nucleation barrier becomes unimportant compared to quantum tunneling through the barrier.[14] This process is "macroscopic," in the sense that it requires the cooperative motion of several hundred helium atoms (of course, "macroscopic" is a great exaggeration). The detailed theory of quantum cavitation was worked out by one of us (Maris) in 1995 and by Montserrat Guilleumas and her colleagues in 1996.[15] Both analyses predicted that quantum cavitation should become important in ^{4}He at temperatures below $T_c = 0.2$ K and at pressures within about 0.3 bars of the spinodal. It is essential in these calculations to allow for the softening of the liquid as the spinodal is approached. This effect was not included in earlier calculations.[16]

At first sight, it looked as though it would be very difficult to test these theoretical ideas. Even with the electron explosions as mileposts, the pressure estimation was still not very accurate. Consequently, to determine that the pressure was 0.3 bars from the spinodal seemed to be equivalent to finding a spot 0.3 feet from the edge of a cliff on a very dark night. Fortunately, our recent experiments at the Ecole Normale Supérieure have produced two results that provide indirect but strong evidence that quantum cavitation has indeed been seen.[17]

When the quantum regime is entered, the pressure at which cavitation occurs should become independent of temperature; the experiments found the onset of such behavior at a temperature of 0.6 K. This temperature was much higher than the T_c of 0.2 K predicted by theory, but the discrepancy was quickly understood. In the experiment, 0.6 K was the measured temperature of the liquid *before* the pressure was reduced; during the expansion of the liquid that took place before cavitation, however, the temperature should decrease by about a factor of three. Thus, the measured critical temperature was in reasonable agreement with theory.

The second piece of evidence for quantum cavitation concerns the statistics of the cavitation. A series of experiments was performed in which the pressure swing applied to the liquid was controlled very precisely. Even though the pressure reached in each sound pulse was the same, sometimes a bubble was produced and sometimes it wasn't (figure 7). The observations that the cavitation is statistical, but independent of temperature, strongly suggest that nucleation is occurring by means of quantum tunneling.

These observations of quantum cavitation have been performed with liquid ^{4}He in the superfluid state. Can bubbles be produced by quantum tunneling only when there is some sort of quantum coherence in the liquid? We hope to answer that question through measurements on liquid ^{3}He, which is not superfluid except at much lower temperatures. For ^{3}He, the crossover temperature from thermal nucleation to quantum tunneling has been predicted[16] to be around 120 mK. In measurements down to 40 mK, our preliminary results show that the cavitation pressure is about three times less negative in ^{3}He than in ^{4}He, as would be expected if cavitation occurs by means of

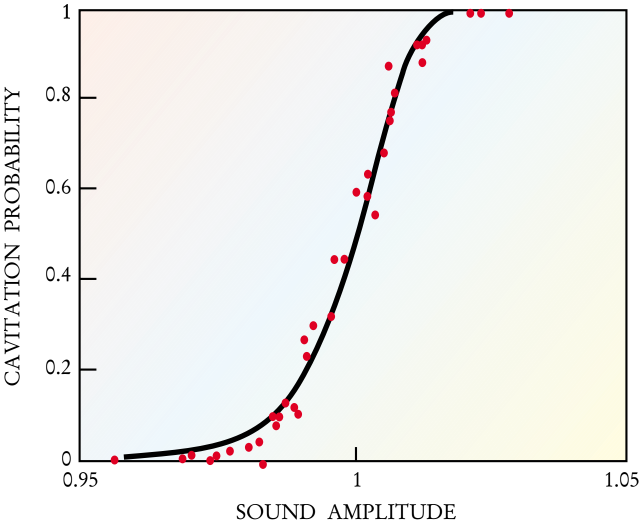

FIGURE 7. ACOUSTIC CAVITATION is a stochastic phenomenon. A high-amplitude burst of sound brought to a focus in the liquid may or may not result in cavitation. We have measured the cavitation probability by sending a series of 100 sound bursts with well controlled amplitude and counting the number of times cavitation occurs. As shown here for liquid helium-4 at 171 mK, the cavitation probability increases continually with the sound amplitude. The solid line is a fit with a theory in which the formation of bubbles is assumed to occur by means of quantum tunneling. The units for the sound amplitude have been chosen such that unit amplitude corresponds to a cavitation probability of 50%.

quantum tunneling very close to the spinodal limit for both isotopes in the low-temperature limit. Furthermore, the results show that the pressure at which bubbles form in ^{3}He continues to vary with temperature down to at least 100 mK, a temperature much lower than in helium-4 (again, as predicted). However, the existence of a temperature-independent regime in ^{3}He has not yet been established.[18]

Much more accurate measurements are now in progress. If a "quantum plateau" below 100 mK is found, it will demonstrate that quantum cavitation can take place without the need for the quantum coherence characteristic of a superfluid. If there is no quantum plateau, it will be necessary to reconsider the theory of quantum cavitation in ^{3}He. For example, since ^{3}He is a Fermi liquid, its compressibility is a function of frequency. This behavior may affect the tunneling process, which occurs on a timescale of around 10^{-11} s. It is also possible that the spinodal line has an unexpected temperature variation, or that the large viscosity of ^{3}He has to be considered. Answering questions about such issues should lead to further improvements in the understanding of liquids close to a spinodal.

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