

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

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The turbidity of the liquid–liquid mixture perfluoroheptane and 2,2,4-trimethylpentane (also known as iso-octane) has been measured and used to determine the correlation length amplitude ξ_0 . By measuring the ratio of the transmitted to incident light intensities over three decades in reduced temperature, we are able to determine that $\xi_0 = 0.253 \pm 0.005$ nm. This value differs significantly from that reported in the literature. The earlier literature value for ξ_0 , when combined with the amplitude A^+ determined in a recent heat capacity measurement on this system, produced the two-scale-factor universality constant $X = A^+ \xi_0^3 / k_B = 0.009 \pm 0.002$, which was not consistent with other experiments and theories that had found a value between 0.018 and 0.020. However, when we combine the value of ξ_0 determined in this experiment with the amplitude A^+ then the two-scale-factor universality constant $X = 0.020 \pm 0.002$, which is quite consistent with other determinations. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518009]

INTRODUCTION

A recent experiment¹ investigating the heat capacity of the liquid–liquid mixture perfluoroheptane and 2,2,4-trimethylpentane (also known as iso-octane) found an amplitude A^+ for the leading divergence which violated two-scale-factor universality when combined with a literature value² of the correlation length amplitude ξ_0 . It was a surprising result and it was speculated¹ that a more careful measurement would find a value of ξ_0 which was consistent with two-scale-factor universality. We report here just such a measurement.

The theory of critical phenomena has described physical processes which are universal for liquid–gas, liquid–liquid mixtures, uniaxial ferromagnetism, and polymer solutions near a critical point. These predictions have, by and large, been verified experimentally.³ 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 ($\nu = 0.630$).⁴ Similarly, a liquid–liquid mixture at its critical composition will have a weak divergence in its heat capacity at constant pressure that is governed by the critical exponent $\alpha = 0.11$. The critical contribution to the heat capacity is^{5,6} $C_{\text{crit}} = (A^+ / \alpha) |t|^{-\alpha}$. Thus, physical phenomena describing a system close to its critical point have a universal form independent of the system involved.

The turbidity τ is the inverse of an effective extinction

length and is defined by $\tau = (-1/L) \ln(I_t / I_0)$, where L is the length of the scattering medium and I_t is the transmitted, and I_0 the incident, light intensity. The turbidity is caused by light scattering from concentration fluctuations in the fluid mixture near the critical point. Assuming Ornstein–Zernike scattering,⁷ an expression for the turbidity can be developed by integrating the light scattered out of the incident beam. A small asymmetry in the forward direction caused Fisher⁸ to introduce a critical exponent η whose value⁸ is small ($\eta = 2 - \gamma/\nu = 2 - 1.2371/0.630 = 0.036$), and results in a negligible effect on the turbidity at the level of this experiment.^{9,10} The turbidity is given by^{7,9}

$$\tau = \tau_0 (1+t) t^{-\gamma} \left[\frac{2a^2 + 2a + 1}{a^3} \ln(1+2a) - \frac{2(1+a)}{a^2} \right], \quad (1)$$

where

$$\tau_0 = \frac{\pi^3}{\lambda_0^4} \left[\frac{\partial n^2}{\partial \phi} \right]^2 k_B T_c \chi_0,$$

$a = 2k_0^2 \xi^2$, $\xi = \xi_0 t^{-\nu}$, $k_0 = 2\pi n / \lambda_0$, $n = 1.327$ is the refractive index of the mixture,¹¹ λ_0 is the vacuum wavelength of the light, the turbidity amplitude τ_0 is a quantity dependent on the system, and ν and γ are universal critical exponents. Good data close to T_c are crucial in determining ξ_0 which enters in a complicated fashion through a . If the system is further from T_c yet still in the asymptotic region described by simple scaling, then the turbidity has a simple power law dependence $\tau = 8\tau_0 t^{-\gamma/3}$. Close to T_c , the turbidity varies much more slowly and is a function of both τ_0 and ξ_0 : $\tau = [\tau_0 / (k_0 \xi_0)^2] \ln(2a)$. In experiments extremely close to T_c , the nonzero value of η becomes important and such a logarithmic dependence is not expected.¹⁰ The compressibility amplitude χ_0 can be estimated from the value of τ_0 deter-

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mined in this study by using the Lorentz–Lorenz relation to estimate the composition dependence of the refractive index, $\partial n^2/\partial\phi$.

