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Abstract. The hierarchical reference theory (HRT) is a unified theory of fluids: in the dense regime it has the accuracy typical of a good theory of the liquid state. At the same time, close to a critical point, it develops the structure of a renormalization group theory in which all non-universal quantities can be deduced from knowledge of the interatomic interaction. The HRT can be applied above as well as below the critical temperature so that the phase diagram, thermodynamic properties and distribution functions are obtained in a unified way. Similar information can be extracted also from models of binary mixtures. In this case, the HRT allows for the determination of the order parameter along lines of critical points and provides an explanation of the strange crossover phenomena found in mixtures.

1. Introduction

For many years, the problem of developing a quantitative microscopic theory of fluids in the region of the critical point of the liquid–vapour phase transition has found no satisfactory answer. A successful theory should aim at deriving, from a realistic interatomic interaction, thermodynamic quantities such as the temperature T_c and density ρ_c of the critical point or the shape of the coexistence curve as well as the correlation functions. At the same time, close to the critical point, the theory should develop the scaling structure of the thermodynamic properties and correlation functions with appropriate critical exponents: such a theory would necessarily be a global theory of the fluid state. In fact at a temperature just 10% below T_c, the two coexisting phases have densities typical of the liquid and gas state: about two thirds of the triple-point value (twice the critical value, ρ_c) on the liquid branch and one third of ρ_c on the gas side. As a consequence, the theory should be able to describe equally well a rather dilute system and a dense fluid with well developed short-range order.

The modern theory of fluids, based on the method of integral equations for the radial distribution function $g(r)$ or on perturbation theory around a reference system, such as hard spheres, is quite accurate for the static properties of simple fluids. These approaches, however, fail close to the critical point. In fact, all of these theories either do not go beyond a mean-field-like description, or they develop some kind of pathology. For instance, one of the most celebrated integral equations [1], the modified hypernetted-chain (MHNC) equation, does not possess a critical point with diverging isothermal compressibility κ_T and correlation length ξ. Rather it has a locus of branch point singularities in the ρ–T plane where κ_T and

ξ reach a finite limit [2]. Therefore, one of the most fundamental properties of a critical point, a diverging correlation length, is not accounted for in the MHNC equation.

Critical phenomena in fluids are understood in terms of a one-component order parameter ψ, as in the Ising model. For a fluid, ψ is the local density of particles. The proper treatment of critical fluctuations is provided by the renormalization group (RG) methods applied to an effective local free energy, the Landau–Ginsburg–Wilson (LGW) functional, for $\psi(\boldsymbol{r})$. On the basis of the universality hypothesis, this description is sufficient for obtaining the so-called universal properties asymptotically close to the critical point, i.e. critical exponents and scaling functions. This leaves, however, a number of questions unanswered. The relation between the parameters entering the LGW functional and the microscopic interaction is obscure and such parameters have to be taken as phenomenological inputs [3]. The extent of the asymptotic region is also largely undetermined.

The situation is even worse in the case of a binary mixture. Mixtures have a rich phase diagram with a variety of topologies. In multicomponent fluids even the identification of the order parameter offers a serious problem because the character of the transition can change continuously from that of pure liquid–vapour to mixing–demixing. Almost all theoretical determinations of the phase diagram do not go beyond van der Waals theory or other mean-field approaches.

About ten years ago we introduced [4] a novel approach in the theory of fluids, that we named the hierarchical reference theory (HRT). The HRT is a proper theory of the fluid state which applies to point particles interacting with a realistic interatomic potential and which develops the RG structure close to a critical point. The approach is sufficiently general that it can be used for one-component fluids, mixtures, lattice models and magnets. A comprehensive review of the HRT can be found in reference [5]. Here we highlight some of the key features of the HRT and present some recent developments. The general aspects are discussed briefly in section 2 and some applications to the case of one-component fluids are presented in section 3. Next we address the question of binary mixtures. In section 4 the order parameter and the nature of criticality in binary fluids are discussed. In section 5 we show how it is possible to derive from the general framework of the HRT a practical scheme which gives the full phase diagram of a mixture, including the coexistence region, along with non-trivial critical behaviour. Finally, we draw some conclusions in section 6.

