Comprehensive Theory of Simple Fluids, Critical Point Included

A. Parola
Scuola Internazionale Superiore di Studi Avanzati, Strada Costiera 11, Trieste, Italy

A. Meroni and L. Reatto
Dipartimento di Fisica dell'Universitá, Milano, Italy

(Received 27 March 1989)

We present a comprehensive theory of fluids which has the typical accuracy of a good liquid-state theory in the dense regime but in addition has a genuine nonclassical critical behavior. The theory is based on the hierarchical reference theory of fluids decoupled with an approximation inspired by the optimized random-phase approximation. The Lennard-Jones interaction is studied in detail above the critical temperature.

PACS numbers: 61.20.Gy, 05.70.−a

We do not have yet a liquid-state theory which is able to treat correctly also the region of the critical point of the liquid-vapor phase transition. Various liquid-state theories can be very accurate elsewhere in the phase diagram but none of them is correct even qualitatively close to the critical point in the sense of having scaling satisfied with reasonable critical exponents. Renormalization-group theory has not yet produced a practical scheme to compute nonuniversal quantities starting from a realistic model of a fluid. A few years back two of the authors[1,2] introduced a new scheme, the hierarchical reference theory (HRT), which held promise to fulfill this goal. This approach, however, leads to an infinite hierarchy of equations and it was not guaranteed that it would lead to a practical and accurate scheme of computation.

We have performed a decisive step to solve this problem. In fact we show in this Letter how a well known and accurate liquid-state theory,[3] the optimized random-phase approximation (ORPA) which has a rather trivial critical-point behavior, can be transformed into a theory with a nontrivial critical behavior. We can consider the new theory either as a sophisticated generalization of ORPA or as the lowest-order approximation of HRT which satisfies the core condition, i.e., the vanishing of the radial distribution function $g(r)$ inside the core.

In ORPA the interatomic pair potential $v(r)$ is decomposed into a repulsive part $v_R(r)$ and an attractive tail $w(r)=v(r)-v_R(r)$, and the effect of $w(r)$ on the properties of the reference system, i.e., the system with interaction $v_R(r)$, is determined. However, following the HRT approach we turn on $w(r)$ not just in one step but selectively in wave-vector space: We consider a family of partially coupled Q systems with potential

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

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

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

When $Q=\infty$, v_Q is just the reference system but when $Q=0$ the fully interacting system is recovered. This procedure allows a gradual turning on of the critical fluctuations on different length scales because density fluctuations with $k<Q$ are strongly depressed in the Q system. In fact in RPA the $S(k)$ of the Q system for $k<Q$ is simply the structure factor of the reference system, and only for $k>Q$ do critical fluctuations show up. Notice, however, that the Q system is treated over all of its length scales and we do not trace out degrees of freedom as in renormalization-group calculations.[4]

The flow of the excess Helmholtz free energy A_Q^{ex} of the Q system is given in three dimensions by the exact equation

$$-\frac{d\mathcal{A}_Q^{\mathrm{ex}}}{dQ}=\frac{Q^2}{4\pi^2}\ln\left[1+\frac{\rho\tilde{\phi}(Q)}{1-\rho\mathcal{C}_Q(Q)}\right], \tag{3}$$

where $\mathcal{A}^{\mathrm{ex}}$ differs from A^{ex} by analytic terms (see I), $\tilde{\phi}(k)=-\tilde{w}(k)/k_BT$, and $\mathcal{C}_Q$ is related to the direct correlation function c_Q of the Q system by

$$\mathcal{C}_Q(k)\equiv c_Q(k)+\tilde{\phi}(k)-\tilde{\phi}_Q(k) \tag{4}$$

evaluated on the shell $k=Q$. The flow of $\mathcal{C}_Q$ is determined by an equation which involves the three- and four-body direct correlation functions, but we truncate the problem at the first equation (3) of the hierarchy by an *Ansatz* for $\mathcal{C}_Q(k)$. Precisely, for $r>d$ we write

$$\mathcal{C}_Q(r)=c_R(r)+\lambda_Q\phi(r)\,, \tag{5}$$

and $\mathcal{C}_Q(r)$ for $r<d$ is determined by the condition of vanishing radial distribution function of the Q system:

$$g_Q(r)\equiv 1+\int\frac{d^3k}{(2\pi)^3}\frac{c_Q(k)}{1-\rho c_Q(k)}e^{i\mathbf{k}\cdot\mathbf{r}}=0,\ \text{for } r<d\,. \tag{6}$$

