Homogeneous nucleation of crystals by acoustic waves

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Abstract. –
In order to study the homogeneous nucleation of crystals in a pressurized liquid, we focused a high intensity acoustic wave in superfluid helium 4. We studied the scattering of light at the acoustic focus and found the first experimental evidence that, beyond a certain wave amplitude, positive pressure swings crystallize the liquid on their path. We discuss measurements of the nucleation time and of the pressure dependence of the scattered light intensity near the liquid-solid equilibrium pressure. Future developments of this work are related to the prediction of a metastability limit for liquid He^4 at high pressure where superfluidity could vanish.

Introduction. – By focusing high intensity acoustic waves in the middle of a pure liquid, it is possible to pressurize it far beyond its liquid-solid equilibrium pressure P_m before crystals nucleate. This is because this method eliminates the influence of walls and impurities, so that, if nucleation occurs, it has to be "homogeneous". In this case, the energy barrier against nucleation is an intrinsic property of the pressurized liquid and it is large except at sufficiently high pressure. We looked for such an acoustic crystallization in liquid helium because it is known to be very pure at low temperature: natural He^4 contains only about 0.1 ppm He^3 and all other impurities are frozen and bound to walls.

In our experiment, the amplitude of the acoustic pressure can be larger than 100 bar, and this method was already used in our group to study homogeneous nucleation of bubbles in the negative swings of the wave [1,2]. In further studies we looked for the nucleation of crystals during the positive swings. For this, a glass plate was first inserted in the focal plane of a hemispherical transducer; from the reflectivity at the glass/liquid interface we measured the wave amplitude [3] and nucleation of He^4 crystals was observed 4.3 bar above $P_m = 25.3$ bar [4]. This overpressure was much larger than what had been observed in ordinary cells (1 to 100 millibars [5,6]), but crystallization was still heterogeneous, occurring on one defect of the glass plate [7]. We then removed the glass plate and increased the wave amplitude with the same transducer. No clear evidence was found for homogeneous crystallization in the bulk liquid up to a pressure which was estimated to be 160 ± 20 bar [8]. However, we shall reconsider the interpretation of this experiment at the end of this article.

In order to further increase the maximum pressure at the acoustic focus, we glued two hemispherical transducers together to make a spherical one. We expected to multiply the

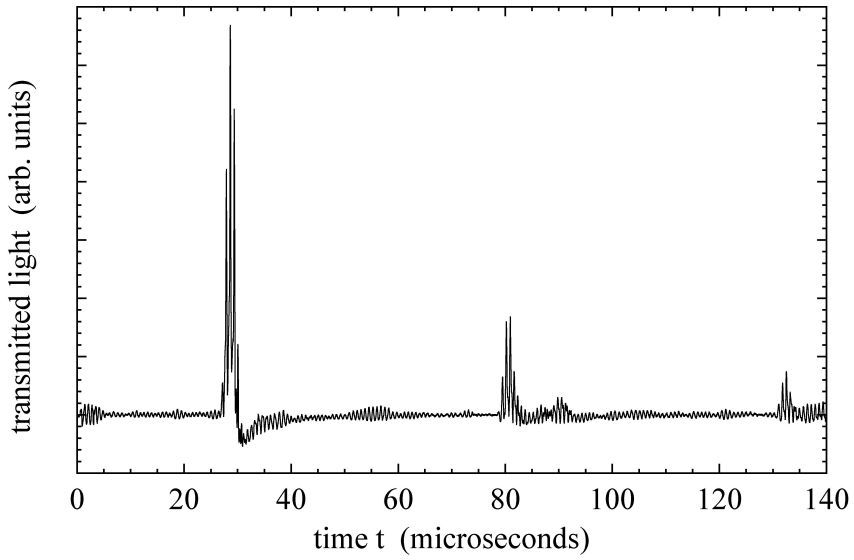

Fig. 1 – A burst of acoustic wave (3 cycles at 1.39 MHz) is emitted at $t = 0$ by a spherical transducer immersed in liquid helium at $P = 25.0$ bar and $T = 600$ mK. From the transmission of light through the central region, one measures the arrival time of this burst at the center and several successive echoes, from which the exact value of the radius is obtained.

