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Supercooling of Liquid Hydrogen

G. M. Seidel, H. J. Maris, F. I. B. Williams,[a] and J. G. Cardon
Department of Physics, Brown University, Providence, Rhode Island 02912

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We describe experiments that we have performed with droplets of supercooled liquid H_2 in the temperature range down to 10.6 K. We have measured the nucleation rate for the production of the solid phase. Using this result, we discuss the prospects for the experimental production of superfluid H_2.

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The normal freezing temperature T_3 for liquid parahydrogen (p-H_2) is 13.81 K. In a recent paper[1] we have considered theoretically the lowest temperature T_s to which liquid H_2 can be supercooled. It was predicted that the amount of supercooling ΔT ($\equiv T_3 - T_s$) should be very large, and that it might even be possible to supercool all the way to $T=0$ K. The large ΔT occurs because quantum-mechanical zero-point motion makes the difference in energy of liquid and solid H_2 fairly small, even at $T=0$ K. If a large amount of supercooling can in fact be achieved, it may be possible to reach the superfluid transition, which for p-H_2 is tentatively estimated[1] to be 2–3 K.

In this Letter we report on experiments that we have performed with supercooled liquid H_2, and we discuss the implications that our results have for attempts to produce superfluid H_2. A major problem in any study of supercooled liquids is heterogeneous nucleation of the solid phase. It is essential to eliminate impurities and to avoid contact with container walls where heterogeneous nucleation is likely to occur. To eliminate nucleation at walls we initially attempted to perform experiments with drops of liquid H_2 of diameter ~ 1 mm which were in free fall either in a vacuum or in low pressure ^{4}He gas ($P \leq 1$ bar). There were several difficulties with these experiments. It was necessary to find a way to tell whether a drop was liquid or solid during the short time that it was falling. In addition, one had to determine the temperature of the liquid and be sure that it was uniform throughout the drop.

To get around these difficulties we have built an apparatus in which liquid-H_2 drops are levitated (Fig. 1). A cylindrical chamber of length 6.5 cm and diameter 5 cm has a thick glass wall and copper end plates. The end plates are held at controlled temperatures, which in a typical case are 15 K for the top plate and 7 K for the lower plate. At the beginning of the experiment the chamber is filled with helium fluid under a pressure P. Liquid H_2 is then introduced through a hole in the upper plate. Because of the vertical temperature gradient in the chamber, the density of the ^{4}He varies with height. If the pressure is chosen to lie in an appropriate range there will be a certain height at which liquid H_2 will be neutrally buoyant, i.e., it will float in the helium. There will be another height (lower) where solid H_2 floats. When the pressure is varied the position and temperature of these places where liquid and solid H_2 float change. Thus, it is possible to levitate either phase of H_2 over a range of temperatures. The temperature of the drops can be determined from the equations of state for helium fluid,[2] and for hydrogen.[3] A small correction was applied to allow for the solubility of H_2 in ^{4}He and vice versa. At a pressure of 14 bars liquid H_2 floats at a temperature of 10.4 K, and at 16 bars the temperature is 11.2 K. Of course, our experiment has the disadvantage that the applied pressure increases the nucleation rate by increasing the difference in free energy between the liquid and solid phases.

The liquid H_2 was introduced through a 5-μm-diam hole in a stainless-steel disk which was in the center of the top plate. We observed the drops with the aid of a microscope with long-focal-length objective. At the buoyancy level for liquid we could observe drops with diameters in the range ~ 50 μm to ~ 1 mm; the range of drop sizes occurs because of the coalescence

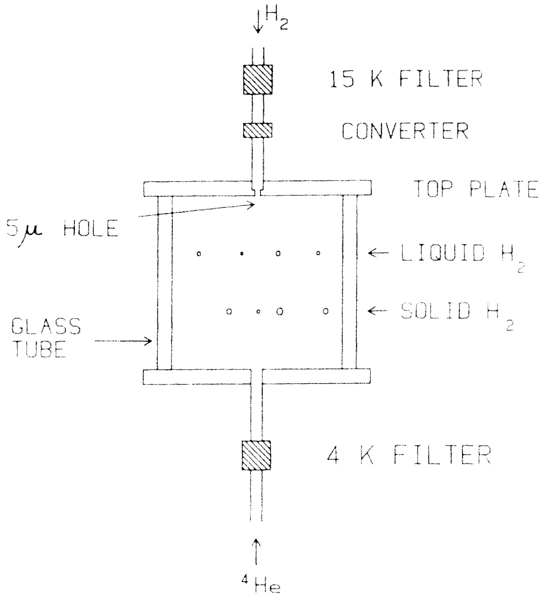

FIG. 1. Schematic diagram of the apparatus.

of small drops. When a drop nucleated it was observed to move to the buoyancy level for solid H_2. The nucleation rate Γ for solid was determined from observations of the lifetimes of liquid drops. Γ is given by

$$\Gamma = 1/\langle V\tau \rangle, \tag{1}$$

where the average is of the product of drop volume V and lifetime before freezing τ. Note that Γ is the nucleation rate per unit volume. In Fig. 2 we show the results that we have obtained for $\Gamma(T)$ in this way.

