

Integral equation study of an ideal Ising mixture

W. Fenz,¹ I. P. Omelyan,^{1,2} and R. Folk¹

¹*Institute for Theoretical Physics, Linz University, A-4040 Linz, Austria*

²*Institute for Condensed Matter Physics, 1 Svientsitskii Street, UA-79011 Lviv, Ukraine*

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We construct an integral equation scheme for magnetic binary mixtures of an ideal soft-core Ising fluid and a soft-sphere fluid by mapping the system onto an equivalent nonmagnetic ternary mixture. We apply the multicomponent Ornstein-Zernike equation together with a closure relation based on the soft mean spherical approximation and a field constraint for the Ising fluid component. Phase coexistence curves are calculated both by directly evaluating the chemical potentials via the bridge function, and by using a Maxwell-like construction which is derived in the text. Our results are compared to Monte Carlo data obtained earlier, and we find that the second method yields a much better agreement with the simulations.

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I. INTRODUCTION

Binary spin fluid mixtures [1,2] form an interesting model system for several reasons. In particular, they can be considered as an extension of the Blume-Emery-Griffiths lattice model for He^3 — He^4 mixtures [3] to continuous space and finite pressures, as it was shown in [2]. In the limit of infinite pressure the mean-field phase diagram of the ideal Ising mixture in the absence of an external field coincides with the well-known Blume-Capel [3–5] diagram exhibiting continuous and discontinuous transitions between superfluid or ferromagnetic and normal or paramagnetic states with a tricritical point separating the second-order λ - or Curie line from the first-order demixing transitions. At low pressures, the line of tricritical points shows a crossover from demixing to gas-liquid type and ends in the tricritical point of the pure ideal Ising fluid (see Fig. 1).

Of course, modeling the superfluid phase using a one-dimensional order parameter can only give a qualitative picture of the real phase behavior of He^3 — He^4 mixtures. There have already been some attempts using instead of Ising spins planar XY spins which fall into the right universality class, both on the lattice [6–8] and recently also in a continuous fluid [9]. However, due to computational complexity it is still reasonable to consider Ising spins for a first integral equation study of a magnetic fluid mixture.

Another reason why especially Ising fluid mixtures are relevant is that due to the discrete spin variable the Ising fluid is mathematically equivalent to a nonmagnetic symmetric binary mixture [10]. Consequently, the Ising mixture corresponds to a ternary system with two of the components forming a symmetric subsystem.

Finally, the Ising mixture serves as a model for studying phase transitions that can occur in realistic mixtures of dipolar fluids or ferrofluids. Just recently the global phase diagram of a similar model, the mixture of two dipolar Stockmayer fluids, has been investigated within a modified mean-field density functional approach [11]. Although those systems are of type II rather than I in the classification of van Konynenburg and Scott [12], i.e., they exhibit a line of consolute points in addition to the plait point line, some of the topologies shown there also appear in our Ising mixture stud-

ies. Furthermore, mixtures of dipolar hard spheres, resembling the ideal Ising fluid in the aspect of a lacking isotropic attractive interaction, were considered in [13,14], and also in the presence of a finite external field [15].

So far, the phase behavior of Ising mixtures has just been explored using a van-der-Waals-like mean-field theory [1], such that comparison with Monte Carlo (MC) simulations was only possible on a qualitative level [2], i.e., by looking at the topology of the phase diagrams. In this paper, we want to improve this situation by establishing a theory that incorporates correlations and allows us to make quantitative predictions of the phase behavior, starting with the most basic case of an ideal Ising mixture.

For the pure ideal Ising fluid, which we studied in [16], we could achieve excellent agreement of the phase bound-

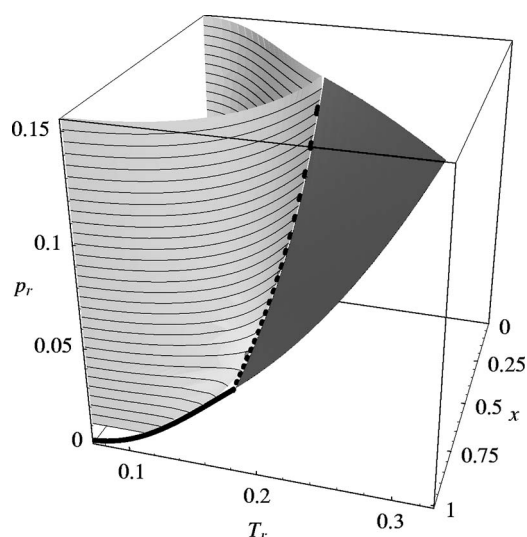


FIG. 1. x - T - P diagram of the ideal Ising mixture at $H=0$ calculated within the mean-field theory (taken from [2]). Thick line, liquid-vapor curve of the pure Ising fluid; thin lines, isobaric curves on the first order surface; dotted line, tricritical line; dark surface, Curie surface; light surface, coexistence surface of para-ferro first-order transitions. T_r and p_r are reduced quantities defined via van-der-Waals parameters [2].

aries obtained from integral equation theory with simulation data by applying the Maxwell construction to the pressure calculated via the virial equation of state, and therefore one of the goals of this work was to generalize this concept to a binary fluid mixture.

The paper is organized as follows: In the next part, the model is defined and the integral equation theory is set up by mapping the binary magnetic mixture onto a ternary non-magnetic one. Conditions for phase equilibria in the x - P and x - T planes are established, and a Maxwell-like construction for two-component systems is derived. In the following section, the details of the numerical calculations are discussed. Subsequently, we present our results, showing both x - P and x - T phase diagrams obtained within the integral equation theory and compare them to previous MC simulation data from [2]. Finally, we give a brief summary of our conclusions and an outlook on future work.

II. MODEL

We consider a system in volume V with N particles in total, consisting of N_a nonmagnetic soft spheres and N_b Ising particles. Its total potential energy can be written as

$$U = \sum_{i<j}^N [\varphi(r_{ij}) + s_i s_j J(r_{ij})] - H \sum_{i=1}^N s_i, \quad (1)$$

where \mathbf{r}_i is the three-dimensional spatial coordinate of the i th molecule, s_i denotes its spin, which is 0 for species a and ± 1 for species b , $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the interparticle distance, and H is the external magnetic field. $J(r)$ denotes the ferromagnetic interaction potential of the Yukawa type given by

$$J(r) = -\varepsilon \frac{e^{-(r-\sigma)/\sigma}}{r/\sigma}, \quad (2)$$

and the soft-core interaction $\varphi(r)$ has the form of a truncated and shifted Lennard-Jones potential,

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

Since the only attractive force present is due to the ferromagnetic interaction, we call the system an *ideal* Ising mixture, in contrast to the *nonideal* system, where also a nonmagnetic attraction is present. We choose the Yukawa and the soft-core interaction to be of equal strength $\varepsilon = \varepsilon$, and both species to have the same diameter σ .

