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PHASE DIAGRAM IN A CONTINUUM MODEL OF THE
CLASSICAL HEISENBERG FERROMAGNET: MEAN
SPHERICAL APPROXIMATION

ЛЬВІВ

Фазова діаграма континуальної моделі класичного гейзенбергівського феромагнетика: середньосферичне наближення

Т.Г.Соколовська

Анотація. Розглядається континуальна Гейзенбергівська модель спінового флюїду. Парні кореляційні функції і одночастинкова функція розподілу феромагнітної фази отримані шляхом самоузгодженого розв'язання рівнянь Орнштейна-Церніке та Ловетта у середньосферичному наближенні. На основі отриманого аналітичного розв'язку розрахована фазова діаграма. Узгодження між теорією і наявним комп'ютерним експериментом є зовсім добре, особливо для лінії співіснування газ-рідина. Середньосферичне наближення передбачає, що і рідинна, і газова фази є впорядкованими поблизу критичної точки переходу газ-рідина. Цей результат підтверджує передбачення підходу Монте-Карло про існування магнітної критичної точки.

Phase diagram in a continuum model of the classical Heisenberg ferromagnet: mean spherical approximation

T.G.Sokolovska

Abstract. The continuum Heisenberg model of spin fluid is considered. The pair correlation functions and the single-particle distribution function of ferromagnetic state are obtained by the self-consistent solution of the Ornstein-Zernike and the Lovett equations in the mean spherical approximation. On the basis of the analytical solution the phase diagram is calculated and compared with the available Monte Carlo results for the same model. The agreement between theory and simulation is quite satisfactory, especially for the liquid-gas coexistence line. The MSA suggests that only ordered states are involved in the gas-liquid transition near the gas-liquid critical point. This result confirms the Monte Carlo prediction about the existence of a magnetic critical point.

1. Introduction

Since the late 1960s there have been reports on the existence of liquid ferromagnetic materials, such as Au-Co alloy [1], the problem of the passing from magnetic lattice models to continuum disordered systems has arisen. In these materials many physical properties are connected to the lack of translational order. For example, these are the effects associated with gas-liquid transitions that can only be strictly accounted for in the context of liquid state theory. Therefore, continuous systems with interparticle spin interactions of classical Heisenberg symmetry have been studied in the past within the framework of classical statistical mechanics, in particular, by means of integral equation approaches. For an isotropic (orientationally disordered) phase the solutions of the Ornstein-Zernike (OZ) equation for some models were obtained in the mean spherical approximation (MSA) [2–4] and within the reference hypernetted chain closure [5]. These methods allow to determine the Curie point. But in ferrofluids the gas-liquid transition cannot be analyzed by the traditional integral equation methods since it involves the anisotropic phase. In other words we have to investigate the region where the isotropic OZ equation does not have any physical sense and must be replaced by the anisotropic OZ equation.

The anisotropic (ferromagnetic) phase of a continuum Heisenberg magnet is an object of special interest. The ordered n-dimensional magnet (for $n \geq 2$) is a system with spontaneously broken symmetry, where without the presence of an external field, the direction of the magnetization is not predetermined. The spontaneous magnetization breaks the isotropic symmetry (the complete rotational invariance) of the system and leads to spin wave excitations (Goldstone modes), which rotate the direction of the magnetization without any energy cost. It can be shown that the anisotropic OZ-equation together with the Triezenberg-Lovett-Mou-Buff-Wertheim (Lovett) equation [6] ensure a correct treatment for the Goldstone modes in uniaxial fluids, such as nematics, polar liquids or magnetic fluids. But there are great difficulties in the obtaining of a self-consistent solution for the integral OZ-equation and the integro-differential Lovett equation.

Therefore, current theoretical results for phase diagrams (that include the first order phase transitions) are obtained with the modified mean field (MMF) theory [7–9] or with the generalized van der Waals approaches [10,11]. The MMF approach gives a pretty good agreement with the simulation results [7,9]. But there exists one qualitative difference in predictions of these theories and Monte Carlo simulations. The theories suggest a phase diagram of the Heisenberg fluid to have the tricritical point whereas the simulations predict instead the existence of the magnetic critical point [5,9]. Considering this contradiction one should understand that the simulation in the vicinity of the critical (or tricritical) point is a process very complicated by finite size effects and the critical slowing down. On the other hand, the mean-field-like methods use approximations that neglect the correlations between spatial and spin variables. Furthermore, all these methods make crude assumptions about the density-density and spin-spin correlations. For example, the MMF theory use the zero-density approximation for the pair correlation function that does not depend neither on the density nor on orientational order parameters. Therefore, the question about the nature of criticality in the Heisenberg fluid remains open. This problem is addressed both by refining the simulation results and by using more sophisticated theories.

In the presented paper we propose a method for the calculation of correlation functions in anisotropic phases with the analytical solution of the anisotropic OZ equation and the Lovett one. The suggested approach stands on a higher level with respect to the mean-field-like theories and does not impose any additional approximations other than a closure for the OZ equation. This approach was used for nematic systems [12,13] and made it possible to calculate analytically the Frank elastic constants by the expressions from the density functional theory [14] and the expressions [15] obtained in the theory of hydrodynamic fluctuations. Both the approaches give the same result that proves the self-consistency of our method.

