

COMPARISON OF FIELD VARIABLES FOR CRITICAL PHENOMENA DESCRIPTION

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We report the findings of the reanalysis of critical phenomena which occur in three different multicomponent systems found in the literature. Multicomponent systems allow for the description of critical phenomena in terms of more than one field variable as the critical curve is approached in the multidimensional phase space. We show empirically that one field variable provides the most relevant description of the critical phenomena over all the others. This relevant field variable displays universality in both the critical exponents and amplitudes. The key feature of this relevant field variable is that its variation toward the critical curve is along paths that are never tangent to the critical curve.

1. Introduction

Numerous researchers have investigated the behavior of single or multicomponent systems that separate into two phases upon approaching a critical point [1]. It has long been known that various quantities (e.g. correlation length, specific heat, etc.) diverge on approach to a critical point with a power law dependence as

$$A = A_0 \epsilon^{-a}, \quad (1)$$

where A_0 is the critical amplitude, ϵ is the field variable, such as reduced temperature, $t = |T - T_c|/T_c$, and a is the critical exponent. Furthermore, the critical exponents and various ratios of the amplitudes appear to be universal [2-4] quantities, independent of the chemical species.

In the majority of these studies the reduced temperature t has been the field variable, usually due to experimental convenience. This is somewhat shortsighted, however, because the phase diagrams used to map the approach to the critical point are two-dimensional slices of more general multidimensional phase diagrams involving other possible variables. In such a phase diagram the critical point is in reality part of a critical curve, an example of which is the critical curve created in a binary liquid consolute system in which pressure is varied [5]. The question then becomes whether eq. (1) can be used for all the

field variables and universality found in each case, or whether there is a preferred or proper field variable? For the case of a non-linear critical curve, universality can only hold for one field variable.

Recently, studies have appeared which investigate critical phenomena near non-linear critical curves [6-9]. The systems studied include closed-loop immiscibility systems in which the upper and lower critical points in a two-dimensional slice of the phase diagram can be made to converge at a hypercritical point (HCP) by variation of a third chemical component, and gas-gas systems in which upper and lower miscibility gaps can be made to converge to a critical double point (CDP) by variation of temperature. In each case critical exponent doubling was seen when eq. (1) was used with the field variable that could approach the critical curve in a tangential manner.

Griffiths and Wheeler [10] described how an asymptotically tangential approach to a critical line can lead to modified critical exponents. Thus, the exponent doubling observed in the references above can be explained as due to a tangential path of approach to an asymptotically quadratic critical curve near the double critical points.

In recent work [11] we have shown again that the amplitudes and exponents depend upon the path of approach to the critical line. For one field variable, however, a set of parallel paths that varied only this

field yielded the same amplitudes and (Ising) exponents, that is, universality was regained. The only distinguishing feature of this more "relevant" field variable was that it was never, at any point along the critical curve, tangent to the critical curve. Because of this behavior we proposed, following Griffiths and Wheeler, that for two fields which share the same plane as the critical curve the field which is "never tangent" to the critical curve will produce exponents and amplitudes common to all paths.

Given the discussion above, it seems appropriate at this time to unify these results into one picture. Hence the purpose of this note is to both substantiate and visually demonstrate with experimental data that, *in general*, use of the "relevant" field variable (that which is never tangent to the critical curve) produces exponents and amplitudes common to all paths of approach. To do this we have reanalyzed three sets of published data. In each case, both the data and the critical curve were extracted from graphs and tables provided in the cited references. The relevant field variable was determined from visual inspection of the critical curve as being that field which never approached tangent to the curve. Conversion from the non-relevant field variable to the relevant field variable was accomplished by measuring the distance from the critical curve along the relevant field direction for all data points, and then replotting those data as a function of that distance.

2. Results for different systems

2.1. 3-methylpyridine/H₂O/D₂O

Sorensen and Larsen [7] measured the correlation length near the HCP found in mixtures of 3-methylpyridine, H₂O, and D₂O, and observed exponent doubling as the path coincided with the HCP. The projection of the critical curve onto the T - $X(\text{D}_2\text{O})$ plane is shown in fig. 1. Here X represents the mole fraction of D₂O in the total water $X(\text{D}_2\text{O}) = \text{D}_2\text{O}/(\text{D}_2\text{O} + \text{H}_2\text{O})$. The critical curve exhibits only a very weak dependence upon the concentration of 3MP and hence we feel justified in using this projection of the critical curve alone.

