

## HOMI JEHANGIR BHABHA MEDAL LECTURE-1993

### PHASE TRANSITIONS AND CRITICAL PHENOMENA IN LIQUID MIXTURES

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The observation of striking universal similarities in the thermal and other properties of diverse systems, like a liquid + gas near its critical temperature or a ferromagnet near its Curie temperature, has opened up a new pathway in the understanding of phase transformations. Critical solution phenomena in binary liquid mixtures offer a conveniently accessible way of studying the universality of the critical point phenomena. Fluctuations dominate in the region. The statics and dynamics of the correlations among the fluctuation then determine the major part of physical properties, over-shadowing the contributions from the chemical and other interaction, thereby yielding a universality of the critical phenomena. The renormalization group theory enables one to calculate mathematically the critical exponents and other parameters, all of which have values significantly different from the predictions of the classical thermodynamic theory. Binary liquid mixtures, besides offering a set of simple systems to study the phenomena, have some features accentuated, like the deviations from the so-called law of rectilinear diameter caused by the deviation from the particle-hole symmetry of statistical physics. They also provide examples of reentrant phase transitions, whose reentry region can be controlled by varying one of the parameters of the system. The double critical point exhibits other symmetries as well as a doubling of the critical exponents. Most of the experimental studies require painstaking control of temperature, impurities and other perturbations.

**Key Words:** Critical Point Phenomena; Liquid Mixtures; Phase Transitions; Critical Exponents; Reentrant Phase Transitions

#### Introduction

It is matter of great responsibility to be allowed in the company of the distinguished Fellows of the Academy who have earlier paid their tributes to the memory of Dr Homi Jehangir Bhabha. Dr Bhabha started his professional career in theoretical studies, later moved to tackle the technological problems of atomic energy and all the time utilized the resources of his country. Giants of such eminence, who strode the science scene like Colassus of the Greek mythology, were the hero models for lesser pigmies like me, who started work in theoretical studies, later moved to work in experimental and technical prob-

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lems, and all the time built their own research facilities indigenously, battling to show that home made equipments can still produce front rank results.

A subject like thermodynamics evokes visions of a mature well settled field of study where the details are well established and are applied to various scientific and technical problems. Thus it is felt to be an area which is unlikely to produce surprising new results, even though statistical thermodynamics may throw up mathematical problems of varying complexity<sup>1,2</sup>.

For instance, more than 150 years ago, Andrews had discovered that a gas like carbon dioxide, if kept above a critical temperature of 32°C, would never become a liquid by applying any high compressive pressure, and that it had to be kept below the critical temperature  $T_c$  before it could be liquified by applying high pressure. This was elegantly explained about fifty years later by Van der Waals through the famous equation of state  $[p + (a/V^2)](V - b) = RT$  which showed the gas like behaviour above  $T_c$  and a gas + liquid behaviour below  $T_c$  when the pressure-volume isotherms are studied. The material is considered to be well understood and is taught in undergraduate science classes.

In the early sixties, when high resolution specific heat measurements were performed by Buckingham and Fairbanks near the superfluid transition of liquid helium<sup>4</sup> and by Vornel and colleagues near the critical temperature of oxygen or nitrogen, a dramatic result emerged that the specific heat was becoming infinitely large, almost like  $\log|T - T_c|$  form. In the conventional thermodynamics theory the heat capacity should vary smoothly and have at best a small jump at  $T_c$ . Even in a more generalized version, the so called mean field theory, the same qualitative behaviour should be seen, classified as the Ehrenfest second order transition. It was also true that when Onsager solved rigorously in 1944 a statistical mechanical model of a system showing phase change, called the Ising model, he obtained the surprising result that the specific heat should show a logarithmic singularity at  $T_c$ . Incidentally this was done only for a two dimensional case and the three dimensional problem is not yet solved mathematically rigorously though approximate solutions of varying refinements are available. Moreover other deviations from the mean field theory predictions had been noted in the early fifties; for example the phase boundary of the coexisting liquid + gas region had a cubic shape rather than the theoretically predicted quadratic shape. However, they were not dramatic enough to draw the attention of the research community. These early studies have not been documented well by Stanley<sup>3</sup>, Domb and Green<sup>4</sup>, Kumar, Krishnamurthy and Gopal<sup>5</sup> and in several other books and reviews.

