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Kumaran, M. K.

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Kumaran, M.K.

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Institute for Research in Construction Institut de recherche en construction Molar Volume and Speed of Sound in the Neighbourhood of the Liquid-liquid Critical Point of (Tetrachloromethane + Tetradecafluoromethylcyclohexane)

Mavinkal K Kumaran Institute for Research in Construction National Research Council of Canada Ottawa, Ontario K1A 0R6 Canada

#### Abstract

The universal critical exponents given by the three-dimensional Ising model and derived through renormalization group calculations accurately describe the gas-liquid critical phenomena of pure fluids and the liquid-liquid critical phenomena of binary liquid mixtures. Thus the behaviour of order parameters, such as density or molar volume, along the respective coexistence curve is well represented by the exponent  $\beta = 0.325$ . For a binary liquid mixture, along the critical isotherm, the critical anomaly of molar volume shall be described by the exponent  $(1 - \alpha)/\beta = 2.74$ . The experimental data obtained for the full range of composition for (tetrachloromethane + tetradecafluoromethylcyclohexane) confirm this requirement.

Speed of sound, though strictly not a generalized density, should be associated with the same set of exponents that describe the behaviour of molar volume. The results on the speed of sound of (tetrachloromethane + tetradecafluoromethylcyclohexane) along the coexistence curve and along the full range of the critical isotherm generally agree with the universality concept.

Keywords: Critical phenomena; Critical indices; Molar volume; Speed of sound

#### 1. Introduction

Three dimensional Ising model captures the details of the gas-liquid critical phenomenon shown by pure fluids and the liquid-liquid critical phenomenon shown by binary liquid mixtures [1,2]. A set of universal critical exponents, derived using renormalization group calculation, quantitatively represents the behaviour of majority of pure fluids and binary liquid mixtures, in the neighbourhood of the respective critical points. As an exception, for a while it was believed that ionic fluids might not be Ising-like asymptotically [3-5]. Although the approach to asymptotic behaviour may be somewhat different in aqueous ionic fluids, the asymptotic behaviour itself is now believed to be Ising-like and described by the same set of universal critical exponents [6]. The universal values of the critical exponents calculated by Le Guillou and Zinn-Justin [7] are as follows:

$$\alpha = 0.11$$
  $\beta = 0.325$ 

The scaling laws [8] have defined exact relationships between the various critical exponents; the Rushbrooke and Griffiths inequalities [9,10] have turned out to be equations. Hence the other commonly used critical exponents have been given the following values [1]:

$$\gamma = 1.24$$
  $\delta = 4.81$   $\mu = 1.26$   $\nu = 0.63$ 

The exponent  $\alpha$  that describes the divergence of constant-volume heat capacity of pure fluids and the exponent  $\beta$  that defines the shape of coexistence curve on a generalized density – temperature plain are the subjects of this paper. For a pure fluid, the exponents  $\gamma$ ,  $\delta$ ,  $\mu$  and  $\nu$  are associated with isothermal compressibility, critical isotherm on the pressure-volume-temperature surface, surface tension and correlation length respectively [1].

Widom and Khosla [11] have concluded that for a binary liquid mixture that shows a liquid-liquid critical phenomenon, the quantity  $|V_m - V_{m,c}|$  approaches the critical solution point as

$$|V_{m} - V_{m,c}| \sim A_{1} |x - x_{c}| + A_{2} |x - x_{c}|^{(1 - \alpha)/\beta}$$
 (1)

where  $V_m$  is the molar volume of the mixture at mole fraction x. The quantities  $V_{m,c}$  and  $x_c$  are respectively the molar volume and mole fraction of the mixture at the critical solution point and  $A_1$ and  $A_2$  two proportionality constants or amplitudes, characteristic of the heterogeneous system under investigation. Constant pressure is implied in equation (1). Kumaran [12] has analyzed a set of experimental results obtained on the molar volume of (methylcyclohexane + tetradecafluoromethylcyclohexane) [13] in terms of equation (1) and obtained quantitative agreement. New sets of results on (tetrachloromethane + tetradecafluoromethylcyclohexane) is reported in this paper and the requirement imposed by equation (1) is reexamined.

