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Supercooling Helium Vapor: Nucleation and Fog Formation induced by Strong Evaporation

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We have studied heterogeneous nucleation of liquid ^4He on cesiated surfaces using calorimetric techniques. Nucleation kinetics are strongly influenced by wetting properties. Since liquid ^4He does not wet cesium below 2K, substantial supercooling of the vapor is expected on theoretical grounds. Experimentally, however, we have been unable to detect any supercooling in our cells. This may be due to microscopic defects in the Cs coating, which in turn may be related to the fact that we have been unable to find a cell construction material which is wetted by Cs.

Somewhat paradoxically, it is possible to supercool helium vapor even in a container made of conventional wetted materials by imposing a large heat and mass flux from the liquid to the vapor across the bulk liquid-vapor interface. When evaporation is sufficiently strong, the vapor above the liquid becomes unstable, and forms a dense fog. Videos of this process show that the fog front propagates rapidly from very near the liquid-vapor interface upward into the vapor. Fog formation near the liquid interface implies that the vapor is in a supercooled metastable state. Qualitative ideas from non-equilibrium thermodynamics and kinetic theory are used to explain this phenomenon.

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1. INTRODUCTION

Metastable phases and nucleation phenomena are an important feature of any system that undergoes a first order phase transition. These issues are particularly interesting in helium because the high purity makes it possible to observe intrinsic behavior, and because of the possibility of observing the crossover from thermally activated to quantum nucleation. The walls of the

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container holding the helium can have important effects on the nucleation process because the walls provide heterogeneous nucleation sites. These can be avoided by using large gradients in temperature or pressure which localize the metastable region away from the walls. For example acoustic lenses have been used to study liquid-vapor[1] and liquid-solid nucleation[2]. Metastable phases can also be studied in containers without gradients if the nucleating phase does not completely wet the wall of the container, i.e. if the contact angle is greater than zero. Using conventional materials, this technique can be used to supercool the liquid-solid transition[3] and the ^{4}He rich branch of the ^{3}He-^{4}He phase separation curve[4]. The discovery that ^{4}He does not wet Cesium suggests the possibility that a cesium-coated container might have qualitatively different nucleation behavior. Pettersen and Saam[5] theoretically analyzed the consequences ^{4}He nonwetting for phase separation kinetics. Experiments on phase separation in a cesiated cell are technically very demanding, but the physics of liquid nucleation from supercooled vapor in a cesiated cell is very similar, which motivated the experiments reported here. We have developed techniques for making glass cells which are coated with cesium and loaded with helium vapor at room temperature. The cells are cooled and nucleation is detected by observing the rate of latent heat release. We have been unable to detect even fractions of a mK of supercooling in a variety of cells. This is presumably due to defects in the cesium coating.

During other unrelated experiments in a cryostat with optical access, we noticed that certain changes in the thermodynamic state of the cell would generate a dense fog of helium. This was surprising because the fog formed in a cell with wetting walls partially filled with bulk liquid, so there should be no barrier to nucleation. This motivated us to make a special test cell which would allow us to control the temperature gradients and to see the entire cell. We found that fog formation was associated with strong evaporation, and that the fog front propagated from the liquid-vapor interface upward into the vapor. We believe that the fog formation is due to homogeneous nucleation in the vapor caused by a local minimum in the temperature near the liquid interface.

2. NUCLEATION IN CESIATED CONTAINERS

The theory of homogeneous nucleation is well established. In homogeneous nucleation of a liquid, the liquid phase grows from small spherical nuclei which are spontaneously generated by statistical process in the supersaturated vapor. The grand free energy Ω of the system has terms proportional to the surface area and the volume of the nucleus. Since the terms

have opposite sign, Ω has a maximum Ω_{max} for a radius called the critical radius. The nucleation rate $J = f_a z e^{-\Omega_{max}/T}$ is a product of three terms: f_a is a kinetic term which characterizes the rate at which atoms from the vapor reach the nucleus. The Boltzmann factor is proportional to the concentration of critical nuclei, and z is the Zeldovich factor which is essentially a normalization constant. The Boltzmann factor can be written in terms of an energy barrier for nucleation E_b and the degree of supercooling δT as $e^{-E_b/(\delta T^2)}$, where $E_b(\sigma, \rho_l, T_0)$ depends on the liquid vapor surface tension σ, the liquid density ρ_l and the coexistence temperature T_0.

