RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 59, NUMBER 4 APRIL 1999

Effect of an external magnetic field on the gas-liquid transition in the Heisenberg spin fluid

T. G. Sokolovska and R. O. Sokolovskii
Institute for Condensed Matter Physics, Svientsitskii 1, Lviv 290011, Ukraine

(Received 10 August 1998)

We present the theoretical phase diagrams of the classical Heisenberg fluid in an external magnetic field. A consistent account of correlations is carried out by the integral equation method. A nonmonotonic effect of fields on the temperature of the gas-liquid critical point is found. Within the mean spherical approximation this nonmonotonic behavior disappears for short-range enough spin-spin interactions. [S1063-651X(99)51204-X]

PACS number(s): 64.70.Fx, 75.50.Mm, 05.70.Jk, 61.20.Gy

The behavior of magnetic fluids in an external field has commanded more and more attention in recent years and has some peculiarities. In the presence of an external magnetic field the orientational (magnetic) phase transition is absent, but there are the first order transitions between ferromagnetic phases of different densities (e.g., gaseous and liquid phases). Physical properties of anisotropic fluids (to these belong also, besides magnetic fluids, nematic liquid crystals) are determined by the interplay between orientational and translational degrees of freedom. Therefore, by varying the magnetic field it is possible to effect structural properties of magnetic fluids, in particular, to change the region of the gas-liquid coexistence. Such investigations with a calculation of phase diagrams were carried out for model spin systems within the mean field (MF) approximation [1,2]. It was found that for fluids of hard spheres carrying Ising spins an external magnetic field decreases the temperature of the gas-liquid critical point. On the other hand, the presence of isotropic van der Waals attractions between molecules can lead to the inverse effect [2]. In Ref. [2] the fluid of hard spheres with the classical Heisenberg spins and strong isotropic attractions was considered also. It was shown that at weak magnetic fields there can be two first order phase transitions in this model: gas-liquid and liquid-liquid. In strong fields the weak liquid-liquid transition disappears.

The need to take into account orientational-translational correlations for the description of physical properties of magnetic fluids stimulated studies of the external field effects by more complex techniques. The effect of an external field on the gas-liquid critical point was studied by the functional integration and Green function methods [3] for the quantum Heisenberg ferrofluid and by the Monte Carlo and integral equation methods for the classical one [4,5]. The pair potentials of those models consisted of contributions of hard spheres and of the spin-spin interaction (the so-called ideal Heisenberg fluid). In these works the conclusion was that an external magnetic field favors the phase separation, i.e., the application of the external field increases the gas-liquid critical temperature. Let us note that the results of Refs. [4,5] are obtained for quite strong fields. In our point of view, it was the effect of small fields that is of special interest. This follows from the fact that at small fields orientational fluctuations are large and the corresponding correlations have a long-range character. Therefore, small external influences can result in significant changes of macroscopic properties of magnetic fluids. Besides, the interplay between orientational and spatial ordering can lead to an interesting behavior of the gas-liquid critical point at small fields. In this Rapid Communication we show that in the systems with the long-range enough spin-spin interactions the nonmonotonic effect of the external fields on the gas-liquid critical temperature takes place. There is a temperature range where weak external fields suppress the gas-liquid phase separation. By the integral equation method we show that while the range parameter of the model potential decreases, this temperature interval first gets smaller and then disappears.

We shall consider the model that was studied before for the case of zero external field [6,7]. The pair potential (analogically to the papers [3,4]) is a sum of the hard sphere potential $\varphi(R_{12})$ for spheres of diameter σ and of the Heisenberg spin-spin potential $\Phi(R_{12},\omega_1,\omega_2)$,

$$\Phi(R_{12},\omega_1,\omega_2)=J(R_{12})\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2, \tag{1}$$

$$J(R)=-K\frac{(z\sigma)^2}{z\sigma+1}\,\frac{\exp[-z(R-\sigma)]}{R/\sigma}, \tag{2}$$

where $\hat{\boldsymbol{S}}_i$ is a unit vector in the direction $\omega_i=(\theta_i,\varphi_i)$ of the magnetic dipole moment $\boldsymbol{\mu}$, referred to the uniform field B_0 as the z direction. The potential of the particle interacting with the field is $v_i=-\mu B_0\cos\theta_i$. In expression (2) the coefficient $(z\sigma)^2/(z\sigma+1)$ is chosen to make the integral

$$I=\frac{N^2}{2V}\int d\omega_1\int d\omega_2\int_{R_{12}>\sigma}d\boldsymbol{R}_{12}\Phi(R_{12},\omega_1,\omega_2)f(\omega_1)f(\omega_2) \tag{3}$$

