

Heat capacity of the liquid-liquid mixture nitrobenzene and dodecane near the critical point

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The heat capacity of the liquid-liquid mixture nitrobenzene-dodecane 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 0.124 ± 0.006 , which was consistent with theoretical predictions. When α was fixed at its theoretical value of 0.11, our value for the amplitude ratio $A^+/A^- = 0.58 \pm 0.02$ 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 a previously published value for the correlation length. © 2007 American Institute of Physics.

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INTRODUCTION

Close to a system's critical point, concentration fluctuations create correlated regions that effectively mask the individual molecules and interact to dominate the behavior of the system.^{1,2} The characteristic size of these fluctuations is called the correlation length ξ ; this correlation length diverges close to the critical point as a power law given by $\xi = \xi_0 t^{-\nu}$, where ξ_0 is the system-dependent amplitude, $t \equiv |(T - T_c)/T_c|$ is the reduced temperature, T_c is the critical temperature, and ν is a universal critical exponent whose value is 0.630.³ Many liquid-liquid mixtures will have an upper critical consolute point that is defined by a critical composition and temperature. A sample at the critical composition cooled from the homogeneous one-phase region will become opalescent due to light scattering from the fluctuations in the concentration. As the temperature is lowered still further, such a sample will spontaneously separate into two phases containing different amounts of each component where the map of composition as a function of temperature is called the coexistence curve.

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, the universal behavior for a liquid-gas system, liquid-liquid mixtures, uniaxial ferromagnetic materials, and polymer solutions.¹ Many material properties satisfy a simple power law when the system is close to the critical point: the susceptibility which follows $\chi = \chi_0 t^{-\gamma}$, the difference in composition between coexisting phases on the coexistence curve which follows $\Delta\phi = Bt^\beta$, etc. The exponents ν, β, γ , etc., are not only universal but are also interrelated so that only two are linearly independent.³ Similarly, while the amplitudes for these power-law relations are not universal, two-scale-factor universality predicts that ra-

tios of them are universal with only two linearly independent amplitudes.³ The diversity of critical systems that can be described by these universal relations indicates the fundamental nature of the theory of critical phenomena.

The heat capacity provides a delicate probe of a system near its critical point and can determine essential amplitude and exponent values. In particular, a precise measurement of the heat capacity of the liquid-liquid mixture nitrobenzene-dodecane at its critical composition will determine the amplitudes of the power-law divergence in the one- and two-phase regions and their ratio, which is predicted to be universal. An independent turbidity experiment has measured the fraction of light scattered from an incident light beam and determined the correlation length amplitude ξ_0 . Combining the one-phase, heat capacity amplitude with the correlation length amplitude allows a test of one of the universal ratios.

The heat capacity has a weak divergence near the critical point that is governed by the critical exponent α , different amplitudes in the one- and two-phase regions, and a critical contribution B_c due to the background heat capacity.⁴ Correction to scaling terms can extend the theoretical description further from the critical point.^{2,4} While a vapor-liquid system measured along the critical isochore would have a weak divergence in the heat capacity at constant volume, a liquid-liquid mixture near its critical consolute point will have the same type of divergence² in its heat capacity at constant pressure when measured along a path of constant, critical composition $x = x_c$. Specifically, the heat capacity is given by

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

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

where C_{px} is the temperature dependent heat capacity at constant pressure and at the critical composition, B_{bg} is the back-

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ground heat capacity for the normal fluids, t is the reduced temperature, $A^{+/-}$ is the amplitude of the leading divergence, and α is the universal exponent ($\alpha=0.1099\pm 0.0007$).³ The one- and two-phase amplitudes are denoted by the + and - superscripts, respectively; the background terms and the critical exponents are predicted⁴ 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. The values of B_{bg} and E can be calculated from the measured heat capacities of the pure components.⁵

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 theoretical predictions for the ratio of the leading singular heat capacity amplitude in the one-phase region to that in the two-phase region were recently reviewed⁶ and are $A^+/A^-=0.537\pm 0.019$ by $d=3$ expansion,⁷ 0.530 ± 0.003 by high-temperature series,³ 0.527 ± 0.037 by ε expansion,⁷ and 0.55 ± 0.01 by Monte Carlo simulation.⁸ One can also relate A^+ to the correlation length amplitude ξ_o in the one-phase region using two-scale-factor universality:³ $X=A^+\xi_o^3/k_B$, where k_B is Boltzmann's constant. The value of X is predicted from a $d=3$ expansion⁹ to be $X=0.019\,66\pm 0.000\,17$ and from high-temperature series³ to be $0.018\,80\pm 0.000\,08$.