The correlation length was measured as a function of temperature along several isopleths of D₂O. In fig.

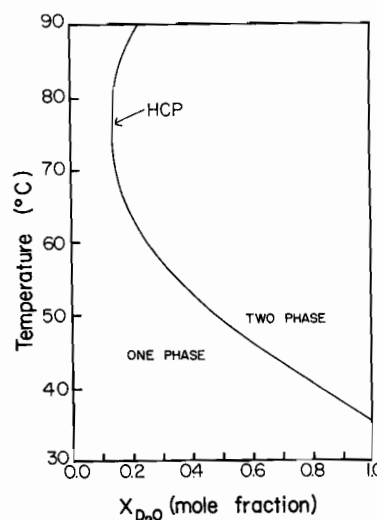


Fig. 1. The projection of the critical curve onto the T - $X(\text{D}_2\text{O})$ plane for the system 3MP/H₂O/D₂O. $X(\text{D}_2\text{O})$ is the mole fraction $\text{D}_2\text{O}/(\text{D}_2\text{O} + \text{H}_2\text{O})$. The concentration of 3MP is constant at 29.9% by weight.

2a the data are represented as a function of the reduced temperature $t = |T - T_c|/T_c^{-1}$, where T_c is the temperature on the critical curve which terminates the path. Exponent doubling is clearly evident as the HCP isochore near D₂O mole fraction 0.13 is approached. We see from the critical curve that temperature is a field which is capable of approaching tangent to the critical curve at some location (namely at the HCP) and hence, we would claim, is not the relevant field variable. On the other hand, paths which vary $X(\text{D}_2\text{O})$ at constant temperature are *never* tangent to the critical curve, hence $X(\text{D}_2\text{O})$ is the relevant field variable. When the correlation length is replotted as a function of the distance away from the critical curve in $X(\text{D}_2\text{O})$ space at various fixed temperatures, the data collapse onto a single curve as displayed in fig. 2b. When analyzed with

$$\xi = \xi_0 [X_c(\text{D}_2\text{O}) - X(\text{D}_2\text{O})]^{-\nu}, \quad (2)$$

where $X_c(\text{D}_2\text{O})$ is the critical curve D₂O concentration for a given isotherm, a common Ising-like exponent, $\nu = 0.60 (\pm 0.05)$, and common amplitude, $\xi_0 = 25 (\pm 5) \text{ \AA}$, is found for all the paths.

In the above analysis we have assumed that $X(\text{D}_2\text{O})$ is a field variable, which means that $X(\text{D}_2\text{O})$ is the same in each phase of the phase-sep-

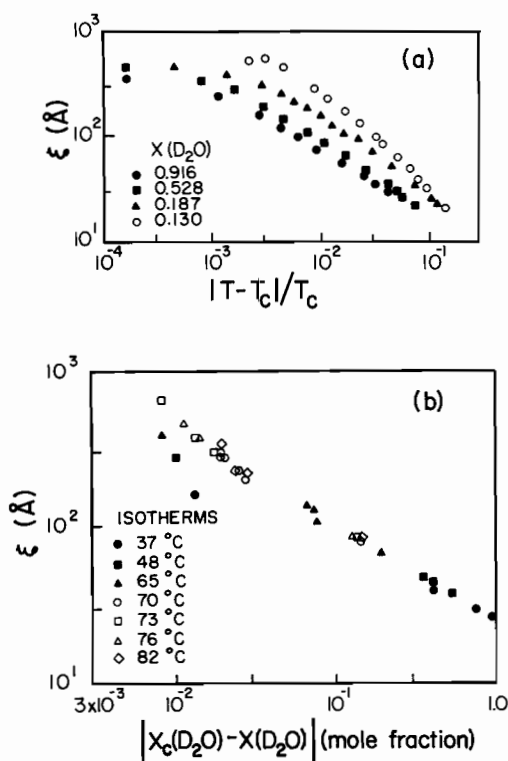


Fig. 2. (a) The correlation length as a function of reduced temperature for the system 3MP/H₂O/D₂O. T_c is the temperature at which each D₂O isopleth intersects the critical curve. (b) The correlation length as a function of the difference in $X(\text{D}_2\text{O})$ from the critical curve along a given isotherm.

arated mixture. This is not exactly true. Given the similarity between H₂O and D₂O compared to 3MP, however, we expect that the water-rich and -poor phases of the phase-separated mixture will in fact have nearly the same $X(\text{D}_2\text{O})$. Thus while $X(\text{D}_2\text{O})$ is strictly not a field variable, we expect it to be a good approximation to one.