[where $f(\omega)$ is a single-particle orientational distribution function], independent of $z\sigma$. The integral I describes a contribution of the spin-spin potential into the free energy functional within the MF approximation (see, for example, [8]). Therefore, within the MF approach the model phase diagram is independent of $z\sigma$, if we use dimensionless units for the temperature $t=k_BT/K$, the density $\eta=(N/V)(\pi\sigma^3/6)$, and the external field strength $h=\mu B_0/K\sqrt{3}$. For the free energy of the hard sphere system we use the "quasiexact" Carnahan-Starling expression [9]. The MF phase diagrams obtained by the well-known double-tangent construction are presented in Fig. 1. One can see a nonmonotonic effect of the external field on the temperature of the gas-liquid critical point at small values of h. With the increase of the external

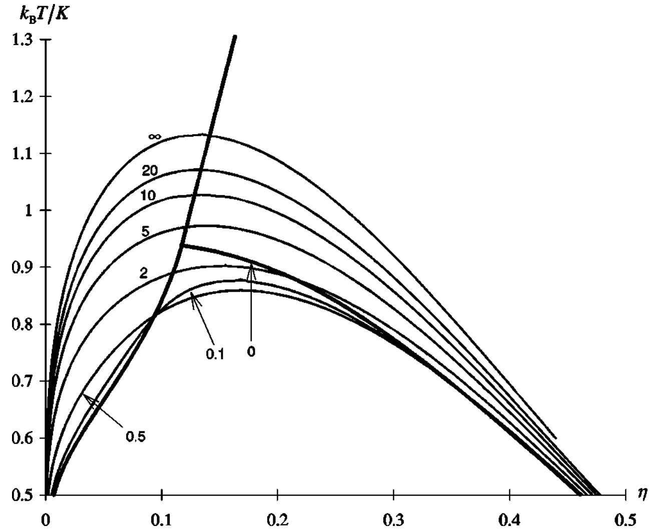

FIG. 1. Phase diagram of the Heisenberg fluid in the external magnetic field within the MF approximation. The results are the same for any $z\sigma$. The thick lines constitute the phase diagram (the Curie line and the gas-liquid binodal) for $h=0$. The thin lines are the gas-liquid coexistence lines for $h=0.1,0.5,2,5,10,20,\infty$.

field strength the gas-liquid critical point first moves down ($h=0.1,0.5$), then moves up ($h=2$), and last ($h=5,10,20,\infty$) grows higher than the top of the zero field binodal. It should be noted that the model potential (2) in the limit $z\sigma\rightarrow 0$ belongs to a family of the so-called Kac potentials, for which the MF approach is accurate. Therefore, relying on the MF results (Fig. 1) we can state that for long-range enough spin-spin interactions ($z\sigma\rightarrow 0$) the nonmonotonous field effect on the critical temperature does take place. But for finite values of $z\sigma$ we are forced to carry out a more accurate investigation.

More consistent consideration of anisotropic fluids can be done on the basis of the integral equation method that allows one to calculate both the one-particle distribution function and the pair distribution function. The task consists [10] of a solution of the anisotropic Ornstein-Zernike (OZ) equation

$$h(1,2)=c(1,2)+\int \rho(3)h(1,3)c(3,2)d(3), \qquad (4)$$

where $d(3)=d\boldsymbol{R}_3 d\omega_3$, $\rho(1)=\rho f(\omega_1)$, $h(1,2)$ and $c(1,2)$ are the total and direct correlation functions of the system. Since Eq. (4) contains the one-particle distribution function, we need (besides a closure relation for the anisotropic OZ equation) some additional relation for the determination of $\rho(1)$. It can be the first equation of the Bogolubov-Born-Green-Kirkwood-Yvon hierarchy [this was used in Refs. [4,5] to obtain a numerical solution of Eq. (4)] or the Lovett equation for anisotropic fluids [11],

