Acoustic crystallization and heterogeneous nucleation

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By focusing a high intensity acoustic wave in liquid helium, we have observed the nucleation of solid helium inside the wave above a certain threshold in amplitude. The nucleation is a stochastic phenomenon. Its probability increases continuously from 0 to 1 in a narrow pressure interval around $P_m + 4.7$ bars ($P_m = 25.3$ bars is the melting pressure where liquid and solid helium are in equilibrium). This overpressure is larger by two to three orders of magnitude than what had been previously observed. Our result strongly supports the recent suggestion by Balibar, Mizusaki and Sasaki [1] that, in all previous experiments, solid helium nucleated on impurities.

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To our knowledge, no one has ever observed that a high intensity sound wave travelling in a liquid can crystallize this liquid. Several experiments have shown that the negative pressure swings of the wave can produce cavitation, in other words nucleate bubbles or trigger the liquid-gas transition [2]. By focusing an acoustic wave in liquid helium, we have found that the positive swings can also trigger the liquid-solid transition. It occurs if the wave amplitude reaches a certain threshold which we have measured. We could also estimate the size of the crystallites formed in the wave (15 μm) and their typical growth velocity (100 ms^{-1}, close to the speed of sound). We believe that it is the ability of helium crystals to grow at very high speed which allowed us to make this observation. The observed threshold corresponds to a pressure 4.7 bar higher than the equilibrium pressure. This overpressure is two to three orders of magnitude larger than what had been observed in all previous experiments [3–7]. Our result strongly supports the recent suggestion by Balibar, Mizusaki and Sasaki [1] that, in all these previous experiments, solid helium nucleated on favourable impurities.

Let us first describe our experimental method. Inside a cryostat with optical access, we have focused an acoustic wave through liquid helium 4. The acoustic focus is located on a clean glass plate which allows us to measure the local instantaneous density of liquid helium [8] (see Fig.1). The acoustic wave is emitted by a hemispherical piezoelectric transducer similar to the one we used for the study of cavitation [2]. It resonates in a thickness mode at 1.019 MHz and we pulse it with bursts of six oscillations, consequently about 6 μs wide. The focusing is achieved by the transducer geometry. Given the characteristics of our RF amplifier, we can reach a maximum acoustic power of 5 kW.cm^{-2} (200 dB) at the focus. The transducer is gently pressed against the glass plate. At the melting pressure, the sound velocity is 366.3 ms^{-1} in the liquid phase [9] , so that the acoustic wavelength

is 360 μm. A lens of focal length 2 cm is located inside the experimental cell and focuses an Ar$^+$ laser beam onto the acoustic focal region. The waist of the laser beam at the focus is 30 μm, less than one tenth of the acoustic wavelength. The light spot position is carefully adjusted at the center of the acoustic focal region by tilting the incident beam and maximizing the modulation of the reflected light from the acoustic wave. We have measured the ratio of the ac-component to the dc-component of the reflected light.
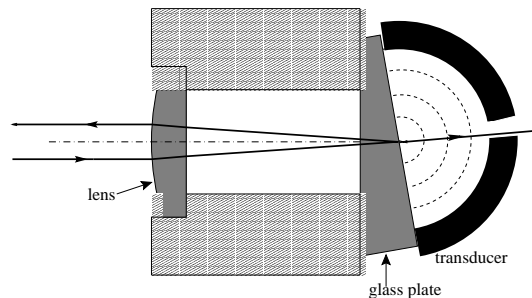

FIG. 1. Experimental setup

The dc-component acts as the reference. It corresponds to the reflection at the interface between the glass and liquid helium at the static pressure in the cell. Here we only present results at low temperature (T = 65 mK) when the static pressure equals P_m. There is some solid helium in the bottom part of the cell. The transducer, the glass plate and the lens are in the liquid above. At the static pressure P_m = 25.324 bar, the static density is ρ_m = 0.17245 g.cm^{-3}. We calculated the refractive index n_{He} of liquid helium from the Clausius-Mossoti relation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi\rho\alpha_M}{3M} \tag{1}$$

where M = 4.0026 g, ρ is the helium density and α_M is the molar polarizability. For 514.5 nm green light, α_M = 0.1245 cm^{3}mol^{-1}. This value is slightly larger than the

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zero frequency polarizability $\alpha_{M0} = 0.1233$ cm^{3}mol^{-1} which is given by Harris-Lowe [10] and cited by Donnelly [11]. Indeed, the polarizability varies with frequency as measured by Cuthbertson [12] cited by M.H.Edwards [13].

