Analysis of the coexistence curve of a liquid system with a global equation of state

F de Pasquale[†], P Tartaglia[†] and P Tombesi[‡]

[†] Istituto di Fisica della Facoltà di Ingegneria, Università di Roma, Italia
and
Gruppo Nazionale di Struttura della Materia del CNR, Roma, Italia
[‡] Istituto di Fisica, Gruppo Nazionale di Struttura della Materia del CNR, Roma, Italia
and
Istituto di Fisica, Università di Camerino, Italia

Abstract. The data of S C Greer on the difference of volume fractions in the coexisting phases of the isobutyric acid–water system are analysed in terms of our equation of state, which is a model for the crossover from the critical region to a van der Waals-like behaviour. Our results provide evidence of the importance of non-scaling correction terms even in a small range close to the critical point. Correspondingly the effective critical index describing the coexistence curve shows a significant departure from its asymptotic value.

1. Introduction

Recently our knowledge of critical phenomena has reached the point where a detailed comparison can be made between theoretical models and accurate experimental data.

From the theoretical side the recently developed techniques of resummation of the perturbation series in powers of the coupling constant allow a precise estimate of critical indices for Ising-like systems in three dimensions (Le Guillou and Zinn-Justin 1977). In particular the critical exponents relevant to this work are $\beta = 0\cdot325 \pm 0\cdot001$ for the coexistence curve and $\Delta_1 = 0\cdot493 \pm 0\cdot007$ for the leading correction to scaling. Previous calculations gave $\beta = 0\cdot328$ (Kadanoff *et al* 1976, see also Greer 1976) and $\beta = 0\cdot320 \pm 0\cdot016$ (Baker *et al* 1976). These calculations are to be compared with $\beta = 0\cdot312 \pm 0\cdot005$ from series expansions (Domb 1974).

In what follows we limit ourselves to consideration of the coexistence curve.

For these results to be useful in the interpretation of experimental data, one should be able to give a reasonable estimate of the size of the region where a single power-law is valid. In fact, especially in fluids (Levelt Sengers *et al* 1976), the use of the leading power to fit the data in larger regions usually leads to values of $\beta = 0\cdot35$, higher than the theoretical expected values (Levelt Sengers *et al* 1976). In addition the index decreases when considering smaller regions around the critical point (Estler *et al* 1975, Hocken and Moldover 1976). Shrinking the range of temperatures considered has therefore been the first attempt to determine the true leading index.

An alternative to this method has been used recently (Greer 1976, Ley-Koo and Green 1977) adapting to fluids the model introduced by Wegner (1972) which describes the lowest-order corrections to simple scaling. The most important result of

the quoted works is that the fitted critical index β tends to the theoretically calculated value on increasing the number of correction terms. A slightly different point of view is adopted by Balfour *et al* (1978) who fix the critical indices to the renormalisation group values, obtaining quite good results with a parametric equation state which includes the first correction to scaling. Moreover the renormalisation group approach, to our knowledge, has not been applied to the calculation of the amplitudes of the non-scaling terms; as a consequence they must be considered as free parameters to be fitted. We will discuss these results in more detail in § 4.

At this point one must note that Ley-Koo and Green (1977), in their analysis of the SF_6 data of Weiner *et al* (1974), stress that the series of terms predicted by Wegner has a relatively small range of applicability which can be related to a crossover to a mean-field behaviour. In fact they use a van der Waals-like equation of state for the data with $(T_c - T)/T_c > 2 \times 10^{-2}$ (T_c is the critical temperature). Consequently, once the necessity of extending simple scaling has been made clear, it is apparent that one needs a global equation of state capable of describing the asymptotic critical regime, the mean-field behaviour and the crossover between the two regions. As we already noted, the renormalisation group has not yet been applied to the detailed calculation of this global behaviour.

