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Out-of-equilibrium nucleation in the solidification of helium

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We observed nucleation in a first-order phase transition in which a nonequilibrium (metastable) solid phase nucleates and grows from overpressured superfluid ^{4}He in preference to the equilibrium solid phase. After a time varying from a fraction of a second to tens of minutes, the stable phase nucleates independently from the liquid, and the nonequilibrium solid phase melts. We examined the possibility of accounting for these events in terms of the known differences in the interfacial free energies between the superfluid and the two solid phases (stable and metastable). The experimental results are not consistent with this explanation, however, and we discuss other possibilities.

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I. INTRODUCTION

Nucleation in a first-order phase transition is the process in which a finite, localized nucleus of a stable phase emerges from a phase rendered unstable by changes in intensive thermodynamic variables, such as temperature or pressure. The current theories of nucleation can be traced back to Gibbs, in the last century, who proposed the idea of a ''work of formation'' required for the new, stable phase to form within the unstable phase. It was Becker and Döring [1] in the 1930s who, following Gibbs' idea, formulated what has become known as classical nucleation theory. Briefly stated, while the bulk new phase nucleating from a metastable (undercooled or overpressured, for example) state will have a lower bulk free energy than the metastable phase, there is an energy cost associated with creating the interface between the two phases. This leads to the existence of an energy barrier for the formation of the new phase.

While this model has served well to describe the vapor-liquid transition, there are some difficulties in the application of the theory to nucleation of the solid from the liquid. Because the densities of the solid and liquid are much closer than the densities of the liquid and vapor, the nucleus itself becomes harder to identify and the interface less distinct. Surface energies for the liquid-solid interface are much more difficult to measure and are known only for a few special cases. In addition, there are still questions about the kinetics of the liquid-solid nucleation process that make quantitative predictions based on the classical nucleation theory less certain. Furthermore, nucleation from a liquid to a solid is a symmetry-breaking transition, unlike nucleation of the isotropic liquid from the isotropic vapor.

Recently, a number of new techniques have been brought to bear on the problem of nucleation of the solid. Computational experiments, in which a model of a Lennard-Jones type of fluid is supercooled to induce nucleation, have been carried out by a number of researchers [2–5]. In addition, density functional methods, treating the solid as an inhomogeneous fluid, have been applied to the problem (for example, [6]). In this paper we present experimental results on nucleation of the solid phase from metastable liquid ^{4}He. In Sec. II we briefly review classical nucleation theory and in Sec. III we describe the experiment. Our observations are presented in Sec. IV and are discussed in light of classical nucleation theory and results from other theoretical and computational investigations in Sec. V.

II. BACKGROUND

In classical nucleation theory, the emerging new phase (in our experiments, the solid) is modeled as a sphere of radius r, surrounded by the metastable initial phase (in our experiments, the overpressured liquid). The change in free energy due to the formation of this nucleus is the free energy required to create the interface between the two phases less the free energy released from converting the bulk of the nucleus to the stable phase. Expressing this free energy change as a function of the radius of the nucleus, one obtains

$$\Delta F = 4\pi r^2 \sigma - \frac{4\pi}{3} r^3 \Delta f_v , \tag{1}$$

where σ is the interfacial free energy and Δf_v is the difference between the specific bulk free energies of the two phases.

For nuclei with a radius smaller than some critical radius r_c, the r^2 term dominates and the change in free energy increases with size; thus smaller nucleii will reduce their free energy by reducing their radius—in the case of these experiments, melting back to liquid. For nucleii with a radius larger than this critical radius, the r^3 term dominates and the change in free energy decreases with size; larger nucleii decrease their free energy by growing. The maximum value of the change in free energy, $\Delta F_{\max}$, which occurs at the critical radius, is an energy barrier to the formation of the new phase. The critical radius r_c in this model is

$$r_c = \frac{2\sigma}{\Delta f_v}, \tag{2}$$

and $\Delta F_{\max}$ has a value of

$$\Delta F_{\max} = \frac{16\pi}{3} \frac{\sigma^3}{\Delta f_v^2}. \tag{3}$$

In order for the new phase to emerge and persist (to nucleate), it must overcome this energy barrier. When this process is thermally activated, the nucleation rate R has the form

$$R = R_0 \exp(-\Delta F_{\max}/kT), \tag{4}$$

where R_0 is some prefactor.

For a liquid that is overpressured, the change in the specific bulk free energy between the liquid and the solid can be written, to first order, as

$$\Delta f_v = \frac{\Delta v \Delta p}{v_s}, \tag{5}$$

where Δv is the difference in molar volume between the liquid and the solid, Δp is the overpressure of the metastable liquid, and v_s is the molar volume of the solid.

