

Comments on Heterogeneous Nucleation in Helium

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We first recall some basic ideas on homogeneous and heterogeneous nucleation. We then reconsider the heterogeneous nucleation of solid helium from liquid helium in the presence of walls. Recent experiments by Ruutu et al. demonstrate that the presence of walls drastically reduces the energy barrier for such "heterogeneous" nucleation events, although walls are usually more favorable to the liquid phase. In order to explain this reduction, we propose a simple model based on the unpinning of an already existing interface. In the light of such results, we then reconsider the nucleation of the B-phase of superfluid helium 3 from its A-phase. We propose a model where the B-phase nucleation is thermally activated on walls, without need of cosmic rays.

1. INTRODUCTION

Being extremely pure, helium at low temperature has shown very useful for the general study of phase transitions. Its thermodynamics only depends on temperature T and pressure P , also on magnetic field H in the case of helium 3, and all these parameters can be very homogeneous and very accurately controlled. Here we focus on first order transitions where a metastable phase 1 needs to be taken outside of its stability region in the phase diagram before a stable phase 2 nucleates. By which nucleation process a system can evolve from a metastable state to a stable one is of course an issue of much wider importance than just for the changes in the states of matter. We believe that this field has progressed thanks to recent experiments in helium. They show why, in most cases, nucleation is more likely to be "heterogeneous," i.e., taking place on particular defects or walls, than "homogeneous" in which case it is an intrinsic property of the bulk matter. In the light of such experiments, we wish to clarify some ideas

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and avoid some misunderstandings or wrong statements. One usually starts any nucleation theory by considering homogeneous nucleation in the “thin wall approximation” as explained in Landau and Lifshitz.¹ One thus assumes that the free energy of a spherical nucleus of phase 2 in the metastable phase 1 writes

$$F(R) = 4\pi R^2 \sigma_{12} - \frac{4}{3}\pi R^3 \Delta G_{12} \quad (1)$$

where the first positive term is a surface energy cost involving the same surface free energy σ_{12} as for a macroscopic surface, and the negative term is a volume energy gain which includes the difference in Gibbs free energy per unit volume ΔG_{12} between phases 1 and 2. From Eq. (1), one deduces a critical radius for nucleation

$$R_c = \frac{2\sigma_{12}}{\Delta G_{12}} \quad (2)$$

and an energy barrier

$$E = \frac{16\pi}{3} \frac{(\sigma_{12})^3}{(\Delta G_{12})^2} \quad (3)$$

Except if ΔG_{12} is very large, or if the surface energy vanishes, the energy E is usually so large that the classical nucleation rate

$$\Gamma = \Gamma_0 \exp -\frac{E}{T} \quad (4)$$

looks totally negligible. This is the striking remark which puzzles physicists since a long time. A well known example in low temperature physics is the nucleation of the B-phase of superfluid helium 3 from its A-phase, where Eq. (1) led D. D. Osheroff² to the estimation $E/T=10^6$. The number $\exp(-10^6)$ is so small that, whatever the attempt frequency Γ_0 can be, Eq. (4) leads to a nucleation probability Γ which is zero. Some years later, Leggett proposed the “baked Alaska model”³ to justify the hypothesis that cosmic rays are responsible for the nucleation of the B-phase. Following refs. 2 and 3, many experimental and theoretical studies have been devoted to the understanding of the B-phase nucleation,^{4,5} a problem which still seems rather controversial.⁶

In the mean time, the understanding of the nucleation of solid helium 4 from liquid helium 4 has substantially progressed. It was first noticed by Balibar *et al.*⁷ that a small overpressure of order 10 mbars was sufficient to nucleate the solid phase in an ordinary cell. From visual observations of

nucleation^{8,9} and measurements of the contact angle of the solid–liquid interface of helium 4 on walls, it is now well established that the nucleation of the solid takes place on walls, although most of these walls are “more favorable” to the liquid phase not to the solid one. By “more favorable,” we mean that usual walls are partially wet by the liquid phase, not by the solid phase, with a contact angle of the liquid–solid interface of about 45°. Furthermore, quantitative studies of this nucleation have been recently published by Ruutu *et al.*¹⁰ and by Sasaki and Mizusaki.¹¹ In this article (Sec. 2), we reexamine Ruutu’s measurements and explain why they demonstrate that the energy barrier is of order 10 K, 9 orders of magnitude smaller than predicted by Eq. (1) (10¹⁰ K!). We then propose a simple explanation for such a drastic reduction, and we suggest an experiment to check it. In Sec. 3, we reconsider the nucleation of the B-phase of helium 3 in the light of Sec. 2. We find analogies between the two cases, and we propose that the B-phase nucleation is heterogeneous, thermally activated on walls, as a possible alternative to the effect of cosmic rays. For this B-phase nucleation also, we propose further experimental checks.

2. THE HETEROGENEOUS NUCLEATION OF SOLID HELIUM 4

Except if a large piece of clean graphite is introduced in the experimental cell, liquid helium 4 can be overpressurized some millibars above the equilibrium melting pressure P_m before it crystallizes. On clean graphite, several authors^{7, 18, 19} showed that hcp helium 4 crystals grow by epitaxy with their c axis perpendicular to the graphite basal planes. As a consequence, no overpressure is observed in the presence of such a clean graphite surface. The hcp phase of solid helium 4 perfectly wets graphite because of some matching of the symmetry and lattice parameters between the two phases. Such a matching is probably needed for any crystalline phase to wet a solid substrate, in which case epitaxial growth takes place. Otherwise, it seems that there is too much stress, consequently too much elastic energy, in the wall-crystal interface. No other case of epitaxial growth has ever been reported, so that we suppose that the contact angle of the solid–liquid interface of helium 4 with most other surfaces is about 45°,^{7–9} showing that the walls favor the liquid phase; one has the usual relation

$$\sigma_{CL} \cos \theta = \sigma_{WC} - \sigma_{WL}, \quad (5)$$

with the wall-crystal interfacial energy larger than that of the wall-liquid interface. In the absence of a clean graphite surface, Balibar *et al.*⁷ found that a typical overpressure of 10 to 15 mbars was necessary for the first crystal to appear. They further observed that, after air had been admitted in

a cell with clean graphite, nucleation occurred only about 5 mbars above P_m . Ruutu *et al.*¹⁰ observed a reproducible overpressure of about 3 mbars if they depressurized their cell by less than 10 mbars below P_m after the observation of each nucleation event. As for Sasaki and Mizusaki,¹¹ they used an electric field to observe nucleation. Their results are qualitatively similar to those of Ruutu *et al.*, except that they measured overpressures of about 30 mbars if each nucleation was followed by a depressurization about 3 bars below P_m . It is now generally accepted that walls can keep crystal seeds at pressures significantly lower than P_m . Both Sasaki and Ruutu observed that the nucleation of solid helium is a stochastic phenomenon, with a nucleation probability varying exponentially with the overpressure $\delta P = P - P_m$. Such stochastic behaviors with exponential probabilities are widely observed with a characteristic “asymmetric S-shape” curve¹² for the nucleation probability as a function of a control parameter. Clear examples of such phenomena have been found in the nucleation of gas bubbles¹² and vortices.¹³ At first sight, the exponential behavior looks easy to understand, at least qualitatively. It is indeed expected when nucleation results from thermal activation over an energy barrier E (see Eq. (3)) or from quantum tunneling through it. The difficulty is to obtain quantitative agreement. Let us try to use Eq. (3) to estimate E for Ruutu’s experiment. As estimated by D. O. Edwards *et al.*¹⁴ a typical value of the energy σ_{CL} for the crystal–liquid interface in helium 4 is 0.2 ergs/cm². As for the difference in free energy per unit volume in Ruutu’s experiment, it is