To minimize the effect of impurities, the ^{4}He gas was admitted to the cell after first having passed through a 1-cm-long filter packed with 1-μm powder. The H_2 passed through a similar filter[4] at 15 K, and also through a powder of nickel silicate to convert normal H_2 to p-H_2. Even with these precautions one needs to be concerned about the possible presence of impurities. As an example, note that H_2 in contact with solid N_2 at 15 K contains an equilibrium concentration[5] of N_2 atoms of 10^{10} to 10^{11} cm^{-3}. Thus, cooling of H_2 saturated with N_2 to lower temperatures could conceivably result in the formation of small clusters of solid N_2, which could in turn cause heterogeneous nucleation of solid H_2. However, it is unlikely that the hydrogen fill line contains enough N_2 on its walls to lead to saturation of the H_2. In one experiment we deliberately introduced impurities by heating briefly a fine tungsten filament which was placed in the fill line near to the cell. The idea was that impurities on the filament surface would be boiled off and enter the H_2. After such a procedure the majority of the drops froze at a temperature very close to 14 K, whereas normally virtually all drops can be supercooled several degrees.

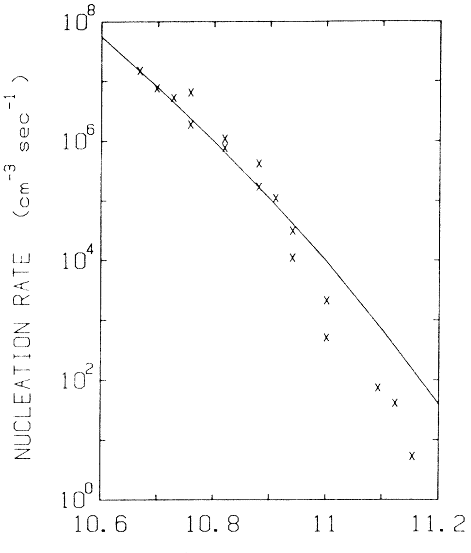

FIG. 2. Experimental results for the nucleation rate Γ. The solid curve is the theoretical value of the classical nucleation rate based on an assumed value of 0.874 cgs for α_{LS}.

Before discussing the results for $\Gamma(T)$ we mention several peculiar hydrodynamic effects which affect the accuracy of the experiment.[6] One finds that the liquid drops do not all float at the same height as the simple buoyancy argument would suggest, but are distributed over a height range which may be as much as 1.5 mm. There are two principal effects which cause this spread in heights. Firstly, the vertical temperature gradient over the drop coupled with the temperature-dependent surface energy of the liquid H_2 produces a tangential force on the surface of the drop.[7] This force generates a flow in the liquid and by viscous drag creates local convection in the ^{4}He gas. The drop can be thought of as trying to pull itself through the gas, and therefore comes to an equilibrium position which depends on its size and differs slightly from that given by the buoyancy condition. A detailed calculation of this effect[6] gives quantitative agreement with the observed height variations. The convection means that our estimated temperatures may be too low by as much as 0.2 K at ~ 11 K. The error should be significantly smaller at lower temperatures (e.g., 10.6 K). Secondly, liquid H_2 in a gas of ^{4}He at 15 bars has a substantial vapor pressure in the temperature range where we are working. If the H_2 concentration in the gas is not close to its saturated value, the liquid will evaporate. This cools the drop and the surrounding gas, and convection currents are set up. These currents produce a force which moves the drop away from the buoyancy height. The sign of this force depends on whether the gas is unsaturated or supersaturated, and the magnitude of the effect is again[8] significantly larger at 11 K than at 10.6 K.

In Fig. 2 we compare the data with the rate predicted from classical nucleation theory.[9] An important parameter in the theory is the liquid-solid surface energy α_{LS} for H_2. The assumed value of α_{LS} is 0.874 cgs. The temperature dependence of the theoretical $\Gamma(T)$ is less than that found experimentally. However, this discrepancy may be just a result of temperature errors (particularly at high T) caused by the hydrodynamic effects. It is for this reason that we have chosen α_{LS} so that theory and experiment match in the lower temperature range.

