

Heat capacity of the liquid–liquid mixture perfluoroheptane and 2,2,4-trimethylpentane near the critical point

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The heat capacity of the liquid–liquid mixture perfluoroheptane and 2,2,4-trimethylpentane (also known as iso-octane) has been measured for the first time near its upper critical consolute point using an adiabatic calorimeter. The theoretical expression for the heat capacity near the critical point was applied to our combined data runs. The critical exponent α was determined to be 0.106 ± 0.026 , which agreed with theoretical predictions. When α was fixed at its theoretical value of 0.11, our value for the amplitude ratio $A^+/A^- = 0.59 \pm 0.05$ was consistent with experimental determinations and theoretical predictions. However, the two-scale-factor universality ratio X , now consistent among experiments and theories with a value between 0.019 and 0.020, was violated in this system when using the published value for the correlation length. © 2001 American Institute of Physics. [DOI: 10.1063/1.1350661]

INTRODUCTION

The theory of critical phenomena takes advantage of common behavior in a wide variety of systems near a critical point. It describes physical processes by realizing, both theoretically and experimentally,¹ the universality for liquid–gas, liquid–liquid mixtures, uniaxial ferromagnetism, and polymer solutions. The diversity of critical systems that can be described by universal relations indicates that experimental measurements on one system should yield complementary information as on another.

Since the spatial extent of concentration fluctuations is very large near the critical point compared to the molecular size, the behavior of a system is not determined by the type of material but by its critical properties, which have universal descriptors. For example, the correlation length ξ diverges close to the critical point as a power law $\xi = \xi_0 t^{-\nu}$ where $t \equiv (T - T_c)/T_c$ is the reduced temperature, ξ_0 is the system-dependent amplitude describing the correlation length, T_c is the critical temperature, and ν is a universal critical exponent ($\nu = 0.630$).² Thus, physical phenomena describing a system close to its critical point have a universal form independent of the system involved.

The heat capacity provides a delicate probe of a system near a critical point and can determine essential amplitude and exponent values. A precise measurement of the heat capacity of a liquid–liquid mixture will determine the amplitude in the one-phase region and its effect on the universal ratio X , and measure the universal ratio of the amplitudes above and below the critical temperature. A liquid–liquid mixture near its critical consolute point will have a weak divergence in its heat capacity at constant pressure when measured along a path of constant, critical composition $x = x_c$ that is governed by the critical exponent α , and has a critical contribution B_c to the background heat capacity.^{3,4}

$$C_{px} = (B_{bg} + B_c) + Et + \frac{A^+}{\alpha} |t|^{-\alpha} \quad (\text{one phase}), \quad (1a)$$

$$C_{px} = (B_{bg} + B_c) + Et + \frac{A^-}{\alpha} |t|^{-\alpha} \quad (\text{two phase}), \quad (1b)$$

where C_{px} is the temperature-dependent heat capacity at constant pressure and at the critical composition, B_{bg} is the background heat capacity far from the critical temperature T_c in the one-phase region, t is the reduced temperature, A^\pm is the amplitude of the leading divergence, and α is the universal exponent ($\alpha = 0.1099 \pm 0.0007$).² The one- and two-phase amplitudes are denoted by the (+) and (–) superscript, respectively; the background terms and the critical exponents are predicted³ to be the same above and below the critical point. A linear background term Et arises from the regular part of the free energy and hence should also be the same above and below the critical point.

Two relevant amplitude ratios are predicted to be true universal quantities that should be the same for all systems in a given universality class (three-dimensional Ising for bulk, liquid–liquid mixtures). The ratio of the leading, singular, heat capacity amplitude in the one-phase region to that in the two-phase region is now predicted to be $A^+/A^- = 0.537 \pm 0.019$ by $d=3$ expansion,⁵ 0.530 ± 0.003 by high-temperature series,² 0.527 ± 0.037 by ϵ expansion,⁵ and 0.56 ± 0.01 by Monte Carlo calculation.⁶ One can also relate A^+ to the amplitude ξ_0 of the correlation length in the one-phase region using two-scale-factor universality:²

$$X = \frac{A^+ \xi_0^3}{k_B},$$

where k_B is Boltzmann's constant. The value of X is predicted from a $d=3$ expansion⁷ to be $X = 0.01966 \pm 0.00017$ and from high-temperature series² to be 0.01880 ± 0.00008 .