III. EXPERIMENT

In these investigations of nucleation, a sample of helium was condensed to liquid and cooled to temperatures between ~1.3 and ~1.6 K. The pressure was then raised and the cell monitored until nucleation of the solid was observed.

The ^{4}He was confined in a cylindrical pressure cell, 10 mm in diameter and 3 mm in depth, bored through a block of oxygen-free, high-conductivity (OFHC) copper. The faces were sealed with sapphire windows to allow optical access.

Temperatures in the cell were measured with a calibrated germanium thermometer, mounted in the block of copper with the cell. The temperature was sampled approximately every 4 s throughout the course of the experiments. Additional germanium and ruthenium oxide thermometers were available as backup devices.

The pressure was measured with a piezoelectric transducer, mounted, due to experimental constraints, outside the cell, and at a different temperature from the cell. Since the liquid in the cell was superfluid, a pressure gradient resulted between the cell and the pressure transducer caused by the thermomechanical effect. This was compensated for by determining differential pressures and calibrating against the known ^{4}He melting curve.

Optical data were taken using a black and white charge-coupled device camera, which generated a standard NTSC video signal (30 frames per second). This was displayed on a monitor and could be recorded on a VCR or captured digitally by computer for subsequent frame-by-frame examination of the data. A high-speed digital camera, which could operate at rates of up to 1000 frames per second, was also available for investigating events that occurred at rates the standard video camera could not resolve.

The temperatures and pressures of our experiments bracket the lower triple point of ^{4}He, where the superfluid phase, the bcc solid phase, and the hcp solid phase coexist (see the helium phase diagram, Fig. 1). The lowest temperatures of our experiments are just above the highest roughening transition for ^{4}He.

In a typical experiment, liquid ^{4}He in the cell at roughly 5 atm below the melting curve was pressurized at roughly constant temperature to within 0.1 atm of the melting curve. (Because this change in pressure leads to a change in T_λ, and thus a change in the thermal load from the thermomechanical effect, the system was allowed to reequilibrate for a few minutes before proceeding. Typical changes in temperature due to this change in pressure were ~2 mK.) The pressure was then increased again, at rates typically around 4×10^{-3} atm/s, until nucleation of the solid was observed. The newly formed solid was monitored before being melted (by dropping the pressure roughly 5 atm) to prepare to repeat the experiment.

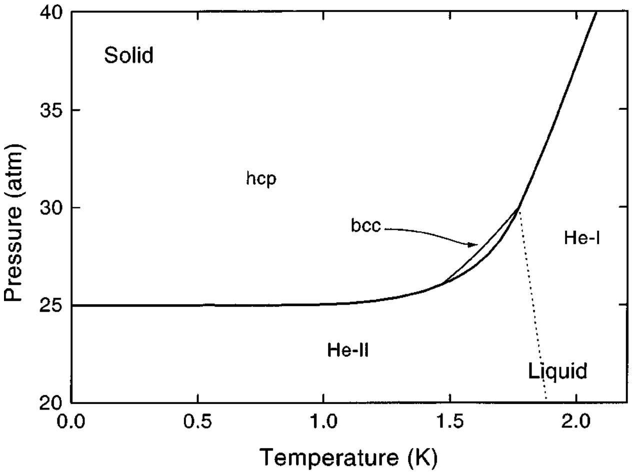

FIG. 1. Schematic of the ^{4}He phase diagram near the melting curve at temperatures below 2 K, showing the bcc and hcp solid phases and the normal and superfluid liquid phases as a function of temperature and pressure.

IV. OBSERVATIONS

A typical pressure and temperature recording for a single nucleation event, the second trace, at ~320 s is shown in Fig. 2. The pressure in the cell was increased until solid was observed to nucleate in the cell, at which point there was a rapid and distinct drop of the pressure to the melting curve. In this example, the solid nucleated at an overpressure of roughly 0.075 atm. (The subsequent drop in pressure, at the time of roughly 355 s, is the point at which the solid was melted back to prepare to repeat the experiment.) Typically, once nucleated, the solid grew rapidly from the copper walls of the cell (only rarely from the sapphire windows) to a size of a few millimeters. At temperatures above the lower ^{4}He triple point T_{TP}, the bcc solid grew macroscopically smooth and rounded. At temperatures below T_{TP}, the hcp crystals grew with nonequilibrium facets that began to erode away once growth had stopped. (These facets were probably due to growth anisotropies.)

