International Journal of Thermophysics, Vol. 25, No. 6, November 2004 (© 2004)

Reanalysis of Microgravity Heat Capacity Measurements Near the SF_6 Liquid–Gas Critical Point

M. Barmatz,[1,2] F. Zhong,[1] and A. Shih[3]

Received April 28, 2004

The earlier microgravity heat capacity measurements in SF_6 by Haupt and Straub have been reanalyzed in this study. A simple power law as well as the minimal-subtraction renormalization (MSR) scheme were used to fit the measurements. In this paper the unexpected result that the SF_6 heat capacity measurements appear to be within the asymptotic critical region all the way out to a reduced temperature $|t| \simeq 10^{-2}$ is presented. This conclusion is in contradiction with the smaller asymptotic region $|t| < 1.6 \times 10^{-4}$ found in the original investigation. These heat capacity measurements were found to be inconsistent with renormalization group predictions using SF_6 compressibility measurements.

KEY WORDS: critical phenomena; heat capacity; liquid–gas critical point; microgravity.

1. INTRODUCTION

An important objective in the study of critical phenomena is the development of theoretical models that accurately predict experimentally observed behavior. The introduction of the scaling hypothesis and the application of renormalization group techniques [1] have provided rather accurate predictions for critical behavior in the asymptotic region very close to a critical point. Over the years, many ground-based studies were performed near liquid–gas critical points to elucidate the expected divergences in thermodynamic quantities. The unambiguous interpretation of these studies very

[1]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, U.S.A.
[2]To whom correspondence should be addressed. E-mail: Martin.B.Barmatz@jpl.nasa.gov
[3]Mechanical Engineering Department, California Polytechnic University at Pomona, Pomona, California 91768, U.S.A.

0195-928X/04/1100-1667/0

near the critical point was hindered by a gravity-induced density stratification. The gravity-induced smearing effect is the main rationale for performing thermodynamic measurements in a microgravity environment. In recent years, attempts have been made to extend asymptotic models of critical phenomena to include thermodynamic behavior farther away from the critical point in what is commonly called the crossover region. In this region, critical fluctuations no longer dominate the behavior of the system. This is also the region where gravity no longer adversely affects experimental measurements. Ground-based measurements farther away from the transition can give insight into the crossover behavior between the asymptotic critical region near the transition and the mean field region farther away. Recently [2], the minimal subtraction renormalization (MSR) scheme [3] was applied to experimental measurements of the isothermal susceptibility and heat capacity along the critical isochore and coexistence curve [4] and earlier measurements of the coexistence curve [5] of ^{3}He near its liquid–gas critical point. This scheme provided a good fit to these thermodynamic measurements in the crossover region out to a reduced temperature $|t| < 10^{-2}$. This MSR fit implied that the asymptotic critical region for ^{3}He extended out to $|t| \approx 2 \times 10^{-4}$.

Given the ^{3}He validation of the MSR crossover model, we decided to see how well this model fit other critical point thermodynamic measurements. One of the most accurate set of heat capacity measurements near a liquid–gas critical point was obtained by Haupt and Straub [6] (HS) in SF_6 during the German Spacelab Mission D-2. That investigation obtained heat capacity measurements over the wide temperature range $3 \times 10^{-6} < |t| < 1 \times 10^{-2}$. In this paper, we present a reanalysis of these microgravity SF_6 measurements.

2. REANALYSIS OF SF_6 MICROGRAVITY HEAT CAPACITY MEASUREMENTS

The theoretically expected behavior of the dimensionless heat capacity at constant volume, C_V^*, along the critical isochore is given by

$$C_V^{\pm *} = (T_c \rho_c / P_c) C_V^{\pm} = A_0^{\pm} |t|^{-\alpha} [1 + A_1^{\pm} |t|^{\Delta_s} + \ldots] + B_{\mathrm{cr}} + C_{\mathrm{B}}, \tag{1}$$

where $\alpha = 0.109$ [1] is a universal critical exponent that defines the strength of the heat capacity divergence and $A_0^{\pm}$ are system-dependent asymptotic critical amplitudes. In this expression, the + sign indicates above the transition and the – sign below. The asymptotic region is very close to the critical point where critical fluctuations dominate the behavior of the system. In this region, the heat capacity is expected to follow a simple power law behavior given by the leading term plus the total constant background term that is the sum of the analytic background C_B and the fluctuation induced background B_{cr}. Farther away from the transition, the system enters the crossover region where it slowly changes from critical behavior to mean-field behavior. In this region, correction-to-scaling terms, shown in the brackets of Eq. (1), become important. These terms are generally called Wegner correction terms. $A_1^{\pm}$ are system dependent amplitudes and $\Delta_s = 0.504$ [1] is another exponent that describes crossover behavior.