2. The hierarchical reference theory of fluids

The HRT can be considered as a way to apply the momentum-space RG theory to a microscopic model of a fluid. In the standard RG approach, the fluctuations of the local order parameter are first decomposed into Fourier series, and then fluctuations of large wavevectors $\boldsymbol{k}$ (say $k > Q$) are integrated out giving rise to a new effective Hamiltonian for the remaining fluctuations with $k < Q$. The procedure can be now iterated by reducing the cut-off Q until all fluctuations are taken into account. In this way one generates a sequence of effective Hamiltonians, each of them describing fluctuations below a certain cut-off. This scheme, although formally exact, has some drawbacks. For instance it is difficult to describe the short-range correlations present in the system and their influence on the large-scale properties. Instead, we do not perform any partial integration nor do we eliminate degrees of freedom: we analyse how the free energy and the correlation functions are modified by the introduction of a cut-off Q in the diagrammatic expansion which defines the observable quantities. An important technical observation is that introducing such a cut-off is equivalent to considering a system with the same number of particles but modified interaction. This has two consequences. At all intermediate steps of the HRT one is dealing

with a proper statistical model of fluid, albeit with a rather peculiar pair interaction which will be discussed below, so one can profit from the deep understanding developed in the framework of liquid-state theories. This will be particularly valuable for the development of approximations necessary to truncate the formally exact infinite set of equations generated by the HRT. Secondly, the intermediate systems are defined over all length scales from the atomic diameter up to arbitrarily large distances. Therefore full information on the correlation functions is retained by the HRT.

We consider systems of structureless classical particles interacting with a central, pairwise-additive interatomic potential $v(r)$. This interaction is written as the sum of a short-range part $v^R(r)$ and a remainder $w(r)$:

$$v(r) = v^R(r) + w(r). \tag{1}$$

The strong repulsive forces at short distance are included in $v^R(r)$ which is often taken as a hard-sphere potential of suitable diameter d. One recognizes here the starting point of a standard perturbation theory of fluids. The properties of the 'reference system', i.e. a system with pair interaction $v^R(r)$, are assumed known from some other theory. If $v^R(r)$ is (essentially) repulsive, the reference system has no phase transition at intermediate densities, where the critical point is located, and the liquid–vapour transition appears only when $w(r)$ is included. Notice that $w(r)$ does not necessarily represent purely attractive forces: the only condition is that $w(r)$ has a well defined Fourier transform $\tilde{w}(k)$ with a finite $k \to 0$ limit. The HRT is based on the following steps. The first is the choice of the partially coupled system, i.e. the precise definition of the cut-off wavevector Q. This corresponds to an interaction $v^Q(r) = v^R(r) + w^Q(r)$ where w^Q is most easily written in Fourier space:

$$\tilde{w}^Q(k) = \begin{cases} \tilde{w}(k) & \text{for } k > Q \\ 0 & \text{for } k < Q. \end{cases} \tag{2}$$

It is clear that as Q is moved from $Q = \infty$ down to $Q = 0$ the system changes from the reference to the fully interacting one. It can be shown that in the partially coupled system (the *Q-system* in the following), density fluctuations of wavevector k are strongly suppressed for $Q > k$, while they are fully included for cut-off $Q \ll k$.

The second step of the HRT consists in the derivation of the exact evolution equations for the properties of the partially coupled system as the cut-off is changed from Q to $Q - \mathrm{d}Q$. Due to the discontinuity in $\delta\tilde{w}^Q(k) = \tilde{w}^{Q-\mathrm{d}Q}(k) - \tilde{w}^Q(k)$, this requires a suitable resummation of the perturbation expansion. In addition, it is convenient to define a modified free energy:

$$\frac{\mathcal{A}^Q}{V} = \frac{A^Q}{V} - \tfrac{1}{2}\rho^2 \left[\tilde{w}(k=0) - \tilde{w}^Q(k=0) \right] + \tfrac{1}{2}\rho \left[w(r=0) - w^Q(r=0) \right] \tag{3}$$

in which the contribution of the missing interaction $\tilde{w}(k) - \tilde{w}^Q(k)$ is included in mean-field approximation. V is the volume of the system. The evolution equation for this quantity reads

$$-\frac{\mathrm{d}}{\mathrm{d}Q} \left(\frac{-\beta\mathcal{A}^Q}{V} \right) = \frac{1}{2} \int_{k=Q} \frac{\mathrm{d}\Omega_k}{(2\pi)^3} \ln\left[1 + \frac{\beta\tilde{w}(Q)}{\mathcal{C}^Q(k)} \right]. \tag{4}$$

