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Theory of the Universal and Nonuniversal Quantities of Fluids at the Critical Point[1]

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We show that the hierarchical reference theory is an accurate global theory of fluids at least above the critical temperature T_c. The hierarchy is truncated at the first equation, the one connecting the free energy to the pair correlation function, with an Ornstein–Zernike ansatz. In this approximation the theory can be considered as a sophisticated generalization of the optimized random phase approximation which has genuine nonclassical critical exponents and for which scaling is satisfied. We study the system of hard spheres plus the Lennard–Jones attractive well and find a good agreement with measured *PVT*, specific heat, correlation length, and structure factor in rare gases. The accuracy of the theory remains very good up to freezing density.

KEY WORDS: critical phenomena; critical point; liquid state theory; rare gases.

1. INTRODUCTION

The need of a theory which treats correctly the region of the critical point of a single-component fluid, in both its universal and its nonuniversal aspect, starting from a microscopic interatomic interaction is widely recognized [1]. From the standard liquid state theories one does not get the correct scaling form for the thermodynamic properties and for the radial distribution function $g(r)$ with nonmean field critical exponents. The renormalization group (RG) approach has not yet produced a practical scheme able to treat directly the statistical mechanics of a fluid. In the last

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few years we have developed [2] a generalized perturbation scheme, the hierarchical reference theory of fluids (HRT), which accomplishes this goal at least for temperatures above T_c, the only region we have treated explicitly so far.

Unlike RG we do not trace out degrees of freedom in building up a recursion relation but we look at how the free energy of the system evolves as we change a cutoff wave vector Q in the *pair interaction.* In this way at each stage we treat completely, i.e., on all length scales, a system which is partially coupled. Having divided $v(r)$ in a "reference" part $v_R(r)$ which contains the strong repulsive part (here we take this as the hard-spheres potential) and in a "weak" part $w(r) = v(r) - v_R(r)$, the partially coupled system (Q–system) is characterized by the interaction

$$v_Q(r) = v_R(r) + w_Q(r) \tag{1}$$

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

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

By this choice the density fluctuations with $k < Q$ of the Q system are strongly depressed compared with those of the fully interacting system and the critical fluctuations are gradually turned on as Q evolves from $+\infty$ down to zero. The evolution of the Helmholtz free energy A_Q and of the n-particle ($n = 2, 3,...$) direct correlation functions $c_n^Q(\mathbf{r}_1,..., \mathbf{r}_n)$ of the Q system for an infinitesimal change of Q is given by an exact hierarchy of equations and the properties of the reference system v_R represent the boundary conditions.

Two aspects should be stressed. First, close to the critical point and at short wavelengths the full hierarchy becomes identical to one of the formulations [3] of the RG. On the other end the hierarchy is much richer because it contains the large wavelengths part not given by RG. Second, the hierarchy is well ordered in many respects. For instance, the first two equations give the correct second virial coefficient of the equation of state at a low density and produce the correct $\varepsilon = 4 - d$ (d is the spatial dimensionality) expansion of the critical exponents up to order ε^2. Two of us [4] have already given the results of HRT when the hierarchy is truncated at the first equation for A_Q by an Ornstein–Zernike (OZ) closure for $c_Q(r)$. The results for the hard-sphere system with an attractive Gaussian well compared favorably with the experimental data for rare gases but the limitation of that computation was that $g(r)$ did not satisfy the core condition. We have extended the theory to take care of this problem by implementing in our scheme the trick of the optimized cluster theory [5], i.e., by a suitable redefinition of $w_Q(r)$ inside the core. Here we present the results for the hard-sphere system with the attractive well of the Lennard–Jones potential.

2. THE HIERARCHICAL REFERENCE THEORY OF FLUIDS

In Paper I (see Ref. 2) we have deduced the exact equation governing the change of the *excess* Helmholtz free energy of the Q system, A_Q^{ex}, when the parameter Q is varied. Specifically, if the *modified* free energy density A_Q^{ex} is defined as

$$A_Q^{\text{ex}} = -\frac{A_Q^{\text{ex}}}{k_B T} - \frac{\rho}{2}[\phi(0) - \phi_Q(0)] + \frac{\rho^2}{2}\int d^d r[\phi(r) - \phi_Q(r)] \tag{3}$$

where $\tilde{\phi}(k) = -\tilde{w}(k)/k_B T$, the *evolution equation* for A_Q^{ex} reads