The theory of heterogeneous nucleation on a solid surface is similar to homogeneous nucleation. In the case of heterogeneous nucleation, the nuclei are spherical caps that meet the solid surface at a contact angle θ_c rather than spheres. The barrier to nucleation as well as the Zeldovich factor depend on θ_c. For the case of ^4He on Cs, θ_c is about 30° at low temperatures, and E_a is about 1% of the bulk vapor homogeneous value. Since the degree of supercooling δT enters quadratically in the nucleation rate formula, the amount of supercooling expected in a cesiated cell is approximately 1/10 of the homogeneous nucleation value. Detailed calculations show that near T_0=1.7K one should expect supercoolings of about 0.05K for nucleation of liquid ^{4}He on Cs.

An important feature of the heterogeneous nucleation rate formulas is that when the contact angle is zero, i.e. when the liquid completely wets the substrate, there is no barrier to nucleation. On a wettable substrate, a thin film of liquid forms even at low pressures. The film thickness grows continuously and eventually diverges as saturation is approached. In order to observe supercooling, it is crucial to eliminate all wettable surfaces in contact with the vapor. In the case of ^{4}He, this requires preparing a cell which contains the helium, and with all exposed surfaces covered with cesium. In an attempt to accomplish this, we used glass cells loaded with a small amount of liquid cesium and an appropriate pressure of ^{4}He at room temperature and formed a molten glass seal using the stem of the cell. The cells were equipped with a resistive heater and a thermometer which was bonded to the outside of the cell. Although cesium does not wet glass, the cesium could be distributed over all visible portions of the glass ampule by melting the cesium, shaking the cell and trapping the molten metal in a metastable configuration, which then solidified.

The cells were attached to a cryostat through a weak thermal link. Nucleation was observed by monitoring the time dependence of the temperature of the cell. Coexistence of liquid and vapor results in a change in slope of the curve, while supercooling gives rise to a discontinuous undershoot in the temperature as shown in Fig 1. The experimental data in Fig. 2 shows no

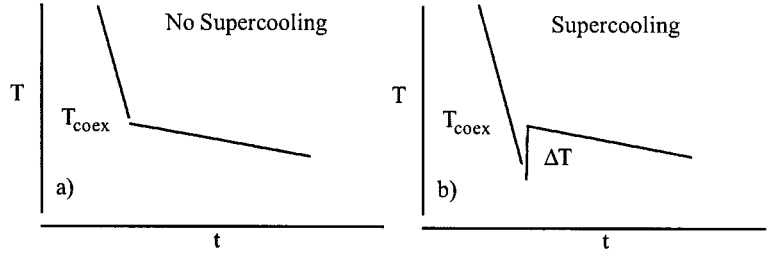

Fig. 1. Schematic plot of the cell temperature T as a function of time t. a) If nucleation of liquid occurs at the coexistence temperature, there is a kink in the cooling curve, but no undershoot. b) If nucleation occurs below the coexistence temperature, latent heat liberation rapidly drives the temperature back to the coexistence curve, resulting in an undershoot in the temperature.

indication of an overshoot, which suggests that nucleation took place on an uncesiated defect in the coating. Possible effects of surface roughness and results using different liquid-vapor systems will be discussed in a forthcoming publication.

3. FOG FORMATION DURING EVAPORATION

A liquid coexisting with its vapor in a container with a temperature gradient will transfer heat and mass from the hot end to the cold end via evaporation and condensation. A careful analysis of this nonequilibrium process leads to some surprising and non-intuitive predictions: very large temperature jumps develop near the liquid-vapor interfaces, and it is possible for the temperature in the vapor to be inverted so that the temperature near the hot evaporating fluid is actually colder than it is near the cold end where the fluid condenses. These non-monotonic temperature profiles are a clear prediction of non equilibrium thermodynamics[7,8] and kinetic theory[9] but have never been experimentally observed.