Here, $\beta = 1/k_B T$ and $\mathcal{C}^Q(k)$ represents a modified Ornstein–Zernike (OZ) correlation function of the Q-system:

$$\mathcal{C}^Q(k) = \check{c}^Q(k) - \beta\tilde{w}(k) - \beta\tilde{w}^Q(k). \tag{5}$$

where our OZ direct correlation functions include the ideal-gas contribution, i.e. $\check{c}^Q(k) = c^Q(k) - \rho^{-1}$. With this definition, $\mathcal{C}^Q(k)$ is a continuous function of k at $k = Q$ while

$\check{c}^Q(k)$ is not. We have obtained the analogous evolution equations for $\mathcal{C}^Q(k)$ as well as for all the higher-order direct correlation functions c_n. The equation for c_n involves w, $\mathcal{C}^Q$, as well as c_j with all $j = 3, \ldots, (n + 2)$. Therefore, HRT generates an infinite hierarchy of differential equations for the free energy and the direct correlation functions describing the evolution of the properties of the system when the cut-off Q is changed.

The full hierarchy of equations simplifies considerably close to a critical point where $\mathcal{C}^{Q=0}(k = 0)$ tends to zero corresponding to the onset of the divergence of the isothermal compressibility. In fact, the full hierarchy acquires a universal form: the interaction $\tilde{w}(k)$ drops out of the equations in the $Q \to 0$ limit and at small momenta. It turns out that these HRT equations coincide, in the critical region, with the Nicoll–Chang differential RG generator [6] for an effective one-component order parameter theory defined by the field theoretical action

$$S[\psi] = \int \mathrm{d}\boldsymbol{x} \; \left\{ \frac{1}{2} |\boldsymbol{\nabla}\psi|^2 + r\psi^2 + u\psi^4 \right\}. \tag{6}$$

Yet, the full HRT equations are much richer because HRT also describes the effects of short-range correlations, absent in RG approaches.

Given the above-mentioned equivalence between the RG theory and the HRT in the critical region, it is clear that HRT describes the universal critical behaviour as given by RG theory and in particular contains non-trivial critical exponents and scaling laws. The values of the critical exponents depend on the approximations introduced in order to make this set of equations tractable. In three dimensions, we have considered so far a simple approximation. It is based on an OZ *ansatz*, i.e. $\mathcal{C}^Q(k)$ is assumed to be an analytic function of k and this corresponds to an exponent $\eta = 0$. The non-linear coupling between density fluctuations is introduced by employing the exact compressibility sum rule

$$\mathcal{C}^Q(k = 0) = \frac{\partial^2(-\beta\mathcal{A}^Q/V)}{\partial\rho^2}. \tag{7}$$

When we insert equation (7) in (4) we find a non-linear partial differential equation (PDE) for $\mathcal{A}^Q$ with respect to Q and ρ which should be studied numerically. Using the standard notation, the critical exponents in 3D turn out to be

$$\gamma = 1.378\ldots \qquad \nu = \gamma/2 \qquad \beta = 0.345\ldots \qquad \alpha = -0.07\ldots. \tag{8}$$

Alternatively, $\mathcal{A}^Q(\rho, T)$ can be expanded around ρ_c up to fourth order. Substituting this parametrization in the PDE and keeping only terms up to quadratic order in the coefficients, we find a set of two coupled differential equations which can be studied analytically. The resulting critical exponents have simple rational expressions satisfying the scaling relations. In particular, in three dimensions, they read

$$\gamma = 1.2 \qquad \nu = 0.6 \qquad \beta = 0.3 \qquad \alpha = 0.2. \tag{9}$$

In order to fully exploit the content of HRT and analyse the whole critical behaviour of specific microscopic models, including the non-universal features, we start from the exact form of the first HRT equation (4) and introduce some realistic approximation for the two-body direct correlation function $\mathcal{C}^Q(k)$ at arbitrary values of Q and k. In this way equation (4) gives rise to a closed equation for the fluid state as discussed in the next section.

