Binary mixtures of magnetic fluids

W. Fenz and R. Folk
University Linz

Theory

We describe a mixture of a van der Waals fluid and a ferromagnetic Ising fluid at zero magnetic field in the framework of mean field theory. Molar Helmholtz free energy:

\[ \frac{\Delta G_m(T_r, V_r, x, m)}{RT} = x \left( 1 - \frac{m}{2} \right) + (1 - x) \ln(1 - x) + x \ln x \]

\[ - \ln(V_r - 1) - \frac{T_m}{RT} \]

Equations of state:

\[ p_r = T_r - 4 \beta(x, m) \]

\[ m = \tanh \left( \frac{2RT_m}{4V_r} \right) \]

(1)

(2)

Quadratic mixing rule:

\[ a(x, m) = \left( 1 + R_m m^2 \right) x^2 + \frac{1 - \Delta}{1 + \Delta} \left( x - 1 + \Delta \right) \]

(3)

\[ \text{and} \]

\[ \zeta = \frac{\Delta}{2} \left( 1 + \frac{3}{R_m} \right) \]

(4)

First order surfaces

Conditions for equilibrium of two phases \( \alpha \) and \( \beta \):

\[ T_r = T_0 \]

\[ \mu (x_\alpha, V_\alpha, m_\alpha) = \mu (x_\beta, V_\beta, m_\beta) \]

\[ \mu (x_\alpha, V_\alpha, m_\beta) = \mu (x_\beta, V_\beta, m_\alpha) \]

Conjugated field \( \Delta \) of the concentration \( x \):

\[ \Delta = m - m_0 \]

\[ \Delta = \frac{1}{1 + \frac{3}{R_m}} \left( x - x_m \right) \]

(5)

(6)

(7)

(8)

(9)

(10)

Second order critical lines

At a second order critical point two phases become identical. The conditions for criticality are

\[ \left( \frac{\partial \Delta \mu}{\partial x} \right)_{T_p} = 0, \quad \left( \frac{\partial^2 \Delta \mu}{\partial x^2} \right)_{T_p} > 0, \]

(11)

where \( \Delta \mu \) is the Gibbs free energy. In terms of the Helmholtz free energy this yields

\[ A_0A_1A_2 - A_0A_3A_4 = 0 \]

\[ A_1A_2 = 3A_0 \]

\[ A_1A_3 = 3A_0 \]

(12)

(13)

(14)

where

\[ A_i \equiv \left( \frac{\partial^i \Delta \mu}{\partial x^i} \right)_{T_p} \]

and

\[ \Delta m = \Delta \mu \left( V_r, x, m \right) \]

\[ \left( V_r, x, m \right) \]

The function \( m \) is implicitly defined by the magnetic equation of state in (2).

Surface of magnetic phase transitions

The locus of second order ferromagnetic-paramagnetic phase transitions is a surface in \( x, T_r, V_r \)-space, given by

\[ V_r = \frac{2}{4R_m T_r} \]

(16)

Via equation (2) a surface in \( x, T_r, V_r \)-space is defined dividing the thermodynamic space into an upper part (\( m > 0 \)) and a lower part (\( m = 0 \)).

Critical lines

Second order critical lines on the surface of magnetic phase transitions are critical lines. Expanding the magnetic equation of state in (2) as

\[ m^2 = \left( 1 - \frac{3}{R_m} \right) \]

where \( \zeta \) is the vicinuity of the magnetic phase transition surface where \( m \ll 1 \), one can take the limit \( m \to 0 \) in (12) and gets an equation in \( T_r \) and \( x \) that can be written as

\[ T_r = \frac{2R_m}{4} \sqrt{\frac{1 - x}{A(x)}} \]

(17)

\[ \zeta = \frac{\Delta}{2} \left( 1 + \frac{3}{R_m} \right) \]

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(18)

Summary

While in ordinary binary fluid mixtures tricritical points occur only under special circumstances, mixtures with a magnetic fluid component show lines of tricritical points, lines of critical end points and magnetic consolute points. Further investigations will include Gibbs Ensemble Monte Carlo simulations [3] of such mixtures which allow for the percolation limit that is not considered in the mean field calculations.

References


Phase diagrams I

\[ \zeta = -1, \quad \Lambda = 1, \quad R_m = \infty, \quad m_0/2m_0 = 0.5 \]

Ideal Ising fluid plus van der Waals fluid

Gibbs first order surface - light grey: liquid-liquid line (magnet-nonmagnetic) - red: critical line

Hot first order surface - yellow: three-phase line

Phase diagrams II

\[ \zeta = 0.5, \quad \Lambda = -0.05, \quad R_m = 0.5 \]

Line of consolute points in the magnetic regime

\[ \zeta = 0.5, \quad \Lambda = -0.25, \quad R_m = 0.5 \]

Critical and tricritical line

\[ \zeta = 0.5, \quad \Lambda = -0.05, \quad R_m = 0.2 \]

Critical and tricritical line

References