These predictions have been tested in liquid-liquid mixtures with mixed results.^{1,2} Experiments¹⁰⁻¹⁷ measuring the heat capacity of liquid-liquid mixtures have determined A^+/A^- as 0.56 ± 0.04 , a value consistently larger than the 0.52 value determined in liquid-vapor systems.¹⁸ The universal ratio X requires the value of the correlation length amplitude ξ_o , which must be determined from a separate experiment. The error in ξ_o usually dominates the error in X since ξ_o enters as the cube. Recent determinations in liquid-liquid systems have found X to be 0.019 ± 0.004 in triethylamine and heavy water,¹³ 0.020 ± 0.002 in 3-methylpentane and nitroethane,¹⁴ 0.028 ± 0.007 in 2,6 dimethyl pyridine and water,¹⁹ 0.019 ± 0.003 in triethylamine and water or succinonitrile and water,¹⁵ and 0.019 to 0.020 in aniline-cyclohexane^{10,17} or *n*-butoxyethanol and water,¹⁷ while the latest liquid-vapor measurement gives 0.023 ± 0.004 in SF₆.¹⁸

There have been a few experiments where the universal ratio X was violated by being more than three standard deviations from the theoretical values. Rebillot *et al.*¹⁰ measured the heat capacity of aniline-cyclohexane and found X to be consistent with the theoretical value using one literature value for the correlation length amplitude but to be violated with another literature value. A later measurement by Pittois *et al.*¹⁷ confirmed the heat capacity data and results for that system. Oby *et al.*¹¹ measured the heat capacity of perfluoroheptane and 2,2,4-trimethylpentane and found $X=0.009\pm 0.002$ when using the literature value for the correlation length amplitude. More recently, Souto-Caride *et al.*²⁰ measured the heat capacity and viscosity for the alkanes hexane, heptane, and octane when mixed with nitrobenzene. Assuming X is universal, the heat capacity measurements give a correlation length amplitude between 0.261 and 0.271 nm

for all three systems. These values are consistent with the literature ξ_o values for the heptane and hexane systems, but not with the value measured for octane and nitrobenzene by Zhou *et al.*²¹

A number of experiments and theories explore the chain-length dependence of several critical properties, usually in polymer solutions in the large chain-length limit. Yelash *et al.*²² also explored the critical concentration and temperature in the small chain-length limit for *n*-alkanes in various solvents, one of which was nitrobenzene. When N is the number of repeating units, the behavior of the critical temperature and concentration changed from the large chain-length limit only after N became less than about 10. Zhou *et al.*²¹ investigated the correlation length amplitude ξ_o dependence on N for a series of *n*-alkanes in nitrobenzene and found the amplitudes to be independent of N within experimental uncertainty. However, recent theory and experiments indicate that $\xi_o \propto N^{(1-\nu)/2} \approx N^{0.185}$ in the large N limit.²³

In this experiment, we perform the first measurement of the heat capacity in the liquid-liquid mixture of nitrobenzene and dodecane near the critical point. Dodecane is one of the alkanes used with nitrobenzene to study the dependence of various quantities with chain length. The coexistence curve for this system has been measured by refractive index²⁴ and by dielectric constant²⁵ measurements. The electric conductivity and dielectric permittivity have also been investigated as a function of temperature, pressure, and electric field.²⁶ Turbidity measurements have determined²⁷ the correlation length amplitude in the one-phase region to be $\xi_o=0.174\pm 0.002$ nm, which can be combined with our measurement of A^+ to test the universal ratio X .

EXPERIMENT

A critical composition sample of nitrobenzene and dodecane was used. The dodecane was 99+% pure from Sigma-Aldrich while the nitrobenzene was purchased from Fluka as 99.5% pure; both were used without further purification. The mixture used in this experiment was 55.20% by mass ($43.39\pm 0.01\%$ by volume) nitrobenzene with a total mass of 15.155 g, which is a volume of 16.02 ml. This concentration is the literature critical concentration²⁴ of 55.2% by mass ($43.4\pm 0.1\%$ by volume) nitrobenzene and is the same composition used by other investigators of this system.^{25,26} 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 one atmosphere. This system exhibits an upper consolute point around 302 K.

