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The asymptotic critical regime in binary mixtures: can it be experimentally observed?

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Abstract. The lack of direct experimental evidence of the detection of the asymptotic critical behaviour in binary mixtures has led to the conjecture that the extent of the critical regime is exceedingly small in these systems. We address this problem from the theoretical side and find that: (i) the strong crossovers which affect the critical phenomena in mixtures are due to the competition between two different renormalization group fixed points; (ii) the crossover temperature is governed by a characteristic parameter which depends on the range of interactions as well as on purely thermodynamic quantities; and (iii) the extent of the asymptotic region is not necessarily small: specific systems and regimes allowing for the experimental observation of the true critical exponents are identified.

The experimental study of the phase diagram and of the critical phenomena in binary mixtures has drawn out a picture considerably richer than that for one-component fluids [1, 2]. On the theoretical side, however, the situation is not firmly established. In particular, the interpretation of critical phenomena in mixtures still rests largely upon the phenomenological approach originally proposed by Fisher in a somewhat different context [3] and subsequently specialized to binary mixtures in a systematic way [4]. Recently, a microscopic justification of this hypothesis has been provided by use of the hierarchical reference theory of fluids (HRT) [5]. The basic *ansatz* of the phenomenological approach is that the singular contribution to the grand potential can be identified, in the critical region, with the scaling function of the one-component system, provided that the 'thermal' and 'magnetic' scaling fields are substituted for with two effective fields that depend analytically on the temperature and on the chemical potentials of the components. This approach has led to several important predictions concerning the critical behaviour of the thermodynamic quantities in binary mixtures, some of which are qualitatively different from the corresponding results for the pure components: for example, a 'renormalization' of the critical exponents along certain thermodynamic paths is predicted, where the renormalizing factor $1/(1-\alpha_I)$ is related to the critical exponent α_I of the constant-volume specific heat for the one-component case. In the following the subscript 'I' will refer to critical exponents for one-component (Ising) systems. Also, the isothermal compressibility at constant composition (κ_T) on the critical isochore is predicted to diverge weakly as a function of temperature with an exponent $\alpha_I/(1-\alpha_I)$, while the specific heat (C_V) does not diverge at all. However, the experimental results [6] have shown that the critical phenomena in binary

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mixtures do not conform to these predictions. This has been explained by invoking strong crossover effects which enormously reduce the asymptotic critical region. This makes it difficult to unambiguously confirm the theoretical predictions: in the case of the isothermal compressibility even the existence of a critical divergence seems to be questionable, as this quantity usually appears to saturate at a constant value rather than diverge. The interest in crossover phenomena in mixtures has now been aroused again, and some studies have been made, at least in the limit of a dilute or a weakly compressible mixture, in the framework of the aforementioned phenomenological approach [7].

In this article, we address the crossover problem in mixtures by the use of HRT [8]: we show that its extension can be estimated in terms of the microscopic properties of the system and find that, under suitable conditions, the crossover region falls in an easily accessible region.

HRT can be regarded as a method for implementing the basic renormalization group (RG) idea of the gradual inclusion of long-wavelength fluctuations in the context of a genuine liquid-state theory. HRT has been applied to a number of systems ranging from simple fluids to Ising models where 'exact' results are available: the comparison has shown that HRT is able to precisely locate the critical points, the coexistence curve and the equation of state of these models [8]. This approach provides a microscopic derivation of the effective, field theoretical action S which governs the long-wavelength fluctuations, starting from the physical Hamiltonian of the model. Moreover, usual RG concepts, like fixed points and flow of coupling constants are naturally present in this framework.