These predictions have been tested in liquid–liquid mixtures with mixed results.^{1,4} Recent experiments^{8–13} measur-

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ing the heat capacity of binary fluid mixtures (including our measurement in triethylamine–water) have determined A^+/A^- as 0.56 ± 0.03 ; a value consistently larger than the 0.52 value determined in liquid–vapor systems.¹⁴

The other universal quantity X requires the value of the correlation length amplitude ξ_0 , which must be determined from a separate experiment. For the system being considered, the value of ξ_0 has been measured. The error in ξ_0 usually dominates the error in X since ξ_0 enters as the cube. Recent determinations in binary fluid systems have found X to be 0.019 ± 0.004 in triethylamine and heavy water,¹⁰ 0.020 ± 0.002 in 3-methylpentane and nitroethane,¹¹ 0.028 ± 0.007 in 2,6 dimethyl pyridine and water,¹⁵ and 0.019 ± 0.003 in triethylamine and water,¹² while the latest liquid–vapor measurement gives 0.023 ± 0.004 in SF₆.¹⁴

In this experiment, we perform the first measurement of the heat capacity in the liquid–liquid mixture of perfluoroheptane and iso-octane near the critical point. The components in this system have quite different densities and the location of the critical point is quite different from that predicted by regular solution theory.¹⁶ Light scattering and diffusivity measurements have determined¹⁷ the correlation length amplitude in the one-phase region to be $\xi_0 = 0.194 \pm 0.025$ nm, which can be combined with our measurement of A^+ to test the universal ratio X .

EXPERIMENT

A critical composition sample of perfluoroheptane and iso-octane (2,2,4 trimethylpentane) was used. The iso-octane was 99+% pure from Aldrich and used without further purification. The perfluoroheptane was purchased as 90% pure from Indofine and further purified by distillation to be 99.7% pure as determined by GC. The mixture used in this experiment was 32.4% by mass iso-octane with a total mass of 20.330 g, which is a volume of 17.46 mL at the critical point. This concentration is the critical concentration¹⁶ of 32.8% by mass ($54.5 \pm 0.5\%$ by volume) iso-octane, and is the same composition used by other investigators of this system.^{17–19} The sample preparation was done in a dry box under a nitrogen atmosphere and a small nitrogen vapor bubble was left above the fluids to keep the pressure close to 1 atm. This system exhibits an upper consolute point around 23 °C.

The heat capacity of the critical composition of perfluoroheptane and iso-octane was measured using an adiabatic calorimeter, which we have already described.^{8,12} The fluid sample was sealed in a cylindrical, gold plated, copper cell with a Kalrez (DuPont perfluoroelastomer) o-ring. The fluids are sloshed while heating to achieve thermal equilibrium, which is especially important in the two-phase region.^{10–12} The cell is heated for a fixed period of time by applying a constant current (to 0.01%) flowing through manganin wire wrapped in grooves on the outside of the cell body. After the heater is turned off and the sloshing stops, the thermostat reaches a constant temperature before the next heating period. This step process has been described previously.⁸

We optimize the experiment so that the temperature of the cell is constant when no current is applied to the heater. Using a temperature control and data acquisition program written in LABVIEW, the resistance of each thermistor in the

TABLE I. The fluid heat capacity C_p of a critical composition of perfluoroheptane and iso-octane as a function of temperature T .