The exponent  $\beta$ , as stated above, is associated with a generalized density. For the liquidliquid critical phenomenon there are several choices for the generalized density. The (mass) density, mole fraction, molar volume and volume fraction – all are equivalent choices. A quite different choice is the speed of sound.

Speed of sound is not really a proper density: it is not of the form (X / Y) where both X and Y are extensive in the restricted sense of each being the sum of the X's and Y's of the constituent parts of a heterogeneous system. Still it is expected that asymptotically on approach to the critical solution point, the same two critical exponents,  $\alpha$  and  $\beta$ , that describe the behaviour of V<sub>m</sub> in the neighbourhood of the critical solution point shall describe the behaviour of speed of sound [14]. According to Van Dael [15], the speed of sound, u, of either coexisting phase will approach u<sub>c</sub>, the speed of sound of the binary mixture at the critical solution point as

$$|u - u_c| \sim B_1 \tau^{\beta} \tag{2}$$

where  $\tau = |T - T_c| / T_c$  and T is the temperature of the coexisting phase and  $T_c$  the critical solution temperature of the binary mixture. For a wide range of temperature, equation (2) is written as [16]

$$|u - u_{c}| = B_{1}\tau^{\beta} + B_{2}\tau^{2\beta} + B_{3}\tau^{\beta+\Delta} + B_{4}\tau^{1-\alpha} + \dots$$
(3)

where  $\Delta$  = 0.5, the Wegner correction exponent [17]. In equations (2) and (3) the B's are proportionality constants similar to A<sub>1</sub> and A<sub>2</sub>.

The exponent  $(1 - \alpha)/\beta$  may then describe the critical anomaly shown by speed of sound at the critical solution temperature on approach to the critical solution point as

$$|u - u_c| \sim C_1 |x - x_c| + C_2 |x - x_c|^{(1 - \alpha)/\beta}$$
 (4)

where C<sub>1</sub> and C<sub>2</sub> are two characteristic proportionality constants, similar to the A's and B's.

This paper also presents results from measurements on the speed of sound of (tetrachlomethane + tetradecafluoromethylcyclohexane) along the coexistence curve and at the critical solution temperature for the full composition range and analyzes those results in terms of equations (3) and (4).

#### 2. Experimental

The tetrachloromethane (Fisher Scientific Co., certified ACS Spectroanalyzed) and tetradecafluoromethycyclohexane (Aldrich Chemical Co., Lot No. 1611KH and showed no significant impurities from a Chromatographic analysis) used in the present investigation are from the same batch as reported in an earlier investigation [18]. The densities of the materials at 298.15 K were respectively 1584.2 kg m<sup>-3</sup> and 1787.4 kg m<sup>-3</sup>. These agree well with literature values: 1584.3 kg m<sup>-3</sup> and 1787.0 kg m<sup>-3</sup> respectively [19, 20]. The critical solution temperature for the mixture at atmospheric pressure was determined to be ( $301.91 \pm 0.04$ ) K by observing the unmixing temperature of several critical mixtures with the composition xc-C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub> = 0.286 ± 0.005 [21]. The excess molar volume of the mixture for the full composition range was determined at ( $301.950 \pm 0.002$ ) K, as indicated by the unmixing temperature of a critical mixture prior to those measurements, using the dilution dilatometer described by Kumaran and McGlashan [22] with an estimated accuracy better than 0.1% (An interesting feature of the excess molar volume data in the critical region is presented in the Appendix). The temperature coefficient of density for the two pure components was determined using a densimeter to be -2.801 kg m<sup>-3</sup> K<sup>-1</sup> for CC<sub>6</sub>F<sub>11</sub>CF<sub>3</sub> and -1.962 kg m<sup>-3</sup> K<sup>-1</sup> for CCl<sub>4</sub>.