The paper is organized as follows. In the next section we review the algebraic representation of the Lovett equation for an uniaxial fluid in the form of exact relations. It will be shown that the representation correctly treats the Goldstone modes. In Sec.3 we solve analytically the anisotropic OZ equation for the classical ferromagnetic fluid. This model was considered in [5]. On the basis of the obtained solution we calculate the phase diagram and compare it with the Monte Carlo [5] and the MMF [7] results in Sec.4. Sec.5 is a summary.

2. Exact algebraic representation of the Lovett equation for anisotropic fluids

The main idea of our method is a principal rejection of the complete rotational invariance form for anisotropic pair correlation functions that is usual in isotropic systems. We use the general expansion in terms of spherical harmonics for the direct correlation function (the form of the

pair correlation function $h(\vec{R}, \omega_1, \omega_2)$ is similar):

$$c(\vec{R}, \omega_1, \omega_2) = \sum_{m,n,l,\mu,\nu,\lambda} c_{mnl}^{\mu\nu\lambda}(R) Y_{m\mu}(\omega_1) Y_{n\nu}^*(\omega_2) Y_{l\lambda}(\omega_{\vec{R}}), \qquad (2.1)$$

$\vec{R}$ is a separation-vector of molecules mass centers, $\omega_i = (\theta_i, \phi_i)$ being an orientation of the linear molecule i. For uniaxial fluids $c(\vec{R}, \omega_1, \omega_2)$ is invariant under a rotation along the ordering direction (z axis). This condition leads to the relation $\mu + \lambda = \nu$. We stress that a complete rotational invariance is broken in anisotropic fluids, and correlation functions can not be represented by rotationally invariant series of Wigner and Blum [16]. The use of such rotationally invariant correlation functions in anisotropic systems is an approximation like the use of a translational invariant form $f_2(|\vec{R}_2 - \vec{R}_1|)$ in crystalline solids. For example, the expansion (2.1) contains the terms $c_{m00}^{000}(R) Y_{m0}(\omega_1) Y_{00}^*(\omega_2) Y_{00}(\omega_{\vec{R}})$, which are excluded in the rotationally invariant series represented by Eqs. (2.8)–(2.10) of Ref. [20]. One can find another differences.

The second principal point is the use of the exact Lovett [6] equation in order to obtain the single-particle distribution function $f(\omega)$ of an anisotropic fluid:

$$\vec{\nabla}_{\omega_1} \ln \rho(\omega_1) = \int c(\vec{R}, \omega_1, \omega_2) \vec{\nabla}_{\omega_2} \rho(\omega_2) \mathrm{d}\vec{R} \mathrm{d}\omega_2, \qquad (2.2)$$

where $\rho(\omega) = \rho f(\omega)$, ρ denotes a number density of the system, $\vec{\nabla}_\omega$ is the angular gradient operator for a linear particle. It should be noted that the substitution of the Lovett equation (2.2) by the "simplified" one (see [17])

$$\ln \rho(\omega_1) = \int c(\vec{R}, \omega_1, \omega_2) \rho(\omega_2) \mathrm{d}\vec{R} d\omega_2 + const$$

is a noncontrollable approximation in anisotropic systems. Therefore, we insist on the solution of the exact equation (2.2).

In uniaxial fluids the orientational distribution function $f(\omega)$ is axially symmetric around a preferred direction (z axis) and depends only on the angle θ between the molecular orientation ω and z axis. It allows to write $f(\omega)$ in the form

$$f(\omega) = \frac{1}{Z} \exp \left\{ \sum_{l>0} A_l Y_{l0}(\omega) \right\}, \qquad (2.3)$$

where the constant Z can be found from the normalization condition $\int f(\omega) \mathrm{d}\omega = 1$. Spherical harmonics $Y_{lm}(\omega)$ satisfy the standard Condon and Shortley phase convention [18] and are normalized in such manner that $\langle |Y_{2m}|^2 \rangle_\omega = 1$ in the isotropic phase, where

$$\langle ... \rangle_\omega = \int f(\omega)(...) \mathrm{d}\omega. \qquad (2.4)$$

The orientational ordering is defined by the parameters

$$S_l = \langle P_l(\cos\theta) \rangle_\omega = \int \mathrm{d}\omega f(\omega) P_l(\cos\theta), \qquad (2.5)$$

where $P_l(\cos\theta)$ are the Legendre polynomials. The space-fixed X, Y and Z components of the angular gradient operator are given by $\vec{\nabla}_\omega = i\vec{l}$, where $\vec{l}$ is the angular momentum operator. Using the expressions (2.1), (2.3) and the relations [18]

$$(\vec{\nabla}_\omega)_y = \frac{\hat{l}_+ - \hat{l}_-}{2}, \qquad (2.6)$$

$$\hat{l}_\pm Y_{m\mu}(\omega) = [m(m+1) - \mu(\mu+1)]^{1/2} Y_{m\mu\pm1}(\omega) \qquad (2.7)$$

we obtained the y-component of (2.2) in the explicit form:

$$\sum_{M>0} \sqrt{M(M+1)} A_M \left[Y_{M1}(\omega_1) - Y_{M-1}(\omega_1) \right] =$$

$$= \sum_{M'>0} \sum_{m,n,\mu} \int c_{mn0}^{\mu\mu0}(R) Y_{00}(\omega_{\vec{R}}) Y_{m\mu}(\omega_1) Y_{n\mu}^*(\omega_2) \times \qquad (2.8)$$

$$\times \sqrt{M'(M'+1)} A_{M'} \left[Y_{M'1}(\omega_2) - Y_{M'-1}(\omega_2) \right] \rho(\omega_2) \mathrm{d}\omega_2 \mathrm{d}\vec{R},$$

where $Y_{00}(\omega_{\vec{R}}) = 1$. Taking into account that only independent of azimuthal angle φ quantities yield nonzero average values and using the orthogonality of Y_{lm}s one gets the following matrix equation

$$\vec{L} = \hat{C}\hat{Y}\vec{L}, \qquad (2.9)$$

where $\vec{L}$ is a column matrix consisting of $L_M = \sqrt{M(M+1)} A_M$, $\hat{C}$ and $\hat{Y}$ are matrices of order $(N \times N)$ with elements

$$C_{mn} = \int \mathrm{d}\vec{R} c_{mn0}^{110}(R) \qquad (2.10)$$

and

$$Y_{mn} = \rho \int \mathrm{d}\omega f(\omega) Y_{m1}(\omega) Y_{n1}^*(\omega), \tag{2.11}$$

where Y_{mn} can be expressed via S_l, N is a number of values of index m (or n) such that $C_{mn} \neq 0$.

On the other hand we can integrate by parts the equation (2.2) and write

$$\vec{\nabla}_{\omega_1} \ln \rho(\omega_1) = - \int \left[\vec{\nabla}_{\omega_2} c(\vec{R}, \omega_1, \omega_2) \right] \rho(\omega_2) \mathrm{d}\omega_2 \mathrm{d}\vec{R}. \tag{2.12}$$

In the similar manner from (2.12) we can obtain a matrix equation for the coefficients of the function $f(\omega)$

$$\vec{L} = \hat{C} \vec{P}, \tag{2.13}$$

where $\vec{P}$ contains the order parameters of the system:

$$P_l = \rho \sqrt{l(l+1)(2l+1)} S_l. \tag{2.14}$$

Thus, the symmetries of the pair potential and of the uniaxial system in whole yield two matrix relations (2.9) and (2.13) which connect the system order parameters, zero Fourier transforms of the direct correlation function harmonics and coefficients A_l of the single-particle distribution function of the system.

Joint use of (2.9) and (2.13) allows to express $f(\omega)$ via the order parameters only:

$$\vec{L} = \hat{Y}^{-1} \vec{P}. \tag{2.15}$$

It follows from the OZ equation [19,17] that an existence of a unit eigenvalue of the integral operator $\tilde{C}(\vec{k} = 0, \omega_1, \omega_2) = \rho^{1/2}(\omega_1) c(\vec{k} = 0, \omega_1, \omega_2) \rho^{1/2}(\omega_2)$ corresponds to an appearance of the Goldstone modes in anisotropic fluids: $h_2(\vec{k} \to 0, \omega_1, \omega_2) \to \infty$. One can see that the Lovett equation (2.2) is an eigenequation for the operator $\tilde{C}$ with the eigenvector $\psi_i(\vec{k} = 0, \omega) = \rho^{-1/2}(\omega) \vec{\nabla}_\omega \rho(\omega)$ and unit eigenvalue. Therefore, the direct correlation function and the single-particle distribution function complying with (2.2) and the OZ equation treat correctly the Goldstone modes in the system.

In order to examine the exact relations (2.9) and (2.13) we consider the OZ equation for anisotropic fluids:

$$h(1,2) = c(1,2) + \int \rho(3) c(1,3) h(3,2) \mathrm{d}(3), \tag{2.16}$$

where $c(1,2)$ and $h(1,2)$ are the direct correlation function and the pair correlation function respectively; $\mathrm{d}3 = \mathrm{d}\vec{R}_3 \mathrm{d}\omega_3$, where $\vec{R}$ denotes mass center coordinates of the particle, $\omega = (\theta, \varphi)$ is the orientation of the molecule. As $\rho(3)$ does not depend on $\vec{R}_3$ then the Fourier-component ($\vec{k} = 0$) of (2.16) can be rewritten in the form of the matrix equations:

$$\hat{H}^{(\mu)} = \hat{C}^{(\mu)} + \hat{C}^{(\mu)} \hat{Y}^{(\mu)} \hat{H}^{(\mu)}, \tag{2.17}$$

where

$$H_{mn}^{(\mu)} = \int \mathrm{d}\vec{R} h_{mn0}^{\mu\mu0}(R) Y_{00}(\omega_{\vec{R}}), \tag{2.18}$$

$$C_{mn}^{(\mu)} = \int \mathrm{d}\vec{R} c_{mn0}^{\mu\mu0}(R) Y_{00}(\omega_{\vec{R}}), \tag{2.19}$$

$$Y_{mn}^{(\mu)} = \int \mathrm{d}\omega f(\omega) Y_{m\mu}(\omega) Y_{n\mu}^*(\omega). \tag{2.20}$$

One can verify (2.17) taking into account that the uniaxial fluid is invariant with respect to rotations around z axis.