T (K)	C_p (J/cm ³ /K)	δC_p (J/cm ³ /K)	T (K)	C_p (J/cm ³ /K)	δC_p (J/cm ³ /K)
294.5310	1.985	0.034	296.3390	2.076	0.073
294.5650	1.994	0.032	296.3490	2.109	0.029
294.6490	2.011	0.032	296.3850	2.093	0.025
294.6820	2.021	0.027	296.4110	2.124	0.054
294.7670	1.981	0.032	296.4240	2.114	0.024
294.8840	1.986	0.034	296.4480	2.123	0.056
294.9240	1.993	0.031	296.4620	2.172	0.029
295.0000	2.006	0.038	296.4870	2.207	0.058
295.1160	2.010	0.033	296.5020	2.203	0.035
295.1170	2.025	0.026	296.5250	2.241	0.058
295.1540	2.018	0.038	296.5410	2.249	0.030
295.1550	2.029	0.055	296.5640	2.027	0.060
295.1920	2.030	0.040	296.5960	1.972	0.035
295.1940	2.038	0.048	296.6030	1.947	0.062
295.2310	2.038	0.039	296.6350	1.917	0.040
295.2320	2.043	0.033	296.6420	1.900	0.057
295.2690	2.046	0.038	296.6820	1.896	0.055
295.2700	2.050	0.043	296.6980	1.884	0.031
295.3070	2.064	0.046	296.7210	1.868	0.049
295.3080	2.037	0.046	296.7380	1.868	0.035
295.3450	2.057	0.045	296.7600	1.864	0.038
295.3830	2.050	0.041	296.7770	1.860	0.027
295.4210	2.053	0.049	296.8790	1.850	0.036
295.4590	2.063	0.058	296.8950	1.849	0.025
295.4650	2.053	0.036	296.9970	1.845	0.031
295.4970	2.061	0.055	297.0030	1.836	0.022
295.5030	2.078	0.038	297.1090	1.828	0.016
295.5340	2.070	0.063	297.1150	1.820	0.031
295.5410	2.085	0.038	297.2270	1.819	0.011
295.5710	2.100	0.067	297.2330	1.807	0.033
295.5790	2.157	0.043	297.3450	1.809	0.014
295.6080	2.190	0.057	297.3520	1.806	0.035
295.6160	2.231	0.042	297.4640	1.806	0.021
295.6450	2.239	0.060	297.4700	1.807	0.033
295.6540	2.012	0.032	297.5890	1.804	0.031
295.6830	1.922	0.066	297.6350	1.807	0.018
295.6920	1.908	0.028	297.7080	1.807	0.029
295.7200	1.890	0.069	297.7550	1.803	0.032
295.7300	1.893	0.026	297.8260	1.808	0.029
295.7570	1.894	0.063	297.9450	1.801	0.028
295.7670	1.863	0.022	297.9930	1.805	0.030
295.7950	1.877	0.055	298.0640	1.802	0.033
295.8050	1.861	0.024	298.1120	1.802	0.025
295.8320	2.031	0.060	298.1830	1.806	0.036
295.8690	2.026	0.063	298.2310	1.861	0.028
295.9060	2.023	0.061	298.3010	1.850	0.035
295.9160	2.034	0.027	298.3510	1.841	0.026
295.9430	2.043	0.071	298.4200	1.838	0.034
295.9530	2.047	0.026	298.4700	1.823	0.030
295.9800	2.035	0.070	298.5380	1.833	0.029
295.9900	2.048	0.024	298.5890	1.825	0.024
296.0170	2.033	0.059	298.7070	1.823	0.028
296.0270	2.055	0.022	298.8550	1.827	0.018
296.0530	2.059	0.054	298.9740	1.824	0.022
296.0640	2.060	0.033	299.1050	1.817	0.026
296.0900	2.055	0.064	299.2240	1.821	0.026
296.1440	2.066	0.027	299.3440	1.817	0.023
296.1800	2.075	0.030	299.4640	1.822	0.027
296.1970	2.076	0.053	299.5840	1.820	0.032
296.2330	2.068	0.047	299.7040	1.818	0.026
296.2680	2.085	0.056	299.8240	1.810	0.019
296.3040	2.093	0.071	299.9440	1.811	0.020
296.3140	2.087	0.033			

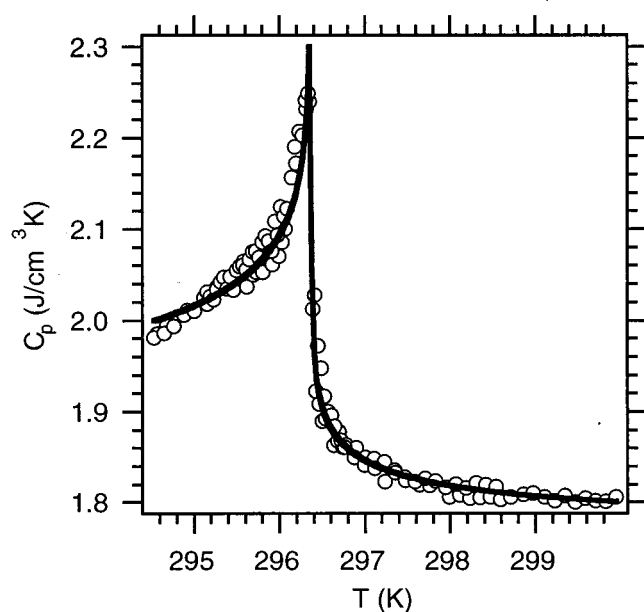


FIG. 1. Heat capacity C_p in perfluoroheptane and iso-octane as a function of temperature T from the data in Table I. All data were taken on the same sample. The solid line is fit 1a from Table II. The errors in the data are slightly larger than the reproducibility and are omitted from the plot for clarity.

thermostat is determined by measuring the voltage across a standard resistor and across each thermistor using a 7 1/2 digit Keithley 2001 multimeter. Near the critical temperature, the cell temperature stays constant within our resolution of 0.2 mK over the 5–10 min when no current is applied to the cell heater. We can correct for any systematic drift in the temperature of this plateau, but only over a limited region, which dictates the temperature interval for the data reported here. The specific heat of the copper cell is taken into account in reporting the heat capacity of a critical composition of the perfluoroheptane and iso-octane system given in Table I and illustrated in Fig. 1.