A. Mapping to a ternary mixture

Similar to the case of the pure Ising fluid [16], the binary ideal Ising mixture can be mapped onto a ternary system with nonmagnetic interactions, whose three components are the soft spheres ($s=0$), the Ising particles with spin up ($s=1$), and those with spin down ($s=-1$). The corresponding particle numbers are

$$N_1 = N_a, \quad N_2 = N_b^+, \quad N_3 = N_b^-, \quad (4)$$

with $N_b = N_2 + N_3$. Now the total energy can be written as

$$U = \sum_{i<j}^N u_{\alpha\beta}(r_{ij}) - HM, \quad (5)$$

where α and β denote the species of particle i and j , respectively, and M is the total magnetization of the system, defined as $M = \sum_{i=1}^N s_i = N_2 - N_3$. The new interaction potentials $u_{\alpha\beta}(r)$ are given by

$$\begin{aligned} u_{11}(r) &= u_{12}(r) = u_{13}(r) = \varphi(r), \\ u_{22}(r) &= u_{33}(r) = \varphi(r) + J(r), \\ u_{23}(r) &= \varphi(r) - J(r), \end{aligned} \quad (6)$$

and fulfill the symmetry relation $u_{\alpha\beta}(r) = u_{\beta\alpha}(r)$. The magnetization m of the Ising fluid is given by $m = M/N_b$. Defining the concentrations of the components as $x = N_b/N$, $x' = N_3/N$, $x - x' = N_2/N$, m can be expressed as

$$m = 1 - 2 \frac{x'}{x}, \quad (7)$$

yielding a connection between the magnetization of the Ising fluid component and the mole fractions of the ternary mixture. The overall particle density of the system is given by $\rho = N/V = \rho_1 + \rho_2 + \rho_3$, where the partial densities are $\rho_\alpha = N_\alpha/V$ or

$$\rho_1 = (1-x)\rho, \quad \rho_2 = (x-x')\rho, \quad \rho_3 = x'\rho. \quad (8)$$

B. Integral equations

The Ornstein-Zernike (OZ) equations for a ternary mixture read [17]

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma=1}^3 \rho_\gamma \int c_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) h_{\gamma\beta}(r') d\mathbf{r}', \quad (9)$$

where $h_{\alpha\beta}(r)$ are the total and $c_{\alpha\beta}(r)$ the direct correlation functions and $\alpha, \beta = 1, 2, 3$. The OZ equations are solved in combination with an approximate closure relation connecting the correlation functions to the interaction potentials:

$$g_{\alpha\beta}(r) \equiv h_{\alpha\beta}(r) + 1 = e^{-\beta u_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) + B_{\alpha\beta}(r)}, \quad (10)$$

where the factor β is now the inverse temperature $1/k_B T$ with k_B being Boltzmann's constant. In our case we use for the bridge function $B_{\alpha\beta}(r)$ a modified soft mean spherical approximation (SMSA), given by

$$B_{\alpha\beta}(r) = \begin{cases} \ln[1 + s_{\alpha\beta}(r)] - s_{\alpha\beta}(r), & s_{\alpha\beta}(r) > 0 \\ 0, & s_{\alpha\beta}(r) \leq 0 \end{cases}, \quad (11)$$

where

$$s_{\alpha\beta}(r) = h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - \beta u_{\alpha\beta}^l(r), \quad (12)$$

and $u_{\alpha\beta}^l(r)$ denotes the long-range part of the potential $u_{\alpha\beta}(r)$. Using a Boltzmann-like switching exponent as in [16] for the pure Ising fluid, the long-range parts $u_{\alpha\beta}^l(r)$ are

$$u_{22}^l(r) = u_{33}^l(r) = J(r)e^{-\beta\varphi(r)},$$

$$u_{23}^l(r) = -J(r)e^{-\beta\varphi(r)},$$

$$u_{1\alpha}^l(r) = 0, \quad \alpha = 1, 2, 3. \quad (13)$$

Setting $B_{\alpha\beta}(r)$ equal to zero (as in the HNC closure) for $s_{\alpha\beta}(r) \leq 0$ in (11) serves the purpose of avoiding negative and thus unphysical values of $g_{\alpha\beta}(r)$ that may occur in the pure SMSA.

C. Thermodynamic quantities

Once the pair correlation functions $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$ are known, thermodynamic quantities such as the pressure and the chemical potential are calculated in a straightforward way, along the lines of the binary case [16]. The pressure P is found via the virial equation of state,

$$P(\rho_1, \rho_2, \rho_3, T) = \rho k_B T - \frac{2\pi}{3} \sum_{\alpha, \beta=1}^3 \rho_\alpha \rho_\beta \int_0^\infty \frac{du_{\alpha\beta}(r)}{dr} g_{\alpha\beta}(r) r^3 dr, \quad (14)$$

whereas the excess part of the chemical potential μ_α^{ex} can be obtained from Lee's formula [18,19] as

$$\begin{aligned} \beta\mu_\alpha^{ex} = & \sum_{\beta=1}^3 \rho_\beta \int_0^\infty \left[\frac{1}{2} h_{\alpha\beta}^2(r) - \frac{1}{2} h_{\alpha\beta}(r) c_{\alpha\beta}(r) - c_{\alpha\beta}(r) \right. \\ & \left. + B_{\alpha\beta}(r) g_{\alpha\beta}(r) - \frac{h_{\alpha\beta}(r)}{s_{\alpha\beta}(r)} \int_0^{s_{\alpha\beta}(r)} B(s') ds' \right] 4\pi r^2 dr, \end{aligned} \quad (15)$$

with the integral over the bridge function given by

$$\int_0^s B(s') ds' = \begin{cases} (1+s) \ln(1+s) - \frac{s(s+2)}{2}, & s > 0 \\ 0, & s \leq 0 \end{cases}. \quad (16)$$

The total chemical potential can then be written as

$$\mu_\alpha(\rho_1, \rho_2, \rho_3, T) = \mu_\alpha^{ex} + k_B T (\ln \rho_\alpha + 3 \ln \Lambda_\alpha), \quad (17)$$

where Λ_α is the thermal de Broglie wavelength.

