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# THE CRITICAL "HUMP" OF $C_V$ UNDER MICROGRAVITY RESULTS FROM THE D1-SPACELAB EXPERIMENT "WÄRMEKAPAZITÄT"

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## ABSTRACT

**The isochoric specific heat $c_v$ was measured at the critical point of Sulphur Hexafluoride under microgravity (µg) conditions. In the high precision thermostat HPT four ramps (3.6, 10, 20, 100 mK/h) were realized within $-100mK < (T_1-T_c) < +100mK$ around the critical temperature $T_c$. Cell capacity $C_0$, which is proportional to $c_v$ did not show a critical peak, but ran even lower than under 1g conditions. Non-equilibrium effects are discussed, comparisons to 1g reference results and former µg-TEXUS-experiments are drawn.**

**Keywords: Critical phenomena, microgravity, specific heat, spacelab, D1-Mission**

## 1. INTRODUCTION

Lots of efforts have been and are still made to reduce or exploit gravitational effects upon experiments near critical points of fluids or to correct the results for the inevitable and "commonly noticeable" presence of gravity on earth. Terrestrial experiments suffer from an inhomogeneous distribution of the local properties, which, in many cases, can hardly be resolved. Caloric measurements requiring a mimimum bulk mass "somehow" average over these local distributions and yield values, e.g. for the specific heat $c_v$, that are not representative for a point of state, but rather for a range of fluid states confined in the test cell over the hydrostatic height.

It is then difficult to relate the results to theoretical calculations or, even more so, to seriously prove the accordance or deviation of the experiment compared to theory. The critical exponent $\alpha$, for instance, characterizing the singularity of the specific heat $c_v$ ranges to $0.110 \pm 0.008$ according to renormalization group calculations /1/, whereas scanning measurements e.g. yield $\alpha = 0.089 \pm 0.010$ /2/ for $SF_6$ and $\alpha = 0.1084$ for $CO_2$ /3/. Apparently, pure fluids seem to behave, at the gas liquid critical point, as the theory of universality predicts. However, 1g measurements of fluid exclude the immediate vicinity of the critical point, even in a flat cell of only 1 mm hydrostatic height, since the diverging compressibility generates the well-known density stratification. Fitting experimental $c_v$ data along the critical isochore is thus restricted only to 2 decades of $t = (T-T_c)/T_c$ above and below the critical point close to $|t| = 7 \cdot 10^{-5}$.

The critical peak itself, the actual task of measurement efforts, seems to evade experimental access. Therefore, experiments in microgravity (µg)-environment have been suggested, along with quantitative estimations. These estimations of possible thermophysical properties to be investigated under µg were published, e.g. /4/.

The D1-Mission in October 1985 opened the opportunity to perform long-term $c_v$ measurements for the first time under µg-conditions. Due to limited experiment time, we focussed on a narrow temperature window of $-100\ mK < (T-T_c) < +100\ mK$, which is affected by gravity on earth.

These temperature bounds border to regions for which reliable results, not affected by gravity, are available /5/. With the recorded µg behavior it was intended to fill the gap in the existing data set, in order to fit the asymptotic model

