XY Spin Fluid in an External Magnetic Field

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A method of integral equations is developed to study anisotropic fluids with planar spins in an external field. As a result, the calculations for these systems appear to be no more difficult than those for ordinary homogeneous liquids. The approach proposed is applied to the ferromagnetic *XY* spin fluid in a magnetic field using a soft mean spherical closure and the Born-Green-Yvon equation. This provides an accurate reproduction of the complicated phase diagram behavior obtained by cumbersome Gibbs ensemble simulation and multiple histogram reweighting techniques.

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Spin fluids are examples of many body systems showing a *rich* variety of phases in the global phase diagram [1–4]. Besides gas-liquid (G-L), liquid-liquid (L-L), and paramagnetic-ferromagnetic (P-F) phase transitions, tricritical, critical end, and triple point behavior is observed. Under special (van Laar) conditions, an unsymmetrical tricritical point exists additionally [5]. This complexity arises due to a *coupling* between spin and spatial interactions. Similar phase diagrams are found in binary mixtures [6–10] with their demixing and G-L transitions, spin lattice gas models [11,12], mixtures of ^{3}He-^{4}He with the superfluid and demixing transitions [13–15], and others.

The properties of spin fluids were studied using mean field (MF) theories [1–4], more accurate integral equation (IE) approaches [5,16–20], and Monte Carlo (MC) simulation techniques [4,16,19,21–24]. Different types of models, such as the well-known discrete 1D spin Ising, or continuous 2D spin *XY* and 3D Heisenberg fluids, have been considered. Despite this, the question concerning the global phase diagram topology of the *XY* spin fluid including the influence of an external magnetic field has *never* been addressed. Moreover, the IE approach has been restricted either to simplified (ideal) Heisenberg fluids [16–20] or to Ising models [5].

Surprisingly, up to now there have been *no* attempts to develop the IE approach for the *XY* spin fluid model. This model may play a crucial role in the description of superfluid transitions in pure ^{4}He and its mixtures in bulk or in media such as porous gold [15] or silica aerogel [25]. It is generally believed [25] that the superfluid transition in ^{4}He belongs to the classical 3D *XY* model universality class (here 3D relates to the dimensionality of spatial coordinates). On the other hand, the fluid of particles with embedded *XY* spins can be treated as one of the simplest models of disordered continuum systems exhibiting ferromagnetic behavior.

The presence of spin interactions and external fields destroys the orientational homogeneity of the fluid, producing nonuniformity or *anisotropy* in the one-body density. Within the standard IE approach this leads to the necessity of performing very complicated joint calculations for one- and two-body distribution functions on the basis of the coupled set of the *anisotropic* Ornstein-Zernike (AOZ) equation, a closure relation, and the first equation of the Born-Green-Yvon (BGY) hierarchy [26]. Such calculations result in *unresolvable* numerical difficulties because of the restricted capabilities of modern supercomputers. Existing IE developments for Ising [5] and Heisenberg [16–20] systems are not applicable to the *XY* fluid, since neither can it be mapped onto a binary nonmagnetic mixture nor its anisotropic correlations be expanded in spherical harmonics. The specific *XY* spin interactions require a separate IE investigation.

Consider an *XY* spin fluid model with the Hamiltonian

$$U = \sum_{i<j}^{N} [\phi(r_{ij}) - I(r_{ij}) - J(r_{ij}) \mathbf{s}_i \cdot \mathbf{s}_j] - \mathbf{H} \cdot \sum_{i=1}^{N} \mathbf{s}_i, \quad (1)$$

where N is the total number of particles, $\mathbf{r}_i$ is the 3D spatial coordinate of the ith body carrying 2D spin $\mathbf{s}_i$ of unit length, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the interparticle separation, and $\mathbf{H}$ is the external magnetic field vector lying like $\mathbf{s}_i$ in the *XY* plane. The exchange integral J of ferromagnetic interactions and the nonmagnetic attraction potential I can be chosen in the form of Yukawa functions,

$$J(r) = \frac{\epsilon\sigma}{r} \exp\left(-\frac{r-\sigma}{\sigma}\right), \qquad I(r) = \frac{J(r)}{R}, \quad (2)$$

where ϵ and σ denote the interaction intensity and the size of the particles, respectively, with R being the ratio defining the relative strength of J to I. The repulsion ϕ between particles can be modeled by a more realistic soft-core (shifted Lennard-Jones) potential [4,5],

$$\phi(r) = \begin{cases} 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] + \epsilon, & r < \sqrt[6]{2}\sigma, \\ 0, & r \geq \sqrt[6]{2}\sigma, \end{cases} \quad (3)$$

rather than by the hard-sphere one.