D. Phase coexistence

Since we intend to find phase boundaries in x - T - P space, we will now switch from the set of variables $(\rho_1, \rho_2, \rho_3, T)$ to a description in terms of the total density and the concentrations (ρ, x, x', T) , using the expressions given in Eq. (8). Two phases I and II characterized by (ρ_I, x_I, x'_I) and $(\rho_{II}, x_{II}, x'_{II})$ are in equilibrium if they share the same pressure

\mathcal{P} and the same chemical potentials μ_α of all three components,

$$P(\rho_I, x_I, x'_I, T) = P(\rho_{II}, x_{II}, x'_{II}, T) = \mathcal{P},$$

$$\mu_1(\rho_I, x_I, x'_I, T) = \mu_1(\rho_{II}, x_{II}, x'_{II}, T),$$

$$\mu_2(\rho_I, x_I, x'_I, T) = \mu_2(\rho_{II}, x_{II}, x'_{II}, T),$$

$$\mu_3(\rho_I, x_I, x'_I, T) = \mu_3(\rho_{II}, x_{II}, x'_{II}, T). \quad (18)$$

For the Ising fluid component, an additional requirement must be fulfilled, the external field constraint (FC), which is a consequence of the mapping between the magnetic binary and the nonmagnetic ternary mixture (see the Appendix for a rigorous derivation). Defining $\Delta\mu$ as

$$\Delta\mu(\rho, x, x', T) \equiv \mu_3(\rho, x, x', T) - \mu_2(\rho, x, x', T), \quad (19)$$

it can be written as

$$\Delta\mu(\rho, x, x', T) = 2H. \quad (20)$$

Equation (20) can be viewed as a constraint on the concentration x' , $x' = x'(\rho, x, T, H)$, allowing us to rewrite the conditions for phase coexistence (18) in terms of the new set of variables $[\rho, x, x'(\rho, x, T, H), T] \equiv (\rho, x, T, H)$ instead of (ρ, x, x', T) . Introducing the chemical potential μ_b of the Ising fluid component (see Appendix and cf. [16]) as

$$\mu_b(\rho, x, T, H) \equiv \frac{\mu_2(\rho, x, T, H) + \mu_3(\rho, x, T, H)}{2}, \quad (21)$$

we can write

$$P(\rho_I, x_I, T, H) = P(\rho_{II}, x_{II}, T, H) = \mathcal{P},$$

$$\mu_a(\rho_I, x_I, T, H) = \mu_a(\rho_{II}, x_{II}, T, H),$$

$$\mu_b(\rho_I, x_I, T, H) = \mu_b(\rho_{II}, x_{II}, T, H), \quad (22)$$

instead of (18), with μ_a being identical to μ_1 . These equations now have the same form as the usual phase equilibrium conditions in a binary mixture. Contrary to the pure fluid case, one has to find both density *and* concentration for each phase, so a system of four equations has to be solved instead of two.

E. Phase coexistence at constant P

If we want to display phase boundaries in an x - T diagram, we are restricted to a constant pressure plane in the thermodynamic space. The corresponding condition,

$$P(\rho, x, T, H) = \mathcal{P}, \quad (23)$$

can be regarded as an additional constraint (pressure constraint, PC) imposed on the density ρ , $\rho = \rho(x, T, \mathcal{P}, H)$. Consequently, we can replace the set of variables (ρ, x, T, H) by the new one $[\rho(x, T, \mathcal{P}, H), x, T, H] = (x, T, \mathcal{P}, H)$. Thus, in this case the conditions of phase equilibrium reduce to the two equations

$$\begin{aligned}\mu_a(x_I, T, \mathcal{P}, H) &= \mu_a(x_{II}, T, \mathcal{P}, H), \\ \mu_b(x_I, T, \mathcal{P}, H) &= \mu_b(x_{II}, T, \mathcal{P}, H),\end{aligned}\quad (24)$$

with only the concentrations of the two coexisting phases as unknowns. Finding the phase boundary is now very similar to the pure fluid case, where one has the equations for equal pressure and equal chemical potential instead of Eqs. (24), and ρ_I and ρ_{II} instead of x_I and x_{II} .

F. Maxwell construction

In [16] we have applied the equal-area Maxwell construction to the isotherms calculated via the virial equation of state in order to locate the phase boundaries for the pure Ising fluid, instead of equating the chemical potentials obtained from the Lee formula (15), as it is usually done. This is only possible because the system of OZ/SMSA/FC equations yields solutions for the correlation functions in a wide range of temperatures and densities, including the two-phase region, whereas for other approximations such as hypernetted chain (HNC) or Percus-Yevick (PY) no solution exists between the spinodal points.

It is worth mentioning that there exists also another type of Maxwell construction that does not depend on the existence of solutions to the OZ equations in the two-phase region, namely the double-tangent construction, which uses only derivatives of the Helmholtz free energy with respect to the density to obtain the pressure (via the energy route) and the algebraic Euler equation connecting the chemical potential to the pressure and free energy. The Helmholtz free energy can be calculated by first integrating the virial pressure (like in the equal-area Maxwell construction), but along a supercritical isotherm (to provide the existence of solutions within either closure anywhere inside the integration region) and then the excess internal energy along an isochore until one reaches the required subcritical temperature. In particular, such a procedure (in tandem with the Euler equation) was successfully applied in Ref. [20] to a simple Lennard-Jones fluid. This procedure as well as the double-tangent Maxwell construction, can be used, in principle, for a wide class of closures including the HNC and PY (despite the fact that no solutions may exist between the spinodal points). However, their implementation leads to much more computational effort (with respect to the standard equal-area Maxwell construction) because it demands the time-consuming evaluation of the Helmholtz free energy, and it also requires that the applied closure provides a high thermodynamic consistency since one is forced to move on different thermodynamic routes.

In general, the two ways of calculating the chemical potential, namely the thermodynamic integration of the virial pressure (standard Maxwell construction) and the application of the direct Lee formula should lead to identical results provided the exact bridge function is used. Of course, in approximate integral equation evaluations, as in our OZ/SMSA/FC case, both routes will yield to some extent different results. Comparing the obtained theoretical results with simulation data [16] has allowed us to conclude that the

Maxwell construction appears to be better than the Lee formula in the particular case of the SMSA closure for ideal Ising fluids, which might be explained by the fortunate cancellation of errors introduced by the approximate SMSA equation. For other systems and other closures, the situation may differ.

In view of these facts regarding the pure ideal Ising fluid, and since the existence of solutions in a large part of thermodynamic space including the phase coexistence region is also provided in the case of a binary mixture, it should be worthwhile to formulate an analogy to the Maxwell equal-area construction for a two-component system and express the chemical potentials in terms of the virial pressure.