At the melting density (and for 514.5 nm), we found $n_{He} = 1.0339$. Since the index of our BK7 glass plate is $n_g = 1.5205$ for the same green light, the reflection coefficient is

$$R = \left(\frac{n_g - n_{He}}{n_g + n_{He}}\right)^2 = 0.036288 \qquad (2)$$

The ac-component is proportional to the modulation of the local density by the acoustic wave. It is measured with an avalanche photodiode (Hamamatsu APD module C5331-03) which has a sensitivity of 15 kV.W^{-1} in the range 4 kHz to 100 MHz. We use low light powers so that the APD responds linearly (the incident power in the experimental cell is about 500 μW and the power received by the diode is about 6 μW). The dc-component is measured with a Si photodiode (Hamamatsu S1406). With its amplifier circuit, it has a sensitivity of 2.35 kV.W^{-1} at low frequency and works up to 400 kHz. We carefully calibrated the sensitivity ratio of our two diodes by modulating the Ar laser beam at 200 kHz, inside the overlap region of their frequency bandwiths. From the known value of the reflection at P$_m$ (the dc-component), we then obtained the value of the instantaneous density at the acoustic focus.

FIG. 2 and FIG. 3 show two recordings of the instantaneous density as a function of time. These recordings were obtained with a LeCroy digital oscilloscope whose sampling rate is 1 GHz. Our transducer has a finite quality factor $Q = 50\pm5$ so that the wave amplitude increases during the six first periods. After six periods, the electric excitation stops and the amplitude relaxes to zero according to the same quality factor. The acoustic burst arrives at the focus 21.84 μs after the beginning of the electrical excitation (time zero).

Two traces are superimposed on these figures. There is also a horizontal line which indicates the static liquid density $\rho_m = 0.17245$ g.cm^{-3}. These traces are not one shot recordings, they correspond to averages on 1000 bursts repeated at a rate of 3 Hz. We checked that our results do not depend on the light intensity nor on the repetition rate. Fortunately, our plate resisted to a very large number of acoustic impacts.

The first trace corresponds to an excitation of 10.4 V, below the threshold for the nucleation of solid helium. The acoustic oscillation is unaltered. It shows a nearly sinusoidal wave with a smoothly varying envelope. The second trace corresponds to a slightly larger excitation (11.0 V) and shows a sharp increase of the density around 27.5 μs, where the maximum sound amplitude is reached.

We attribute this increase to the nucleation of solid helium at the acoustic focus. This nucleation occurs on the glass surface since the reflectivity measurement only probes this surface and the crystallization starts when the density is maximum there.
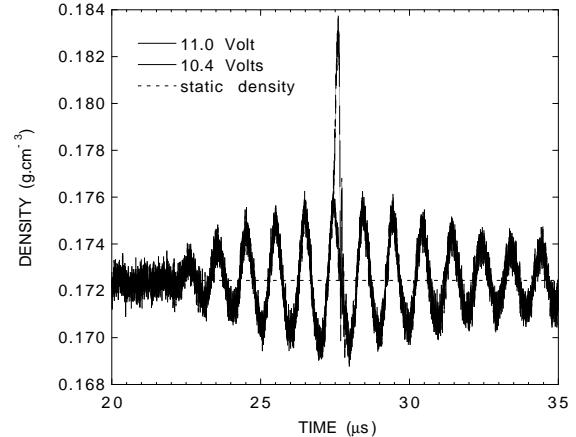

FIG. 2. Two recordings of the density at the acoustic focus as a function of time. One trace corresponds to an excitation (10.4 V) below the crystallization threshold; the other one (11.0 V) is superimposed on the first one and shows a peak corresponding to the nucleation of solid helium.
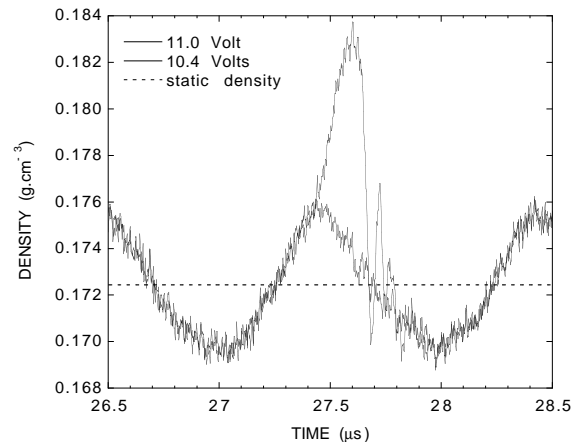