The pulse-echo overlap method combined with a dilution technique [18,23, 24] was used to measure the speed of sound with a reproducibility of 0.02 m s<sup>-1</sup> and an accuracy better than 0.2 m s<sup>-1</sup> for completely miscible binary mixtures. The measurement details for compositions along the coexistence curve were reported earlier [18]. Two separate series of dilution measurements were carried out at (301.878  $\pm$  0.002) K , as indicated by the unmixing temperature of a critical mixture prior to those measurements.

#### 3. Results

The critical composition was assigned  $xc-C_6F_{11}CF_3 = 0.2855$  [19]. From the excess molar volume measurements,  $V_{m,c} = 128.50 \text{ cm}^3 \text{ mol}^{-1}$ . As reported earlier [18], for a critical mixture with an unmixing temperature of (301.901 ± 0.002) K, the speed of sound at the critical point was determined to be (701.21 ± 0.02) m s<sup>-1</sup> (The frequency at which this measurements were made was not recorded). The above four values are used to derive the quantities listed in Tables 1 to 4.

Table 1. The change in the quantity  $|u - u_c|$  with  $\tau$  along that branch of the coexistence curve where xc-C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub> is > 0.2855.

τ	u – u <sub>c</sub>  , m s <sup>-1</sup>	τ	u – u <sub>c</sub>  , m s <sup>-1</sup>
0.002531	40.32	0.000593	26.48
0.00206	38.41	0.000454	24.27
0.001716	36.46	0.000325	21.52
0.001418	34.62	0.000222	18.81
0.001156	32.64	0.000149	16.04
0.000951	30.68	0.000103	12.88
0.000752	28.65	5.63E-05	9.08

Table 2. The change in the quantity  $|u - u_c|$  with  $\tau$  along that branch of the coexistence curve where  $xc-C_6F_{11}CF_3$  is < 0.2855.

τ	u – u <sub>c</sub>  , m s <sup>-1</sup>	τ	u – u <sub>c</sub>   , m s <sup>-1</sup>
0.002806	52.1	0.000232	20.75
0.002289	48.84	0.000195	19.66
0.001984	46.19	0.000129	16.29
0.001514	41.72	9.61E-05	14.65
0.001163	37.9	7.95E-05	12.31
0.000778	32.71	6.96E-05	10.26
0.00052	27.89	2.65E-05	6.14
0.000368	24.43		

x – x <sub>c</sub>	$ V - V_{m,c} $ , cm <sup>3</sup> mol <sup>-1</sup>	x – x <sub>c</sub>	$ V - V_{m,c} , cm^3 mol^{-1}$
0.0011	0.115	0.1300	13.493
0.0238	2.486	0.1647	17.045
0.0272	2.839	0.1851	19.122
0.0433	4.517	0.2700	27.646
0.0492	5.133	0.3620	36.647
0.0653	6.807	0.5613	55.196
0.1009	10.495		

Table 3. The change in the quantity  $|V - V_{m,c}|$  with  $|x - x_c|$  along the critical isotherm where  $xc-C_6F_{11}CF_3$  is > 0.2855.

Table 4. The change in the quantity  $|V - V_{m,c}|$  with  $|x - x_c|$  along the critical isotherm where  $xc-C_6F_{11}CF_3$  is < 0.2855.

x – x <sub>c</sub>	$ V - V_{m,c} $ , cm <sup>3</sup> mol <sup>-1</sup>	x – x <sub>c</sub>	$ V - V_{m,c} $ , cm <sup>3</sup> mol <sup>-1</sup>
0.0147	1.534	0.1581	16.72
0.0375	3.918	0.1854	19.685
0.0626	6.553	0.2142	22.863
0.0861	9.032	0.2402	25.77
0.1134	11.927	0.2673	28.85
0.1353	14.263		

The speed of sound along the critical isotherm was measured at a frequency of 2.36 MHz and from the knowledge of the critical composition,  $u_c$  at that frequency is estimated to be (702.85  $\pm$  0.02) m s<sup>-1</sup>. (As reported earlier, the frequency used has a measurable effect on the speed of sound [18].) This value is used to derive the quantities listed in Tables 5 and 6.

x – x <sub>c</sub>	u – u <sub>c</sub>  , m s <sup>-1</sup>	x – x <sub>c</sub>	u – u <sub>c</sub>  , m s <sup>-1</sup>
0.0218	18.5	0.2034	71.0
0.0421	25.8	0.2546	81.8
0.0622	33.2	0.3112	91.5
0.0779	38.2	0.3700	100.0
0.0954	43.5	0.4398	115.7
0.1140	48.9	0.5132	122.6
0.1350	54.9	0.6018	128.8
0.1584	60.8	0.7145	134.2

Table 5. The change in the quantity  $|u - u_c|$  with  $|x - x_c|$  along the critical isotherm where  $xc-C_6F_{11}CF_3$  is > 0.2855.