$$-\frac{dA_Q^{\text{ex}}}{dQ} = \frac{1}{2}\int_{p=Q} \frac{d\Omega_p}{(2\pi)^d} \ln[1 + \check{\mathscr{F}}_Q(p)\,\tilde{\phi}(p)] \tag{4}$$

where the correlation function $\check{\mathscr{F}}_Q(k)$ is given by

$$\check{\mathscr{F}}_Q(k) = \frac{\rho}{1 - \rho\mathscr{C}_Q(k)} \tag{5}$$

The *modified direct correlation function* $\mathscr{C}_Q$ is related to the usual direct correlation function of the Q system $c_Q(k)$ by

$$\mathscr{C}_Q(k) \equiv c_Q(k) + \tilde{\phi}(k) - \tilde{\phi}_Q(k) \tag{6}$$

We have chosen to express all the physical quantities in terms of this *modified* correlation function because, due to the discontinuity in the potential of the Q system (2), the usual one has a discontinuity at wave vector $k = Q$.

Equation (4) should be solved by imposing the appropriate boundary condition at $Q = \infty$, where the potential $v_Q(r)$ reduces to the reference one and therefore the free energy is assumed to be known. However, the evolution equation, (4), contains the unknown correlation function of the Q system $\mathscr{C}_Q(k)$. A possible solution of this problem is to write an evolution equation for the quantity $\mathscr{C}_Q(k)$ analogous to the one for the free energy (4). This has been done in Paper I, where it was shown that the resulting equation suffers from a similar problem: it depends upon the three- and four-particle correlation functions of the Q system, which are solutions of analogous evolution equations, and so on. This set of equations thus defines an exact hierarchy of differential equations for the free energy and the correlation functions of the system. The resulting hierarchy can be explicitly analyzed in the critical region *and* at long wavelengths (i.e., for $Q \to 0$ and $k \to 0$) and it can be shown to develop a renormalization group structure from which the usual dimensionality expansion (ε expansion) can be obtained.

However, in this note we are interested in a theory of the liquid state able to describe both the critical region and the dense fluid regime. We have therefore chosen to approximate the correlation function appearing into Eq. (4) using the understanding gained by the study of perturbation approaches in the framework of liquid state theory [6]. In order to preserve the renormalization group structure of the equation near the critical point, it is sufficient that the exact sum rule

$$\mathscr{C}_Q(k=0) = \frac{\partial^2 A_Q^{\text{ex}}}{\partial \rho^2} \tag{7}$$

is satisfied [2] within our approximation at each Q: the evolution equation becomes a *partial* differential equation (PDE) because the relation (7) couples different densities.

Starting from Eqs. (4) and (7) an elegant analysis of the critical universal properties can be performed. In fact in Paper I we demonstrated that, when the sum rule (7) is satisfied and the long-wavelength limit of the direct correlation function is analytic in k^2 (that is, the critical exponent η vanishes), the critical behavior of the system is *universal* and *nonclassic*: the critical exponents can be obtained studying the fixed point solution of a suitably rescaled form of Eq. (4) in complete analogy with the renormalization group method. The explicit values of the critical indices for such an Ornstein–Zernike closure are (in three dimensions)

$$\nu = 0.689, \qquad \gamma = 1.378, \qquad \beta = 0.345, \qquad \delta = 5 \tag{8}$$

These values, being 10% higher than the commonly accepted ones, are the best estimates of the critical exponents obtained within the framework of a theory of the liquid state, and this suggests that the approach we have adopted can be used for an extensive investigation of the universal as well as nonuniversal properties of a simple fluid in the critical region even if we limit ourselves to this class of OZ closures which preserve the analyticity in k of the correlation functions at the critical point.

The simplest closure satisfying the above prescriptions corresponds to the well-known random phase approximation (RPA):

$$\mathscr{C}_Q(k) = c_R(k) + \lambda_Q \tilde{\phi}(k) \tag{9}$$

where λ_Q is a parameter determined so that Eq. (9) satisfies the sum rule (7). The thermodynamics resulting from this approximation [eqs. (4), (7), (9)] has been analyzed in a previous publication [4]: its weakest feature is probably the poor representation of the short-range structure of the liquid induced by the RPA *ansatz* (9). In fact it is known that RPA does not satisfy the short-range constraint on the radial distribution function: $g(r) = 0$ when r is less than the hard-sphere diameter σ *(core condition)*. We have succeeded in including this requirement in our theory using an optimization procedure analogous to the one proposed by Weeks et al. [5] with the optimized cluster theory (OCT), in liquid state theory. This amounts to redefining the potential at separations smaller than the hard-sphere diameter in such a way as to obey the core condition. We stress in our case that the core condition must be satisfied by the *true* radial distribution function of the Q system for each value of the parameter Q. Therefore in place of Eq. (9) we have analyzed the approximation

