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# Theory of critical phenomena in fluids

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**Abstract.** We discuss a differential approach to the theory of fluids, the hierarchical reference theory, which, above the critical temperature, has been shown to be (i) as accurate as the most widespread theories of liquid state in the high density region and (ii) able to reproduce the renormalization group results in the critical region. In this region it predicts both the universal and the non-universal quantities. We have studied the Lennard-Jones fluid in detail but the method can be directly applied to more realistic interactions between molecules. The treatment of temperatures below the critical one presents some additional difficulties due to the presence of the (inhomogeneous) two-phase region. Preliminary results indicate that our theory gives the coexistence curve with the correct scaling behaviour without any need for an *ad hoc* Maxwell construction. The extension of the formalism to binary mixtures is under way.

## 1. Introduction

The accurate description of equilibrium properties of simple fluids has been one of the major goals of liquid state theory in the past decades. The most sophisticated liquid state theories are now able to achieve an accuracy better than 2% both in thermodynamics and correlations in most of the phase diagrams for simple and isotropic systems [1]. Careful tests against numerical simulations have shown that integral equations have now reached the level of confidence which allows the study of very detailed questions such as the accuracy of intermolecular pair potentials in dense phases, or the extent of many-body forces in simple fluids [2].

An exception to this positive situation is in the region of the critical point of the liquid-vapour phase transition.

Large-scale fluctuations, which are essentially neglected in the integral equation approach, play an important role in the system only near the phase transition region. In fact they are responsible for the universal, and non-mean field, features of the critical regime, as well as for the convexity of the free energy below the liquid-vapour coexistence curve. Therefore, it is not surprising that liquid state theories fail to reproduce the correct behaviour of the system in these regions of the phase diagram [3].

The crucial role of fluctuations in the critical region has been recognized by the renormalization group (RG) approach which represents the only accurate method for taking into account their effects in a consistent way [4]. The RG has been able to

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explain the observed universality of critical phenomena and to provide quantitative estimates for the critical exponents and other universal properties in the critical region. Unfortunately, the RG cannot be directly used within liquid state theory because it needs a preliminary coarse graining onto the system in order to trace out fluctuations at short wavelengths. This prevents the combining of the powerful methods of field theory with the accurate approaches devised in the framework of liquid state theory.

In the following we briefly review the basic ideas which lead us to the formulation of a liquid state theory, the hierarchical reference theory of fluids (HRT), which is able to describe accurately the critical region [5]. We present evidence in favour of this claim by comparing the results of the theory with numerical simulations and experiments on rare gases [6]. The problems related to the coexistence region are also addressed and preliminary results are shown.

## 2. Theory

Following the procedure described in [5], we consider a sequence of systems ( $Q$ -systems) defined by the two-body interaction  $v_Q(r)$  which interpolates between a repulsive singular reference potential  $v_R(r) = \lim_{Q \rightarrow \infty} v_Q(r)$  and the physical interaction  $v(r) = v_R(r) + w(r)$  which is recovered in the limit  $Q \rightarrow 0$ . More precisely:

$$v_Q(r) = v_R(r) + w_Q(r) \quad (1)$$

where the Fourier transform of  $w_Q(r)$  is  $\tilde{w}_Q(q)$

$$\tilde{w}_Q(q) = \begin{cases} \tilde{w}(q) & \text{for } q > Q \\ 0 & \text{for } q < Q. \end{cases} \quad (2)$$

The role of the parameter  $Q$  is to depress density fluctuations of wavevector  $k < Q$ . Therefore the family of  $Q$ -systems can be also considered as a sequence of approximations to the fully interacting system where fluctuations on length scales larger than  $1/Q$  are depressed. In this respect, our approach is similar in spirit to the RG procedure, where fluctuations are introduced selectively on the wavevector, but it differs from some implementations of the RG because degrees of freedom are not eliminated and information on all length scales is retained at each step.