maximum wave amplitude by more than a factor 2 because of non-linear effects [9, 10]. This article describes the results of this new experiment. We first summarize our experimental method. We then discuss how we could distinguish nucleation of bubbles in the negative swings from nucleation of crystals in the positive swings. This was done by measuring nucleation times and the influence of the static pressure $P_{\rm stat}$ in the cell. Eventually, we compare our results to those previously obtained by Werner *et al.* [8]. Our goal is to verify the existence of a metastability limit for liquid He^4 where superfluidity could vanish [11–13].

Experimental procedure. – We have used two hemispherical transducers (PZT 5800 from Channel Industries) with an inner radius $R = 9.42 \pm 0.02$ mm and a 1.6 mm thickness. They were chosen with similar electrical characteristics, glued together with GE varnish, and electrically connected with copper wires and silver paint. We could excite them either in their first thickness mode at 1.39 MHz or in a 132 kHz mode which is presumably the fundamental breathing mode. Four slits allow optical access to the center in two perpendicular directions. Thanks to a lens outside the cryostat, a laser beam is focused through the transducer center; we can detect either the transmitted light (Fig. 1) or the light scattered 0.5 to 5 degrees off the optical axis (Fig. 2). The exact value of the inner radius R is important to know for the analysis of nucleation times (see below). It was measured from the time delay between echoes inside the spherical cavity. For a better accuracy, we used 1.39 MHz bursts and Fig. 1 shows a time recording of the transmitted light. The delay between echoes is $2t_f = 2R/c = 51.6 \pm 0.1$ μs, where c is the sound velocity (365 m/s at 25.0 bar [14]).

We have checked our analysis of flight times by comparing signals recorded at different static pressures $P_{\rm stat}$ in the cell. Fig. 2 shows light scattered by the acoustic wave which is now excited at low frequency (140 kHz). The successive peaks correspond to the sharp positive pressure peaks which are predicted to occur [9] due to non-linearities in the focusing