A weighted, nonlinear, least-squares routine was used to fit Eq. (1) to the data by finding the best set of parameters that minimize²⁰ the reduced chi-square χ^2/N . In analyzing the heat capacity data shown in Table I, we simplify Eq. (1) by using a parameter $C_{p_0} \equiv (B_c + B_{bg})$. We force equal exponent values above and below the critical point as predicted by theory.^{3,4} A smooth, continuous background specific heat near the critical point is expected,^{3,4} which means the background amplitudes C_{p_0} and E are the same in the one- and

two-phase region. We simultaneously fit these equations to the one- and two-phase data.

The combined runs were fit over the entire 5° temperature region around the critical temperature. In the following, our quoted parameter errors are those given by the program and should be considered the 1σ error. These 125 data points were well described by six adjustable parameters: C_{p_0} , E , A^+ , A^- , T_c , and α . The parameter E should reflect the noncritical fluid behavior and has²¹ a small negative value of -0.87 J/(cm³ K) for the composition used. Allowing E to vary does not improve the fits (see Table II) and thus we fix its value for most fits to the data. Allowing the critical exponent α to vary gives a value of 0.106 ± 0.026 , consistent with the theoretical value of 0.11, but doing so substantially increases the errors in the amplitudes. Because of the interdependence of the fitting parameters, it is important to fix critical exponents at their theoretical values so consistent amplitudes can be compared through universal ratios such as X . Thus, most fits have α fixed. The best is fit 1a because the resulting equation is the simplest that fits the combined data.

The heat capacity fits given in Table II provide a consistent set of amplitude values when $E = -0.87$ J/(cm³ K) and $\alpha = 0.11$ are fixed. The background amplitude of Eq. (1) is then: $B_c = -0.27 \pm 0.02$ J/(cm³ K), while $A^+ = 0.0172 \pm 0.0013$, $A^- = 0.0294 \pm 0.0013$ J/(cm³ K), where all the errors are one standard deviation estimates. Our value of the universal ratio $A^+/A^- = 0.59 \pm 0.05$ is consistent with experimental values determined in several liquid–liquid systems recently and with theoretical predictions.

The two-scale-factor universality ratio

$$X = \frac{A^+ \xi_0^3}{k_B}$$

can be calculated from our value of $A^+ = 0.0172 \pm 0.0013$ J/(cm³ K) and the literature value¹⁷ of $\xi_0 = 0.194 \pm 0.025$ nm, which gives $X = 0.009 \pm 0.002$. This value substantially disagrees with other recent experimental determinations and with theoretical predictions. Two-scale factor universality would predict a value of $\xi_0 \approx 0.25$ nm using our heat capacity amplitude.

CONCLUSION

The heat capacity of the liquid–liquid mixture perfluoroheptane and iso-octane (2,2,4 trimethylpentane) has been measured near its upper critical consolute point using an adiabatic calorimeter. The critical exponent α was deter-

TABLE II. Parameter values resulting from fitting Eq. (1) to the heat capacity data in Table I. The units on C_{p_0} , E , and A are J/cm³K, while α is dimensionless, and T_c is in K. The reduced chi-square χ^2/N was equivalent for all three fits (≈ 0.18). The three fits are to the combined data from the two runs over the 5° temperature region where correction-to-scaling terms were negligible. Values in parentheses were fixed; the errors are one standard deviation.

	C_{p_0}	E	A^-	A^+	α	T_c
1a	1.54 ± 0.02	(-0.87)	0.0294 ± 0.0013	0.0172 ± 0.0013	(0.11)	296.375 ± 0.005
1b	1.54 ± 0.02	-1.1 ± 1.0	0.0296 ± 0.0013	0.0173 ± 0.0013	(0.11)	296.376 ± 0.005
1c	1.52 ± 0.11	(-0.87)	0.031 ± 0.011	0.018 ± 0.009	0.106 ± 0.026	296.375 ± 0.005

mined to be 0.106 ± 0.026 , in agreement with theoretical predictions. When α was fixed at its theoretical value of 0.11, our values of $A^+ = 0.0172 \pm 0.0013$, $A^- = 0.0294 \pm 0.0013$ J/($\text{cm}^3 \text{K}$), gave a ratio of A^+/A^- consistent with previous experiments and theory. Two-scale-factor universality could be directly tested in this system and was found to disagree with theoretical predictions. We suspect that a remeasurement of ξ_0 using techniques that reduce or account for multiple scattering and that more closely approach the critical temperature would give a value that is more consistent with universality predictions.

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