Equation (2.17) can be presented in the form :

$$\begin{aligned}
\sqrt{\hat{Y^{(\mu)}}} \hat{H}^{(\mu)} \sqrt{\hat{Y^{(\mu)}}} \ &= \ \left\{ 1 - \sqrt{\hat{Y^{(\mu)}}} \hat{C}^{(\mu)} \sqrt{\hat{Y^{(\mu)}}} \right\}^{-1} \\
&\times \sqrt{\hat{Y^{(\mu)}}} \hat{C}^{(\mu)} \sqrt{\hat{Y^{(\mu)}}}.
\end{aligned} \tag{2.21}$$

The matrix $\hat{H}^{(\mu)}$ is singular, if

$$\det \left(1 - \sqrt{\hat{Y^{(\mu)}}} \hat{C}^{(\mu)} \sqrt{\hat{Y^{(\mu)}}} \right) = 0.$$

The last condition is satisfied for $\mu = 1$ in uniaxial fluids due to the obtained relation (2.9). Thus, the Goldstone modes are connected with the corresponding harmonics of the pair correlation function ($h_{mn0}^{110}(\vec{k} = 0)$). Since these harmonics are coupled with the transverse correlations of spins in magnets, the divergences $h_{mn0}^{110}(\vec{k} = 0) \to \infty$ are responsible for a long-range character of the above-mentioned correlations in the ordered phase.

3. Solution of the anisotropic OZ equation in the MSA for the classical Heisenberg ferromagnet

We consider the model that was proposed in [5]. This is the fluid of hard spheres of diameter σ with embedded Heisenberg spins, whose coupling constant is given by a Yukawa interaction:

$$v(1,2) = \begin{cases} \infty, & R < \sigma \\ J(R)\vec{s}_1 * \vec{s}_2, & R > \sigma \end{cases} \qquad (3.1)$$

with

$$J(R) = -K(z\sigma)^2 \frac{\exp(-zR)}{R/\sigma}, \qquad (3.2)$$

where $K > 0$ (ferromagnetic case), $\vec{s}_i$ being the unit vector describing the orientation of the spin in particle i. In other words $\vec{s}_1 * \vec{s}_2 = \cos\omega_{12}$, ω_{12} being the relative spin orientation. Let we note that in [5] $J(R)$ is chosen in a slightly different form $(J(R) = -3K\exp(-z(R-\sigma))/R)$.

For this model we shall solve the anisotropic OZ equation (2.16) with the MSA closure:

$$\begin{array}{lll} h(1,2) = -1 & \text{for} & R < \sigma \\ c(1,2) = -\beta v(1,2) & \text{for} & R > \sigma \end{array} , \qquad (3.3)$$

For the closure (3.3) the general form (2.1) is reduced [12] to the form:

$$\begin{aligned} c_2(R,\omega_1,\omega_2) &= c_{000}(R) + c_{100}(R)(Y_{10}(\omega_1) + Y_{10}(\omega_2)) + \\ &+ \sum_{|m| \leq 1} c_{11m}(R)Y_{1m}(\omega_1)Y_{1m}^*(\omega_2). \end{aligned} \qquad (3.4)$$

The expression for $h_2(R,\omega_1,\omega_2)$ is analogous. It should be noted that the structure of (3.4) is different from the one for the isotropic phase. In particular, in (3.4) there are the terms with $c_{100}(R)$.

For the expansion (3.4) the exact relations (2.9) and (2.13) can be written in a simple form:

$$1 = \rho\langle|Y_{11}(\omega)|^2\rangle_\omega \int c_{111}(R)\mathrm{d}\vec{R}, \qquad (3.5)$$

$$A_1 = \rho\langle Y_{10}(\omega)\rangle_\omega \int c_{111}(R)\mathrm{d}\vec{R}. \qquad (3.6)$$

On the other hand due to uniaxial symmetry of the ferromagnetic phase the equation (2.16) separates into the independent integral equations with different values of m. For $|m| = 1$ we get:

$$\begin{aligned} h_{11m}(R_{12}) &= c_{11m}(R_{12}) \\ &\quad + \rho\langle|Y_{1m}(\omega)|^2\rangle_\omega \int c_{11m}(R_{13})h_{11m}(R_{32})\mathrm{d}\vec{R}_3, \\ h_{11m}(R_{12}) &= 0, \ R_{12} < \sigma \\ c_{11m}(R_{12}) &= \beta K(z\sigma)^2\frac{\exp(-zR_{12})}{3R_{12}/\sigma}, \ R_{12} > \sigma. \end{aligned} \qquad (3.7)$$