3. A differential theory of simple fluids

Let us assume that the reference system is the hard-sphere one with suitable diameter d. This diameter is possibly a function of density and temperature if we wish to mimic a
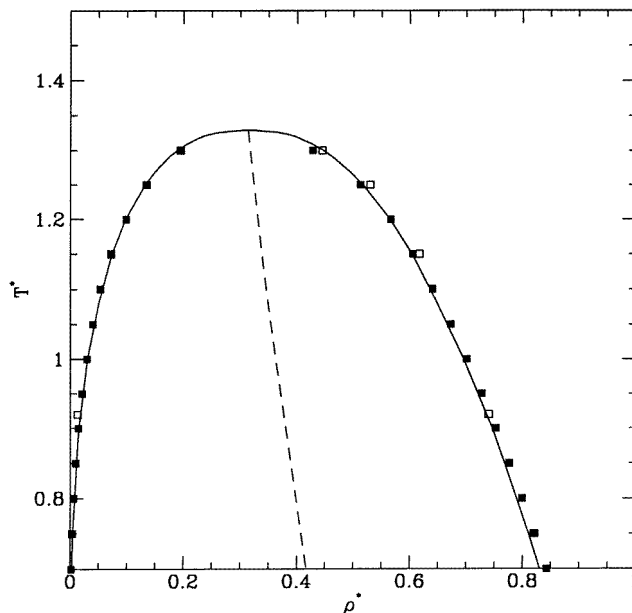
Figure 1. The coexistence curve and diameter of a Lennard-Jones fluid in the (ρ^*, T^*) plane. Full curve: the HRT. Open symbols: the MHNC result [17]. Full symbols: simulations [8].

soft-core repulsive potential, like that of the Lennard-Jones (LJ) fluid. In this case, we have studied equation (4) together with the closure relation

$$\mathcal{C}^Q(k) = \check{c}^R(k) - \lambda^Q \beta \tilde{w}(k) + \mathcal{G}^Q(k) \tag{10}$$

where $\check{c}^R(k)$ is the direct correlation function of the reference system (including the ideal-gas term), $\mathcal{G}^Q(k)$ is a function determined by the core condition for the partially coupled system (i.e. $g^Q(r) = 0$ for $r < d$) and λ^Q is determined by the sum rule (7). If λ^Q were unity, equation (10) would correspond to the mean-spherical approximation (MSA). The non-trivial critical behaviour arises from the presence of this parameter λ^Q which couples the *ansatz* for the direct correlation function (10) to the evolution equation for the free energy (4) and leads to the critical exponents (8). Solution of the full equations (4), (10) gives the thermodynamics of the fluid throughout the phase diagram, including the universal and non-universal properties in the critical region. Computations for the LJ potential give results in good agreement with simulations. It is interesting to notice that at temperatures $T < T_c$ the integration of this hard-core HRT equation (HC-HRT) gives rigorously a flat isotherm over a finite range of density: the coexistence of liquid and vapour is obtained as an effect of the proper treatment of long-wavelength fluctuations and not as a result of an *ad hoc* Maxwell construction. The coexistence curve for the LJ fluid is shown in figure 1 and compared to simulation and MHNC results. Notice that only HRT is able to give the full coexistence curve up to the critical point.

Recently we have developed a more general closure than (10) which allows for the direct treatment of soft-core potentials thereby avoiding the preliminary mapping to a hard-core reference system. This approximation is inspired by the soft MSA (SMSA) of liquid-state theory [7] which can be written as

$$c(r) = c^R(r) - \beta w(r) + \left[g(r) - g^R(r) \right] (1 - e^{\beta v^R(r)}). \tag{11}$$

Again, equation (11) can be generalized to the partially interacting systems, leading to the same formal expression for $\mathcal{C}^Q(k)$ as before (10). The only difference being the definition of the function $\mathcal{G}^Q(r)$, which is now explicitly given by

$$\mathcal{G}^Q(r) = \left[g^Q(r) - g^R(r)\right]\left(1 - e^{\beta v^R(r)}\right). \tag{12}$$

This form becomes equivalent to the core condition in the limit of hard-sphere reference system but is also applicable to soft-core reference potentials. The parameter λ^Q in equation (10) is still determined by the compressibility sum rule (7) which guarantees the validity of the critical exponents (8) within this approximation.

