

Search for the effect of pressure on liquid–liquid critical phenomena

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Abstract. The coexistence curve of methanol + cyclohexane has been reanalyzed using an intrinsically simpler equation to study the influence of pressure on its asymmetry. The results confirm that no pressure dependence is discernible in the coexistence curve. Suggestions for future work in this direction are made.

Keywords. Liquid–liquid transitions; critical phenomena; pressure effect; critical exponents.

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1. Introduction

We intend to explore the effect of pressure (P) on liquid–liquid (L–L) critical phenomena (Kumar *et al* 1983; Sengers and Levelt Sengers 1986) employing the coexistence curve of a binary fluid mixture as an example. These systems belong to the Ising universality class (spin dimensionality, $n = 1$). Pressure is not expected to affect (Kadanoff 1966; Griffiths 1970 and Stauffer *et al* 1972) the critical exponents and certain dimensionless amplitude ratios in binary fluid mixtures. This is a consequence of the fact that (a) P is not a field conjugate to the order parameter (difference of concentration of one of the two fluids in both phases) and (b) P does not change the symmetry of the order parameter.

At a highly quantitative level, the pressure independence of various universal parameters has been shown near the superfluid transition of liquid ^4He ($n = 2$) (Ahlers 1980) and the Curie temperature of nickel (Yousuf and Kumar 1989) ($n = 3$). The λ -line in ^4He and the line of Curie temperatures in Ni, do not display any pronounced curvatures when scanned with pressure. Historically the investigations along the λ -line of ^4He (Ahlers 1980) regarding the thermo-hydrodynamic quantities were pivotal in highlighting the significance of the confluent singularity (or correction-to-scaling) terms as well as in testing the results of the renormalization group theory (RGT) of phase transitions (Wilson and Kogut 1974; Le Guillou and Zinn-Justin 1980, 1989) in a rigorous manner.

The comprehension of multicritical points is better facilitated with the aid of pressure instead of an additional component – in binary (Prافulla *et al* 1992) and ternary (Schneider 1991) liquid mixtures.

A meticulous investigation concerning the influence of pressure on the L–L

coexistence curve of methanol + cyclohexane (M + CH) has been reported (Aizpiri *et al* 1988). These data are carefully reanalysed using a simpler expression.

2. Reanalysis of the data of Aizpiri *et al*

Two of us (RGR and AGA) measured the coexistence curve (Aizpiri *et al* 1988) of (M + CH) in the pressure range $0.1 < P/\text{MPa} < 13.0$. Several isobars were obtained interpolating in various visually determined isopleths. The temperature, pressure and composition resolutions were ± 1 mK, ± 0.01 MPa and ± 0.002 respectively. The shape of the phase diagram and its diameter (Greer 1976; Greer *et al* 1983; Vani *et al* 1986; Aizpiri *et al* 1988) can be combined to yield a general expression,

$$|X - X_c| = \pm A_1 t \pm A_2 t^{1-\alpha} + A_3 t^\beta + A_4 t^{\beta+\Delta} \quad (1)$$

where $t = |(T_c - T)/T_c|$, T_c being the critical temperature. X can be any concentration variable of the coexistence curve. $A_1 - A_4$ are the parameters to be fitted. The critical exponents β and α describe the shape of the coexistence curve and specific heat singularity respectively as $t \rightarrow 0$. According to RGT (Wilson and Kogut 1974; Le Guillou and Zinn-Justin 1980, 1989), $\beta = 0.325$ and $\alpha = 0.110$. The correction-to-scaling exponent (Greer 1978; Kumar *et al* 1983; Sengers and Levelt Sengers 1986) has a value $\Delta = 0.50$ and X_c is the critical concentration. When the chosen composition variable does not provide the preferred order parameter, the $t^{1-\alpha}$ term may be hidden under a strong $t^{2\beta}$ anomaly, but very often the data do not allow to distinguish between the two (Greer 1978; Kumar *et al* 1983; Greer *et al* 1983). In the data analysis reported here, equation (1) is used to fit the data of Aizpiri *et al* (1988). The data were fitted using a nonlinear-least-squares fit program CURFIT (Bevington 1969). This program has been extensively used earlier for similar expressions (Greer 1976; Greer *et al* 1983; Vani *et al* 1986). The criterion for a good fit (Bevington 1969) was that χ^2_ν should be close to 1.0 (apart from the reasonable randomness of the residuals of the fits).