The equations (3.7) and (3.5) constitute a complete system now. It allows to obtain $\langle|Y_{11}(\omega)|^2\rangle_\omega$ as a function of the model parameters βK, $z\sigma$ and $\eta = \pi\rho\sigma^3/6$. The solution (3.7) under the condition (3.5) means the calculation of the single-particle distribution function in the MSA. By the factorization method of Baxter (see [20,12,21]) the equation (3.7) for $m = 1$ results in the system of algebraic equations:

$$\frac{12}{3}\tilde{\eta}\beta K = \tilde{D}[1 - \tilde{Q}(z)], \qquad (3.8)$$

$$2\pi\tilde{g}_{111}(z)[1 - \tilde{Q}(z)] = \frac{1}{2}\exp(-2z\sigma)[1 - 2\pi\tilde{g}_{111}(z)]\tilde{D}, \qquad (3.9)$$

$$-\tilde{C} = [1 - 2\pi\tilde{g}_{111}(z)]\tilde{D}, \qquad (3.10)$$

where $\tilde{\eta} = \eta\langle|Y_{11}(\omega)|^2\rangle_\omega$, $\tilde{D}$ and $\tilde{C}$ are dimensionless coefficients of the factor correlation function:

$$Q(R) = \frac{z}{\rho\langle|Y_{11}(\omega)|^2\rangle_\omega}[Q_0(R) + \tilde{D}\exp(-zR)] \qquad (3.11)$$

with the short-range part

$$Q_0(R) = \tilde{C}[\exp(-zR) - \exp(-z\sigma)], \ R < \sigma \qquad (3.12)$$

$$Q_0(R) = 0, \ R > \sigma. \qquad (3.13)$$

$\tilde{Q}(z)$, $\tilde{g}_{111}(z)$ are the dimensionless Laplace transforms of $Q(R)$ and the harmonic of the pair correlation function $h_{111}(R)$:

$$\begin{aligned} \tilde{Q}(z) &= \rho\langle|Y_{11}(\omega)|^2\rangle_\omega \int_0^\infty e^{-zt}Q(t)\mathrm{d}t, \\ \tilde{g}_{111}(z) &= \frac{\rho\langle|Y_{11}(\omega)|^2\rangle_\omega}{z}\int_\sigma^\infty e^{-zt}h_{111}(t)t\mathrm{d}t. \end{aligned} \qquad (3.14)$$

From the definition of the factor correlation function it follows that

$$1 - \rho \langle |Y_{11}(\omega)|^2 \rangle_\omega \int c_{111}(R) d\vec{R} = [Q(k=0)]^2, \qquad (3.15)$$

where $Q(k)$ is defined by the expression:

$$Q(k) = 1 - \rho \langle |Y_{11}(\omega)|^2 \rangle_\omega \int_0^\infty dR e^{ikR} Q(R). \qquad (3.16)$$

The joint use of (3.15) and (3.5) gives us the additional equation to determine $\langle |Y_{11}(\omega)|^2 \rangle_\omega$:

$$Q(k=0) = 0, \qquad (3.17)$$

and in the explicit form

$$1 = \tilde{D} + k\tilde{C}, \qquad (3.18)$$

where $k = e^{-z\sigma} \Delta_1(z\sigma)$. Here and below we use the symbols

$$\Delta_n(x) = \exp(x) - \sum_{l=0}^n \frac{1}{l!} x^l. \qquad (3.19)$$

The formulae (3.18) and (3.9), (3.10) yield the expression for $\tilde{D}$:

$$\tilde{D} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \qquad (3.20)$$

where

$$a = -k \exp(-2z\sigma) - (k-1)\left(k - \Delta_0^2(-z\sigma)\right),$$
$$b = (k-1)c - k + \Delta_0^2(-z\sigma) + k\exp(-2z\sigma). \qquad (3.21)$$
$$c = 2k - \Delta_0^2(-z\sigma),$$

Now from the equation (3.8) we can obtain the dependence between the ordering parameter $\langle |Y_{11}(\omega)|^2 \rangle_\omega$ and the system parameters η, βK and $z\sigma$:

$$\beta K \eta \langle |Y_{11}(\omega)|^2 \rangle_\omega = \frac{1}{8} \tilde{D} \left[2 - \frac{\Delta_0^2(-z\sigma)}{k} - \tilde{D}\left(1 - \frac{\Delta_0^2(-z\sigma)}{k}\right) \right]. \qquad (3.22)$$

Substituting in (3.22) $\langle |Y_{11}(\omega)|^2 \rangle_\omega = 1$ we determine the loci of the Curie points in the temperature-density plane for the fixed $z\sigma$.

It follows from the (3.6) that the self-consistent $f(\omega)$ in the MSA has the form:

$$f(\omega) = const \exp\left(\langle Y_{10}(\omega) \rangle_\omega Y_{10}(\omega) / \langle |Y_{11}(\omega)|^2 \rangle_\omega\right). \qquad (3.23)$$

Using (3.23), (3.22) and definition (2.4) one can calculate all order parameters. For the order parameter $s_1 = \frac{1}{\sqrt{3}} \langle Y_{10}(\omega) \rangle_\omega$ Eq. (2.4) is rewritten as the well-known self-consistency equation:

$$s_1 = \coth(Ms_1) - \frac{1}{Ms_1}, \qquad (3.24)$$

where $M = \frac{3}{\langle |Y_{11}(\omega)|^2 \rangle_\omega}$.