In addition to events like this one, however, below T_{TP} we recorded ''double nucleation'' events, in which two distinct, consecutive nucleation events were observed with two distinct plateaus at two different liquid-solid coexistence pressures. An example of the pressure and temperature data for such an event is the first trace, at ~100 s, shown in Fig. 2. In this example, as in the last example, the pressure was increased until nucleation occurred, at roughly 0.075 atm, at which point the pressure dropped—but only by about 0.01 atm; not to the equilibrium melting curve. After about 20 s another pressure drop, associated with the sudden emergence of a second solid and the melting of the first, was

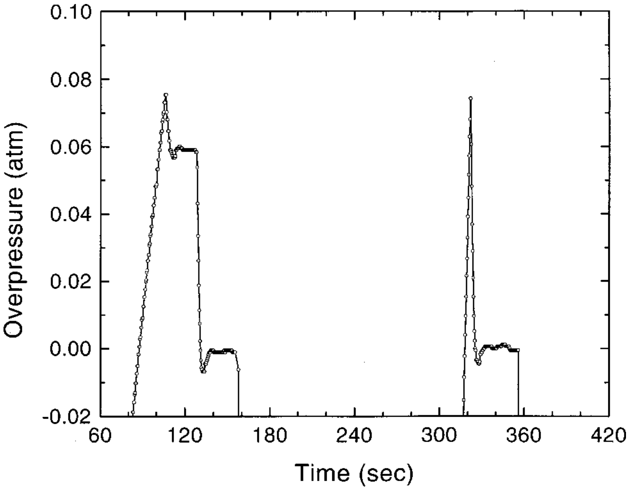

FIG. 2. Overpressure (measured with respect to the hcp melting curve) recorded during two consecutive nucleation events. The nucleation overpressure in both cases is ~0.075 atm. In the event that occurred at 320 s, only the hcp solid was observed, and the pressure dropped to the melting curve. (The subsequent drop in pressure, at 355 s, was induced to melt the solid and prepare the cell for the next event.) In the event that occurred at 100 s, the metastable bcc solid nucleated first, and the pressure in the cell dropped to the metastable bcc-liquid coexistence pressure. After approximately 20 s, the hcp solid nucleated from the liquid, the bcc melted, and the pressure dropped to the hcp melting curve. The temperature of these events is roughly 1.30 K.

recorded, with the pressure this time dropping to the stable melting curve (again, the third drop in the pressure trace occurs when the pressure was reduced to melt the solid and prepare the cell for another event). The camera captured the emergence of a crystal of helium with the first pressure drop, followed by the emergence of a second, independently nucleated crystal of helium and the melting of the initial crystal of helium coincident with the second pressure drop. The initially nucleated crystal grew macroscopically smooth (typical of bcc crystals nucleated above T_{TP}) and the subsequently nucleated crystal grew with the nonequilibrium facets characteristic of hcp ^{4}He crystals grown below T_{TP}. Growth of the second crystal and melting of the first all occur within a single frame of video, $\frac{1}{30}$th of a second. In order to resolve the event, the high-speed digital camera was used. This revealed that growth of the new solid and melting of the initial solid typically required ~0.02 to ~0.03 s. We were also able to determine that the stable solid was emerging independently from the liquid (also growing from the cell wall), and not as a solid state transformation of the metastable solid. The high-speed images also showed the nucleation of the second solid prior to noticeable melting of the first solid, establishing the sequence of events. Lifetimes of the initially nucleated, metastable solid (in the case of Fig. 2, just under a minute long) have been observed to range from fractions of a second up to tens of minutes. The initially nucleated solid phase has been identified as the metastable bcc solid, the subsequent nucleation as the stable hcp solid. Again, these double nucleation events were observed only for temperatures below T_{TP} where hcp is the stable solid phase; never above T_{TP} where the bcc solid is stable.

An example of the pressure and temperature recording for a series of consecutive nucleation events is shown in Fig. 3. Note that some of the individual events in this series have the appearance of the single nucleation event of Fig. 2 (though shown on a much compressed time scale); others, however, exhibit the two distinct pressure drops and two distinct liquid-solid coexistence pressures (plateaus in the trace) of Fig. 2.