A complete thermodynamic and magnetic description of system (1) can be performed in terms of orientationally dependent one-body $\xi(\varphi)$ and two-body $g(r, \varphi_1, \varphi_2) = h(r, \varphi_1, \varphi_2) + 1$ distribution functions. The angles φ are

referred to spin directions with respect to $\mathbf{H}$, so that $\mathbf{H}\cdot\mathbf{s} = H\cos\varphi$ and $\mathbf{s}_1\cdot\mathbf{s}_2 = \cos(\varphi_1 - \varphi_2)$. According to the liquid state theory [26], the total correlation function h satisfies the AOZ equation which in our case reads

$$h(r, \varphi_1, \varphi_2) = c(r, \varphi_1, \varphi_2) + \frac{\rho}{2\pi}\int_V d\mathbf{r}' \int_0^{2\pi} d\varphi \xi(\varphi) \times c(|\mathbf{r} - \mathbf{r}'|, \varphi_1, \varphi) h(r', \varphi, \varphi_2), \quad (4)$$

where $\rho = N/V$ is the particle number density, V is the volume, and $c(r, \varphi_1, \varphi_2)$ is the direct correlation function (note that a positionally homogeneous and orientationally anisotropic system is being investigated).

The AOZ equation (4) must be complemented by a closure relation. The most general form of it is

$$g = \exp(-\beta u + h - c + B), \quad (5)$$

where $u(r, \varphi_1, \varphi_2) = \phi(r) - I(r) - J(r)\cos(\varphi_1 - \varphi_2)$ with $\beta^{-1} = k_B T$ being the temperature, and B is the bridge function. It cannot be determined exactly for *any* system of interacting particles, but a lot of approaches exist allowing us to present it approximately [26]. One way is to use the soft mean spherical approximation (SMSA) [5,27]

$$B(r, \varphi_1, \varphi_2) = \ln[1 + \tau(r, \varphi_1, \varphi_2)] - \tau(r, \varphi_1, \varphi_2), \quad (6)$$

where $\tau = h - c - \beta u_1$. The long-ranged part u_1 can be extracted [5] from the total potential u as $u_1(r, \varphi_1, \varphi_2) = -[I(r) + J(r)\cos(\varphi_1 - \varphi_2)]\exp[-\beta\phi(r)]$.

Evaluation of pair correlations from AOZ equation (4) requires the knowledge of $\xi(\varphi)$. The latter is obtained from the first member of the BGY hierarchy [26],

$$\frac{d}{d\varphi}\ln\xi(\varphi) = \frac{d}{d\varphi}\beta H\cos\varphi - \beta\frac{\rho}{2\pi} \times \int_V d\mathbf{r}\int_0^{2\pi} d\varphi' \xi(\varphi') g(r, \varphi, \varphi') \times \frac{du(r, \varphi, \varphi')}{d\varphi'}. \quad (7)$$

Equations (4), (5), and (7) constitute a very complicated set of coupled AOZ-SMSA-BGY nonlinear integro-differential equations with respect to h (or g), c, and ξ. The main problem in solving it is that the unknowns h and c depend on up to three variables. This leads to unresolvable numerical difficulties, and thus a method is needed to remedy such a situation.

Any periodic function of two angle variables can be expanded in sine and cosine harmonics as

$$f(r, \varphi_1, \varphi_2) = \sum_{n,m=0}^{\infty}\sum_{l,l'=0,1} f_{nmll'}(r) T_{nl}(\varphi_1) T_{ml'}(\varphi_2) \quad (8)$$

using the orthogonal Chebyshev polynomials $T_{n0}(\varphi) = \cos(n\varphi)$ and $T_{n1}(\varphi) = -\frac{1}{n}dT_{n0}(\varphi)/d\varphi = \sin(n\varphi)$. Expansion (8) can readily be applied to our two-body functions $\{h, g, c\} \equiv f$ with the simplification $f_{nmll'} = f_{nml}\delta_{ll'}$ because they are invariant with respect to the transformation $(\varphi_1, \varphi_2) \leftrightarrow (-\varphi_1, -\varphi_2)$ in view of the symmetry of Hamiltonian (1). Then exploiting the orthonormality condition $\int_0^{2\pi} T_{nl}(\varphi) T_{ml'}(\varphi) d\varphi = t_n \delta_{nm}\delta_{ll'}$, where $t_n = \pi(1 - \delta_{n0}) + 2\pi\delta_{n0}$, yields the expansion coefficients

$$f_{nml}(r) = \frac{1}{t_n t_m}\iint f(r, \varphi_1, \varphi_2) T_{nl}(\varphi_1) T_{ml}(\varphi_2) d\varphi_1 d\varphi_2. \quad (9)$$