In order to implement the closure (10), (12) within the HRT equation (4) it is convenient to expand the function $\mathcal{G}^Q(r)$ in a basis of short-range functions, project equation (12) on this basis and write differential equations for the expansion coefficients [5]. Following this procedure, an efficient algorithm for the solution of the resulting PDE has been set up [9].
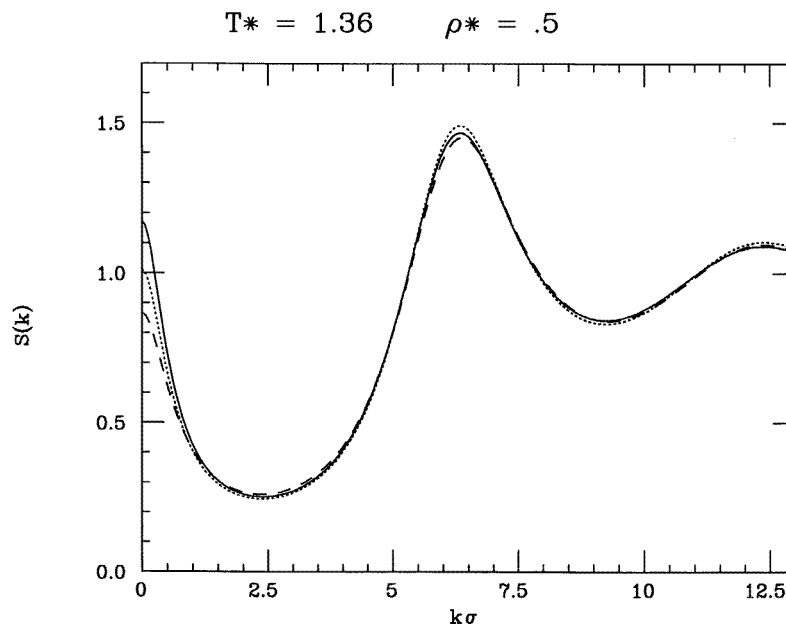
Figure 2. The structure factor of a Lennard-Jones fluid at reduced temperature $T^* = 1.36$ and density $\rho^* = 0.5$. Solid line: SC-HRT; dotted line: the HC-HRT; dashed line: the MHNC result.

As an example, in figure 2 we show the soft-core HRT (SC-HRT) results for the structure factor of a Lennard-Jones fluid compared with the previously described approximation (HC-HRT) and to the MHNC result. The SC-HRT result is clearly closer to the MHNC result at all wavevectors except the small ones. It is known that the MHNC model describes quite accurately the short-range part of the correlations including near-critical states, so we conclude that the new closure SC-HRT is superior to HC-HRT.
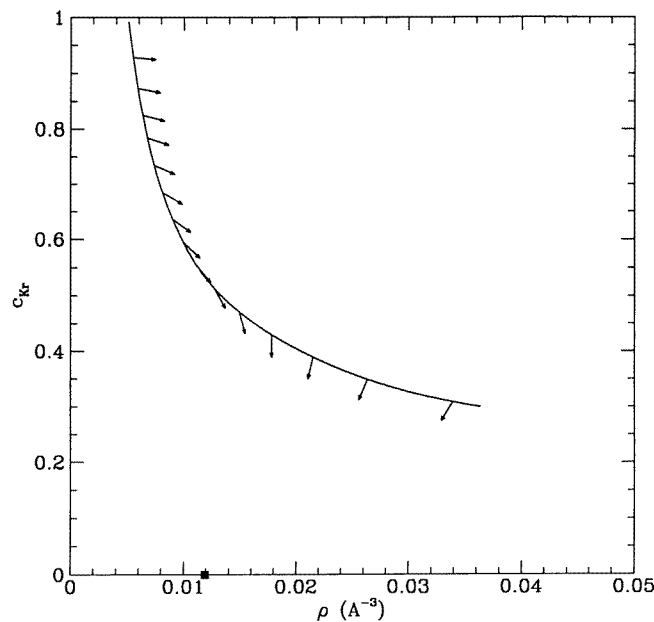
4. The order parameter and criticality in mixtures

The HRT can be formally generalized to mixtures [10], the only difference with respect to one-component fluids being the presence of species indices in the interactions and correlation

functions. As a first step, the two-body potential is written as a sum of a reference part and a remainder: $v_{ij}(r) = v_{ij}^R(r) + w_{ij}(r)$. After having introduced a cut-off Q in the Fourier components of all the tails w_{ij}, analogously to equation (2), we can derive exact evolution equations for the free energy and the correlation functions which describe the inclusion of fluctuations on length scales $1/Q$. For instance, the equation for the free energy reads

$$-\frac{\mathrm{d}}{\mathrm{d}Q}\left(\frac{-\beta\mathcal{A}^Q}{V}\right) = \frac{1}{2}\int_{k=Q}\frac{\mathrm{d}\Omega_k}{(2\pi)^3}\,\ln\det\left[\mathbf{1} + \beta\left[\mathcal{C}^Q(k)\right]^{-1}\tilde{w}(k)\right].\qquad(13)$$

Here matrix notation for $\mathcal{C}^Q$ and $\tilde{w}$ is understood. This evolution equation is just the first of the formal HRT hierarchy, but for the present discussion it is not necessary to elaborate the detailed structure of the equations for the correlation functions. Notice that in order to derive this hierarchy we need not specify the nature of the phase transitions that we want to describe: our equations are valid far from the critical regime as well as in the critical region, independently of the character of the transition, liquid–vapour, demixing or of mixed character. In this respect HRT differs from the usual RG treatments which start from the definition of the local order parameter and the associated effective Hamiltonian which governs its fluctuations.