Table 6. The change in the quantity  $|u - u_c|$  with  $|x - x_c|$  along the critical isotherm where  $xc-C_6F_{11}CF_3$  is < 0.2855.

x – x <sub>c</sub>	u – u <sub>c</sub>  , m s <sup>-1</sup>	x – x <sub>c</sub>	u − u <sub>c</sub>  , m s <sup>-1</sup>
0.0232	9.2	0.1846	97.6
0.0417	24.0	0.2078	122.1
0.0810	30.1	0.2325	145.6
0.1101	47.7	0.2568	171.0
0.1361	64.9	0.2806	198.3
0.1623	84.0	0.2855	204.2

#### 4. Analysis in terms of universality

Figure 1 shows the speed of sound data in Table 1 expressed in terms of the limiting relation given by equation (2). The statistics of the curve fit show a systematic and not a random scatter. The standard deviation is 1.04 m s<sup>-1</sup> and is much higher than the estimated precision of 0.2 m s<sup>-1</sup>. The low value of the overall correlation factor  $r^2 = 0.992$  for the curve fit is not justifiable. Therefore, in subsequent analyses equation (3) was used with successively adding the second, third and fourth terms. The statistics are given in Table 7.

Table 7. The influences of the second, third and fourth terms in equation (3) in accounting for the critical behaviour of speed of sound as given in Table 1.

Terms used from equation (3)	r <sup>2</sup> (95 % confidence limits)	Standard deviation, m s <sup>-1</sup>
First	0.992	1.04
First and second	0.992	1.07
First, second and third	0.998	0.52
All terms	0.9996	0.26

As shown in Table 7 and Figure 2, inclusion of all the terms given by equation (3) for the analyses gives a representation of the data in Table 1 within the limits of the experimental uncertainty. Van Dael [25] had already shown that the higher terms in equation (3) are not negligible even for  $\tau = 2 \times 10^{-4}$ . The results from Table 2 also follow the same behaviour, though the r<sup>2</sup> is only 0.999 (when all the terms are included) and the standard deviation of 0.62 is higher than the experimental uncertainty.

The molar volume data in Tables 3 and 4 were analyzed in terms of equation (1) and the following statistics show that the data give an excellent fit to the equation, well within the limits of the experimental uncertainty. For the results in Table 1:  $r^2 = 0.999998$  with a standard deviation = 0.02 cm<sup>3</sup> mol<sup>-1</sup> and for the results in Table 4:  $r^2 = 0.9999988$  with a standard deviation = 0.005



Figure 1. The speed of sound data in Table 1 expressed in terms of equation (2). The points are the experimental data and the continuous curve is obtained from equation (2):  $B_1 = 288.46 \text{ m s}^{-1}$ .



Figure 2. The speed of sound data in Table 1 expressed in terms of equation (3). The points are the experimental data and the continuous curve is obtained from equation (3):  $B_1 = -216.4 \text{ m s}^{-1}$ ,  $B_2 = 31541 \text{ m s}^{-1}$ ,  $B_3 = -243256 \text{ m s}^{-1}$ ,  $B_4 = 241095 \text{ m s}^{-1}$ .