In terms of these coefficients the AOZ equation (4) reduces to

$$h_{nml}(k) = c_{nml}(k) + \rho\sum_{n',m'} c_{nm'l}(k)\xi_{n'm'l} h_{n'ml}(k), \quad (10)$$

where $\xi_{nml} = \frac{1}{2\pi}\int_0^{2\pi}\xi(\varphi) T_{nl}(\varphi) T_{ml}(\varphi) d\varphi$ are the moments of $\xi(\varphi)$, and the 3D Fourier transform $f(k) = \int_V f(r)\exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{r}$ has been used. The algebraic representation (10) looks like the OZ equation corresponding to a mixture of simple homogeneous fluids of *nonmagnetic* particles. This is a very important feature because the problem can now be solved by adapting algorithms already *known* for isotropic systems.

Furthermore, we perform the one-body polynomial expansion

$$\ln\xi(\varphi) = \beta H\cos\varphi + \sum_{n=0}^{\infty} a_n T_{n0}(\varphi), \quad (11)$$

where only cosine harmonics appear due to the property $\xi(-\varphi) = \xi(\varphi)$. Then the cumbersome integro-differential equation (7) is able to be solved analytically,

$$a_n = \frac{\beta\rho}{2n}\int d\mathbf{r}\sum_{\substack{m=0\\ l,l'=0,1}}^{\infty}(-1)^{l+l'}\xi_{m1l} g_{\tilde{n}ml}(r) J(r) \quad (12)$$

for $n \geq 1$, where $\tilde{n} = n - 1 + 2l'$, while the coefficient a_0 is determined from the normalization $\frac{1}{2\pi}\int_0^{2\pi}\xi(\varphi) d\varphi = 1$.

Handling the SMSA closure (5) also presents no difficulties, because for distances $r \geq 2^{1/6}\sigma$ [where $\phi(r) = 0$] we obtain from Eqs. (5) and (6) that $c(r, \varphi_1, \varphi_2) = \beta[I(r) + J(r)\cos(\varphi_1 - \varphi_2)]$. Taking into account the equality $\cos(\varphi_1 - \varphi_2) = T_{10}(\varphi_1)T_{10}(\varphi_2) + T_{11}(\varphi_1) \times T_{11}(\varphi_2)$, one finds $c_{000}(r) = \beta I(r)$ and $c_{110}(r) = c_{111}(r) = \beta J(r)$, while all other c coefficients are equal to zero at $r \geq 2^{1/6}\sigma$. For $r < 2^{1/6}\sigma$, we should perform a numerical integration [see Eq. (9)] of the right-hand side of Eq. (5) in order to obtain the expansion coefficients $g_{nml}(r)$.

Another important feature is that only a *small* number $\mathcal{N}$ of harmonics should be, in fact, involved because the expansion coefficients rapidly tend to zero with increasing $\mathcal{N}$. Then the sums $\sum_{n,m}^{\infty}$ can be replaced without loss of precision by finite ones with $n, m \leq \mathcal{N}$. In our case the anisotropic potential is presented by zeroth and first harmonics [see above the expansion for $\cos(\varphi_1 - \varphi_2)$], while a slight anharmonicity ($\mathcal{N} > 1$) in the correlation functions appears due to the nonlinearity of the closure.

Once the expansion coefficients are found, *all* the magnetic and thermodynamic properties of the system are obtained in a straightforward way. In particular, the magnetization is $M = \frac{1}{2\pi}\int_0^{2\pi}\cos(\varphi)\xi(\varphi)d\varphi \equiv \xi_{100}$, while the pressure P can be calculated from the virial equation

$$\frac{\beta P}{\rho} = 1 - \frac{1}{6}\frac{\beta\rho}{(2\pi)^2}\int d\mathbf{r}d\varphi_1 d\varphi_2 \xi(\varphi_1)\xi(\varphi_2)g(r,\varphi_1,\varphi_2)r\frac{du(r,\varphi_1,\varphi_2)}{dr}$$
$$= 1 - \frac{\beta\rho}{6}\sum_{n,m}\int r d\mathbf{r}\left[\frac{d[\phi(r)-I(r)]}{dr}\xi_{n00}\xi_{m00}g_{nm0}(r) - \frac{dJ(r)}{dr}\sum_{l=0,1}\xi_{n1l}\xi_{m1l}g_{nml}(r)\right]. \quad (13)$$