The ratio of certain amplitudes is expected to be universal for all systems in a given universality class (three-dimensional Ising for bulk, liquid–liquid mixtures). One of those combines the leading, singular, heat capacity amplitude A^+ with the correlation length amplitude ξ_0 in the one-phase region using two-scale-factor universality.⁴

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

where k_B is Boltzmann's constant. The value of X (also referred to as Q^+) is predicted from a $d=3$ expansion¹² to be $X=0.019\,66\pm 0.000\,17$ and from high-temperature series⁴ to be $0.018\,80\pm 0.000\,08$. Experimentally, the error in ξ_0 usually dominates the error in X since ξ_0 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,¹⁵ 0.020 in nitroethane and 2,2,4-trimethylpentane,⁶ 0.019 ± 0.003 in triethylamine and water,¹⁶ 0.019 ± 0.001 in succinonitrile and water,¹⁷ but a small 0.009 ± 0.002 in perfluoroheptane and 2,2,4-trimethylpentane.¹ The latest liquid–vapor measurement gave 0.023 ± 0.004 in SF_6 .¹⁸ All of the experimental values were within experimental error of the theoretical values except for the perfluoroheptane system, which we investigate here.

In this experiment, we perform the first measurement of the turbidity in the liquid–liquid mixture of perfluoroheptane and 2,2,4-trimethylpentane near the critical point. The components in this system have very different densities and the location of the critical point is quite different from that predicted by regular solution theory.¹⁹ Light scattering and diffusivity measurements have determined² the correlation length amplitude in the one-phase region to be $\xi_0=0.194\pm 0.025$ nm along with a critical exponent $\nu=0.65\pm 0.03$, but these values are based on measurements over only one decade in reduced temperature and without a correction for multiple scattering.²⁰ Our turbidity measurement will extend over several decades in reduced temperature and determine a value of ξ_0 which is not significantly influenced by multiple scattering over the temperature region investigated.²¹

EXPERIMENT

The coexistence curve of perfluoroheptane and iso-octane (2,2,4 trimethylpentane) was crudely measured by Hildebrand *et al.*¹⁹ using seven data points. From this data, the critical composition is approximately 32.8% by mass (54.5% by volume) iso-octane, which is the composition used by other investigators of this system.^{2,22,23} 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. This system exhibits an upper consolute point around 23 °C.

We collected turbidity data on a sample transferred in the one-phase region from the heat capacity experiment,¹ which had a composition of 32.4% by mass iso-octane, (sample 1). However, we noticed that the meniscus did not appear in the center of the cell when the fluids were just into the two phase region as it would if the composition were the critical composition. By measuring the meniscus location as we went deeper into the two-phase region, a corrected composition could be determined.²⁴ Thus, we found the critical composition to be a slightly lower 31.4% by mass (53.3% by volume) iso-octane. The turbidity was also measured for this composition (sample 2), which had the meniscus appear in the middle when close to, but below, the critical temperature.

Our light scattering cells were commercial (Spectrocell) made of optical glass with a cylindrical design 22 mm in diameter and a path length of 1.00 cm. Each had a fill tube which was heated and drawn closed to seal the sample. The temperature of the cell was controlled by immersion in a well-stirred, filtered water bath, as described previously.^{9,17,25} The temperature was controlled with a Tronac PTC-41 to give ± 0.2 mK maximum excursions over 1 h. The temperature was monitored with a calibrated Thermometrics thermistor whose resistance was measured with a Keithley 2010 digital multimeter to an accuracy of ± 10 mK and a precision of ± 0.1 mK.

The optical system optimized the precision and accuracy of the light intensity measurements that allowed the turbidity to be determined. The optics has been fully described^{17,25} and includes a laser power amplitude controller that provided an incident intensity that varied less than 0.1% long term. The low power laser beam ($\lambda_0=632.8$ nm) traveled through the water bath where the cell was oriented with the laser beam along the cell's cylindrical axis. The cell could be moved out of the beam path to determine the absolute turbidity of the fluid sample. The transmitted light intensity was detected by a photodiode with an acceptance angle of 0.3° .

The procedure of taking intensity measurements with the cell in and out of the beam path corrects for reflected and absorbed light from the bath, but not for reflected light from the cell windows. The turbidity due to reflections from the cell windows contributes to a “background” turbidity τ_b , which is determined by the value of the turbidity well above the critical temperature and is subtracted from the measured turbidity at each temperature to obtain the absolute turbidity τ .

$$\tau = -\frac{1}{L} \ln\left(\frac{I_1}{I_2}\right) - \tau_b, \quad (2)$$

where I_1 and I_2 are the ratios of the transmitted to reference intensities with and without the cell in the beam, respectively.

Reproducible data were taken for both samples 1 and 2 in the one-phase region when $2\times 10^{-6} < t < 10^{-2}$ ($0.0006^\circ < T - T_c < 3^\circ$). The critical temperature was slightly different for each cell, but neither drifted in time. In this mixture, no difference in the turbidity was measured between the two samples. The absolute turbidity data are listed in Table I and shown in Fig. 1.