Motivated by initial observations in a previous experiment, we constructed a test cell to study strong evaporation. The cell consisted of a glass tube with copper end plates, as shown in Fig. 3. The top end plate, which has a fill line to add helium gas, was attached to a pumped ^{4}He refrigerator. The cell was in vacuum in an optical cryostat so we could visually observe its behavior. We found that fog was remarkably easy to make[6]. One of the most controllable ways of producing it involved adding gas at approximately 1 atmosphere of pressure through the fill line while maintaining the

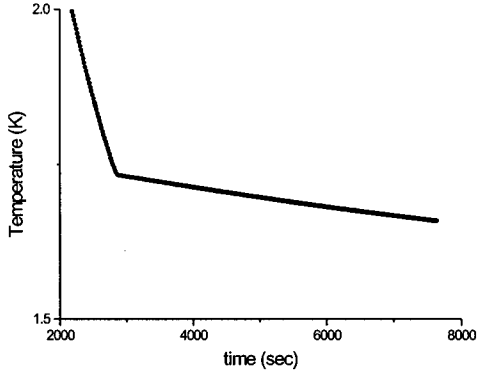

Fig. 2. Temperature of cesiated cell as a function of time. Cell is weakly coupled to a reservoir at T=1.6K. The change in slope of the cooling curve near T=1.7K is due to liberation of latent heat of condensation. Note that there is no thermal undershoot, indicating that there is no supercooling of the vapor.

top (cold) end plate at around 2K. Liquid would form on the top plate and drain down to the bottom plate, which was thermally floating and which stabilized around 3K. Shortly after the valve to the fill line was closed, fog would be seen starting near the liquid surface and propagating up the cell. The initial stage of the fog generation is too fast to follow with a standard video camera. The picture on the right of Figure 3 was taken approximately 1 second after the fog began to form; it will eventually fill 3/4 of the cell.

Model calculations based on a kinetic theory treatment of evaporation suggest the following interpretation of our observations. Although the difference in vapor pressure at the two ends of the cell is about 1/4 of an atmosphere, the pressure in the interior of the cell is almost uniform. This implies that there are large jumps in the pressure near both liquid interfaces which drive the mass flux. The temperature of the gas also has large jumps that occur in a region within a few mean free paths of the interface. The size of these jumps is proportional to the evaporative flux. For sufficiently strong evaporation, the gas in the interior can be driven into a supercooled metastable state. When the supercooling becomes sufficiently strong, the vapor undergoes homogeneous nucleation and forms a dense fog, which we see in our cell. More detailed calculations confirm that the most strongly supercooled region is expected at the interface near the hot fluid. Further

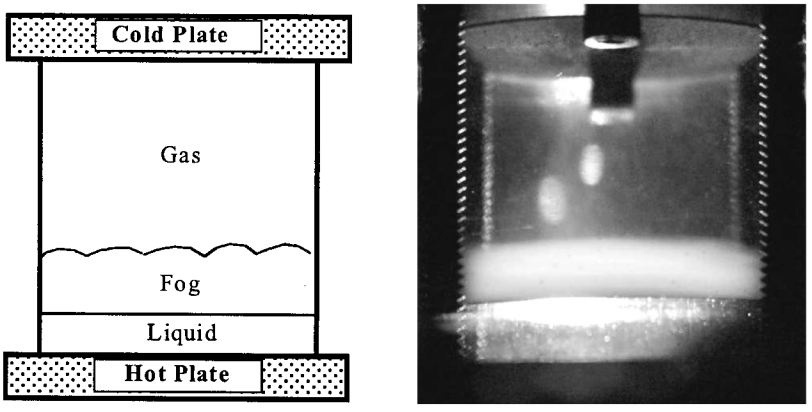

Fig. 3. Glass tube cell 3 cm dia. with copper end plates. T=3K at hot end, T=1.5K at cold end. Left: Schematic diagram of cell showing helium liquid level with fog which forms above it. Right: Picture of cell showing fog above liquid.

experiments to investigate the systematics of this phenomenon are planned for the future.

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