Binary mixtures of magnetic fluids

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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:

$$\frac{A_m(T_r, V_r, x, m)}{RT} = x\left(\frac{1-m}{2}\ln\frac{1-m}{2} + \frac{1+m}{2}\ln\frac{1+m}{2}\right) + (1-x)\ln(1-x) + x\ln x - \ln(V_r - 1) - \frac{27}{4}\frac{\alpha(x,m)}{V_r T_r} \quad (1)$$

Equations of state:

$$p_r = 8\frac{T_r}{V_r - 1} - 54\frac{\alpha(x,m)}{V_r^2}, \qquad m = \tanh\left(\frac{27 R_m}{4}\frac{xm}{V_r T_r}\right) \quad (2)$$

Quadratic mixing rule:

$$\alpha(x,m) = \left(1 + R_m m^2\right)x^2 + 2\frac{1-\Lambda}{1+\zeta}x(1-x) + \frac{1-\zeta}{1+\zeta}(1-x)^2 \quad (3)$$

3 parameters characterize the mixture:

$$\zeta = \frac{a_{22} - a_{11}}{a_{11} + a_{22}}, \qquad \Lambda = \frac{a_{11} - 2a_{12} + a_{22}}{a_{11} + a_{22}}, \qquad R_m = \frac{1}{2}\frac{a_m}{a_{22}} \quad (4)$$

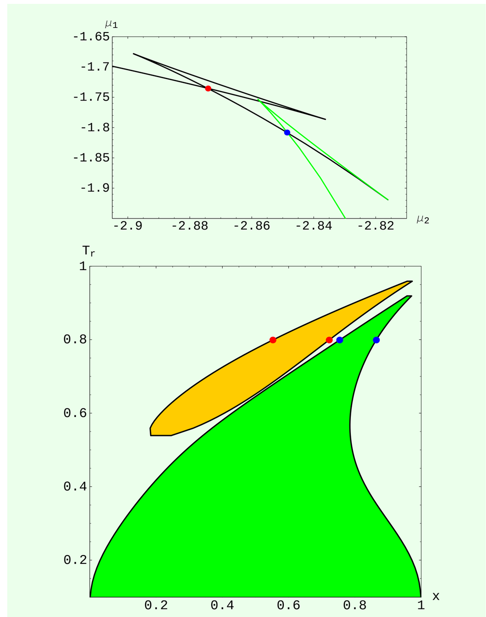
First order surfaces

Conditions for equilibrium of two phases α and β:

$$T_\alpha = T_\beta \quad (5)$$
$$p(x_\alpha, V_\alpha, m_\alpha) = p(x_\beta, V_\beta, m_\beta) \quad (6)$$
$$\mu_1(x_\alpha, V_\alpha, m_\alpha) = \mu_1(x_\beta, V_\beta, m_\beta) \quad (7)$$
$$\mu_2(x_\alpha, V_\alpha, m_\alpha) = \mu_2(x_\beta, V_\beta, m_\beta) \quad (8)$$

Conjugated field Δ of the concentration x:

$$\Delta = \mu_1 - \mu_2 \qquad \in [-\infty, +\infty] \quad (9)$$
$$\xi(\Delta) = \frac{1}{1+e^{-\frac{\Delta}{RT}}} \qquad \in [0,1] \quad (10)$$



Second order critical lines

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

$$\left(\frac{\partial^2 G_m}{\partial x^2}\right)_{T,p} = 0, \qquad \left(\frac{\partial^3 G_m}{\partial x^3}\right)_{T,p} = 0, \quad (11)$$

where G_m is the Gibbs free energy. In terms of the Helmholtz free energy this yields

$$A_{2V}A_{2x} - A_{Vx}^2 = 0 \quad (12)$$
$$A_{3V}A_{2x}^2 - 3A_{2Vx}A_{Vx}A_{2x} + 3A_{V2x}A_{Vx}^2 - A_{3x}A_{2V}A_{Vx} = 0 \quad (13)$$
$$A_{3x}A_{2V}^2 - 3A_{2xV}A_{Vx}A_{2V} + 3A_{x2V}A_{Vx}^2 - A_{3V}A_{2x}A_{Vx} = 0 \quad (14)$$

where

$$A_{iVjx} \equiv \left(\frac{\partial^{i+j}A_m}{\partial^i V_m \partial^j x}\right)_T \quad \text{and} \quad A_m = A_m(V_r, x, m(V_r, x)) \quad (15)$$

