Liquid-Vapor Transition from a Microscopic Theory: Beyond the Maxwell Construction

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A smooth cutoff formulation of the hierarchical reference theory (HRT) is developed and applied to a Yukawa fluid. The HRT equations are derived and numerically solved leading to the expected renormalization group structure in the critical region, nonclassical critical exponents and scaling laws, a convex free energy in the whole phase diagram (including the two-phase region), finite compressibility at coexistence, together with a fully satisfactory comparison with available numerical simulations. This theory, which also guarantees the correct short range behavior of two body correlations, represents a major improvement over the existing liquid-state theories.

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Given that the physics of the liquid-vapor phase transition is a textbook topic in thermodynamics, it is disappointing that so far no liquid-state theory has been able to describe it satisfactorily. In fact, when faced with phase coexistence, mean-field approaches such as (generalized) van der Waals theories give a nonconvex free energy, while integral equations [1] fail to converge altogether in some domain inside the coexistence region. In both cases, the coexistence boundary must be recovered via the Maxwell construction, namely, by imposing thermodynamic equilibrium *a posteriori*. Aside from first-principles considerations, it should also be noted that this procedure may turn out to be cumbersome to implement, especially in the case of integral equations, because of the need to circumvent the forbidden domain and the ambiguities entailed by this procedure for theories lacking thermodynamic consistency. When dealing with mixtures of fluids, this becomes a serious hindrance to the theoretical determination of the phase diagram.

The approach that comes closest to a realistic description of the liquid-vapor transition is the hierarchical reference theory (HRT) of fluids [2], a genuine microscopic approach that implements the renormalization group (RG) method within the liquid-state framework. HRT is able to reproduce nonclassical critical exponents, scaling laws, and, what is most relevant for this discussion, a rigorously convex free energy, so that flat isotherms at coexistence naturally emerge from the theory, leading to accurate predictions of phase boundaries. However, the implementation of HRT developed so far is plagued by an unphysical divergence of the compressibility on the coexistence boundary [3]. In liquid-state theory jargon, HRT forces the spinodal and the binodal curve to coincide. If flat isotherms are obtained at this price, one may have some doubts about how reliable the description of the first-order phase transition given by HRT really is. This also prevents one from achieving any information on the possible occurrence of metastable pure phases that, in the usual approaches, are located between the binodal and the spinodal.

In this Letter we show that a novel implementation of HRT based on a smooth cutoff procedure [4] is able to reproduce correctly the physics at the phase boundary and provide a criterion to discriminate between unstable and metastable states, while also improving on the representation of short range correlations. This qualifies HRT as the only liquid-state theory able to provide a satisfactory description of the liquid-vapor phase transition.

Following the lesson of the RG [5], HRT is based on the gradual introduction of (density) fluctuations starting from short wavelengths. The two body potential $v(r)$ is first split into the sum of a (repulsive) reference part $v_R(r)$ and a (mostly attractive) tail $w(r)$. The properties of the reference system, usually a hard sphere fluid, are assumed to be known, and a sequence of intermediate systems is introduced, labeled by a parameter $t \in (0, \infty)$ "interpolating" between the reference and the physical model. The interaction potential of the t system is $v_t(r) = v_R(r) + w_t(r)$ where the Fourier components $\tilde{w}_t(k)$ of $w_t(r)$ are strongly suppressed for wave vectors $k \lesssim e^{-t}$. The change in the free energy of the system when the parameter t undergoes an infinitesimal change can be evaluated exactly, leading to the HRT differential equation.

The purpose of the procedure outlined above is to suppress the liquid-vapor transition throughout the whole sequence of intermediate t systems, due to the long range repulsive tail present in $w_t(r)$. As in the RG, the long-wavelength fluctuations that drive the phase transition must be allowed to develop only in the $t \to \infty$ limit, when $w_t(r)$ tends to the physical attractive interaction $w(r)$. The sharp cutoff formulation of HRT, which has been successfully applied to several model systems [6], fulfills this condition. The sharp cutoff is defined by the choice $\tilde{w}_t(k) = \tilde{w}(k)$ for $k > e^{-t}$ while $\tilde{w}_t(k) = 0$ for $k < e^{-t}$ and gives rise to an HRT equation which, close to the critical point and at long wavelengths, reproduces the Wegner-Houghton RG scheme [7]. When a simple, analytic closure for the correlations is inserted into this equation, some flaws occur close to the first-order boundary, where, as previously

