

## Homogeneous nucleation temperature of liquid $^3\text{He}$

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We report measurements of the liquid-to-vapor homogeneous nucleation temperature of  $^3\text{He}$  in the reduced-pressure range  $(0.05-0.5)P/P_c$  using the technique of transient superheating. These measurements extend the range over which Becker-Doring classical nucleation theory has been tested using the transient superheating technique to new limits of low temperature and quantum influence. Our results are consistent with predictions based on this theory and show the general behavior expected of a liquid with a large de Boer parameter.

### I. INTRODUCTION

The classical theory of kinetics involved in the nucleation of one phase from another has received much attention since its original formulation by Volmer and Weber,<sup>1</sup> Becker and Doring,<sup>2</sup> and others.<sup>3</sup> Such phase transitions are associated with the existence of a thermodynamic energy barrier to the formation of droplets of a second phase in a homogeneous metastable parent phase. The nucleation of the phase transition is assumed to be accomplished by the thermal activation of incipient droplets of the second phase over the top of this barrier. One application of the Becker-Doring nucleation theory is the prediction of an effective kinetic limit of metastability of a parent liquid phase with respect to the transition to the vapor phase.<sup>3</sup> In this case a vapor bubble which manages to attain critical size corresponding to the peak of the barrier can grow without further limitation.

Although attempts at experimental verification of Becker-Doring theory for the liquid-vapor transition have met with considerable success, there are some areas in which agreement between theory and experiment has not been observed. The verification experiments have generally taken one of two forms. Many workers have used some type of superheating technique in which the temperature of the liquid is raised at constant pressure up to the limit of metastability, at which point bubbles of vapor are observed.<sup>3,4</sup> Other investigations have employed a variety of methods in which the pressure is lowered at more or less constant temperature (quasiadiabatically) until nucleation of the vapor phase is observed. The latter type of experiment can also be used to probe the tensile strength of the liquid if the pressure can be reduced to negative values before nucleation occurs. As a result of these efforts it was established that, for organic liquids, both superheating and tensile-strength experiments yielded values of the homogeneous nucleation temperature,  $T_h$ , and ultimate tensile strength which were in good agreement with the predictions of Becker-Doring nucleation theory.<sup>3-5</sup>

However, for cryogenic liquids the situation is not so clear. For example, a variety of methods has been employed in attempts to measure the ultimate tensile

strength of liquid argon, nitrogen, oxygen, and helium,<sup>6-8</sup> but no values even approaching the predictions of classical nucleation theory in the negative-pressure region have been reported. This discrepancy has been attributed to a number of possible factors including impurity nuclei in the liquid or at the container walls, the production of ions by cosmic rays or radioactivity, and, in the case of liquid helium, the quantum nature of the liquid and the role of quantized vortex lines.<sup>9,10</sup> Since Skripov and co-workers have used superheating, expansion chamber, and acoustic cavitation techniques to stress liquid argon, krypton, and xenon, and have found good agreement with theory in the positive-pressure region,<sup>11-13</sup> it seemed possible that the strongly quantum nature of liquid helium might be an important cause of the discrepancy between theory and experiment for liquid helium. Indeed, Lifshitz and Kagan have pointed out that under certain conditions the probability that a subcritical size nucleus could tunnel through the nucleation barrier becomes equal to or exceeds the probability of thermal activation over the top of the barrier.<sup>14</sup> Under these conditions the Becker-Doring theory is not expected to apply. However this particular mechanism for the breakdown of Becker-Doring theory is not expected to occur until rather extreme conditions are reached: a temperature of 0.3 K and a negative pressure of 14.6 atm in liquid  $^4\text{He}$ , and 0.2 K and negative 5.2 atm in liquid  $^3\text{He}$  (Refs. 15 and 16). One would therefore expect the predictions of the Becker-Doring theory to hold for the liquid-vapor transition in liquid helium at higher temperatures and at positive pressures. As an experimental test of this prediction, measurements of  $T_h$  in liquid  $^4\text{He}$  were carried out in this laboratory, employing a transient superheating technique, with the result that good agreement was observed with the Becker-Doring theory.<sup>16</sup> Results consistent with these also have recently been obtained in  $^4\text{He}$  by Nishigaki and Saji.<sup>17</sup> The purpose of this paper is to report the results of similar measurements of the homogeneous nucleation temperature in the case of liquid  $^3\text{He}$ .