FIG. 3. An enlargement of the central part of Fig. 2

We have also observed that the nucleation is stochastic. The nucleation probability increased continuously from zero to one as the excitation increased in a small voltage interval [14]. The probability was 3% for 10.6 V, 35% for 10.8 V and 98% for 11.0 V. The first trace is an average on bursts which never nucleated the solid. On the contrary, the second trace is an average on bursts which nearly always nucleated the solid. We also have to remember that the laser beam is focused onto a region about 30 μm wide. Since the density of solid helium [15]

is 0.19076 g.cm^{-3} , our observation of a maximum density around 0.183 g.cm^{-3} indicates that once the solid has nucleated, it grows up to about 15 μm in size, half the waist of the laser beam at the focus. As we further increased the excitation, our signal saturated around 0.191 g.cm^{-3}. It shows that the nucleated phase is hcp helium. When starting from a lower static density, we obtained the same nucleation threshold (0.1758 g.cm^{-3}). We expected these crystals to grow as long as the local pressure is larger than P_m and to melt only when it becomes less than P_m. FIG. 3 shows that our signal decreases slightly sooner, also that it oscillates a few times before vanishing. This surprising behaviour may be due to oscillations of the crystal itself (acoustic resonances inside it ?) or to the existence of a non-monotonic density field in the liquid. We also remark that the crystal grows in about 150 ns, which corresponds to a very large growth velocity, about 100 m.s^{-1}. It is well known [16] that the helium crystals grow very fast at low temperature. With any classical crystal, the necessary evacuation of the latent heat introduces a resistance to the growth which would hardly allow growth velocities comparable to the sound velocity. This is probably the reason why acoustic crystallization was never observed before. Let us finally notice that the wave amplitude corresponds to a relative density oscillation of order 2%, so that the temperature at the acoustic focus should also oscillate, but only by the same 2 % if we assume that the wave is adiabatic, which is reasonable.

How can one understand our results? Several authors [3–7] had observed that solid helium appeared in their cells if liquid helium was pressurized a few millibars only above the equilibrium pressure P_m. This is a very small overpressure. Indeed, a rough estimate [1] of the energy barrier for homogeneous nucleation is 10^{10} K for an overpressure $\delta P = 3$ mbar. Since Ruutu et al. [6] measured an energy barrier of order 10 K, 9 orders of magnitude less, Balibar et al. [1] had suggested that their energy represented the pinning energy of an already existing liquid-solid meniscus, not the energy cost for creating the interface (as assumed in the elementary homogeneous nucleation theory). Balibar et al. [1] further suggested that impurities such as graphite particles were present in all ordinary cells. Indeed, solid hcp helium 4 is known to grow by epitaxy on graphite [17,3,18–20] . If there is a small area of such graphite somewhere in the cell, solid helium only needs to escape from it to invade the cell. The pinning energy being typically the product of a surface energy by the size of the pinning site which can be very small, Balibar et al. [1] explained why the energy barrier for the appearance of solid helium in an ordinary cell can be small even for slight overpressures. One important check of the above suggestions was to measure the nucleation threshold δP for solid helium in the absence of favourable impurities. Balibar et al. [1] predicted that δP would be much higher in this clean case. According to the preliminary results which are presented here, this is indeed true. We studied our nucleation events as a function of static pressure and temperature. We also performed other experiments [14] with static pressures smaller than P_m and temperatures up to 1 K. The results are similar but this study is not yet completed. In this letter, we restrict our main comments to FIG.2 and FIG.3. These figures demonstrate that the nucleation mechanism is significantly different from what had been observed in all previous studies [3–7].