### Universality of Critical Phenomena

The observation of a singular behaviour, the divergence to infinite values, in the heat capacity was qualitatively different and dramatic. The similarity to the unexpected Ising model logarithmic singularity also caught the attention of many workers. It was realized that another system, studied again under mean field theories, showed similar anomalies. Ferromagnets when heated above the Curie temperature become paramagnetic. The Curie-Weiss theory is analogous to the Van der Waals model in the mean field approximation. The paramagnet-

ic state with random oriented spins is analogous to the gas phase with random positions, whereas the ordered ferromagnetic state is analogous to the lattice model of a liquid. Careful measurements of heat capacity of the ferromagnetic iron near its Curie temperature had shown the possibility of an infinitely large value for the specific heat.

Detailed studies revealed a very striking universality in the behaviour of diverse systems like the behaviour of oxygen gas near its critical temperature, i.e., liquid + gas system, or the behaviour of a ferromagnet like iron near its Curie temperature. The behaviour was governed by a simple power law behaviour and the power law exponents, called now critical exponents, had the same value for different systems. The results of these studies are summarized schematically in Fig. 1.

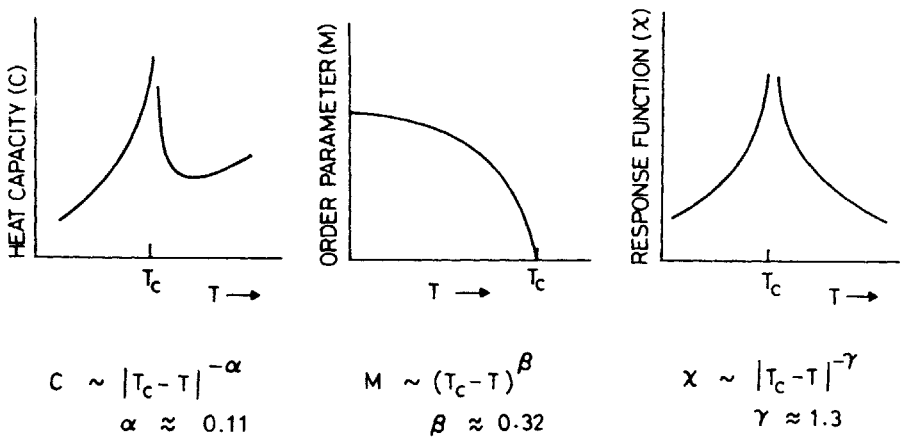


Fig 1 Universality and simple power law behaviour near the critical temperature  $T_c$ . Numerous systems show this behaviour. Behaviour of heat capacity (exponent  $\alpha$ ), order parameter (exponent  $\beta$ ) and response function (exponent  $\gamma$ ) is shown schematically.

The heat capacity of liquid + gas system at constant volume  $C_v$  or the heat capacity of a ferromagnet at constant magnetization  $C_M$  has the functional form

$$C = A |T - T_c|^{-\alpha} \dots (1)$$

for the leading singular part.  $\alpha$  is called the critical exponent for heat capacity and has a value of about 0.11. This equation is a more accurate description of the experimental behaviour of the 3-dimensional systems than the approximate logarithmic behaviour mentioned earlier.

