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Phase diagram and critical behavior of the ferromagnetic Heisenberg fluid from density-functional theory

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We have investigated the phase behavior of the ferromagnetic Heisenberg fluid using two versions of density-functional theory, viz., the mean-field and modified mean-field approximations. In the latter, configurations in the average of the perturbative part of the energy are weighted by the zero-density approximation of the pair distribution function. This is known to yield an improved description of the phase diagram of dipolar fluids. Both theories predict, in addition to isotropic liquid and vapor phases, a ferromagnetically ordered liquid phase at moderate to high (fluid) densities. The topology of the phase diagram depends sensitively on the relative strengths of the isotropic and anisotropic parts of the intermolecular potential. For weakly anisotropic potentials, the order-disorder transition is always continuous and terminates at a critical endpoint on (the liquid side of) the liquid-vapor coexistence curve. Increasing the anisotropy above a certain threshold drives the transition first order at low temperatures, thus leading to the appearance of a tricritical point and a ferromagnetic liquid-isotropic liquid-vapor triple point. For strongly anisotropic potentials, ordinary liquid-vapor phase separation is preempted by a direct (condensation-ordering) transition between a low-density disordered phase and a ferromagnetic liquid that becomes continuous at a tricritical point. Results are in agreement with earlier theoretical work and, moreover, are compatible with recent Monte Carlo simulations of the same system. These provide evidence of a magnetic critical point (with the Curie line ending at a critical endpoint on the vapor side of the liquid-vapor coexistence curve). Owing to finite size effects, however, the existence of a tricritical point cannot be ruled out. The latter is predicted, for the same model, by both theories. In this context, we looked for coexistence between orientationally ordered fluid phases in generalized Heisenberg models and found it, within mean-field theory, for a class of fluids characterized by *soft repulsive* isotropic interactions, in addition to the hard-core and ferromagnetic Heisenberg potentials.

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I. INTRODUCTION

Recent computer simulations by Patey and co-workers [1,2] and Weis and co-workers [3,4] have revealed that systems of strongly interacting dipolar soft or hard spheres can exhibit a ferroelectric nematic phase at high densities. Results seem, however, to depend very sensitively on the boundary conditions used in the simulations, which aim to reproduce, as faithfully as possible, the effects of long-range interactions in what is of necessity a finite model system [5]. Moreover, there remains some uncertainty as to the precise location of the ferroelectric phase transition.

Although several theories have been proposed for the true dipolar fluid with long-range interactions [6–12], considerable conceptual difficulties remain. Indeed, there is not even consensus among specialists on whether the thermodynamic limit of a positionally disordered, but orientationally ordered phase, exists (but see [13]). On a more practical level, the theoretical treatment of as strongly anisotropic an interaction as the dipole-dipole potential, beyond the simplest perturbative approaches, constitutes a formidable challenge.

By contrast, the simpler Heisenberg fluid [14–19] is much more easily studied by either theory or simulation, while retaining a considerably rich behavior. Since the intermolecular potential is now short ranged, no complications arise in connection with the thermodynamic limit. Furthermore, it includes no coupling between positional and orientational degrees of freedom of the molecules, thereby eliminating the possibility of chain formation as obtained in zero-density dipolar fluids [20,21]. For the Heisenberg model, Landau and density-functional theories can thus be constructed in the usual way.

Recently, Lomba and co-workers have performed Monte Carlo (MC) simulations of both the ferromagnetic and the antiferromagnetic Heisenberg fluid [22,23]. The former was found to exhibit a ferromagnetic order-

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disorder as well as a gas-liquid transition. The latter transition seems to occur between a ferromagnetic liquid and a ferromagnetic gas close to the gas-liquid critical point, whereas it occurs between a ferromagnetic liquid and a paramagnetic gas farther away from the critical point. If real, this effect would in a sense be similar to the novel solid-solid critical point seen in simulations of simple atomic fluids interacting via very short-ranged attractive potentials [24,25]. There is also evidence from simulation for an order-disorder transition in the antiferromagnetic fluid, for which, however, no gas-liquid coexistence is found. The ordering transition is now between an isotropic and a nematically ordered phase.

The same authors have also treated these systems by means of integral equation (mean spherical approximation and reference hypernetted chain) methods. Both equations capture the essentials of the order-disorder transitions, but fail to elucidate the nature of gas-liquid coexistence in either system. In this paper we calculate the phase diagram of the ferromagnetic Heisenberg fluid using the mean-field (MF) and modified mean-field (MMF) approximations of density-functional theory (DFT). The latter consists in weighting configurations in the perturbative part of the energy by the zero-density approximation of the radial distribution function [26]. This is known to describe angular correlations which are missed in simple MF treatments [11,12,26–28]. Recently, Groh and Dietrich [11,12] have investigated the phase behavior of the Stockmayer fluid using MMF theory. Besides predicting liquid-vapor coexistence, they found evidence for a high density ferroelectric phase. Note, however, that owing to the long-ranged nature of the interactions, their results appear to have the correct thermodynamic limit only for infinitely long needle-shaped systems [12,13]. By contrast, the thermodynamic limit is well established for the (short-ranged) Heisenberg fluid, for which detailed computer simulation results are also available, allowing a quantitative test of MMF-DFT for ordered fluid phases.

This paper is organized as follows. In Sec. II we formulate the MF and MMF theories of the Heisenberg fluid. The different types of phase diagram they yield are presented in Sec. III, where we also show that our results are compatible with recent simulation data. Two sets of MC simulations have been performed: a first set [22] employed the full interaction potential to study the global phase diagram; in a second set [29], the potential was truncated at 2.5σ and the magnetic transition line was accurately located, taking into account finite size effects. In Sec. IV we address the issue of criticality in the Heisenberg fluid, and derive explicit expressions for the location of the critical and tricritical points which occur in these systems. In this context we also derive the condition for the existence of a fourth-order critical point (where the sixth derivative of the free energy with respect to the magnetization, at fixed temperature and chemical potential, vanishes), which is a necessary condition for a crossover between tricritical behavior and magnetic criticality (i.e., criticality between ordered magnetic phases). Within the MF theories studied in this paper, this condition *can* be fulfilled by a variant of the Heisenberg model which includes long-ranged isotropic repulsions. These results also suggest that the existence of magnetic critical points may be expected in simple magnetic fluids. Finally, in Sec. V we summarize our results.

II. DENSITY-FUNCTIONAL THEORIES OF THE FERROMAGNETIC HEISENBERG FLUID

A. General density-functional formalism

The grand potential free energy Ω of a nonuniform, one-component fluid is the minimum of the functional

$$\Omega[\rho(\mathbf{r},\omega)] = \mathcal{F}[\rho(\mathbf{r},\omega)] + \int d\mathbf{r}d\omega\,\rho(\mathbf{r},\omega)V_{\text{ext}}(\mathbf{r},\omega) -\mu\int d\mathbf{r}d\omega\,\rho(\mathbf{r},\omega), \tag{1}$$

where $\rho(\mathbf{r},\omega)$ is the density-orientational profile in the presence of the external potential $V_{\text{ext}}(\mathbf{r},\omega)$ and μ is the chemical potential. $\mathbf{r} = (x,y,z)$ is the set of position coordinates and $\omega = (\phi,\theta,\chi)$ the set of orientation coordinates (Euler angles) of a molecule. $\mathcal{F}[\rho(\mathbf{r},\omega)]$ is a unique functional of the density which is independent of the external potentials and represents the intrinsic Helmholtz free energy of the inhomogeneous fluid. If the fluid is characterized by a pairwise intermolecular potential, $\phi(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)$, it can be shown [30] that

$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r},\omega)] = \mathcal{F}_{\text{ref}}[\rho(\mathbf{r},\omega)] + \frac{1}{2}\int_0^1 d\alpha \int d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2 \\ \times g(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2;\alpha) \\ \times\rho(\mathbf{r}_1,\omega_1)\phi_p(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2)\rho(\mathbf{r}_2,\omega_2),\end{aligned} \tag{2}$$

where we have defined a "perturbative" interaction

$$\phi_p(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2) = \phi(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2) - \phi_{\text{ref}}(\mathbf{r}_1,\mathbf{r}_2). \tag{3}$$

In Eq. (2), $\mathcal{F}_{\text{ref}}[\rho(\mathbf{r},\omega)]$ corresponds to a reference system in which the particles interact via a pairwise potential $\phi_{\text{ref}}(\mathbf{r}_1,\mathbf{r}_2)$ and the density is constrained to be $\rho(\mathbf{r},\omega)$. This is treated in a local-density approximation, viz.,

$$\mathcal{F}_{\text{ref}}[\rho(\mathbf{r},\omega)] = \int d\mathbf{r}d\omega\, f_{\text{ref}}(\rho(\mathbf{r},\omega)). \tag{4}$$

$g(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2;\alpha)$ is the pairwise distribution function for a fluid with density $\rho(\mathbf{r},\omega)$ and in which the intermolecular potential is

$$\begin{aligned}\phi_\alpha(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2) = \phi_{\text{ref}}(\mathbf{r}_1,\mathbf{r}_2) + \alpha[\phi(\mathbf{r}_1,\omega_1,\mathbf{r}_2,\omega_2) \\ -\phi_{\text{ref}}(\mathbf{r}_1,\mathbf{r}_2)].\end{aligned} \tag{5}$$

This is the familiar coupling-constant algorithm, where α parametrizes a linear integration path between the reference system and the real system.

Equation (2) is an *exact* result. Besides the local-density approximation, Eq. (4), further approximations will now be made to the pair distribution function, which is in general not known. Note that, since we shall be dealing with uniform systems, g depends on the position coordinates only through $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$.