$$\Delta G_{CL} = \left(\frac{\rho_C}{\rho_L} - 1 \right) \delta P = 0.3 \text{ mbars}, \quad (6)$$

so that $E = 1.5 \times 10^{-6}$ ergs = 10^{10} K! Such activation energies are absurd, of course, since $\exp(-10^{10})$ is an incredibly small number.

In fact, Ruutu’s experimental results provide strong evidence that $E = 12$ K, not 10^{10} K, around $T = 0.5$ K. As we shall now see, this more realistic value is implicit in their analysis. Ruutu *et al.* observed a temperature independent overpressure below about 300 mK, and a decrease of this overpressure above 300 mK. This is convincing evidence for a crossover from quantum to thermal nucleation, and they assumed that the prefactor Γ_0 in the nucleation rate is about $k_B T/h$. We agree with that and wish to go a little further in the interpretation. Let us introduce a time τ_0 which is the typical time during which nucleation is observed in their experiment. This time depends on the rate c at which they pressurize their cell. Assuming that c is constant, the pressure increases with time as

$$\delta P = ct, \quad (7)$$

and the nucleation probability is the time integral of the rate:

$$\Sigma = 1 - \exp - \left[\Gamma_0 \tau_0 \exp - \left(\frac{E}{T} \right) \right] \quad (8)$$

with $\tau_0 = -T/(cE')$ and $E' = \partial E/\partial \delta P$. Here, we only need to consider the thermal nucleation regime. As could be expected, τ_0 is the time necessary for the activation energy E to change by an amount T during the pressurization. This time is about 0.3 s, as can be easily estimated from the width of their probability curves ($T/E' = -0.06$ mbars so that $E' = \partial E/\partial \delta P \approx -8$ K/mbar from the curve at 500 mK (Fig. 2 in ref. 10), and $c = 0.2$ mbar/s). As usual, we then define the nucleation threshold $\delta P_{1/2}$ as the overpressure corresponding to a nucleation probability 1/2; there, the activation energy has the value $E_{1/2}$ such that

$$E_{1/2} = T \ln \left(\frac{\Gamma_0 \tau_0}{\ln 2} \right) \quad (9)$$

At $T = 500$ mK, one has $\Gamma_0 = k_B T/h = 7 \times 10^{10}$ Hz and one finds $E_{1/2} = 12$ K. In fact, this value is a direct consequence of the hypothesis that nucleation is thermally activated around 1 K at one single site in an experiment which lasts for about one second.

More interesting is the fact that it can be further checked. Indeed, the value of the activation energy also determines how fast the nucleation pressure decreases as T increases. When writing Eq. (6), we have implicitly assumed that the difference in free energy ΔG does not depend on T . This is a good approximation in liquid helium 4 below 1 K where the thermodynamic properties depend more on P than on T (for example, the slope of the melting line is very small). If we keep assuming that nucleation is thermally activated over an energy barrier E , we can take the T derivative of Eq. (9) and show that the quantity

$$\frac{\partial(E_{1/2}/T)}{\partial T} = -\frac{E_{1/2}}{T^2} + \frac{E'}{T} \frac{\partial \delta P_{1/2}}{\partial T} \quad (10)$$

is about 0 since $\partial(\ln(\Gamma_0 \tau_0))/\partial T$ is negligible. From $E_{1/2} = 12$ K (at $T = 0.5$ K) and $E' = \partial E/\partial \delta P = -8$ K/mbar, we can then calculate the T derivative of the threshold $\delta P_{1/2}$ and compare with Ruutu's data. We find $\partial \delta P_{1/2}/\partial T = -3$ mbars/K, in very good agreement with their results (Fig. 3 in ref. 10). We thus believe that Ruutu's experiment provides strong evidence that solid helium is nucleated on walls either by thermal activation or by

quantum tunneling, with an energy barrier of about 12 K at 500 mK. It nucleates on walls because they see it, also because activation energies for homogeneous nucleation in the bulk are unrealistic. It cannot be triggered by mechanical noise nor by cosmic rays because the prefactor Γ_0 would then be much smaller than 10^{10} , leading to a much smaller activation energy which would then be contradictory with the T dependence of their nucleation threshold above 500 mK.

The next important issue is to understand how this activation energy can be only about 12 K at 500 mK. Let us try geometrical effects first. As explained by Uwaha,²¹ as soon as the walls are not perfectly wet by the metastable phase (the liquid), the nucleation has to take place on these walls, because the free energy of a truncated spherical nucleus touching the wall with a contact angle θ is smaller than the energy of a fully spherical nucleus in the bulk. The energy of the truncated nucleus is

$$E = \frac{16\pi (\sigma_{12})^3 f(\theta)}{3 (\Delta G_{12})^2} \quad (11)$$

where $f(\theta) = 1 - (1 - \cos \theta)^2 (2 + \cos \theta)/4$. Except very close to perfect wetting by the stable phase ($\theta = 180^\circ$), the reduction in activation energy is not very large. For example, $f(\theta) = 0.94$ if $\theta = 45^\circ$. Obviously, it is far from enough to reduce the homogeneous activation energy by a factor 10^9 . The next idea is thus to consider a crack in the wall with a particular geometry. Such a crack has to be able to keep a solid nucleus at $P < P_m$ and it also has to let it escape at pressures only a few mbars higher than P_m . As already noticed by Ruutu *et al.* themselves, this looks rather difficult to imagine. If the solid seed remains at pressures much lower than P_m , as was often observed by us, we could find no geometry for a suitable crack in the wall.