$$c_v/R = A/\left|\frac{T-T_c}{T_c}\right|^{-\alpha} + B \qquad (1)$$

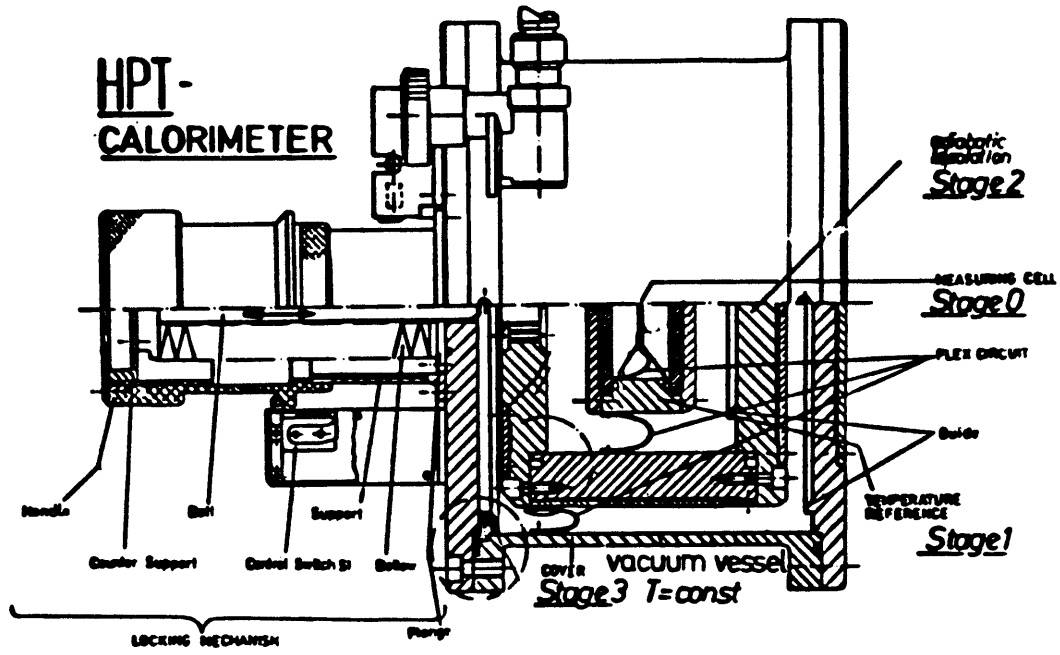


Fig. 1 Mechanical set-up of the four-stage HPT Calorimeter

closer to the critical temperature.

The results in this work are assumed to be rather independent of gravitational fields, since the acceleration jitter showed an average level of less than $5 \cdot 10^{-5}$ g with occasional peaks during manouvering and sled runs. In order to quantify relaxational effects in the absence of gravity, now being of great influence upon phase transition, four temperature-time ramps ($dT/dt$=3.6, 10, 20 and 100 mK/h) could be accomplished within 4 days experimental time.

The sections below briefly sketch the experimental apparatus and outline the method of measurement. The documentation of µg data displays a comparison with the corresponding 1g measurements. However, the results are still to be considered preliminary, since the data evaluation has not been completed yet. In the discussion the discrepancy is pointed out between the µg $c_v$ behavior as measured, and as expected.

## 2. EXPERIMENTAL APPARATUS AND MEASUREMENT METHOD

An assembly drawing of the HPT scanning ratio calorimeter used is shown in Fig 1. It is described in greater detail in Ref /6/ and resembles the one developed by Buckingham et al. /7/ for $c_v$-measurements of $CO_2$ and the apparatus used by Würz /8/ to measure $c_p$ of binary liquid mixtures. A description of the preceeding laboratory prototype version is given in /5/. This consisted of voluminous commercial analog control devices, like Princeton 1281 lock-in amplifiers and HP data recording systems. A further calorimeter of the scanning type is presented in Ref /9/, where also different modes for cooling and heating are discussed. A recent high precision calorimeter was developed by Edwards /3/ who also outlines the electronic circuit to compensate for non-linear bridge effects in the thermometry.

The special constraints imposed on operating an orbital calorimeter were basically determined by limited space (19" rack) reduced electrical energy supply and little crew attendance, as well as mechanical resistance to sustain shaking and acceleration during lauch and landing. Fig. 1 shows four concentric cylindrical vessels (stage 0-3). The coin-shaped test cell (stage 0), reference (stage 1) and the adiabatic shield (stage 2) are heated through the critical temperature of $SF_6$ (45.583°C) applying constant power to stage 1. The electronic control system minimizes the temperature difference $T_0$-$T_1$ by supplying electrical power to stage 2 and 0. The energy fluxes of stage 0 and 1 can be modelled by a system of diffential equation

$$C_0 (dT_0/dt) = P_0 + P_{T,0} + \dot{Q}_{01} \quad (2)$$

$$C_1 (dT_1/dt) = P_1 + P_{T,1} - \dot{Q}_{01} + \dot{Q}_{12} \quad (3)$$

where $C_0 \cdot (dT_0/dt)$ is the capacity of stage 0 times the

temperature ratio $P_0$ denotes the servo power, $\dot{Q}_{01}$ the heat leakage from 0 to 1 and $P_{T,0}$ the thermistor dissipation. The interstage heat flux $\dot{Q}_{ij}$ is very small, because of high vacuum insulation and excellent temperature control and can be measured or determined from data of different heating ramps by means of extrapolation to a ramp rate $dT/dt = 0$. Both techniques are discussed in Ref /10/ and account for non-linear effects of the thermistor bridges.