Recently, we proposed a model of this kind which applies to Ising-like systems (de Pasquale and Tombesi 1977). The model is essentially based on ideas which come from the renormalisation group approach to critical phenomena (i.e. the fixed point and the expansion in $\epsilon = 4 - d$, where d is the dimensionality) although we use a somewhat different technique, the so called skeleton expansion. The model corresponds to the first step of this expansion which already gives a partial resummation of the series in ϵ. Its main features are summarised in § 2. Our most important result is the fact that we are able to give a closed form for the equation of state both near the critical point and far from it, where a 'classical' type of behaviour is expected. At the same time we obtain values of the critical indices and the explicit form of the crossover function. When expanded in reduced temperature, the latter gives the same functional form as that used by Wegner (1972) close to the critical point, with the difference that the amplitudes of the non-asymptotic terms all depend on a single non-universal parameter. This in turn implies some universal relations among the amplitudes themselves.

In § 3 we analyse the accurate coexistence curve data of Greer (1976) for the binary liquid system isobutyric acid–water with our global equation of state. Although these data only cover a small range around the critical point, we find evidence for the need of 'effective' correction terms to simple scaling. In fact the critical index which describes the coexistence curve shows a 30% deviation from its asymptotic value.

In § 4 we discuss our results and compare them with similar analyses of fluid systems, where it it shown that discrepancies of the exponents with the theoretically calculated values may be attributed to an overestimation of the size of the asymptotic region.

2. The global equation of state

2.1. The model

The problem is the derivation of a parametric equation of state from a statistical model of a critical system. Our model Hamiltonian (de Pasquale and Tombesi 1977)

is a slightly modified version of the usual Landau–Ginzburg–Wilson Hamiltonian for an Ising system (Wilson and Kogut 1974). The partition functional is

$$Z(h, J) = \int d\psi \int d\sigma \, \exp\left(-\int d^d x \left[\tfrac{1}{2}(\nabla\psi(x))^2 + \tfrac{1}{2}ig\sigma(x)\psi^2(x)\right.\right.$$

$$\left.\left. + \tfrac{1}{2}\sigma^2(x) - h(x)\psi(x) - J(x)\sigma(x)\right]\right) \tag{2.1}$$

which reduces to the usual one with a functional integration over the field $\sigma(x)$. The use of the dummy field $\sigma(x)$ (Halperin *et al* 1974, Coleman *et al* 1974) describing the weak fluctuations of the system, i.e. the energy fluctuations, allows the introduction of the coupled external field $J(x)$ which has the physical meaning of distance in temperature from the critical point. The strong fluctuations of the order parameter are described by the field $\psi(x)$ coupled to the external magnetic field $h(x)$; g is the usual bare coupling constant.

By means of a Legendre transformation over the partition function we get the functional $\Gamma(\phi, J)$ which allows the definition of the one-particle irreducible Green functions (or vertices):

$$\Gamma(\phi, J) = \ln Z(h, J) - \int d^d x \, h(x)\phi(x) \tag{2.2}$$

with the averaged field $\phi(x)$:

$$\phi(x) = \frac{\delta \ln Z(h, J)}{\delta h(x)}\bigg|_J. \tag{2.3}$$

The vertices are

$$\Gamma_{n,m}(\phi, J) = \frac{\delta^{n+m}\Gamma(\phi, J)}{\delta\phi^n \, \delta J^m}. \tag{2.4}$$

The results we will use in the following were obtained by de Pasquale and Tombesi (1977); we confine ourselves here to a brief account of the procedure we used. The important point is to establish a relation among the 'natural' thermodynamic variables h and J associated with the strong and weak fluctuations and the variables characteristic of the parametric representation of the equation of state (Schofield 1969). In our scheme this is accomplished with the use of the skeleton expansion (de Pasquale and Tombesi 1972, Tsuneto and Abrahams 1973, Ginzburg 1974) which allows us to establish self-consistent functional relations among the vertices. Our approximation is checked in the limit of dimensionality close to 4 ($\epsilon = 4 - d \to 0$). The topological structure of the skeleton expansion, together with the usual approximation of zero momentum transfer, allows the use of differential relations instead of functional differential ones. These equations involve the effective coupling constants u and v defined through the vertices

$$u \sim \Gamma_{4,0}(\Gamma_{2,0})^{-\epsilon/2}, \qquad v \sim (\Gamma_{3,0})^2 (\Gamma_{2,0})^{-1-(\epsilon/2)} \tag{2.5}$$

as a function of the variables ϕ and J. A crucial point is then the inversion of the differential equation to get ϕ and J in terms of u and v, which in the model play the role of the variables in the parametric representation of the equation of state. It is in fact easy to verify that on varying u from 0 to 1 the system goes from critical conditions to a regime of independent fluctuations (i.e. a mean-field or van der

