Recent High Resolution Measurements of the Specific Heat and Isothermal Compressibility Near the ^{3}He Liquid-Gas Critical Point

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Measurements of the specific heat at constant volume and isothermal compressibility have been made along a near critical isochore in the liquid–gas critical region of ^{3}He. The critical density was determined to within 0.1% from pressure-density measurements along a near critical isotherm in the single phase region. The specific heat was measured in the gravity affected region in the reduced temperature range $|T/T_c - 1| \leq 3 \times 10^{-4}$ using a slow cooling drift technique. The present specific heat data will be compared to previous measurements. A new electrostriction technique was developed to measure the isothermal compressibility along isochores and isotherms near the critical point. Initial measurements that validate this new technique will also be presented.

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1. INTRODUCTION

The unusual thermodynamic properties near a liquid-gas critical point have intrigued scientists for over a century. During the 1960's and 70's significant advances were made in explaining this unusual behavior. In particular, the introduction of the homogeneous postulate for the singular part of thermodynamic quantities[1] led to a set of scaling relations between the critical exponents that describe the power law divergences. With this full set of thermodynamic scaling relations one can determine all the thermodynamic exponents in terms of two of them. The application of Renormalization Group (RG) theory to the study of critical points[2] has provided a more fundamental justification for the scaling relations. This RG calculational tool has produced highly accurate values for the critical exponents for a wide range of universality classes.[3]

Many ground-based (1g) experimental studies were previously performed to test the critical exponents and scaling predictions near a liquid-gas critical point. Unfortunately, the strong divergence of the isothermal compressibility near the transition leads to a gravity induced density gradient in an experimental cell of finite height. This density gradient limits the experimentally accessible range within the asymptotic region near the critical point. This situation has hindered efforts to provide a rigorous test of the RG scaling predictions. In an attempt to rectify this situation, a ^{3}He liquid-gas critical point experiment was proposed to be performed in a microgravity environment. This experiment called MISTE (MIcrogravity Scaling Theory Experiment) was accepted by the National Aeronautics and Space Administration and is now in a space–flight definition program. The objective of this experiment is to accurately determine several static critical exponents (α, γ and δ) from measurements taken in the same experimental cell. A precise determination of the ^{3}He critical point parameters ($T_c \approx 3.31K, \rho_c \approx 0.041g/cm^3, P_c \approx 0.117MPa$) are crucial to the success of this experiment. Thermodynamic measurements along several near critical isochores are planned for the space–flight experiment in order to accurately determine the critical isochore and isotherm. The measured critical exponents will be compared to the theoretically predicted exponent values and the expected scaling relations.

2. THEORETICAL CONSIDERATIONS

The critical point is a unique thermodynamic state (T_c, ρ_c, P_c) where the liquid and gas densities become equal. Extensive theoretical and experimental studies have been made on the behavior of various thermodynamic quantities as the critical point is approached along the critical isochore, ρ_c, and critical isotherm, T_c. This experiment is designed to perform precision measurements of the specific heat at constant volume, C_V, and the isothermal compressibility, κ_T. The power law divergence of these quantities along the critical isochore will provide accurate values of the critical exponents α and γ. Measurements of the compressibility along the critical isotherm are also planned to determine the critical exponent δ.

In order to determine the critical exponents α and γ to 1% in microgravity it is necessary to fill the sample cell to a density very near the critical value. For the case of C_V and κ_T, an analysis of their sensitivity to density variations in the asymptotic region[4] shows that a reduced density of

$\leq 0.1\%$ is needed to achieve the required accuracy. For the current 0.05 cm high sample cell filled to the critical density, the effect of gravity was calculated to produce a 1% density gradient at a reduced temperature of $t \equiv T/T_c - 1 = 2 \times 10^{-4}$ in $1g$, 5×10^{-8} in $10^{-4}g$ and 1×10^{-9} in $10^{-6}g$. These calculations clearly demonstrate the need for a low gravity environment to perform accurate thermodynamic measurements in the asymptotic region near the ^{3}He critical point.

3. GROUND–BASED EXPERIMENT

The objective of the present flight definition stage is to demonstrate experimental measurement techniques on the ground that have the precision needed to achieve the proposed goals of the microgravity experiment. The following sections describe recent specific heat and compressibility measurements near the critical point of ^{3}He.