The SF_6 microgravity flight experiment of HS [6] employed a scanning calorimeter to obtain a large number of heat-capacity measurements for analysis. There were six cooling runs and five heating runs at various drift rates performed during the D-2 mission [7]. Only data from several cooling runs were included in their final analysis [6]. Over 70,000 data points were assembled, mainly from the slowest runs through the transition. A data averaging approach was used to create a smaller reduced 2500 point data set. In order to minimize the computer time required to perform a regression analysis, they further reduced the data set to only 40 data points per decade in reduced temperature. The critical temperature of their sample was experimentally found to be $T_c = 318.680\,\mathrm{K} \pm 0.5\,\mathrm{mK}$. These authors estimated the uncertainty in each data point as the deviation between the measured heat capacity and a smoothing cubic spline fit to the data in logarithmic form. This estimation process was repeated using several spline smoothing parameters. Using a range shrinking procedure, this reduced data set was fit to the simple power law,

$$C_V^{\pm *} = A_0^{\pm} |t|^{-\alpha} + B_0, \tag{2}$$

with no constraints on the critical exponent, α, leading asymptotic amplitudes, $A_0^{\pm}$, critical temperature, T_c, or constant background term B_0. By observing when the goodness of fit, χ_ν^2, significantly increased, they concluded that a simple power law was only valid in the range $|t| < 1.6 \times 10^{-4}$. From this global fit they obtained a critical temperature $T_c = 318.6801\,\mathrm{K}$, critical exponent $\alpha = 0.1105^{+0.025}_{-0.027}$ and an asymptotic amplitude ratio $A_0^-/A_0^+ = 1.919^{+0.24}_{-0.27}$ that were consistent with theoretical predictions [1] $\alpha = 0.109 \pm 0.004$ and $A_0^-/A_0^+ = 1.862 \pm 0.066$. They also attempted to fit data outside their asymptotic region by including the first and second Wegner correction terms. They again used the range shrinking method. The critical exponent Δ_s was fixed to the theoretical value 0.5, and the other parameters were varied. The asymptotic power law extended by the first Wegner correction term provided a good representation of the data out to $|t| < 1.0 \times 10^{-3}$; however, the inclusion of the second Wegner correction term gave insufficient representation of the total data set. Haupt [8] found $A_1^+ = -0.72$ and $A_1^- = -1.61$ from his fit including only the first Wegner correction term. This result suggests that α_{eff} is larger than α, which is inconsistent with the theoretical prediction [9] that α varies monotonically from its finite positive value near the critical point to zero in the mean-field region farther away. Allowing a large number of parameters to simultaneously vary can lead to spurious results. Another approach, which is employed in this reanalysis, uses the predictions of recent well-developed crossover models for the critical exponents and critical amplitude ratios. In this way, the number of adjustable parameters is significantly reduced and experimental measurements can be used to more precisely determine crossover behavior consistent with the theoretical predictions. This is the main approach that we have taken.

The original complete data set used by HS is unfortunately no longer available for further analysis. However, the reduced set of 2500 SF_6 data points was obtained from Haupt. A repeat of the range shrinking approach used by HS to determine the asymptotic region was initially attempted using several methods for assigning uncertainties to the measurements. This effort failed to find an obvious initial deviation from a simple power law for reduced temperatures $|t| \geqslant 1.6 \times 10^{-4}$. As a matter of fact, by holding T_c constant at values within the experimental range found by HS, a good fit to the entire data set was obtained using a simple power law. This result implies that the critical region for SF_6 extends much farther away from the transition than is generally expected from analyses of thermodynamic measurements near other liquid–gas critical points [2]. The data were also fit to a simple power law while holding the asymptotic critical exponent and amplitude ratio constant at values expected from various theories [2, 9, 10]. Again, in every case, a good fit was obtained over the entire experimental measurement range.

To provide a check on this surprising result, the MSR crossover model [2, 3] was used to analyze these measurements. This model was chosen because it provided a good joint fit to heat capacity, susceptibility, and coexistence curve measurements near the ^{3}He liquid-gas critical point [2]. In this approach, the critical exponents and critical amplitude ratios are determined within the theory and only the system dependent critical amplitudes are obtained from the model parameters that are fit to experimental measurements. The MSR model has three system-dependent parameters [2], u, μ, and a; however, only two of these are independent in the case of the heat capacity. For this analysis, μ and a were chosen as the model fitting parameters. A constant analytical background term, C_B, was also included in the fit. These parameters determined the asymptotic and crossover behavior from the fit. In this fit, $u \equiv 0.999u^*$, where u^* is the fixed-point value.