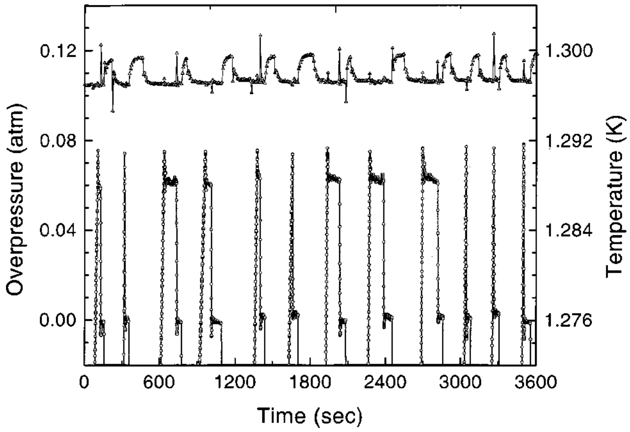

FIG. 3. Pressure and temperature data recorded during a number of successive nucleation events, all at the same temperature of ~1.30 K. The upper trace is temperature, the lower trace is pressure. Again, the nucleation overpressure is ~0.075 atm, the metastable bcc solid–liquid coexistence is at an overpressure of ~0.06 atm. The peaks in the temperature trace are due to the change in thermal loading from the thermomechanical effect when the pressure is changed (at this temperature, roughly 3 mK for a 5 atm change in pressure). Some of the events show evidence of the metastable solid, and some do not. (The first two events in the series are those shown, at an expanded scale, in Fig. 2.)

An interesting feature of the data, which can be seen in Fig. 3, is that the pressures at which nucleation occurs for the stable hcp solid, in events in which only the stable solid is observed, and for the metastable bcc solid, in double nucleation events, is roughly the same. This is contrary to what might be expected from classical nucleation theory. If the nucleation prefactor [see Eq. (4)] is about the same for both solid phases, then for both of them to have a nucleation rate approaching 1, ΔF_{max} should be the same for both. Yet both phases have different surface and bulk free energies, and a different coexistence pressure. The possibility that all these differences happen to balance out such that the pressure at which nucleation occurs is approximately the same for both phases, across the temperature range of the experiments, seems remote.

If we examine the overpressures for roughly 1000 events in which only the hcp solid was observed, where the overpressure is measured as the difference between the nucleation pressure and the equilibrium melting curve, we get Fig. 4. Despite the scatter in this plot there are some trends, and a line generated by a least squares fit of the data is shown with the plot. As expected for thermally activated nucleation, the overpressure increases with decreasing temperature; dP/dT_{hcp} is roughly -0.23 ± 0.01 atm/K. The overpressure for the bcc form in roughly 400 double nucleation events, when measured with respect to the same equilibrium melting curve, looks similar, as shown in Fig. 5; the temperature dependence dP/dT^{*}_{bcc} found from the least squares fit is

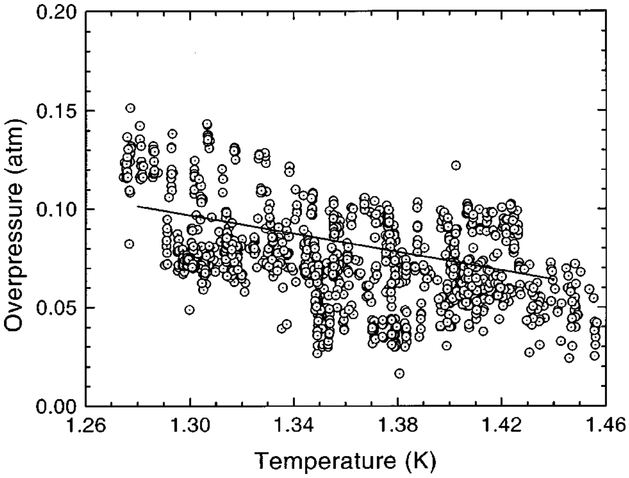

FIG. 4. Nucleation overpressure (with respect to the equilibrium melting curve), as a function of temperature, for events in which only the hcp solid was observed. The solid line represents the least squares linear fit.

roughly -0.26 ± 0.02 atm/K. In fact, the difference between the fits of the two data sets is much less than the scatter in either dataset. (The fit for the bcc data falls roughly 0.01 atm below the fit for the hcp data; however, it is not clear that this difference is significant: the standard deviation in either data set is more than twice this value, and over the course of a given sequence of events at one temperature, there is no discernible, systematic difference between the nucleation overpressure of the hcp-only events and the nucleation overpressure of the double nucleation events). However, when we calculate the overpressure for the bcc solid with respect to the natural choice of the metastable bcc coexistence curve and plot that as a function of temperature, the results are quite different, as can be seen in Fig. 6. Again, the data are shown with the least squares fit, which now has a much smaller, *positive* temperature dependence; $dP/dT_{\mathrm{bcc}}=0.04\pm0.02$ atm/K. A nearly zero temperature dependence is characteristic of quantum nucleation, rather than thermally activated nucleation. Although quantum mechanical properties play a significant role in the behavior of ^{4}He at the temperatures of our experiments, other investigators have suggested that, at these temperatures, nucleation of the solid proceeds classically, that is, by thermal activation [7].