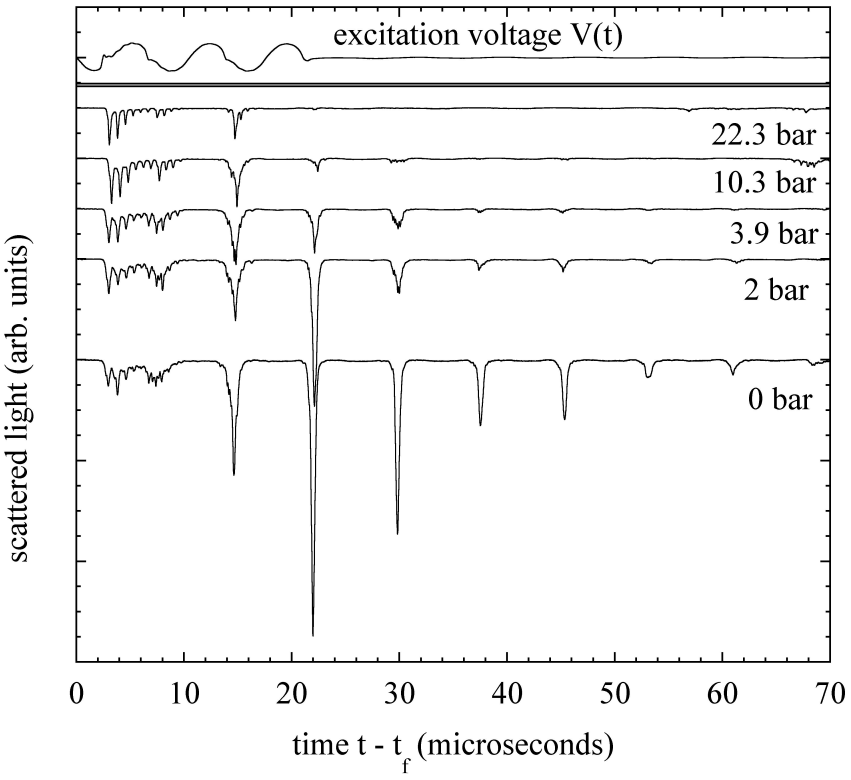

Fig. 2 – Upper part: the excitation voltage $V(t)$ (3 cycles at 140 kHz) is sinusoidal but slightly distorted by the amplifier. Lower part: the light scattered by an acoustic burst as a function of time $(t - t_f)$. As predicted by Appert *et al.* [9], non-linear effects in the focusing produce sharp positive pressure peaks every one sound period (7.6 μs), especially at low pressure. The high frequency oscillations from 2 to 10 μs are due to the distortions of $V(t)$.

when the equation of state itself is non-linear. Since the equation of state is more curved at low pressure, the effect is less pronounced at high pressure. At each pressure, the flight time t_f is caculated from the known value of R and the sound velocity from ref. 14. After subtracting t_f, the time scale starts when the acoustic pulse arrives at the center. All signals being now synchronized, our measurement of the transducer radius is confirmed. The spacing between sharp peaks also allows to measure the period of the wave which is emitted when the transducer is excited at the nominal frequency $f = 140$ kHz during 3 cycles only (top of Fig. 2). We found 7.6 ± 0.1 μs corresponding to 132 ± 2 kHz for the real frequency.

For the study of nucleation, we used the low frequency mode because nucleated crystals had more time to grow and were easier to detect. Compared to previous experiments in our group [8], there were thus two main differences: the geometry was spherical instead of hemispherical and the sound frequency was 132 kHz instead of 1 MHz. Furthermore, we measured the nucleation probability by counting nucleation events in series of 200 bursts repeated at 1 Hz as before [1, 2, 7, 8]. The voltage threshold V_c corresponds to a probability 0.5. On Fig. 3, the two recordings were obtained at the threshold for nucleation during the second cycle. We also observed nucleation during the first or third cycles (Fig. 4) but at voltages which were different because of the finite quality factor of the transducers. The

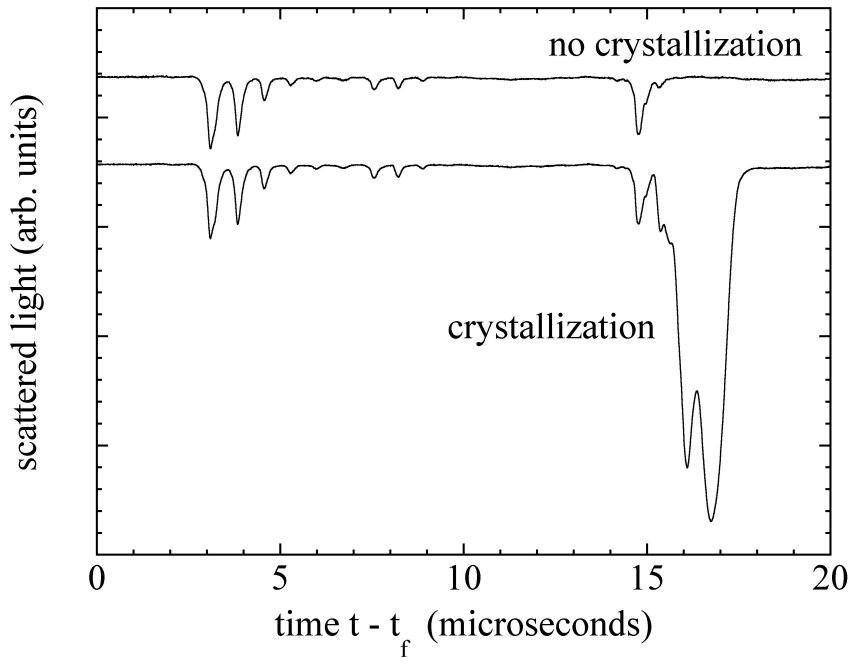

Fig. 3 – Two typical recordings of the scattered light at 25.3 bar and 600 mK. The upper one shows scattering by the acoustic wave only. The lower one shows additional scattering due to the nucleation of a crystal. The time scale starts when the beginning of the acoustic burst arrives at the center.