$c_R(r)$ is the direct correlation function of the reference system, d is its hard-core diameter, and λ_Q is determined by the compressibility sum rule which reads

$$\mathcal{C}_Q(k=0)=\partial^2\mathcal{A}_Q^{\mathrm{ex}}/\partial\rho^2\,. \tag{7}$$

If $\lambda_Q=1$, Eqs. (4)–(6) are simply the ORPA for the Q

system. Generalizations of ORPA or of related equations similar to (5) in the sense that a parameter is introduced which is determined by a condition of thermodynamic consistency like Eq. (7) have been already considered in the literature[5] but in all these formulations the effect of the full perturbation $w(r)$ is considered. Our approach differs in a fundamental way because the condition (7) is applied all along the Q integration and only in this way one finds nontrivial critical exponents. In fact with our *Ansatz* $\mathcal{C}_Q(k)$ is analytic in k so that $\eta=0$ and the other critical exponents have been already computed in I. By performing a dimensional expansion these turn out to be correct to linear order in $\epsilon=4-d$, and for $d=3$ an explicit computation of the fixed point of Eqs. (3)-(7) gave

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

We have applied our theory to the Lennard-Jones fluid: $v_{\mathrm{LJ}}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$ and v_{LJ} is decomposed with the Andersen-Chandler-Weeks rule.[3] The repulsive part of the interaction, i.e., $v_R(r)=v_{\mathrm{LJ}}(r)+\epsilon$ for $r<2^{1/6}\sigma$ and $v_R(r)=0$ for $r>2^{1/6}\sigma$, is replaced by the hard-sphere potential with a state-dependent diameter $d(\rho,T)$ given by the Andersen-Chandler-Weeks rule.[3] As usual with ORPA Eq. (6) is approximately solved by expanding $\mathcal{C}_Q(r)$ for $r<d$ on a polynomial basis (the first five Legendre polynomials are adequate) and the coefficients $u_n(Q)$ $(n=0,\ldots,4)$ are determined from Eq. (6).

Combining Eqs. (3)-(7) one obtains a system of six partial differential equations for $\mathcal{A}_Q$ and $\{u_n(Q)\}$ as functions of Q and ρ (the temperature T has the role of an external parameter). These equations become decoupled if in the equations for $u_n(Q)$ one neglects the feedback of density fluctuations on the short-range properties of the system. The accuracy of this approximation is verified *a posteriori* by verifying that the core condition (6) is satisfied as in a standard ORPA computation. The flow equation for the excess chemical potential $\beta\mu_Q^{\mathrm{ex}} \equiv \partial\mathcal{A}_Q^{\mathrm{ex}}/\partial\rho$ is a flux-conserving parabolic equation in Q and in ρ which is integrated[6] starting from $Q=\infty$ down to $Q=0$ in the density range (0,1) for $\rho^*=\rho\sigma^3$. For the moment we have considered only a solution corresponding to a homogeneous state so that we study temperatures above the critical one T_c because the equation becomes unstable for $T<T_c$ inside the two-phase region. The properties of hard spheres[7] [the Carnahan-Starling equation of state and the Verlet-Weiss parametrization of $c_R(k)$] enter as initial conditions at $Q=\infty$. The boundary condition at $\rho=0$ is obtained by solving the ordinary differential equation which is obtained by expanding to second order in density all quantities appearing in Eq. (3). At $\rho^*=1$ we use the ORPA solution; i.e., we put $\lambda_Q=1$ for all Q.

First we compare our results with those of simulation. In Fig. 1 the compressibility factor $Z\equiv P/\rho k_BT$ on the isotherm[7] $T^*=T/\epsilon=1.35$ is shown over the full density range. The agreement is excellent up to the highest density and comparable with the results of accurate liquid-state theories. We find that the critical point of the LJ system is at $T^*=1.3330$ and $\rho^*=0.3155$ whereas simulation leads to the estimate[8] $T^*=1.31$ and $\rho^*=0.31$.

