ISOCHORIC SPECIFIC HEAT OF SULPHUR HEXAFLUORIDE AT THE CRITICAL POINT
A SPACELAB EXPERIMENT FOR THE GERMAN D1-MISSION IN 1985

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ABSTRACT

The mechanical and functional concept of a space qualified scanning ratio calorimeter is presented for measuring the isochoric specific heat of SF₆ near the critical point. The micro-gravity relevance of this experiment is discussed and underlined by laboratory measurements, the hydrostatic height of the specimen being varied. In 1-g reference experiments the critical exponent and parameters for cᵥ have been determined. Critical relaxation effects are taken into account by a suitable functional time profile for the HPT spacelab experiment.

Keywords: Critical phenomena, micro-gravity, critical exponents, isochoric specific heat, scanning ratio calorimeter, Spacelab, D1-mission

1. INTRODUCTION

Studies of critical phenomena have grown to a considerable field in theoretical physics. In the recent years a global theory, the "renormalization group" has focused great expectations of scientists, for it predicts macroscopic thermodynamic properties around critical points without considering the molecular structure of the system to be investigated. This theory is applicable to physically different kinds of critical phenomena such as magnetisation of a solid body near the Curie Point as well as phase separations of binary mixtures or phase changes of pure liquids near critical temperature. The universality of this model has gained importance since up to the present day it has not been possible in most cases to describe the macroscopic behaviour including phase transitions out of molecular interaction using methods of statistical physics. However, the range in which the renormalization group holds is confined to a small region around critical points. This region is characterized such that macroscopic properties can be expressed in terms of simple power laws. For example the specific heat at constant volume cᵥ becomes

\[ \frac{cᵥ}{R} = A \left( \frac{T - T_c}{T_c} \right)^{\alpha} + B \]  

(1)

where R denotes the gas constant, Tc the critical temperature and A, \( \alpha \) and B parameters for which theoretical calculation yield numerical values.

Terrestrial investigations have been performed that show a reasonably good agreement of the experimentally determined parameters in Eq. (1) with the corresponding theoretical results. Unfortunately, like in many other measurements at fluid critical states, these results suffer from gravitational influences that enhance their dominating significance just at the critical point, the target of all experimental efforts.

The D1-Mission in 1985 will open an opportunity to perform longterm cᵥ-measurements under micro-gravity (u-g) conditions. It will supply data free from systematic errors induced by gravitational effects. For this purpose a space qualified calorimeter has been developed which is housed in a high precision thermostat ("HPT") and integrated in the MEDEA-rack of the spacelab.

2. EXPERIMENTAL PROBLEMS AND MICRO-GRAVITY RELEVANCE

The experimental determination of the parameters A, \( \alpha \) and B in the equation (1) for the isochoric specific heat cᵥ is inhibited by the fact that the power laws describe the...
behaviour of state only within a small temperature range 
\( /T / < 2 \times 10^{-3} \) around the critical point where 
\( T = (T - T_C)/T_C \) (LANGE, 1983). Therefore, experimentation 
ear critical state requires extraordinary efforts in 
threshold stabilization, electronic measuring and control and 
can be performed only in samples of small dimensions. 
Fluid at critical temperature is very sensitive to external 
fields like temperature gradients and gravity forces. The 
disturbing influence of gravity, however, can only be 
suppressed in \( \mu \)-g environment since in earthbound 
experiments the finite hydrostatic height in the test 
substance cannot be sufficiently reduced to layer 
thicknesses of order of the largest density fluctuations to 
achieve critical state throughout the complete fluid 
volume. Therefore, \( 1-g \) results are affected by an 
averaging error which can merely be estimated in data 
evaluations (Hohenberg and Barmatz, 1972). The closer to 
the critical point refined experimentation techniques 
enable measurements, the more influences of 
gravitational body forces gain dominance.

Since near the critical point C.P. the isotherms in a 
pressure-density diagram are almost horizontal (Fig. 1)

![Figure 1: Pressure-density diagram of a pure fluid near critical state](image)

already a small hydrostatic pressure difference

\[
\Delta p = \rho g H
\]

(2)
in the specimen of height \( H \) is sufficient to produce 
density profiles. In addition the isothermal compressibility

\[
K_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial p} \right)_T
\]

(3)
approaches infinity ( \( \partial \rho / \partial p = 0 \) ) with the result that 
small pressure changes cause considerable density 

\[
(\partial \rho / \partial H)_T = -\rho^2 K_T g (a/g)
\]

(4)

where \( h \) is the hydrostatic length coordinate and a 
characterizes the actual gravitational field imposed on 
the fluid. These layers of different density are measurable 
or can be computed applying an equation of state. Fig. 2 
and 3 show such density profiles under variation of 
temperature near its critical value. Consequently 
measurements of caloric properties like \( c_v \) represent 
integral values over all states existing in a fluid volume 
of finite dimensions. Gravity induced density gradients 
falsify measurements because these caloric properties are 
no more significant for a thermodynamic point of state 
but represent a somehow integral average.