signals in Fig. 3 are typical of what we observed when the static pressure $P_{\rm stat}$ in the cell was close or equal to $P_{\rm m}$. For a precise determination of the nucleation time, we substracted the upper signal from the lower one. An example of this is shown on Fig. 4 but it corresponds to a different recording.

Results and discussion. – In fact, we could observe two different regimes: nucleation at low $P_{\rm stat}$ (typically 0 to 3 bar) and at high $P_{\rm stat}$ (23 to 25.3 bar) but our sensitivity was apparently not high enough to detect it in between. It is natural to assume that it was bubbles at low $P_{\rm stat}$ and crystals at high $P_{\rm stat}$, but this needs to be demonstrated. Since cavitation occurs in negative swings and crystallization in positive ones, their respective times should be shifted by half a period. Figure 4 shows a comparison of nucleation signals at low and high $P_{\rm stat}$. The time scale starts when the acoustic burst arrives at the center, and we subtracted the light scattered without nucleation from the one with nucleation. The nucleation event at 25.3 bar starts at $t = 21.1$ μs which is close to two and three quarters of a period (7.6 μs). We have checked with a hydrophone and the transducer in water that our excitation generated a pressure pulse which started with a negative swing so that the maximum pressure was indeed reached $2 + 3/4$ periods later. Furthermore, Fig. 4 shows a time delay of 3.6 ± 0.1 μs between the the starting times of the two nucleation signals; this corresponds to half a period, which shows that the low pressure nucleation is cavitation. We had already observed such a shift in a preliminary experiment done at 1.3 MHz [15], but, at that time, our measurement of t_f was not yet precise enough for a definite conclusion. The sharp oscillation in the low pressure trace is what remains after subtraction of positive pressure peaks similar to those shown in Fig. 2.

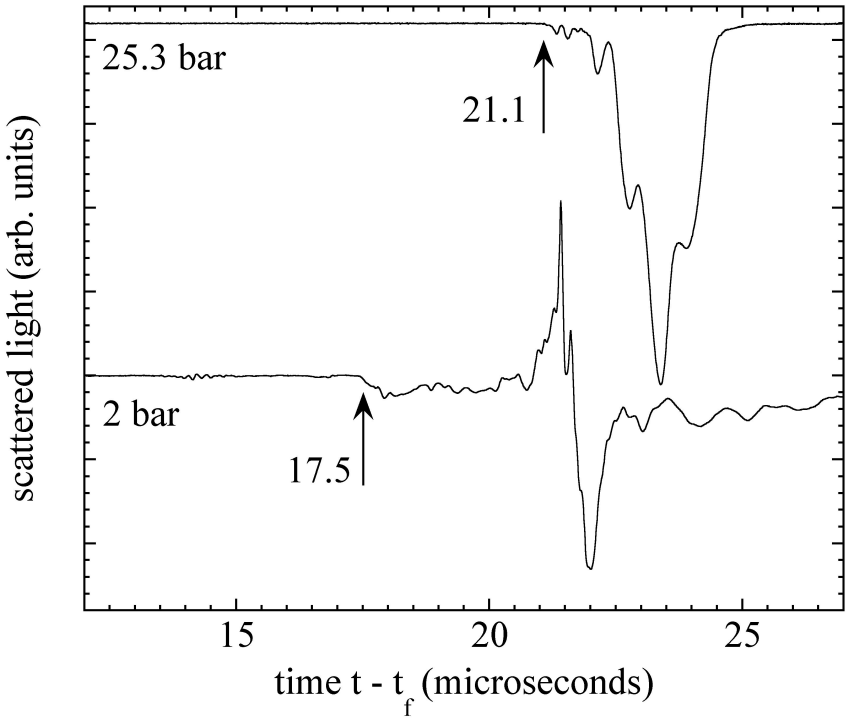

Fig. 4 – Comparison of nucleation times for bubbles at 2 bar and crystals at 25.3 bar at their respective threshold voltages. Crystals nucleate 3.6 ± 0.1 μs – about half an acoustic period – later than bubbles. Each trace is a difference between signals with and without nucleation.