In order to do so we define the excess Helmholtz free energy of a binary mixture as $F^{ex}(N_a, N_b, T, V, H) \equiv F - F^{id}$, where F^{id} is the free energy of a pure ideal gas. F^{ex} is connected to an excess pressure P^{ex} via

$$P^{ex}(N_a, N_b, T, V, H) = P - P^{id} = - \left(\frac{\partial F^{ex}}{\partial V} \right)_{N_a, N_b, T, H}. \quad (25)$$

From F^{ex} one can derive the excess chemical potentials μ_a^{ex} and μ_b^{ex} as

$$\begin{aligned}\mu_a^{ex}(N_a, N_b, T, V, H) &= \left(\frac{\partial F^{ex}}{\partial N_a} \right)_{N_b, T, V, H}, \\ \mu_b^{ex}(N_a, N_b, T, V, H) &= \left(\frac{\partial F^{ex}}{\partial N_b} \right)_{N_a, T, V, H}.\end{aligned}\quad (26)$$

By integrating Eq. (25) one obtains the excess free energy,

$$F^{ex}(N_a, N_b, T, V, H) = - \int_{\infty}^V P^{ex}(N_a, N_b, T, V', H) dV', \quad (27)$$

and its density $f^{ex}(\rho, x, T, H)$

$$\begin{aligned}f^{ex}(\rho, x, T, H) &\equiv \frac{F^{ex}}{V} = \rho \int_0^{\rho} P^{ex}(\rho', x, T, H) \frac{1}{\rho'^2} d\rho' \\ &= \rho \int_0^{\rho} \left(\frac{P(\rho', x, T, H)}{\rho'^2} - \frac{k_B T}{\rho'} \right) d\rho',\end{aligned}\quad (28)$$

where the ideal gas equation of state $P^{id} = \rho k_B T$ has been used. With the relations

$$\begin{aligned}\left(\frac{\partial F^{ex}}{\partial N_a} \right)_{N_b, T, V, H} &= \left(\frac{\partial f^{ex}}{\partial \rho} \right)_{x, T, H} - \frac{x}{\rho} \left(\frac{\partial f^{ex}}{\partial x} \right)_{\rho, T, H}, \\ \left(\frac{\partial F^{ex}}{\partial N_b} \right)_{N_a, T, V, H} &= \left(\frac{\partial f^{ex}}{\partial \rho} \right)_{x, T, H} + \frac{1-x}{\rho} \left(\frac{\partial f^{ex}}{\partial x} \right)_{\rho, T, H},\end{aligned}\quad (29)$$

we obtain for the chemical potentials

$$\begin{aligned} \mu_a^{ex}(\rho, x, T, H) &= \frac{P(\rho, x, T, H)}{\rho} - k_B T \\ &+ \int_0^\rho \left(\frac{P(\rho', x, T, H)}{\rho'^2} - \frac{k_B T}{\rho'} \right) d\rho' \\ &- x \int_0^\rho \frac{P_x(\rho', x, T, H)}{\rho'^2} d\rho' \end{aligned} \quad (30)$$

and

$$\begin{aligned} \mu_b^{ex}(\rho, x, T, H) &= \frac{P(\rho, x, T, H)}{\rho} - k_B T \\ &+ \int_0^\rho \left(\frac{P(\rho', x, T, H)}{\rho'^2} - \frac{k_B T}{\rho'} \right) d\rho' \\ &+ (1-x) \int_0^\rho \frac{P_x(\rho', x, T, H)}{\rho'^2} d\rho', \end{aligned} \quad (31)$$

where $P_x(\rho, x, T, H) \equiv [\partial P(\rho, x, T, H) / \partial x]_{\rho, T, H}$. In view of the conditions for phase coexistence,

$$P(\rho_I, x_I, T, H) = P(\rho_{II}, x_{II}, T, H) = \mathcal{P}, \quad (32)$$

$$\mu_a(\rho_I, x_I, T, H) = \mu_a(\rho_{II}, x_{II}, T, H), \quad (33)$$

$$\mu_b(\rho_I, x_I, T, H) = \mu_b(\rho_{II}, x_{II}, T, H), \quad (34)$$

we can now write Eq. (33) as

$$\begin{aligned} \frac{\mathcal{P}}{\rho_I} - k_B T + \int_0^{\rho_I} \left(\frac{P(\rho, x_I, T, H)}{\rho^2} - \frac{k_B T}{\rho} \right) d\rho \\ - x_I \int_0^{\rho_I} \frac{P_x(\rho, x_I, T, H)}{\rho^2} d\rho + k_B T \ln[\rho_I(1-x_I)] \\ = \frac{\mathcal{P}}{\rho_{II}} - k_B T + \int_0^{\rho_{II}} \left(\frac{P(\rho, x_{II}, T, H)}{\rho^2} - \frac{k_B T}{\rho} \right) d\rho \\ - x_{II} \int_0^{\rho_{II}} \frac{P_x(\rho, x_{II}, T, H)}{\rho^2} d\rho + k_B T \ln[\rho_{II}(1-x_{II})], \end{aligned} \quad (35)$$

and Eq. (34) as

$$\begin{aligned} \frac{\mathcal{P}}{\rho_I} - k_B T + \int_0^{\rho_I} \left(\frac{P(\rho, x_I, T, H)}{\rho^2} - \frac{k_B T}{\rho} \right) d\rho \\ + (1-x_I) \int_0^{\rho_I} \frac{P_x(\rho, x_I, T, H)}{\rho^2} d\rho + k_B T \ln(\rho_I x_I) \\ = \frac{\mathcal{P}}{\rho_{II}} - k_B T + \int_0^{\rho_{II}} \left(\frac{P(\rho, x_{II}, T, H)}{\rho^2} - \frac{k_B T}{\rho} \right) d\rho \\ + (1-x_{II}) \int_0^{\rho_{II}} \frac{P_x(\rho, x_{II}, T, H)}{\rho^2} d\rho + k_B T \ln(\rho_{II} x_{II}). \end{aligned} \quad (36)$$