The Helmholtz free energy  $\mathcal{A}_Q$  of systems characterized by different values of the parameter  $Q$  are related by a differential equation involving the two-particle correlation function of the  $Q$ -system. The same procedure can be repeated for the correlation functions thereby generating an exact hierarchy of differential equations which describe the change in the physical properties of the system when  $Q$  is decreased. We have studied an approximate *closure* to this hierarchy which is obtained by expressing the two-particle direct correlation function  $\mathcal{C}_Q$  of the  $Q$ -system in terms of the density derivative of the free energy itself. In fact, in close analogy to the well known optimized random-phase approximation [1] (ORPA), we set

$$\mathcal{C}_Q(r) = c_R(r) + \lambda_Q \phi(r) \quad (3)$$

for  $r > d$ , while  $\mathcal{C}_Q(r)$ , for  $r < d$ , is determined by the condition of a vanishing radial distribution function of the  $Q$ -system (core condition) which is rigorously valid for

potentials containing a hard core term of diameter  $d$ . The parameter  $\lambda_Q$  in (3) is determined by the compressibility sum rule which reads

$$\mathcal{C}_Q(k=0) = \partial^2 \mathcal{A}_Q^{\text{ex}} / \partial \rho^2. \quad (4)$$

This last thermodynamic constraint is essential for an accurate description of the critical region because it couples the direct correlation function to the free energy of the fluid in a non-trivial way, introducing non-linearities in the evolution equation which now becomes a partial differential equation. In fact in [5] we showed that, provided the approximate form for  $\mathcal{C}_Q(k)$  is analytic in  $k^2$  and equation (4) is satisfied for every  $Q$ , the resulting free energy satisfies scaling laws in the critical region, with critical exponents given by

$$\nu = 0.689 \quad \gamma = 1.378 \quad \beta = 0.345 \quad \delta = 5 \quad (5)$$

in three dimensions. Moreover near four dimensions the critical exponents has been proven correct [5] to leading order in  $\epsilon = 4 - D$ .

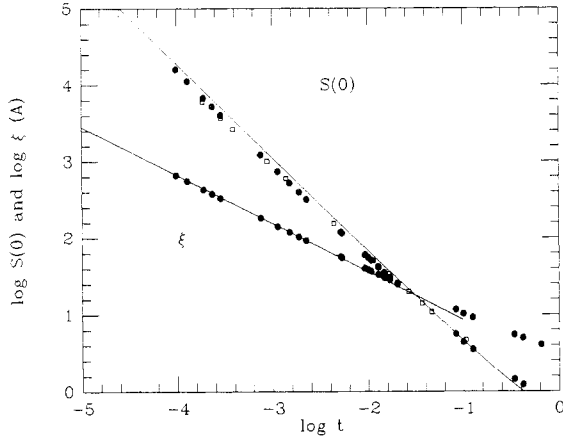
Such a theory contains, at the same time, the basic ingredients which allow for a good description of short-range correlations in dense fluids (ORPA, (3)) and of long-range correlations in the critical regions (RG structure). We therefore expect this approach to give a realistic description of the thermodynamics and correlations in the whole phase diagram of the system. Extension of this formalism to binary mixtures is straightforward and gives rise to an evolution equation for the free energy which is coupled both to density and concentration fluctuations. The analysis of such an equation along the same lines we have just reviewed is currently under way.

### 3. Comparison with experiments—above $T_c$

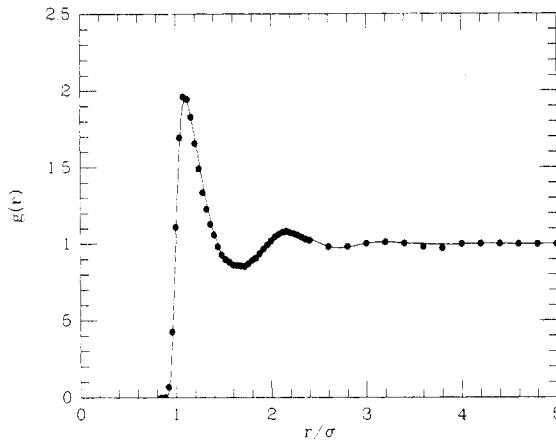
We have applied our theory to the Lennard-Jones fluid:  $v_{\text{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$  and  $v_{\text{LJ}}$  is split with the WCA [1] rule. The repulsive part of the interaction is replaced by the hard-sphere potential with a state-dependent diameter  $d(\rho, T)$  given by the AWC prescription [1]. Our estimate for the critical point is  $\rho^* = 0.3155$  and  $T_c^* = 1.3330$  (in units of  $\epsilon/k_B$ ). These values have to be compared with the simulation estimates [7]  $T_c^* = 1.31$  and  $\rho^* = 0.31$ . A detailed comparison with experimental data on rare gases and with numerical simulations has been published separately [6]. The agreement between theory and experiments is good both for the compressibility and for the correlation length as shown in figure 1. Preliminary results [9] of our theory in the case of a more accurate pair interaction for krypton plus three-body forces are also shown in the same figure.