For the equation with $m = 0$ that follows from (2.16) we obtain a more complicated expression. In the Fourier space it may be presented in matrix form:

$$\hat{H}(k) = \hat{C}(k) + \hat{C}(k)\hat{\rho}\hat{H}(k), \qquad (3.25)$$

where

$$\hat{H}(k) = \begin{pmatrix} h_{000}(k) & h_{010}(k) \\ h_{100}(k) & h_{110}(k) \end{pmatrix}, \ \hat{C}(k) = \begin{pmatrix} c_{000}(k) & c_{010}(k) \\ c_{100}(k) & c_{110}(k) \end{pmatrix},$$
$$\hat{\rho} = \rho \begin{pmatrix} 1 & \langle Y_{10}(\omega) \rangle_\omega \\ \langle Y_{10}(\omega) \rangle_\omega & \langle |Y_{10}(\omega)|^2 \rangle_\omega \end{pmatrix}. \qquad (3.26)$$

The closures of the correlation functions in the $\vec{R}$-space are as follows:

$$R < \sigma: \qquad h_{000}(R) = -1, \text{ the other harmonics are equal to 0;}$$
$$R > \sigma: \qquad c_{110}(R) = \frac{\beta K(z\sigma)^2 \sigma}{3} \frac{\exp(-zR)}{R}, \text{ the others equal 0.}$$

Since the elements of the matrix $\hat{\rho}$ are calculated from (2.4) one can solve Eq. (3.25) now with the Baxter factorization technique in the usual way. A detailed discussion of the factorization method can be found elsewhere and therefore we omit any details and refer the reader to the previous publications [12,20,21].
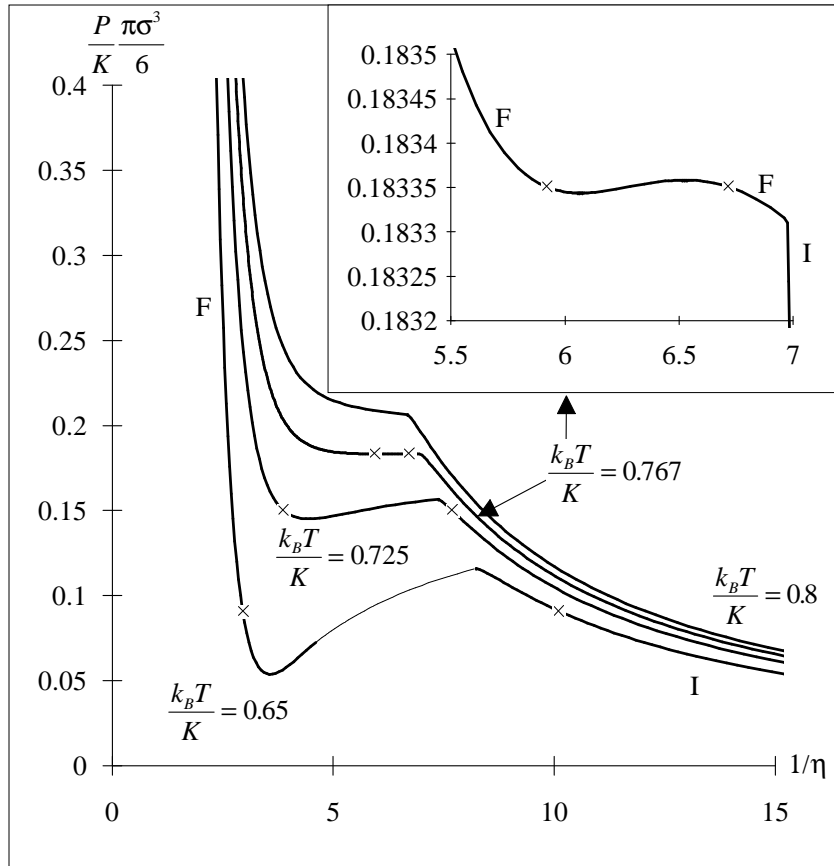
Figure 1. Pressure-volume isotherms of the Heisenberg fluid with $z\sigma = 1$, in reduced units, as obtained by the virial theorem at $\frac{k_B T}{K} = 0.8$, 0.767, 0.725 and 0.65. Both isotropic (I) and ferromagnetic (F) branches are shown. Solid lines are the theoretical results, the thin line is a spline. The break points of the isotherms correspond to the Curie points. The crosses are the points of the gas-liquid coexistence obtained with the Maxwell construction. On the inset the isotherm $\frac{k_B T}{K} = 0.767$ is shown (detail).

4. Phase diagram of the Heisenberg fluid

In order to determine the gas-liquid equilibrium we should have thermodynamically consistent expressions for the pressure and chemical potential. For the MSA in the isotropic phase there are three thermodynamically consistent approaches obtained via: 1) the compressibility relation, 2) the virial theorem, 3) the internal energy [22]. But the results of the remarkable paper of Høye and Stell are not applicable for the case of anisotropic phases. A derivation of the thermodynamically consistent pressure and chemical potential for the anisotropic MSA is a problem for a special serious investigation. In this paper we shall avoid this problem using the generally known Maxwell construction.