In what follows we shall consider the simple Heisenberg fluid characterized by the potential

$$\phi_{\text{ref}}(r) = \begin{cases} +\infty, & r \le \sigma \\ 0, & r > \sigma, \end{cases} \tag{6}$$

$$\phi_p(r, \omega, \omega') = \begin{cases} 0, & r \le \sigma \\ -I(r) - J(r)\cos(\omega, \omega'), & \sigma < r \le r_c \\ 0, & r > r_c, \end{cases} \tag{7}$$

where σ is the hard sphere diameter, r_c is a cutoff (introduced for the purpose of comparing our results with simulations), $I(r)$ and $J(r)$ are the isotropic and anisotropic parts of the potential, respectively, and $\cos(\omega, \omega') = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi')$. Within MF theory only the integrated strengths of the interactions [i.e., the volume integrals of $I(r)$ and $J(r)$] contribute to the thermodynamics; consequently their detailed analytical form is immaterial, provided that they decay faster than $1/r^3$ as $r \to \infty$ [see Eqs. (13) and (14)]. $J > 0\,(< 0)$ corresponds to a ferromagnetic (antiferromagnetic) system. In this paper we shall be concerned with the ferromagnetic case only; in addition, all the results presented are for $r_c = \infty$ unless otherwise stated.

The free energy density of the reference system is now approximated by

$$f_{\text{ref}}(\rho(\mathbf{r}, \omega)) = f_{\text{hs}}(\rho(\mathbf{r})) + \rho(\mathbf{r}) k_B T \langle \ln[4\pi \hat{f}(\mathbf{r}, \omega)] \rangle, \tag{8}$$

where $\hat{f}(\mathbf{r}, \omega)$ is the orientational distribution function (ODF) defined through $\rho(\mathbf{r}, \omega) = \rho(\mathbf{r})\hat{f}(\mathbf{r}, \omega)$, $\langle A \rangle = \int A \hat{f}(\mathbf{r}, \omega)\, d\omega$ and $f_{\text{hs}}(\rho(\mathbf{r}))$ is the free energy density of a hard-sphere system given by the "quasiexact" Carnahan-Starling expression [31]

$$f_{\text{hs}}(T, \rho) = \frac{\rho}{\beta}\left[\ln(\rho\Lambda^3) - 1 + \frac{4\xi - 3\xi^2}{(1-\xi)^2}\right], \tag{9}$$

where Λ is the thermal de Broglie wavelength and $\xi = \frac{\pi}{6}\rho\sigma^3$ the packing fraction.

B. The mean-field approximation

The simplest MF approximation amounts to taking g to be given by its long-distance limit, i.e., $g(r_{12}, \omega_1, \omega_2) = 1$. We then obtain, for the Helmholtz free energy $\mathcal{F}[\rho(\mathbf{r}, \omega)]$,

$$\mathcal{F}_{\text{MF}}[\rho(\mathbf{r}, \omega)] = \mathcal{F}_{\text{ref}}[\rho(\mathbf{r}, \omega)] + \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2 \times \rho(\mathbf{r}_1, \omega_1)\phi_p(\mathbf{r}_{12}, \omega_1, \omega_2)\rho(\mathbf{r}_2, \omega_2). \tag{10}$$

Substitution of Eqs. (6), (7), and (8) into Eq. (10) then yields, for the free energy density of an orientationally ordered, but positionally disordered, phase,

$$f_{\text{MF}}(\rho, [\hat{f}_{\text{MF}}(\omega)]) = f_{\text{hs}}(\rho) + \rho k_B T \langle \ln[4\pi \hat{f}_{\text{MF}}(\omega)] \rangle - \frac{1}{2} I_{\text{int}}\rho^2 - \frac{1}{2} J_{\text{int}}\rho^2\eta_1^2, \tag{11}$$

where η_1 is the (MF) *polar order parameter*, defined as

$$\eta_1 = \int P_1(\cos\theta)\hat{f}_{\text{MF}}(\theta)\, d\omega, \tag{12}$$

$P_1(\cos\theta)$ being the first Legendre polynomial, and

$$I_{\text{int}} = \int_\sigma^{r_c} I(r)\, d\mathbf{r}, \tag{13}$$

$$J_{\text{int}} = \int_\sigma^{r_c} J(r)\, d\mathbf{r}. \tag{14}$$

Minimizing the free energy with respect to $\hat{f}_{\text{MF}}(\omega)$ [33], we obtain

$$\hat{f}_{\text{MF}}(\omega) = \frac{\exp(\beta J_{\text{int}}\rho\eta_1\cos\theta)}{\int \exp(\beta J_{\text{int}}\rho\eta_1\cos\theta)\, d\omega}, \tag{15}$$

$$\eta_1 = \coth(\beta J_{\text{int}}\rho\eta_1) - \frac{1}{\beta J_{\text{int}}\rho\eta_1}, \tag{16}$$

from which it follows, for the equilibrium pressure and chemical potential,

$$p(\rho) = p_{\text{hs}}(\rho) - \frac{1}{2}\rho^2\left(I_{\text{int}} + J_{\text{int}}\eta_1^2\right), \tag{17}$$

$$\mu(\rho) = \mu_{\text{hs}}(\rho) - I_{\text{int}}\rho + \beta^{-1}\ln\left[\frac{\beta J_{\text{int}}\rho\eta_1}{\sinh(\beta J_{\text{int}}\rho\eta_1)}\right], \tag{18}$$

where $\beta = 1/k_B T$, η_1 is the solution of Eq. (16), and $p_{\text{hs}}(\rho)$ and $\mu_{\text{hs}}(\rho)$ are, respectively, the pressure and the chemical potential of the hard-sphere system. We note that the MF Helmholtz free energy density may also be written in terms of ρ and η_1 [using $f = -p + \mu\rho$ and Eqs. (17) and (18)]. When this expression is used, Eq. (16) for the equilibrium polar order parameter is obtained by minimizing f_{MF} with respect to η_1, at constant density (and temperature). We will return to this point in Sec. IV, where the equations for the critical and multicritical points of the Heisenberg fluid are derived, within this approximation.

C. The modified mean-field approximation

The simplest way to include correlations due to the perturbative part of the potential is to use for $g(\mathbf{r}_{12}, \omega_1, \omega_2; \alpha)$ the zero-density approximation,

$$g(\mathbf{r}_{12}, \omega_1, \omega_2; \alpha) = e^{-\beta\phi_\alpha(\mathbf{r}_{12}, \omega_1, \omega_2)}, \tag{19}$$

which gives

$$\mathcal{F}_{\text{MMF}}[\rho(\mathbf{r}, \omega)] = \mathcal{F}_{\text{ref}}[\rho(\mathbf{r}, \omega)] + \frac{1}{2\beta}\int d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2\, e^{-\beta\phi_{\text{ref}}(\mathbf{r}_{12})}\left[1 - e^{-\beta\phi_p(\mathbf{r}_{12}, \omega_1, \omega_2)}\right]\rho(\mathbf{r}_1, \omega_1)\,\rho(\mathbf{r}_2, \omega_2). \tag{20}$$

Putting the various approximations for the reference free energy together and neglecting the external field, the (variational) grand potential density can be written

$$\frac{1}{V}\Omega_{\rm MMF}\left(\rho,[\hat{f}_{\rm MMF}(\omega)]\right) = \frac{\mathcal{F}\left(\rho,[\hat{f}_{\rm MMF}(\omega)]\right) - \mu\int d\mathbf{r}\rho(\mathbf{r})}{V}$$

$$= f_{\rm hs}(\rho) + \rho k_B T\langle \ln[4\pi \hat{f}_{\rm MMF}(\omega)]\rangle - \mu\rho + \frac{1}{V}\Omega_{\rm int}, \qquad (21)$$

where the interaction contribution (for a system with no isotropic attractive interactions) is given by

$$\frac{1}{V}\Omega_{\rm int} = -\frac{\rho^2}{2\beta}\int_\sigma^{+\infty} d\mathbf{r}d\omega_1 d\omega_2 \left[e^{\beta J(r)\cos(\omega_1,\omega_2)} - 1\right] \times \hat{f}_{\rm MMF}(\omega_1)\hat{f}_{\rm MMF}(\omega_2). \qquad (22)$$

To proceed further it is convenient to expand $\hat{f}_{\rm MMF}(\omega)$ in terms of Legendre polynomials:

$$2\pi \hat{f}_{\rm MMF}(\omega) = \varphi(\cos\theta) = \sum_{l=0}^{\infty} \varphi_l\, P_l(\cos\theta), \qquad (23)$$

$$\varphi_l = \frac{2l+1}{2}\int \hat{f}_{\rm MMF}(\theta) P_l(\cos\theta)\, d\omega = \frac{2l+1}{2}\eta_l, \qquad (24)$$

where η_l are *generalized order parameters*, and similarly for the exponential term in Eq. (22):

$$e^{t\cos(\omega_1,\omega_2)} = \sum_{n=0}^{\infty}(2n+1)\sqrt{\frac{\pi}{2t}}\; I_{n+1/2}(t)\; P_n\left(\cos\theta_{12}\right). \qquad (25)$$

Here $I_{n+1/2}$ is a modified spherical Bessel function of the first kind [32].