Waals-like behaviour). At the same time the variable v defines the different paths of approach to critical conditions. Thus our model gives a set of generalised parametric equations since it determines not only the asymptotic but the whole global behaviour up to 'classical' conditions. It must be noted that the approximation used in the inversion procedure may be checked to every order in ϵ, for each order giving a set of well defined differential equations. The integration of these equations introduces a partial resummation of the ϵ expansion, in fact it gives $\beta = (1 - \frac{1}{2}\epsilon)/(2 - \frac{1}{3}\epsilon)$ for the asymptotic value of the critical exponent for the coexistence curve.

In conclusion the first step of the skeleton expansion gives the following explicit form of the parametric equation of state:

$$\phi/N_{\phi} = G^{1/\epsilon}\theta(1-u)^{(1/\epsilon)-\frac{1}{2}}u^{-1/\epsilon} \qquad (2.6a)$$

$$t = G^{2/\epsilon}(1-\tfrac{3}{2}\theta^2)(1-u)^{(2/\epsilon)-\frac{1}{3}}u^{-2/\epsilon} \qquad (2.6b)$$

$$h/N_h = G^{3/\epsilon}\theta(1-\theta^2)(1-u)^{(3/\epsilon)-\frac{1}{2}}u^{-3/\epsilon} \qquad (2.6c)$$

where the usual parametric variable $\theta^2 = v/3u$ has been introduced. $t = (T - T_c)/T_c$ is the reduced temperature and N_{ϕ}, N_h are normalisation constants which allow the interpretation of ϕ and h as the physical order parameter and external field respectively. G is related to the bare coupling constant.

2.2. Crossover function for the coexistence curve

The two branches of the coexistence curve are given for $\theta = \pm 1$, so that from the parametric equation of state (equations (2.6)) one gets for the order parameter difference in the two coexisting phases $\Delta\phi$ and the reduced temperature t:

$$\Delta\phi = 2G^{1/\epsilon}N_{\phi}(1-u)^{(1/\epsilon)-\frac{1}{2}}u^{-1/\epsilon} \qquad (2.7a)$$

$$t = -\tfrac{1}{2}G^{2/\epsilon}(1-u)^{(2/\epsilon)-\frac{1}{3}}u^{-2/\epsilon}. \qquad (2.7b)$$

It is now possible to eliminate the parameter u with the result

$$\left(\frac{\Delta\phi}{N_{\phi}}\right)^3 - 2^\epsilon G[(-8t)^{3/4}]^{2-\epsilon}\left(\frac{\Delta\phi}{N_{\phi}}\right)^{2/3} - [(-8t)^{3/4}]^2 = 0. \qquad (2.8)$$

This is the functional form for the coexistence curve which can be made explicit in the temperature for the case of physical interest $\epsilon = 1$, i.e.

$$-t = \frac{1}{8}\left(\frac{\Delta\phi}{N_{\phi}}\right)^{2/3}\left\{-G + \left[G^2 + \left(\frac{\Delta\phi}{N_{\phi}}\right)^2\right]^{1/2}\right\}^{4/3}. \qquad (2.9)$$

Although the preceding equation would be sufficient, the expression of $\Delta\phi$ as a function of t is more suitable for the analysis of experimental data, since the measurements are performed at fixed temperature. Moreover knowledge of $\Delta\phi(t)$ allows a direct comparison with the renormalisation group models (Wegner 1972). To this end the following transformation of variables is useful:

$$x = \frac{1}{5}\left(-\frac{2t}{G^2}\right)^{\Delta_1}, \qquad y = \left(\frac{\Delta\phi}{2GN_{\phi}}\right)^{1/2}\left(-\frac{G^2}{2t}\right)^{\beta/2} \qquad (2.10)$$

with the asymptotic exponents given by $\beta = 0\cdot 3$, $\Delta_1 = 0\cdot 6$. Then the coexistence curve

assumes the simple form

$$y^6 - y = 5x \qquad (2.11)$$

from which the following Lagrange expansion (Abramowitz and Stegun 1965) of y as a function of x can be easily obtained:

$$y(x) = 1 + \sum_{k=1}^{\infty} A_k x^k \qquad (2.12)$$

with the coefficients given by

$$A_k = \frac{1}{k!} \left[\frac{\mathrm{d}^{k-1}}{\mathrm{d}y^{k-1}} (y + y^2 + y^3 + y^4 + y^5)^{-k} \right]_{y=1}$$

$$= \sum_{a_1 a_2 a_3 a_4 a_5} \frac{(-1)^{a_1+a_2+a_3+a_4+a_5}}{5^k k!} \frac{(k-1+a_1+a_2+a_3+a_4+a_5)!}{a_1! a_2! a_3! a_4! a_5!}$$

$$\times 2^{2a_2+a_4} 3^{a_1+a_3+a_4} 5^{-a_4-a_5} \qquad (2.13)$$

summed with the condition $a_1 + 2a_2 + 3a_3 + 4a_4 + 5a_5 = k - 1$. The expansion up to the sixth order is given explicitly by

$$y = 1 + x - 3x^2 + 14x^3 - 78x^4 + 478 \cdot 8x^5 - 3125x^6 + \dots \qquad (2.14)$$

and in terms of universal variables

$$\Delta\phi^* = \frac{\Delta\phi}{2N_\phi G}$$

$$= (-t^*)^\beta \left(1 + \sum_{k=1}^{\infty} B_k (-t^*)^{k\Delta_1} \right)$$

$$= (-t^*)^\beta [1 + 0 \cdot 4(-t^*)^{\Delta_1} - 0 \cdot 2(-t^*)^{2\Delta_1} + 0 \cdot 176(-t^*)^{3\Delta_1} - 0 \cdot 1904(-t^*)^{4\Delta_1}$$

$$+ 0 \cdot 2296(-t^*)^{5\Delta_1} - 0 \cdot 2962(-t^*)^{6\Delta_1} + \dots] \qquad (2.15)$$

with

$$t^* = \frac{2t}{G^2}; \qquad B_m = \frac{1}{m} \sum_{k=1}^{m} (3k - m) A_k B_{m-k}. \qquad (2.16)$$

The expression (2.15) of $\Delta\phi$ as a function of T has been used to fit the experimental data.

At this point we note some features of our equations:

(i) A comparison with Wegner's (1972) results shows immediately that the expansion of our crossover function for the coexistence curve is of the same functional form. We are able to get the values of the amplitudes of the non-asymptotic terms; in particular B_2 turns out to be negative, in agreement with the sign obtained when fitting fluid systems (Greer 1976, Ley-Koo and Green 1977, Balfour *et al* 1978).

(ii) The correction terms to asymptotic scaling only depend on the parameter G, so that one can in general say that the ratio B_k/B_1^k is a universal quantity. As a consequence one can represent the experimental data on a universal plot $(t^*, \Delta\phi^*)$.

(iii) The use of the scaling variables x and y confirms the effect of the correction terms. In fact asymptotic scaling corresponds to $y = 1$, the first non-scaling term to $y = 1 + x$ and so on.

A particularly suitable tool to confirm the crossover phenomenon is the intro-
duction of an effective critical index β_{eff}† (Riedel and Wegner 1974), which is given by

$$\beta_{\text{eff}} = \frac{d \lg \Delta\phi}{d \lg(-t)} = \beta + 2\Delta_1 \frac{x}{6x + y(x)} \tag{2.17}$$

where $y(x)$ is given implicitly by equation (2.11) or by the expansion equation (2.14).
It is apparent that when $x \to 0$ (i.e. the critical point) β_{eff} tends to its asymptotic value
$\beta = 0\cdot 3$ while for large values of x it tends to the 'classical value' $\beta_{\text{eff}} = \beta + \frac{1}{3}\Delta_1 = 0\cdot 5$.
Surprisingly our analysis in § 3 will show a variation of β from $0\cdot 30$ to $0\cdot 38$ even if the
maximum distance from the critical point is only $-t \simeq 10^{-2}$.

3. Analysis of isobutyric acid–water data

In order to test our global equation of state we analysed the published data of Greer
(1976). We use the two runs reported there and refer to the original paper for the
details of the experiment.