Defining the functions Q_1 and Q_2 as

$$\begin{aligned} Q_1(\rho_I, \rho_{II}, x_I, x_{II}, T, H) \\ = \mathcal{P} \left(\frac{1}{\rho_{II}} - \frac{1}{\rho_I} \right) + k_B T \ln \frac{1-x_{II}}{1-x_I} \\ + \int_0^{\rho_{II}} \frac{1}{\rho^2} [P(\rho, x_{II}, T, H) - x_{II} P_x(\rho, x_{II}, T, H)] d\rho \\ - \int_0^{\rho_I} \frac{1}{\rho^2} [P(\rho, x_I, T, H) - x_I P_x(\rho, x_I, T, H)] d\rho, \end{aligned} \quad (37)$$

and

$$\begin{aligned} Q_2(\rho_I, \rho_{II}, x_I, x_{II}, T, H) \\ = \mathcal{P} \left(\frac{1}{\rho_{II}} - \frac{1}{\rho_I} \right) + k_B T \ln \frac{x_{II}}{x_I} \\ + \int_0^{\rho_{II}} \frac{1}{\rho^2} [P(\rho, x_{II}, T, H) + (1-x_{II}) P_x(\rho, x_{II}, T, H)] d\rho \\ - \int_0^{\rho_I} \frac{1}{\rho^2} [P(\rho, x_I, T, H) + (1-x_I) P_x(\rho, x_I, T, H)] d\rho, \end{aligned} \quad (38)$$

the conditions for phase equilibrium (32)–(34), obtained via the Maxwell-like construction, can be cast into the form

$$P(\rho_I, x_I, T, H) = P(\rho_{II}, x_{II}, T, H) = \mathcal{P}, \quad (39)$$

$$0 = Q_1(\rho_I, \rho_{II}, x_I, x_{II}, T, H), \quad (40)$$

$$0 = Q_2(\rho_I, \rho_{II}, x_I, x_{II}, T, H). \quad (41)$$

If both x_I and x_{II} are set equal to 1, Eq. (41) becomes

$$Q_2(\rho_I, \rho_{II}, T, H) = \mathcal{P} \left(\frac{1}{\rho_{II}} - \frac{1}{\rho_I} \right) + \int_{\rho_I}^{\rho_{II}} \frac{1}{\rho^2} P(\rho, T, H) d\rho = 0, \quad (42)$$

reproducing the equation for the usual Maxwell construction in a pure fluid, as applied in [16].

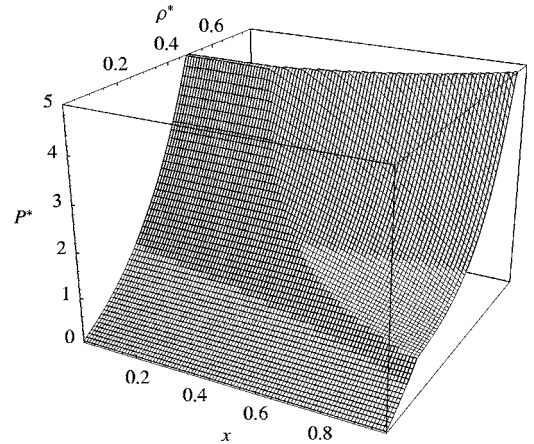


FIG. 2. The virial pressure $P^*(x, \rho^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC integral equation theory for $T^* = k_B T / \varepsilon = 4$, $H = 0$ ($P^* = P \sigma^3 / \varepsilon$, $\rho^* = \rho \sigma^3$).

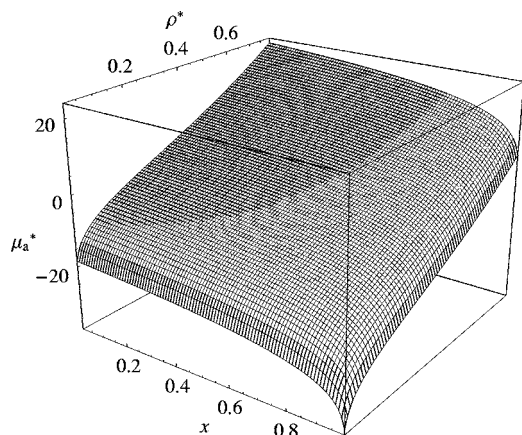


FIG. 3. The chemical potential $\mu_a^*(x, \rho^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC integral equation theory for $T^*=4$, $H=0$ ($\mu_a^* = \mu_a/\varepsilon$).

III. NUMERICAL DETAILS

By applying the three-dimensional Fourier transform

$$\tilde{f}(k) = \int_V f(r) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} = \int_0^\infty 4\pi r^2 f(r) \sin(kr)/(kr) dr, \quad (43)$$

where f is any function of r , the OZ integral equations (9) can be transformed into a system of linear algebraic equations,

$$\tilde{h}_{\alpha\beta}(k) = \tilde{c}_{\alpha\beta}(k) + \sum_{\gamma=1}^3 \rho_\gamma \tilde{c}_{\alpha\gamma}(k) \tilde{h}_{\gamma\beta}(k), \quad \alpha, \beta = 1, 2, 3, \quad (44)$$

which can be written in 3×3 matrix form as $\tilde{\mathbf{h}}(k) = \tilde{\mathbf{c}}(k) + \boldsymbol{\rho} \tilde{\mathbf{c}}(k) \tilde{\mathbf{h}}(k)$, with $\boldsymbol{\rho}$ being the diagonal matrix $\boldsymbol{\rho} = \text{diag}(\rho_1, \rho_2, \rho_3)$. The OZ equations (9), SMSA closure (10)–(12), field constraint (20) and pressure constraint (23)

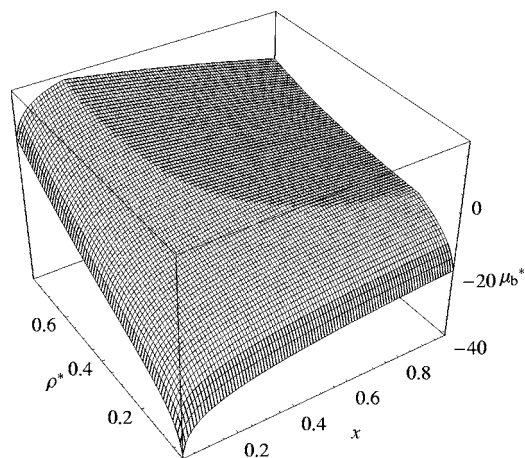


FIG. 4. The chemical potential $\mu_b^*(x, \rho^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC integral equation theory for $T^*=4$, $H=0$ ($\mu_b^* = \mu_b/\varepsilon$).

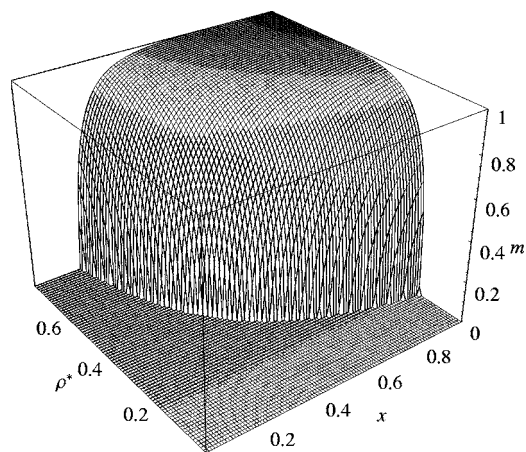


FIG. 5. The magnetization $m(x, \rho^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC integral equation theory for $T^*=4$, $H=0$.