The interaction contribution in Eq. (21) can now be expressed as

$$\frac{1}{V}\Omega_{\rm int} = \rho^2 \sum_{l=0}^{\infty} u_l\, \varphi_l^2, \qquad (26)$$

where the coefficients u_l are given by

$$u_l = -\frac{2}{\beta}\int d\mathbf{r}\left[\frac{i_l(t)}{2l+1} - \delta_{l,0}\right], \qquad (27)$$

with use of the abbreviations

$$i_l(t) = \sqrt{\frac{\pi}{2t}}\; I_{l+1/2}(t), \qquad (28)$$

$$t = \beta\, J(r). \qquad (29)$$

Finally, as remarked in [11,12], an alternative expression for Eq. (26), useful to derive the equilibrium density distribution, is

$$\frac{1}{V}\Omega_{\rm int} = \frac{\rho^2}{2}\int_{-1}^{+1} dx \int_{-1}^{+1} dx' \varphi(x)\,\varphi(x')\,\kappa(x,x'), \qquad (30)$$

where

$$\kappa(x,x') = \sum_{l=0}^{\infty}\frac{(2l+1)^2}{2}\, u_l\, P_l(x)\, P_l(x'). \qquad (31)$$

For fixed temperature T and chemical potential μ the equilibrium one-particle density satisfies the condition

$$\frac{1}{V}\,\frac{\delta\Omega}{\delta\rho(\mathbf{r},\omega)} = 0, \qquad (32)$$

which is equivalent to simultaneous minimization of Ω with respect to ρ and $\varphi(\omega)$ [33]:

$$\frac{1}{V}\,\frac{\partial\Omega}{\partial\rho} = 0, \qquad (33)$$

$$\frac{1}{V}\,\frac{\delta\Omega}{\delta\varphi(\omega)} = \lambda, \qquad (34)$$

where λ is a Lagrange multiplier which ensures normalization of the ODF. Equations (33) and (34) lead to

$$\mu_{\rm hs}(\rho) + \frac{1}{\beta}\int_{-1}^{+1} dx\, \varphi(x)\ln[2\varphi(x)] + 2\rho\sum_{l=0}^{\infty} u_l\varphi_l^2 - \mu = 0, \qquad (35)$$

and

$$\varphi(x) = C\,\exp\left[-\beta\rho\sum_{l=0}^{\infty}(2l+1)\,u_l\,\varphi_l\; P_l(x)\right], \qquad (36)$$

where

$$C = \frac{1}{\int_{-1}^{+1} dx\, \exp\left[-\beta\rho\sum_{l=0}^{\infty}(2l+1)u_l\varphi_l P_l(x)\right]} \qquad (37)$$

is the normalization constant.

From Eq. (36) it follows that

$$\int_{-1}^{+1} dx\, \varphi(x)\ln[2\varphi(x)] = \ln(2C) - 2\beta\rho\sum_{l=0}^{\infty} u_l\,\varphi_l^2, \qquad (38)$$

so that Eq. (35) can be rewritten as

$$\mu_{\rm hs}(\rho) + \frac{1}{\beta}\ln(2C) - \mu = 0. \qquad (39)$$

Finally the projections φ_l satisfy the integral equations [27]

$$\varphi_l = \frac{2l+1}{2} \frac{\int_{-1}^{+1} dx\, P_l(x)\, \exp\left[-\rho\beta \sum_{l=1}^{\infty}(2l+1)\, u_l\, \varphi_l\, P_l(x)\right]}{\int_{-1}^{+1} dx\, \exp\left[-\rho\beta \sum_{l=1}^{\infty}(2l+1)\, u_l\, \varphi_l\, P_l(x)\right]} \quad (l \neq 0), \tag{40}$$

$$\varphi_0 = 1/2. \tag{41}$$

We have examined the possibility of coexistence between an isotropic gas at density ρ_i and a magnetic liquid at density ρ_f. The coexistence conditions are obtained by requiring the equality of the pressures and chemical potentials of the two phases at fixed temperature, namely [11,12]

$$\frac{\Omega}{V}\left[T, \mu_f, \rho_i, \varphi = 1/2\right] = \frac{\Omega}{V}\left[T, \mu_f, \rho_f, \varphi(x)\right], \tag{42}$$

$$\left.\frac{\partial\Omega}{\partial\rho}\right|_{\rho=\rho_i, \varphi=1/2} = 0, \tag{43}$$

$$\left.\frac{\partial\Omega}{\partial\rho}\right|_{\rho=\rho_f, \varphi(x)} = 0, \tag{44}$$

$$\left.\frac{\delta\Omega}{\delta\varphi}\right|_{\rho=\rho_f, \varphi(x)} = \lambda. \tag{45}$$

Making explicit these relations and eliminating μ_f, the common chemical potential of the coexisting phases, it follows that the unknowns ρ_i, ρ_f, and φ_l $(l \geq 1)$ are solutions of the equations [11,12]

$$f_{\text{hs}}(\rho_i) - \rho_i \mu_{\text{hs}}(\rho_i) - \frac{1}{4}\rho_i^2 u_0 = f_{\text{hs}}(\rho_f) - \rho_f \mu_{\text{hs}}(\rho_f) - \rho_f^2 \sum_{l=0}^{\infty} u_l \varphi_l^2, \tag{46}$$

$$\mu_{\text{hs}}(\rho_i) + \frac{1}{2}\rho_i u_0 = \mu_{\text{hs}}(\rho_f) + \frac{1}{2}\rho_f u_0 + \frac{1}{\beta}\left[\ln 2 - \ln \int_{-1}^{+1} dx\, \psi_f(x)\right], \tag{47}$$

and

$$\varphi_l = \frac{2l+1}{2} \int_{-1}^{+1} dx\, P_l(x) \psi_f(x) \bigg/ \int_{-1}^{+1} dx\, \psi_f(x). \tag{48}$$

In Eqs. (47) and (48) we have introduced the notation

$$\psi_f(x) = \exp\left[-\beta\rho_f \sum_{l=1}^{\infty}(2l+1) u_l \varphi_l P_l(x)\right]. \tag{49}$$

(Note that the sum starts at $l = 1$.)

III. RESULTS AND DISCUSSION

Figures 1–3 illustrate the different types of phase diagrams obtained from MF theory for different values of $R = J_{\text{int}}/I_{\text{int}}$, which are identical with those originally calculated by Hemmer and Imbro [15]. Three types of transitions have been identified in these phase diagrams: a continuous order-disorder transition between ferromagnetic and isotropic dense fluid phases, and two first-order condensation transitions. The discontinuous transitions are characterized by a finite density jump and involve either two disordered fluids ("ordinary" isotropic condensation) or an isotropic gas and a magnetic liquid (condensation-ordering transition, where both the density and the magnetization change). At sufficiently low temperatures, a condensation-ordering transition occurs. (In reality, if R is small enough, corresponding to very weakly anisotropic potentials, this transition will be preempted by the solid phase [15]. In this work, however, we have only considered fluid phases, which we believe to be stable with respect to the solid for densities $\rho^* \leq 0.8$. This includes the various types of fluid phase diagrams presented here and in the following sections, for which

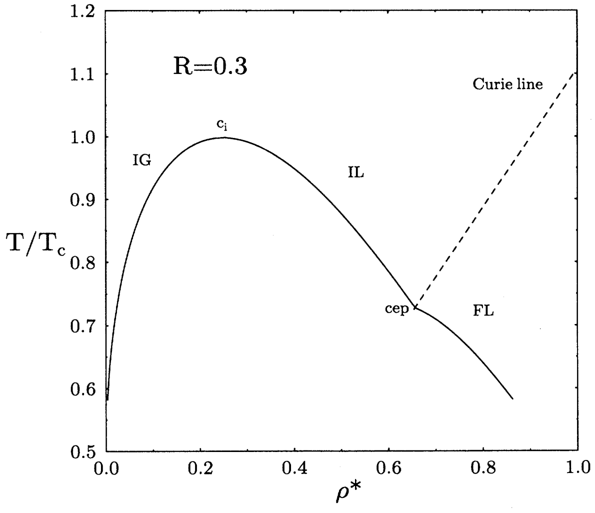

FIG. 1. MF phase diagram of the ferromagnetic Heisenberg fluid for $R = 0.3$. $\rho^* = \rho\sigma^3$, and T/T_c are the reduced density and temperature, respectively, where T_c is the temperature of the (isotropic) liquid-vapor critical point. FL, ferromagnetic liquid; IL, isotropic liquid; IG, isotropic gas; solid lines, first-order transitions; dashed line, continuous ordering transition (Curie line); c_i, (isotropic) critical point; cep, critical endpoint.

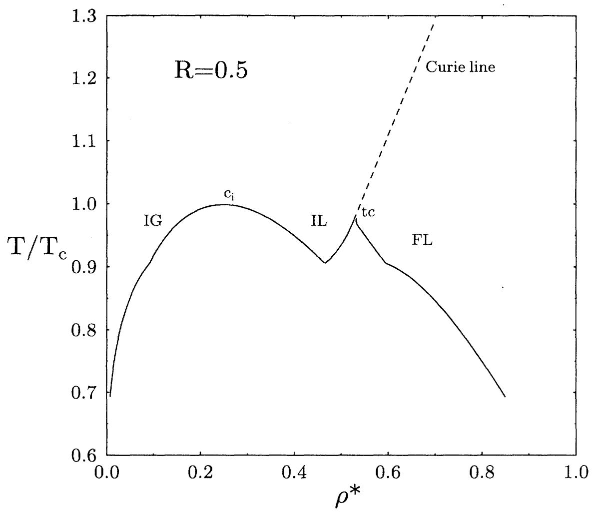

FIG. 2. MF phase diagram of the ferromagnetic Heisenberg fluid for $R = 0.5$ (same reduced units as in Fig. 1). FL, ferromagnetic liquid; IL, isotropic liquid; IG, isotropic gas; solid lines, first-order transitions; dashed line, continuous ordering transition (Curie line); c_i, (isotropic) critical point; t_c, tricritical point.

$R \geq 0.3$. The stability of these magnetic fluids is consistent with computer simulation results and with the phase diagrams of Ref. [15], which include solid-fluid coexistence. Similarly, the continuous order-disorder transition (where the magnetization density becomes finite) occurs, at sufficiently high temperatures and densities, for any value of R. The temperature at which the line of continuous order-disorder transitions meets the condensation-ordering phase boundary depends sensitively on R. Furthermore, the nature and stability of this point depends on the relative strength of the anisotropic interactions (see Ref. [15]).