Several fitting procedures were performed. For this study, the uncertainty in all of the data was estimated to be 0.6%. This value was obtained from the average difference between each measurement and the theoretical fit $((1/N)\sum |C_V(\text{exp.}) - C_V(\text{fit})|)$. If our earlier fitting result for a simple power law was correct and all the data were within the asymptotic region, the parameters μ and a would be completely correlated and holding one of them constant would not change the goodness of the fit. This is essentially the situation observed in the case of SF_6. Thus, a was held constant for a range of values and T_c, μ, and C_B were allowed to vary for each fixed a. We found that the goodness of the fit given by χ^2_ν decreased as a function of a in the range $a \leqslant 20$. For larger values of a, χ^2_ν remained essentially constant at its best fit value.

The log–log plot in Fig. 1a shows the results of a fit using $a = 50$. The best fit critical temperature $T_c = 318.6804$ K obtained from this analysis was still below the experimentally estimated maximum value given in the previous study [6]. The magnitude and uncertainty in the critical amplitudes as well as the fluctuation induced background term, B_{cr}, were determined from the best fit parameters, μ and C_B [2]. The difference between the measured heat capacity and the best fit value is also shown at the top of the figure. This plotted difference for the data in the range $|\tau| > 1 \times 10^{-5}$ is consistent with the chosen experimental uncertainty of 0.6%. This fit again indicates that almost all the measurements were within the asymptotic region! One possibility for this unusual result is that there is a strong background effect. To test this possibility, we included in the fit a background term that is linear in temperature. This did not change the range of the asymptotic region or the quality of the fit.

A more sensitive representation of the fitting quality and crossover behavior can be obtained by scaling the critical part of the heat capacity ($C^*_V - C_B - B_{cr}$) by $|t|^{-\alpha}$. The results of both the scaled experimental measurements and the fit are shown in Fig. 1b. The solid horizontal lines represent the MSR prediction for the asymptotic critical amplitudes, $A^\pm_0$. These asymptotic critical amplitudes, determined from this MSR fit, are still consistent with the values found by HS (≈7% higher). The main difference between the present and previous analysis is the absence of any measurable crossover behavior as indicated by the very small values of the first Wegner critical amplitudes, $A^\pm_1$, obtained in this reanalysis. Haupt [8] found much larger negative values from his fit including only the first Wegner correction term.

We have recently developed a 1D computer code to predict the error in drift heat capacity measurements through the liquid-gas critical point.

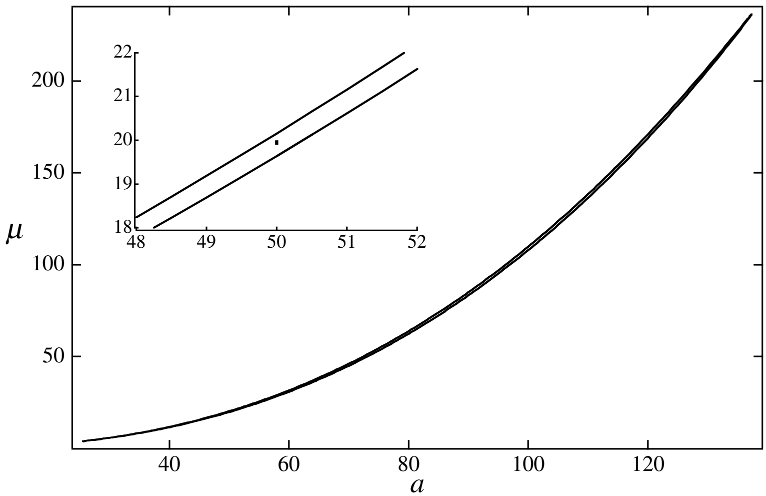

Fig. 1. (a) Fit of the MSR model to SF_6 microgravity heat-capacity measurements in both the single-phase region (dark symbols) and two-phase region (gray symbols). u/u^*, a was arbitrarily set equal to 50, and T_c, μ and C_B were adjusted. The lines represent the theoretical fit. The difference between the experimental and fitted heat capacity is also shown. (b) Scaled critical part of the SF_6 heat capacity versus reduced temperature. Horizontal lines represent the asymptotic critical amplitudes obtained from the fit.