Let us consider some orders of magnitude. A solid-liquid meniscus can be in equilibrium at a pressure $P_m + \delta P$ if it is properly curved. According to the Gibbs-Thomson relation, the curvature radius needs to be

$$R(\delta P) = \frac{2\sigma_{CL}}{(\rho_C/\rho_L - 1)\delta P} \quad (12)$$

For $\delta P = +5$ mbars, the equilibrium curvature radius has to be 8 microns. As shown on Fig. 1, one could imagine a kind of ink bottle (also called “lobster pot” by Leggett and Yip²⁰) with a neck of radius 8 microns, so that the meniscus escapes spontaneously from the bottle at $\delta P = 5$ mbars, and at 3 mbars it has to overcome an energy barrier. This is somehow similar also to the “cavity in the wall” suggested by Ruutu *et al.* who

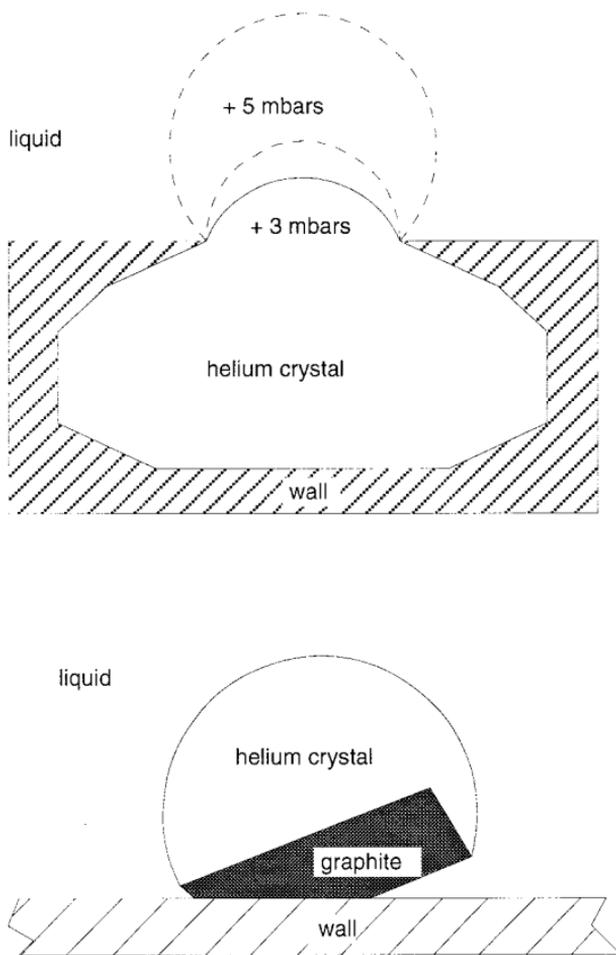


Fig. 1. A helium crystal can be trapped inside an "ink bottle" below the melting pressure (top). 3 mbars above P_m , it is anchored on the orifice (solid line). 5 mbars above P_m it would escape spontaneously if the bottle neck is 8 microns in radius (broken lines). However, thermal fluctuations are not sufficient to overcome the macroscopic energy barrier between the position at 3 mbars and the one at 5 mbars. If the crystal has grown by epitaxy on a graphite particle, it only needs to overcome a small pinning energy to escape in the cell (bottom).

indeed claim that the liquid would be totally unstable at 5 mbars but that the solid nucleates at 3 mbars.

We agree with them that the system has to be close to an instability point, a kind of surface spinodal limit at some critical value δP_c . Indeed, the analysis of Ruutu's data not only provides $E_{1/2} = 12$ K for $\delta P = +3$ mbars but also $\partial E_{1/2} / \partial \delta P = -8$ K/mbar, so that the activation energy

$E_{1/2}$ has to vanish at a certain δP_c , 1 or 2 mbars above 3 mbars. As a consequence, Ruutu *et al.* present a very general argument showing that the energy barrier has to be proportional to $(\delta P - \delta P_c)^{3/2}$. Their fit leads to $\delta P_c = 5$ mbars. However, if the wall defect is only geometric like such an ink bottle, the energy barrier would be nearly as large as the homogeneous nucleation barrier except if the pressure is extremely close to the instability limit ($\delta P_c = 5$ mbars). Since 3 mbars is not very close to 5 mbars, the ink bottle model leads to an activation energy at 3 mbars which is inconsistent with the experimental results.

If geometry does not solve our problem, we have to imagine another kind of wall defect. We propose a defect with a different chemical composition, so that the local contact angle is very different. More precisely, we propose that the solid grows continuously from a region with 180° contact angle (perfect wetting by the solid), and that it is pinned there with a small pinning energy. The size of this region has to be comparable to the equilibrium curvature radius. Since graphite is known to be wet by hcp solid helium 4, we can imagine a graphite particle somewhere on the wall (Fig. 1). If this graphite particle is about 10 microns in size, solid helium can grow on it spontaneously and reach a curvature radius of several microns. Dust particles from cars are a few microns in size and might exactly provide what we need. Now, in order that the solid meniscus escapes in the cell, it has to overcome a pinning energy. The pinning site might be the edge of the graphite particle or a micro-aggregate of solid air. In fact, no one has ever made a systematic search for substrates which solid helium could perfectly wet, and graphite might not be the only one at all. Anyhow, the pinning energy corresponds to a change in surface energy on a scale comparable to the size of the pinning site. It can be written as

$$E_p \approx \delta A \sigma_{\text{CL}} \left(1 - \frac{\delta P}{\delta P_c} \right)^{3/2} \quad (13)$$

where δA is the typical area of the pinning site, and δP_c is again a limit in overpressure at which the meniscus would spontaneously escape from its pinning site, even in the absence of fluctuations (another surface spinodal limit). Note that we use the same 3/2 exponent as Ruutu *et al.*, because this is a general property of stability limits.

The order of magnitude of the surface energy term is $0.1 \text{ K}/\text{\AA}^2$ since $\sigma_{\text{CL}} \approx 0.2 \text{ ergs/cm}^2$. To obtain 12 K for the pinning energy, one needs a site area of about 120 \AA^2 , slightly more if we account for the pressure term. This is about the square of the thickness of the solid-liquid interface, so that the description in terms of the macroscopic surface tension is only an approximation.

At this stage of our reasoning, it seems important to note that finding a microscopic scale (120 \AA^2) is not surprising; it is the only way to build a microscopic energy (12 K). As long as one uses a macroscopic curvature radius, as long as one sticks to a theory related to homogeneous nucleation in the thin wall approximation, it is impossible to find a microscopic energy barrier. This is why we propose a rather different scenario where the energy barrier no longer represents a cost for creating a solid-liquid interface but the pinning energy of an already existing interface. A first check of this model would be to study the nucleation of solid helium in a cell with very smooth glass walls carefully cleaned in a white room, as was done for the A-B transition of superfluid helium 3. This is not an easy experiment since one cannot isolate a part of a cell from the influence of the rest with the aid of a magnetic field as in the case of superfluid helium 3. However, a clean porous vycor plug glued with stycast might work. The goal would be to pressurize liquid helium up to much higher pressures than ever done before just by carefully avoiding the presence of dust particles. If this could be achieved, it would be a strong support to our model. However, one might discover other kinds of surfaces which help the nucleation of solid helium. We also notice that Balibar, Maris and their collaborators have tried to nucleate solid helium 4 in the absence of any influence from walls. They tried it with the same acoustic transducers as was used for the study of the homogeneous nucleation of bubbles from liquid helium. Up to now, they have not detected the nucleation of solid helium by this method, although liquid helium was overpressurized by much more than 10 bars above P_m . Homogeneous nucleation of solid helium 4 clearly requires a very much higher overpressure than heterogeneous nucleation.