The spontaneous magnetization  $M_s$  of a ferromagnet is a measure of the ordering or alignment of the magnetic moments. When the temperature is increased, the thermal energy tends to disorder the system and  $M_s$  goes to zero at the Curie temperature, after which in the high temperature paramagnetic phase  $M_s = 0$ . In the case of a liquid + gas system the density difference  $\rho_L - \rho_G$  between the liquid and the gas is a measure of ordering which goes to zero at  $T_c$  is reached. It was surprising that in all these cases the order parameter  $M$  has a simple power law behaviour

$$M = B(T_c - T)^\beta \quad \dots (2)$$

just below the critical temperature. The critical exponent  $\beta$  has a value 0.32, the careful experiments revealing it to be slightly different from the simple number 1/3 mentioned earlier and significantly different from the classical value of 1/2.

The compressibility  $\chi_T = -(1/V)(\partial V/\partial P)_T$  is a measure of the mechanical response of the system to the external perturbation i.e. change of volume on the application of pressure. In a similar way the magnetic susceptibility  $\chi_T = (\partial M/\partial H)_T$  is a measure of the response of the magnetisation when an external magnetic field is applied. It was unexpectedly discovered that the response function  $\chi$  has again a universal simple power law function

$$\chi_T = C|T - T_c|^{-\gamma} \quad \dots (3)$$

becoming very large near the critical temperature with the critical exponent  $\gamma$  having a value of about 1.24. The mean field theories give  $\gamma=1$ , the Curie-Weiss formula.

In addition to these simple power law behaviours with universal values of these and other critical exponents, it was also discovered that one has scaling behaviour of the properties. In other words, in terms of suitable reduced variables the response function for instance could be plotted as a single universal curve.

It was somewhat of a sensation that different systems like magnetic systems, liquid + gas systems, order-disorder alloy, ferroelectric materials, and binary liquid mixtures all showed such universal features<sup>3,5</sup>. The reason for the unexpected behaviour became clear when one realized that near the critical temperature the response function becomes infinitely large (eq. 3). When there is a slight pressure fluctuation, the density fluctuations become large. This can be readily observed in a liquid + gas system as the critical opalescence, caused by the corresponding large fluctuations of the refractive index and the consequent pronounced scattering of light. The critical opalescence and the reasoning based on fluctuation phenomena had been known since the beginning of this century. As  $T_c$  is approached not only the magnitudes of fluctuations increase but also the length scale over which the fluctuations are correlated. The inter particle spacing becomes small by comparison. The near neighbour interactions, which are responsible for the magnetic ordering or ordering of the gas into the liquid state etc., also become less significant in the fluctuation dominated region. The universality of the behaviour was the consequence of the fluctuation dominated process. The scaling laws were also seen as arising from the same origin. Based on this logic one could also deduce some relationships among the critical exponents which were also approximately verified.

The rigorous formulation of this problem had to wait for the brilliant development of the Renormalization Group theoretical method, by K.G. Wilson in the early seventies. It provided a new pathway to understand the critical phenomena<sup>4</sup>, justifying the award of Nobel Physics Prize in 1982. The theory showed that the behaviour depends upon the spatial dimensionality,  $d$ , of the

system (i.e., 3 dimension  $d=3$ , 2 dimension  $d=2$  etc.) and also on the spin dimensionality  $n$  of the interacting particles. The isotropic Heisenberg interaction in magnetism has  $n=3$  spin dimension whereas the Ising model using only up or down spins has  $n=1$ . The RG theory shows for example the specific heat exponent  $\alpha$  to have the values

$$\alpha = \frac{4-n}{2(n+8)} (d-4) - \frac{(n+2)^2(n+28)}{4(n+8)^3} (d-4)^2 - \frac{(n+2)}{8(n+8)^5} [n^4 + 50n^3 + 920n^2 + 3472n + 4800 - 192(5n+22)(n+8) \times 0.60103](d-4)^3 + \dots \dots (4)$$