One of the most important results of the analysis performed by Greer is that the
best choice for the order parameter of the binary liquid system isobutyric acid–water is
the volume fraction of one of the components in the mixture. For this reason we
assumed the order parameter ϕ which appears in our model to be proportional,
through the constant N_ϕ, to the volume fraction.

The best fit to the data was performed mainly with a modified version of the
general non-linear fitting program CURFIT reported by Bevington (1969), and only
occasionally, and whenever possible, checked with a linear fitting program. We
started reproducing the fit to the simple power law reported by Greer and getting the
same results within statistical error. Then we analysed the data with our equation of
state, both in the explicit form $t = t(\phi)$ (equation (2.9)) and in the form $\phi = \phi(t)$ of
equation (2.15). In both cases we got the same results for the free parameters T_c, G
and N_ϕ which are reported in table 1 together with their estimated errors (three times
the standard deviation) and the average standard deviation of the data $\bar{\sigma}$. The fits we
obtain seem to be very accurate and comparable with the ones performed by Greer.
However, it must be stressed that we use a global equation which only depends on
three parameters, namely the critical temperature, the amplitude of the leading power

Table 1. Results of fit to the differences of volume fractions in the coexisting phases of the
isobutyric acid–water system. Data refer to the two runs reported in Greer (1976). χ_ν^2
and $\bar{\sigma}$ are respectively the normalised chi-squared and the average standard deviation of
$\Delta\phi$ (Bevington 1969).

	Run 1	Run 2
T_c	$(25\cdot 9967 \pm 0\cdot 0012)\,°C$	$(25\cdot 9697 \pm 0\cdot 0011)\,°C$
G	$0\cdot 278 \pm 0\cdot 023$	$0\cdot 365 \pm 0\cdot 038$
N_ϕ	$0\cdot 572 \pm 0\cdot 080$	$0\cdot 521 \pm 0\cdot 090$
χ_ν^2	$1\cdot 59$	$1\cdot 21$
$\bar{\sigma}$	$7\cdot 68 \times 10^{-4}$	$6\cdot 70 \times 10^{-4}$

† The definition of β_{eff} is mistaken in de Pasquale and Tombesi (1977). In equation (3.4a) one should read
β_{eff}^{-1} instead of β_{eff}.

of t and the parameter which determines all the non-asymptotic correction terms; whereas in the analysis of Greer (1976), the number of free parameters increases on adding correction terms to the simple scaling form.

The main difference between our approach and Greer's is in the already stated fact that we think that the corrections to the leading behaviour are noticeable even in this case, where the maximum distance from the critical point is of the order 10^{-2}. On the contrary the conclusion reached in the previous analysis of the same data is that no additional term is necessary to the leading behaviour.

In order to test this fact, as we noted in the introduction, we made an F-test (Bevington 1969) to establish the need for these corrections. We fixed the critical temperatures of the two runs and the critical indices β and Δ_1 and performed a test on the necessity of adding further terms to the leading one. The indices were fixed at the already quoted values recently obtained in three dimensions with renormalisation group techniques (Le Guillou and Zinn-Justin 1977), which should be among the best available estimates. The F-test gives the following results. For run 1 the inclusion of the first correction term is justified with a 99% probability (i.e. this is the probability that the χ_{ν}^2 is not decreased by chance) and the inclusion of the second term is justified with 28% probability. For the second run the corresponding probabilities are 80% and 60%.

The reason for the disagreement between our analysis and Greer's can, in our opinion, be understood considering that she fitted both the critical index β and the amplitudes of the scaling and correction terms. The effect of this procedure is less evident in the case of the isobutyric acid–water system, where the data are confined to a small range, but it is apparent in Greer's analysis of the data of Gopal *et al* (1973) on the carbon disulphide–nitromethane system which extend up to $-t = 0{\cdot}2$. In this case there is a definite decrease of β from $0{\cdot}352$ to $0{\cdot}306$ and at the same time the various amplitudes do not show a tendency to remain constant when adding correction terms. We think this shows that the fitting procedure introduces an effective critical index.

The analysis of Ley-Koo and Green (1977) does not show this phenomenon, since they increase the range of the data together with the number of correction terms. In this way they succeed in obtaining stable values of β and the amplitudes. We observe that the indices thus obtained are quite close to the calculated ones, so that it looks natural to fix their values and fit only the amplitudes. This has been done recently for steam by Balfour *et al* (1978).