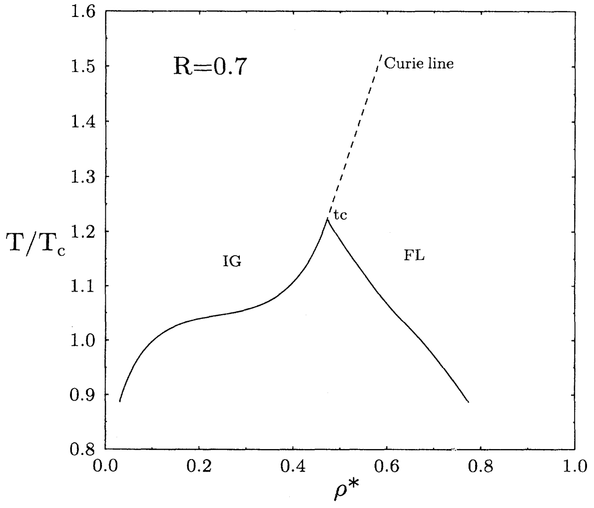

FIG. 3. MF phase diagram of the ferromagnetic Heisenberg fluid for $R = 0.7$. Symbols and units as in Fig. 2.

For weakly anisotropic fluids ($R < 0.38$) the continuous order-disorder transition (which is known as the Curie line) ends at a critical endpoint, cep, on the condensation phase boundary. (The critical endpoint is thus obtained by the simultaneous solution of the equations for liquid-vapor coexistence and the Curie line.) The corresponding temperature, T_{cep}, separates a regime of isotropic liquid-vapor condensation ($T > T_{\text{cep}}$) from a regime of condensation-ordering transitions ($T < T_{\text{cep}}$). At temperatures below T_{cep} (i.e., inside the condensation phase boundary), the Curie line is globally unstable (see Sec. IV). This type of diagram is illustrated in Fig. 1 (type I diagram) [34]. For stronger magnetic anisotropies, $0.38 < R < 0.63$, the critical endpoint becomes locally unstable (see Sec. IV) and a tricritical point occurs at a temperature T_{tc}, where the Curie line terminates. For a system with $R = 0.38$ this point is located exactly on the condensation phase boundary. The tricritical temperature increases with the anisotropy R, and this point separates two regimes of magnetic transitions. Above T_{tc} the magnetic transition is continuous (Curie line), while below T_{tc} it becomes first order. In this case, the transition is characterized by a finite jump in the magnetization accompanied by a similar jump in the density, as illustrated in Fig. 2 (type II diagram). This is what we call a condensation-ordering transition (see also Sec. IV). In a pressure-temperature diagram the two condensation lines, which correspond to isotropic-condensation and condensation-ordering transitions, meet at a triple point at a temperature T_{tr}, where a dilute isotropic gas, an isotropic liquid, and a denser magnetic liquid coexist (the densities of these phases are shown in the temperature-density diagram of Fig. 2, for a system with $R = 0.5$). (The triple point is obtained by simultaneously solving the four equations for the constancy of the pressure and chemical potential of the three coexisting phases).

As R increases, the triple-point temperature also increases. For a system with anisotropy ratio $R = 0.63$ the triple-point temperature is equal to the isotropic liquid-vapor critical point. For systems with $R \geq 0.63$, the isotropic critical point occurs at a temperature which is below T_{tr} and thus it is no longer globally stable (type III phase diagram, see Fig. 3). In this regime there is a single first-order transition, namely a condensation-ordering transition. This transition ends at a tricritical temperature T_{tc}, above which only a continuous order-disorder transition remains. This type of phase diagram, characterized by first-order coexistence between an isotropic vapor and a magnetic liquid ending at a tricritical point, persists up to $R = \infty$, i.e., for systems with no isotropic attractive interactions.

We further note that the MF phase diagram of a fluid with $R = \infty$ is compatible with the simulation results of Lomba and co-workers for the same model (see Fig. 4). These results are, however, not too precise as to the location of the critical point, nor are they conclusive as to its nature, presumably due to finite size effects.

The MMF phase diagram of the same model for $R = \infty$, and where the coupling between spins is given by a Yukawa interaction,

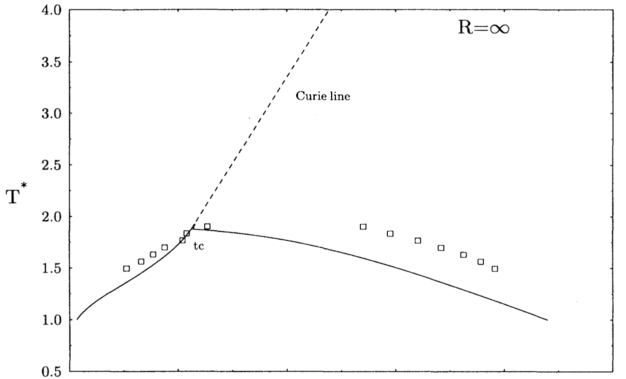

FIG. 4. MF phase diagram of the ferromagnetic Heisenberg fluid for the potential of Ref. [22] [Eqs. (6) and (7) with $I(r) = 0$, and (50)]. Temperature in reduced units of $T^* = k_BT/J$; other symbols as in Fig. 3. The squares are Gibbs ensemble MC data from Ref. [22].

$$J(r) = J\,\frac{e^{-z(r-\sigma)}}{(r/\sigma)}, \tag{50}$$

with $z = \sigma^{-1}$, was obtained by solving the set of Eqs. (46)–(49) and is shown in Fig. 5. These results correspond to retaining coefficients φ_l up to $l = 6$ in the expansion of the ODF, Eq. (23). We have checked that the inclusion of more terms does not change the phase boundaries. MMF-DFT predicts a phase diagram which is qualitatively the same as that of MF theory, namely first-order coexistence between a low-density isotropic vapor and a high-density ferromagnetic liquid, ending at a tricritical point where the Curie line also terminates. The MMF tricritical temperature is found to be $T^*_{\rm tc} = 2.06$, which is somewhat higher than the MF prediction, $T^*_{\rm tc} = 1.876$ (reduced temperatures are defined as $T^* = k_BT/J$). Above this temperature one finds a line of order-disorder critical points separating the isotropic and ferromagnetic phases (Curie line). We note that the absolute stability conditions for the isotropic phase, within the zero-density approximation, $c(12) = g(12) = e^{-\beta\phi(12)}$ used in MMF theory, can be written as

$$1 + \frac{2l+1}{2}\rho\beta u_l > 0, \tag{51}$$

for all $l \geq 1$. These relations are always satisfied for $l \geq 2$, so the density above which the isotropic phase is unstable is the solution of

$$\rho = -\frac{2}{3\beta\, u_1(T)}, \tag{52}$$

where

$$u_1 = -\frac{8\pi}{3\beta}\int_\sigma^{r_c} r^2 dr\,\frac{1}{\beta J(r)}\left[\cosh\left(\beta J(r)\right) - \frac{\sinh\left(\beta J(r)\right)}{\beta J(r)}\right]. \tag{53}$$

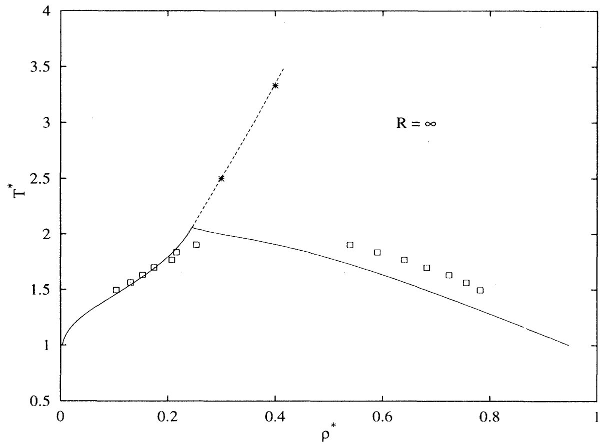

FIG. 5. MMF phase diagram of the ferromagnetic Heisenberg fluid (same potential as in Fig. 4). Solid lines, first-order phase transitions; dashed line, Curie line. The squares are the Gibbs ensemble MC data, and the diamonds the RHNC results, of Ref. [22]. For error bars on the GEMC results, see Ref. [22]. Temperature and density are in reduced units of $T^* = k_BT/J$ and $\rho^* = \rho\sigma^3$, respectively.

The limit of stability of the isotropic phase with respect to ferromagnetic fluctuations coincides with the line of critical points (Curie line) obtained from Eqs. (36), (39), (40), and (41), since the order-disorder transition is continuous above the tricritical temperature (see Fig. 5 [35]). In Sec. IV we discuss the stability (spinodals) of the various fluid phases, in connection with the derivation of the critical and multicritical behavior of the Heisenberg fluid.

Simulation results for the liquid-vapor coexistence curve, obtained using Gibbs ensemble Monte Carlo (GEMC) [36], are included in Fig. 5. The coexistence vapor densities obtained by DFT are very close to the simulation data points except at the highest temperature considered in the simulations ($T^* = 1.903$), where the theoretical density is too low. On the other hand, liquid densities are systematically underestimated. The overall agreement between simulated and theoretical curves is, however, quite remarkable, in view of the drastic approximations involved in the theory.

The simulation results of Ref. [22] indicate that the Curie line ends at a critical endpoint on the vapor side of the liquid-vapor coexistence curve, or at a tricritical point. The former scenario implies the existence of an order-order critical point between two ferromagnetic phases. In the range of temperatures above the critical endpoint, the phase diagram would then describe coexistence between a magnetic liquid and a magnetic gas. Neither DFT, suitably modified to describe coexistence between ordered phases, nor Hemmer and Imbro's MF theory [15] predict such phase diagrams for any value of (positive) R (see, however, Sec. IV). Although Ref. [22] provides some evidence for the coexistence of two magnetic phases, this could turn out to be a finite size effect.