The heat capacity of the critical composition of nitrobenzene and dodecane was measured using an adiabatic calorimeter, which we have already described.^{10,11,15} 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.¹³⁻¹⁵ The cell is heated for a fixed period of time (approximately 240 s) by applying a constant current (to 0.01%) through manganin wire wrapped in grooves on the outside of the cell body. After the heater is turned off and the sloshing stops, the

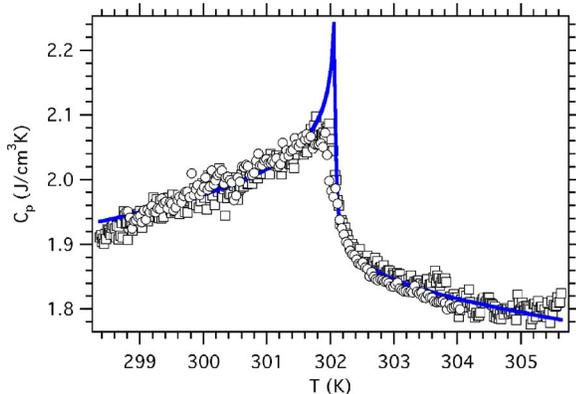


FIG. 1. (Color online) The measured heat capacity of nitrobenzene-dodecane plotted as a function of temperature T for two data runs of different heater powers. Consistency between runs indicates a good adiabatic environment. The error bars are omitted for clarity but are about ± 0.03 J/(cm³ K) for run 1 (squares) and ± 0.05 J/(cm³ K) for run 2 (circles), which is the scatter in the data. The solid line is fit 1 from Table I.

thermostat reaches a constant plateau temperature before the next heating period. The time from one plateau to the next is approximately 15 min. The heating power is either 4.28 mW (run 1) or 7.83 mW (run 2) resulting in temperature steps of approximately 20 mK or 35 mK, respectively. This step process has been described previously.^{10,11}

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 thermostat is determined by measuring the voltage across a standard resistor and across each thermistor using a 7 1/2 digit Keithley 2001 multimeter. The cell thermistor's resistance is determined from an average voltage measured by a Keithley 2182 nanovoltmeter synchronized to a low-frequency, switching ± 10 μ A current from a Keithley 2400 sourcemeter; the average of the alternating voltages corrects for thermocouple effects. The cell thermistor was calibrated against a platinum resistance thermometer (Guildline 9540) with an accuracy of ± 0.02 K. When no heat is applied to the cell heater, the equilibrium cell temperature stays constant within our resolution of 0.1 mK. We correct for any systematic drift in the temperature of this plateau, which reflects small heat leaks in the thermostat and control system. The specific heat of the copper cell was determined from a cali-

bration using nanopure water and was taken into account in reporting the heat capacity of a critical composition of the nitrobenzene and dodecane system 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 minimize²⁸ the reduced chi-square χ^2/N . In analyzing the heat capacity data, we simplify Eq. (1) by using a parameter $C_{po} = (B_c + B_{bg})$. A smooth, continuous background specific heat near the critical point is expected, which means the background amplitudes C_{po} and E are the same in the one- and two-phase regions, and we force equal exponent values above and below the critical point as predicted by theory.^{2,4} We simultaneously fit these equations to the one- and two-phase data, which are sufficiently close to the critical point to neglect correction to scaling terms.

The combined runs were fitted over the entire 7 K temperature region around the critical temperature. Those points in the two-phase region within $t < 10^{-4}$ were omitted from the fit due to rounding in the heat capacity that occurs as the system goes through the critical point. In the following, our quoted parameter errors are those given by the analysis program IGOR²⁹ and should be considered the 1σ error. These 552 data points were well described by six adjustable parameters: C_{po} , E , A^+ , A^- , T_c , and α . In all the fits, the critical temperature was 302.09 ± 0.01 K, a value consistent with published values ranging from 300.3 to 302.7 K. Variation of the critical temperature among samples is common due to the effect of small amounts of impurities.³⁰ The parameter E should reflect the noncritical fluid behavior and had a small negative value of -3.8 ± 0.5 J/(cm³ K) for the composition used.⁵ Allowing the critical exponent α to vary determined a value of 0.124 ± 0.006 , 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 intercompared through universal ratios such as X . Thus, the other two fits have α fixed.

The heat capacity fits given in Table I provide a consistent set of amplitude values. The background amplitude of Eq. (1) is then $B_c = -1.83 \pm 0.02$ J/(cm³ K), while $A^+ = 0.0143 \pm 0.0009$ and $A^- = 0.0248 \pm 0.0009$ J/(cm³ K), where all the errors are one standard deviation estimates. Our value of the universal ratio $A^+/A^- = 0.58 \pm 0.02$ is consistent

TABLE I. Parameter values resulting from fitting Eq. (1) to all our heat capacity data except some two-phase data very close to the critical point. The units on C_{po} , E , A^- , A^+ are J/(cm³ K) while α is dimensionless. In fits 1 and 2, the critical exponent α was fixed at its theoretical value of 0.11, while the universal ratio of the one-phase and two-phase amplitudes A^+/A^- was fixed at 0.53 for fits 2 and 3. Parameter uncertainties represent one standard deviation estimates from the fitting program. The critical temperature for all fits was the same 302.09 ± 0.01 K; these fits have equivalent reduced chi squares.