Indeed, we see that the liquid density needs to reach values as high as 0.1758 ± 0.0002 g.cm^{-3} for the solid to appear. The main source of uncertainty is the noise in the intensity of the reflected light. By measuring the sound velocity as a function of pressure Abraham et al. [9] established the following equation of state for liquid helium:

$$P - P_m = 567.42 \, \delta\rho + 11115 \, (\delta\rho)^2 + 74271 \, (\delta\rho)^3 \quad (3)$$

where $\delta\rho = (\rho - \rho_m)$, the pressure P is in bars and the density ρ in g.cm^{-3}, $P_m = 25.324$ bar and $\rho_m = 0.17245$ g.cm^{-3}. We note that this equation of state is very accurate and almost indistinguishable from the equation by Maris once one corrects it for the fact that he took pressures in bars when they are in atm in the original paper by Abraham *et al*. We also note that the liquid density at melting is very slightly different from Grilly's value [15] 0.17293. Using Abraham's measurement we deduce the value of the liquid pressure at the nucleation threshold, $P = 30.0 \pm 0.3$ bar $= P_m + 4.7 \pm 0.3$ bar. We further remark that crystal seeds do not survive on the glass plate, although the static pressure differs from P_m by a very small hydrostatic pressure only. We believe that there is no defect on the glass plate which is able to keep a crystal seed, but we cannot yet exclude that seeds are washed out by the negative pressure swing which follows the positive one.

From the temperature variation of the nucleation statistics, we hope to measure the activation energy E. It should be of order 10 K [1]. Before we do this, it is interesting to estimate what would be the energy barrier for the homogeneous nucleation of solid helium at $P_m + \delta P$ = 30.0 bar, using the thin wall approximation as a crude approximation [22]. It is given by

$$E = \frac{16\pi}{3}\alpha^3 \left(\frac{\rho_L}{(\rho_C - \rho_L)\delta P} \right)^2 \quad (4)$$

where $\alpha = 0.17$ erg.cm^{-2} is the average value of the surface energy of helium crystals [23]. For $\delta P = 4.7$ bar, we found E = 2700 K and a critical radius for the nucleation $R_c = 72$ Å. This is still too large, but not at all as absurd as 10^{10} K. We know [3,24,25] that ordinary walls are partially wet by liquid helium, with a contact angle for the liquid/solid interface $\theta = 45$ deg. As explained by Uwaha [26], a critical nucleus with the shape

of a truncated sphere touching the glass wall with a contact angle $\theta = 45$ deg would have nearly the same energy ($0.94 \times$ E $= 2540$ K).

We cannot exclude that there is some roughness on the glass plate, which lowers the energy barrier. But the van der Waals attraction from the glass wall should be the most important effect. One needs to account for the density gradient near this wall and to calculate the activation energy with a density functional method. Let us finally comment on homogeneous nucleation of solid helium. In this experiment, solid helium nucleates on the glass wall. In our previous experiments where the acoustic wave was focussed in the middle of liquid helium, we never saw any solid nucleation even by exciting our transducers with a much higher voltage. Given the maximum output power of our RF amplifier, we must have reached $25 + 17 = 42$ bar, and we now know that we should have detected the solid if it had nucleated. At that time, we looked at the light transmitted through the focus. This is not the technique used for the recordings of Figs. 2 and 3, but we also looked at the transmitted light in this experiment. The nucleation of the solid was easy to see without any averaging, and we now use this method for the complementary measurement of the nucleation probability. If we use homogeneous nucleation theory, now with δP $= 70$ bar, we find E $= 8$ K, so that a more powerful RF amplifier should allow us to observe the homogeneous nucleation of solid helium in the absence of glass plate. This would also be very interesting to observe. Indeed, at such pressures, we expect the roton gap of liquid helium to vanish, and we consider this as the spinodal limit for the liquid-solid transition (rotons are not related to any vortices but to local order in the liquid which extends to infinity if the roton gap vanishes).

We have observed crystallization inside an acoustic wave. This new phenomenon allowed us to bring new information on the nucleation of solid helium, more precisely on heterogeneous nucleation on a clean wall, a situation which is intermediate between homogeneous nucleation and heterogeneous nucleation on unknown impurities. We have found that nucleation occurs 4.7 bar above the melting pressure P_m. This overpressure is much more than in previous experiments where it is likeley that favourable impurites were present. It is also less than what we expect for homogeneous nucleation (δP > 70 bar). Our experiment is still in progress. We hope that it triggers new calculations of the nucleation threshold for solid helium.

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