Furthermore, the simulations are not very accurate in the critical region, and thus the nature of the point where the Curie line terminates cannot be ascertained from the available Monte Carlo results. In order to settle this issue, new simulations are in progress which approach the critical point more closely. These simulations include free energy calculations as well as a careful analysis of finite size effects, which are particularly important in the critical region.

In Fig. 5 we also compare MMF theory with the reference hypernetted chain equation (RHNC) for the continuous order-disorder transition [22]. In RHNC, as well as in other integral equation theories, the location of continuous transitions is determined from the divergence of the corresponding isothermal susceptibility. In general, this yields the spinodals (or lines where the stability of a bulk phase is lost with respect to a given type of fluctuations), which coincide with the phase boundaries when the transition is continuous (see also Sec. IV). For the Curie line the diverging susceptibility is magnetic. The agreement between the Curie lines obtained with this sophisticated theory and MMF is rather good. As mentioned in the previous paragraph, for the model given by Eqs. (6), (7), and (50) only qualitative MC estimates of the order-disorder transition were obtained, and are thus of little value in testing the theoretical results. The line of Curie points has, however, been determined with great precision [29] by a MC method based on finite size scaling analysis of the fourth-order magnetization cumulant [37] combined with histogram techniques [38] for an interaction potential similar to that of Eqs. (6), (7), and (50), with a cutoff distance $r_c = 2.5\sigma$. (The choice of a cutoff guarantees identical potentials for the various system sizes considered in the MC calculations.) These results are compared in Fig. 6 with MMF-DFT predictions for the same (truncated) potential. The agreement is again remarkably good. The large change in slope entailed upon truncation of the potential and the drop in the tricritical point temperature (from $T^* = 2.06$–1.39) are captured fairly accurately by MMF. (A similar drop of the critical point temperature is observed for the spherically symmetric Yukawa potential upon restricting the range of the potential [39,40].) The slope of the MMF-DFT Curie line is, however, somewhat small when compared with MC results.

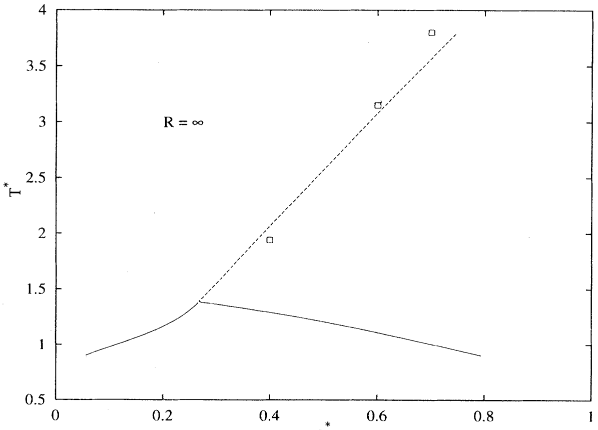

FIG. 6. MMF phase diagram of the truncated ferromagnetic Heisenberg fluid [same potential as in Figs. 4 and 5 but with $J(r) = 0$ for $r \geq 2.5\sigma$]. Solid lines, first-order phase transitions; dashed line, Curie line. The diamonds are MC results from Ref. [29]. The error bars are of the same size as the symbols. Temperature and density are in reduced units of $T^* = k_B T/J$ and $\rho^* = \rho\sigma^3$, respectively.

IV. CRITICALITY IN THE HEISENBERG FLUID

A. Stability of bulk phases and spinodals

Using Eqs. (17) and (18), the MF Helmholtz free energy density is rewritten as

$$f(\rho,\eta_1) = f_{\rm hs}(\rho) - \frac{1}{2}I_{\rm int}\rho^2 + \frac{1}{2}J_{\rm int}\rho^2\eta_1^2 + \rho k_B T\alpha(x), \tag{54}$$

where

$$\alpha(x) = \ln\left(\frac{x}{\sinh x}\right), \tag{55}$$

and we have introduced the variable $x = \beta J_{\rm int}\rho\eta_1$. The equilibrium chemical potential, μ, and the external magnetic field, H, are obtained by partial differentiation of the free energy density, Eq. (54), with respect to ρ and η_1:

$$\mu(\rho,\eta_1) = \left(\frac{\partial f(\rho,\eta_1)}{\partial\rho}\right)_{\eta_1} = \frac{\partial f_{\rm hs}(\rho)}{\partial\rho} - I_{\rm int}\rho + J_{\rm int}\rho\eta_1^2 + k_B T\alpha(x) + k_B T x\,\alpha'(x), \tag{56}$$

$$H(\rho,\eta_1) = \left(\frac{\partial f(\rho,\eta_1)}{\partial\eta_1}\right)_{\rho} = J_{\rm int}\rho^2\left[\eta_1 + \alpha'(x)\right], \tag{57}$$

where the prime denotes differentiation with respect to the function's argument. In zero magnetic field, Eq. (57) is equivalent to Eq. (16) for the equilibrium polar order parameter, η_1. The equilibrium thermodynamic fields, μ and H, may also be determined by requiring that the grand potential functional Ω be stationary with respect to density fluctuations, i.e.,

$$\frac{1}{V}\Delta\Omega = \frac{1}{V}\sum_i \frac{\partial\Omega}{\partial\rho_i}\Delta\rho_i = 0, \tag{58}$$

with the densities $\rho_1 = \rho$ and $\rho_2 = \eta_1$, or

$$\frac{1}{V}\frac{\partial\Omega}{\partial\rho} = 0 \tag{59}$$

and

$$\frac{1}{V}\frac{\partial\Omega}{\partial\eta_1} = 0. \tag{60}$$

Local stability of the bulk phases further requires that this stationary point be a minimum, i.e., that the second variation of the grand potential functional be strictly positive,

$$\frac{1}{V}\Delta^2\Omega = \frac{1}{2V}\sum_{ij}\frac{\partial^2\Omega}{\partial\rho_i\partial\rho_j}\Delta\rho_i\,\Delta\rho_j > 0. \tag{61}$$

Equation (61) is satisfied when the matrix of second derivatives of Ω with respect to the densities ρ and η_1 has positive eigenvalues. When one of these eigenvalues vanishes, the bulk phase is unstable with respect to fluctuations in ρ and/or η_1 associated with the eigenvector corresponding to that zero eigenvalue. This will occur when

$$\det \mathbf{M} = 0, \tag{62}$$

where $\mathbf{M}$ is the stability matrix, defined as

$$M_{ij} = \frac{1}{V}\frac{\partial^2\Omega}{\partial\rho_i\partial\rho_j}. \tag{63}$$

Using Eqs. (62) and (63), we find that the grand potential Ω becomes locally unstable when

$$\left(\frac{\partial^2 f(\rho,\eta_1)}{\partial\rho^2}\right)_{\eta_1}\left(\frac{\partial^2 f(\rho,\eta_1)}{\partial\eta_1^2}\right)_{\rho} - \left(\frac{\partial^2 f(\rho,\eta_1)}{\partial\rho\partial\eta_1}\right)^2 = 0, \tag{64}$$

which is easily calculated for the Heisenberg fluid within MF theory, as

$$\left[1+\frac{J_{\rm int}\rho}{k_BT}\alpha''(x)\right]\left\{\frac{1}{J_{\rm int}}\frac{\partial^2 f_{\rm hs}}{\partial\rho^2} - \frac{I_{\rm int}}{J_{\rm int}} - (\alpha'(x))^2\left[1-\frac{J_{\rm int}\rho}{k_BT}\alpha''(x)\right]\right\} - x^2(\alpha''(x))^2 = 0. \tag{65}$$

At equilibrium in zero magnetic field, it follows from Eq. 57 that $\eta_1 = -\alpha'(x)$, which upon substitution into the previous equation yields the simple result

$$\left[1+\frac{J_{\rm int}\rho}{k_BT}\alpha''(x)\right]\left(\frac{1}{J_{\rm int}}\frac{\partial^2 f_{\rm hs}}{\partial\rho^2} - \frac{I_{\rm int}}{J_{\rm int}}\right) - (\alpha'(x))^2 = 0. \tag{66}$$

The solution(s) of Eq. 66 is (are) the mean-field spinodal(s) of the Heisenberg fluid. This spinodal has several branches, associated with instabilities of the bulk phases with respect to different density fluctuations.

In the isotropic phases $\eta_1 = 0$ and so is $\alpha(x)$ and all its odd-order derivatives. In this case, there are two different solutions to Eq. (66). The first of these is given by

$$\frac{1}{J_{\rm int}}\frac{\partial^2 f_{\rm hs}}{\partial\rho^2} - \frac{I_{\rm int}}{J_{\rm int}} = 0, \tag{67}$$

which for a finite $J_{\rm int}$ is the usual MF liquid-vapor spinodal of an isotropic fluid with attractive interactions of strength $I_{\rm int}$.

A second solution of Eq. (66) with $\eta_1 = 0$ corresponds to

$$1+\frac{J_{\rm int}\rho}{k_BT}\alpha''(0) = 0, \tag{68}$$

which, using Eq. (55) to calculate the second derivative of $\alpha(x)$ at $x=0$, becomes

$$\rho = \frac{3k_BT}{J_{\rm int}}. \tag{69}$$

This is the well known result for the MF Curie line.

Finally, the zeros of Eq. (66) when $\eta_1 \neq 0$ correspond to instabilities caused by fluctuations in both ρ and η_1. One such spinodal is associated with a first-order transition from a disordered vapor to a magnetic liquid (for $R > 0.38$, below the tricritical temperature). We call this a condensation-ordering transition, since both density and magnetization change at the corresponding phase boundary. Additionally, the system may (at least in principle) exhibit condensation between two magnetic fluids. We call this an order-order transition, since the two fluid phases exhibit orientational order. This is a novel transition for the ferromagnetic Heisenberg fluid, evidence for which has been suggested by the simulations of Ref. [22].