What do these results mean for the prospects of making superfluid H_2? At lower temperatures, Γ from classical nucleation reaches a maximum and then decreases rapidly. If H_2 can be cooled rapidly through this maximum into the relatively stable regime at lower temperature, it may be possible to achieve superfluidity. The magnitude of Γ_{max} together with the rate of cooling determine the largest-volume drop which can be cooled in this way. To estimate Γ_{max} we have to assume some model for the temperature dependence of α_{LS}. In Fig. 3 we show the results for

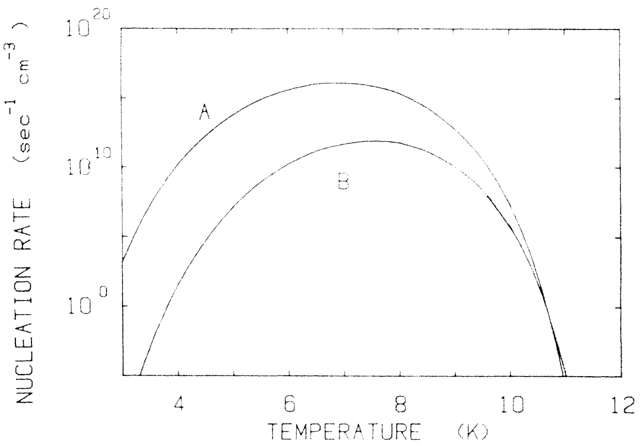

FIG. 3. Theoretical rates for classical nucleation at zero pressure. Curve A assumes $\alpha_{LS}=0.874$ independent of T. Curve B assumes a temperature-dependent α_{LS} as discussed in the text.

$\Gamma(T)$ at zero applied pressure under different assumptions about $\alpha_{LS}(T)$. (Note that Γ is much reduced at zero pressure because of the pressure dependence of the free-energy difference between the liquid and solid phases.[10]) Curve A is for $\alpha_{LS}=0.874$ cgs independent of T. This gives $\Gamma_{max}\sim 10^{16}$ sec^{-1} cm^{-3} at $T_{max}\sim 7$ K. In this case an experiment would have to be done with very small drops, since even a 0.1-μm-diam drop will decay in 0.2 sec at T_{max}. In the case of curve B we assume an $\alpha_{LS}(T)$ suggested by Woodruff.[11] We take the temperature-dependent term in the liquid-vapor surface energy[12] $\alpha_{LV}(T)$, and reduce it by the ratio of α_{LS} to α_{LV}. We also require that $\alpha_{LS}(T)=0.874$ at 10.7 K. This gives

$$\alpha_{LS}=1.014-0.001\,22T^2. \qquad (2)$$

In this case Γ_{max} is $\sim 10^{12}$ sec^{-1} cm^{-3} and so 1-μm drops would have a lifetime of 2 sec at T_{max}. Thus, even a small temperature dependence of α_{LS} has a very large effect on nucleation rates at lower T, and thereby on experiments to produce the superfluid phase.[13] We are currently constructing an apparatus to cool smaller drops at a high rate in the absence of applied pressure, and will report on these experiments subsequently.

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[a] Permanent address: Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaire de Saclay, F-91191 Gif-sur-Yvette Cédex, France.

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[2] R. W. Hill and O. V. Lounasmaa, Philos. Trans. Roy. Soc. London **252**, 44 (1960).

[3] H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Nat. Bur. Stand. **41**, 379 (1948). The data for the liquid had to be extrapolated into the supercooled regime.

[4] This filter is unlikely to remove HD or D_2 impurity. We have studied experimentally the effect of deliberately adding D_2 impurities. We found that a 1% D_2 concentration raises the temperature at which the nucleation rate is 10^5 cm^{-3} sec^{-1} from 11.0 to 11.5 K. Thus, the naturally occurring HD or D_2 impurities which result from the natural abundance (0.015%) of D in H are expected to have only a small influence on the nucleation process.

[5] This estimate is made with use of the higher-temperature data of M. N. Omar and Z. Dokoupil, Physica (Utrecht) **28**, 461 (1962).

[6] We will discuss these effects in more detail in a subsequent paper.

[7] N. O. Young, J. S. Goldstein, and M. J. Block, J. Fluid Mech. **6**, 350 (1959).

[8] The first effect is reduced because the flow is inhibited by the increased viscosity of the liquid H_2; the second effect is reduced because the H_2 vapor pressure has decreased.

[9] The calculation is the same as in Ref. 1, but modified to include the effect of the pressure of the ^{4}He gas. Note that this pressure depends on T.

[10] There may also be a pressure dependence to α_{LS}.

[11] D. P. Woodruff, *The Solid-Liquid Interface* (Cambridge, London, 1972), p. 30.

[12] V. N. Grigoriev and N. S. Rudenko, Zh. Eksp. Teor. Fiz. **47**, 92 (1964) [Sov. Phys. JETP **20**, 63 (1965)]. These authors fit their data with a linear T dependence, but this implies a constant surface entropy as $T\rightarrow 0$.

[13] If α_{LS} stays constant at 0.874 the *quantum* nucleation rate is predicted to be very large ($\sim 10^{19}$ sec^{-1} cm^{-3}) for $T\leq 2$ K (see Ref. 1). This would be an additional, and major, problem for superfluidity experiments. On the other hand, if α_{LS} varies with temperature as assumed in model B [Eq. (2)], the quantum nucleation rate at low T would be only $\sim 10^8$ sec^{-1} cm^{-3}.