(in the case of constant P calculations) constitute a coupled set of nonlinear equations that was solved iteratively using the efficient method of modified direct inversion in the iterative subspace (MDIIS) [21]. For given values of ρ (or P), x , T , and H , the iteration starts with initial guesses for $\mathbf{c}(r)$ and x' as well as ρ in case of fixed P . After calculating the Fourier transformed functions $\tilde{\mathbf{c}}(k)$, the total correlation functions in Fourier space are found analytically via $\tilde{\mathbf{h}}(k) = [\mathbf{I} - \boldsymbol{\rho} \tilde{\mathbf{c}}(k)]^{-1} \tilde{\mathbf{c}}(k)$, and transformed back to real space using the inverse Fourier transformation

$$f(r) = 1/(2\pi)^3 \int_0^\infty 4\pi k^2 \tilde{f}(k) \sin(kr)/(kr) dk. \quad (45)$$

Now the residuals of the SMSA, FC, and PC equations are evaluated with the current values of $\mathbf{c}(r)$, $\mathbf{h}(r)$, x' , and ρ .

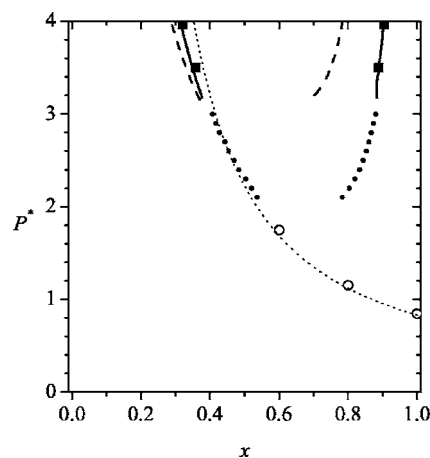


FIG. 6. x - P phase diagram of the ideal Ising mixture at $T^*=4$, $H=0$. Dashed line, coexistence curve from the OZ/SMSA/FC integral equation theory [Eqs. (22)]; solid line, coexistence curve obtained via Maxwell construction [Eqs. (39)–(41)]; dotted line, Curie line; squares, results from Gibbs ensemble MC simulations; filled circles, results from semigrand canonical MC simulations and multihistogram reweighting; open circles, para-ferro magnetic critical points from simulations in the isobaric-isothermal ensemble. All simulation results are taken from Ref. 2.

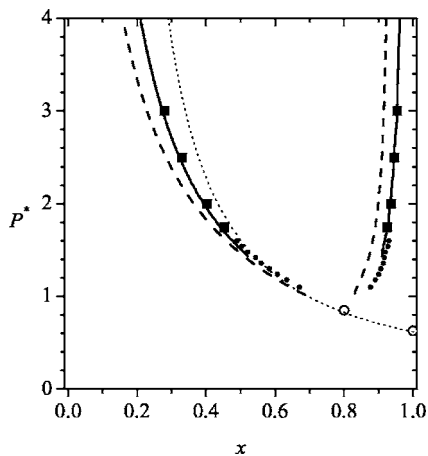


FIG. 7. x - P phase diagram of the ideal Ising mixture at $T^*=3.5$, $H=0$. Symbols as in Fig. 6.

New values of $\mathbf{c}(r)$, x' , and ρ are then obtained from the MDIIS algorithm, and the iteration continues until the relative root-mean-square magnitude of the residuals is below 10^{-7} .

Using Eqs. (14) and (15), pressure and chemical potentials can thus be found at a certain constant temperature T in a range of concentrations x and densities ρ . In practice, we obtained P , μ_a , and μ_b on a discretized grid with $0.001 \leq x \leq 0.999$ and $\Delta x = 0.001$, $0.001 \leq \rho \leq 0.899$, and $\Delta \rho = 0.001$. Equations (22) were then solved using bilinear interpolation for the functions $P(x, \rho)$, $\mu_a(x, \rho)$, and $\mu_b(x, \rho)$ and a Hybrid-Newton algorithm to find the roots of the equations. For the calculations with the Maxwell-like construction we applied bilinear interpolation for the function $P(x, \rho)$ only and solved Eqs. (39)–(41) using the same algorithm as before. The derivatives of the pressure with respect to concentration, occurring in Eqs. (37) and (38), were calculated by bilinear interpolation between the slopes in four adjacent grid points.

In the case of constant pressure, the chemical potentials μ_a and μ_b were calculated for $0.001 \leq x \leq 0.999$ and $\Delta x = 0.001$, for temperatures in a specified range. Here the equations of phase coexistence (24) could be solved for each

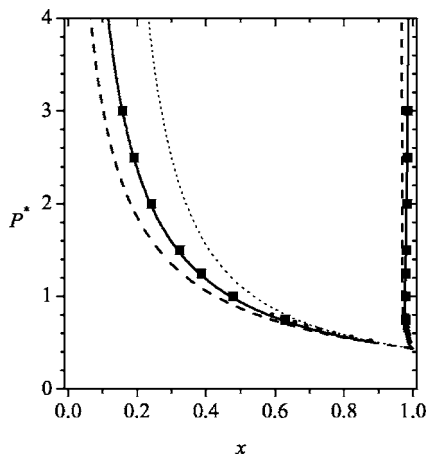


FIG. 8. x - P phase diagram of the ideal Ising mixture at $T^*=3$, $H=0$. Symbols as in Fig. 6.

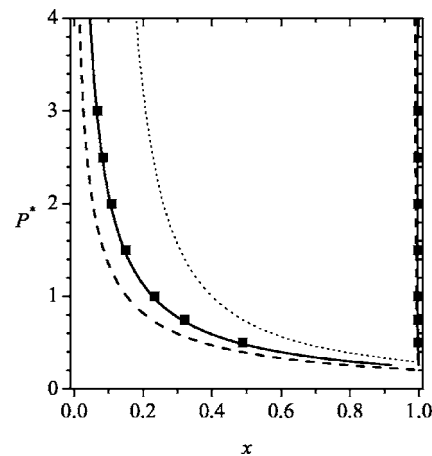


FIG. 9. x - P phase diagram of the ideal Ising mixture at $T^*=2.5$, $H=0$. Symbols as in Fig. 6.

temperature independently, using only the functions $\mu_a(x)$ and $\mu_b(x)$, obtained from cubic spline interpolation.