The solutions of Eq. (66) were found numerically by solving it simultaneously with the equilibrium conditions, Eqs. (56) and (57), in zero magnetic field and fixed T, as a function of the density. We note that the density is restricted to be larger than the Curie density [i.e., the solution of Eq. (69)], in order that nonzero (equilibrium) values of η_1 may be obtained. We solved the equations for the whole range of (positive) R's, over a wide range of temperatures, and found at most one zero with finite magnetization. This implies that for this system (at least within the MF approximation), no first-order transitions may occur between ordered fluid phases, and thus the possibility of a magnetic (order-order) critical point [22] seems to be excluded, in agreement with the results of Hemmer and Imbro [15] (we will return to this point in Sec. IV C).

B. Criticality

If the stability matrix $\mathbf{M}$ has a zero eigenvalue, higher order derivatives need to be considered to establish the local stability of the system. If this is stable, a zero eigenvalue of $\mathbf{M}$ corresponds to criticality [41]. Suppose the determinantal equation, Eq. (62), has a simple zero for the critical values of the densities ρ_1 and ρ_2. Then a special direction in density space is defined by the eigenvector $\mathbf{v} = (v_1, v_2)$ of $\mathbf{M}$ corresponding to that zero eigenvalue [42]. Consider deviations from the critical densities in the direction of $\mathbf{v}$ in density space, measured by the small parameter δ:

$$\boldsymbol{\rho} = \boldsymbol{\rho_c} + (v_1, v_2)\,\delta. \tag{70}$$

An expansion which is analogous to a Landau expansion in δ is given by

$$\frac{1}{V}\Omega(\boldsymbol{\rho}) = \frac{1}{V}\Omega(\boldsymbol{\rho}_c) + \sum_{n=3}^{\infty} \frac{\delta^n C_n(\boldsymbol{\rho}_c)}{n!}, \tag{71}$$

where $C_n(\boldsymbol{\rho})$ is the nth derivative of Ω (divided by the volume V) in the direction of $\mathbf{v}$. Note that the expansion, Eq. (71), of Ω/V about the critical point begins with the $n = 3$ term. The equilibrium conditions, Eqs. (59) and (60), imply that the term linear in δ vanishes (Ω is stationary with respect to both ρ and η_1). In addition, at criticality, the term quadratic in δ also vanishes, since $\mathbf{v}$ is the eigenvector corresponding to the zero eigenvalue. A necessary condition for a stable critical point is that the third derivative of Ω/V in the direction of $\mathbf{v}$ vanishes,

$$C_3 = \frac{1}{V}\frac{\partial^3 \Omega}{\partial v^3} = 0, \tag{72}$$

otherwise instead of a minimum the system would have a saddle point.

The Heisenberg fluid may exhibit three classes of critical points, which are associated with the different zeros of the determinant, Eq. (66). The first class corresponds to the solution of Eq. (67). In this case the stability matrix has a single nonzero element, namely M_{22}. The eigenvector corresponding to this zero eigenvalue is the solution of

$$M_{22}\, v_2 = 0, \tag{73}$$

from which the normalized eigenvector is $\mathbf{v} = (1, 0)$. Recalling that $\rho_1 = \rho$, we conclude that the instability is driven by (number) density fluctuations, and thus the order parameter of the corresponding phase transition is simply the density difference $\Delta\rho$. Condition 72 is now written

$$\left(\frac{\partial^3 f(\rho,\eta_1)}{\partial \rho^3}\right)_{\eta_1} = \frac{\partial^3 f_{\rm hs}(\rho)}{\partial \rho^3} = 0, \tag{74}$$

which is the usual MF condition for the liquid-vapor critical point of an isotropic fluid. Note that, within the simplest MF approximation, the anisotropic interactions do not contribute to the thermodynamic functions of the isotropic phases, and consequently the liquid-vapor critical point is independent of $J_{\rm int}$ (this is not true in an exact theory and is no longer the case in MMF-DFT).

The second class of critical points of the Heisenberg fluid corresponds to the solution of Eq. (66) given by Eq. (69). Now M_{11} is the only nonzero element of the stability matrix, and the eigenvector corresponding to the zero eigenvalue of $\mathbf{M}$ is given by

$$M_{11}\, v_1 = 0, \tag{75}$$

from which the normalized eigenvector is $\mathbf{v} = (0, 1)$. Clearly, the instability is driven, in this case, by fluctuations in the magnetization density, and the order parameter of the corresponding critical point is the magnetic density or polar order parameter, η_1. The condition for criticality, Eq. (72), is now

$$\left(\frac{\partial^3 f(\rho,\eta_1)}{\partial \eta_1^3}\right)_{\rho} = 0, \tag{76}$$

which is identically zero when $\eta_1 = 0$. This is an order-disorder (Curie) critical point: the fluid is isotropic in the high-temperature, low-density phase, and magnetic otherwise.

Finally, if there is a root of Eq. (66) with nonzero η_1 for which condition 72 is satisfied, the system exhibits an order-order (or magnetic) critical point. We have checked, within MF theory, that these two conditions are not simultaneously satisfied for any (positive) ratio R of magnetic to isotropic interactions. Thus, no MF magnetic critical point is to be expected for Heisenberg fluids characterized by positive R.

So far we have derived the necessary conditions for the existence of (various types of) critical points. Further conditions are required to guarantee their local and global stability. The condition for local stability is easily written in terms of the coefficients of an appropriate Landau expansion. By contrast, global stability requires that the local minimum be the absolute one, which cannot be written in terms of a local expansion. Indeed, this condition requires the knowledge of all the stationary solutions of the grand potential functional, for the given set of thermodynamic fields, which is often a rather difficult task. Here we have simplified this task, by considering fluid phases only.

C. Landau expansions

Close to a critical point, a Landau expansion can be derived for the free energy in terms of the corresponding order parameter, as was originally proposed by Landau [43] and later developed by Bogolubov [44]. This (phenomenological) approach was applied to tricritical phenomena by Griffiths [45], and the connection between such an expansion and the MF theory of microscopic models of metamagnets has been reviewed by Kincaid and Cohen [46].

The order parameters of two of the critical points discussed in the previous paragraphs were easily identified with the density difference, $\Delta\rho = \rho - \rho_c$, and the magnetization, η_1. We define (by suitable Legendre transforms) the free energy densities (of two fields, and one density or order parameter)

$$g_\rho(T,H,\rho) = \frac{1}{V}\Omega(T,H,\mu) + \mu\rho, \tag{77}$$

$$g_{\eta_1}(T,\mu,\eta_1) = \frac{1}{V}\Omega(T,H,\mu) + H\eta_1. \tag{78}$$

The fields μ and H can be eliminated from the right-hand side of Eqs. (77) and (78) using the equilibrium conditions, Eqs. (56) and (57). To construct the Landau free energy close to the isotropic liquid-vapor critical point, we expand g_ρ in a power series in $\Delta\rho$ about $\rho = \rho_c$. The coefficients of the expansion are partial derivatives of the Helmholtz free energy density $f(\rho,\eta_1)$ with respect to ρ, at fixed temperature and magnetic field $H = 0$. Since in the isotropic phase $H = 0$ implies $\eta_1 = 0$, the calculation of these coefficients is quite trivial.

In an analogous fashion, we can construct a Landau free energy close to the Curie critical point by expanding g_{η_1} in a power series in η_1 about $\eta_1 = 0$. The coefficients of the expansion are now partial derivatives of the Helmholtz free energy density $f(\rho, \eta_1)$ with respect to η_1, at fixed temperature and chemical potential μ, which are evaluated at $\eta_1 = 0$. By symmetry, the expansion of g_{η_1} contains no odd powers of η_1, thus we can write

$$g_{\eta_1}(T, \mu, \eta_1) = g_{\eta_1}(T, \mu, 0) + \sum_{n=1}^{\infty} \frac{1}{(2n)!} \left(\frac{\partial^{2n} g_{\eta_1}}{\partial \eta_1^{2n}} \right)_{T,\mu} \eta_1^{2n}. \tag{79}$$

Many of the thermodynamic properties of the Heisenberg fluid including its (order-disorder) phase diagram can be deduced from the free energy g_{η_1} obtained from Eq. (79). The behavior of the free energy is determined by the behavior of the coefficients of the expansion as functions of T and μ, which in turn depend on the parameters of the Hamiltonian, I_{int} and J_{int} [46]. For the Heisenberg fluid this depends critically on the parameter R. In [46] a full discussion can be found of the phases and phase diagrams that may occur in a metamagnet, including a series of graphs which illustrate the behavior of g. Here we restrict our attention to the critical order-disorder transitions (Curie line and tricritical points) discussed in Sec. III.

The Curie line is given by the condition that the second derivative of g_{η_1} with respect to η_1, at fixed T and μ, vanish when $\eta_1 = 0$. Using Eq. (78) the first derivative of g_{η_1} is easily shown to be

$$\left(\frac{\partial g_{\eta_1}}{\partial \eta_1} \right)_{\mu} = H, \tag{80}$$

where the field H is to be evaluated with the help of the equilibrium conditions, Eqs. (56) and (57). Now the second derivative of g_{η_1} with respect to η_1, at constant μ, can be written in terms of derivatives of H and μ [Eqs. (56) and (57)] with respect to the densities ρ and η_1, as

$$\left(\frac{\partial^2 g_{\eta_1}}{\partial \eta_1^2} \right)_{\mu} = \left(\frac{\partial H}{\partial \eta_1} \right)_{\mu} = \left(\frac{\partial H}{\partial \eta_1} \right)_{\rho} + \left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu} \left(\frac{\partial H}{\partial \rho} \right)_{\eta_1}, \tag{81}$$

where the derivative of ρ with respect to η_1, at constant μ, is given by

$$\left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu} = - \left(\frac{\partial \mu}{\partial \eta_1} \right)_{\rho} \left(\frac{\partial \mu}{\partial \rho} \right)_{\eta_1}^{-1}. \tag{82}$$

Note that Eq. (82) vanishes when $\eta_1 = 0$. It is then straightforward to check that, by setting $\left(\frac{\partial H}{\partial \eta_1} \right)_{\mu} = 0$, the result for the Curie line, Eq. (69) is (again) obtained. Local stability of the order-disorder critical points requires that the fourth derivative of g_{η_1} with respect to η_1 be positive.