as an asymptotic function. Thus the critical exponents are not simple algebraic quantities like  $1/2$ ,  $1/3$ ,  $0$  etc. but may be irrational numbers. For  $d=3$  the three dimensional system  $\alpha$  has the values  $-0.12$  ( $n=3$ ),  $-0.02 \pm 0.04$  ( $n=2$ ) and  $0.11$  ( $n=1$ ). Uniaxial ferromagnets or binary liquids or liquid + gas systems belong to  $d=3$ ,  $n=1$  case. Planar ferromagnets and superfluid liquid He<sup>4</sup> belong to  $d=3$ ,  $n=2$ . Ordinary ferromagnets like iron, nickel belong to the class  $d=3$ ,  $n=3$ . The best experimental values<sup>5</sup> are  $-0.13$  ( $n=3$ ),  $0.01$  ( $n=2$ ),  $0.10 \pm 0.03$  ( $n=1$ ) for the three dimensional system, showing remarkable agreement now between the theoretical calculations and the experimental observations. In fact, the RG theory has occasionally lead the experimenters to look for the predicted effects<sup>4</sup>.

### Critical Solution Phenomena in Liquid Mixtures

It had been known for quite a long time in physical chemistry that pairs of liquids like alcohol and water are miscible in all proportions to form a single solution phase, while mercury and water do not mix and remain as two separate phases. Binary systems like carbon disulphide and methyl alcohol are miscible in all proportions above a (upper) critical solution temperature of about 39°C while at lower temperatures the mutual solubility is limited, giving a two phase region. The analogy with liquid + gas system wherein there is only one vapour phase above  $T_c$  and the possibility of a two phase region below  $T_c$  is obvious. It was recognized in late sixties that the analogy extended to quantitative levels. The analog of the density of liquid + gas system is the concentration of one species. Thus the phase diagram of co-existing phases has the same features.

Fig. 2 shows the phase diagram of the binary liquid system carbon disulphide + nitromethane, a pair of commonly available liquids which can be obtained in sufficiently high purity<sup>6</sup>. The temperature region is also accessible easily. The control of temperature, constancy in time as well as over the spatial dimensions of the experimental volume, is crucial and has been done at  $\pm 1$  millidegree centigrade level. When one recognizes that the boiling point of water changes by 3 mK over a height difference of 1 meter, one realizes that a good deal of experimental skill and care is needed in these experiments. The order parameter is  $x' - x''$  the difference in compositions of the phase boun-

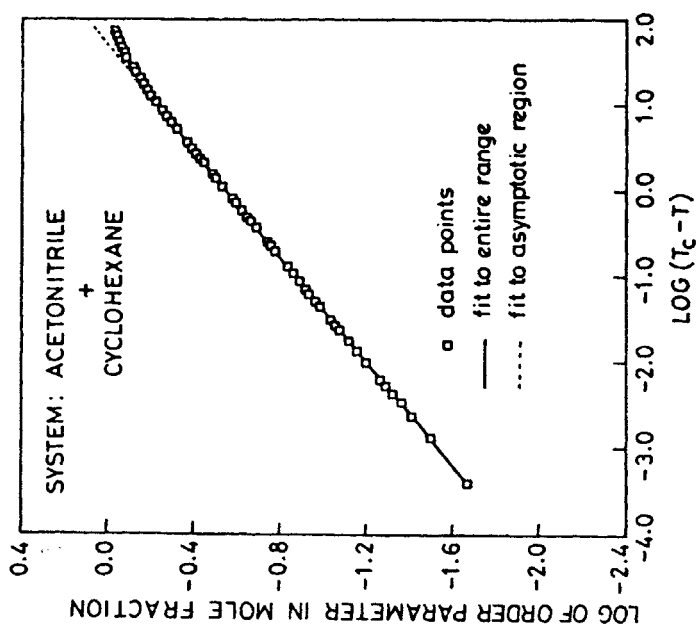


Fig 3 Analysis of the order parameter of the binary liquid system acetonitrile + cyclohexane. The  $\beta$ -exponent has a value 0.32 and  $\Delta = 0.5$ .