As can be seen, the crystal nucleation occurs at the same time as these positive pressure peaks, which again supports our analysis. Eventually, Fig. 4 shows that the cavitation signal at 2 bar lasts for a longer time than the crystallization signal at $P_{\rm m}$. This is probably due to non-linear effects distorting the wave: the negative swings last longer than the positive ones, so that bubbles could survive to the positive pressure peaks which last for a short time only. On the opposite, crystals are melted by the negative swings which follow the narrow time during which they nucleate and grow. As we shall now see, our interpretation is further supported by the dependence of the signal amplitude on the static pressure $P_{\rm stat}$.

Fig. 5 shows the signal area, or time integral of the light scattered by the crystals near $P_{\rm m} = 25.3$ bar (dotted line). The signal increases sharply as $P_{\rm stat}$ approaches $P_{\rm m}$. When working at $P_{\rm m}$, we had some crystal in the bottom part of the cell but the transducer was in the liquid above. A signal increase close to $P_{\rm m}$ is of course consistent with our interpretation: the objects which nucleate at high pressure are crystals, not bubbles; they have more time to grow if the liquid is close to $P_{\rm m}$; one could hardly imagine such a signal increase if the objects nucleating at high $P_{\rm stat}$ were bubbles. However, some of these observations were already made by Werner *et al.* [8] whose conclusions were opposite and need to be reconsidered in the light of the present work.

Werner *et al.* have proposed that the wave nucleated bubbles at high $P_{\rm stat}$, not crystals. Their main reason came from an analysis of the dependence of the threshold voltage V_c on $P_{\rm stat}$. They showed that the quantity ρV_c – where ρ is the pressure dependent density of the liquid

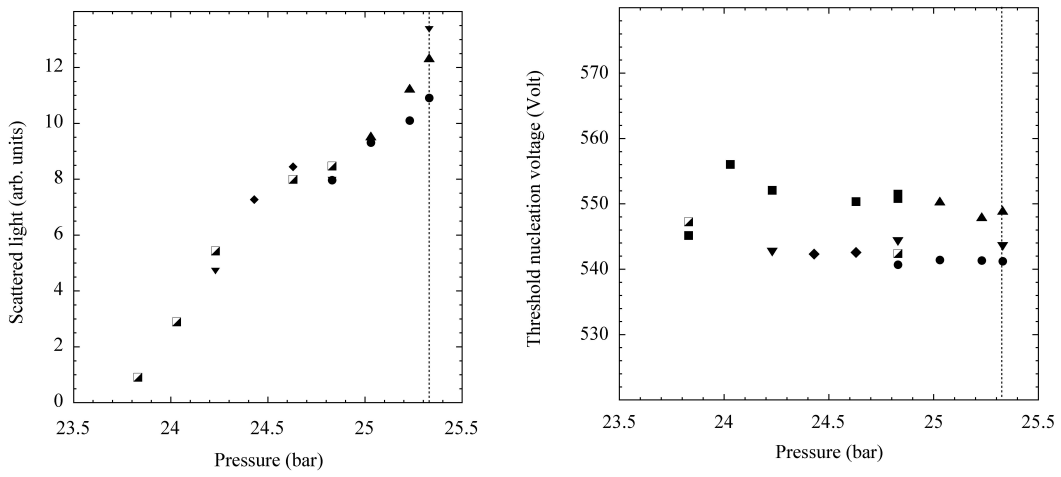

Fig. 5 – Left: the variation of the time integral of the scattered light, as a function of the static pressure in the cell $P_{\rm stat}$. The dotted line indicates the liquid-solid equilibrium pressure $P_m = 25.3$ bar. Right: the pressure dependence of the nucleation threshold voltage V_c.