We have applied this code to ^{3}He with a drift rate equivalent to the slowest SF_6 cooling rate (−0.06 K/hr) at $t = 1 \times 10^{-5}$. From this analysis, we predict a systematic flaring downward in the heat capacity in the single-phase region with an error of ~1% at $t = 1 \times 10^{-6}$. This accumulated error is consistent with the flaring effect in SF6 shown in Fig. 1. This possible cause for the flaring effect is further substantiated by the long diffusive relaxation time of 227 hours estimated at $t = 1 \times 10^{-5}$ for the microgravity SF_6 cell. If we remove the measurements for $|t| < 1 \times 10^{-5}$ affected by the flaring, the best fit critical temperature increases to $T_c = 318.6807$ K and the goodness of the fit is reduced to $\chi_\nu^2 = 0.27$ from the value $\chi_\nu^2 = 0.51$ obtained in Fig. 1.

The uncertainty in the model adjustable parameters, μ and C_B, can be determined from confidence contour plots [11]. We obtained the 1σ standard deviation for a joint variation in these quantities from the confidence contour ($\Delta\chi_\nu^2 = 2.3$) shown in Fig. 2. The standard deviations in the asymptotic and Wegner first-order amplitudes and other calculated quantities shown in Fig. 1 were then obtained from the uncertainties in μ and C_B.

The correlation between the MSR model parameters, μ and a, can also be investigated by generating a joint contour plot [11]. If the parameters

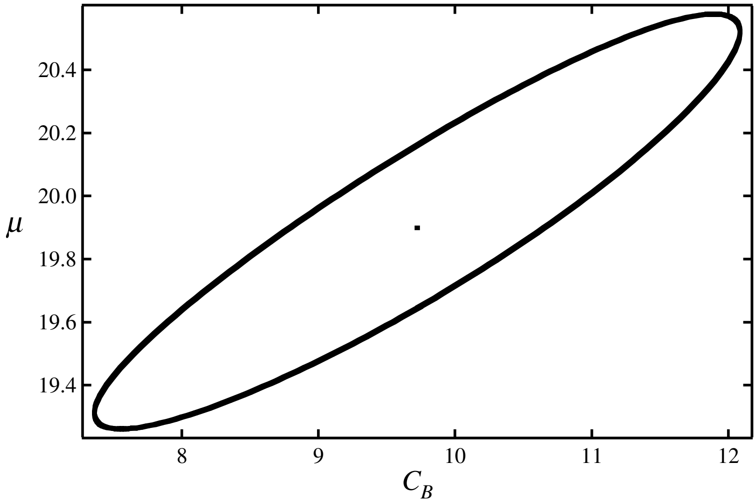

Fig. 2. 1σ contour plot of MSR model parameters μ and C_B. The individual standard deviation for each parameter taken separately is obtained from the projections of the contour onto the parameter axis.

are completely uncorrelated, one would have a circle in the contour plot, while if the parameters are completely correlated, one obtains a single curve. Figure 3 shows such a plot for μ and a using a 1σ joint confidence level of 68.3%, i.e, there is approximately a 68.3% probability that the true values of the measured parameters will lie within this confidence region. We see that these two parameters are almost completely correlated as assumed in the reanalysis of the SF_6 measurements. The contour shown in Fig. 3 provides a good fit to a quadratic polynomial, i.e., $\mu \propto a^2$.

3. DISCUSSION

In this study, a good fit between the MSR theory and experiment was obtained over more than three decades in reduced temperature using a variety of fitting approaches. The most important result of this study is that the entire SF_6 microgravity measurements appear to lie within the asymptotic region. It would be of considerable interest to extend this SF_6 heat-capacity analysis by including additional measurements farther away from the transition ($|t| > 10^{-2}$). This would allow an unambiguous determination of the beginning of crossover behavior. There were many earlier studies of the critical behavior of the heat capacity in SF_6; however, none of the published (or unpublished) investigations we encountered discussed measurements beyond $|t| \geqslant 10^{-2}$.