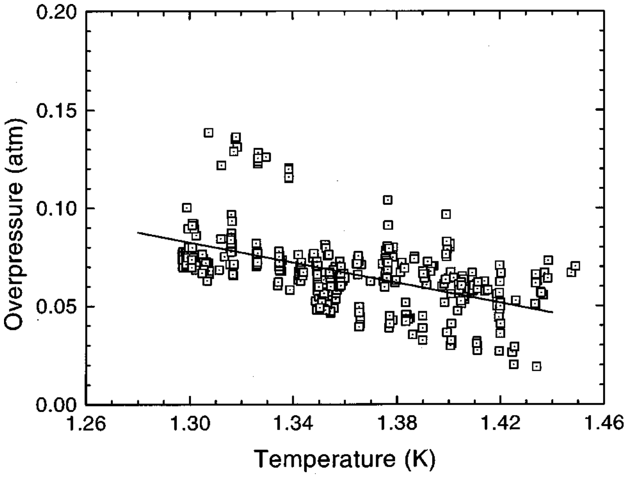

FIG. 5. Nucleation overpressure (with respect to the equilibrium melting curve), as a function of temperature, of the metastable bcc solid in double nucleation events. The solid line is the least squares linear fit.

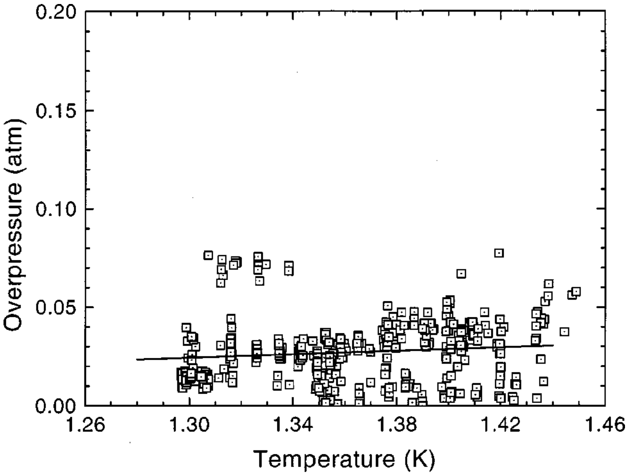

FIG. 6. Nucleation overpressure (with respect to the metastable solid–liquid coexistence pressure), as a function of temperature, of the metastable solid in double nucleation events. The solid line is the least squares linear fit.

V. DISCUSSION

To rule out the possibility that the nucleation of the metastable bcc solid might proceed from seeds of unmelted solid retained in cracks or crevices, the pressure was reduced roughly 5 atm between events in our experiments. As other investigators have determined that a pressure drop of about 1 atm is sufficient to ensure that there is no unmelted solid remaining in the cell to seed subsequent nucleation [8], this seems an adequate precaution. Furthermore, the solid in the cell immediately prior to a new nucleation event, and before the 5 atm drop in pressure to prepare the cell for a new event, was in almost all cases the stable hcp phase. More significant, perhaps, is the fact that nucleation of the metastable solid has been observed in the first nucleation event following the cooling of the cell from its rest temperature, approximately 10 K when the refrigerator is not running, and in the first nucleation event following the cooling of the Dewar and refrigerator from room temperature. Certainly in the latter case, there is no possibility that solid helium of either the bcc or hcp phase was preserved in the cell. We do not suspect any peculiarity of the sample cell as responsible either; while the basic geometry and materials of the cell design were not significantly changed over the course of these experiments, three different sample cells have been used, and double nucleation events have been observed in all three cells. Although some materials have been reported to lead to barrier-free nucleation of stable or metastable phases in ^{4}He or ^{3}He (for example, carefully degassed Grafoil (which has a hexagonal structure) has been reported to lead to barrier-free nucleation of stable and metastable solid hcp ^{4}He [9], and MgO has been reported to lead to nucleation of barrier-free bcc solid in ^{3}He [10]), there are no such reports for the common materials used in our experimental cells.

In classical nucleation theory, the nucleation barrier

$\Delta F_{\rm max}$ [see Eq. (3)] is a function of both the bulk free energy of the solid with respect to the liquid and the interfacial energy of the solid with respect to the liquid. Although the stable solid (hcp in our experiments) always has the lower bulk free energy, the two solids have different interfacial energies with respect to the superfluid, and this can lead to a nucleation barrier that is lower for the metastable bcc solid than for the stable hcp solid. Interfacial free energies for both solids at temperatures near $T_{\rm TP}$, have been reported in [11]. The extrapolated values for the metastable bcc solid, between 1.3 K and $T_{\rm TP}$, at least, are lower than the values for the stable hcp solid. Assuming that the nucleation prefactor R_0 [see Eq. (4)] is roughly the same for both the bcc and the hcp solids, the relative nucleation probabilities can be determined by comparing $\Delta F_{\rm max}$ of the two solids. At a temperature of 1.40 K, for example, $\Delta F_{\rm max}$ of the hcp and $\Delta F_{\rm max}$ of the bcc are equal at an overpressure of ~0.14 atm with respect to the hcp melting curve. The hcp solid has a higher *relative* probability of nucleating at lower overpressures; the bcc solid has a higher *relative* probability of nucleating at higher overpressures. Qualitatively, then, we would expect to find that events which led to the nucleation of the metastable bcc solid occurred at higher overpressures than events which led to the nucleation of the stable solid. The distribution of overpressures for the nucleation of either solid is broad, and both have roughly the same median value—suggesting that the phase which nucleates is not a function of the overpressure, in contrast to the predictions of the classical nucleation theory.