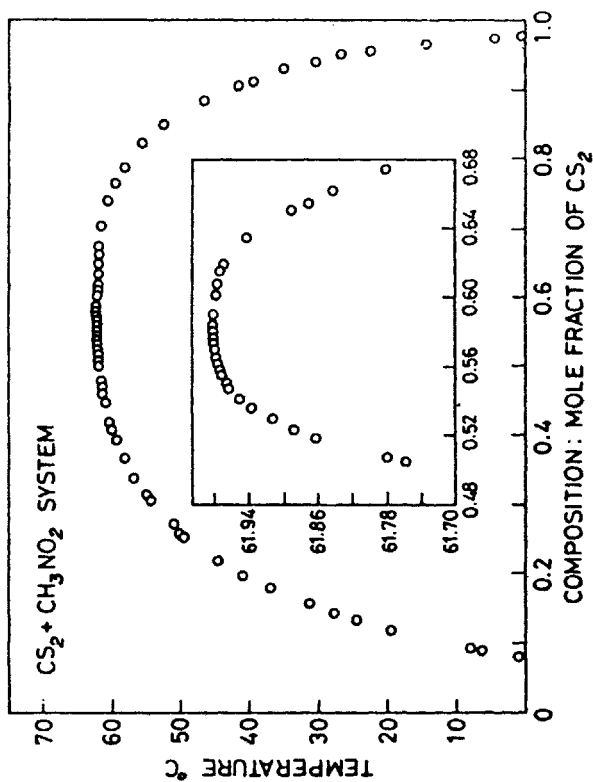


Fig 2 Phase diagram of the binary liquid system carbon disulfide + nitromethane. Inset is the critical region. Temperature control is  $\pm 1$  mK and composition is accurate to  $\pm 0.005$ .

dary at a temperature  $T$ . The log-log plot of  $|x' - x''|$  against  $(T_c - T)$  is shown in Fig. 3, for the system acetonitrile + cyclohexane. One sees that over five orders of magnitude, eq. (2) is obeyed<sup>7</sup>, a nice illustration of the power law behaviour. Further as one moves far away from  $T_c$ , deviations from the straight line behaviour appear. This is because eq. (2) is valid only in the asymptotic region close to  $T_c$ . Far away from  $T_c$ , higher order terms appear of the form

$$|x' - x''| = B_1(T_c - T)^\beta + B_2(T_c - T)^{\beta + \Delta} + \dots \quad \dots (5)$$

where  $\Delta = 0.5$  is called the correction-to-scaling exponent. Studies on several binary liquid mixtures have shown the same universal behaviour.

In the case of ferromagnetic materials the up-alignment of the magnetic moment has the same behaviour as the down-alignment. This arises from various factors like the time reversal symmetry, which also leads to the symmetry between the (bare) particles and holes in statistical physics: In the case of liquid + gas system, this implies that the diameter  $x' + x''$  has the functional form

$$|x' + x''|/2 = x_c + D(T_c - T) \quad \dots (6)$$

which is called the Cailletet-Mathias law of rectilinear diameter having been discovered more than a hundred years ago. The dominant influence of fluctuations in the critical region suggested that this rectilinear diameter law may break down and one should get

$$|x' + x''|/2 = L + D(T_c - T) + E(T_c - T)^{-a} + \dots \quad \dots (7)$$

The prediction was however difficult to check. In ferromagnets the particles (i.e. magnetic moments) are the same as also the state of aggregation making  $L$ ,  $D$ ,  $E$  all zero. In a liquid + gas system the particles are the same but the states of aggregation (i.e., liquid or vapour) are different. In a binary liquid system even the particles are different. So one may hope that the effect should be more pronounced.