The coupled set of OZ-SMSA-BGY equations (5), (10), and (12) was solved by adapting the algorithm used in Ref. [5]. The integration in angle variables has been performed by Gauss-Chebyshev quadratures. The number of harmonics involved was $\mathcal{N} = 3$. A further increase of $\mathcal{N}$ does not affect the solutions. The phase coexistence densities between gas and liquid states has been evaluated by applying the well-known Maxwell construction to Eq. (13). The P-F transition has been determined as a boundary (Curie) curve in the temperature-density plane, where nonzero (spontaneous) magnetization $M \neq 0$ becomes possible at $H = 0$. Other computational details are similar to those of Ref. [5] when solving the Ising IEs. The dimensionless quantities $\rho^* = \rho\sigma^3$, $T^* = k_B T/\epsilon$, and $H^* = H/\epsilon$ were chosen in the presentation of the results.

The simulations were carried out using the Gibbs ensemble MC (GEMC) [28] and multiple histogram reweighting (MHR) [29] techniques for evaluating the G-L and L-L coexistences, while the Binder crossing scheme [24,30] was utilized to determine the P-F magnetic transition (at $H = 0$). Other simulation details are similar to those reported in Refs. [4,5,24].

We first compare in Fig. 1 the OZ-SMSA-BGY results for the *ideal XY* fluid at different external fields H with the GEMC and MHR simulation data {according to the classification of Refs. [3,5], the term "*ideal*" indicates here a simplified model with the nonmagnetic attractive interaction switched off, $I(r) = 0$ [see Eqs. (1) and (2)], i.e., $R = \infty$}. At $H = 0$, a tricritical (TC) point separates the second order P-F magnetic phase transition line from the first order transition between a P gas and an F liquid. The H dependence of the G-L critical temperature and density is *nonmonotonic*. Samples of the MF binodals are included in Fig. 1 as well to demonstrate the obvious advantage of the IE theory. These samples were obtained [for $I(r) = 0$] on the basis of a soft-core version of the MF theory introduced recently by us in Ref. [4]. Note that contrary to the theoretical binodals, the GEMC and MHR coexistence curves break up when approaching the critical regions. This is because of the appearance of huge density fluctuations which cannot be properly handled within finite simulation boxes. The MHR technique allows us to approach to critical points more closely (see Fig. 1) and should be considered as more preferable than the GEMC method.

The OZ-SMSA-BGY and MHR phase diagrams of the *nonideal XY* fluid are shown in Figs. 2 and 3 for different ratios R and magnetic fields H. *Four* types of phase diagram topology can be identified overall. For large $R \geq 0.415$ (type I), the system exhibits an *ideal-like* behavior with the existence of a TC point at $H = 0$ and G-L transitions at $H \neq 0$ for each R [Fig. 2(a)]. At moderate values $0.26 < R < 0.415$ (type II), the transition between a P liquid and an F liquid arises at $H = 0$ *additionally* to the transition between a P gas and a P liquid. Here a triple point (TP) *occurs,* too, where a rare P gas, a moderately dense P liquid, and a highly dense F liquid all coexist at the same T and P [see Figs. 2(b) and 3(a)]. The TPs can *exist* at $H \neq 0$ as well and describe then the phase coexistence between a weakly magnetized gas, a moderately magnetized liquid, and a strongly magnetized liquid [Fig. 3(b)]. With increasing H, either the G-L ($0.376 < R < 0.415$, type IIa) or L-L ($0.26 < R < 0.376$, type IIb) critical line *terminates* in a critical end (CE) point at some finite H. For instance, even if R is slightly smaller than the boundary value $R_{vL} = 0.376$, namely, $R = 0.37$, the L-L critical line ends (type IIb) at some $H^* \sim 1$ [Fig. 3(a)], while the G-L

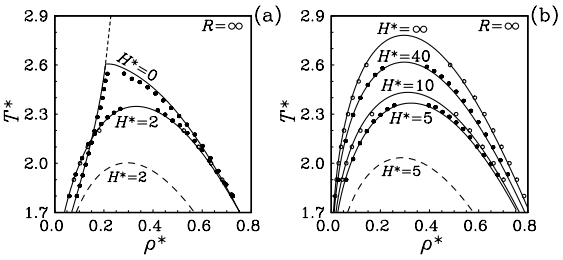

FIG. 1. The G-L binodals obtained for the ideal ($R = \infty$) *XY* fluid within the OZ-SMSA-BGY approach (full curves) versus the GEMC (open circles) and MHR (full circles) simulation data. The P-F transition is plotted by the short-dashed line. The MF samples are shown by long-dashed curves.