$$\boldsymbol{\nabla}_{\omega_1}\ln\rho(1)+\boldsymbol{\nabla}_{\omega_1}\frac{v(1)}{k_BT}=\int c(1,2)\boldsymbol{\nabla}_{\omega_2}\rho(2)d(2), \qquad (5)$$

where $\boldsymbol{\nabla}_{\omega_1}$ is an angular gradient operator; $v(1)$ is a potential of interaction with a uniform external field, its spherical harmonic expansion is of the form

$$v(1)=-\sum_l v_l Y_{l0}(\omega_1). \qquad (6)$$

For a self-consistent solution of Eqs. (4) and (5) we shall use the method suggested in [7,12]. The method is based on the algebraic representation of the Lovett equation for uniaxial fluids. Using the general expansion for the direct correlation function of linear molecules

$$c(1,2)=\sum_{\substack{mnl\\ \mu\nu\lambda}} c_{mnl}^{\mu\nu\lambda}(R)Y_{m\mu}(\omega_1)Y_{n\nu}^{*}(\omega_2)Y_{l\lambda}(\omega_R) \qquad (7)$$

and the exponential form of the one-particle distribution function

$$f(\omega)=Z^{-1}\exp\left(\sum_{l>0} A_l Y_{l0}(\omega)\right), \qquad (8)$$

we obtain, following Refs. [7], an algebraic representation of the Lovett equation for a uniaxial fluid in the external field

$$L_l=\sum_{mn} C_{lm}Y_{mn}L_n+V_l=\sum_m C_{lm}\mathcal{P}_m+V_l, \qquad (9)$$

where all indices take the values greater or equal to 1, $V_l=v_l/k_BT$, $C_{mn}=\int c_{mn0}^{110}(R)d\boldsymbol{R}$, $Y_{mn}=\rho\langle Y_{m1}(\omega)Y_{n1}^{*}(\omega)\rangle_\omega$, $\langle\cdots\rangle_\omega=\int f(\omega)(\cdots)d\omega$, $L_l=\sqrt{l(l+1)}A_l$, $\mathcal{P}_l=\rho\sqrt{l(l+1)(2l+1)}\langle P_l(\cos\theta)\rangle_\omega$, $P_l(\cos\theta)$ is the lth order Legendre polynomial. Let us note that the average values $\langle P_l(\cos\theta)\rangle_\omega$ play the role of order parameters in anisotropic fluids. Relations (9) are accurate, and their use, as well as the use of the integro-differential equation (5), does not introduce any approximation into the theory.

Due to Eq. (9) it turns out to be possible to obtain for our model [Eqs. (1) and (2)] an analytical solution of the anisotropic OZ equation (4) within the mean spherical closure,

$$\begin{aligned} c(1,2)&=-\Phi(R_{12},\omega_1,\omega_2)/k_BT, & R_{12}&>\sigma,\\ h(1,2)&=-1, & R_{12}&<\sigma. \end{aligned} \qquad (10)$$

Condition (10) for $h(1,2)$ follows directly from the fact that hard spheres do not overlap. The mean spherical closure (10) restricts correlation functions of our model to those of the form

$$f(1,2)=\sum_{l_1l_2m} f_{l_1l_2m}(R_{12})Y_{l_1m}(\omega_1)Y_{l_2m}^{*}(\omega_2), \qquad (11)$$

($l_1,l_2=0,1$), and representation (9) results in equalities

$$\begin{aligned} A_1&=A_1\rho\langle|Y_{11}(\omega)|^2\rangle_\omega\int c_{111}(R)d\boldsymbol{R}+\frac{v_1}{k_BT},\\ A_1&=A_1\rho\langle Y_{10}(\omega)\rangle_\omega\int c_{111}(R)d\boldsymbol{R}+\frac{v_1}{k_BT}. \end{aligned} \qquad (12)$$