– was linearly related to $P_{\rm stat}$ in the pressure interval from 18 to 25 bar. Furthermore, they found that ρV_c extrapolated to 0 at $P_{\rm stat}= -9.5$ bar (the spinodal pressure), in agreement with earlier studies of cavitation [2]. It looked natural to Werner *et al.* that the voltage necessary for the nucleation of bubbles increased with $P_{\rm stat}$. However, the extrapolation to -9.5 bar could have been a coincidence and non-linear effects in the wave focusing could make positive pressure peaks higher at low $P_{\rm stat}$ than at large $P_{\rm stat}$ [16]. The observation of a linear variation of $\rho V_c(P_{\rm stat})$ in a limited pressure range (18 to 25 bar) was perhaps not sufficient to claim that non-linear effects were negligible in their geometry and at their frequency (1 MHz). In the present experiment, we found that ρV_c was independent of $P_{\rm stat}$ in the narrow range from 23.8 to 25.3 bar (Fig. 5). Further measurements are needed to understand this pressure dependence. In particular, we wonder how non-linearities vary with frequency and geometry.

Werner *et al.* could not measure nucleation times accurately because, in their hemispherical geometry, there were no echoes to measure the radius R with enough acccuracy. They also looked at the pressure variation of the signal and they found the same kind of increase as shown in Fig. 5. However, they used a lens inside their experimental cell in order to better focus the light at the center and improve the detection sensitivity; but the focal length of this lens depended on $P_{\rm stat}$ via the pressure variation of the index of helium. The lens focused the light onto the acoustic focus only at $P_{\rm m}$, and they attributed the pressure variation of their nucleation signal to the optical focus moving away from the acoustic focus when $P_{\rm stat}$ decreased away from $P_{\rm m}$. In the present experiment, the light is focused with a lens outside the cryostat, so that the sensitivity is not as good but nearly independent of $P_{\rm stat}$.

Werner *et al.* had concluded that He^4 could remain in a metastable liquid state up to 160 bar, but we now think that this needs to be further checked and their conclusion possibly corrected. For this, we need to measure the local instantaneous pressure inside the acoustic wave. This is a rather difficult task but it should be possible with Brillouin scattering [17].

Conclusion and perspectives. – We have presented the first experimental evidence for homogeneous nucleation of crystals in the bulk of a liquid which is pressurized by an acoustic

wave. Further studies should allow us to measure at which pressure or density this phenomenon occurs, thanks to the combination of Brillouin light scattering with our ultrasonic method. We might have to consider the limit where the roton gap vanishes [11] and the liquid becomes unstable. According to a preliminary estimate by F. Caupin and H.J. Maris [18], this limit should be reached for a density of 0.24 g.cm^{-3} corresponding to about 200 bar, but the recent Monte Carlo calculation by Vranjes *et al.* [19] shows that this density corresponds to 275 bar where the roton gap is not yet zero. Considering this issue is one goal of our experiment. Furthermore, this density being much higher than that of liquid helium at 25 bar (0.17 g.cm^{-3}) or even solid helium at 25 bar (0.19 g.cm^{-3}), quantum exchange of atoms should be difficult near this limit and it is interesting to know if the liquid is still superfluid [12,13]. Vranjes *et al.* [19] have predicted that liquid He^4 should be superfluid at 0.24 g.cm^{-3} and sufficiently low T. Boninsegni *et al.* [20] also found that superfluidity is possible at such densities, even in a glass state. If liquid He^4 was not superfluid when nucleation occurs, the crystals would not grow fast enough to be detected in our experiment, except if we really reached the instability. In any case, it is interesting to measure the lambda line in the metastable region of liquid He^4 at very high pressure, and the observation of a second sound line in Brillouin scattering could allow us to do it. This is another goal for future developments of our experiment.

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