Integral Equation Approach for XY Spin Fluids in an External Magnetic Field

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TASK

Development of an integral equation (IE) approach for anisotropic fluids with planar spins. Evaluation of phase diagrams for ferromagnetic XY spin fluid models with different ratios R of strengths of magnetic to nonmagnetic interactions in an external field H. Classification of the phase diagram topology. Determination of the dependence of the critical temperature and density of the gas-liquid (G–L) and liquid-liquid (L–L) transitions on H and R. Comparison with Gibbs ensemble Monte Carlo (GEMC) and histogram reweighting (HR) techniques.

METHOD

The IE method of anisotropic Ornstein-Zernike (AOZ) equations is used in tandem with proper expansions of the anisotropic correlation functions in terms of orthogonal polynomials. The Born-Green-Yvon (BGY) equation and soft mean spherical approximation (SMSA) for the closure are also applied. The resulting integro-differential equations are solved by utilizing an algorithm basing on the method of modified direct inversion in the iterative subspace.

MOTIVATION

Up to now there were *no* attempts to develop the IE approach for the XY spin fluid model. 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 as well.

PROBLEM

- How to map the XY AOZ equations to those of ordinary isotropic fluids?
- What is the total number of types of the XY phase diagram topology?
- How depend the G–L and L–L critical temperatures and densities on H at given R?

MODEL

Consider an XY spin fluid model with the Hamiltonian

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

where $\mathbf{s}_i\in$ 2D XY and $\mathbf{r}_i\in$ 3D. The exchange integral J of ferromagnetic interactions and the nonmagnetic attraction potential I are chosen in the form of Yukawa functions,

$$J(r)=\frac{2(z_1\sigma)^2}{1+z_1\sigma}\frac{\epsilon\sigma}{r}\exp[-z_1(r-\sigma)]\,,\qquad I(r)=\frac{2(z_2\sigma)^2}{1+z_2\sigma}\frac{\epsilon\sigma}{r}\exp[-z_2(r-\sigma)]/R$$

with

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

being the soft-core Lennard-Jones-like repulsion potential.
A complete description of the system 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 which are connected with the direct correlation function $c(r,\varphi_1,\varphi_2)$ by the AOZ equation

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

where $\rho=N/V$, and angle φ is defined as $\cos\varphi=\mathbf{H}\cdot\mathbf{s}/H$, so that $\mathbf{s}_1\cdot\mathbf{s}_2=\cos(\varphi_1-\varphi_2)$.

THEORY

The functions $\{h,g,c\}\equiv f$ are periodic with respect to two angle variables and thus can be expanded in sine and cosine harmonics as

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

using the orthogonal Chebyshev polynomials $T_{n0}(\varphi)=\cos(n\varphi)$ and $T_{n1}(\varphi)=\sin(n\varphi)$ with the simplification $f_{nmll'}=f_{nml}\delta_{ll'}$ following from the invariance of f to the transformation $(\varphi_1,\varphi_2)\leftrightarrow(-\varphi_1,-\varphi_2)$ in view of the symmetry of Hamiltonian, where $f_{nml}(r)=\frac{1}{t_nt_m}\iint f(r,\varphi_1,\varphi_2)T_{nl}(\varphi_1)T_{ml}(\varphi_2)\mathrm{d}\varphi_1\mathrm{d}\varphi_2$ and $t_n=\pi(1-\delta_{n0})+2\pi\delta_{n0}$.
Then the AOZ equation reduces to

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

where $\xi_{nml}=\frac{1}{2\pi}\int_0^{2\pi}\xi(\varphi)T_{nl}(\varphi)T_{ml}(\varphi)\mathrm{d}\varphi$ are the moments of $\xi(\varphi)$, and the 3D Fourier transform $f(k)=\int_V f(r)\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\mathrm{d}\mathbf{r}$ has been used. It looks like the OZ equation corresponding to a mixture of simple homogeneous fluids. 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 $\ln\xi(\varphi)=\beta H\cos\varphi+\sum_{n=0}^{\infty}a_nT_{n0}(\varphi)$. Then the cumbersome integro-differential BGY equation

$$\beta^{-1}\frac{\mathrm{d}}{\mathrm{d}\varphi}\ln\xi(\varphi)=\frac{\mathrm{d}}{\mathrm{d}\varphi}H\cos\varphi-\frac{\rho}{2\pi}\int_V\mathrm{d}\mathbf{r}\int_0^{2\pi}\mathrm{d}\varphi'\xi(\varphi')g(r,\varphi,\varphi')\frac{\mathrm{d}u(r,\varphi,\varphi')}{\mathrm{d}\varphi'}$$

for $\xi(\varphi)$, where $\beta^{-1}=k_{\mathrm{B}}T$ is the temperature, allows to be solved in quadratures,