The original data from Aizpiri *et al* (1988) i.e. (T, P) at a given X , were converted to (X, T) at a given P by means of an interpolation method (Aizpiri *et al* 1988). These data were fitted to each branch of the coexistence curve to generate the coexisting compositions at a given T , from which the corresponding values of the order parameter and of the diameter were obtained and fitted. The essential conclusions (Aizpiri *et al* 1988) were that (a) P effect on the asymmetry of the coexistence curve, was masked by uncertainties and (b) the diameter shows no statistically significant anomaly. Here it should be noted that the original precision of the measurements, which was remarkable, possibly suffered due to two steps of interpolation (which could also introduce small systematic errors and as a consequence a certain systematicity in the distribution of residuals). Since this research was the *first* careful endeavour to probe the pressure effect on L-L critical phenomena, it was decided to reanalyze and reexamine these data using (1). The temperature range covered in the data analysis is $1.5 \times 10^{-4} \leq t \leq 5 \times 10^{-2}$ which is outside the range of gravity effects for (M + CH), even for the smallest t approached (Kumar *et al* 1983; Greer 1978; Aizpiri *et al* 1988). The two data points closest to T_c were neglected as was done in the reference of Aizpiri *et al* (1988). The critical exponents α , β and Δ were kept fixed at their theoretical values as is the common practice (Greer *et al* 1983; Aizpiri *et al* 1988).

The minimum in χ_v^2 was achieved by varying X_c and T_c . These values of X_c and T_c were then held fixed and parameters $A_1 - A_4$ were determined. The term $A_4 t^{\beta+\Delta}$ in (1) was not found to improve the fit significantly and was discarded. This result is in agreement with the assumption that for L-L critical systems the first correction-to-scaling amplitude is small as has been reported recently (Singh and Pitzer 1989).

It is also inferred that the anomalous term, $A_2 t^{1-\alpha}$, in the diameter [equation (1)] cannot be excluded from the data—this finding is not in consonance with the work of Aizpiri *et al* (1988). However, a careful examination of the residuals of the diameter fits of Aizpiri *et al* (1988) (unpublished) does *not* rule out the possibility that those data were consistent with the existence of a $(1 - \alpha)$ term in (1).

According to our results, amplitude A_2 seems to be the best index to reveal the effect of P on the coexistence curve of (M + CH). Equation (1) treats the order parameter as mole fraction, which is the preferred order parameter for this system (Greer *et al* 1983; Aizpiri *et al* 1988). The results of the fit are shown in tables 1 and 2.

Table 1. Results of fits to equation (1) [Right: $R(X > X_c)$ Left: $L(X < X_c)$]. The values of X_c and T_c were kept fixed. A small variation in steps of ± 0.001 for X_c did not affect the results. The right branch of the coexistence curve gave a better fit than the left branch, possibly due to paucity of data points very close to X_c .

P/MPa	T_c/K	A_1	A_2	A_3	χ_v^2
0.1 R	318.445	-11.1 ± 0.8	8.1 ± 0.6	0.79 ± 0.01	1.02
0.1 L	318.445	14.2 ± 1.1	-11.6 ± 0.9	0.69 ± 0.02	0.07
1 R	318.749	-11.9 ± 0.8	8.7 ± 0.6	0.79 ± 0.01	0.96
1 L	318.749	9.9 ± 1.0	-8.4 ± 0.8	0.74 ± 0.01	0.21
2.5 R	319.264	-11.2 ± 0.8	8.2 ± 0.6	0.79 ± 0.01	1.18
2.5 L	319.264	15.3 ± 1.2	-12.6 ± 0.9	0.67 ± 0.02	0.02
5 R	320.070	-11.8 ± 0.8	8.6 ± 0.6	0.79 ± 0.01	1.06
5 L	320.070	10.5 ± 0.9	-8.7 ± 0.8	0.75 ± 0.01	0.70
10 R	321.688	-11.5 ± 0.8	8.6 ± 0.6	0.77 ± 0.01	0.51
10 L	321.688	14.4 ± 1.1	-11.9 ± 0.9	0.68 ± 0.02	0.10
13 R	322.600	-9.9 ± 0.7	7.2 ± 0.6	0.80 ± 0.01	1.13
13 L	322.600	15.5 ± 1.0	-12.4 ± 0.8	0.69 ± 0.02	0.17

Table 2. Ratios of the amplitudes A_1 , A_2 and A_3 for the right and left branches (taken from table 1). These ratios are expected to articulate the effect of pressure on the coexistence curve. None of the ratios show any systematic trend up to 13 MPa.