2.2. Glycerol/guaiacol/H₂O

Johnston et al. [8,12] measured the correlation length along various paths toward the critical curve in the system glycerol/guaiacol/H₂O (ggw) and also observed exponent doubling near the HCP. The critical curve provided in fig. 3 is analogous to that of the 3MP/H₂O/D₂O. Again fig. 3 is only a projection

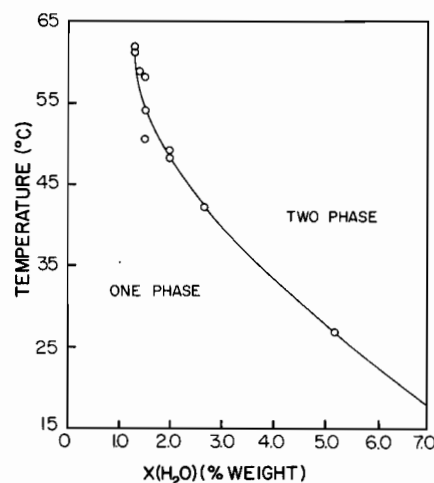


Fig. 3. The projection of the critical curve onto the T - $X(\text{H}_2\text{O})$ plane for the system glycerol/guaiacol/H₂O. $X(\text{H}_2\text{O})$ is the percent by weight of H₂O to H₂O plus glycerol. The weight fraction of guaiacol is approximately 0.5. The circles are measurements of the critical points provided by ref. [12]. The line represents the fit used for the present analysis.

of the true critical curve, but the dependence upon guaiacol is very weak.

In fig. 4a, the correlation length is represented as a function of the reduced temperature. Since $X(\text{H}_2\text{O})$ is the field which is never tangent to the critical curve, it is the relevant field. The analysis for ggw differs slightly from that outlined above for 3MP/H₂O/D₂O. A plot of the correlation length as a function of the distance away from the critical curve in $X(\text{H}_2\text{O})$ -space ($\Delta X(\text{H}_2\text{O}) = |X(\text{H}_2\text{O}) - X_c(\text{H}_2\text{O})|$) lacked sufficient data points in the low $\Delta X(\text{H}_2\text{O})$ range. Instead of plotting isotherms, the isochore data in fig. 4a have been replotted in terms of $\Delta X(\text{H}_2\text{O})$, which changes due to changes in $X_c(\text{H}_2\text{O})$ as T is varied. Upon replotting the data versus the relevant field variable, the data collapse onto a single curve. A fit to eq. (2) using $X(\text{H}_2\text{O})$ yields a common Ising-like exponent, $\nu = 0.63 (\pm 0.03)$, an roughly common amplitude, $\xi_0 = 50 (\pm 10)$ Å, for all the paths, as shown in fig. 4b. The small systematic differences between paths in fig. 4b may be due in part to the substantial difficulty of locating the critical curve.

Here again, similar to the 3MP/H₂O/D₂O system,

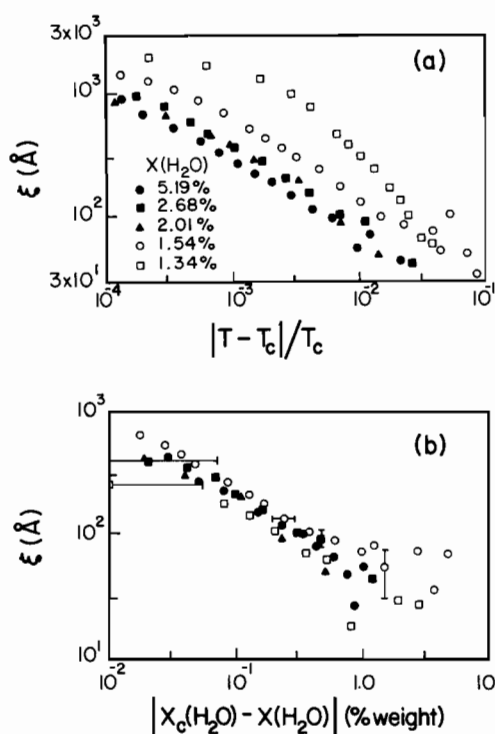


Fig. 4. (a) The correlation length as a function of reduced temperature for the system glycerol/guaiacol/ H_2O for various H_2O isochores. T_c is the temperature at which each H_2O isochore intersects the critical curve. (b) The correlation length as a function of the difference in $X(\text{H}_2\text{O})$ from the critical curve.

we have assumed $X(\text{H}_2\text{O})$ is a field variable, i.e. that is the same in the glycerol-rich and guaiacol-rich phases. Johnston [12] remarks that this is probably a good approximation due to the small amount of H_2O present in the system to cause phase separation.