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

where $n\geq1$, while a_0 is determined from the normalization $\frac{1}{2\pi}\int_0^{2\pi}\xi(\varphi)\mathrm{d}\varphi=1$.
In the next step, we introduce the closure relation

$$g(r,\varphi_1,\varphi_2)=\exp\big[-\beta u(r,\varphi_1,\varphi_2)+h(r,\varphi_1,\varphi_2)-c(r,\varphi_1,\varphi_2)+B(r,\varphi_1,\varphi_2)\big]\,,$$

where the bridge function is cast in the SMSA form

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

Here $\tau(r,\varphi_1,\varphi_2)=h(r,\varphi_1,\varphi_2)-c(r,\varphi_1,\varphi_2)-\beta u_{\mathrm{lr}}(r,\varphi_1,\varphi_2)$ is the modified indirect correlation function and $u_{\mathrm{lr}}(r,\varphi_1,\varphi_2)=-[I(r)+J(r)\cos(\varphi_1-\varphi_2)]\exp[-\beta\phi(r)]$ denotes the long-ranged part of the potential.
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 $M=\frac{1}{2\pi}\int_0^{2\pi}\cos(\varphi)\xi(\varphi)\mathrm{d}\varphi\equiv\xi_{100}$, while the pressure P is calculated from the virial equation

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

The number of harmonics involved was $\mathcal{N}=3$. Further increase of $\mathcal{N}$ does not affect the solutions. The G-L and L-L phase coexistence densities have been evaluated by applying the *Maxwell construction* to P. The results below were presented for the case $z_1=z_2=1/\sigma$ using dimensionless quantities $\rho^*=\rho\sigma^3$, $T^*=k_{\mathrm{B}}T/\epsilon$, and $H^*=H/\epsilon$

RESULTS

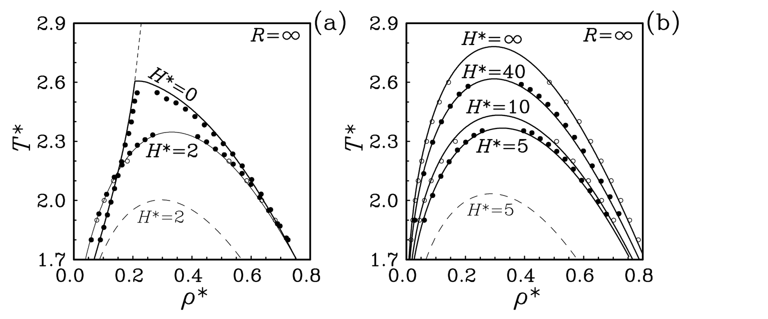

FIG. 1. AOZ/BGY/SMSA phase diagrams of the ideal XY spin fluid ($R=\infty$) versus GEMC/HR data (circles) and MF results (dashed curves).

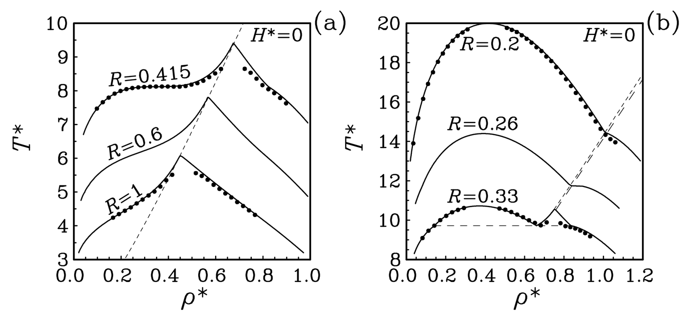

FIG. 2. AOZ/BGY/SMSA binodals of the nonideal XY fluid at $H=0$. The magnetic transition is plotted (as in Fig. 1(a)) by dashed lines.