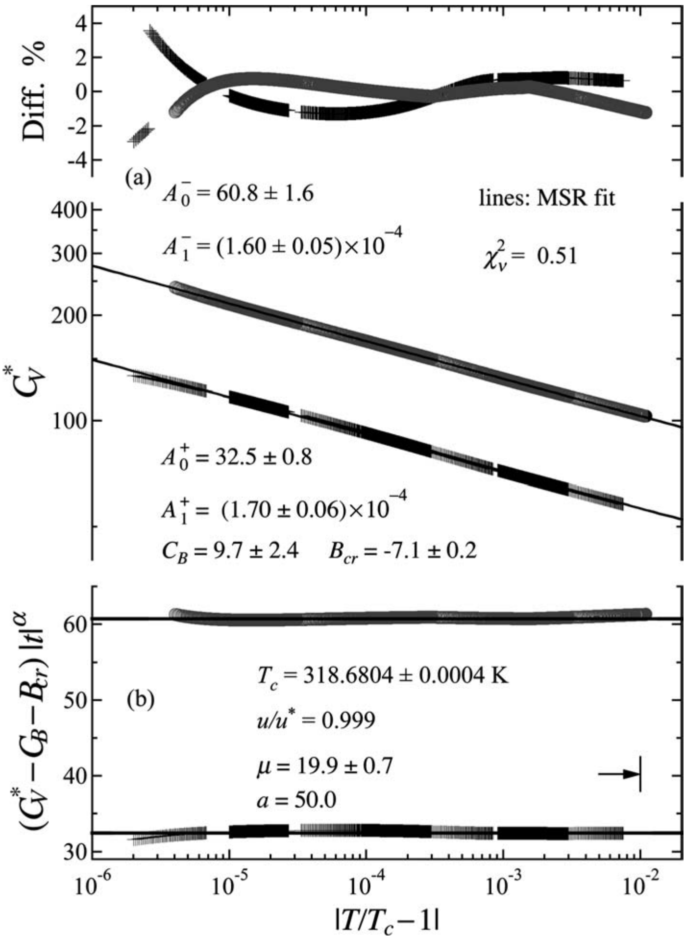

Fig. 3. Contour plot of MSR model parameters μ and a for a 68.3 % (1σ) confidence level. The insert shows the magnitude of the separation that defines the narrow contour area near the best fit (dot). This contour demonstrates that μ and a are almost completely correlated.

An alternative way to obtain additional insight is to investigate other thermodynamic measurements near the SF_6 liquid-gas critical point. The susceptibility measurements in SF_6 show crossover behavior not too different from what was found in ^{3}He. Garrabos [12] obtained a susceptibility amplitude $\Gamma_1^+ = 1.14$ from a reanalysis of the earlier measurements of Cannell [13]. Critical phenomenon theories based on renormalization group analyses predict a universal amplitude ratio between the Wegner first-order heat capacity and susceptibility amplitudes. The MSR model predicts $A_1^+/\Gamma_1^+ = 0.894$ for this universal amplitude ratio [2]. Similar values for this ratio are found in other crossover models [9, 10]. Using this MSR ratio, one obtains a predicted $A_1^+ = 1.02$, which is comparable to the ^{3}He value [2], $A_1^+ = 1.01$. However, this predicted Wegner first-order heat capacity amplitude is much larger than the value obtained in this reanalysis $A_1^+ = 0.0002$. This inconsistency between presently accepted renormalization group predictions and experimental measurements in SF_6 needs to be resolved.

ACKNOWLEDGMENTS

We are indebted to Dr. Haupt for fruitful discussions regarding the earlier studies. The research described in this article was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

REFERENCES

1. R. Guida and J. Zinn-Justin, *J. Phys. A*: *Math. Gen.* **31**:8103 (1998).
2. F. Zhong, M. Barmatz, and I. Hahn, *Phys. Rev. E* **67**:021106 (2003).
3. R. Schloms and V. Dohm, *Nucl. Phys. B* **328**:639 (1989).
4. M. Barmatz, I. Hahn, F. Zhong, V. A. Agayan, and M. A. Anisimov, *J. Low Temp. Phys.* **121**:633 (2000).
5. E. Luijten and H. Meyer, *Phys. Rev. E* **62**:3257 (2000).
6. A. Haupt and J. Straub, *Phys. Rev. B* **59**:1795 (1999).
7. J. Straub, A. Haupt, and L. Eicher *Int. J. Thermophy.* **16**:1033 (1995).
8. A. Haupt, *Ph.D. Thesis*, Technische Universität München (1997).
9. C. Bagnuls and C. Bervillier, *Phys. Rev. E* **65**:066132 (2002).
10. V. A. Agayan, M. A. Anisimov, and J. V. Sengers, *Phys. Rev. E* **64**: 026125, (2001).
11. P. R. Bevington and D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, 2nd Ed. (McGraw-Hill, New York, 1992).
12. Y. Garrabos, *J. Physique* **47**:197 (1986).
13. D. S. Cannell, *Phys. Rev. A* **12**: 225 (1975).