Fig. 4 shows the diameter of the binary liquid mixture carbon disulphide + nitromethane<sup>6</sup>. The deviation from the rectilinear behaviour is readily seen. This observation was made in India first, barely months before the reports from USSR and USA. The deviation becomes even more pronounced if one deals with a metallic liquid and its vapour. This has been observed in the case of cesium and rubidium<sup>8</sup>.

In addition to these equilibrium properties, the non-equilibrium properties like thermal conduction, diffusion, electrical conductivity etc. also display unusual features. In the case of liquids, there is an additional class of surface phenomena, like the interfacial tension between the two co-existing liquids going to zero as  $T \rightarrow T_c$ . This leads to interesting partial and complete wetting transitions of the interface, which have also been studied well. They have applications in chemical engineering processes, for instance in the supercritical extraction of oils and essences from natural products.

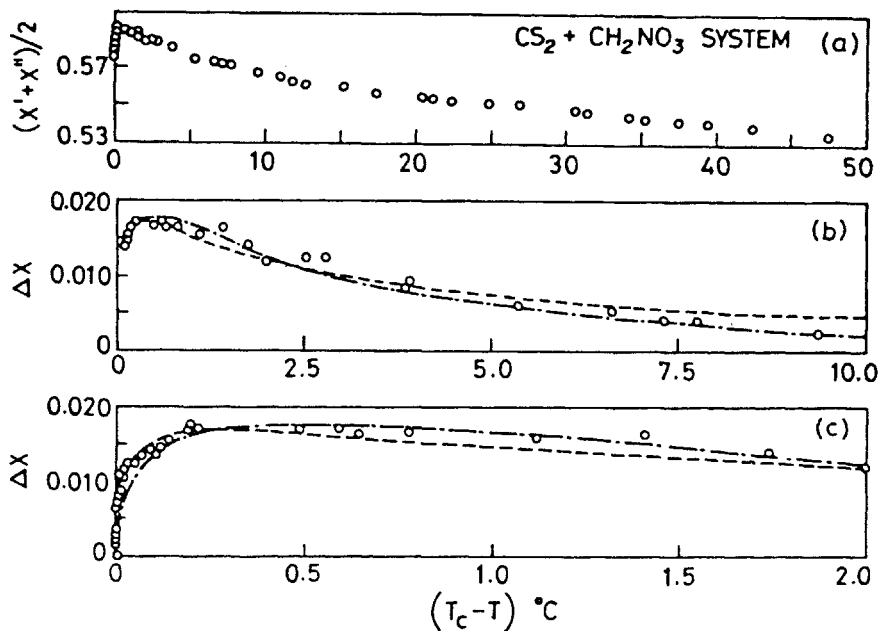


Fig 4 Behaviour of the diameter of the binary liquid system carbon disulphide + nitromethane. Top curve (a) shows the diameter while (b) and (c) show the deviations from the rectilinear behaviour. Lines are different computer fits.