discussed, a diverging compressibility is predicted by the sharp cutoff HRT. Remarkably, it has been recently shown, in the framework of scalar field theories, that this unphysical behavior can be eliminated by changing the cutoff procedure, i.e., by modifying the definition of the intermediate potentials $w_t(r)$ [8,9]. Whether this property survives in the framework of a liquid-state theory is not known, and it is addressed here. In this Letter, we adopt the following form:

$$w_t(r) = w(r) - e^{-dt}\psi(t)w(re^{-t}), \tag{1}$$

where $d = 3$ is the space dimensionality and $\psi(t)$ is a decreasing function of t with $\psi(0) = 1$ and asymptotic behavior $\psi(t) \propto e^{-2t}$ for $t \to \infty$. The precise definition of $\psi(t)$ will be discussed later. Note the t dependence of the range of the second (weakly repulsive) contribution to $w_t(r)$: in the large t limit, the amplitude of this term decreases while its range grows.

The differential equation expressing the change in the free energy when the parameter t (and hence the interaction v_t) is changed follows from first-order perturbation theory [10]:

$$\frac{dA_t}{dt} = \frac{\rho^2}{2}\int d\mathbf{r} g_t(r)\frac{d\phi_t}{dt}, \tag{2}$$

where A_t is $(-\beta)$ times the Helmholtz free energy per unit volume of the fluid interacting via $v_t(r)$ and $g_t(r)$ is the corresponding radial distribution function, while $\phi_t(r) = -\beta w_t(r)$. This equation is formally exact but, as usual in the HRT approach, it requires a closure relation expressing the two body correlations in terms of the free energy. Analogous to the standard implementation of the sharp cutoff HRT [6], we adopt the following mean spherical approximation (MSA)-like representation [10]:

$$g_t(r) = 0 \quad \text{for } r < 1, \tag{3}$$

$$c_t(r) = \phi_t(r) + \lambda_t\phi(r) \quad \text{for } r > 1, \tag{4}$$

where the direct correlation function $c_t(r)$ is related to $g_t(r)$ by the usual Ornstein-Zernike (OZ) equation [10]. The key feature of this closure is the presence of the λ_t parameter, which is introduced in order to enforce the compressibility sum rule:

$$\frac{\partial^2 A_t}{\partial\rho^2} = -\frac{1}{\rho} + \int d\mathbf{r} c_t(r). \tag{5}$$

Equations (2)–(5) form, together with the definition (1), a closed set of integrodifferential equations for the thermodynamics and correlations of the model. The numerical solution of this problem poses highly demanding computational tasks, which may, however, be simplified by choosing a particularly favorable model system: the Yukawa fluid, i.e., a hard sphere fluid with attractive tail

$$\phi(r) = -\beta w(r) = \frac{1}{T}\frac{e^{-z(r-1)}}{r}, \tag{6}$$

where T is the dimensionless temperature and z is the inverse range. Lengths are normalized to the hard sphere diameter. This one-parameter family of interaction potentials actually represents one of the most studied systems in liquid-state theory: because of the simple analytical form of $w(r)$ and the flexibility due to the tunable inverse range parameter z, it provides a reasonable description of simple fluids (for the celebrated choice $z = 1.8$) as well as colloidal suspensions, where typically $z \gg 1$. A major advantage of this particular form of the interaction follows from the availability of an exact analytical solution of the OZ integral equation with the ansatz (3) and (4) [11], which provides the explicit expression of the radial distribution function $g_t(r)$. By use of this solution, the right-hand side of the HRT Eq. (2) can be written in terms of λ_t or, by use of Eq. (5), in terms of the free energy density A_t, leading to a closed nonlinear partial differential equation.