TABLE I. The absolute turbidity τ for different reduced temperatures t for both samples 1 and 2. The error in the reduced temperature was 3×10^{-6} (1 mK) and in the absolute turbidity it was 0.01 cm^{-1} . The critical temperature for sample 1 was 296.220 K and 296.362 K for sample 2.

Sample 1		Sample 2	
t	τ	t	τ
0.000 012	2.041	0.004 832	0.009
0.000 019	1.720	0.004 398	0.005
0.000 027	1.493	0.003 439	0.013
0.000 036	1.325	0.002 584	0.005
0.000 042	1.250	0.001 650	0.054
0.000 053	1.085	0.001 224	0.090
0.000 064	1.017	0.000 796	0.121
0.000 077	0.904	0.000 367	0.298
0.000 082	0.891	0.000 165	0.583
0.000 091	0.830	0.000 122	0.724
0.000 101	0.777	0.000 102	0.816
0.000 112	0.703	0.000 089	0.889
0.000 119	0.730	0.000 077	0.978
0.000 129	0.695	0.000 066	1.049
0.000 133	0.671	0.000 049	1.210
0.000 146	0.629	0.000 042	1.295
0.000 154	0.588	0.000 033	1.433
0.000 165	0.582	0.000 027	1.579
0.000 168	0.539	0.000 023	1.605
0.000 202	0.493	0.000 018	1.746
0.000 223	0.467	0.000 013	1.894
0.000 242	0.421	0.000 010	2.006
0.000 265	0.392	0.000 005	2.190
0.000 284	0.374	0.000 002	2.505
0.000 315	0.345	0.000 587	0.176
0.000 406	0.267	0.001 013	0.087
0.000 420	0.271	0.000 845	0.150
0.000 631	0.204	0.000 743	0.131
0.000 841	0.159	0.000 886	0.119
0.001 136	0.096	0.001 419	0.062
0.001 345	0.071	0.003 401	0.019
0.002 769	0.045	0.004 649	0.006
0.004 009	0.016	0.006 923	0.002
0.009 965	0.004	0.012 794	0.001
0.010 921	0.004		

ANALYSIS AND DISCUSSION

The data from both samples shown in Table I were analyzed using a properly weighted least-squares fit²⁶ where the parameters ξ_0 , τ_0 , ν , and γ can all be adjusted in Eq. (1). The resulting values of the parameters are given in Table II, along with the one standard deviation uncertainties. The data reported in Table I were well explained by an $n=1$ Ising model as shown by the four fits in Table II.

The first three fits in Table II use the exponents ν and γ fixed at their theoretical values,⁴ which gave equivalent values for the other parameters independent of which sample's data were fit. The first two fits confirm the visual observation illustrated in Fig. 1 of the consistency of the measured turbidity in the two samples despite the slightly different compositions. The third fit varies the background turbidity by about the resolution in the turbidity. The last fit allowed the five parameters τ_0 , ξ_0 , ν , γ , and τ_b to vary freely. When all 71 points were fit by Eq. (1), the values of the exponents were $\nu=0.66 \pm 0.02$ and $\gamma=1.29 \pm 0.08$, which are close to the known Ising model values⁴ of $\nu=0.6300 \pm 0.0002$ and

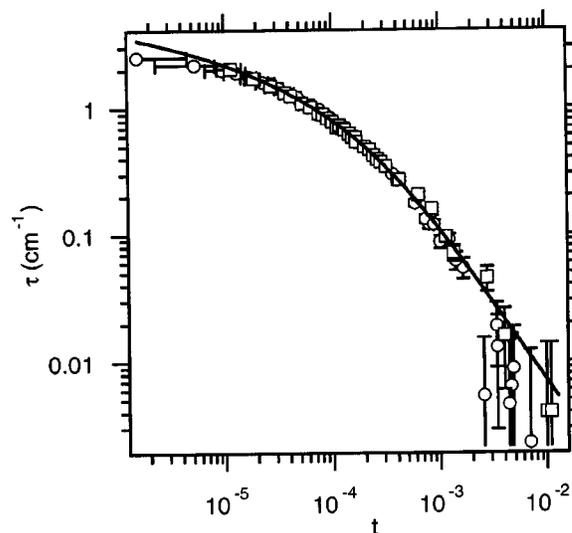


FIG. 1. Turbidity τ in perfluoroheptane and iso-octane as a function of reduced temperature $t=(T-T_c)/T_c$ from the data in Table I. The squares are sample 1 while the circles are sample 2. The solid line is the second fit from Table II.

$\gamma=1.2371 \pm 0.0004$. Since the turbidity has a complicated dependence on the critical exponents, it was not possible to accurately determine the critical exponents from this experiment. However, the exponents are consistent with the Ising universality class. Because of the sensitive dependence of the amplitudes on the values of the critical exponents, the best fit is chosen as the second fit where the exponents are fixed at the theoretical values and the background turbidity was that determined experimentally.