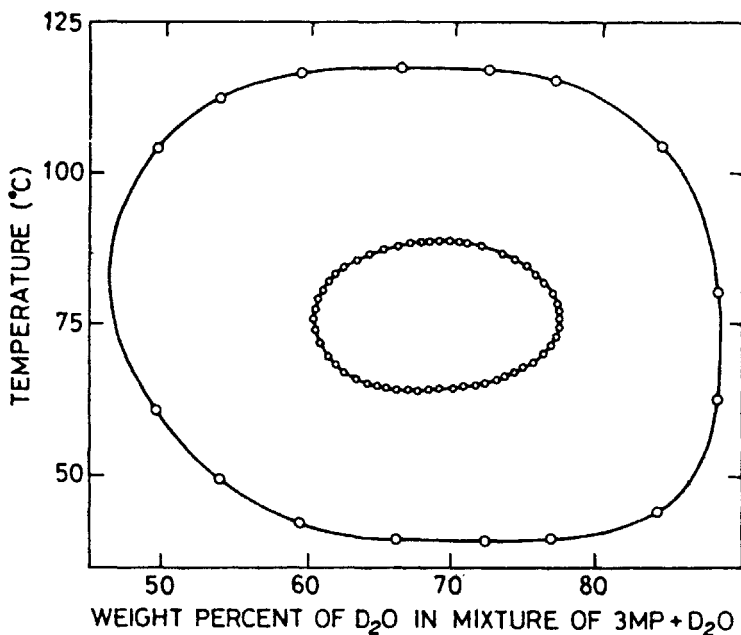


Fig 5 Closed loop phase diagram of 3 methyl pyridine +  $D_2O$ , showing reentrant phenomena of one phase  $\rightarrow$  two phase  $\rightarrow$  one phase when say temperature is reduced from  $125^\circ C$  at a weight percent of 0.7 of  $D_2O$  in the mixture. The addition of  $H_2O$  reduces the loop size. The  $22^\circ C$  loop size plot is plotted as a function of weight fraction of  $(D_2O + H_2O)$ , with weight fraction of  $D_2O$  in  $D_2O + H_2O$  mixture fixed at 0.24.



### Reentrant Phase Transitions

So far one had talked about liquid mixtures like methanol + cyclohexane which show an upper critical solution temperature (UCST). Above  $T_c$  there is only one phase, the liquids being miscible in all proportions. Below  $T_c$  one has the possibility of a two phase region. There are a few pairs of liquids like triethylamine + water where one has a lower critical solution temperature (LCST). In this case below  $T_c$  the liquids are miscible in all proportions giving a one phase region. Above  $T_c$  one has the possibility of a two phase region. There are even fewer pairs of liquids like nicotine + water which show both UCST and LCST. In other words the two phase region is a closed loop, bounded on the high temperature side by UCST and on the low temperature side by LCST. It is interesting that Dr McEwen, working in the Nizam College, Hyderabad, was among the first to study this in the early twenties.

Fig. 5 shows such a closed loop diagram<sup>9</sup> of 3 methyl pyridine +  $D_2O$ . The UCST is  $117.1^\circ C$  and the LCST is  $38.5^\circ C$ . The interesting feature of the system is that the loop size  $\Delta T = UCST - LCST$  can be altered by the application of a third field, in this case by addition of  $H_2O$ . As seen in figure 5, the loop size decreases and ultimately the loop disappears when  $X = \text{Wt. of } D_2O / [\text{Wt. of } D_2O + \text{Wt. of } H_2O]$  is below 0.17. There is then only a single phase region. The locus of the UCST and LCST is shown in Fig. 6. The point where the two coalesce  $t_d = 76.56^\circ C$ ,  $X_d = 0.172$  is called the double critical point. The theory predicts that the shape of curve should be symmetric quadratic