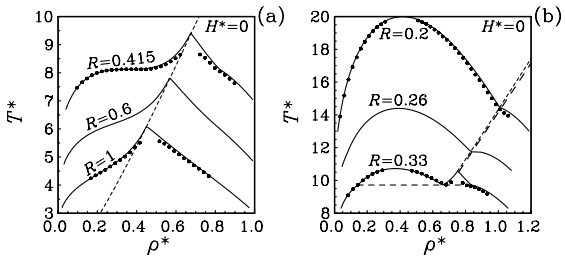

FIG. 2. The G-L and L-L binodals of the nonideal *XY* fluid within the OZ-SMSA-BGY approach (full curves) versus the MHR data (circles). The P-F transition is plotted by the short- (theory) and long- (simulation) dashed curves. The triple point is represented by the horizontal dashed line.

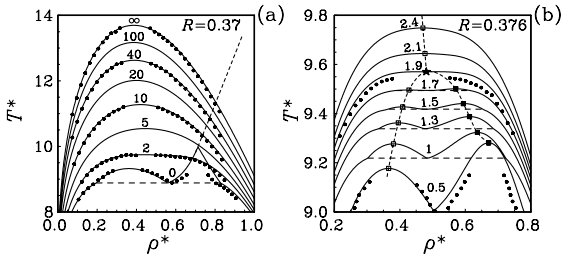

FIG. 3. The binodals near (a) and at (b) the boundary value $R = R_{\mathrm{vL}}$. The G-L and L-L critical points are shown in subset (b) for different H^* as open and full squares, respectively, connected by dashed curves. The curves meet in the TC point (star). Other notations are the same as for Fig. 2.

critical line extends to infinite field. In the special case $R = R_{\mathrm{vL}}$, the G-L and L-L critical lines *merge* into the TC van Laar point at $H^* = 1.9$ [Fig. 3(b)]. For small $R \leq 0.26$ (type III), the spatial interaction dominates over the spin one, preserving the G-L transition, whereas the TC point at $H = 0$ *transforms* into a CE point [Fig. 2(b)]. For $H \rightarrow \infty$, the system at any R behaves like a *simple* fluid with $u(r) = \phi(r) - I(r) - J(r)$ (then all the spins align along **H**).

As can be seen, the agreement between the theory proposed and the simulations is *quite* satisfactory. Slight deviations appear only in the vicinity of critical points. This is explained by finite size effects in the simulations and an approximate character of the SMSA closure used in the theory. For the latter reason, the classical value $\beta = 1/2$ of the critical exponent describing the G-L binodal behavior $|\rho - \rho_{\mathrm{c}}| \sim |T - T_{\mathrm{c}}|^{\beta}$ near the criticial point $(\rho_{\mathrm{c}}, T_{\mathrm{c}})$ is recovered (in particular, at $R = \infty$ and $H \neq 0$), instead of the value $\beta \approx 1/3$ known from the renormalization group analysis [31]. On the other hand, the crossover to the TC value $\beta = 1/4$ can be observed near the van Laar point at $R = 0.376$ and $H^* = 1.9$ [Fig. 3(b)].

More precise IE calculations near critical points are *possible* provided a more accurate closure is used. For instance, the self-consistent OZ ansatz [7–9] (which in its present formulation was implemented only for simple isotropic hard-sphere Yukawa systems) can be *extended* to our anisotropic soft-core XY fluid by introducing a state dependent function $K(\rho, T, H)$ as a multiplier at the inverse temperature in the SMSA closure [Eqs. (5) and (6)]. Then K is determined by the requirement of thermodynamic *consistency* between the energy and compressibility routes. In view of the anisotropy and softness, this leads to a significant sophistication of the calculations. They go beyond the scope of the present Letter and will be considered elsewhere.

In conclusion, we point out that a *novel* technique to study orientationally ordered fluids with planar spins has been proposed. It combines the standard IE method with the appropriate expansions of the anisotropic correlation functions in terms of orthogonal polynomials. This reduces the calculations to those inherent in a homogeneous mixture of simple monoatomic fluids and thus presents now *no* numerical difficulties. Detailed comparisons with our simulations have shown that the proposed approach is powerful enough to give a *quantitative* description of phase transitions in the XY spin fluid systems.

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