![Figure 2: Measured density sedimentation of \( N_2O \) near critical state (STRAUB, 1977)](image)

![Figure 3: Computed density profiles of \( SF_6 \) near critical state (LANGE, 1983)](image)

3. EXPERIMENTAL APPARATUS

Fig. 4 and 5 show the mechanical and the corresponding 
fractional set up of the "HPT" scanning ratio calorimeter 
which in principle is similar to the ones used by
BUCKINGHAM (1973) and WÜRZ (1980). The calorimeter consists of four cylindrical vessels elastically suspended in each other: the central stage 0 containing the test substance, reference stage 1 constantly heated up, stage 2 adiabatically shielding the center from the thermal environment and the vacuum vessel 3 kept at constant temperature. While turning the handle of the locking mechanism a bolt is moved along the center axis and pushes stage 1 and 2 towards 3 till they rest in guiding edges in order to prevent the suspension from being overstressed by shaking and accelerations during the shuttle launch. Additionally locking shortens cooling the calorimeter since heat from the center (except stage 0) transfers by conduction across the touching vessel surfaces.

The structure of the test cell (stage 0) resembles the one used by BUCKINGHAM (1973). The design requirements to be fulfilled are: low heat capacity of the stainless steel container compared to the test substance, a sufficient mechanical resistance against an inner pressure of about 40 bar, a small hydrostatic height for preceding 1-g reference tests. Fig. 6 shows cross sections of the coin-shaped cell.

Due to the extremely reduced wall thickness a machined spiral supports the upper and the lower transverse face soldered together. Furthermore, by this means the thermal diffusion lengths are minimized and thermal equilibrium is eased.

In operation the calorimeter is evacuated to pressures of $10^{-5}$ mbar gained by an ion getter pump to reduce heat
leaks between the nickel plated vessels which are all electrically heated. Thermistors are used to measure temperature differences as well as to determine the overall process temperature $T_1-T_c$ relatively to critical temperature $T_c$.

A constant current source supplies stage 1 with adjustable power and linearly raises the temperature $T_1$. The two control loops 0 and 1 balance the temperature differences between the stages such that $T_0-T_1=0$ and $T_2-T_1=0$, respectively. Both control systems are essentially identical. They consist of an AC-bridge B to convert temperature differences between two adjacent stages into voltage signals, a lock-in amplifier LA including an oscillator and a variable current source $Q$. According to a PID-algorithm $Q$ is regulated by a central processor unit that also controls house keeping and frontpanel display. In the open loop 2 bridge B2 measures the process temperature with respect to a constant resistor $R$ chosen such that the output signal is proportional to $T_1-T_c$ where $T_c=45.58^\circ C$ is the critical temperature of $SF_6$.

Data relevant for scientific evaluation is encoded in a 12 bit format, other parameters in 8-bit words. With a frequency of 128 byte per 0.6 sec data is transferred to an external data handling module for high rate multiplexing and is finally sent to ground for online monitoring in Oberpfaffenhofen nearby Munich. In addition a computer link between the German ground station and the laboratory of the authors at the Technical University in Munich permits quasi online data evaluation which provides a means to advise the astronauts while they manually operate the apparatus in case of disturbance or mission termination.

4. METHOD OF MEASUREMENT

The method of measurement is, very simplified, based on the fact that controllable heating the specimen (stage 0) is gained by force such that the temperature-time gradient stays constant. An energy balance applied on stage 0 and 1 yields a system of equations

\[
C_0 \left( \frac{dT_0}{dt} \right) = P_0 + \dot{Q}_{01} + P_{T,0} \tag{5}
\]
\[
C_1 \left( \frac{dT_1}{dt} \right) = P_1 + \dot{Q}_{01} + \dot{Q}_{12} + P_{T,1} \tag{6}
\]

where $C_0 \left( \frac{dT_0}{dt} \right)$ denotes the capacity of stage 0 times temperature ramp, $P_0$ the electrical heating power, $\dot{Q}_{01}$ the heat flux from 0 to 1 and $P_{T,0}$ the electrical power dissipated in the thermistor.

In the following outline the correction terms $\dot{Q}_{ij}$ and $P_{T,i}$ are neglected, i.e. it is assumed that there is no thermal coupling between the calorimeter vessels and ideal, nondissipative thermistors are used.