3. THE CASE OF THE A-B TRANSITION

Let us now consider the nucleation of the B-phase in the light of the above analysis. It was first claimed^{2,3} that the B-phase nucleation is a unique puzzle because the homogeneous nucleation theory gives an extraordinarily large activation energy. As explained above, the nucleation of solid helium is even more striking from this point of view.

It was further claimed^{2,3,25} that since walls are more favorable to the A-phase than to the B-phase, nucleation has to take place in the bulk, not on the walls. For this to be true, walls would need to be perfectly wet by the A-phase, and we do not believe that they are. Indeed, in this case, experimental cells would never keep a memory of the B-phase, whereas they often do so. Leggett²⁰ has noticed that in order to achieve large degrees of supercooling of the A-phase, once the cell has seen the B-phase, it is necessary to warm up this cell in the normal phase (above T_c).

Otherwise, during the next cool down, the B-phase nucleates much closer to T_{AB} than during the first cool down. This has been confirmed by several authors, including recently by Ruohio *et al.*²⁸ Some experiments have shown that the nucleation takes place at particular, reproducible, places in the cell.¹⁵ D. D. Osheroff *et al.* have achieved larger supercoolings by improving the smoothness of their cell walls.^{2,4,5} Other experiments also showed that the B-phase can be superheated inside the stability region of the A-phase.²² All these observations are strong indications that the contact angle of the AB interface with walls is intermediate between 0 and 180°, probably also that wall defects play some role.

Furthermore, as we understand, this contact angle has been measured, but unfortunately never published. Indeed, according to D. D. Osheroff²³ and M. Cross,²⁵ J. Landau and A. White measured a contact angle of 68°. This result agrees with two theoretical estimates. Indeed, Cross²⁵ calculated a contact angle in the range 60 to 80° and Thuneberg²⁶ found 39 to 65°; in both works, the angle depends on the nature of the scattering of quasiparticles on the wall. We thus understand that walls are only slightly more favorable to the A-phase, and certainly not enough to induce perfect wetting. Of course, a new and precise measurement of this contact angle looks highly desirable to us. At least, we do not think that nucleation on walls can be ruled out by saying that walls are more favorable to the A-phase.

Of course, one could say that nucleation takes place on the walls when they are rough but maintain that nucleation takes place in the bulk when walls are perfectly clean as in the last experiments by O'Keefe.⁵ This is hard to rule out, but a good test is to look for memory effects. After one nucleation event in ultraclean cells, we suggest that superfluid helium 3-B is warmed up to a temperature only slightly higher than T_{AB} , and cooled down again. If nucleation of the B-phase occurs at a much smaller undercooling, then the system has a memory. Since the bulk has no memory, this is a strong indication that nucleation takes place on walls where there exist particular defects which are favorable to the B-phase. If the system has no memory, so that the nucleation of the B-phase takes place at the same very low temperature as when the system is warmed above T_c , then it is a strong indication that nucleation takes place in the bulk. Since various authors gave us contradictory answers for this question, we hope that it can be more systematically studied.

For the nucleation to take place in the bulk, Leggett has proposed that the large necessary energy is provided by the impact of cosmic rays. We do not claim that this is impossible. We do not wish either to enter the controversy⁶ about quasiparticle mean free path, and the comparison between the Kibble mechanism and the "baked Alaska" model. These two models claim that radiation is necessary for nucleation to occur. But none

of these models explain how cosmic rays or gamma rays or neutrons can combine with surface roughness to decrease the possible undercooling of the A-phase in the presence of rough walls.

The life time of the A-phase is lowered when a radioactive source is approached to the cell. In itself, this observation does not necessarily support the idea that, in the absence of radioactive source, the nucleation is due to cosmic rays. As a comparison, let us consider another phase transition, namely the liquid-gas transition in helium. Su and Maris²⁴ demonstrated that cavitation occurs in liquid helium at pressures which are about 5 times less negative in the presence of electrons from a radioactive source than in their absence. This allowed the same research group to interpret quantitatively how bubble chambers work.¹⁶ Still, the fact that cavitation occurs in a liquid helium bubble chamber is no proof that, in the absence of radioactive source, acoustic cavitation is due to cosmic rays! In fact it cannot be, since it was observed on such small volumes and times that the effect of cosmic rays is totally negligible.

The Stanford group carefully analyzed the effect of radiations. They compared the relative efficiency of cosmic rays and Cobalt sources and found agreement within a factor 2 to 4, that is the right magnitude for the respective fluxes of particles. More puzzling is the fact that, in all their fits, Osheroff *et al.* use an exponent 3/2 in the exponential variation of the lifetime which is different from the one calculated by Leggett in his baked Alaska model (3 to 5). We do not claim that cosmic rays are irrelevant. We want to present an alternative interpretation of all the results, where nucleation takes place on the walls and involves no cosmic rays. As we shall see, our model fits all the existing measurements of the lifetime of helium 3-A, whether obtained with smooth or with rough walls.

We assume that the invasion of the cell by the B-phase occurs when an already existing AB interface unpins from some wall defect (Fig. 2). The depinning could be either activated by thermal fluctuations or due to quantum tunneling. For simplicity, we calculate a thermal activation from one single site as follows.

Osheroff's group studied the B-phase nucleation as a function of undercooling, not as a function of pressure as in the liquid-solid case. This makes an important difference because, now, the variation of T affects not only the amplitude of thermal fluctuations but also the magnitude of the free energy difference ΔG_{AB} between the two phases, a central quantity.

As described in the review by Schiffer *et al.*,⁴ the difference ΔG_{AB} is linear in $(T - T_{AB})$ near T_{AB} , and it saturates below 0.5 mK at the value $\Delta G_{AB}(0) = 1.47$ ergs/cm³. From 1.1 mK to $T_{AB} = 1.93$ mK, it writes:

$$\Delta G_{AB} = 3.36(1 - t) - 0.692(1 - t^4) \quad (14)$$

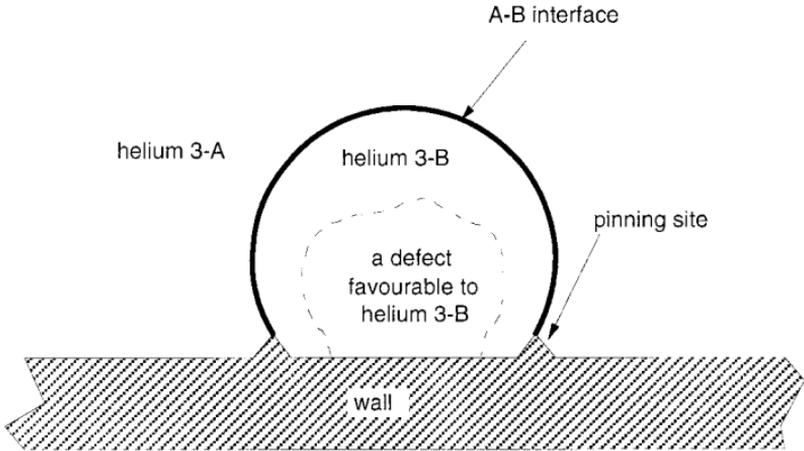


Fig. 2. Schematic view of a wall defect favourable to helium 3-B. In order to escape from this favourable site, the B phase has to unpin from a nearby edge.

in ergs/cm^3 with $t = T/T_{AB}$, but Eq. (14) is not valid in the low T limit. In order to make fits easier, we have adjusted a 5th order polynomial to represent the full temperature variation of ΔG_{AB} from $T=0$ to T_{AB} . As shown on Fig. 3, we have obtained a good approximation with

$$\Delta G_{AB} = 1.4782 - 0.302T + 2.0947T^2 - 4.381T^3 + 2.5633T^4 - 0.47718T^5 \quad (15)$$

in ergs/cm^3 with T in mK.