Our results are shown in figures 1 to 5. Figures 1 and 2 show the experimental data and the fitted coexistence curves; figure 3 shows the associated deviation plot for the two runs. Figure 4 exhibits a first indication of the deviation from a simple power law (lower curve) in the universal plot $(t^*, \Delta\phi^*)$. This deviation is confirmed in figure 5 using the scaling variables x and y; in this plot a horizontal line starting from $y = 1$ would represent true asymptotic behaviour, the straight line $y = 1 + x$ represents the first correction to it and the lower curve our model. Finally, figure 6 shows the variation of β_{eff} in the actual range of temperatures considered. One can see a maximum variation of β_{eff} of the order of 30%. In order to check this unexpected behaviour we estimated β_{eff} for the already mentioned fit with fixed $\beta = 0{\cdot}325$ and $\Delta_1 = 0{\cdot}493$ and a single correction term. We get a maximum value of the order of $0{\cdot}40$ in good agreement with our result.

Finally, we must note that the average value of β_{eff} over the range of temperatures we considered is of the order of $0{\cdot}34$, i.e. the order of magnitude usually found when fitting a simple power law up to the non-asymptotic region.
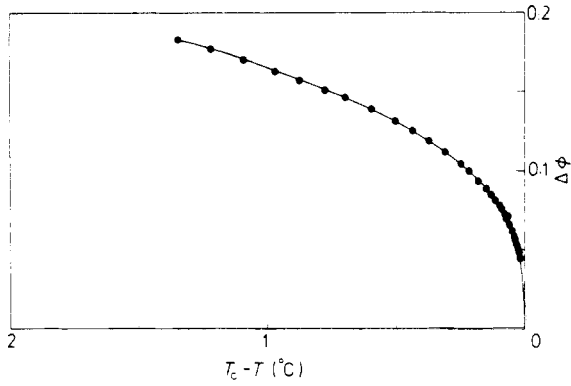
Figure 1. Coexistence curve of isobutyric acid–water: difference in volume fraction of the two phases as a function of temperature for run 1 (Greer 1976). The full curve is our fitted equation of state. $T_c = 25 \cdot 997$ °C.

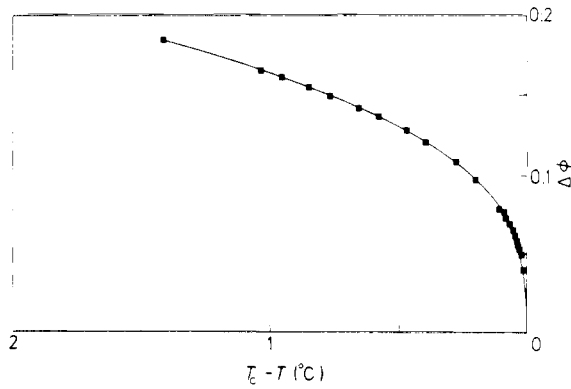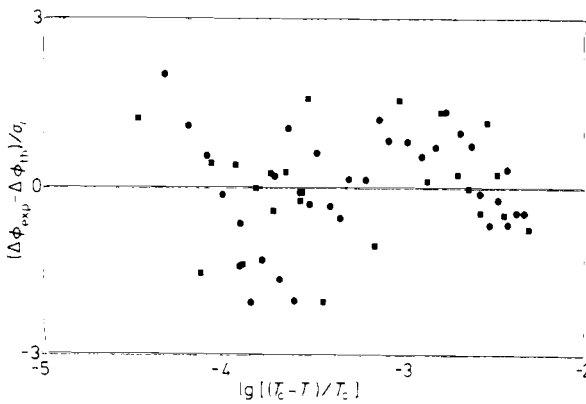**Figure 2.** Coexistence curve for run 2 (Greer 1976). See figure 1. $T_c = 25 \cdot 970$ °C.