Capacity $C_0$ of the specimen consists of the constant background part $C_{container}$ of the cell and the temperature dependent term $m_{fluid} \cdot c_{v,fluid}$, the former will be measured after completing the 1g reference tests by cutting the container wall and running ramps with an empty cell.

However, the critical enhancement of $c_v$ is already visible in the behavior of $C_0$, and as Eq. (2) shows, in $P_0$, $P_{T,0}$ and $\dot{Q}_{01}$ being neglected. In the sections below we use either heating power $P_0$ or cell capacity $C_0$ for further discussion.

## 3. RESULTS

Three heating runs of different temperature time gradients within a temperature window of $-100mK \ll (T-T_c) \ll +100mK$ were planned. However, hardware problems with the evacuation system ventline and an anomal servo loop imbalance required the experiment time line to be completely rearranged. Ramp 3.6 mK/h was aborted and therefore an additional ramp 20 mh/h was conducted. Fig. 2 documents the originally planned and finally executed experimental time profile as a plot of the overall process temperature $T_1-T_2$ versus mission elapsed time MET. The bars "3.6, 100, 10, 20 mK/h" indicate the 4 ramps discussed below.

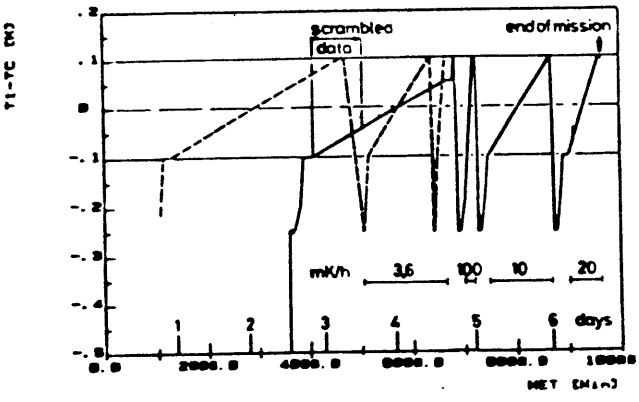


Fig. 2 Experimental time profile, dashed line: as planned, solid line as finally executed. MET: Mission ellapse time.

The original data recording density of 1264, 414, 180, 88 frames/mK in µg runs and 680, 579, 283, 85 frames/mK in 1g reference tests was condensed to uniformly 250 points per file associated with each ramp. Great efforts were made to minimize the noise to signal ratio, and to eliminate oscillations in the servo power to the cell, due to LSB-jitter in the AD and DA converters. In order not to smear out the weak $c_v$ peak, which was predicted to be extremely enhanced under µg-conditions, the PI control circuit servoed stage 0 emphasizing the P-characteristic. A LSB-change in the temperature sensor (1 LSB = 8µk) was thus detected with great amplification in measuring servo power $P_0$. Simple averaging did not yield satisfactory curves. To receive data free of an over-amplified and periodic digital jitter, a Fourier smoothing routine /11/ was implemented on the HP 1000 computer based on virtual memory and, thus, capable of smoothing "any" amount of data.

The four ramps recorded under µg-conditions were repeated on earth in the authors' laboratory. The apparatus was not changed, neither were the electronics (bridges) readjusted in order to ensure the same experimental condition, except gravity and long-term drifting.

Fig. 3 und 4 display the results for the capacity $C_0$ under µg- and 1g-conditions, respectively, as cubic spline representations. $C_0$ is proportional to the specific heat $c_v$. In addition to the curves for the four heating runs, a dotted line indicates the model behavior of equation (1), but recalculated for the complete cell capacity $C_0$. However, the computation contains an estimated value for the metal capacity of the cell shell. At least, it qualitatively reveals a theoretical guide line of how $C_0$ is "supposed" to be shaped. The maxima in the 1g lines may not be confused with the actual locations of the critical peaks relative to each other, since gravity corrections (/12/,/13/) have not yet been applied to the raw data.