As in Sec. 2, we further assumed that there exists a wall defect which is favorable enough to the B-phase, so that the AB interface already exists somewhere, that it is pinned there and that it only has to overcome a small pinning energy to escape (Fig. 2). At some critical value ΔG_c of the free energy difference between A and B, the AB interface would spontaneously unpin. Since this is the same kind of spinodal limit as in Sec. 2, the same general arguments apply, and the pinning energy writes

$$E = E_0 \left(1 - \frac{\Delta G_{AB}}{\Delta G_c} \right)^{3/2} \quad (16)$$

The pinning and unpinning having to do with surface tension equilibrium, it seems natural to suppose that ΔG_c has the same temperature variation as σ_{AB} . At least, ΔG_c has to vanish at T_c where σ_{AB} vanishes. The temperature variation of σ_{AB} is given by Schiffer *et al.*⁴ from a fit of experimental measurements and writes

$$\sigma_{AB} = 1.2675 \times 10^{-5} \left(1 - \frac{T}{T_c} \right)^{1/2} \quad (17)$$

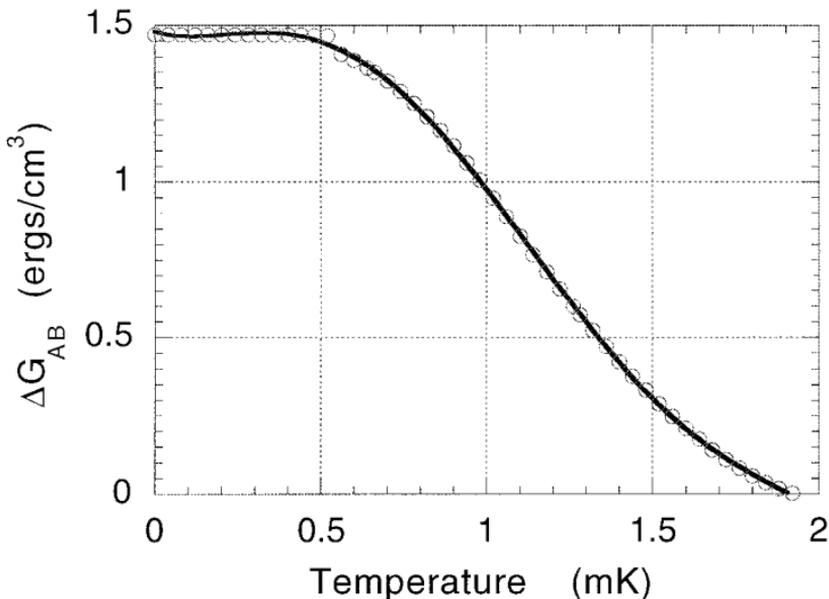


Fig. 3. A polynomial fit (Eq. (15), solid line) of the free energy difference ΔG_{AB} between helium 3-A and helium 3-B as calculated by P. Schiffer, D. D. Osheroff, and A. J. Leggett (circles)⁴ at melting pressure.

in ergs/cm² with $T_c = 2.49$ mK. We thus decided to use the same 1/2 power variation and to write

$$\Delta G_c = B \left(1 - \frac{T}{T_c}\right)^{1/2} \quad (18)$$

Finally it looked natural to include the same temperature variation in the quantity E_0 , and write the energy barrier as follows:

$$E = A \left(1 - \frac{T}{T_c}\right)^{1/2} \left(1 - \frac{\Delta G_{AB}}{\Delta G_c}\right)^{3/2} \quad (19)$$

with ΔG_c given by Eq. (18). The lifetime τ being the inverse of the nucleation rate, we finally used the following equation to fit the various data presented in the review by Schiffer *et al.*:⁴

$$\tau = \frac{h}{k_B T} \exp \left(\frac{A}{T} \left(1 - \frac{T}{T_c}\right)^{1/2} \left(1 - \frac{\Delta G_{AB}}{B \left(1 - T/T_c\right)^{1/2}}\right)^{3/2} \right) \quad (20)$$

Note that in doing this we force the attempt frequency to be as high as a thermal frequency, as in Sec. 2.

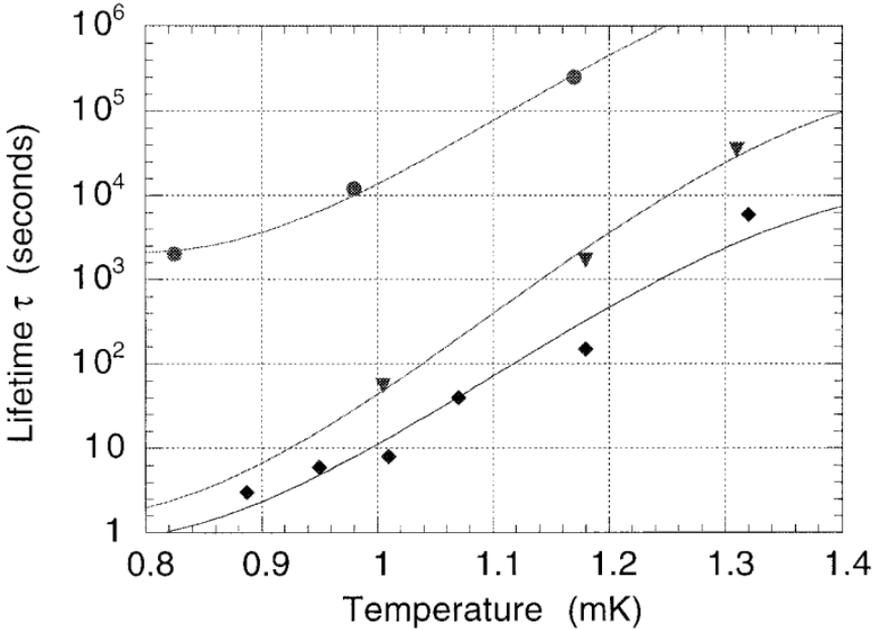


Fig. 4. The lifetime τ of helium 3-A versus temperature, as measured by Schiffer *et al.*⁴ Fits are obtained with Eq. (20). Circles: without radioactive source (called “background” by Schiffer *et al.*); triangles: in the presence of a neutron source; losanges: in the presence of a gamma-ray (Co60) source.