Figure 3. Mean-field critical lines and the direction of the order parameter in the density–concentration plane for a neon–krypton mixture. The critical line originating from the critical point of pure Ne (marked with a square in the figure) stops almost immediately upon addition of Kr.

Near a critical point and in the long-wavelength limit, the equations simplify acquiring a universal structure due to the generalized compressibility sum rule:

$$\mathcal{C}_{ij}^Q(k=0) = \frac{\partial^2(-\beta\mathcal{A}^Q/V)}{\partial\rho_i\,\partial\rho_j}\qquad(14)$$

which relates the divergence of *any* second derivative of the free energy to the vanishing of the determinant of the direct correlation functions in the $(k, Q) \to 0$ limit. Notice that the

exact vanishing of $\det[\mathcal{C}^{Q=0}(k=0)]$ occurs at a critical point, irrespective of the physical nature of the order parameter and implies that (at least) one eigenvalue of the second-derivative matrix (14) vanishes. The corresponding eigenvector defines a particular direction in the density–concentration plane (ρ, c) specified by an *angle* φ. Here we specialize the discussion to binary fluids and we use standard notation: $\rho = \rho_1 + \rho_2$, $c = \rho_2/\rho$. Physically, this direction identifies the particular combination of density and concentration which shows strong fluctuations at that critical point. This observation suggests that we define the order parameter ψ_1 of the transition as the linear combination

$$\psi_1 = \delta\rho \cos\varphi + \delta c \sin\varphi \qquad (15)$$

where $\delta\rho = \delta\rho_1 + \delta\rho_2$, $\delta c = (\rho_1 \delta\rho_2 - \rho_2 \delta\rho_1)/\rho$. Therefore, the angle φ determines, via equation (15), the order parameter which generally turns out to be neither pure density (liquid–vapour) nor concentration (demixing) except for for the special values $\varphi = 0$ and $\varphi = \pi/2$ respectively. An arrow in the density–concentration plane conveniently gives a visual representation of the order parameter angle at the critical point. As an example we report in figure 3 the mean-field critical lines for a neon–krypton mixture, modelled by LJ potentials, in the density–concentration plane. The arrows, according to the previous definition, identify the character of the transition, which is seen to change continuously along the critical line from mostly liquid–vapour at moderate densities to mostly demixing in the high-density region. We also notice that the angle defining the order parameter in mixtures can be related by exact identities to purely thermodynamic quantities (e.g. the partial molar volumes) or to the concentration and volume difference of the two coexisting phases just below the critical point [5]. These identities may be useful for an experimental determination of the order parameter in binary fluids.

The asymptotic critical properties of a binary mixture can be studied within HRT by extending the same analysis and approximations as were discussed in the one-component case. In particular, under the assumption that all of the partial direct correlation functions $\mathcal{C}_{ij}^Q(k)$ remain analytic in k even at the critical point, the evolution equation for the free energy (13) can be closed by use of the compressibility relation (14). The resulting equation is again a PDE, now involving three variables: the density ρ, the concentration c and the evolution parameter, i.e. the cut-off, Q. Again, the HRT equations in the long-wavelength limit become identical to RG equations for an effective action involving *two* fluctuating fields: besides the local order parameter ψ_1 previously introduced, a further weakly fluctuating variable ψ_2 appears in the effective action:

$$S[\psi_1, \psi_2] = \int d\boldsymbol{x} \left[\frac{1}{2}|\nabla\psi_1|^2 + r\psi_1^2 + g^2\psi_2^2 + u\psi_1^4 + wg\psi_1^2\psi_2 \right]. \qquad (16)$$

Physically, the field ψ_2 represents the further linearly independent combination of density and concentration $\psi_2 = \delta\rho \cos\varphi - \delta c \sin\varphi$.