## 4. DISCUSSION

The arrangement of the curves in Fig. 3 and 4 relatively to each other as well as the absolute ordinates may slightly change after the measurements with an empty cell have been completed. These ultimate calibrations will also reveal the true dependence of the interstage heat transfer on the process temperature $T_1-T_c$ and heating rate $dT/dt$ and will result in a slight rotation. Especially the profile for 3.6 mK/h still ranges high since, for

reduced heating rates, the relative share of the heat leakage $\dot{Q}_{12}$ at the servo power $P_0$, the measurement signal, increases. However, this will by no means explain the most obvious deviation of the µg curves from the 1g results: there is evidently no enhanced peak in any of the µg runs. Instead, $C_0$ reveals a surprisingly gentle rise and smooth drop and shapes rather a hump as in 1g measurements with an increased hydrostatic height /14/. This surprising result is discussed in the following:

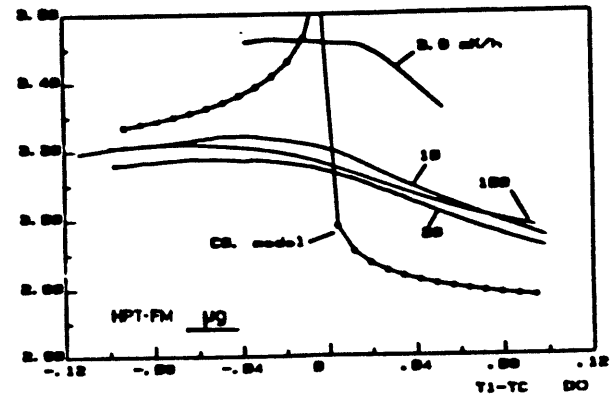


Fig. 3 Total cell capacity $C_0$, which is proportional to the specific heat $c_v$, under µg-conditions versus the overall process temperature $T_1$-$T_c$. The curves represent four heating rates. The dotted line indicates the theoretical behavior of $C_0$.

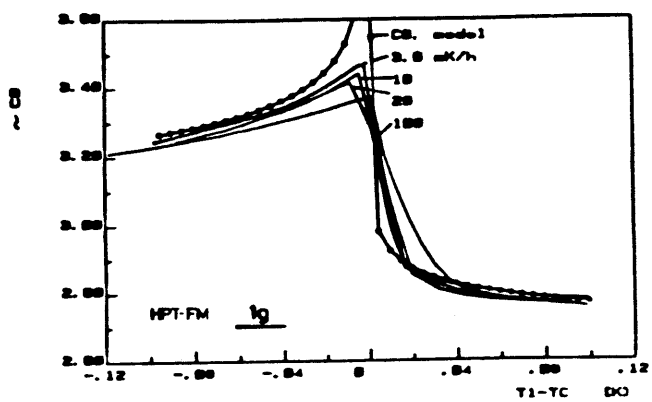


Fig. 4 Total cell capacity $C_0$ from 1g reference tests.

## 4.1 PERFORMANCE OF THE APPARATUS

After landing, the experiment racks were dismounted and the HPT-calorimeter was delivered as one unit to the authors' lab in the original flight configuration. The critical peak reappeared under 1g (Fig.4) and proved the apparatus to be in proper condition as it was before.

## 4.2 AVERAGE DENSITY

First apprehensions the cell filling may have lost its critical density seemed to be confirmed in the four sequential runs, since for four different heating rates this damped behavior of $c_v$ was reproduced. However, even phase transitions of first order indicate a drastic change of $c_v$ as repeatedly measured, e.g. by Voronel /15/, who investigated $c_v$ of Argon for different isochores $\varrho = \varrho_c$ and $\varrho \neq \varrho_c$ on earth. Also theoretical calculations of $c_v$ for 1g and µg, based on the linear model and assuming uniform temperature $T=T_c$, exhibit a sudden drop of some 70% even for different densities $\varrho \neq \varrho_c$ /12/. This behavior becomes even more distinct as gravity is reduced. However, the cell had maintained its density as post mission 1g tests evidenced, besides proper mission performance of the apparatus. For, heating power $P_0$ indicated no significant deviation comparing post and pre-mission 1g data of the cell. They both showed the typical critical peak.