Figure 4 shows a comparison with the experimental results by Schiffer *et al.*⁴ Clearly, the quality of the fits is good, but it is important to discuss the magnitude of the two adjustable parameters E_0 and ΔG_0 . The respective values of the parameters A and B are

- “background” curve: $A = 118$ mK; $B = 2.325$ ergs/cm³
- “neutrons”: $A = 109.2$ mK; $B = 2.67$ ergs/cm³
- “Co60”: $A = 98.9$ mK; $B = 2.19$ ergs/cm³

As can be seen, it is possible to fit the data corresponding to the irradiated cells, not only the “background” data where no radioactive source is approached. Let us first consider the non-irradiated cell. The value of B gives the magnitude of the critical supercooling. It is a little larger than the maximum value $\Delta G_{AB}(0) = 1.47$ ergs/cm³, so that it might be possible to supercool the A-phase down to $T = 0$.

As for the typical pinning energy, it is given by A and found of order 100 mK. As we did in Sec. 2, we can think of this pinning energy as being the product of the surface energy σ_{AB} by the area of a pinning site δA . We thus find that δA is about $100 \times 100 \text{ \AA}^2$ since σ_{AB} is slightly less than 10^{-5} K/\AA^2 . Such a size is smaller than the typical roughness of the cell

walls.⁴ It is also comparable to the correlation length ξ_0 near the melting pressure. We see no fundamental objection to all these results, except that at this scale, of course, any description in terms of the macroscopic surface tension is only an approximation again. Indeed, the width of the AB interface is comparable to ξ_0 . We further note that the correlation length is also comparable to the ratio $\sigma_{AB}/\Delta G_{AB}$. A more rigorous calculation looks difficult to us and would require that the nature and the shape of the wall defect are known.

We now need to understand the effect of radiations. Figure 4 shows that Eq. (20) fits the data obtained in the presence of radiation just as well as the data obtained without radioactive source. Only a slight modification of the parameters is needed. We have no quantitative calculation of this, but we wish to suggest two possible explanations. It is well known that when one injects electrons in liquid helium, they repel the neighboring atoms and form bubbles a few nanometers in size.²⁴ These bubbles may have bound states at the AB interface. If so, σ_{AB} should be reduced by the adsorption of electron bubbles. A reduction of order 10% seems to be sufficient to explain the observed reduction in lifetime of the A-phase. However, Doug Osheroff²⁹ recently estimated the binding energy of electron bubbles to the AB interface and the number of electrons required for a 10% change of σ_{AB} . His conclusion was that it is impossible. If he is right, another possibility might be that moving electrons create vortices or textures which might be the defects favorable to the B-phase. Clearly, this issue needs further theoretical and experimental studies.

Let us now consider the field dependence of the lifetime. Schiffer *et al.*⁴ performed three sets of measurements, corresponding to a cell irradiated with a Co60 source, under magnetic fields of 14, 28.2, and 100 mT. They could fit the field dependence with the baked Alaska model without much further adjustment of parameters. They only used a field dependence of the free energy, which can be written as

$$\Delta G_{AB}(H) = \Delta G_{AB}(H=0) \left(1 - 3 \left(\frac{H}{H_c} \right)^2 \right) \quad (21)$$

Their data are consistent with a zero temperature critical field $H_c = 0.55$ Teslas, which is satisfactory since they explain that it has to be between 0.47 and 0.63 Teslas. Within their model, there should be not much difference between the results at 14 and 28.2 mT which are small fields, and the increase in lifetime at 100 mT is well associated to a small reduction in the free energy difference ΔG_{AB} . The same is true within our model. Figure 5 shows that a good fit of the two sets of data can again be obtained with Eq. (20). The respective values of the parameters are

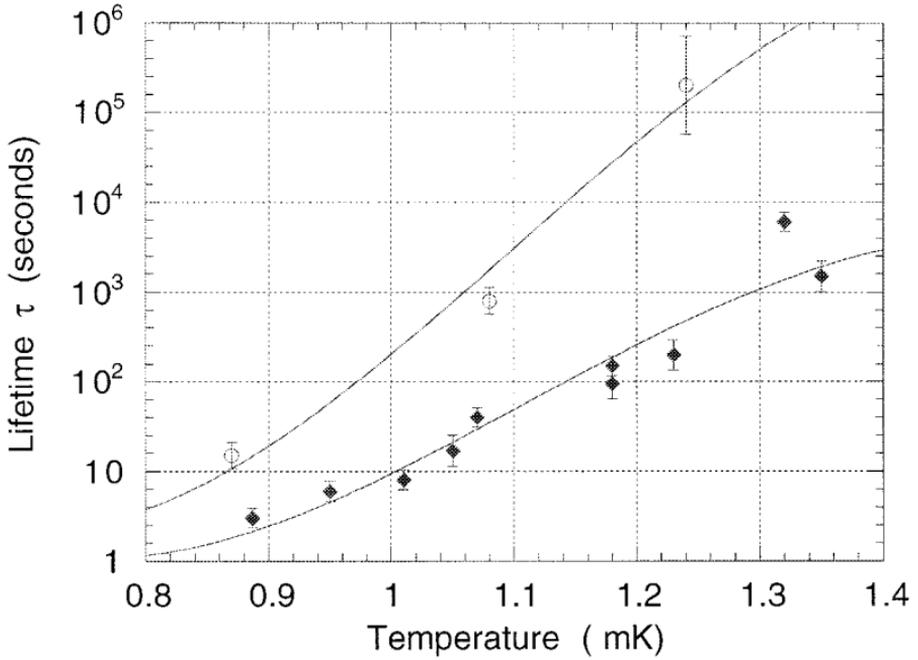


Fig. 5. The lifetime of helium 3-A increases with magnetic field H . Open circles: $H=100$ mT; filled losanges: 14 and 28 mT. The data are measurements by Schiffer *et al.*⁴ in the presence of a Co60 gamma ray source. The fits are obtained with Eq. (20).

— for $H=100$ mT: $A=123.4$ mK; $B=2.10$ ergs/cm³

— for $H=14$ and 28 mT: $A=94.5$ mK; $B=2.23$ ergs/cm³.