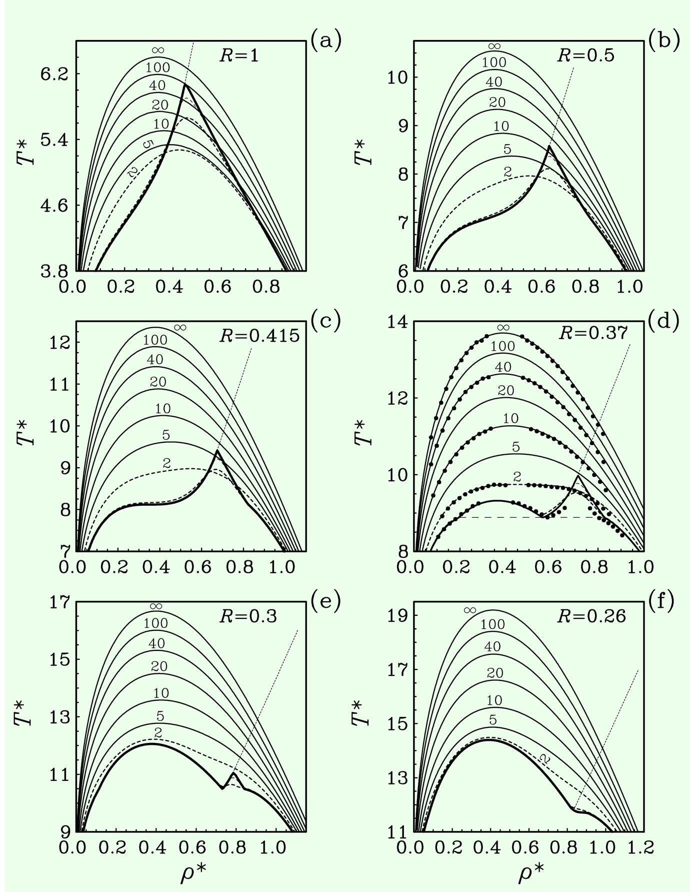

FIG. 3. AOZ/BGY/SMSA phase diagrams of the nonideal XY fluid for typical values of R and H^*.

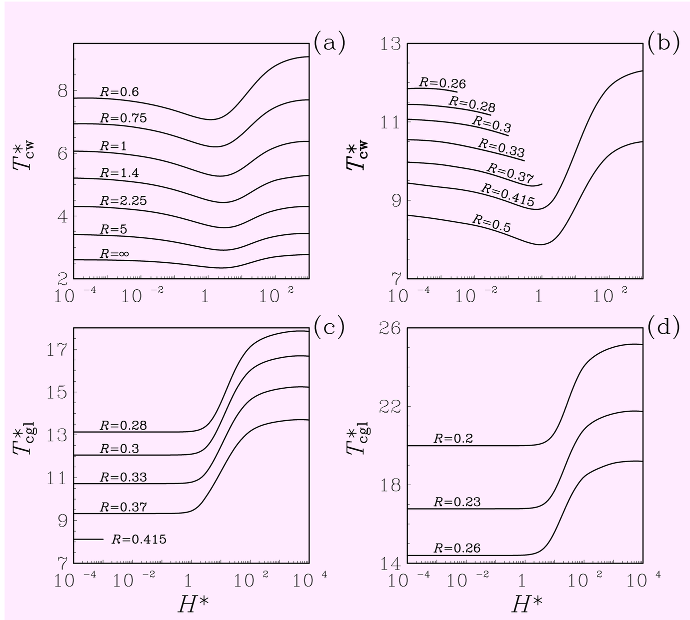

FIG. 4. The critical temperatures of G-L and L-L phase transitions as functions of H at different R.

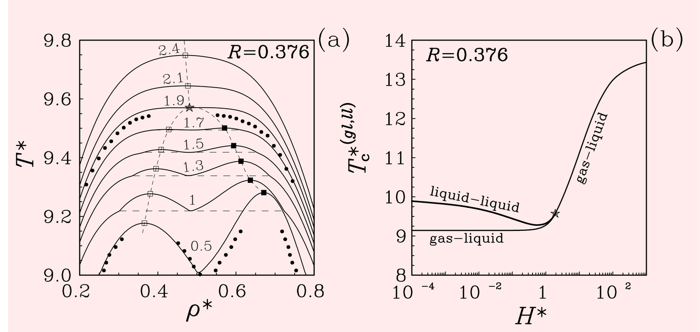

FIG. 5. The same as in Figs. 3 and 4 but at a specific van Laar value of $R=R_{\mathrm{vL}}$. The triple points are represented by horizontal dashed lines.

Four types of the phase diagram topology can be identified overall. For large $R\geq0.415$ type I, the system exhibits an *ideal-like* behavior with the existence of a tricritical point (TCP) at $H=0$ and G-L transitions at $H\neq0$ for each R. At moderate $0.26<R<0.415$ (type II, the transition between a paramagnetic (P) liquid and a ferromagnetic (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. For $H\neq0$, the TPs can *exist* as well. With increasing H, either the G-L ($0.376<R<0.415$, type IIa) or L-L ($0.26<R<0.376$, type IIb) transition line *terminates* in a critical end point (CEP) at some finite H. In the special case $R=R_{\mathrm{vL}}=0.376$, the G-L and L-L transition lines *merge* into the TC van Laar point at $H^*=1.9$. For small $R\leq0.26$ (type III), the spatial interaction dominates over the spin one, remaining the G-L transition, whereas the TCP at $H=0$ *transforms* into a CEP. For $H\to\infty$, the system at any R behaves like a *simple* fluid with $u(r)=\phi(r)-I(r)-J(r)$.
The G-L or L-L critical temperatures T_{c} are *nonmonotonic* in H for $0.376<R<\infty$. The position of the minimum in T_{c} shifts from $H^*\sim3$ to 1 with decreasing R. For $R\leq0.376$, the G-L critical temperature increases always monotonically with increasing H.

CONCLUSION

A *novel* AOZ/BGY/SMSA technique has been proposed to study orientationally ordered fluids with planar spins. It is powerful enough to give a *quantitative* description of the complicated phase diagram behavior in the XY spin fluid systems.

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