$$\mathscr{C}_Q(k) = c_R(k) + \lambda_Q \tilde{\phi}(k) + \sum_{j=0}^{M} u_Q^j \tilde{P}_j(k) \tag{10}$$

where $P_j(r)$ is a basis of polynomials in the range $0 < r < \sigma$ and the coefficients u_Q^j are determined at each Q by the requirement that

$$g_Q(r) \equiv 1 + \int \frac{d^3k}{(2\pi)^3} \frac{c_Q(k)}{1 - \rho c_Q(k)} e^{i\mathbf{k}\cdot\mathbf{r}} = 0 \qquad \text{for} \quad r < \sigma \tag{11}$$

and the relation between $\mathscr{C}_Q(k)$ and $c_Q(k)$ is given by (6). We have followed the standard prescription of liquid state theory limiting the basis set to the first five Legendre polynomials. Even in this case the equations turn out to be exceedingly difficult because the core condition is to be imposed at each Q and ρ and is coupled to the partial differential equation for the free energy (4). We have approximated the evolution equations for the coefficients u_Q^j by neglecting the feedback of fluctuations on the short-range properties of the system. In this way the problem simplifies, allowing for an explicit numerical analysis. We have verified that this approximation is highly successful, $g_Q(r)$ being below 10^{-2} inside the core as is standard in OCT computations.

Equation (4) can be written as a *flux conservative* parabolic equation [7] by taking its derivative with respect to the density and considering the dimensionless excess chemical potential

$$\beta\mu_Q^{\text{ex}} \equiv \frac{\partial A_Q^{\text{ex}}}{\partial \rho} \tag{12}$$

as the basic unknown function. In these terms the explicit equation becomes

$$\frac{\partial \beta \mu_Q^{\mathrm{ex}}}{\partial Q} = -\frac{Q^2}{(4\pi^2)} \frac{\partial}{\partial \rho} \ln \left[1 + \frac{\rho \tilde{\phi}(Q)}{1 - \rho \mathscr{C}_Q(Q)} \right] \tag{13}$$

where $\mathscr{C}_Q(k)$ is given by Eq. (10) and the parameter λ_Q is expressed in terms of the chemical potential by Eq. (7):

$$\lambda_Q = \left(\frac{\partial \beta \mu_Q^{\mathrm{ex}}}{\partial \rho} - c_{\mathrm{R}}(k=0) - \sum_{j=0}^{4} u_Q^j \tilde{P}_j(k=0) \right) \frac{1}{\tilde{\phi}(k=0)} \tag{14}$$

The reference system has been taken as a hard-sphere fluid and its properties have been computed using the Verlet–Weis parameterization of the correlation functions and the Carnahan Starling equation of state [6]. The attractive part of the interaction $w(r)$ is a Lennard–Jones potential computed following the WCA procedure [5]:

$$w(r) = \begin{cases} -\varepsilon & \text{if} \quad r \leqslant 2^{1/6}\sigma \\ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] & \text{if} \quad r > 2^{1/2}\sigma \end{cases} \tag{15}$$

The five coefficients u_Q^j are determined at each density by solving the set of evolution equations

$$\begin{aligned} \sum_{n=0}^{4} M_{jn}(Q) \frac{du_Q^n}{dQ} &= \frac{Q^2}{(2\pi^2)} \tilde{P}_j(Q) \frac{\check{\mathscr{F}}_Q^2(Q)\, \tilde{\phi}(Q)}{1 + \check{\mathscr{F}}_Q(Q)\, \tilde{\phi}(Q)} \\ \frac{d}{dQ} M_{jn}(Q) &= -\tilde{P}_j(Q)\, \tilde{L}_n(Q) \frac{Q^2}{(2\pi^2)} \left[\check{\mathscr{F}}_Q^2(Q) - \left(\frac{\check{\mathscr{F}}_Q(Q)}{1 + \check{\mathscr{F}}_Q(Q)\, \tilde{\phi}(Q)} \right)^2 \right] \\ M_{jn}(Q = \infty) &= \rho^2 \int \frac{d^3k}{(2\pi)^3} \tilde{P}_j(k)\, \tilde{L}_n(k)\, S_R^2(k) \\ \tilde{L}_n(k) &= \tilde{P}_n(k) - \tilde{P}_n(0) \frac{\tilde{\phi}(k)}{\tilde{\phi}(0)} \end{aligned} \tag{16}$$