The MC simulations for the ideal Ising mixture were already performed earlier and are described in [2].

IV. RESULTS

We have investigated the x - T - P phase diagram of the ideal Ising mixture in the absence of a magnetic field ($H=0$), by calculating phase boundaries in several constant- T and constant- P sections via the integral equation theory described in Sec. II. The topology of the overall phase behavior is visualized in Fig. 1, showing the mean-field (MF) diagram for this system, as calculated in [2]. As stated there, the MF results can only be qualitatively compared to MC data.

Figures 2–5 show the reduced virial pressure $P^* = P\sigma^3/\varepsilon$, chemical potentials $\mu_a^* = \mu_a/\varepsilon$, $\mu_b^* = \mu_b/\varepsilon$ and magnetization m as functions of density $\rho^* = \rho\sigma^3$ and concentration x calculated within the OZ/SMSA/FC integral equation theory at a temperature $T^* = k_B T/\varepsilon = 4$. One can see the kink in the P and

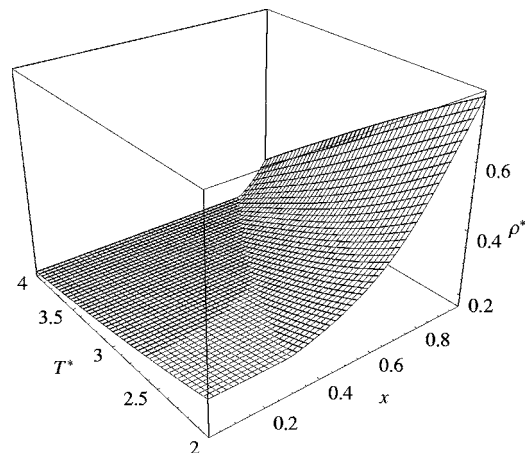


FIG. 10. The density $\rho^*(x, T^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC/PC integral equation theory for $P^*=1$, $H=0$.

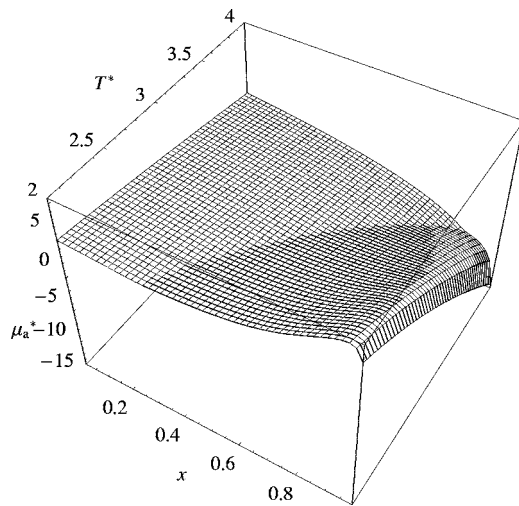


FIG. 11. The chemical potential $\mu_a^*(x, T^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC/PC integral equation theory for $P^*=1, H=0$.

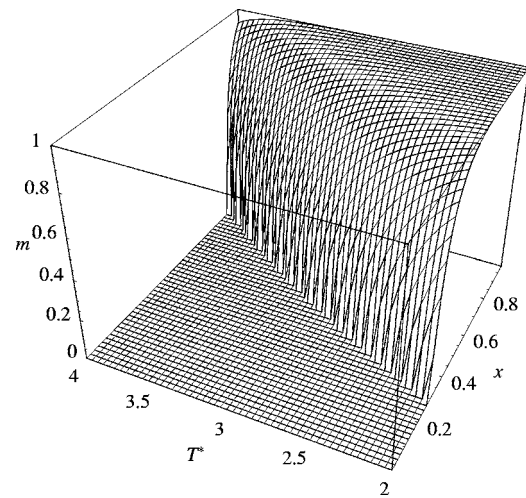


FIG. 13. The magnetization $m(x, T^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC/PC integral equation theory for $P^*=1, H=0$.

μ_b surfaces where the magnetization becomes finite. In Fig. 6 we present the phase coexistence curves obtained from these functions both via Eqs. (22) and by applying the Maxwell construction (39)–(41). Also shown is the Curie line indicating the transition from zero to finite magnetization. For comparison, we have added our results from simulations in the Gibbs ensemble and the semigrand ensemble [2] for the same system. Obviously, the Maxwell construction yields a large improvement over the integral equation results obtained by the usual method, and the corresponding binodal curve almost coincides with the MC data. Still, neither of the methods allows us to approach the critical region where we expect to find a tricritical point. For the first method this is not surprising, since the same is already true in the one-component case, but in the pure Ising fluid the Maxwell construction allowed us to calculate the binodal curve up to the

(tri)critical points [16]. However, the higher complexity of the mixture (four unknowns instead of two) and the numerical subtleties of solving the Maxwell construction equations (39)–(41) prevent convergence in the critical region of the two-component system.

When going to lower temperatures (Figs. 7–9) the difference between the two routes becomes smaller but the Maxwell construction is still superior and agrees very well with the MC data. As to the Curie line, it is also in good agreement with the results of our simulations performed in the isobaric-isothermal ensemble [2].

If we want to look at the x - T diagrams in the constant- P plane, we use the OZ/SMSA/FC/PC version of our theory which applies the pressure constraint, Eq. (23) to the solutions. Figures 10–13 show the reduced density ρ^* , chemical potentials μ_a^*, μ_b^* , and magnetization m as functions of

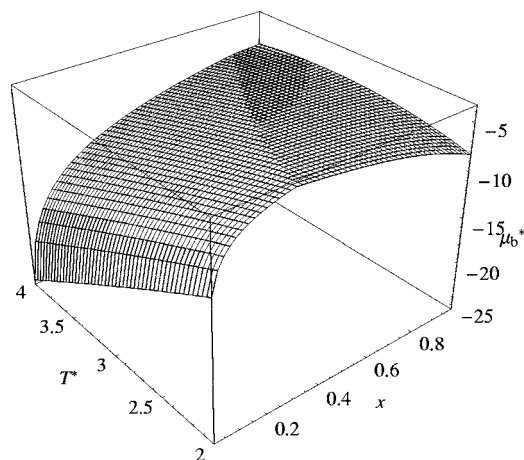


FIG. 12. The chemical potential $\mu_b^*(x, T^*)$ of the ideal Ising mixture obtained from the OZ/SMSA/FC/PC integral equation theory for $P^*=1, H=0$.