Figures 3 and 4 show the speed of sound data in Tables 5 and 6 analyzed in terms of equation (4). The statistics of the analysis are the following - for Table 5 results:  $r^2 = 0.959$  with a standard deviation = 8.7 m s<sup>-1</sup> and for Table 6 results:  $r^2 = 0.998$  with a standard deviation = 2.9 m s<sup>-1</sup>. Figure 4 shows that the results in Table 6 are reasonably well represented by equation (4) whereas Figure 3 shows that those in Table 5 are only poorly represented. The latter covers a much broader range in x: from 0.2855 to 1 while the former covers the shorter range from 0 to 0.2855. Therefore the next term was introduced as,  $C_3 | x - x_c |^{1/\beta}$  in equation (4) and the results in Table 5 were reanalyzed. The statistics were  $r^2 = 0.985$  with a standard deviation = 5.3 m s<sup>-1</sup>, a significant improvement over equation (4), but still inadequate to represent the experimental data. The results of this analysis are shown in Figure 5.



Figure 3. The speed of sound data in Table 5 expressed in terms of equation (4). The points are the experimental data and the continuous curve is obtained from equation (4):  $C_1 = 351 \text{ m s}^{-1}$ ,  $C_2 = -314 \text{ m s}^{-1}$ .



Figure 4. The speed of sound data in Table 6 expressed in terms of equation (4). The points are the experimental data and the continuous curve is obtained from equation (4):  $C_1 = 386.8 \text{ m s}^{-1}$ ,  $C_2 = 2940 \text{ m s}^{-1}$ .



Figure 5. The speed of sound data in Table 5 expressed in terms of equation (4) adding the next term in the scaled equation; the points are the experimental data and the continuous curve is obtained from equation (4) with the additional term.

#### 5. Concluding remarks

The analyses presented above show that the liquid-liquid critical phenomenon of (tetrachloromethane + tetradecafluoromethycyclohexane) belongs to the universality class of the 3D Ising model. The universal set of critical exponents quantitatively describes the behaviour of molar volume. Speed of sound can not be regarded as an order parameter equivalent to molar volume because terms other than the lead term may be necessary, even very close to the critical

point, for a proper representation of its behaviour. Appropriate higher terms may be introduced for this purpose.

Indeed the results presented here do not contradict the universality concept. Neither do they rigorously prove the concept. For example, the value of A<sub>1</sub> in equation (1) can be directly determined from the dilution measurements as  $(104.2 \pm 0.2)$  cm<sup>3</sup> mol<sup>-1</sup>. With this value,  $(1-\alpha)/\beta = 2.61 \pm 0.02$  perfectly represents the experimental results on the larger branch of the isotherm. The Ising value for  $(1-\alpha)/\beta$  is 2.74. Therefore direct determination of the critical exponents from experimental data on real systems continues to be rather challenging.

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#### 7. Nomenclature

A, B, C	Proportionality constants or Amplitudes in equations (1) to (4)
с	Critical (subscript)
m	Molar (subscript)
r <sup>2</sup>	Overall correlation coefficient for a least-squares fit
т	Temperature
u	Speed of sound
V	Volume
x	Mole fraction
α, β, γ, δ, μ, ν	Critical exponents
τ	Reduced temperature
Δ	Wegner correction exponent

#### Appendix:

The second derivative of excess molar volume with respect to mole fraction vanishes at the critical solution points of binary liquid mixtures [13,26]. This makes the critical isotherm of excess molar volume nearly linear for a measurable range of mole fraction, about the critical composition. This in turn probably results in the behaviour of the quantity  $V_m^{E}/x_1x_2$  shown in Figure A1: there is a clear minimum at the critical composition of CCl<sub>4</sub> + C<sub>7</sub>F<sub>14</sub>. Similar behaviour is found with methylcyclohexane + tetradecafluoromethylcyclohexane [13]. As shown in Figure A2, all three types of isotherms- critical, supercritical and sub-critical - have a minimum at the critical composition.



Figure A1. Excess molar volume of tetrachloromethane + tetradecafluoromethylcyclohexane at the critical solution temperature; the quantity  $V_m^{E}/x_1x_2$  shows a clear minimum at the critical composition.



Figure A2. Excess molar volume of methylcyclohexane + tetradecafluoromethylcyclohexane at three different temperatures; the quantity  $V_m^{E}/x_1x_2$  shows a clear minimum at the critical composition for the supercritical, the critical and the sub-critical isotherms.

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