As stage 1 is heated with constant power $P_1$ its temperature rises linearly over time, the heat capacity $C_1$ assumed constant. Both control systems regulating cell 0 and stage 2 govern the temperature $T_0$ and $T_2$ according the profile $T_1(t)$ such that

\[
\frac{dT_0}{dt} = \frac{dT_1}{dt} = \frac{dT_2}{dt}. \tag{7}
\]

This control condition combines the energy balance (5 and 6) to an explicit function of the temperature depending heat capacity of stage 0 to

\[
C_0(T) = C_1 \frac{P_0(T)}{P_1} \tag{8}
\]

with

\[
C_0(T) = C_{0,\text{container}} + m_{f1} c_{v,f1}(T) \tag{9}
\]

where $c_{v,fi}(T)$ is the specific heat of the test substance to be measured versus temperature.

5. EXPERIMENTAL TIME PROFILE

In order to achieve negligible disturbances of the thermodynamic equilibrium in the fluid volume the realization of heating rates as small as possible is essential. Only if this is guaranteed the continuous method of measurement can be assumed quasi-stationary. For earthbound experiments temperature gradients of $\frac{dT}{dt}=10^{-6}$ K/sec still lead to the establishment of equilibrium around the critical point except within a temperature span of $\tau < 3.5 \times 10^{-5}$ mK (LANGE, 1983). Owing to the reduced thermal diffusivity, finite spatial temperature gradients remain. However, these values of experience are superimposed by density relaxation effects which do not exist in $\mu$-g environment. Thus reliable reference data of thermal relaxation under reduced gravity is not available yet. This information is expected from the data evaluation of the three different temperature ramps of the HPT-experiment (fig. 7).

The sample is heated up with three gradients that vary in orders of ten. $\mu$-g reference data of the same profile will be acquired immediately after the D1-mission using the same apparatus. A comparison will reveal valuable information about pure, isolated thermal diffusion in a fluid at critical state.
fig. 7: Temperature-time profile of the HPT spacelab calorimeter with three different temperature ramps (total duration of the experiment: 108 hours).

6. PRELIMINARY RESULTS

The μ-g relevance of the HPT-phase change experiment is well documented in fig. 8.

Fig. 8: Heating power $P_0$ for different hydrostatic heights in the fluid cell.

For constant power input $P_1$ in stage 1 the controlled heating power $P_0$ is proportional to the specific heat $c_V(T)$ (Eq. 8 and 9). For an inclination angle $\Phi = 0^\circ$ (minimum, 1mm, of the hydrostatic height, fig.6) the characteristic peak at $T_1-T_{cr}=0$ reaches its maximum and diminishes as the angle grows to $-5^\circ$ or to $+5^\circ$, respectively. For $45^\circ$ or ultimately at $90^\circ$ (30 mm) the enhancement vanishes completely. This data is obtained from a laboratory test of the HPT-engineering model.

In previous experiments $c_V$-measurements have been performed using a laboratory version of a scanning ratio calorimeter (LANGE, 1983). As can be seen in fig. 9 the behaviour of the specific heat $c_V$ clearly exhibits a singularity at the critical temperature $45.58^\circ$C ($SF_6$).

Fig. 9: The isochoric specific heat $c_V$ of $SF_6$ near the critical temperature $T_{cr}=45.58^\circ$C.

Data fitting yields parameter values for the power equation (1)

$$c_V/R = A \left| \frac{T-T_{cr}}{T_{cr}} \right| ^{-\alpha} + B \quad (10)$$

with $B = 2.54$, $\alpha = 0.0977$ and $A = 10.07$ in the one-phase region and $A' = 18.41$ in the two-phase region. These parameters are in accord with theoretically derived values (CAMP et al., 1978; BAKER et al. 1976).

The critical enhancement of $c_V$ measured as $T$ approaches its critical value is well represented by equation 10 as exhibited in the double logarithmic plot of fig 10.

Fig. 10: (1): curves expected for micro-gravity, the curves are extrapolated after data fitting according Eq. 10 for $3.5*10^{-5} < \tau / \tau < 10^{-2}$

(2): measured curves of $c_V$ for 1-g and 1 mm cell height

A constant exponent $\alpha$ leads to a linear $c_V$-behaviour in fig. 10 which is not the case for $\tau / \tau \leq 3.5*10^{-5}$ according to the measured values. Mixed effects of density and thermal relaxation cause this deviation.
7. CONCLUSIONS

The German D1-Mission will provide adequate experimental conditions in micro-gravity environment for longterm $c_v$ measurements. The HPT-calorimeter mechanically and functionally described in this paper is expected to furnish valuable data of the isochoric specific heat $c_v$ that is free from gravitational influences. The experimental results will serve as important references for further theoretical investigations. Furthermore terrestrial experiments still have no access to the immediate vicinity around the critical point not even with highly sophisticated electronic control systems. It will be the aim of HPT $μ$-g experiment program to intrude this region and supply data without the disturbing effects of density sedimentation.

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9. REFERENCES


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