2.3. Ne/Kr

Tufeu, Keyes and Daniels [9] measured the intensity of light scattered at 90° from a mixture of neon and krypton near a CDP. The projection of the critical curve onto the P - T plane is reproduced in fig. 5. Intensity measurements were obtained along the three paths indicated in this figure. Since the scattered intensity is proportional to the osmotic susceptibility, χ , plots of I^{-1} should obey

$$I^{-1} \sim \chi^{-1} = \Gamma^{-1} \epsilon^\gamma. \quad (3)$$

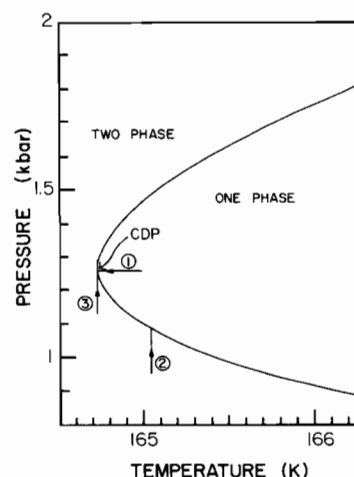


Fig. 5. The projection of the critical curve onto the P - T plane for the binary system Ne/Kr. Measurements of the intensity of scattered light were obtained by ref. [9] along the three numbered paths.

As shown in fig. 6a, path 3 exhibits exponent doubling when plotted versus reduced pressure (the non-relevant field variable in this instance). Upon conversion of paths 2 and 3 to the relevant field variable, t , we obtain the same exponent and amplitude. This is shown in fig. 6b. To compare these paths (two phase regime) with path 1 (one phase regime), I^{-1} for paths 2 and 3 has been multiplied by the amplitude ratio, Γ_I/Γ_{II} , of the susceptibility in the one- and two-phase regimes. Hocken and Moldover [13] have observed values of Γ_I/Γ_{II} ranging from 4.5 for Xe and 5.0 for binary systems. The value predicted by the series Ising model is 5.07. We have chosen to use $\Gamma_I/\Gamma_{II}=4.9$. With this correction all three paths come in line and universality is achieved.

3. Summary

In conclusion we have demonstrated and further developed the ideas presented by Griffiths and Wheeler by contending that there exists a "relevant" field variable for describing the divergence of various quantities as a critical curve is approached. We find empirically that when the divergence is described using the field variable which is nowhere tan-

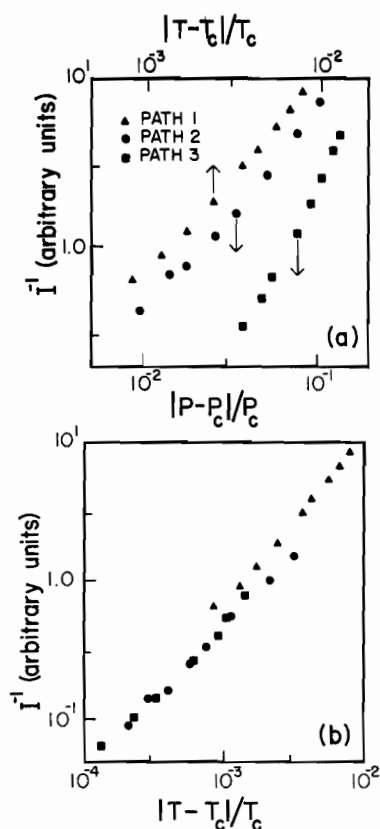


Fig. 6. (a) The inverse scattered intensity versus reduced temperature (path 1) or versus reduced pressure (paths 2 and 3) for the system Ne/Kr. (b) The inverse scattered intensity as a function of reduced temperature for all the paths. I^{-1} along paths 2 and 3 have been multiplied by 0.204 to account for the difference in critical amplitudes of one-phase and two-phase states.

gent to the critical curve, *both* the critical exponents and critical amplitudes will be common to all paths.

The systems we have investigated have critical lines

that fall, to a good approximation, on a plane. More complex systems where this approximation does not hold can be envisioned, and our results here would have to be generalized.

Acknowledgement

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