The virial theorem provides the most convenient way to calculate pressure on the basis of the MSA results obtained in the previous section:

$$P_v = \rho k_B T - \frac{\rho^2}{6} \int \mathrm{d}\vec{R}_{12} d\omega_1 d\omega_2 R_{12} \frac{\partial v(1,2)}{\partial R_{12}} f(\omega_1)(1 + h(1,2))f(\omega_2).$$

In Fig. 1 we present pressure-density isotherms of the model with $z\sigma = 1$ at different temperatures ($\frac{k_B T}{K} = 0.8, 0.767, 0.725, 0.65$). **I** marks the isotropic branch, **F** denotes the ferromagnetic one. At $\frac{k_B T}{K} = 0.8$ the orientational (ferromagnetic) phase transition of the second order takes place in the system. The break point of the isotherm is a locus of the Curie point. At $\frac{k_B T}{K} = 0.725$ the orientational phase transition is coupled with a condensation. The crosses are the points of the gas-liquid coexistence obtained with the Maxwell rule of areas. The coexisting densities are $\eta_I = 0.130$, $\eta_F = 0.259$. In the range between these densities there is the two-phase region. We note that one should not expect a physical solution of the anisotropic OZ equation (2.16) in the whole two-phase region, because Eq. (2.16) describes spatially uniform systems. Indeed, at low temperatures (e. g. $\frac{k_B T}{K} = 0.65$) the nonsolution domain appears, and we interpolate the isotherm behaviour in this domain with splines. In Fig. 1 the spline for the isotherm at $\frac{k_B T}{K} = 0.65$ is depicted by a thin line. At this temperature the coexisting densities are $\eta_I = 0.099$, $\eta_F = 0.339$.

The isotherm at $\frac{k_B T}{K} = 0.767$ is of special interest. It allows us to determine the type of criticality in this model. In Fig. 1 the inset allows to discern the sequence of phase transitions at this temperature. At the lower η the order-disorder transition of the second order occurs. The break between **I** and **F** branches is its manifestation. At the greater η the phase transition ferrogas-ferroliquid of the first order takes place (coexisting densities are $\eta_{\mathbf{F}\mathrm{gas}} = 0.149$ and $\eta_{\mathbf{F}\mathrm{liq}} = 0.168$). Thus, the
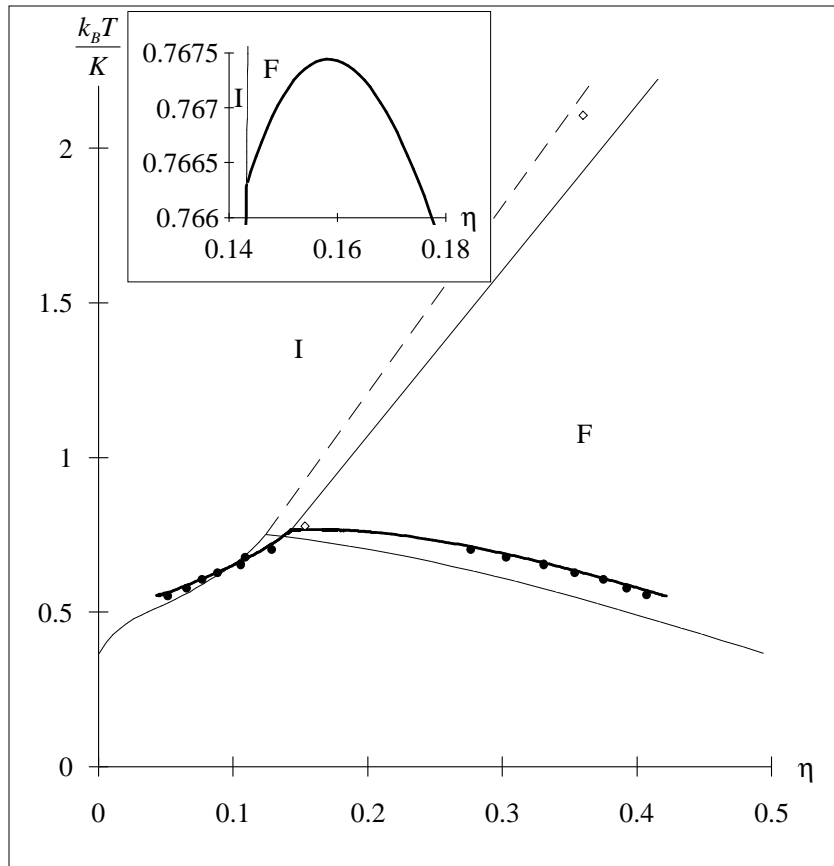
Figure 2. Phase diagram for the Heisenberg fluid in reduced temperature-density units, with parameter $z\sigma = 1$. I and F mean isotropic and ferromagnetic phases. The gas-liquid coexistence and the Curie points obtained in the MSA are given as thick and thin lines respectively. On the inset the vicinity of the magnetic critical point is depicted (the MSA results). The dashed lines are results of the MMF theory [7]. It should be noted that $\frac{k_B T}{K}$ equals $\frac{T^*}{3e}$ from Ref. [5] (or T^*/e from Ref. [7]). The diamonds correspond to the Monte-Carlo results of Lomba et. al. [5] for the Curie points. Gibbs ensemble simulations for the gas-liquid coexistence [5] are represented by solid circles.