D. Tricritical line

Not all the solutions of Eq. (69) correspond to stable critical points. Some fall below the condensation phase boundary and are thus globally unstable, while a second class is locally unstable. The point at which local stability is lost is the tricritical point. The fourth derivative of g_{η_1}, or the third derivative of H, with respect to η_1, at fixed T and μ, is given by

$$\begin{aligned} \left(\frac{\partial^3 H}{\partial \eta_1^3} \right)_{\mu} = {} & \left(\frac{\partial^3 H}{\partial \eta_1^3} \right)_{\rho} + 3 \left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu} \left(\frac{\partial^3 H}{\partial \rho \partial \eta_1^2} \right) + 3 \left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu}^2 \left(\frac{\partial^3 H}{\partial \rho^2 \partial \eta_1} \right) + \left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu}^3 \left(\frac{\partial^3 H}{\partial \rho^3} \right)_{\eta_1} \\ & + 3 \left(\frac{\partial^2 \rho}{\partial \eta_1^2} \right)_{\mu} \left(\frac{\partial^2 H}{\partial \rho \partial \eta_1} \right) + 3 \left(\frac{\partial \rho}{\partial \eta_1} \right)_{\mu} \left(\frac{\partial^2 \rho}{\partial \eta_1^2} \right)_{\mu} \left(\frac{\partial^2 H}{\partial \rho^2} \right)_{\eta_1} + \left(\frac{\partial^3 \rho}{\partial \eta_1^3} \right)_{\mu} \left(\frac{\partial H}{\partial \rho} \right)_{\eta_1}, \end{aligned} \tag{83}$$

which, when $\eta_1 = 0$, simplifies to

$$\left(\frac{\partial^3 H}{\partial \eta_1^3} \right)_{\mu} = \left(\frac{\partial^3 H}{\partial \eta_1^3} \right)_{\rho} + 3 \left(\frac{\partial^2 \rho}{\partial \eta_1^2} \right)_{\mu} \left(\frac{\partial^2 H}{\partial \rho \partial \eta_1} \right). \tag{84}$$

Using the MF expressions for the derivatives of H and μ with respect to the densities, evaluated on the Curie line, Eq. (69), the third derivative of H, Eq. (84), becomes

$$\left(\frac{\partial^3 H}{\partial \eta_1^3} \right)_{\mu} = 27 (k_B T)^2 \left[\frac{6}{5 J_{\text{int}}} - \left(\frac{\partial^2 f_{\text{hs}}}{\partial \rho^2} - I_{\text{int}} \right)^{-1} \right]. \tag{85}$$

Positive values of Eq. (85) correspond to stable Curie (order-disorder) criticality. Tricritical behavior is obtained when the right-hand side of Eq. (85) vanishes [45,46], i.e.,

$$\frac{\partial^2 f_{\text{hs}}}{\partial \rho^2} = I_{\text{int}} + \frac{5}{6} J_{\text{int}}. \tag{86}$$

Since the density is given by Eq. (69), the (scaled) tricritical temperature is uniquely determined by R. Thus for a given R, the Curie critical point is locally stable in the region where the right-hand side of Eq. (85) is positive. The tricritical line (as a function of R) is given by the solution of Eq. (86). Note, however, that for weakly anisotropic systems the tricritical point given by Eq. (86) will fall below the isotropic-liquid-vapor coexistence curve, thus becoming globally unstable. This implies, as was found numerically, that there is a lower threshold of anisotropy ratios R below which tricriticality does not occur. This threshold is not given by the expansion of g_{η_1} since the latter is a local expansion.

The MF equation for the tricritical line may also be derived by several alternative methods. One which is similar to the above, but requires much less algebra, is the following [41]: we consider variations in ρ and η_1 about the Curie point, of the type

$$(\rho, \eta_1) = (\rho_{\text{Curie}}, 0) + (0,1)\,\delta + (x,y)\,\delta^2, \tag{87}$$

where $\mathbf{v} = (0,1)$ is the direction along which the second and third derivatives of f vanish, and $\mathbf{u} = (x,y)$ is an as yet arbitrary direction in density space. The corresponding grand potential free energy density can be written as

$$\frac{1}{V}\Omega(\rho,\eta_1) = \frac{1}{V}\Omega_{\text{Curie}} + D\,\delta^4 + O\left(\delta^6\right), \tag{88}$$

where the coefficient D is given by

$$D = \frac{1}{4!}\frac{\partial^4 f}{\partial v^4} + \frac{1}{2}\frac{\partial^2 f}{\partial u^2} + \frac{1}{2}\frac{\partial^3 f}{\partial u \partial v^2}, \tag{89}$$

evaluated at the Curie critical point. The differential operators on the right-hand side of Eq. (89) are derivatives of the Helmholtz free energy density in the directions of $\mathbf{v}$ and $\mathbf{u}$. Evaluating these derivatives on the Curie line and minimizing D with respect to x and y, we find that the direction in density space which minimizes D is given by

$$x_{\min} = \frac{3}{2}k_B T\left(\frac{\partial^2 f_{\text{hs}}}{\partial \rho^2} - I_{\text{int}}\right)^{-1}, \tag{90}$$

and arbitrary y. We obtain for $D_{\min}$,

$$D_{\min} = \frac{9}{8}(k_B T)^2\left[\frac{6}{5J_{\text{int}}} - \left(\frac{\partial^2 f_{\text{hs}}}{\partial \rho^2} - I_{\text{int}}\right)^{-1}\right]. \tag{91}$$

By setting $D_{\min} = 0$, we find (again) the equation for the line of tricritical points, Eq. (86).

A third derivation of the tricritical line, which has a clear physical meaning, follows from the requirement that the derivative of the MF pressure with respect to ρ vanish in the limit of zero magnetization ($\eta_1 = 0$) on the ordered side of the order-disorder transition. Using Eq. (17) for the pressure and Eq. (16) for the equilibrium polar order parameter, the above limit can be evaluated explicitly, and we find once more Eq. (86) for the MF tricritical line.

We note, in passing, that the MF equation for the tricritical line of the Heisenberg fluid can also be obtained from Eq. (7.24) of Ref. [12] by restricting the expansion, Eq. (23), for the orientational distribution function to terms up to $l = 1$.

Lastly, in Fig. 7 we plot the results for the tricritical density obtained from solving Eq. (86), as a function of R. Note that for positive R's the line of tricritical points has a limiting lower density $\rho^* = 0.224$, which occurs for $R = \infty$. The stability of the tricritical points is further discussed in the next subsection.

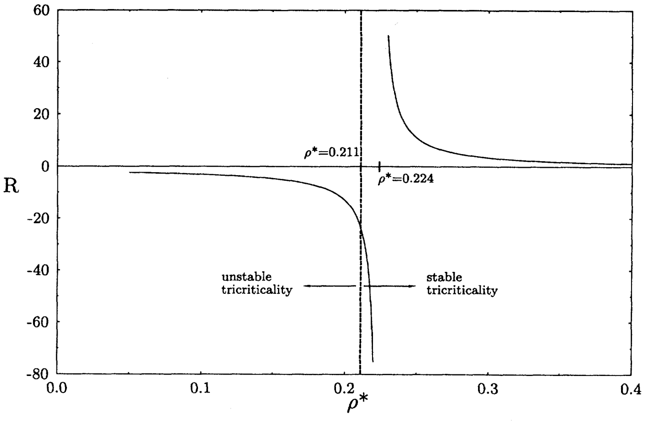

FIG. 7. MF tricritical line of the ferromagnetic Heisenberg fluid vs R. The limiting (reduced) density (for $|R| \to \infty$) is $\rho^* = 0.224$. The short-dashed line marks the fourth-order critical point, where the system crosses over from tricritical behavior to a regime where an order-order critical point may exist; note that it occurs for a *negative* value of R and $\rho^*_{4\text{th}} = 0.211$.

E. Magnetic critical points

The calculation of the sixth derivative of g_{η_1} is long and tedious, but its knowledge is required not only to check that the tricritical points derived earlier are locally stable but, more importantly, to establish if there is a set of parameters for which they become unstable. At this point the system will cross over from tricritical behavior to a regime where an order-order critical point may be found [46,47]. After somewhat lengthy algebra, $\left(\frac{\partial^5 H}{\partial \eta_1^5}\right)_\mu$ at $\eta_1 = 0$ is found to be

$$\begin{aligned}\left(\frac{\partial^5 H}{\partial \eta_1^5}\right)_\mu = {} & \left(\frac{\partial^5 H}{\partial \eta_1^5}\right)_\rho + 10\left(\frac{\partial^2 \rho}{\partial \eta_1^2}\right)_\mu \left(\frac{\partial^4 H}{\partial \rho \partial \eta_1^3}\right) \\ & + 15\left(\frac{\partial^2 \rho}{\partial \eta_1^2}\right)_\mu^2 \left(\frac{\partial^3 H}{\partial \rho^2 \partial \eta_1}\right) \\ & + 5\left(\frac{\partial^4 \rho}{\partial \eta_1^4}\right)_\mu \left(\frac{\partial^2 H}{\partial \rho \partial \eta_1}\right),\end{aligned} \tag{92}$$

which, after calculating the derivatives within MF and evaluating them at a point which satisfies simultaneously Eqs. (69) and (86), becomes

$$\left(\frac{\partial^5 H}{\partial \eta_1^5}\right)_\mu = \frac{972(k_B T)^2}{5J_{\text{int}}}\left(\frac{1}{7} + \frac{18 k_B T}{5J_{\text{int}}^2}\frac{\partial^3 f_{\text{hs}}}{\partial \rho^3}\right). \tag{93}$$

This derivative is positive at all points which are simultaneous solutions of Eqs. (69) and (86), for systems characterized by *positive* ratios R of anisotropic to isotropic interaction strengths, thus confirming the local stability of the MF tricritical points found in Sec. III including the result for $R = \infty$.