where $S_{\mathrm{R}}(k)$ is the structure factor of the reference system. This PDE has been solved by a Lax–Wendroff finite-difference method [7]. The initial condition at $Q = \infty$ is given in terms of the reference system properties, while the boundary condition at $\rho = 0$ is obtained by expanding all the quantities appearing in Eq. (13) in powers of the density, equating the coefficients of corresponding powers and solving the resulting ordinary differential equations. The numerical scheme we have employed also needs a boundary condition at high densities, which has been imposed at $\rho\sigma^3 = 1$ using the optimized random phase approximation (ORPA).

3. RESULTS

The numerical solution of Eq. (13) provides a complete description of the thermodynamics as well as the structure of a Lennard–Jones fluid, meaningful also in the critical region. It is interesting to discuss our results and to make a comparison with the available experimental data in simple fluids and computer simulations for Lennard–Jones systems. As a first step we briefly comment upon the evaluation of the universal quantities. The approximation (10) we have considered preserves, as noted before, the analyticity of the direct correlation function at the critical point and therefore we expect that the universal asymptotic properties of the system in the critical region are described by the set of critical exponents (8). This expectation will be satisfied by the present numerical computation provided that, at the critical point, the solution of Eq. (13) evolves toward the fixed point we analyzed in Paper I. In our computation we have verified that this is the case: the critical exponents computed from the numerical solution of Eq. (13) agree with the values (8) previously obtained.

In discussing the nonuniversal quantities in the critical region and, more generally, the properties far from the critical region, we face the problem of comparing our result with experimental data, which necessarily refer to a different interaction. In fact the potential we choose in our computation is unrealistic at short distances, having a hard core, and does not reproduce correctly the shape of the attractive well as predicted by more refined interactions. For these reasons we first compare our result with a Monte Carlo simulation performed by Stell and Weis for a system interacting by exactly the same potential we have used [8]. Our estimate for the critical temperature has been obtained by a power-law fitting of the values of $S(k=0)$ along the critical isocore $\rho^* = 0.312$ (in units of σ^{-3}). The critical exponent γ is in excellent agreement with Eq. (8) and the critical temperature is $T_c^* = 1.3502$ (in units of ε/k_B). This result is consistent with the observation made by Stell and Weis [8] that the state $\rho^* = 0.3$, $T^* = 1.35$, is already in the metastable region for this potential. In Table I we compare the values of the compressibility factor $Z \equiv P/\rho k_B T$, obtained from the chemical potential from the solution of Eq. (13) (compressibility route), the evaluation via the virial theorem and the Monte Carlo result. We also report the values $g(1)$ of the radial distribution function at $r = \sigma$ at densities and temperatures where the simulation data are available. In Fig. 1 we plot the radial distribution function in our approximation together with the

Table I. Comparison Between the MC Results for the Compressibility Factor Z_{MC} and the Value of $g(r)_{\mathrm{MC}}$ at Contact for Hard Spheres with the Attractive Well Eq. (15) and the Results from the HRT, Z_c from Compressibility, and Z_v from the Virial Relation

ρ^*	T^*	Z_{MC}	Z_c	Z_v	$g(1)_{\mathrm{MC}}$	$g(1)$	$g(1)_{\mathrm{ORPA}}$[a]
0.2	1.6	0.67	0.666	0.636	1.94	1.810	1.708
0.6	1.6	1.12	1.09	1.142	2.57	2.6	2.592
0.91	1.35	5.41	5.313	6.032	4.90	5.193	5.202
0.91	2.74	8.75	8.330	8.652	5.15	5.23	5.255

[a] This column is the results from ORPA for $g(r)$ at contact $[g(r)_{\mathrm{ORPA}}]$.