In the case of binary mixtures, HRT predicts a long-wavelength effective action of the general form

$$\begin{aligned} S[\phi_1,\phi_2] &= \int \mathrm{d}\boldsymbol{x}\ \left\{\frac{1}{2}|\boldsymbol{\nabla}\phi_1|^2 + H[\phi_1,\phi_2]\right\} \\ H[\phi_1,\phi_2] &= r\phi_1^2 + g^2\phi_2^2 + u\phi_1^4 + wg\phi_1^2\phi_2 \end{aligned} \tag{1}$$

where the *two* fluctuating fields (ϕ_1, ϕ_2) physically represent suitable combinations of density and concentration fluctuations. The difference in character of the fluctuations in the two directions (ϕ_1, ϕ_2) is manifest in the effective action (1), where the gradient term of ϕ_2 which describes the spatial fluctuations of the order parameter is absent, resulting in the lack of a natural length scale for ϕ_2. This effective action is a natural generalization of the usual ϕ^4-form for one-component fluids and refers to the region of the phase diagram where odd operators in the field ϕ_1 vanish. Analogously to the one-component system, all fixed points lie in this symmetric manifold. The four coupling constants which define $S[\phi_1,\phi_2]$ are non-universal parameters related, by HRT, to the microscopic features of the model.

The momentum-space RG equations which describe the long-wavelength behaviour of this model are obtained by introducing an infrared cut-off Q on fluctuations and examining how $S[\phi_1,\phi_2]$ is modified when fluctuations with wavevector $k > Q$ are integrated out. As usual, the effective action maintains the same formal structure, at least near the upper critical dimensionality ($d = 4$), while the coupling constants (r, g, u, w) change their values according to differential equations [5] which can be obtained by standard methods, at least to leading order in the ϵ-expansion (where $\epsilon = 4 - d$). The evolution stops when the cut-off Q matches the inverse correlation length: $Q \sim \xi^{-1} \sim Q\, r_Q^{1/2}$, i.e. when the system is mapped out of the critical regime.

The possible fixed points of this set of RG equations have been studied in reference [5] and include, among others, the 'one-component' (1C) and the 'two-component' (2C) fixed points. By linearizing the evolution equations around their fixed-point solutions we can investigate the stability of these solutions In the symmetric subspace, the 1C fixed point

is characterized by two relevant eigenvalues: the thermal one $\Lambda_T = 2 - \epsilon/3$ which leads to Ising critical exponents; and an additional 'mixing' eigenvalue $\Lambda_\times = \epsilon/3$ leading to the crossover exponent $\Lambda_\times/\Lambda_T = \alpha_I$. Instead, the 2C fixed point has a single relevant (thermal) operator with eigenvalue $\Lambda_T = 2 - 2\epsilon/3$ which gives a diverging correlation length with exponent $\nu = 1/\Lambda_T = \nu_I/(1-\alpha_I)$ in agreement with the phenomenological approach. Asymptotically close to a generic point on the critical line of a binary mixture, the RG flow is governed by the 2C fixed point which leads to a strong divergence of fluctuations of the ϕ_1-field with exponent $\gamma_I/(1-\alpha_I)$, and to a weak divergence of ϕ_2-fluctuations with exponent $\alpha_I/(1-\alpha_I)$. The basic difference between the structure of the 1C (unstable) and 2C (stable) fixed points is the vanishing of the 'mixing term' w^* in the former case. Clearly, if this term happens to be small at the beginning of the RG evolution, i.e. at a mean-field level, the flow will first feel the influence of the unstable 1C fixed point, giving rise to effective critical exponents of the Ising type, as observed experimentally. Eventually, the presence of the relevant crossover eigenvalue $\Lambda_\times > 0$ will drive the RG flow away from the 1C fixed point and the real asymptotic critical exponents associated with the 2C fixed point will be detectable. But this will occur only at reduced temperatures smaller than $t_\times$, which can be estimated [5] on the basis of the RG evolution equations:

$$t_\times \propto (r - r_c) \simeq \left(\frac{w}{w^*}\right)^{2/\alpha_I} \tag{2}$$

with $\alpha_I \simeq 0.12$ in a three-dimensional system. Although this estimate does not give a unique definition of the crossover temperature, it clearly shows how this basic quantity *scales* with the microscopic parameters, and particularly with the 'mixing ratio' w/w^*. Due to the large exponent in equation (2), $t_\times$ is quite sensitive to this parameter.