In order to assess the quality of our approximations for correlation functions, we compare HRT results with simulations [10] performed for the LJ potential and one such comparison is shown in figure 2. The nice agreement we find shows that, within our approach, it is possible to obtain the typical accuracy of a good liquid state theory (like ORPA) outside the critical region and, at the same time, the correct scaling behaviour near the critical point. This feature is not shared by any other liquid state theory.

Up to now, the numerical analysis of HRT equations has been confined to the region above the critical isotherm. This limitation is due to the fact that (4) involves density derivatives and, in the coexistence region, these derivatives might be negative inducing



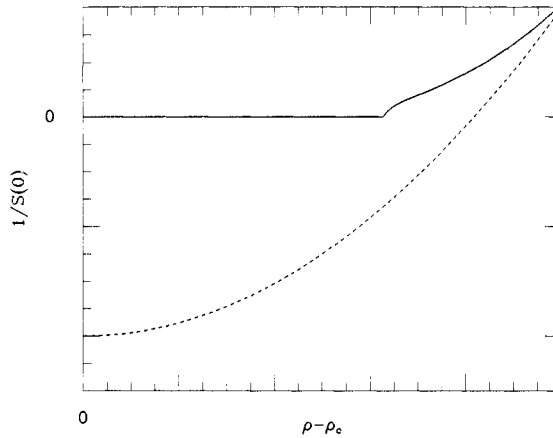
**Figure 1.** Reduced isothermal compressibility  $S(0)$  and correlation length  $\xi$  as a function of the reduced temperature  $t = (T - T_c)/T_c$  on the critical isotherm. HRT results ( $\bullet$ ) for LJ potential and ( $\square$ ) for an accurate pair interaction (Kr) plus three-body terms. Fit [8] of experimental data in Xe (—).



**Figure 2.** Radial distribution function for a LJ system at  $\rho^* = 0.5$  and  $T^* = 1.36$  as given by HRT (—) and simulation [10] ( $\bullet$ ).

numerical instabilities in our algorithm. However, a careful integration of the partial differential equation shows that it does not have spurious singularities below  $T_c$ . On the contrary, the theory is able to guarantee the convexity of the free energy in a self-consistent way, without the *ad hoc* Maxwell construction used in other formulations. In figure 3 we plot the inverse compressibility as a function of  $\rho - \rho_c$  for an isotherm below the critical temperature. The calculation so far has been performed for the simplest model which retains the full complexity of the original problem (basically a  $\phi^4$  field theory).

From figure 3 we conclude that the introduction of fluctuations strongly flattens the inverse compressibility in the region where ‘unstable’ (or ‘metastable’) behaviour is predicted at a mean field level. The density at coexistence can be accurately evaluated from our numerical solution as the end point where  $S(0)^{-1} = 0$  and is shown to scale



**Figure 3.** Inverse compressibility  $1/S(0)$  as a function of density (in arbitrary units) along an isotherm below the critical temperature for a  $\phi^4$  theory. Results are symmetric around the critical density. Mean-field result (---), before fluctuations are introduced, and final HRT prediction (—). The region where  $1/S(0)$  is negative is thermodynamically unstable.

with temperature following the expected power-law behaviour:  $\rho_{\text{coex}}/\rho_c \sim 1 \pm At^\beta$  where  $t$  is the reduced temperature and  $\beta = 0.345$  (see (5)).

The inverse compressibility should exhibit a discontinuity across the coexistence curve but, from our preliminary results, we are not able to evaluate the amount of this discontinuity because the numerical algorithm tends to enforce the continuity of the solution. Further analysis on this very interesting issue is in progress.

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