Here we use the notations of Eq. (11) for harmonics of the direct correlation function $c(1,2)$; $v_1=\mu B_0/\sqrt{3}$. Thus, the use of the mean spherical closure yields for our model vanishing of coefficients A_l with $l>1$ in Eq. (8), and the self-consistent one-particle distribution function in the mean spherical approximation (MSA) takes the form

$$f(\omega)=\exp[A_1Y_{10}(\omega)]\bigg/\int\exp[A_1Y_{10}(\omega)]d\omega. \qquad (13)$$

A uniaxial symmetry of our system leads to factorization of Eq. (4) on the equations with different m. At $m=\pm1$,

$$h_{11m}(R_{12})=c_{11m}(R_{12})+\rho\langle|Y_{1m}(\omega)|^2\rangle_\omega \times\int c_{11m}(R_{13})h_{11m}(R_{32})d\boldsymbol{R}_3. \qquad (14)$$

For $m=0$ we have a system of integral equations that after the Fourier transformation gains the matrix form

$$H_{ij}(k)=C_{ij}(k)+\sum_{i'j'}C_{ii'}(k)\rho_{i'j'}H_{j'j}(k), \qquad (15)$$

where $H_{ij}(k)=h_{ij0}(k)$, $C_{ij}(k)=c_{ij0}(k)$, $\rho_{ij}=\rho\langle Y_{i0}(\omega)Y_{j0}(\omega)\rangle_\omega$, indices take the values 0 and 1. The problem of a self-consistent solution of the anisotropic OZ and Lovett equations has reduced at this stage to the solution of Eqs. (14) and (15) under conditions (12) and the self-consistent $f(\omega)$ given by relation (13). On the basis of the Wertheim-Baxter factorization method [13] one can find the analytical solution of such equations in the form of a set of algebraic equations. The detailed derivation of similar solutions can be found in the literature, and therefore we omit any details and refer the reader to the previous publications [7,12]. The explicit form of the solution is quite unwieldy and will be given in a future presentation. Here we point out only that it is efficiently computable, and we use it for calculation of isotherms by the virial route to thermodynamics in order to locate the gas-liquid transition by the Maxwell construction.

The configuration of the MSA zero-field phase diagrams slightly differs from that of the MF theory (Fig. 1). The MSA via the virial route to thermodynamics demonstrates (Fig. 2) the lack of the tricritical point [7] in the Heisenberg fluid [Eqs. (1) and (2)] contrary to the MF and modified MF theories [8]. Within the MSA the Curie line joins the gas-liquid binodal at its vapor branch (see the insets to Fig. 2). This result is in whole agreement with the available zero-field simulations for the same model [6]: the liquid phase is ferromagnetic and the gaseous phase is mainly paramagnetic, except in the neighborhood of the critical point, where the transition ferroliquid-ferrogas takes place. The quantitative agreement with simulations is also quite perfect [see Fig. 2(a)]. In the insets to the figure one can distinguish the critical point (CP, the top of the gas-liquid binodal) and the critical end point (CEP) in which the Curie line joins the binodal. In the temperature range from $t_{\rm CEP}$ to $t_{\rm CP}$ three spatially uniform phases (isotropic gas, ferrogas, and ferroliquid) can exist. For long-range enough potentials this interval ($t_{\rm CP}-t_{\rm CEP}$) decreases with the decrease of $z\sigma$ (see Table I) and tends to zero for small values of $z\sigma$: the CP and the CEP coincide and form the tricritical point, as is shown in Fig. 1. In practice we cannot distinguish the CP and the CEP by the MSA virial route already at $z\sigma=0.1$.