In order to analyse the extent of crossover phenomena in realistic models of mixtures, the key ingredients, missing in the usual RG treatments of this problem, are (i) the relationship between the scaling fields (ϕ_1, ϕ_2) and the density–concentration fluctuations together with (ii) a realistic estimate of the bare parameters (r, u, g, w). This connection is provided by HRT which gives a precise correspondence between physical variables and effective, field theoretical actions. In particular, a previous study [9] showed that the direction of strong fluctuation ϕ_1 in the density–concentration plane is related to experimentally available quantities such as the partial molar volumes $v_i \equiv (\partial V/\partial N_i)_{T,P}$. Here V, T, P are respectively the volume, the temperature, and the pressure of the mixture, and N_i is the number of particles of i-type. In order to identify the essential features of the crossover phenomena, here we adopt a simplified analysis where short-wavelength effects are treated at a mean-field level. This leads to an analytic relationship between the parameters defining the effective action and the physical variables. A careful analysis shows that, along the mean-field critical lines, the key parameter w, which governs the flow towards the 2C fixed point, can be written as the product of two terms: a 'fluctuation' contribution $w_{\rm fl}$, which involves the range of the interparticle interactions; and a term $w_{\rm th}$ which instead contains only thermodynamic quantities like the aforementioned partial molar volumes v_i, the molar fraction $x \equiv N_2/(N_1 + N_2)$, the volume per particle $v \equiv V/(N_1 + N_2)$, the isothermal compressibility at constant composition κ_T, and the temperature T. Specifically, one finds

$$w_{\rm fl} = \frac{v_1^2 + v_2^2}{b_{11}v_2^2 + b_{22}v_1^2 - 2b_{12}v_1v_2}\,\frac{3}{\pi Q_0^{1/2}} \tag{3}$$

$$w_{\rm th} = \left(\frac{k_B T}{\kappa_T}\right)^{1/2} \frac{v^3}{v_1^2 + v_2^2}\,\frac{1}{1-x}\left(\frac{\partial v_2}{\partial x}\right)_{T,P}. \tag{4}$$

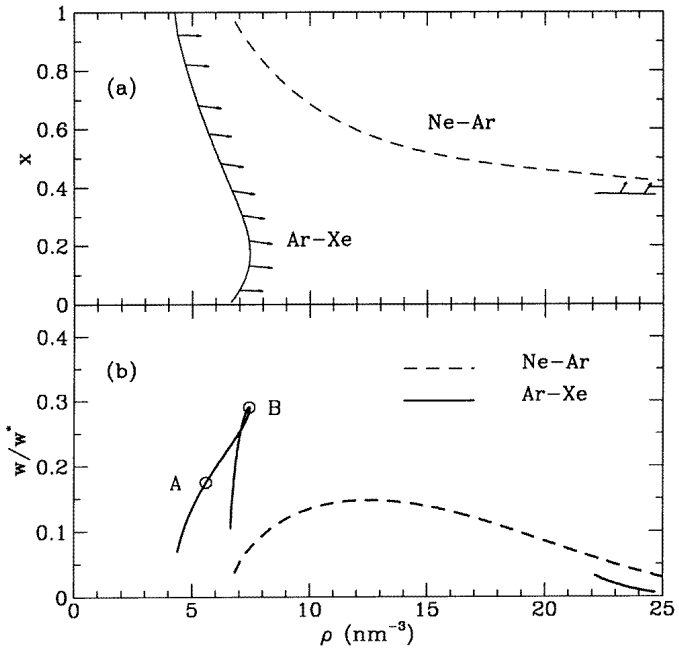

Figure 1. (a) Mean-field critical lines on the density–concentration plane for a neon–argon mixture (dashed line) and an argon–xenon mixture (full line). The arrows along the argon–xenon critical lines point in the direction of the strong fluctuation, which gives the order parameter of the transition. (b) The mixing ratio appearing in equation (2) for an argon–xenon and a neon–argon mixture.