There are also significant quantitative inconsistencies between our results and those of classical nucleation theory. Nucleation overpressures in our experiments are typically about 0.1 atm. At a temperature of 1.4 K, the interfacial energy σ for the hcp solid is about 0.15 erg/cm^2 and the ratio of $\Delta v/v$ is roughly 0.1. Thus, the classical model of nucleation gives a value for the nucleation energy barrier on the order of 10^6 K [see Eqs. (3)–(5)]. (Similarly, we find from the classical model that an overpressure of over 20 atm is required to lower the nucleation barrier sufficiently for nucleation to occur.) Such a large energy barrier leads to vanishingly small nucleation rates for any realistic value of the preexponential factor [see Eq. (4)].

Of course, the classical model of nucleation is predicated on homogeneous nucleation, while nucleation in our experiments is heterogeneous. Heterogeneous nucleation, nucleation on a substrate, has a lower energy barrier than homogeneous nucleation. Consider a model of heterogeneous nucleation in which a truncated sphere of the new phase emerges on a flat, uniform substrate. The contact angle between the solid and the substrate is determined by the relative interfacial energies of the nucleus with respect to the liquid and with respect to the substrate. The total change in free energy on the formation of a nucleus on a flat homogeneous substrate can be expressed as a function of this contact angle:

$$\Delta F^* = g(\theta)\Delta F, \tag{6}$$

where ΔF is the change in free energy for homogeneous nucleation, θ is the contact angle, and

$$g(\theta) = \tfrac{1}{4}(2 - 3\cos\theta + \cos^3\theta). \tag{7}$$

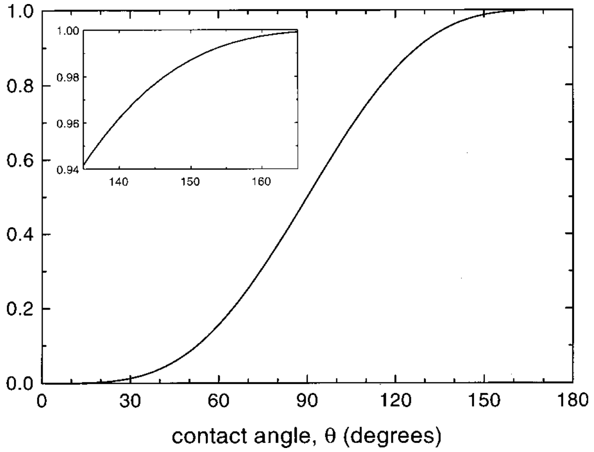

FIG. 7. A graph of $g(\theta)$, the correction term for heterogeneous nucleation, as a function of the contact angle θ between the nucleus and the substrate.

The nucleation barrier for this model of heterogeneous nucleation is thus

$$\Delta F^*_{\rm max} = g(\theta)\Delta F_{\rm max}. \tag{8}$$

Contact angles for solid ^{4}He on a copper substrate (such as our cell) have been determined experimentally for both phases [11]. The values for the two phases are similar, roughly between 140° and 160°, and are about the same for a wide range of substrates. For these values of the contact angle, however, the nucleation barrier $\Delta F^*_{\rm max}$ differs from the value of that for homogeneous nucleation by only a few percent [$g(\theta) > 95\%$—see Fig. 7], where a reduction by orders of magnitude is required to get an appreciable probability of nucleation.