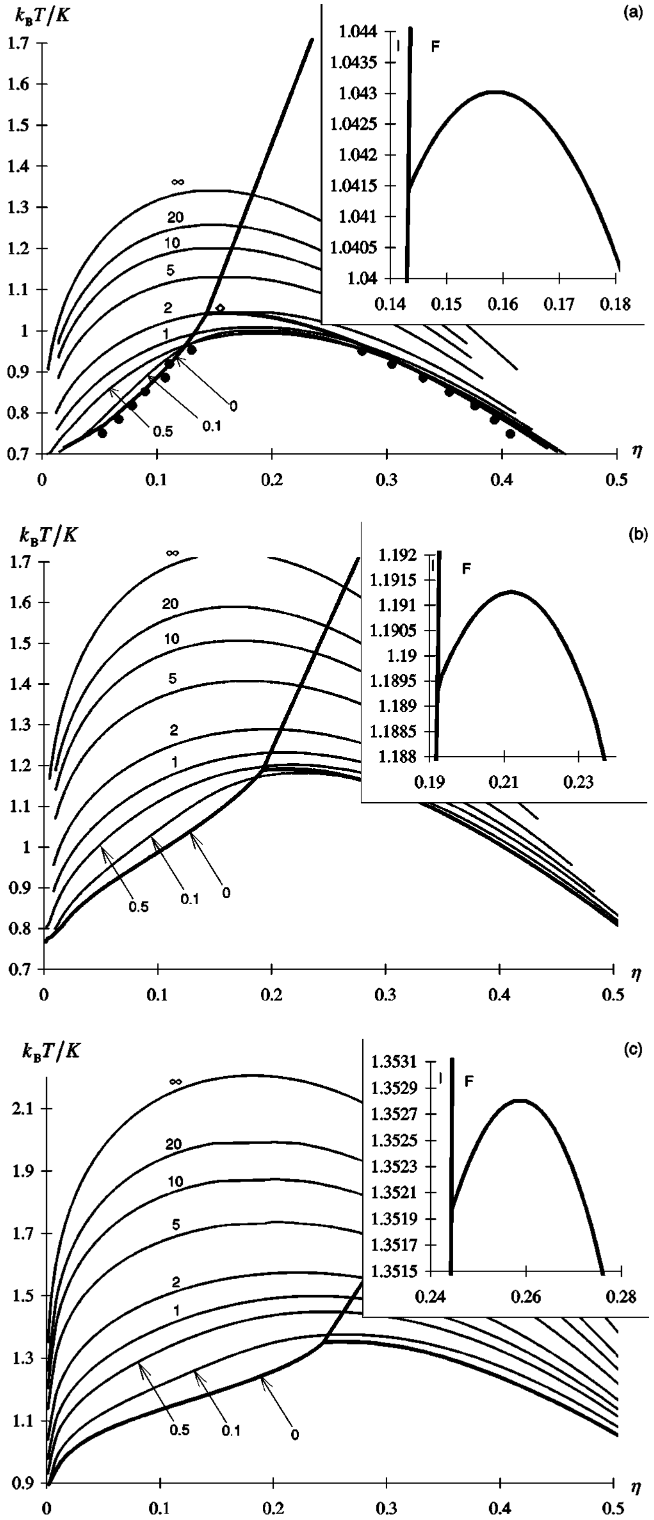

FIG. 2. Phase diagram of the Heisenberg fluid in the external field for $z\sigma=1$ (a), $z\sigma=2$ (b), and $z\sigma=3$ (c). Lines are results of the MSA. The thick line is the case of zero field. In the insets the vicinity of the ferrogas-ferroliquid critical point is shown, and I and F mark isotropic and ferromagnetic domains. The thin lines are the gas-liquid binodals of the fluid in the magnetic field (the attached numbers are the values of the field h). Simulation data [6] ($h=0$) for $z\sigma=1$ (a) are shown as black circles (the gas-liquid coexistence) and diamonds (Curie points). It should be noted that $k_BT/K=T^*/6$ from Ref. [6].

TABLE I. Coordinates of the gas-liquid critical point and its distance from the critical endpoint at different $z\sigma$.