### II. BACKGROUND

The results of superheating experiments with various classical and quantum cryogenic liquids are summarized

in Fig. 1 from Sinha *et al.*<sup>16</sup> which shows the scaled homogeneous nucleation temperature  $T_h/T_c$  plotted as a function of the scaled bath pressure  $P/P_c$ .  $T_c$  and  $P_c$  are the critical temperature and pressure, respectively. The solid lines are predictions of the theory. Although the data for the classical cryogenics all fall on the same line, representing a relationship of corresponding states, it is clear that the data for hydrogen and  $^4\text{He}$  differ substantially from the classical line. However, it must be emphasized that this deviation of the quantum liquids from the classical relation of corresponding states does not represent a breakdown of the Becker-Doring nucleation theory. Rather, the deviation of the quantum liquids is a reflection of the relatively larger quantum mechanical influence on the thermophysical properties of those liquids. The magnitude of these deviations has been scaled to the de Boer quantum parameter,  $\Lambda$ , in a quantum extension to the theory of corresponding states.<sup>16,17</sup> The de Boer parameter is the ratio of the de Broglie wavelength  $\lambda$  to the range parameter  $r_0$  of the Lennard-Jones potential:  $\Lambda = \lambda/r_0 = (h^2/r_0^2 m \epsilon)^{1/2}$ , where  $h$  is Planck's constant,  $m$  is the atomic mass, and  $\epsilon$  is the strength parameter of the Lennard-Jones potential.

Figure 1 also includes the theoretical prediction for liquid  $^3\text{He}$ . In accordance with its large de Boer parameter ( $\Lambda = 3.1$ ), the prediction for  $^3\text{He}$  falls still further below the classical liquids than  $\text{H}_2$  and  $^4\text{He}$ . A next logical step following the verification of Becker-Doring nucleation theory for positive pressure in  $^4\text{He}$  was to extend the studies of bubble nucleation in cryogenic liquids to the extreme limit of relative quantum influence and to still lower temperatures by measuring the homogeneous

nucleation temperature of liquid  $^3\text{He}$ . From a theoretical point of view, liquid  $^3\text{He}$  is interesting because it is the most strongly quantum liquid known, as measured by its de Boer parameter, and thus should show the largest deviation from the corresponding state predictions based on the classical liquids. Experimentally, it affords the easiest access to the lowest temperatures of any liquid. Also, it exhibits no superfluid transition down to very low temperatures, an important practical consideration when using a transient superheating method.

In the classical nucleation theories, the formation of critical-sized nuclei in the metastable liquid as a result of thermal heterophase fluctuations is described in terms of a thermally activated transition across a thermodynamic energy barrier. The height of this energy barrier is determined by the minimum work of formation  $W_{\text{cr}}$  of a critical (vapor-filled) nucleus.

The rate of formation of these critical nuclei per unit volume  $J$  is generally described by an Arrhenius-type expression:

$$J = J_0 \exp(-W_{\text{cr}}/k_B T), \quad (1)$$

where  $J_0$  is an attempt frequency determined by the dynamics of nucleus formation process,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant. This equation can be expressed more completely in a form recently given by Blander and Katz:<sup>3</sup>

$$J = N(2\sigma/\pi m B)^{1/2} \exp[-16\pi\sigma^3/3k_B T(P_e - P_l)^2 \delta^2], \quad (2)$$

where  $\sigma$  is the bulk surface tension,  $N$  is the molecular density of the liquid,  $m$  is the molecular mass,  $B$  is a