P/MPa	T_c/K	$A_1(\text{R})$	$A_2(\text{R})$	$A_3(\text{R})$
		$A_1(\text{L})$	$A_2(\text{L})$	$A_3(\text{L})$
0.1	318.445	-0.783	-0.701	1.141
1	318.749	-1.203	-1.039	1.070
2.5	319.264	-0.732	-0.652	1.186
5	320.070	-1.120	-0.984	1.061
10	321.688	-0.800	-0.720	1.136
13	322.600	-0.642	-0.579	1.158

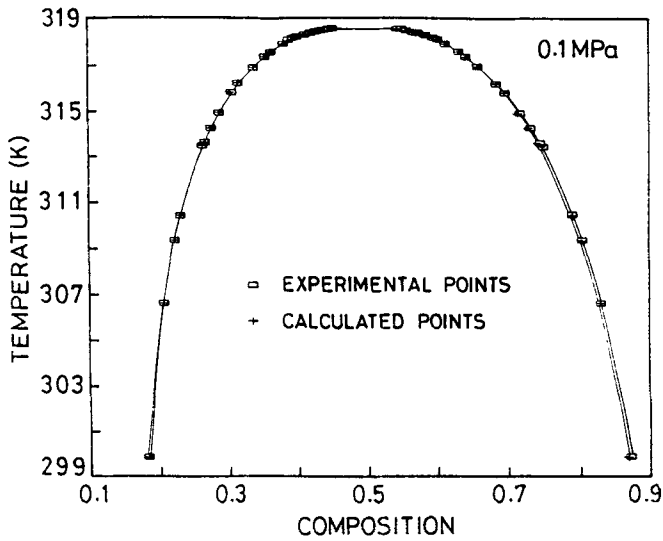


Figure 1. Experimental and calculated phase diagram (using equation (1)) of methanol + cyclohexane at 0.1 MPa. The continuous line is guide to the eye.

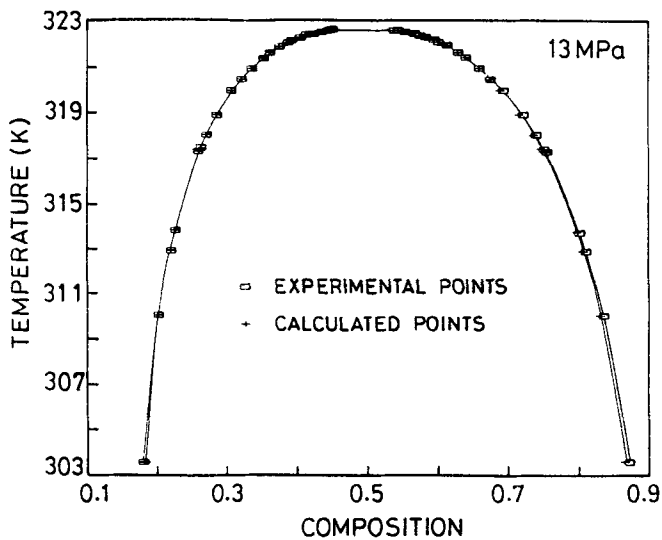


Figure 2. Experimental and calculated phase diagram (using equation (1)) of methanol + cyclohexane at 13 MPa. The continuous line is guide to the eye.

Figures 1 and 2 display the complete coexistence curve at two extreme pressures along with the fitted values.

3. Discussion

It is evident from tables 1 and 2 that there is no noticeable effect of P on A_2 i.e. the increased pressure has not enhanced the asymmetry of the coexistence curve. A similar result persists if $(1 - \alpha)$ is replaced by 2β in (1). The non observation of

the effect of P is not in conflict with the ideas of universality and the RGT (Kadanoff 1966; Griffiths 1970; Stauffer *et al* 1972; Wilson and Kogut 1974; Le Guillou and Zinn-Justin 1980, 1989).

The debatable question is whether the effect of pressure on the L-L coexistence curve can be measured at all. Here one must refer to the situation in the study of the superfluid transition in liquid ^4He as pressure was increased to nearly 3 MPa along the λ -line (Ahlers 1980). The pressure dramatically increased the amplitude of correction-to-scaling terms for the superfluid fraction, thermal expansion and thermal conductivity. Nonetheless, it should be recognized that a modest pressure of ≈ 3 MPa is fairly close to the freezing pressure for liquid ^4He . Perhaps one has to extend the range of pressure to a few *hundred* MPa in binary fluid systems to observe its influence. The ultimate pressure will be limited by the solidification of one of the liquids.

4. Suggestions for future work

It is fortuitous that a highly symmetric system (i.e. a system with X_c almost at 0.5 and a very symmetric coexistence curve), (M + CH), was chosen to see the effect of pressure. It seems prudent to choose a system like polystyrene + cyclohexane, that is extremely asymmetric, for a molecular weight of 10^5 or 10^6 of polystyrene. The critical volume fraction of polystyrene (Nakata *et al* 1975, 1978) is 0.0321 in this system.

It is suggested that a *direct* isobaric determination of the coexistence curve should be made, preferably with a single sample technique, avoiding interpolation at any step.

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