It is apparent the similarity between the self-consistent Ornstein-Zernike approximation (SCOZA) [12] and this novel formulation of the HRT approach: both theories satisfy Eqs. (3)–(5), and in both cases use is made of the analytic solution of the OZ equation for a Yukawa potential. Moreover, the consistency condition at the basis of SCOZA may be written in the form (2) for a specific choice of the turning-on procedure of the attractive interaction: in SCOZA the t parameter (often identified with the inverse temperature) only affects the amplitude of $w(r)$ without changing its range. This seemingly minor difference has profound implications on the behavior of the theory in the critical region and close to the phase boundary.

The cutoff function $\psi(t)$ in Eq. (1) has been chosen in order to guarantee the numerical stability of the HRT differential equation: $\psi(t) = (1 + zt/2)^{-2}$ for $t < t^*$ and $\psi(t) = (\cosh t)^{-2}$ for $t > t^*$, where t^* is defined by imposing the continuity of $\psi(t)$ [13]. Full details will be given in a forthcoming publication.

Close to the critical point and in the $t \to \infty$ limit, the HRT Eq. (2) simplifies and, when the thermodynamical variables are properly rescaled, acquires a RG structure. The precise form of the rescaled equation actually depends on the specific form of the attractive part of the interaction $\phi(r)$ (6), which in HRT plays the role of the smooth cutoff of the RG approach. A fixed point analysis, similar to that performed for a Φ^4 theory [9], shows that the HRT equa-

TABLE I. HRT estimates of the critical exponents and compressibility amplitude ratio in three dimensions for $z = 1.8$ compared to the exact values [14].

Exponent	α	β	γ	δ	η	$U_2 = C_+/C_-$
"Exact"	0.110	0.327	1.237	4.789	0.036	4.76
HRT	0.01	0.332	1.328	5	0	4.16

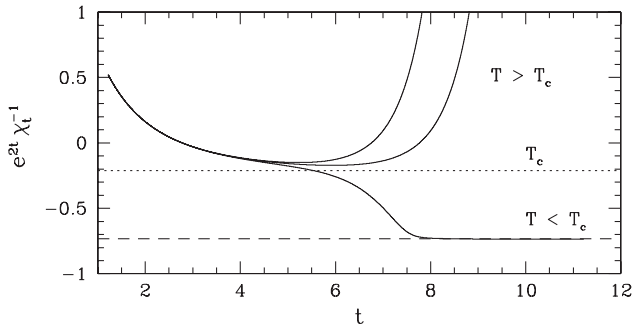

FIG. 1. Rescaled inverse compressibility for $z = 1.8$ during the t evolution at the critical density and reduced temperatures $(T - T_c)/T_c = 1.1 \times 10^{-5}$, 2.6×10^{-6}, -1.4×10^{-5} from top to bottom. The dotted line is the fixed point critical value and the dashed line is the "zero temperature" fixed point obtained by a RG analysis of the HRT equation.

tion satisfies scaling and hyperscaling with the nonclassical critical exponents shown in Table I. The numerical solution of the full HRT Eq. (2) allows one to justify the fixed point analysis on microscopic grounds: very close to the critical point, the quantity

$$\chi_t^{-1} = -\rho\left[\frac{\partial^2 A_t}{\partial \rho^2} + \psi(t)\int d\mathbf{r}\phi(r)\right], \tag{7}$$

when multiplied by the rescaling factor e^{2t}, falls into the basin of attraction of the fixed point, as shown in Fig. 1. However, at very long wavelength (i.e., for $t \to \infty$), the small deviations from the critical point drive the system either to the "infinite temperature" or to the "zero temperature" fixed point. The physical meaning of χ_t^{-1} is apparent from its definition: it is proportional to the inverse compressibility (5) supplemented by the mean-field contribution associated with the residual part of the potential $w(r) - w_t(r)$. In order to understand how the singularity associated with the first-order liquid-vapor transition develops within HRT, it is instructive to follow the "evolution" of the inverse compressibility χ_t^{-1} for a fixed