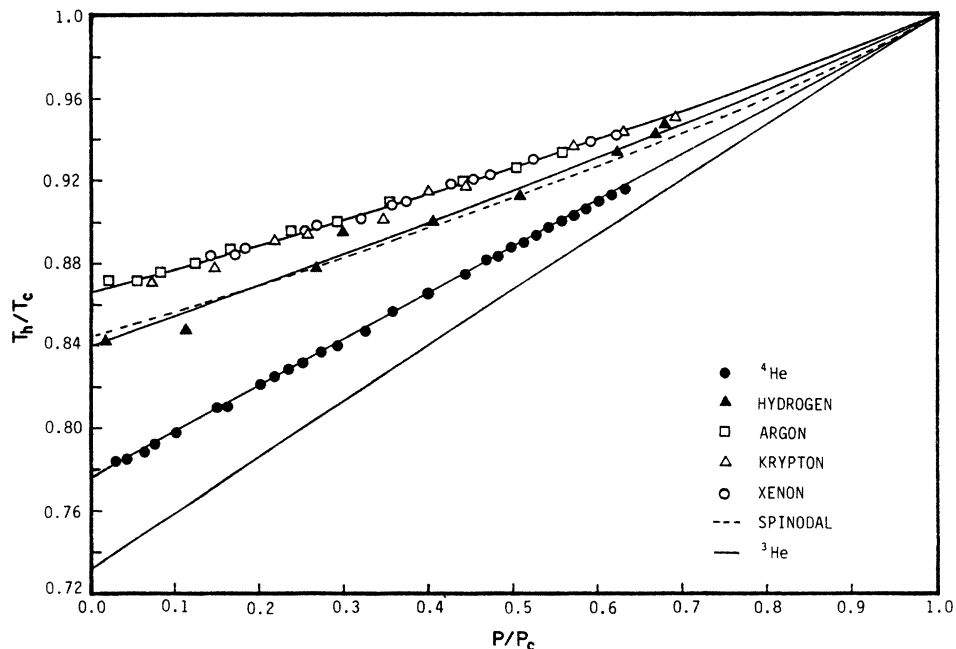


FIG. 1. Scaled homogeneous nucleation temperature  $T_h/T_c$  vs scaled pressure  $P/P_c$  (Ref. 16). The data for Ar, Kr, and Xe are from the experiments of Skripov *et al.* (Ref. 11), the  $\text{H}_2$  data are selected from Hord *et al.* (Ref. 18), and the  $^4\text{He}$  data are taken from Sinha *et al.* (Ref. 16). The solid lines represent theoretical predictions from Eq. (2). The theoretical curve for  $^3\text{He}$  was obtained with the surface tension data of Zino'eva (Ref. 19). The dotted line shows the van der Waals spinodal.

constant ( $B = \frac{2}{3}$  in our superheating experiment),  $P_e$  is the equilibrium vapor pressure, and  $P_l$  is the ambient pressure. The Poynting correction factor  $\delta$  relates  $P_v$ , the vapor pressure of the liquid under an ambient pressure  $P_l$ , to the equilibrium pressure:  $\delta = (P_v - P_l) / (P_e - P_l)$ .

Equation (2) is extremely sensitive to small changes in temperature so that an effective homogeneous nucleation temperature can be defined by arbitrarily setting  $J$  equal to one critical nucleus per cubic centimeter per second and then solving the resulting equation for  $P_l$  as a function of  $T$ . The kinetic coefficient in the preexponential factor of Eq. (2) does not include the modifications due to viscous or inertial forces that affect the dynamics of nuclei growth. However, these effects have been estimated to be unimportant for homogeneous nucleation in  $^3\text{He}$  or  $^4\text{He}$ .<sup>16,20</sup> In addition, the estimated relaxation time to establish steady state nucleation is several orders of magnitude smaller than the time scales considered here.

### III. EXPERIMENTAL PROCEDURE

Our measurements are made using the technique of fast transient superheating discussed in detail elsewhere.<sup>16</sup> In this technique a single crystal of bismuth immersed in the liquid helium is employed as both heater and thermometer, the magnetoresistance of the bismuth serving as the thermometric property. A step pulse of electric heating power is applied to the heater-thermometer crystal, and its temperature response is recorded as a function of time. When the temperature of the liquid helium in contact with the solid surface reaches the homogeneous nucleation temperature, a sudden break is observed in the temperature-time curve. The superheat at which the break occurs is added to the bath temperature to obtain  $T_h$ .

The use of this technique in  $^4\text{He}$  measurements<sup>16</sup> was adapted in several ways to liquid  $^3\text{He}$ . In particular, the limited availability of  $^3\text{He}$  necessitates the use of a smaller-sized bismuth crystal in a more restrictive geometry than that used earlier in  $^4\text{He}$ . The experimental apparatus is also fitted into a  $^4\text{He}$  cryomagnetic dewar to control the  $^3\text{He}$ -bath temperature and allow for easy vapor recycling.

### IV. RESULTS

Figure 2 shows the maximum superheat temperature  $T_m$  as a function of applied power. It will be noticed that  $T_m$  increases slightly and linearly with increasing applied power. Although there are several possible factors that might contribute to the observed increase in maximum superheat with increasing heater power, our results suggest that the Kapitza resistance is the overwhelming factor.<sup>21,22</sup>

In measurements of the homogeneous nucleation temperature of  $^4\text{He}$ , Sinha *et al.* reported that the observed maximum superheat remained constant over a wide range of applied heater powers.<sup>16</sup> It is possible that the earlier failure to observe the Kapitza  $\Delta T$  was due to a combination of factors. These include the less-restrictive geometry and higher crystal quality which allowed the