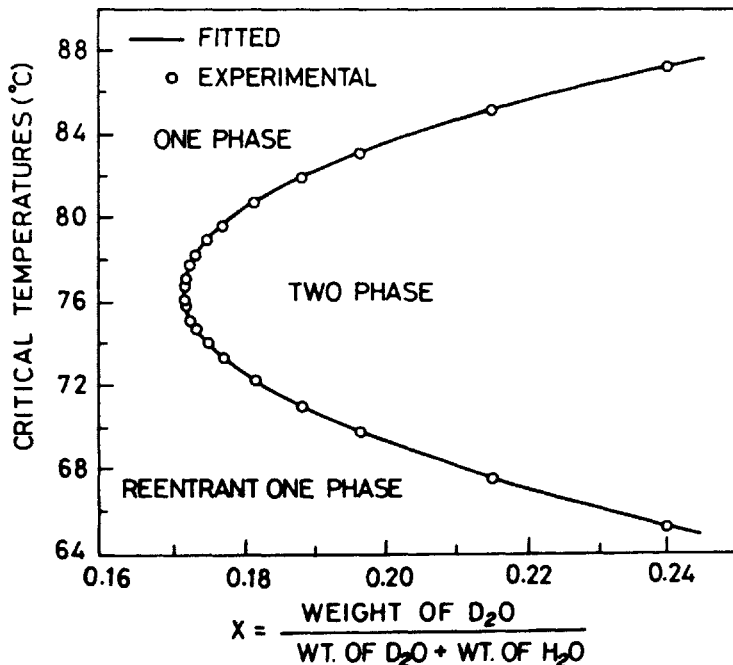


Fig 6 The locus of UCST and LCST as a function of water addition in the system 3 MP +  $D_2O$  +  $H_2O$ . The line is the theoretically fitted curve. The system 3 MP +  $H_2O$  is miscible in all proportions showing only one phase.

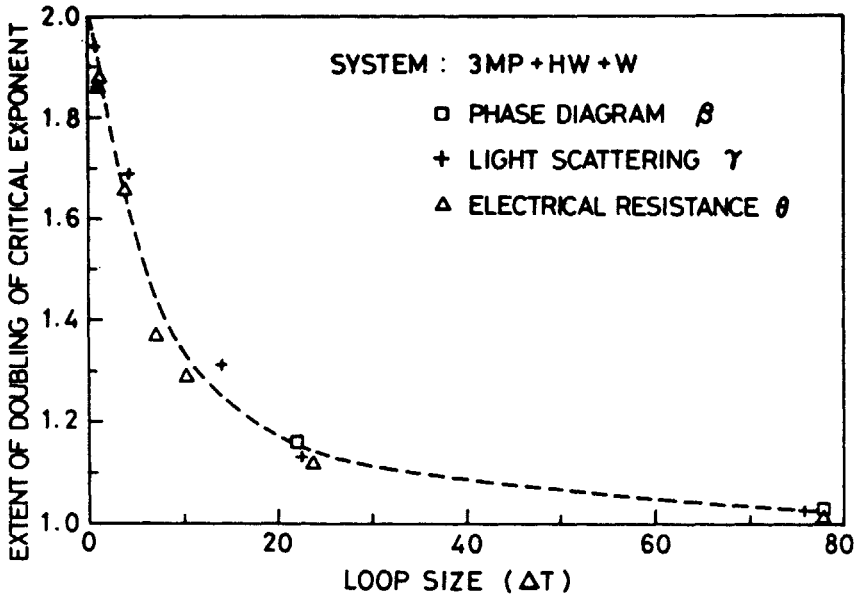


Fig 7 Doubling of the effective critical exponents when the double critical point is approached. When the loop size  $\Delta T$  is very large one gets the Ising values of the exponents  $\beta=0.32$ ,  $\gamma=1.24$ ,  $\theta=0.65$ .

$$\Delta T = E |x - x_d|^{1/2} \quad \dots (8)$$

and that  $(T_U + T_L)/2 = T_d + F(x - x_d) \quad \dots (9)$

with  $F=0$ . The experiments give this within the limit of experimental error and the exponent of eq. (8) is  $0.51 \pm 0.04$ . Fig. 6 has the curve showing a very good agreement between experiment and theory<sup>10</sup>.

A more striking prediction is that near  $T_d$ , the numerical values of critical exponents must become double the values far away from  $T_d$ . It had not been possible to check this with good accuracy, because of the difficulties in the experiments. Using these convenient liquids and temperature region it has been possible to produce with some effort a loop with  $\Delta T=240$  mK far lower than any reported so far by others. Using techniques of light scattering, electrical resistivity and phase diagrams, it has been possible to measure various critical exponents as a function of  $\Delta T$ . Fig. 7 shows the effective exponents as a function of  $\Delta T$  the loop size. The doubling the exponent is clearly evident<sup>11</sup> and constitutes an important addition to the information on critical phenomena. Over this temperature the curve appears to be quadratic in  $\Delta T$ , whose significance is not clear now. New work may throw up yet other interesting results<sup>12</sup>.

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