Figure 3. Deviation plot for the two runs (●, run 1; ■, run 2). The abscissa is $\lg[(T_c - T)/T_c]$ and the ordinate $(\Delta\phi_{exp} - \Delta\phi_{th})/\sigma_i$ where σ_i is the estimated standard deviation for each point.
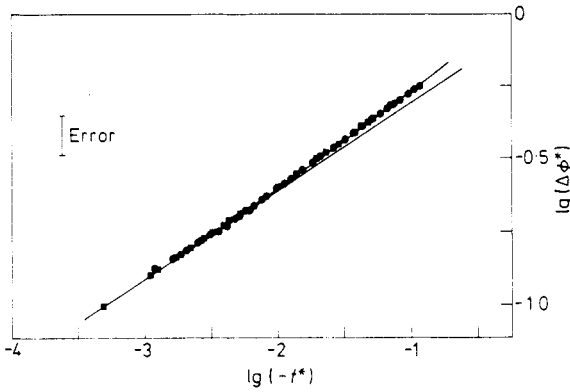
Figure 4. Universal plot (●, run 1; ■, run 2) in the variables t^* and $\Delta\phi^*$ defined in the text. The lower curve is a single power law with $\beta = 0\cdot3$, the upper curve our fitted equation of state.
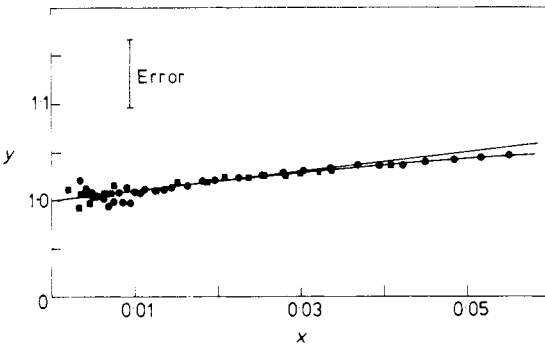

Figure 5. Universal plot (●, run 1; ■, run 2) in the variables x and y defined in the text. The upper curve is the first non-scaling correction $y = 1 + x$; the lower curve our fitted equation of state.
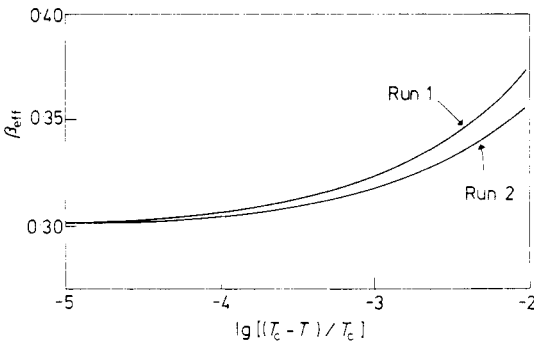

Figure 6. Variation of β_{eff} for the two runs.

4. Discussion and summary

The most recent approach to critical phenomena in fluids seems to be successful in overcoming the difficulties of connecting their behaviour to that of an Ising system.

The new strategy consists in assuming the validity of the theoretically estimated indices and explaining the apparent discrepancies, which arises when considering only asymptotically valid power laws, with the addition of non-scaling correction terms, i.e. fitting only the amplitudes of these terms (Balfour *et al* 1978, Sengers and Moldover 1978). Moreover it seems by now widely accepted that these corrections are important both in restricted ranges around the critical point and far from it, where there are indications that the system should be described by a van der Waals equation of state (de Pasquale *et al* 1976, Ley-Koo and Green 1977). Unfortunately the calculation of the amplitude of the non-asymptotic terms and the resummation of the Wegner expansion to describe the global behaviour of fluids has not yet been made with the accuracy that the renormalisation group has achieved in the case of critical exponents.

The main advantage of our model is to describe the global behaviour between critical and classical regimes in terms of only three parameters. In other words, we calculate on the same footing both the critical indices and the crossover function. The success of the analysis of § 3 makes us confident that our approach is in the right direction.

In conclusion, the challenging problem, from the theoretical side, is to determine the structure of the crossover consistent with the accurately known critical indices. Our model is a first attempt in this direction; its limitations are apparent because our critical exponents are quite far from the 'true' ones. The next step, in the context of the skeleton expansion approach, would be to improve our evaluation of the critical exponents and the structure of the crossover function. From the experimental point of view one gets the natural suggestion to extend the range of the data in order to have a complete understanding of the critical phenomena.

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