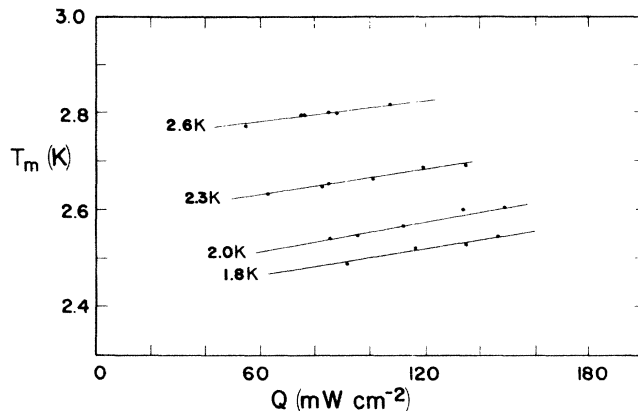


FIG. 2. Maximum superheat  $T_m$  of liquid  $^3\text{He}$  as a function of the applied power for several bath temperatures.

use of relatively lower applied powers, an analog data acquisition and analysis system which may have made correction of errors due to non-Ohmic effects more difficult than with our digital equipment, and the relatively lower Kapitza resistance at the higher temperatures existing in the  $^4\text{He}$  research.

Although the individual measurements of  $T_m$  reported above fall somewhat above the predicted homogeneous nucleation temperature for  $^3\text{He}$  we feel that the physically relevant quantity is the extrapolated zero-power intercept of a series of experiments taken at different powers. This extrapolation is expected to yield the values of the temperature of the liquid at the crystal surface without any influence of the Kapitza  $\Delta T$ . This approach is supported by the fact that the calculated slopes of the  $\Delta T$ -versus-power curves are close to those expected from a prediction based on Kapitza thermal-boundary resistance calculations.<sup>21,22</sup>

Our final experimental results for  $T_h$  are tabulated in Table I and plotted in Fig. 3 which is a scaled temperature-versus-scaled-pressure graph similar to Fig. 1. The  $^3\text{He}$  data points shown are actually the extrapolated zero-power intercepts of a large number of individual transient superheating experiments. It can be seen that these results are close to the theoretical predic-

TABLE I. Tabulation of final experimental results. Each experimental value of  $T_h/T_c$  is the extrapolated zero power intercept of a large number of individual transient superheating experiments. The theoretical values were calculated from Eq. (2), using the surface tension data of Iino *et al.* (Ref. 23).

$P_l/P_c$	$T_h/T_c$	$T_h/T_c$	$T_h/T_c$
	Experimental	Theory $J=1$	Theory $J=10^8$
0.0441	0.7181	0.7225	0.7337
0.1175	0.7401	0.7434	0.7532
0.1732	0.7630	0.7594	0.7682
0.2437	0.7837	0.7797	0.7872
0.3308	0.8072	0.8048	0.8109
0.4359	0.8324	0.8354	0.8399
0.5609	0.8724	0.8718	0.8747

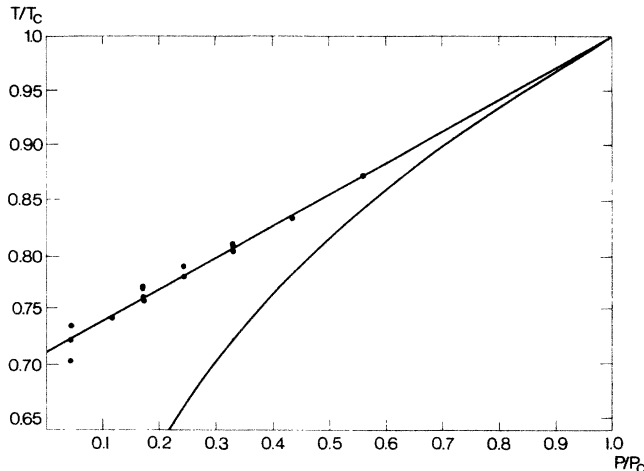


FIG. 3. Scaled homogeneous nucleation temperature  $T_h/T_c$  vs scaled pressure  $P/P_c$  for liquid  $^3\text{He}$ . Each data point is the extrapolated zero-power intercept of a large number of individual transient superheating experiments. The upper solid line is the theoretical prediction for liquid  $^3\text{He}$ , calculated from Eq. (2) using Iino's surface tension data (Ref. 23), and the liquid and vapor densities of Kerr (Ref. 24). The lower curve is the liquid-vapor coexistence curve of  $^3\text{He}$  taken from Sydoriak *et al.* (Ref. 25).