The universal critical behavior given by our equations can be studied separately and this leads, for instance, to the critical exponents (8) and to the scaled equation of state displayed below. The solution of the full equation flows to this fixed point; for instance, on the critical isochore the asymptotic behavior for the isothermal compressibility corresponding to the exponent $\gamma=1.378$ is roughly reached for a reduced temperature $t=(T-T_c)/T_c\simeq10^{-4}$ as shown in Fig. 2. Here the fit[9] of the experimental data in Xe is also shown. Notice that in the theory there is no adjustable parameter once ϵ and σ are fixed and these have been chosen to get agreement with the experimental critical point ($\epsilon/k_B=217.3$ K, $\sigma=4.16$ Å). These values are very close to the standard ones,[7]

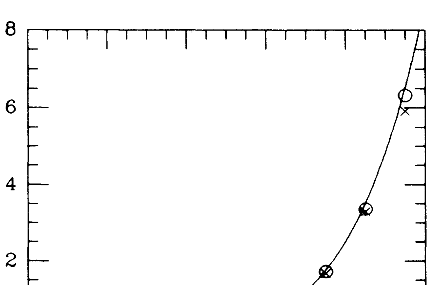

FIG. 1. Compressibility factor Z of the LJ system for the isotherm $T^*=1.35$: simulation (Ref. 7) (○), ORPA (×), and HRT (——).

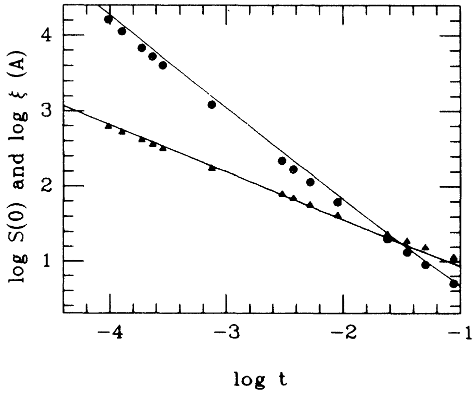

FIG. 2. Reduced isothermal compressibility $S(0)=nk_BT\kappa_T$ and correlation length ξ as functions of $t=(T-T_c)/T_c$ on the critical isotherm. HRT results for $S(0)$ (●) and ξ (▲), and fits of experimental data (Refs. 9 and 10) for Xe (——).

$\epsilon/k_B = 225.3$ K, $\sigma = 4.07$ Å. There is an excellent agreement between theory and experiment but at smaller t one notices the larger slope of the theoretical result and this is due to the larger value of γ compared with the experimental one ($\gamma = 1.24$). Excellent agreement is also found for the correlation length and in Fig. 1 the data[10] for Xe are shown.

Close to the critical point scaling with the exponents (8) is satisfied by the present approximation and in Fig. 3 the scaling function $h(x)$, defined by the relation

$$\Delta\mu = \Delta\rho \, |\Delta\rho|^{\delta-1} h\left[\frac{t}{|\Delta\rho|^{1/\beta}}\right], \qquad (9)$$

is shown {here $\Delta\rho = (\rho - \rho_c)/\rho_c$ and $\Delta\mu = [\mu(\rho,T) - \mu(\rho_c,T)]/T_c$}. We display both $h(x)$ obtained from the asymptotic analysis and the results of the full equation for a number of isotherms in the density range $0.2 < \rho^* < 0.4$. Also shown is the result of a fit[11] of experimental data in Xe. At large x theory and experiment give a different slope for $h(x)$, which is equal to γ, and this is again a manifestation of the small deviation between our value and the experimental value of γ. To a very good extent the results of the full equation are symmetric around ρ_c and on the scale of Fig. 3 the asymmetry is not visible. The region of validity of the asymptotic behavior appears to be smaller both in t and in $\Delta\rho$ in comparison to experiment.[11] This parallels the slow setting in of the asymptotic behavior on the critical isocore (Fig. 2) and presumably is due to the constraint $\eta = 0$ of the present approximation.

In Fig. 4 we compare the experimental structure factor $S(k)$ for krypton[12] for a state in the region of the critical point ($T = 237$ K, $\rho = 5.582$ atoms/nm^3) with theory with the LJ parameters $\epsilon/k_B = 157$ K and $\sigma = 3.64$ Å which give the correct critical point in our approximation. The agreement is reasonable and the main origin of the discrepancy is due to the use of the LJ potential and not to the approximations of the theory. This is demonstrated by comparing the results of the modified hypernetted chain equation[7] (MHNC) for the LJ potential and for an accurate pair interaction plus the three-body Axilrod-Teller potential.[13] It can be noticed that the present result is very close to the MHNC result when the same potential is used.