"exact" result from simulation for the states $\rho^* = 0.6$, $T^* = 1.60$, and $\rho^* = 0.91$, $T^* = 1.35$. At these high densities our basic approximation for the correlations, similar to ORPA, is satisfactory, as can also be seen from the good degree of thermodynamic consistency between A_c and Z_v shown in Table I, and our theory represents an improvement with respect to ORPA. At low densities our results are not as good because Eq. (10) is not a good representation of the correlations in the system and it does not correctly reproduce the virial expansion as $\rho \to 0$.

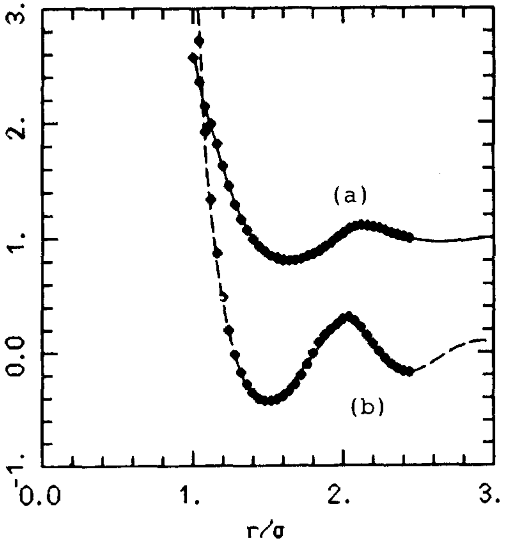

Fig. 1. Comparison between Monte Carlo simulation of Stell and Weis and the results of HRT. (a) $g(r)$ at $T^* = 1.6$ and $\rho^* = 0.6$. The solid line is the HRT result and filled circles are the MC data. (b) $g(r) - 1$ at $T^* = 1.35$ and $\rho^* = 0.91$. Dashed line, HRT; filled circles, MC data.

The dimensionless compressibility $S(0)$ is plotted in Fig. 2 versus the reduced temperature $t = (T - T_c)/T_c$ along the critical isocore. The continuous curve is the fit of scattering data in xenon taken from Ref. 9. The fit contains both the asymptotic power-law behavior and the correction to scaling terms. Keeping in mind that we have no adjustable parameters, the agreement is remarkable but our computation systematically overestimates the experimental results in the whole range of temperatures. This could be due either to approximation (10), which is inaccurate at these densities, or to the difference between the interatomic potential we have used and the true potential. In Fig. 2 we also show our results for the correlation length ξ (with $\sigma_{\mathrm{LJ}} = 4.07$ Å) together with the asymptotic fit of experimental measures in xenon [10]. We observe a very good agreement except at the lowest temperatures, where the effect of the difference between our estimate of the critical exponent ν (8) and the correct one is important.

In Fig. 3 we compare the compressibility factor Z_c to experimental data in argon [11] along the isotherm −110°C. We plot the numerical results corresponding to the same *absolute* temperature (using the standard Lennard–Jones representation of argon with $\varepsilon/k_B = 119.8$ K) and to the same *reduced* temperature t, which corresponds to a different absolute temperature (10% higher) due to the discrepancies between our estimate of the

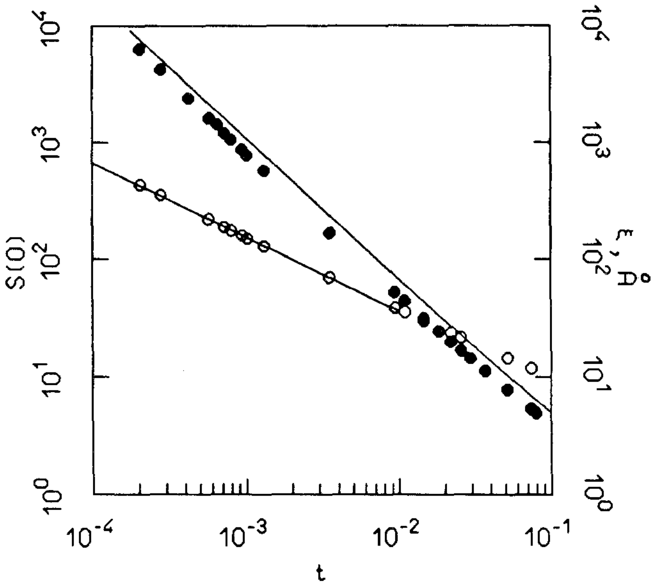

Fig. 2. $S(0)$ and correlation length ξ from the HRT (respectively, filled and open circles) compared with the fits of the data in xenon. On the X axis $t = (T - T_c)/T_c$.