To discuss whether the original bulk filling itself is critical, the precision of the cell density shall be estimated. According to Michels /16/ the critical density of $SF_6$ amounts to 0.737 g/cm³ with an assumed error of less than 1%. The precision of the cell density including the error of the volume determination and the weighing error ranges to some 0.5% /17/, which is less than the literature value above. It is evident that, due to density stratification, gravity assists to confine one thin layer of fluid in critical state within the sample volume, i.e. small deviations $\varrho - \varrho_c$ will yield a peak as long as the critical fluid layer stays between the top and the bottom of the fluid container. As gravity is reduced, the local values approach the average density. Neglecting possible boundary effects due to critical wetting at the stainless steel cell shell or due to adsorption, an assumed homogeneous density would be rather within $(\varrho - \varrho_c) <$ 10% for which Ref. /12/ still predicts a measurable change in $c_v$, as mentioned above.

## 4.3 IMPURITIES

Contamination of the test substance on earth leads to similar $c_v$ shapes as received when deviating from the critical density. Voronel /18/ measured $c_v$ of relatively pure Nitrogen (99.88%) and contaminated with impurities (N-77.4%). In all cases $c_v$ appreciably increased at the

critical point. However, the samples are stirred which is proved to reduce rounding. The HPT-calorimeter was filled with $SF_6$ of 99.993% (liquid purity) according to the manufacturer (Matheson Gas Products). Several cycles of evacuating (24h) and flushing the cell guaranteed a high specimen purity. In as much impurities increase their relatively small 1g influence in µg-experiments was not found in literature.

### 4.4 THERMAL EQUILIBRATION

The continuous scanning measurement technique applied generates a permanent spatial temperature gradient in the sample cell. Heating rates have to be chosen gentle enough to render the inhomogenouities of the temperature field negligible. It is often discussed that, when approaching the critical point, the establishment of thermal equilibrium is retarded, since the isochoric thermal diffusivity decreases for $T \rightarrow T_c$. High ramp rates lead to the typical damped peaks (Fig.4) in 1g runs. To study this effect without gravity, 4 ramps down to 3.6 mK/h = $10^{-6}$ =11K/day were conducted. This is the lowest ramp that is possible considering measurement techniques and available experiment time in space. It is tempting to simply account the poor thermal equilibration for this smeering effect, for the temperature gradients remain in the cell and depend on the temperature ramp rate and the transport coefficients of the fluid, which are functions of the temperature themselves. Regarding this, the partial differential equation of Fourier's law for heat conduction can only be solved numerically using locally temperature-dependent properties. In a simplified solution the thermal diffusivity is the leading combination of properties, which is

$$D_{th} = \frac{\lambda}{\rho \cdot c}$$

with $\lambda$ as the thermal conductivity, and $\rho$ the fluid density. The heat capacity c depends on the process of heating. In case of an isobaric process $c_p$, the heat capacity at constant pressure and in case of the isochoric process $c_v$ the heat capacity at constant volume has to be chosen. In the case of the constant volume calorimeter, $c_v$ is generally the right property. It is important to point out that especially near the critical point we have to clearly distinguish between the two thermal diffusivities, calculated with $c_p$ or $c_v$. It is known that the thermal conductivity diverges at $T_c$, but $c_p$ diverges about twice as strongly , so the isobaric thermal diffusivity converges with an exponent of about 0.8. This means that in an isobaric process the temperature equalization is strongly retarded. This is the common understanding in the discussion of thermal relaxation near the critical point.

The heat capacity at constant volume diverges less than the thermal conductivity in the critical region. The isochoric thermal diffusivity goes to infinity and equalizes the temperature gradients. This is the essential point to be regarded when discussing temperature equilibration effects at $T_c$.

In terrestrial isochoric bulk measurements, there are local changes in density according to the density stratification upon change of the system temperature. This means that locally there neither is a purely isochoric nor an isobaric process. Close to $T_c$ the isobaric component will dominate in the critical fluid layer. Therefore, disregarding convection, a retardation of temperature equilibration could not be strictly excluded, since the isobaric diffusivity rules the process.

An isochoric system at super-critical state under µg-conditions stays even locally isochoric with no thermal retardation to be expected, since the isochoric diffusivity governs the heat conduction process. In the two-phase region below $T_c$, the bulk is isochoric, but locally the phase transition brings about a change in density as T approaches $T_c$. In the liquid phase, the density decreases, whereas in the vapor phase it grows. This change of density is a process of vaporisation and requires mass transport. Nevertheless there is no indication of the temperature equilibration being retarded.

What we discussed above was experimentally confirmed in the TEXUS 8 experiment /19/, which documents thermal equilibrium.