Once more, as expected from the exponential dependence, a small change in the parameters leads to a large change of the lifetime. Within our model, we do not see why the pinning energy or the spinodal limit should be independent of field, but we can still try to force the field dependence to be only inside ΔG_{AB} (as done by Schiffer *et al.*⁴) and use Eq. (21) for it. As shown on Fig. 6, if we do so, we obtain fits whose quality is not as good as on Fig. 5. However, we clearly obtain the right magnitude for the change in lifetime. Indeed, by imposing now $A=108.95$ mK, we respectively find $B=2.2333$ ergs/cm³ for the 100 mT data and $B=2.0554$ ergs/cm³ for the 14 and 28 mT data. This corresponds to a reduction of ΔG_{AB} by 8%, when the field goes up to 100 mT, as expected if H_c is about 0.6 Teslas. Note that not much change should be observed from 14 to 28 mT, so that the scatter in the data gives an estimate of the true error bars in this series of experiments which must have been long and difficult. Our feeling is that both the pinning energy and the unpinning limit are likely to depend on H . In summary, our model is able to fit all the lifetime measurements by Schiffer *et al.*⁴

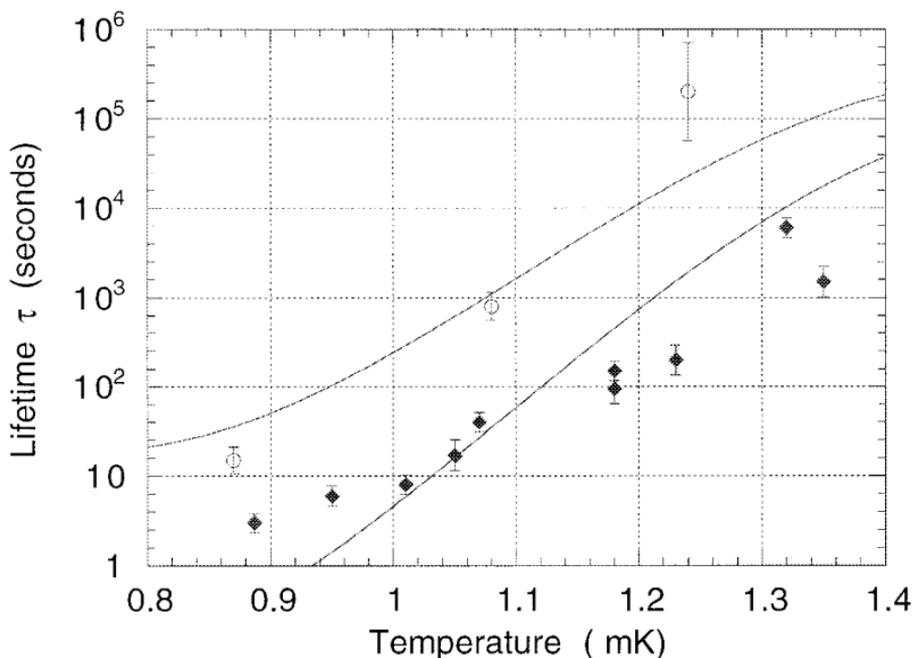


Fig. 6. On this figure, the data are the same as on Fig. 5. The fits are obtained with only one adjustable parameter (B) instead of two. At 100 mT (circles), B is found larger by 8% than at low field (14 and 28 mT, losanges). This is expected since, according to Eq. (21), the difference in free energy between the two superfluid phases decreases by about 8% from 28 to 100 mT.

We finally wish to compare smooth cells such as in the experiments done at Stanford and rough cells where measurements were done a longer time ago. One good example of data obtained with a cell whose walls are supposed to be rough is described by Hakonen *et al.*³ in their comment to Leggett's letter on the baked Alaska model. Nucleation takes place in a narrower temperature range, also at higher temperature, in Hakonen's cell than in Schiffer's cell. Hakonen shows a histogram of 18 events which extends over 0.15 mK while, in Schiffer's experiment, the lifetime varies by about 2 orders of magnitude over 0.4 mK. The narrow temperature region where nucleation occurs in rough cells was called a "catastrophe line." The steeper temperature variation of the lifetime in rough cells was considered by several authors as evidence that nucleation in rough cells is due to a different mechanism. However, as we shall now see, Eq. (20) fits Hakonen's data as well as Schiffer's data. We had first to estimate the lifetime τ from Hakonen's histogram. He observed nucleation during cool down at a rate of about $20 \mu\text{K}/\text{min}$. By integrating the number of events and normalizing by 18 we calculated the cumulative probability $\Sigma(T)$ that nucleation occurs above a certain T . As shown on Fig. 7, the curve $\Sigma(T)$ is asymmetric and

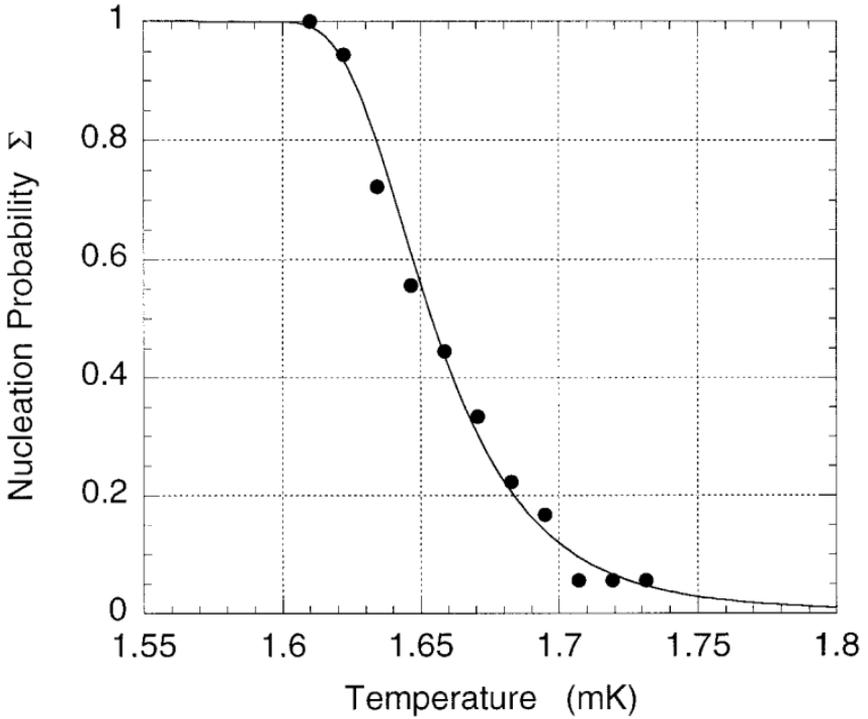


Fig. 7. An estimation of the nucleation probability Σ in the experiment by Hakonen *et al.*³ We estimated this probability from their histogram of events and their typical cooling rate (see text). The solid line corresponds to a fit with Eqs. (20) and (23).

reminiscent of all “asymmetric S-shape” curves which have been observed in experiments where the relevance of statistical fluctuations (either thermal or quantum) was proven.^{10–13} The typical time τ_0 of their experiment is the ratio of the width of the histogram by the cooling rate, about 5 min. We finally obtained an estimate of the lifetime of helium 3-A in their experiment as

$$\tau = -\frac{\tau_0}{\ln(1-\Sigma)} \quad (22)$$

As shown on Fig. 8, we found good agreement with Eq. (20). Since these experiments were performed at 29.3 bars, we took $T_c = 2.43$ mK and $T_{AB} = 2.075$ mK from Greywall’s work.³⁰ We obtained $A = 161$ mK and $B = 1.17$ ergs/cm³. The solid line on Fig. 7 corresponds to Eq. (8) with E from Eq. (19) and the same respective values for A and B .