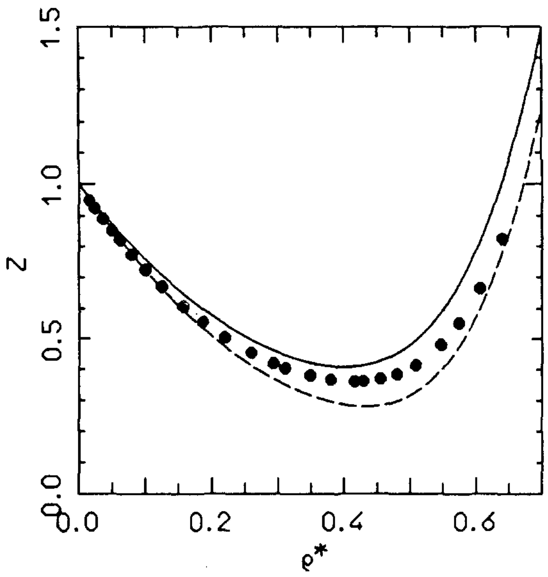

Fig. 3. Equation of state for argon at $T = -110°\mathrm{C}$ (filled circles) compared with the results of the theory at the same absolute temperature (dashed line) and at the same reduced temperature t (solid line).

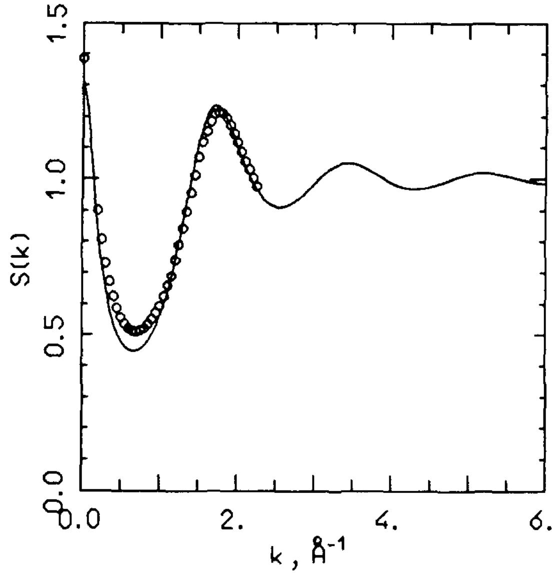

Fig. 4. Structure factor $S(k)$ for krypton from the theory (solid line) compared with the experimental data.

critical temperature ($T_c^* = 1.3502$) and its value in argon ($T_c^* = 1.258$). We see that these two curves bracket the experimental result, suggesting that the origin of the deviation is related to the different critical temperatures of the two systems.

In Fig. 4, the structure factor of our approximation is compared to scattering measurements in krypton [12] at temperature $T = 297$ K and at a density ($\rho = 6.19 \times 10^{27}$ atoms $\cdot$ m^{-3}) which is close to the critical value. In terms of reduced units ($\varepsilon/k_B = 166.2$ K, $\sigma = 3.68$ Å), this corresponds to $T^* = 1.79$ and $\rho^* = 0.308$.

4. DISCUSSION

We can summarize the comparison with experiments by noting that our results for the thermodynamics are as accurate as the most reliable theories of liquids in the dense fluid regime but, at the same time, are meaningful also in the critical region where all the theories of liquid state fail. The correlations are reproduced with the same accuracy as ORPA, which is considered a successful theory of the liquid state in the dense region. An improvement of approximation (10) is needed at lower densities, where the low density virial expansion should be built in our closure for the direct correlation function. An additional way for improving our basic ansatz (10) is to parameterize $\mathscr{C}_Q(k)$ with an additional coefficient to be determined by imposing thermodynamic consistency between the compressibility and the virial route. The study of such a fully consistent HRT with OZ closure is currently under way. The other way to improve the present theory is to consider also the second equation of the full hierarchy by introducing a suitable closure at the level of $c^{(3)}$ and $c^{(4)}$.

In liquid state theory one often introduces an improved description by imposing condition of thermodynamic consistency (see, for instance, Ref. 13). This consistency, however, is imposed with respect to the full interaction. In our theory a consistency condition such as Eq. (7) is imposed all along the Q integration, i.e., it operates as we turn on the density fluctuations on the different length scales. It is this fundamental difference which distinguishes the two approaches and builds scaling and nonclassical critical exponents in our approach.

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