Some investigators have speculated on the possibility that other geometries might increase the change in free energy [12], but for contact angles that are greater than 90°, these changes will not be sufficient to reduce the predicted nucleation barrier to a value compatible with experimental observations. Consider a simple model for heterogeneous nucleation in which the nucleus forms in a conical pit of arbitrary angle at the apex ϕ. The contact angle of the solid with the substrate, θ, remains the same. One obtains for the change in free energy (as a function of θ and ϕ)

$$\Delta F^{\dagger} = q(\theta,\phi)\Delta F \tag{9}$$

where

$$q(\theta,\phi) = \frac{1}{4}\Bigg[2 - 3\sin(\theta+\phi) + \sin^3(\theta+\phi) - \cos^3(\theta+\phi)\frac{\cos\phi}{\sin\phi}\Bigg]. \tag{10}$$

When the value of the contact angle is greater than 90°, this function has a minimum with respect to the angle of the pit—see Fig. 8. For the reported values of the contact angle for solid helium on a copper substrate, this minimum leads to

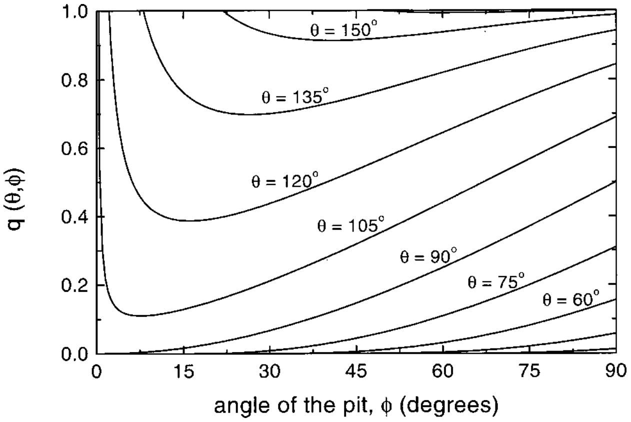

FIG. 8. A plot of $q(\theta,\phi)$, the correction term for heterogeneous nucleation in a pit, as a function of ϕ, the angle of the pit, for values of the contact angle θ between 30° and 165°, at 15° intervals.

no more than ~30% decrease in the nucleation barrier $\Delta F_{\max}$; again, not nearly enough to be consistent with the observations.

The similarity of the nucleation *pressure* recorded for events in which only the hcp solid was observed and for those events in which we recorded double nucleation suggests that either the nucleation process for the metastable bcc solid is substantially different from that of the stable hcp solid, or the critical nucleus in both types of events may be the same.

When we measure the bcc nucleation overpressure with respect to the bcc metastable coexistence pressure the temperature dependence is distinctly different from that seen in events in which only hcp is observed. As seen in Fig. 6, the best linear fit of the data has very little temperature dependence compared to the results from the hcp data (Fig. 4). A temperature independent nucleation overpressure is characteristic of quantum mechanical nucleation. Such an explanation for the bcc nucleation would have to include an account of why the hcp nucleation, over the same temperature range, has the temperature dependence one would expect from a thermally activated process, and would also mean that the bcc nucleation *overpressure* was such as to cause the bcc nucleation *pressure* to coincide with the hcp nucleation *pressure* across the temperature interval investigated—which seems unlikely.

On the other hand, the nucleation pressure for both phases would be the same if it were the case that the critical nuclei for both phases were the same.

It is possible that the events in which only a single pressure plateau at the hcp melting pressure is recorded may actually have had the metastable bcc phase with a lifetime that is too brief to record less than 1 s. We have modeled the distribution of lifetimes of the metastable liquid in the presence of the bcc solid (at the melting pressure of the metastable bcc solid) as an exponential decay process, and estimated the number of events we expect to find at times of less than 1 s. The number of events in which metastable bcc was not observed, however, far exceeds the number of events that were determined from these calculations.

Another possibility is that the critical nucleus in both cases is the same, but that sometime after nucleation, and before reaching macroscopic size, the nucleus transforms into either the hcp or the bcc phase. Recent developments in computer simulations of the liquid-solid phase transition, and in numerical results from density functional approaches to the same, have suggested the possibility that, for liquids with a Lennard-Jones type potential, the interface of a nucleus of solid may have considerable bcc-like ordering, even when the stable phase is a close-packed phase (fcc in the works cited).

In the late 1970s, molecular dynamics simulations of systems of particles in a Lennard-Jones potential were carried out by Mandell, McTague, and Rahman [2]. They found that nucleation in simulations with 500 particles resulted in the formation of a nucleus with a bcc-like structure. The number of particles in their simulation was small, however, and it is likely that the boundary conditions or other size dependent factors strongly influenced the development of the nucleus. Much later, Swope and Andersen [3] performed molecular dynamics simulations on much larger systems, up to 10^6 atoms. Their simulations seemed to suggest that $\sim 10^4$ atoms were sufficient to overcome system size dependencies in nucleation simulations. While they observed the formation of fcc, hcp, and bcc precritical crystallites, the solid that formed in their simulations was fcc, and the fcc solid did not emerge from bcc precritical nuclei. However, their simulation required extremely large supercoolings, for nucleation to occur within a reasonable amount of time. It is possible that the magnitude of the supercooling reduced the nucleation barriers for all phases to such an extent that any preference for a bcc-like phase was insignificant. In an attempt to examine the nucleation process in a Lennard-Jones system with smaller supercooling, van Duijneveldt and Frenkel [4] pioneered the use of ''umbrella sampling'' in Monte Carlo simulations of nucleation. This technique was exploited by ten Wolde, Ruiz-Montero, and Frenkel [13] on a system of 10^4 particles with ~20% supercooling; they found evidence of a lower nucleation barrier for metastable bcc nucleation and of a bcc-like structure of the interface of the nucleus.