tion based on Eq. (2). The slight scatter is consistent with the calculated standard deviation of the zero-point intercepts. This was calculated for each extrapolation and was typically in the range of 20 to 40 mK, a figure which is consistent with our expectations based on analysis of the experimental apparatus, associated electronics, and bath-temperature uncertainty.<sup>26</sup>

Although our results agree with present theory, there are a number of factors that could systematically influence the experiment. Nishigaki and Saji have suggested that the slight discrepancy between their quasi-steady-state measurements and homogeneous nucleation theory could be due to early spontaneous bubble formation as predicted by fluctuation nucleation theory.<sup>17</sup> Sinha *et al.* had suggested that because of the relatively small superheated layer and the transient nature of that experiment, which is similar to the one reported here, such spontaneous as well as heterogeneous nucleation should be negligible.<sup>16</sup>

We found that the measurements could not be extended much above a reduced pressure of about 0.5, probably because normal circulation was reduced by the restricted geometry referred to previously. Above this pressure we would observe that the coefficient of heat transfer, even for relatively low heat fluxes, was substantially reduced from what we normally found in liquid  $^3\text{He}$ , and a normal temperature-time curve could not be observed. Although not rigorously tested, our best explanation of this phenomenon is that a turbulent foam of liquid and vapor develops in the experimental vessel as a result of the pulsed heating. The inhibited heat transfer does not revert to normal until a substantial amount of time has elapsed and the temperature of the liquid  $^4\text{He}$  bath surrounding the  $^3\text{He}$  vessel is reduced, resulting in conden-

sation of the  $^3\text{He}$ . Because our pulsed experiments take place in a few milliseconds and the heat penetration into the  $^3\text{He}$  bath in this time interval is less than 0.1 mm, we do not believe that this problem is a significant source of measurement error for the results reported here.

A factor which can result in measured values lower than expected is the heat conduction from the bismuth crystal heater thermometer along the copper resistance-sensing leads into the nonsuperheated liquid-helium bath a short distance away.<sup>27-29</sup> We have so far been unable to calculate precisely the expected magnitude of this error but results of experiments with differing wire and crystal sizes, which would be expected to lead to different results, suggest that this factor may be safely neglected in our fast transient experiments.

## V. DISCUSSION

Since the value of  $T_h$  predicted by Eq. (2) is very sensitive to surface tension, it is important to note that the theoretical  $^3\text{He}$  curve calculated by Sinha and reproduced in Fig. 1 was obtained with the data of Zeno'veva.<sup>19</sup> However, in Fig. 3 we have used the more recent surface-tension data of Iino *et al.*<sup>23</sup> which differ enough from Zeno'veva to result in theoretical predictions of  $T_h$  for  $^3\text{He}$  several percent lower than those published previously.<sup>16</sup> Thus our experimental values for  $T_h$  in  $^3\text{He}$  do differ measurably from what was originally expected. To the extent that our experimental results can be used as a benchmark, it seems clear that the  $^3\text{He}$  surface-tension data of Iino *et al.* provide better agreement.

The results reported above represent a verification of Becker-Doring classical nucleation theory in the most strongly quantum liquid, as measured by its de Boer parameter, and the completion of the positive pressure phase of a more extensive program of mapping out the entire boundary of the metastable region of liquid  $^3\text{He}$ .

These measurements were made in the temperature range of approximately 2.4 to 2.9 K and correspond to a bath temperature range of about 1.4 to 2.8 K. Previous superheating work in  $^4\text{He}$  was limited by the  $\lambda$  transition at 2.18 K which corresponds to a homogeneous nucleation temperature of about 4.0 K.<sup>16</sup> It would be interesting to extend measurements of the kinetic limit of metastability in liquid helium to still lower temperatures and into the negative pressure regime with a tensile strength experiment. The motivations for this are twofold. First, it is desirable to extend the range of verification of the classical nucleation theory for the liquid to vapor phase transition to as low a temperature as possible. In particular, one would like to go below the limit of about 0.8 K to which the general theory has been tested, in this case in  $^3\text{He}$ - $^4\text{He}$  phase-separation experiments by Sinha and Hoffer<sup>30</sup> and Alpern *et al.*<sup>31</sup> Second, we are approaching the temperature of several hundred mK at which the rate of formation of critical-sized vapor nuclei by subbarrier quantum-tunneling transitions<sup>14-16</sup> is predicted to equal the rate of formation by thermally activated transitions over the top of the energy barrier.

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