The third derivative of $f_{\text{hs}}(\rho)$, however, changes sign as a function of the density and consequently it is possible that Eq. (93) has a zero which also satisfies Eqs. (69) and (86) for a different set of parameters. This occurs at a value of J_{int} which is the solution of

$$\frac{\partial^3 f_{\text{hs}}}{\partial \rho^3} = -\frac{5}{126}\frac{J_{\text{int}}^2}{k_B T}, \tag{94}$$

which, when coupled with Eqs. (69) and (86), defines the density and the ratio R of anisotropic to isotropic interactions at which this fourth-order critical point may occur. These three equations have indeed a solution, and this (fourth-order critical) point is also plotted in Fig. 7, where it is seen to occur at a finite *negative* value of R and at a density $\rho^* = 0.211$. Since our Eq. (69) is only valid for positive J (i.e., ferromagnetic interactions), this implies that, within MF theory, a fourth-order critical point may occur for a ferromagnetic Heisenberg fluid with additional long-ranged *repulsive* interactions. This higher-order critical point [46] has been given particular names which are, however, a matter of some controversy [47]. Since that discussion is not particularly relevant in the context of this paper, we avoided the use of any of those names.

Within the MF approximation, we thus find that the tricritical point is locally stable over the whole range of positive R's for which it occurs, becoming unstable at a finite *negative* value of the ratio of anisotropic to isotropic interaction strengths R. For sufficiently strong isotropic repulsions (for $|R| < |R_{4\text{th}}|$), the critical behavior of the Heisenberg fluid is characterized by an order-order (magnetic) critical point [46,47]. A typical phase diagram in this regime is shown in Fig. 8. In these systems, the Curie line ends at a critical endpoint on the low-density branch of the first-order phase diagram and, for temperatures between the critical endpoint and the magnetic critical point, phase coexistence is between two magnetic fluids. A systematic investigation of the MF phase diagram for the whole range of negative R's, and of the existence of magnetic critical points for similar systems within MMF theory, is currently being conducted. The existence of such points in generalized Heisenberg fluids, however, is significant in the context of the simulations of Ref. [22] since, in contrast to the theoretical results of MF and MMF theory for a system with $R = \infty$, it indicates that magnetic critical points may be expected for Heisenberg fluids with sufficiently "strong" anisotropic interactions. Whether the missing anisotropic correlations neglected by MF and MMF theories are enough to induce a magnetic critical point in the system with $R = \infty$, as suggested in Ref. [22], remains an open question. We are currently addressing this problem both by refining the simulation results and by using more sophisticated theories.

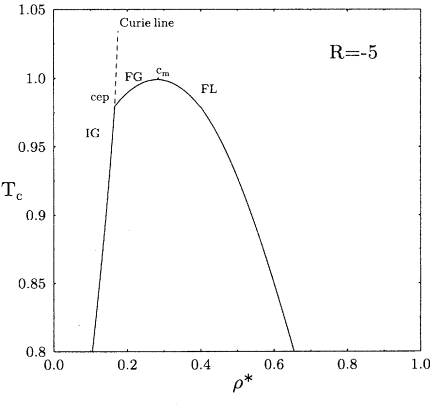

FIG. 8. MF phase diagram of the ferromagnetic Heisenberg fluid in the magnetic criticality regime ($R = -5$). ρ^* is as before, but T_c is now the temperature of the (magnetic) liquid-vapor critical point, c_m. Solid lines, first-order phase transitions; dashed line, Curie line; IG, isotropic gas; FG, ferromagnetic gas; FL, ferromagnetic liquid. The Curie line terminates at a critical endpoint (cep) on the vapor side of the liquid-vapor coexistence curve, as seen in the simulations of Ref. [22].

We finish this section by indicating an alternative method to derive the fourth-order critical point, which is computationally simpler. Furthermore, it provides a means of checking the previous, rather lengthy, derivation. We start, as in the preceding section, by considering variations in ρ and η_1 of the type

$$(\rho, \eta_1) = (\rho_{\text{tricritical}}, 0) + (0,1)\,\delta + (x_{\text{min}}, y)\,\delta^2, \tag{95}$$

where $\mathbf{v} = (0,1)$ is the direction along which the second, third, and fifth derivatives of f vanish, and $\mathbf{u} = (x_{\text{min}}, y)$ is a direction in density space. x_{min} is given by Eq. (90), and y is as yet arbitrary. The corresponding grand potential free energy density can be written as

$$\frac{1}{V}\Omega(\rho, \eta_1) = \frac{1}{V}\Omega_{\text{tricritical}} + \mathcal{D}\,\delta^6 + O\left(\delta^8\right), \tag{96}$$

where the coefficient $\mathcal{D}$ is given by

$$\mathcal{D} = \frac{1}{6!}\frac{\partial^6 f}{\partial v^6} + \frac{1}{3!}\frac{\partial^3 f}{\partial u^3} + \frac{1}{4}\frac{\partial^4 f}{\partial u^2 \partial v^2} + \frac{1}{4!}\frac{\partial^5 f}{\partial u \partial v^4}, \tag{97}$$

evaluated at a point on the tricritical line, and the differential operators on the right-hand side of Eq. (97) are derivatives of the Helmholtz free energy density in the directions of $\mathbf{v}$ and $\mathbf{u}$. Evaluating the MF derivatives for the Heisenberg fluid on the tricritical line and minimizing $\mathcal{D}$ with respect to y [x is given by Eq. (90)], we find that the direction in density space which minimizes $\mathcal{D}$ is given by $(x_{\text{min}}, 0)$. We obtain for $\mathcal{D}_{\text{min}}$,

$$\mathcal{D}_{\text{min}} = \frac{3^3}{100 J_{\text{int}}}(k_B T)^2\left(\frac{1}{7} + \frac{18}{5 J_{\text{int}}^2}\frac{\partial^3 f_{\text{hs}}}{\partial \rho^3}\right). \tag{98}$$

By setting $\mathcal{D}_{\text{min}} = 0$, we find (again) the equation for the fourth-order critical point, Eq. (94).

V. CONCLUSIONS

In this paper we have studied the phase diagram and the criticality of the Heisenberg fluid using MF and MMF-DFT. The latter is a more sophisticated version of MF theory, which weighs configurations in the average of the perturbative part of the energy by the zero-density approximation of the pair distribution function. For a fluid characterized by anisotropic attractive interactions ($R = \infty$), both theories predict a phase diagram with a first-order (condensation) transition between a disordered gas and an ordered (magnetic) liquid, which ends at a tricritical point where the Curie line (order-disorder transition) also terminates. The MMF-DFT phase diagram is in semiquantitative agreement with the results of recent Monte Carlo simulations, Ref. [22], which may, however, suggest a different type of criticality.

In order to throw some light on the critical behavior of this class of fluids, we used simple MF theory to study the global phase diagram of these systems as a function of the ratio of anisotropic to isotropic interaction strengths, R. For positive R's the results of Ref. [15] are reproduced. These include three different types of phase diagram. For weakly anisotropic potentials, the order-disorder transition is always continuous and terminates at a critical endpoint on (the liquid side of) the liquid-vapor coexistence curve. Increasing the anisotropy above a certain threshold drives this magnetic transition first order at lower temperatures, thus leading to the appearance of a tricritical point and a ferromagnetic liquid-isotropic liquid-vapor triple point. For strongly anisotropic potentials, ordinary liquid-vapor phase separation is preempted by a direct transition between a low-density disordered phase and a ferromagnetic liquid which becomes continuous at a tricritical point. We have studied the stability of the Heisenberg fluid by deriving explicit expressions for the MF spinodal, which was found to possess three different branches: isotropic condensation, a Curie line, and a third branch corresponding to simultaneous condensation and ordering transitions. The last branch may, in principle, involve one or two ordered phases. For systems with positive R, i.e., ferromagnetic systems with additional isotropic interactions, only the first possibility was found to occur, indicating the absence of an order-order (magnetic) critical point in these fluids (at least within this approximation).

We have also derived explicit expressions for the isotropic and Curie critical points and studied their local and global stability. The Curie critical endpoint becomes locally unstable at a tricritical transition. The line of tricritical transitions was also derived and its stability was further analyzed. It was found that MF tricriticality, when it occurs above the condensation curve, is stable for the whole range of positive R. We have also found that the tricritical line survives for systems with negative R, i.e., ferromagnetic systems with additional (long-range) isotropic repulsions. As the strength of the isotropic repulsions is further increased, a fourth-order critical point is found where the sixth derivative of the free energy with respect to the magnetization, at fixed temperature and chemical potential, vanishes. Here, the tricritical line becomes locally unstable, and the phase diagram of systems with stronger isotropic repulsions is characterized by a Curie critical endpoint on the vapor side of the coexistence curve, as well as a magnetic critical point, i.e., criticality between two ordered magnetic phases. The latter coexist for a range of temperatures between the Curie critical endpoint and the magnetic (order-order) critical point. These results also suggest that the existence of magnetic critical points may be expected in simple magnetic fluids, but whether or not this is the criticality of the fluid with no isotropic interactions, $R = \infty$, remains an open question.

The possibility of finding magnetic colloids with sufficiently strong ferromagnetic interactions (including colloids with additional repulsive isotropic interactions) to exhibit a magnetic critical point seems (to us) remote but not out of reach.

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