The coefficients b_{ij} in equation (3) represent the second moment of the attractive interactions between two particles of species i and j while Q_0 is a characteristic ultraviolet cut-off which gives a measure of the region in momentum space where fluctuations become important, and can be estimated as the typical inverse diameter of the molecules. It is worthwhile to observe that the values of b_{ij} do not affect the phase diagram at the mean-field level, so nothing can be said about the value of $w_{\rm fl}$ by considering the shape of the critical lines. The form of $w_{\rm fl}$ accounts for the well known Ginsburg result [10], which states that short-range interactions are more effective than long-range ones in revealing the asymptotic critical behaviour of the system. Although to be expected, this piece of information is clearly out of the reach of the phenomenological approach.

Since $w_{\rm fl}$ behaves smoothly along the critical lines, the main qualitative features of w are embodied in the thermodynamic contribution $w_{\rm th}$. It must be explicitly recalled that equation (4) for $w_{\rm th}$ refers to a mean-field or 'coarse-grained' action (1), so from a phenomenological point of view its validity is limited to the pre-asymptotic region: in fact, in the very neighbourhood of a critical point, that is for $Q \to 0$, both $1/\kappa_T$ and $\partial v_2/\partial x$ would vanish [11]. A region that gives rise to small (although not exactly vanishing) values of w as a consequence of the behaviour of $w_{\rm th}$ is the high-density, high-pressure portion of the critical lines. This part of the phase diagram, where the character of the transition is generally of the demixing type, with strong concentration fluctuations, is not favourable for the detection of the true asymptotic regime in an experimentally accessible range.

Two specific examples are considered in figure 1, where we present the mean-field

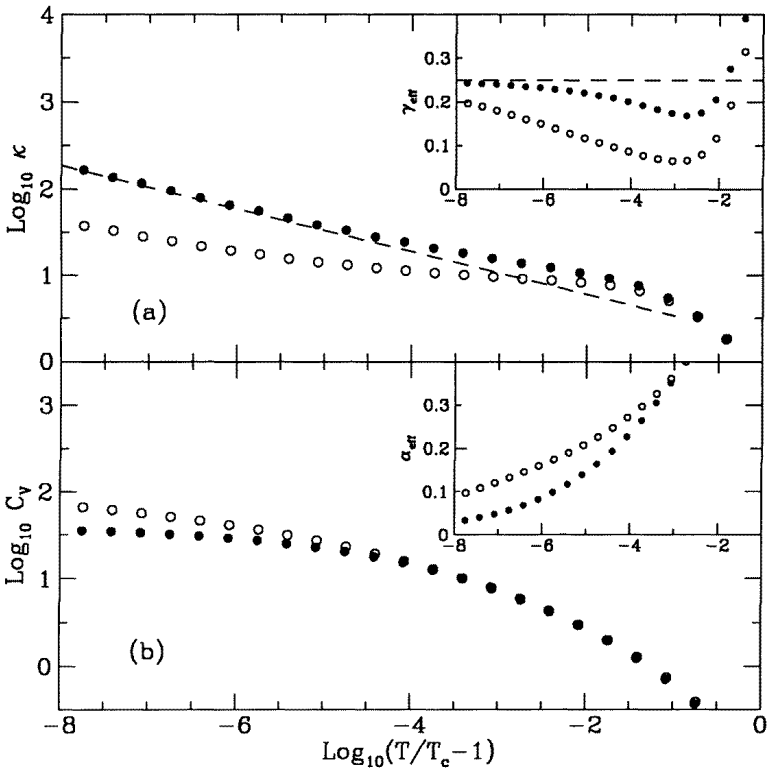

Figure 2. A log–log plot of (a) the reduced isothermal compressibility at constant concentration $\kappa_{\rm red}$ and of (b) the specific heat at constant volume and concentration C_V of an argon–xenon mixture as functions of the reduced temperature t for the two critical points A (open dots) and B (full dots) of figure 1, as calculated from RG equations. The asymptotic behaviour of the compressibility is shown by a dashed line. In the insets the corresponding effective critical exponents are reported. The asymptotic value of $\gamma_{\rm eff}$ is shown in panel (a).

critical lines and the dimensionless mixing ratio appearing in equation (2) for a simple model made up of additive spheres interacting via a hard-core plus a Lennard-Jones-tail potential. Two different choices of the diameters σ_i and of the depth of the attractive well ϵ_{ij} were made [12], so as to model a neon–argon and an argon–xenon mixture. In the figure the direction of the strong fluctuation in the density–concentration plane is also shown. It can be seen that in the case of the neon–argon mixture the mixing ratio, and therefore the crossover temperature, is small everywhere on the critical line. This is actually the situation encountered in most cases, irrespective of the topology of the phase diagram. In the case of the argon–xenon mixture, however, the reduced crossover temperature raises very sharply, and in a narrow region around a xenon concentration $x \simeq 0.15$ reaches a relatively large value which can be estimated in the experimentally accessible range between 10^{-2} and 10^{-3}.