Fit	C_{po}	E	A^-	A^+	α
1	1.61 ± 0.02	-3.2 ± 0.4	0.0248 ± 0.0009	0.0143 ± 0.0009	0.11
2	1.656 ± 0.002	-4.3 ± 0.2	[0.0223]	0.0118 ± 0.0001	0.11
3	1.652 ± 0.003	-3.4 ± 0.4	[0.0233]	0.0123 ± 0.0003	0.124 ± 0.006

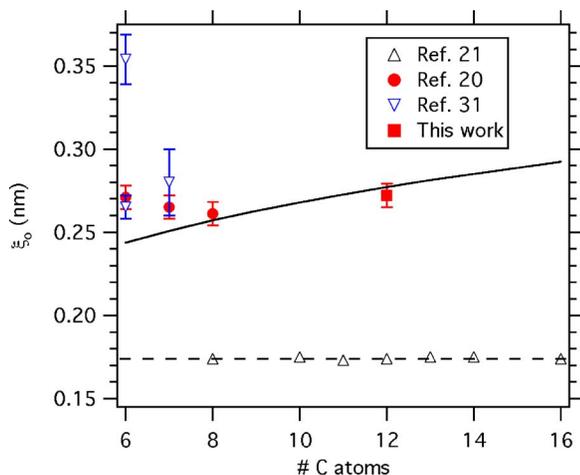


FIG. 2. (Color online) The correlation length amplitudes are shown for different n -alkanes with nitrobenzene. The values determined by light or x-ray scattering are indicated by open symbols while values calculated from heat capacity measurements assuming X is universal are solid symbols. The dashed line connects Zhou's measurements from Ref. 21, whose error bars are smaller than the plot symbols. The solid line shows the large chain-length limit $N^{0.185}$.

with experimental values determined in several liquid-liquid systems recently and with theoretical predictions. As fit 2 in Table I shows, our data can be fitted just as well when the ratio is fixed at the theoretical value of $A^+/A^- = 0.53$. Thus, we use an average from fits 1 and 2 for our value of $A^+ = 0.013 \pm 0.001$ J/(cm³ K) from this experiment.

The two-scale-factor universality ratio X can be calculated from our value of A^+ and the literature value from Zhou *et al.*²⁷ of $\xi_o = 0.174 \pm 0.002$ nm, which gives $X = 0.0050 \pm 0.0006$. This value substantially disagrees with other recent experimental determinations and with theoretical predictions. If we assume two-scale factor universality with $X = 0.019$, then our A^+ value would predict a value of $\xi_o = 0.272 \pm 0.007$ nm.

We compare the values of the correlation length amplitude ξ_o for several n -alkanes with nitrobenzene in Fig. 2. Some values were measured using light or x-ray scattering³¹ while other values were calculated from heat capacity amplitudes assuming a universal value of X .²⁰ With the exception of the turbidity experiments of Zhou *et al.*²¹ that gave a uniform ξ_o of 0.175 nm, all the other values are in the range of 0.26–0.35 nm. Our calculated value for $\xi_o = 0.272 \pm 0.007$ nm is consistent with these larger values. While it is possible that X is not universal, substantial experimental evidence suggests that X is a universal quantity whose value is consistent with, though slightly larger than, the theoretical estimates of 0.019. Our calculated value for ξ_o together with other values calculated from heat capacity measurements or determined optically suggests an effectively constant value as the number of repeating units N increases (see Fig. 2). It is also possible that the weak dependence on N represented by the large chain-length limiting result of $N^{0.185}$ has occurred in the correlation length amplitude values with only $N \approx 10$ (see solid line in Fig. 2). Zhou

*et al.*²¹ also found the correlation length amplitude to be virtually a constant for different N , although the value was significantly smaller than these other values.

CONCLUSION

The heat capacity of the liquid-liquid mixture nitrobenzene and dodecane has been measured near its upper critical consolute point using an adiabatic calorimeter. The critical exponent α was determined to be 0.124 ± 0.006 , in agreement with theoretical predictions. When α was fixed at its theoretical value of 0.11, our data give $A^+ = 0.013 \pm 0.001$ J/(cm³ K) and 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 when using the literature value for the correlation length amplitude. If the universal ratio X is valid, then we calculate the correlation length amplitude ξ_o to be 0.272 ± 0.007 nm in this nitrobenzene-dodecane system.

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