3.1. Experimental Cell

High purity ^{3}He fluid is contained in a cylindrical sample cell of 0.05 cm high by 11.2 cm in diameter. A low temperature valve is attached directly on the cell. The temperature of the OFHC copper walls is measured with a high resolution magnetic susceptibility thermometer.[5] A capacitor with a 60 μm gap located in the middle of the fluid layer serves as a density sensor. The sample density is obtained from the measured capacitance using the Clausius–Mossotti equation. A Straty–Adams type gauge, also attached to the cell, allows for a measurement of the pressure in the fluid sample. An advantage of this cell design is the ability to perform continuous in–situ PVT measurements during the experiment.

In the present ground–based studies, a near critical density is experimentally obtained by measuring the pressure–density curve for an isotherm slightly above the critical temperature. This is achieved by initially over–filling the cell. Then the sample is slowly leaked from the cell while its temperature is regulated. Figure 1a is a pressure–density curve obtained for an isotherm at a reduced temperature $t = 6 \times 10^{-4}$ in the single phase region. The derivative of this curve, shown as an insert in Fig. 1a, is obtained using a tension spline fit. This derivative is associated with the symmetrized isothermal compressibility, $\chi_T = \rho^2 \kappa_T = \rho(\partial\rho/\partial P)_T$. The maximum of the χ_T versus ρ curve occurs at the critical density for isotherms close to the critical point. The density, corresponding to the maximum, can easily be determined to within 0.1%. Once the capacitance associated with the maximum is determined, the experimental cell is refilled and sealed at this capacitance value.

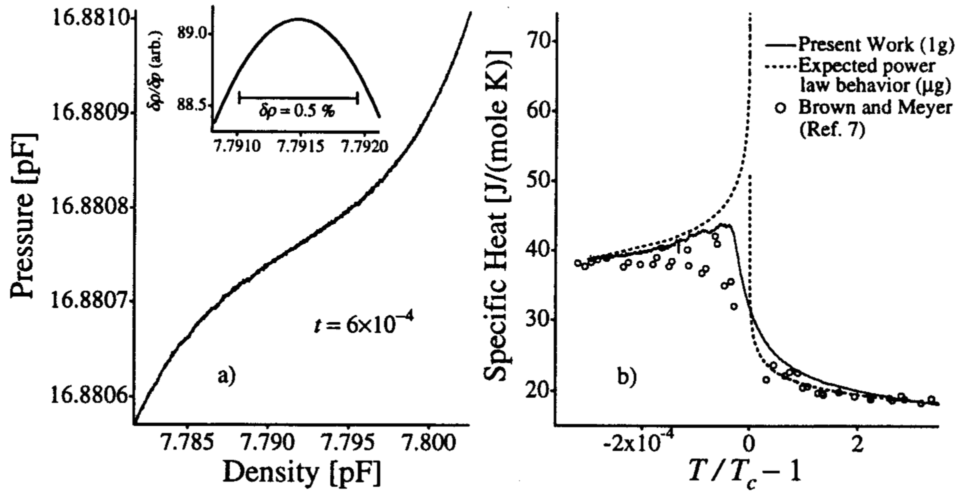

Fig. 1. a) Experimental determination of the critical density from the inflection point of a $P-\rho$ curve at $t = 6 \times 10^{-4}$. Insert shows the derivative of the $P - \rho$ curve. b) Cooling drift measurement of the specific heat at constant volume along an isochore within 0.1% of the critical isochore.

3.2. Specific Heat

One of the most important thermodynamic properties for testing theories near a liquid-gas critical point is the specific heat at constant volume. A goal of this experiment is to develop an apparatus that will be capable of measuring C_V to a reduced temperature of 10^{-7} with an accuracy of 1%. In the present experimental study, the sample stage is surrounded by a radiation shield whose temperature is controlled slightly below the critical temperature. The sample is initially regulated at a reduced temperature of 3×10^{-4} above the transition. Then the sample is slowly cooled to the shield temperature. Figure 1b shows recent heat capacity data along an isochore within 0.1% of the critical isochore. These data were taken with an average cooling drift rate of 3×10^{-4} K/hr. For this drift rate the density gradient due to the "piston effect",[6] which is in addition to the gravity stratification, is estimated to be $\leq 0.1\%$ in the sample in the single phase region. Also shown is the power law divergence expected in a microgravity environment as well as earlier experimental data.[7] The present work has significantly less scatter compared to the previous measurements due to the improved high resolution temperature control. These data also clearly show the rounding effect of the earth's gravitational field. The 1% resolution in C_V required for the flight experiment has been achieved.