Fig. 5 shows the thermal response in the center of a cylindrical test cell (2.5 cm inner diameter, 1.5 cm long) following a linear temperature ramp of the metal walls under µg and 1g conditions, respectively. On earth an almost constant temperature difference of 0.1 K between cylinder center and wall is maintained throughout the complete ramp of 0.9 K in 340 s. Heat transfer is supported by strong convection as was observed through the cell windows at the flat cylinder faces. It can be seen in Fig. 5 that in µg the temperature in the center of the fluid follows the wall temperature with nearly the same constant temperature difference as in 1g. This phenomenon was also measured in a parallel cooling run from $T_c$+0.4 K down to $T_c$-0.4 K. Pictures from the movie

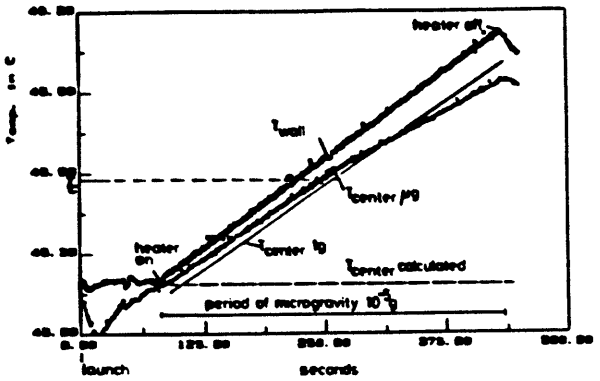


Fig. 5 Results of the TEXUS 8 experiment:
Center temperature of a cylinder filled with $SF_6$ as response to the linearly increased wall temperature. The calculated line is based on a pure thermal diffusion model with temperature dependent diffusivity.

film exhibit a bubble-droplet conglomerate created by the initial rocket spin. The clearly visible interfaces fade out as T exeeds $T_c$ in the heating run. The inhomgeneous density field with local concentrations and dilutions remains until the end of the experiment at $T=T_c+0.4$ K. The kinetics of the gentle µg phase transition looks totally different compared to the 1g transition, which is distorted by whirling convection. Thus, we can conclude that heat is transferred only by conduction in this TEXUS µg-experiment with the fast heating rate of 9.4 K/h.

According to numerical simulations using a temperature-dependent isobaric thermal diffusivity as measured by means of light scattering on earth /20/, the center temperature would not change at all. This is indicated by a straight horizontal line in Fig. 5., which is based on a pure heat conduction model. Therefore, in this case, the effective thermal diffusivity is the isochoric one as discussed before. This is valid in both the one and the two-phase region.

All the more thermal equilibrium is guaranteed in the DI-calorimeter cell, since the HPT-temperature ramps range a hundred to a thousand times below those in TEXUS. As a further proof for thermal equilibrium we consider the similar rounding of the four µg curves in Fig.3. Apart from the absolute height of the 3.6 mK/h line, no ramp rate effects could be detected. This can be regarded as a strong indication of thermal equilibrium in all runs. Considering only thermal equilibrium, a steep ramp rate of 100 mK/h seems to be sufficiently small in experiments at the gas-liquid critical point. This may be a valuable result planning µg-experiments in the future.

## 4.5 MASS EQUILIBRATION

It is known /21/ from terrestrial measurements of the local density that the establishment of the equilibrium profile, caused by high compressibility, takes many hours. After a perturbation in an isothermal probe of $T-T_c=25$mK, for example, 38h are required for the establishment of the equilibrium profile. In continuous $c_v$ measurements under 1g, the density profiles are permanently rearranged to follow the temperature-density-pressure relation in equilibrium. If higher temperature ramp rates are applied to the critical fluid, it seems that, close to $T_c$, the density profile is still behind its equilibrium distribution. This could be one explanation for the observation that at 1g the curves are flatter with faster ramp rates (Fig. 4). During such heating processes, mass is transferred from regions of higher density to lower ones. In the experiment discussed here, which starts in the two phase region, mass is transferred from the liquid to gas phase as long as $T < T_c$. This mass transfer passes the interphase and, under terrestrial conditions, in opposite direction to the gravity field. The shift of mass can be regarded as a self-diffusion process, in which the mass diffusion coefficient diverges to zero at $T_c$. There are no concrete facts on this diffusion coefficient, but one can assume that it displays a similar or the same temperature dependence as the isobaric thermal diffusion coefficients, which tend to zero in approaching $T_c$.