In addition to the various efforts at computer simulation, there have been advances in the theoretical methods used to address the nucleation process. In their 1978 paper, Alexander and McTague [14] presented an argument, based on Landau's theory of phase transitions [15], that the bcc solid should be uniquely favored in nucleation from an isotropic liquid for reasons of symmetry. Obviously not all solids crystallize from the liquid as bcc, but their work suggests a relationship between the liquid and the bcc solid that is consistent with the observations of a bcc-like interface of the nucleus seen in the simulations of ten Wolde, Ruiz-Montero, and Frenkel.

Finally, density functional methods have been applied to the problem of nucleation. For example, Shen and Oxtoby [6] explored the structure of a nucleus forming from a Lennard-Jones fluid with density functional techniques. Their results also show an interfacial layer of the nucleus that has a bcc-like structure, consistent with the computer simulations and with the results of Alexander and McTague. Thus, a picture emerges of a symmetry-breaking process in the transition from an isotropic, simple liquid to a crystalline solid, in which the formation of a bcc structure is favored, regardless of the ultimate, stable solid structure.

In our experiments, the initially emerging nuclei may be ‘‘all interface,’’ and, like the nuclei modeled by ten Wolde, Ruiz-Montero, and Frenkel, may have a bcc-like structure. Although the stable phase in the models discussed was fcc, the results strongly suggest that the emergence of the bcc-like nucleus is due to symmetry properties and energy barriers of the bcc phase with respect to the liquid, and not the stable solid. Beyond a certain size, the core of the nucleus will transform into the stable or metastable phase, but in either case, the initial nucleation barrier would be determined by the cost of creating the ‘‘all-interface’’ critical nucleus. In our case, an ‘‘all-interface’’ bcc-like solid may have an enhanced probability of becoming a metastable bcc solid instead of a stable hcp solid.

We have noted that we did not observe metastable nucleation at pressures above T_{TP} (nucleation of metastable hcp where bcc is the stable solid). In a previous study of solidification in ^{4}He, Jung and Franck [16] investigated the nucleation of the solid from the liquid at much higher temperatures and pressures, near the fcc-hcp-He(I) triple point. They did not observe the nucleation of any metastable phases. This is consistent with a model in which the metastable bcc phase arises from the postulated bcc-like interface. Because the bcc phase is unstable at those temperatures and pressures, a macroscopic bcc phase cannot form from the ‘‘all interface’’ nucleus; because the interface is bcc-like, it does not lead to the formation of metastable hcp or fcc phases.

We have also explored the lifetime of the metastable superfluid at the metastable bcc coexistence pressure P_m(bcc) for several temperatures. While the characteristic lifetime of the metastable bcc-superfluid system within the temperature range of our experiments and at P_m(bcc) is between ~80 and ~400 s, depending on the temperature, the lifetime of the superfluid at P_m(bcc) when no metastable bcc solid has been nucleated is very large—no nucleation was seen for waiting times in excess of 2 h. Thus, the lifetime of the bcc-superfluid system may be determined by the presence of a nonequilibrium population of nuclei, generated at the nucleation pressure of the metastable bcc solid. (We note that the lifetime of the supercooled liquid gets longer as the temperature gets higher; this is because of the temperature dependence of the bcc metastable coexistence pressure; the overpressure of the liquid gets smaller with increasing temperature—it is not an indication that nucleation in these events is not thermally activated.)

VI. SUMMARY

We have observed the frequent occurrence of nucleation and growth of metastable bcc solid from superfluid ^{4}He, at temperatures below the lower triple point (1.46 K) where the hcp is the stable phase. This bcc solid persists for times ranging from a fraction of a second to tens of minutes, before hcp solid independently nucleates and grows, and the bcc solid melts. In other events, we observe only the growth of the hcp solid. Nucleation pressures for the two events are the same, and we have speculated on mechanisms that might lead to such behavior. Specifically, we note that our results are consistent with the picture of nucleation as a symmetry-breaking process in which the bcc structure is uniquely favored in transitions from an isotropic, simple liquid, and with numerical and computational models of nucleation that reveal the emerging nucleus as bcc-like or having a bcc-like interfacial layer.

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