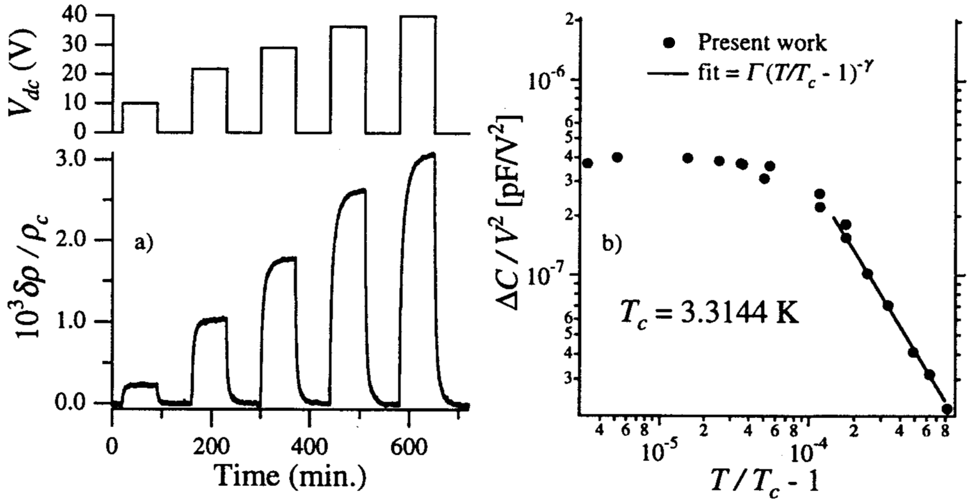

Fig. 2. a) Density response to a DC bias voltage at $t = 3.6 \times 10^{-5}$. b) Effective isothermal compressibility measurements along a near critical isochore.

3.3. Isothermal Compressibility

The isothermal compressibility, κ_T, diverges more strongly than the specific heat as the critical point is approached. An electrostrictive technique has been developed to measure the compressibility. This technique takes advantage of the fact that an electric field gradient can produce a pressure change within a dielectric fluid.[8] In this experiment, an electric field is applied to the same parallel plate capacitor used for the local density measurement. In this case the pressure change associated with the application of a DC voltage, V, between capacitor plates, induces a density change. This density change can be detected by a capacitance change ΔC. The effective isothermal compressibility is obtained from the ratio of the density to pressure change which is proportional to $\Delta C/V^2$.

An example of the electrostriction effect near the critical point of ^{3}He is shown in Fig. 2a. These data were obtained at $t = 1.2 \times 10^{-4}$. Density changes are shown for a DC bias ranging from 10 – 40 volts. The effective κ_T is obtained by plotting $\Delta C/V^2$ as a function of V^2 and extrapolating the data to zero voltage. Figure 2b shows a log-log plot of the effective isothermal compressibility versus reduced temperature. The rounding at $t < 10^{-4}$ is possibly caused by a slight tilt of the cell that can lead to an increased density deviation from ρ_c at the capacitor location as T_c is approached. This rounding effect near the transition, associated with gravity and density shifts, makes it difficult to accurately determine the critical temperature. The critical temperature for this preliminary analysis was chosen to be consistent with the value obtained from the specific heat measurements. This choice of T_c yields $\gamma = 1.25$ which is close to the theoretical value.

4. CONCLUSIONS

High resolution measurements of the specific heat, C_V, and isothermal compressibility, κ_T, were performed in ^{3}He along an isochore determined to within 0.1% of the critical isochore using in-situ pressure, density and temperature sensors. The specific heat, measured using a cooling drift technique, clearly shows the gravity rounding effect near the transition. Even though the ground-based cell has a small fluid heat capacity ($\approx$ 2 J/K) due to the small vertical height, it is still capable of demonstrating the required sensitivity in microgravity. The space–flight cell is planned to have a significantly larger volume (designed not to increase the relaxation time) that will lead to enhanced temperature stability and resolution. Preliminary isothermal compressibility data near the critical point were also determined for the first time using an electrostrictive technique. Improvements in the sensitivity of this technique are now in progress that will permit measurements closer to the critical point using a lower excitation voltage.

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