A direct analysis of the critical properties displayed by the HRT equations leads to the conclusion that the critical phenomena in binary fluids are governed by a fixed point where the two fields (ψ_1, ψ_2) are non-trivially coupled ($w^* \neq 0$). However, this asymptotic critical behaviour is masked by the presence of strong crossover effects due to the competition of another (unstable) fixed point where the two fields are decoupled ($w^* = 0$). In both cases the critical exponents turn out to be related to those of one-component systems. The asymptotic behaviour agrees with the predictions of Fisher's 'phenomenological *ansatz*' [11]: the isothermal compressibility at fixed concentration diverges weakly with temperature with an exponent $-\alpha/(1-\alpha)$, while the specific heat at constant volume attains a finite limit at the critical point. Instead in the crossover region the isothermal compressibility remains
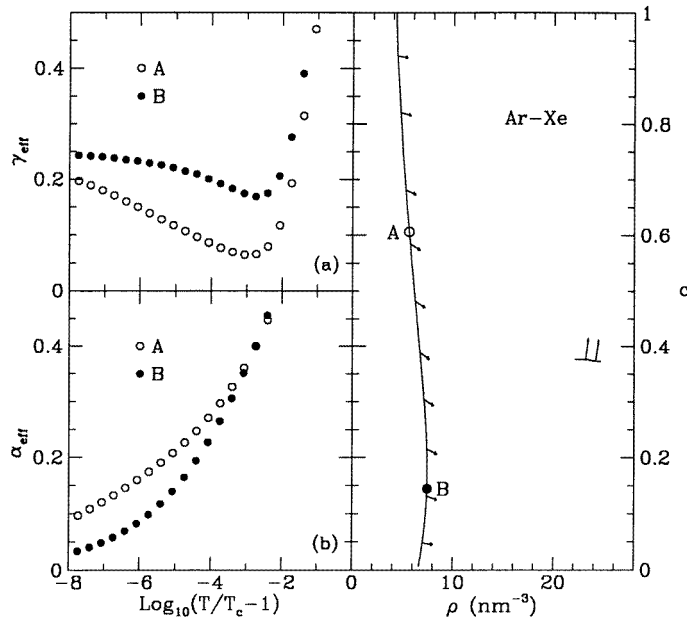
Figure 4. Effective critical exponents close to two points A and B along the critical lines of an argon–xenon mixture. Left-hand panel: compressibility (γ) and specific heat (α) effective exponents as functions of the reduced temperature. Right-hand panel: mean-field critical lines of the mixture projected on the density–concentration plane.

flat and the specific heat grows with an exponent $-\alpha$ as in one-component systems. In general, we find that the asymptotic behaviour sets in so close to the critical point that only the crossover region is experimentally accessible. This agrees with the experimental findings [12]. Under certain circumstances, however, the asymptotic regimes become wider. We have studied the extent of the crossover region by use of the simple 'quartic' approximation to the HRT equations already discussed in the framework of one-component systems, which gives $\alpha = 0.2$ according to equation (9). As an example, we have estimated the effective critical exponent for the divergence of compressibility (γ_{eff}) and specific heat (α_{eff}) for parameters chosen so as to mimic an argon–xenon mixture at two points on the 'liquid–vapour' critical line. The results of figure 4 show that the expected crossover temperature changes considerably at different points along the same critical line. The crossover temperature strongly correlates with the strength of the coupling between (ψ_1, ψ_2) in the effective action (16). A general analysis has shown that mixtures near critical end points or with phase diagrams close to a change in the topology are favourable situations where the asymptotic critical behaviour can be experimentally detected [13].