Our determination for $\xi_0=0.253 \pm 0.005 \text{ nm}$ and $\tau_0=(8.88 \pm 0.16) \times 10^{-6} \text{ cm}^{-1}$ can be compared to the value $\xi_0=0.194 \pm 0.025 \text{ nm}$ Dubois and Berge² reported for this system. Dubois and Berge collected and analyzed diffusivity data over a limited temperature region ($2^\circ < T-T_c < 16^\circ$) and determined $\nu=0.65 \pm 0.03$ and a ξ_0 that was significantly smaller than our value. The difference in amplitude may be due to the additional decades in reduced temperature that we explored. Had Dubois and Berge known about and used the currently accepted value of the critical exponent ν , their value of ξ_0 would have been less than the value published and even further from the value we found with ν fixed at 0.63. However, as shown by the last fit in Table II when we allow all the amplitudes and exponents to vary, we obtain values of ξ_0 and ν that are consistent with those of Dubois and Berge. This is because of the coupling among the amplitudes and the exponents combined with the large uncertainties that arise when the exponents can vary in the fit. Comparisons to universal amplitude ratios should use exponents fixed at the now well-determined theoretical values when determining the relevant amplitudes.

We can also do a crude test on our amplitude $\tau_0=(8.88 \pm 0.16) \times 10^{-6} \text{ cm}^{-1}$, which is related to χ_0 as shown in Eq. (1) provided the concentration dependence of the refractive index can be determined. While no measurements exist, we can estimate $\partial n^2/\partial \phi=0.28 \pm 0.01$ from the Lorentz-Lorenz relation and refractive index measurements we have taken on the pure components. This allows the uni-

TABLE II. Parameter values resulting from fitting Eq. (1) to either sample 2 or the combined turbidity data in Table I. Values in parentheses are fixed while errors are one standard deviation estimates. χ^2/N is the reduced chi-square. $\delta\tau_b$ is an adjustment to the background turbidity used in Eq. (2).

	$\tau_0(\times 10^6 \text{ cm}^{-1})$	ξ_0 (nm)	γ	ν	$\delta\tau_b(\times 10^2 \text{ cm}^{-1})$	χ^2/N
Sample 2	8.42 ± 0.24	0.236 ± 0.007	(1.237)	(0.63)	(0)	1.19
Combined	8.88 ± 0.16	0.253 ± 0.005	(1.237)	(0.63)	(0)	1.23
Combined	9.50 ± 0.26	0.268 ± 0.007	(1.237)	(0.63)	-0.9 ± 0.3	1.20
Combined	6.0 ± 3.2	0.20 ± 0.03	1.29 ± 0.08	0.66 ± 0.02	(0)	1.23

versal amplitude ratio R to be estimated,²⁴ where theory predicts⁴

$$R = (Q_c)^{1/3} = \xi_0 \left(\frac{B^2}{k_B T_c \chi_0} \right)^{1/3} = 0.6931 \pm 0.0007,$$

and B is the amplitude of the coexistence curve (in volume fraction) that we determined from the few data points in the literature¹⁹ to be 0.93 ± 0.02 when $\beta = 0.326$. Our values of ξ_0 and τ_0 from the second fit in Table II give a value of $R = 0.59 \pm 0.06$, which is quite consistent with the theoretical prediction considering the assumptions and systematic errors unaccounted for in the one standard deviation, random error quoted.

The two-scale-factor universality ratio $X = A^+ \xi_0^3 / k_B$ can be calculated directly from our value¹ of $A^+ = 0.0172 \pm 0.0013 \text{ J}/(\text{cm}^3 \text{ K})$ and $\xi_0 = 0.253 \pm 0.005 \text{ nm}$, which gives $X = 0.020 \pm 0.002$. This value agrees with other recent experimental determinations and with theoretical predictions.

CONCLUSION

The turbidity of the liquid–liquid mixture perfluoroheptane and iso-octane (2,2,4 trimethylpentane) has been measured near its upper critical consolute point over several decades in reduced temperature. The critical exponent ν and γ were consistent with three-dimensional, $n = 1$ (Ising) values. When the exponents were fixed at their theoretically predicted values then the amplitudes were determined to be $\xi_0 = 0.253 \pm 0.005 \text{ nm}$ and $\tau_0 = (8.88 \pm 0.16) \times 10^{-6} \text{ cm}^{-1}$. Our value of ξ_0 is determined from a wide range of reduced temperatures and is a value that is consistent with universal amplitude relations. Two universal ratios could be calculated. One can be directly verified from ξ_0 and the value of A^+ determined by measuring the heat capacity in the same system; we find $X = 0.020 \pm 0.002$, which is consistent with previous experiments and theory. The other amplitude R could only be estimated from existing measurements, but it also appears to be verified.

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