In conclusion, we have presented the first theory which, starting from a realistic pair interaction, allows the accurate computation of the properties of a fluid over the full density range, the region of the critical point included. By using the method of the HRT we have transformed a successful liquid-state theory, ORPA, into a theory with a nontrivial critical behavior without losing (actually improving) its accuracy far from the critical point. The results for the universal quantities in the critical region are not competitive with those of accurate renormalization-group computations[4] but since the present theory is within the framework of the general formulation of HRT we know how to introduce systematic improvements on it. If in place of *Ansatz* (5) we consider the second equation of the hierarchy with a suitable decoupling at this level the critical exponents should improve since these turn out[1] to be correct to second order in ϵ and not just to first order as in the case of the present computation.

Presently[7] liquid-state theory is mainly based on the method of the integral equation for $g(r)$ but often it has been drawn to consider differential conditions via thermodynamic consistency requirements. The present approach is fully differential but at a higher level since it involves also the parameter Q which controls the turning on of the interaction and of the density fluctuations and this is central to obtain the renormalization-group structure close to the critical point. We have considered the LJ potential but nothing prevents the use of a more realistic pair interaction.

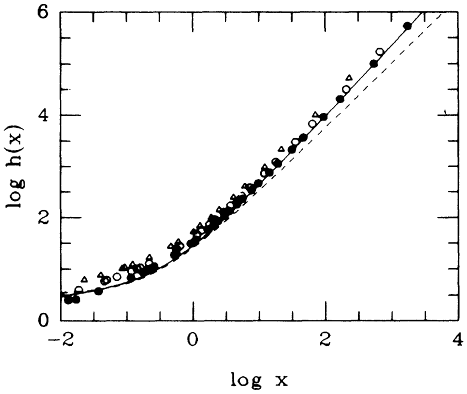

FIG. 3. Scaled equation of state $h(x)$ as function of x. HRT results for $T^* = 1.33313$ (●), $T^* = 1.33338$ (○), and $T^* = 1.334$ (△), from HRT asymptotic analysis (——), and fitted experimental data (Ref. 11) for Xe (---).

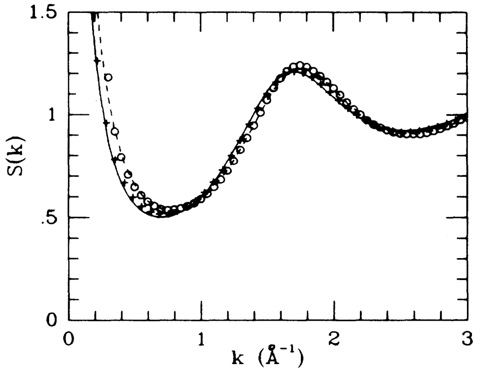

FIG. 4. Structure factor for krypton at $T = 237$ K and $\rho = 5.582$ atoms/nm^3: experimental (Ref. 12) (○), HRT result for LJ (——), and modified hypernetted chain results for LJ (+) and for an accurate pair-plus-three-body interaction (Ref. 13) (---).

[1] A. Parola and L. Reatto, Phys. Rev. Lett. **53**, 2417 (1984).

[2] A. Parola and L. Reatto, Phys. Rev. A **31**, 3309 (1985), referred to as paper I.

[3] H. C. Andersen, D. Chandler, and J. D. Weeks, Adv. Chem. Phys. **34**, 105 (1976).

[4] See, for instance, K. G. Wilson and J. B. Kogut, Phys. Rep. **12C**, 75 (1974).

[5] J. S. Høye and G. Stell, Mol. Phys. **52**, 1071 (1984).

[6] A. Parola, A. Meroni and L. Reatto, Int. J. Thermophys. (to be published).

[7] See, for instance, J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).

[8] A. Z. Panagiotopoulos, Int. J. Thermophys. (to be published).

[9] H. Güttinger and D. S. Cannell, Phys. Rev. A **24**, 3188 (1981).

[10] J. V. Sengers and M. R. Moldover, Phys. Lett. **66A**, 44 (1978).

[11] M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. Green, Phys. Rev. Lett. **22**, 389 (1969).

[12] J. A. Youden, M.Sc. thesis, Guelph, 1987 (unpublished).

[13] M. Tau, L. Reatto, R. Magli, P. Egelstaff, and F. Barocchi (to be published).