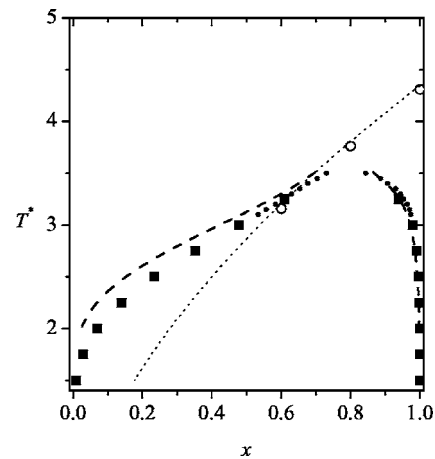


FIG. 14. x - T phase diagram of the ideal Ising mixture at $P^*=1, H=0$. Symbols as in Fig. 15.

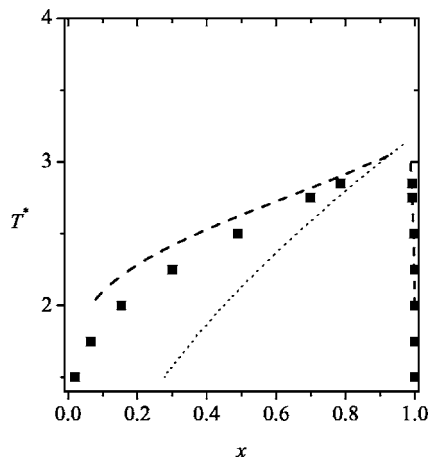


FIG. 15. x - T phase diagram of the ideal Ising mixture at $P^* = 0.5$, $H = 0$. Dashed line, coexistence curve from the OZ/SMSA/FC/PC integral equation theory [Eqs. (24)]; other symbols as in Fig. 6.

temperature and concentration obtained in this manner at fixed pressure $P^* = 1$. Equations (24) were then solved to calculate the binodal curve in Fig. 14 from the chemical potentials. Coexistence curves for other pressures, $P^* = 0.5$ and $P^* = 2$, can be seen in Figs. 15 and 16. With increasing pressure, the deviations between integral equation theory and simulations, especially near the critical region, get larger.

The Maxwell construction of course cannot be combined with the pressure constraint, since calculating the integrals occurring in Eqs. (37) and (38) requires knowledge of the function $P(x, \rho)$ in the whole x - ρ region. Solving (39)–(41) for the fixed pressure yields only one pair of points on the coexistence curve, so in order to find the whole phase boundary in the x - T diagram, $P(x, \rho)$ has to be calculated for each value of T in the considered range, which turns out to be too time consuming. For this reason, we do not show a coexistence curve obtained via Maxwell construction in the constant- P diagrams.

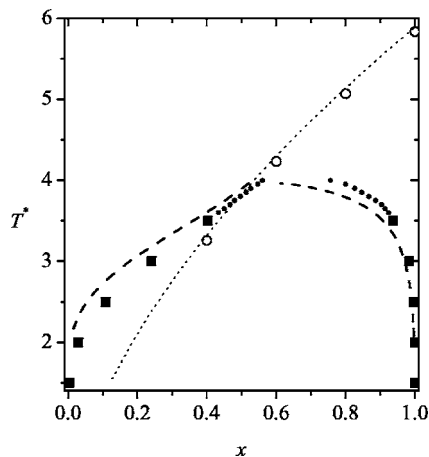


FIG. 16. x - T phase diagram of the ideal Ising mixture at $P^* = 2$, $H = 0$. Symbols as in Fig. 15.

V. CONCLUSIONS

We have formulated an integral equation theory for a magnetic mixture of an ideal Ising fluid and a soft-core fluid by mapping it onto the equivalent nonmagnetic ternary system with two symmetric components. We have calculated total and direct correlation functions by numerically solving the Ornstein-Zernike equation, the SMSA closure relation, and the field constraint. Via applying a Maxwell-like construction for the determination of phase equilibria in the x - P plane, we have achieved an almost exact coincidence with MC simulation data. The usual method of equating the chemical potentials obtained from Lee's formula yields significantly inferior results, but it is also applicable in constant-pressure calculations. Our theory is also suitable for more complicated systems such as mixtures of nonideal Ising fluids with Lennard-Jones fluids, which will be considered in future studies.

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APPENDIX

The Gibbs free energy of a magnetic binary mixture in the presence of an external field has the form

$$G = \mu_a N_a + \mu_b N_b - HM. \quad (\text{A1})$$

On the other hand, the Gibbs free energy of a nonmagnetic ternary mixture is

$$G = \mu_1 N_1 + \mu_2 N_2 + \mu_3 N_3. \quad (\text{A2})$$

Taking into account that $N_a = N_1$, $N_b = N_2 + N_3$, and $M = N_2 - N_3$ [see Eqs. (4) and (5)], one obtains that both forms of G are equivalent if and only if

$$\mu_a = \mu_1, \quad \mu_b = \frac{\mu_2 + \mu_3}{2}, \quad H = \frac{\mu_3 - \mu_2}{2}. \quad (\text{A3})$$

Thus we come to Eqs. (19)–(21) and can immediately map Eqs. (18) to Eqs. (22).

It is interesting to remark that when flipping all N_2 spins from up ($s = +1$) to down ($s = -1$) and all N_3 spins from down to up without changing their spatial coordinates, the total change of the potential energy [Eq. (5)] will be completely determined by the change in the Gibbs free energy. Indeed, then $\Delta U = 2HM = -H\Delta M$, because the terms related to interparticle interactions do not contribute to ΔU due to the symmetry [see Eq. (6)] of the potentials (in particular, due to the property $u_{22} = u_{33}$), while the change in the magnetization is $\Delta M = -2(N_2 - N_3) = -2M$, since $M \rightarrow -M$. During the above mutual exchange $N_2 \leftrightarrow N_3$, the change in the Gibbs free energy according to Eqs. (A1) and (A2) is equal to $\Delta G = -H\Delta M = (\mu_3 - \mu_2)(N_2 - N_3) = 2HM$, and thus $\Delta G = \Delta U$.

This result is, of course, consistent with the thermodynamic relation $G=U-TS+PV$, because the pressure P and entropy S are invariant [$\Delta P=0$ and $\Delta S=0$; see, for instance, the virial equation of state, Eq. (14)] with respect to the above

transformation $N_2 \leftrightarrow N_3$ due to the same symmetry [Eq. (6)] in the interparticle potentials. Therefore, in a constant NVT ensemble (note that $N=N_1+N_2+N_3$) we have that $\Delta G=\Delta U-T\Delta S+\Delta PV=\Delta U$.

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