MSA with virial route to thermodynamics suggests the existence of the magnetic critical point. Now let us consider the compressibility route to thermodynamics. In the isotropic MSA the orientational and spatial contributions to the pair correlations are decoupled to the point that the structure factor of our model reduces to that of the hard sphere fluid. Therefore, within this route the compressibility of the model is finite in the whole isotropic phase including its boundary (the Curie line). In the MSA for an anisotropic phase the spatial distribution (the structure factor) depends on the order parameter and does not coincide with that of the hard sphere fluid [23]. Therefore, a gas-liquid critical point can be located only in an anisotropic phase in principle. Thus, the compressibility route also excludes the existence of the tricritical point. One can see that the MSA is in marked disagreement with the mean field and the MMF theories and supports available simulation results [5,9] on the criticality of the system.

It should be noted, that in [7,9] the treatment of critical behaviour was done by stability analysis of the free energy functional adopted in the MMF approximation. For a pity, such general analysis of the free energy functional on the MSA level is a much more complex problem, if it is possible at all. The point is that the MSA pair correlation function is sensitive to the density and the ordering in the system in opposite to any mean field approach. Therefore, we are forced to calculate the correlation functions in the MSA for each model individually, whereas in the MMF one uses the simple Ansatz (namely a zero-density approximation) for the pair correlation function:

$$h(1,2) = \exp(-\beta v(1,2)) - 1$$

Figure 2 shows the temperature-density phase diagram of the model ($z\sigma = 1$). Also included for the sake of comparison are the MMF results (dashed lines) as well as the Gibbs ensemble Monte-Carlo results of the Lomba et al [5] for the gas-liquid coexistence (solid circles) and their estimates of the Curie points by the canonical ensemble Monte Carlo (diamonds). It follows from the figure that at high temperatures we have the second order phase transition paramagnet-ferromagnet. The Curie points of the MSA [2] are represented by the straight (thin) line in Fig. 2. The agreement between theory and simulation (diamonds) is satisfactory, though in [5] it is noted that the Monte Carlo estimates of the Curie temperature are not accurate enough. A more precise Monte Carlo location of the Curie line is possible for very short-range potentials, e. g., for the Yukawa interaction truncated at 2.5 hard sphere diameters [8,9].

There is the first order phase transition at low temperatures. The equilibrium between the paramagnetic gas and ferromagnetic liquid takes place. But near the gas-liquid critical point only ordered states are involved in the gas-liquid transition (see the inset to Fig. 2). The magnetic critical point has coordinates $\frac{k_B T}{K} = 0.7674$, $\eta = 0.16$. Thus within the MSA the system will lack a tricritical point and the line of Curie points will end up on the vapour side of the gas-liquid coexistence curve. This result confirms available simulations. One can see in Fig. 2 that quantitative agreement between the theory and simulation [5] (solid circles) is quite perfect.

5. Summary

In this paper we have obtained the analytical solution for the fluid of hard spheres with interparticle spin interactions of classical Heisenberg symmetry (3.1). The analytical results in the MSA for the ferromagnetic phase is represented by a system of algebraic equations.

Our method is based on the self-consistent solution of the anisotropic Ornstein-Zernike and the Lovett equations. This approach does not impose any approximations other than a closure for the OZ equation. It correctly treats the Goldstone modes and can be used for any uniaxial fluid. A principal difference of our approach from the early studies in the anisotropic fluid theory [19,17] is the rejection of the complete rotational invariance form [16] for the anisotropic (ferromagnetic) correlation functions. This allows us to treat correctly a system symmetry and to get rid of noncontrollable procedures like the rotational average of correlation functions [17,19].

Using the pair correlation function (in the MSA) the phase diagram of the considered model ($z\sigma = 1$) has been obtained. The calculation is based on the virial theorem and the Maxwell construction. The temperature-density phase diagram shows that at high temperatures the second order ferromagnetic phase transition takes place. At low temperatures there is the gas-liquid transition. This transition could not be analyzed by the integral equation methods before since it involves anisotropic phases, where the isotropic OZ equation does not have any physical sense. For the MSA the invalidity of the isotropic solution manifests in the fact that the real solution of the isotropic OZ equation disappear. But the anisotropic OZ equation does have real solution in the anisotropic phase for any reasonable closure (including the MSA). The anisotropic MSA provides the consistent treatment of correlations in both the phases, and it is of great importance in the vicinity of critical points, where the fluctuations are large. Probably, due to this the MSA phase diagram is in whole agreement with available [5] simulations: the liquid phase is ferromagnetic and the gas phase is mainly paramagnetic, except in the neighbourhood of the critical point, where the transition ferroliquid-ferrogas takes place. The MSA via virial and compressibility routes to thermodynamics demonstrate the lack of tricritical point for the model (3.1) in opposite to the MMF theory [7]. We have compared the calculated phase diagram with the Monte Carlo simulation [5] for the same model. The agreement between our theory and the available simulations is quite remarkable, especially for the liquid-gas coexistence line.

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