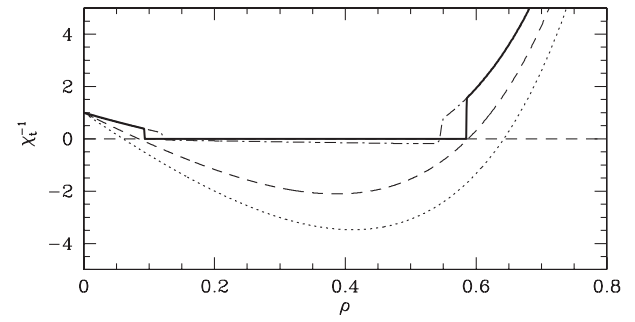

FIG. 2. Snapshots of the inverse compressibility along the density axis for $z = 1.8$ and $T = 1.1$ at three different values of the parameter t: $t = 0$ (dotted line), $t = 0.2$ (dashed line), $t = 2.6$ (dot-dashed line), and $t \to \infty$ (solid line).

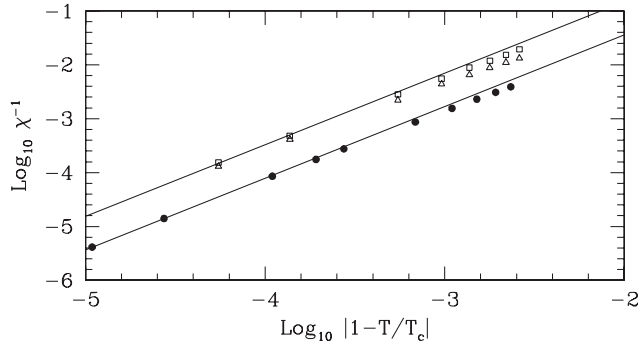

FIG. 3. Log-log plot of the inverse compressibility as a function of the reduced temperature above (circles) and below the critical temperature along the low-density (triangles) and the high-density (squares) branch of the binodal for $z = 1.8$. Solid lines show the expected power law behavior defined by the exponent of Table I ($\gamma = 1.328$).

temperature below the critical point and different values of t (see Fig. 2). Long-wavelength fluctuations force the inverse compressibility to vanish identically in the $t \to \infty$ limit inside the binodal, as customary in the HRT approach [3]. The novel feature displayed by the smooth cutoff formulation, and clearly visible in Fig. 2, is the jump of χ_∞^{-1} across the phase boundary. A closer inspection of the t evolution of χ^{-1} at coexistence reveals that the approach toward zero proceeds differently deep inside the binodal, where χ^{-1} remains negative throughout the evolution, and close to the phase boundary, where long-wavelength fluctuations first drive the system towards stability ($\chi^{-1} > 0$) and then push the inverse compressibility to zero. It is

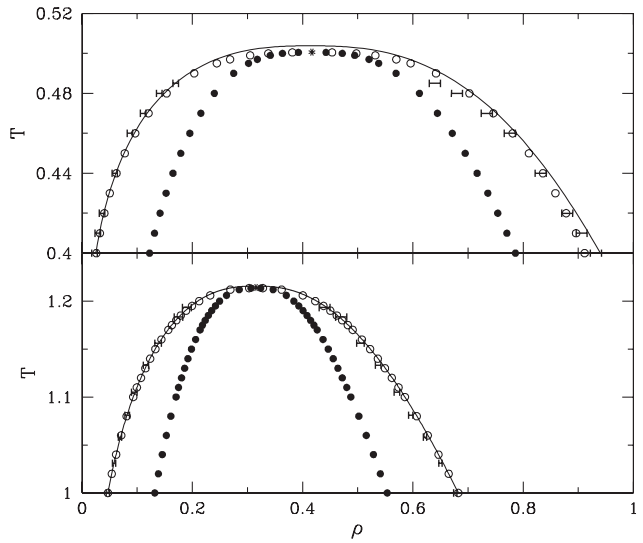

FIG. 4. Coexistence curve as obtained by HRT (open circles), SCOZA (solid line) and Monte Carlo data (bars) for $z = 5$ (upper panel) [17] and $z = 1.8$ (lower panel) [12]. The HRT spinodals are also shown (full circles).