$z\sigma$	t_{CP}	η_{CP}	$t_{\mathrm{CP}}-t_{\mathrm{CEP}}$	$\eta_{\mathrm{CP}}-\eta_{\mathrm{CEP}}$
2	1.1913	0.2119	0.0016	0.0185
1	1.0430	0.1587	0.0015	0.0151
0.5	0.9811	0.1316	0.0008	0.0063
0 (MF theory)	0.938	0.117	0	0

The effect of strong magnetic fields on the Heisenberg fluid [Eqs. (1) and (2)] consists of a considerable increase of the critical temperature. Strong external fields spread the gas-liquid coexistence region on the phase diagram, in other words, it favors the gas-liquid phase separation. This result agrees with the conclusions of Refs. [3–5]. But it follows from the MSA phase diagrams in Fig. 2 that small fields can suppress the gas-liquid transition at finite values of $z\sigma$ (not only in the limit $z\sigma\rightarrow 0$). For example, one can see in Fig. 2(a) ($z\sigma=1$) that the external field of strength $h=0.1$ totally removes the phase separation at temperatures from $t_{\mathrm{CP}}(0.1)=1.002$ to $t_{\mathrm{CP}}(0)=1.043$. In the systems with more short-range anisotropic interactions this temperature interval decreases. For example, in Fig. 2(b) ($z\sigma=2$) the temperature interval, where the external field $h=0.1$ removes the gas-liquid separation, is much less. For short-range enough potentials even very weak fields do not suppress separation, e.g., for $z\sigma=3$ the same field $h=0.1$ increases t_{CP} [Fig. 2(c)]. Thus, the MSA predicts that the suppression effect of small fields on the gas-liquid separation gets weak and finally disappears for short-range enough spin-spin interactions.

The field effects may be explained by the existence of two concurrent tendencies. *The first* tendency is that the external field aligns the spins and, therefore, causes a more effective attraction between particles. This raises the binodal (e.g., in simple nonmagnetic fluids the binodal goes up when the interaction increases). *The second* tendency takes place if the susceptibility of the rarefied phase is larger than that of the coexistent dense phase. In this case the magnetization and the effective attraction between particles grow better in the rarefied phase. This decreases the energetical gain of the phase separation. Therefore, the second tendency suppresses the gas-liquid separation in the fluid. The second tendency is very strong at $h=0$ in the vicinity of the gas-liquid critical point. In this region the vapor branch of the binodal almost coincides with the Curie line (where the susceptibility tends to infinity), whereas the branch of the coexistent liquid phase rapidly deviates from the Curie line. The proximity of the vapor branch to the Curie line is the most considerable when the tricritical point takes place, and the suppression effect is the most pronounced in the case $z\sigma=0$. The susceptibilities of the coexistent phases level with increasing $z\sigma$, and the second tendency gets weak for short-range potentials. The similar external field effect has also been noticed in the recent study of the Ising magnetic fluid within the cluster approach [14].

We are grateful to I. M. Mryglod, for he compelled our attention to the problem.

[1] T. Kawasaki, Prog. Theor. Phys. **58**, 1357 (1977).
[2] F. Schinagl, H. Iro, and R. Folk, Eur. Phys. J. B (to be published).
[3] I.O. Vakarchuk, H.V. Ponedilok, and Yu.K. Rudavskii, Theor. Math. Phys. **58**, 445 (1984).
[4] F. Lado, E. Lomba, and J.J. Weis, Phys. Rev. E **58**, 3478 (1998).
[5] F. Lado, and E. Lomba, Phys. Rev. Lett. **80**, 3535 (1998).
[6] E. Lomba *et al.*, Phys. Rev. E **49**, 5169 (1994).
[7] T.G. Sokolovska, Physica A **253**, 459 (1998).
[8] J.M. Tavares *et al.*, Phys. Rev. E **52**, 1915 (1995).
[9] N.F. Carnahan, and K.E. Starling, J. Chem. Phys. **51**, 635 (1969).
[10] D. Henderson, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), Chap. 4.
[11] R.A. Lovett, C.Y. Mou, and F.P. Buff, J. Chem. Phys. **65**, 570 (1976).
[12] M.F. Holovko, and T.G. Sokolovska, Ukr. Phys. J. **41**, 933 (1996) (in Ukrainian).
[13] M.S. Wertheim, J. Math. Phys. **5**, 643 (1962).
[14] R.O. Sokolovskii, e-print cond-mat/9901024.