We now understand that, in Hakonen’s case, the critical value ΔG_c is reached by ΔG_{AB} at a finite temperature, while in Schiffer’s case ΔG_{AB} was

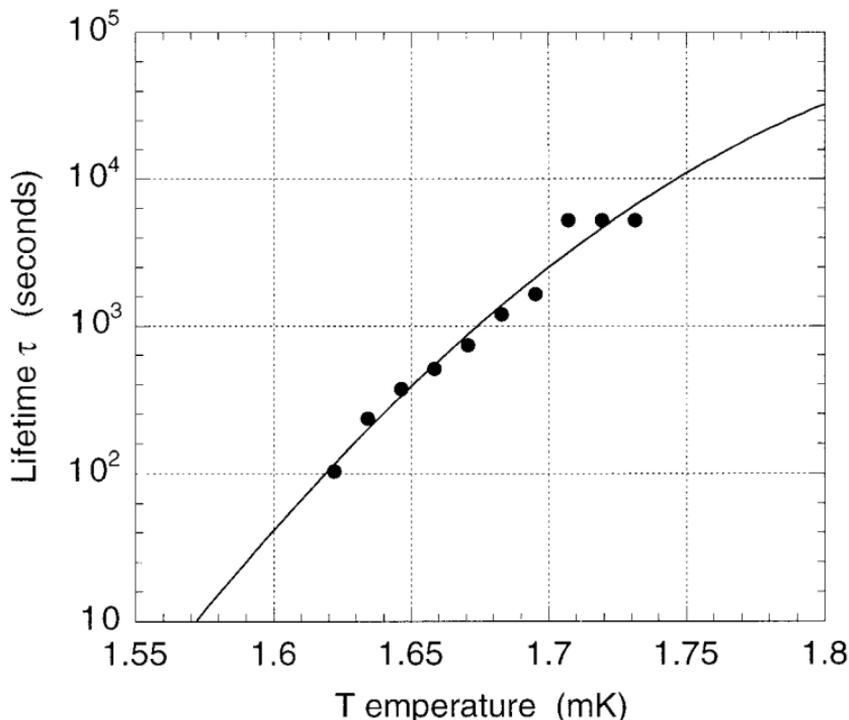


Fig. 8. An estimation of the lifetime τ of helium 3-A in the experiment by Hakonen *et al.*³ We used Eq. (22) to estimate this lifetime from their histogram of events and their typical cooling rate. The solid line corresponds to a fit with Eq. (20).

less than ΔG_c even at $T=0$. This is the main difference. Otherwise, the model is the same. According to our description, there is an absolute metastability limit at $T=1.18$ mK in Hakonen's experiment, and the B-phase nucleates around 1.6 mK because of the existence of thermal fluctuations. Without thermal fluctuations, Hakonen's histogram would have no width; on the contrary, Hakonen's histogram is asymmetric with a narrow but finite width for the same reasons as in cavitation studies¹² or in solidification studies.^{10,11} We believe that the "catastrophe line" is a nucleation region close to a pinning stability limit which could be called a "surface spinodal line."

Let us now consider the values of the parameters A and B. That A is larger in Hakonen's case than in Schiffer's case indicates that the rough cell has pinning sites larger than the smooth cell. We could have slightly improved our model by allowing a finite density of sites on the whole surface instead of considering only one. To contribute together, these sites need to be similar, otherwise those with the lowest energy dominate those with higher energy which are irrelevant. Taking an arbitrary number of

10 000 similar sites leads to the same good quality fit and slightly higher energies ($A = 200$ mK; $B = 1.3$ ergs/cm³). Finding a smaller B is more surprising, at first sight. It means that the AB interface needs a smaller undercooling to escape when the walls are rough than when they are smooth. One possible explanation is that the contact angle is 68° with smooth walls but larger than 90° with rough walls. Indeed, only flat walls favor the A-phase. This is clearly another interesting property to be checked.

More mysterious for us is the remark by Hakonen that the B phase does not nucleate at fixed temperature, only during cool down, although no dependence on the cooling rate could be found. Does this mean that cooling down produces temperature gradients, hydrodynamic flows, vortices, textures...? Could a flow unpin an AB interface? We do not know. Our model assumes the existence of at least one defect in each cell, and there is indeed one boojum at least in a closed cell, but we do not know if these boojums are more likely to be responsible for the nucleation than other possible defects. Leggett calculated the elastic energy in a boojum. If one takes the last published values for the surface tension and the free energy difference, one finds that the line-defect is marginally favorable to the B-phase at low enough temperature. We also note that recent studies of the superfluid transition in aerogels show that the presence of silica fibers tends to suppress the A-phase from the phase diagram. Various theories also seem to predict that scattering on walls or defects can suppress the A-phase.²⁷

It should also be interesting to study the nucleation of superfluid helium 3-B in smaller or shielded cells, in order to decrease the flux of cosmic rays to a negligible level. It is only about 1 muon per cm² and per minute at ground level, so that it is already small in Schiffer's experiment. If one finds longer lifetimes in smaller or shielded cells, it means that cosmic rays are involved. If not, it could mean that the smaller cell has the same number of defects as the larger one. An experiment done in a much shorter time should allow to measure the lifetime at lower temperature, and it would be interesting to see if a crossover exists from the thermally activated nucleation which we considered above to a quantum nucleation regime. Indeed, Eq. (20) predicts that the lifetime increases in the limit of very low temperatures. This is expected as a consequence of the vanishing of thermal fluctuations, but such a possible increase should be replaced by a plateau in the quantum regime. We have not yet calculated the crossover temperature for this new effect nor any upper bound of the lifetime of superfluid helium 3-A in a metastable state at $T=0$. O'Keefe⁵ extended Schiffer's results down 0.5 mK. His lowest temperature measurement might be in such a quantum nucleation regime.

4. CONCLUSIONS

We have tried to progress in the understanding of heterogeneous nucleation. In the case of the liquid-solid transition, we have shown that geometric defects such as cracks in walls are not sufficient to understand the experimental results of Ruutu *et al.*¹⁰ We have proposed that the nucleation barrier does not correspond to the creation of the liquid-solid interface, and that it is in fact the pinning energy of an already existing interface. We also proposed that this interface spontaneously appears at the melting pressure if chemical defects are present in the cell, such as graphite particles. It would be interesting to search for other substrates on which hcp helium 4 crystals grow by epitaxy. Why not the (111) surfaces of Si, for example? In the case of superfluid helium 3-B we have proposed a new model which allows to understand why the nucleation is influenced by the presence of walls. We do not claim that the "Baked Alaska" model is irrelevant; we prefer pointing out that there are symmetric difficulties in the two models. The baked Alaska model gives no explanation for the effect of walls on nucleation, but naturally explains why the presence of a radioactive source shortens the lifetime. Inversely, our model starts from the experimentally demonstrated influence of walls but does not yet provide a quantitative interpretation for the influence of radiation. We also showed that the nucleation mechanisms in rough and smooth cells are not necessarily different.

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