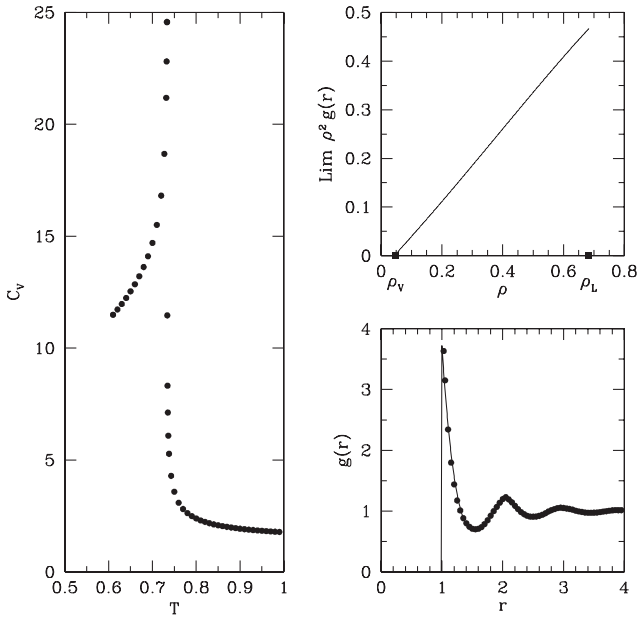

FIG. 5. Left panel: HRT specific heat along the critical isochore $\rho = 0.3605$ for $z = 3$. Lower-right panel: radial distribution function for $z = 1.8$, $T = 1$, $\rho = 0.8$. Line: HRT result; points: Monte Carlo simulations [12]. Upper-right panel: $r \to \infty$ limit of $\rho^2 g(r)$ inside the coexistence curve for $z = 1.8$ and $T = 1$.

tempting to identify the boundary between these two regimes as the boundary of metastability, i.e., the spinodal curve. A power law fit of the compressibility in the critical region $\chi \sim C|T - T_c|^{-\gamma}$, shown in Fig. 3, is fully consistent with the critical exponent γ reported in Table I both above and below the critical temperature. The amplitude ratio C_+/C_-, also shown in Table I, agrees well with the field theoretical expectation. The phase diagram of a Yukawa fluid with $z = 1.8$ and $z = 5$ is compared with Monte Carlo simulations and SCOZA results in Fig. 4. The constant volume specific heat can be obtained by differentiation of the free energy density at convergence $A_\infty(\rho, T)$. In Fig. 5 we plot the specific heat per particle C_v along the critical isochore: the data below the critical temperature are obtained by use of the free energy inside the coexistence curve, which is directly accessible in HRT. A typical radial distribution function of a $z = 1.8$ Yukawa liquid as obtained by HRT is shown in Fig. 5. The core condition is exactly fulfilled due to Eq. (3) and the use of the analytical solution of the OZ equation. However, the linear dependence of $c(r)$ on the attractive interaction $w(r)$ implied by the MSA-like closure (4) limits the accuracy of HRT for the description of the local structure of the fluid, particularly at low density. Nevertheless, the accurate treatment of the physics underlying the first-order transition has important consequences on the form of $g(r)$ inside the binodal. In the two-phase region, density correlations are linear combinations of those of the two stable phases (liquid L and vapor V). This implies the exact relation $\lim_{r\to\infty}\rho^2 g(r) = \rho(\rho_V + \rho_L) - \rho_V\rho_L$, which is satisfied by the numerical solution of the smooth cutoff HRT equation, as displayed in Fig. 5.

In summary, we have shown how a smooth cutoff formulation of HRT provides a consistent picture of the equilibrium thermodynamics of a fluid, including the complex, singular behavior at first- and second-order phase transitions, a distinction between unstable and metastable states, and quantitative predictions for the coexistence curve, equation of state, and specific heat. The present formulation of the theory is specific to a single Yukawa interaction, but the available analytical solution of the OZ equation for a sum of an arbitrary number of Yukawa potentials foreshadows possible generalizations. A better representation of correlations may also be achieved within the HRT framework, either by adopting parametrizations more elaborate than Eqs. (3) and (4) or by closing the hierarchy at the level of the second equation, which embodies the effects of density fluctuations on the structure of the fluid [6]. Applications to binary mixtures [15] and nonuniform fluids [16] are also possible.

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