The critical behaviours of the compressibility and specific heat, together with the corresponding 'effective' critical exponents ($\gamma_{\rm eff}$ and $\alpha_{\rm eff}$ respectively), are plotted in figure 2 as functions of the reduced temperature for two different points, labelled A and B, on the Ar–Xe critical lines. The effective exponents are defined as the local slope, in a log–log

plot, of the physical quantity versus the reduced temperature. In the case of point A, γ_{eff} approaches its asymptotic value ($\gamma_{\text{eff}} = 0.25$ in our approximation) only at extremely small reduced temperatures, while the specific heat does not even show a well defined power-law behaviour and the corresponding effective exponent is everywhere larger than half of its Ising value ($\alpha_I = 0.2$ in this approximation). An estimate of the crossover temperature can be obtained by considering the inflection point of γ_{eff} leading to $t_\times^A \simeq 10^{-5}$ for point A. Instead, the asymptotic critical behaviour can be more easily achieved for point B, at least as far as the divergence of the compressibility is concerned. By the same criterion as was introduced for point A, we can estimate $t_\times^B \simeq 10^{-3}$ which falls in the experimentally accessible range. Similarly, the effective exponent α_{eff} vanishes more rapidly, showing the asymptotic saturation of the specific heat in mixtures. It is noteworthy that the ratio between the two estimated crossover temperatures $t_\times^A/t_\times^B \sim 10^{-2}$ agrees with the corresponding mixing ratio (w^A/w^B) raised to the power $2/\alpha_I$, as predicted by equation (2).

It can be seen that a sharp increase of the parameter w such as the one just considered occurs when a portion of the critical lines gets close to a stability limit. The stability condition that has to be satisfied for every point in the phase diagram amounts to requiring that the free energy must have the correct convexity. A critical end-point is an obvious case in which the stability limit is exactly reached: low-density critical end-points should therefore be good candidates for the observation of the asymptotic critical behaviour in mixtures. On the other hand, a stability limit can be approached also along a critical line. A favourable situation in this respect occurs when the system considered is close to a change of topology in the phase diagram from class II to class III [1], since at the boundary between these classes two critical lines touch—at least at the mean-field level—and the intersection is a point of marginal stability. The argon–xenon mixture actually corresponds to such a case. It must be noted that this system was chosen in the present context since in this case the assumption of spherically symmetric interactions postulated in the simple model considered here is not unrealistic. However, other examples which are probably much easier to handle experimentally can be pointed out: for instance, it is well known that in mixtures formed by carbon dioxide or CHF_3 plus an aliphatic hydrocarbon (the so-called CO_2 or CHF_3 families) a gradual transition from class II to class III is found by considering hydrocarbons of increasing lengths [1, 13].

On the basis of the present analysis the proximity to a low-density critical end-point or to a change of topology in the critical lines are then identified as conditions that favour the experimental detection of the true asymptotic behaviour in binary systems. It must also be remarked that, since the crossover temperature varies sharply along the critical lines, the favourable regions are in any case predicted to be rather narrow.

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[11] A case can be found (apart from the trivial one of a very dilute mixture) in which the thermodynamic contribution vanishes also at the mean-field level: this is due to the vanishing of $\partial v_2/\partial x$ that occurs whenever the temperature along the critical lines has an extremum (provided that it does not coincide with a critical end-point). In this case, strong and weak fluctuations are decoupled throughout the RG flow. The 1C fixed point is then stable leading to finite compressibility and unrenormalized critical exponents. This feature agrees with the prediction of the phenomenological theory [4, 7].

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