In orbit the experiment in the HPT is started at $T < T_c$ and heated up to a temperature above $T_c$. Therefore, the fluid initially consists of two inhomgeneous phases, but an equilibration time of four hours before the heating assures us that the fluid was in thermodynamic equilibrium. In absence of gravity, we can assume that, despite surface tension, the liquid wets the cell walls, and vapor stays in the center of the cell, surrounded by liquid. The µg mass equalization process at subcritical temperature resembles the diffusion-like process under terrestrial conditions, but takes place across an enlarged area at the interface. The mass transport does not act against the gravity vector, and thus it can be assumed that mass equilibration should be faster than under terrestrial conditions. Furthermore, curves (Fig. 3) of the four different temperature time ramps, with a maximum ratio of 3.6/100=1:28, show neither a significant change at all nor relative deviations that could be correlated to the heating rates like for those under 1g (Fig. 4).

Consequently, we are still endeavoring an incontestable explanation for the result of the D1-experiment, which cannot be found exclusively on the basis of the mass equilibration effect.

### 4.6 LIFETIME AND RELAXATION OF FLUCTUATIONS

The theory of critical phenomena today is based on the spatial extention of the fluctuations in a critical probe, expressed by the correlation length $\xi$, which diverge as

$$\xi = \xi_0 / \frac{T-T_c}{T_c} /^{-\nu} \qquad (4)$$

This increase of the fluctuations can be observed and is known as the so-called critical opalescence, which yields a yellow and brownish coloring of the probe, since the correlation length approaches the the wave length of visible light. A system near the critical state can only be in equilibration when the fluctuations related to the temperature are completely developed. Considering a system subdued to a continuous temperature change, the question arises whether the fluctuations can follow the temperature fast enough. If one assumes a fluctuation to be a sphere with the diameter of the correlation length $\xi$, the time necessary to establish the equilibrium can be calculated by solving the Fourier heat flow equation. For the case that the equlibrium is reaches close to $10^{-4}$ of the final temperature, the equilibration time can be calculated by

$$t = \frac{\xi^2}{D_{th,p}} . \qquad (5)$$

A fluctuation can be regarded as an isobaric process within an overall isochoric bulk system, so for the local process the isobaric diffusivity applies. With the temperature-dependent measurements of $D_{th,p}$ /20/ and eq. 5, the equilibration time can be estimated: at $T-T_c$=1mK, $t=2.26\cdot10^{-2}$s and at $T-T_c$=0.1mK, t=3.67s. Using gentle heating ramps, we can be sure that up to 0.1mK to $T_c$ the fluctuation equilibrium is established and cannot be the reason for the rounded curvature of the µg measurement in Fig. 3.

## 5. CONCLUSIONS

The fundamental motivation for our µg experiment was to measure $c_v$ much closer to $T_c$, than it is possible on earth owing to gravity influence. Under gravity the mass ratio of the fluid layer at critical state and of the total specimen mass is 1:1000 for $/(T-T_c)/T_c/=10^{-6}$ and a cell height of 1mm. Therefore, the results for $c_v$ measured for an inhomogeneous bulk system cannot be regarded representative of the critical state. In orbit the complete cell volume is at critical state. Thus, we expected the theoretically predicted peak to appear much more enhanced than on earth and thus the theory becomes confirmed. However, the measured µg curves are surprisingly low and even smoother than on earth. These unexpected results cannot be explained simply by mal-function of hardware, wrong filling of the specimen cell or impurities of the substance, as it was discussed above. We cannot completely exclude equilibration effects, but it seems to us that the thermal equilibrium is not retarded, the kinetics of the fluctuation is not hindered like on earth /22/, and the relaxation time of a fluctuation increases only in narrow temperature span of 0,1 mK to an extend that can influence the results. The rounded hump of $c_v$ measured under µg could possibly be generated by a retarded mass transport mechanism from the liquid to the gaseous phase, which is not exactly understood and investigated yet.

A comparison of the µg- and 1g $c_v$ curves does not yield an incontestable result. After a final review of our results we are almost tempted to ask presumptiously in as much the theory, which was developed for magnetic systems, is able to describe critical phenomena in pure fluids without any specific constraints.

## 6. ACKNOWLEDGEMENTS

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