5. The phase diagram of binary fluids

In order to study the phase diagram of a microscopic model of mixtures on the basis of a realistic approximation, we have generalized the MSA closure (10) already successfully applied for one-component fluids. As a first step, we have not implemented the core condition, i.e. we have simply dropped the function $\mathcal{G}^Q(k)$ in (10). By substituting this approximation into the evolution equation for the free energy (13), we get a PDE which
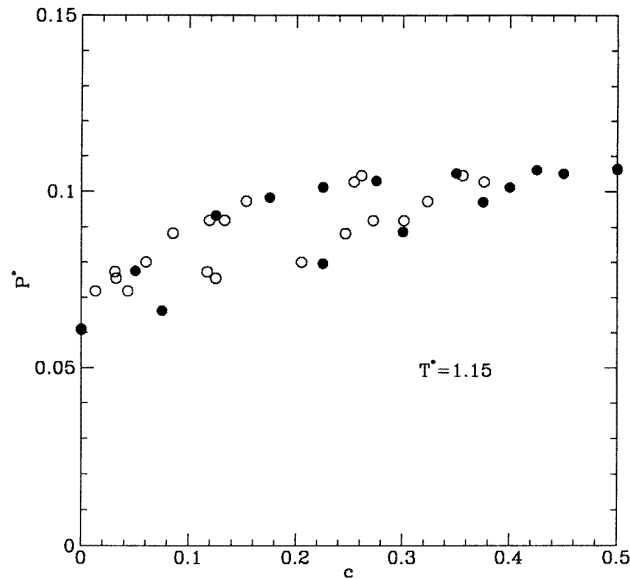
Figure 5. The coexistence region for a symmetric Lennard-Jones mixture with strength ratio $\epsilon_{12}/\epsilon_{11} = 0.75$ at a temperature $T^* = 1.15$. Full symbols: numerical integration of the HRT PDE. Open symbols: simulation results from reference [15].
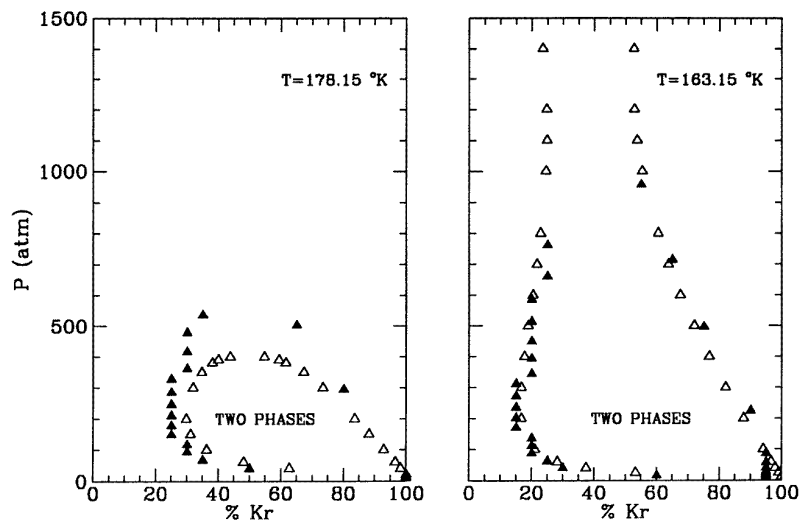
Figure 6. Isothermal sections of the coexistence region for a neon–krypton mixture. Full symbols: numerical integration of the HRT PDE for a mixture of Lennard-Jones molecules. Open symbols: experimental results from reference [16].

can be numerically integrated [14]. We have first applied this theory to the study of the phase diagram of a simple model where simulation results are available: a mixture of two LJ fluids with equal strengths and diameters between like particles and different strength between unlike molecules. The shape of the coexistence region at the reduced temperature

$T^* = 1.15$ is compared to simulation results [15] in figure 5. We have also studied a Lennard-Jones mixture with parameters suitable to represent a neon–krypton mixture. Sections of the coexistence curve at two temperatures are shown in figure 6 together with the experimental results of reference [16]. The good agreement both with simulation and experiment is encouraging and suggests that the HRT equation can be successfully applied to the quantitative study of phase diagrams in binary fluids.

6. Conclusions

The present application of the HRT has shown that this scheme is a flexible and powerful approach for dealing with equilibrium fluctuations over all length scales. At short distance it has an accuracy comparable to that of standard liquid-state theories. At longer range, the proper critical behaviour is recovered if the system is close to the critical point. HRT appears to be the only available theoretical scheme which has the merits of liquid-state theories and of RG models. A number of applications to models of simple fluids, and of mixtures and also to lattice models have shown that it is possible to close the full infinite HRT hierarchy in a reasonable way at the first equation so that rather accurate results are obtained for thermodynamic quantities and for correlation functions. Among the most prominent results we recall the microscopic characterization of criticality and of crossover phenomena in binary fluid mixtures and the development of a practical scheme for obtaining the phase boundaries in binary fluids, beyond mean-field approximations. Applications and extensions of HRT to other models, to coulombic mixtures and to magnetic models with competing interactions are under way. The complexity of the HRT hierarchy when we go beyond the first equation suggests that an accuracy in the values of the critical exponents comparable with that of the most sophisticated RG schemes will not be achieved easily using HRT. In this respect, one can predict another use of HRT as a tool to generate, from the microscopic interactions, the effective coupling parameters which enter the phenomenological action which can then be treated by field theoretical techniques.

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