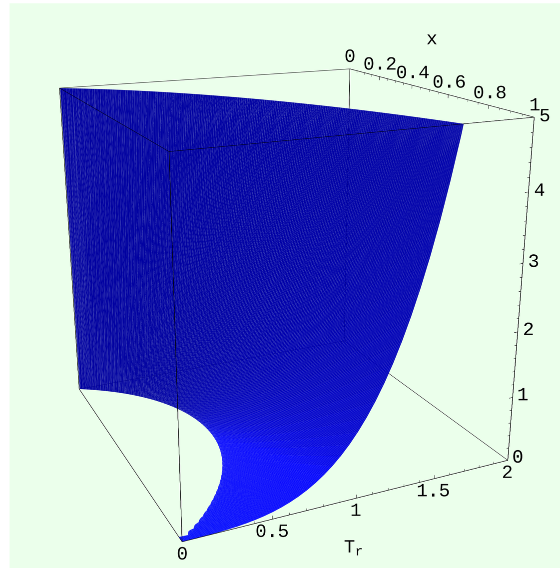
The function $m(V_r, x)$ is implicitly defined by the magnetic equation of state in (2).

Surface of magnetic phase transitions

The locus of second order ferromagnetic-paramagnetic phase transitions is a surface in x, T, V-space, given by

$$V_r = \frac{27}{4R_m}\frac{x}{T_r} \quad (16)$$

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



Tricritical lines

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

$$m^2 \sim 3\left(1 - \frac{4}{27R_m}\frac{V_r T_r}{x}\right) \quad (17)$$

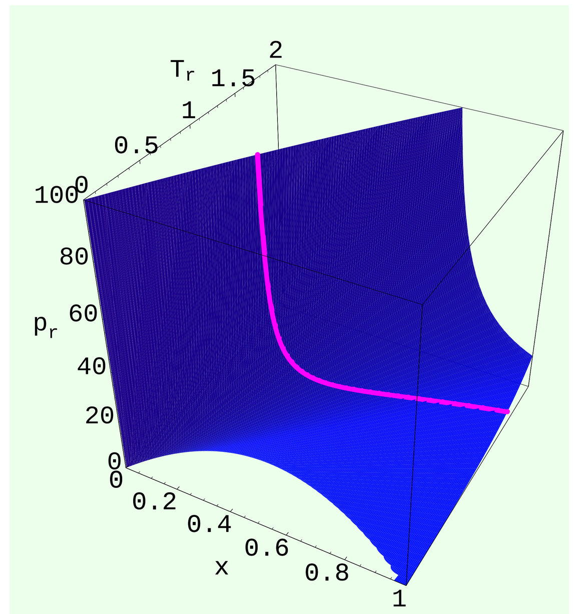
which is valid in the vicinity of the magnetic phase transition surface where $m \ll 1$, one can take the limit $m \to 0$ in (12) and gets an equation in T_r and x that can be written as

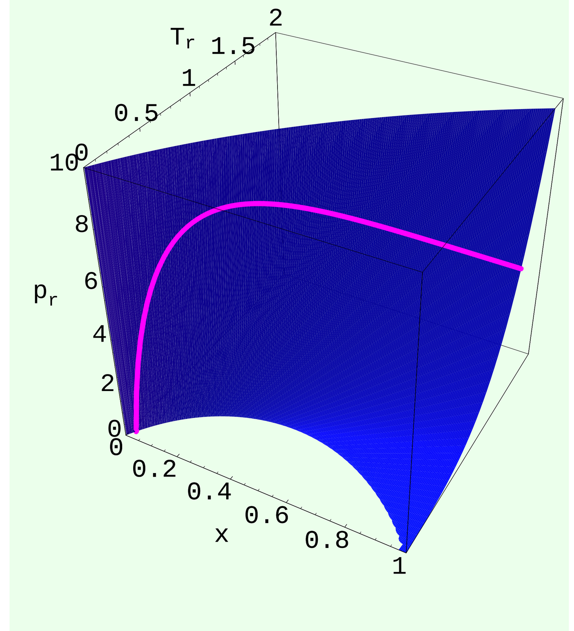
$$T_r = \frac{27R_m}{4}\left(x - \sqrt{\frac{x^3}{A(x) - \frac{B^2(x)}{C(x) - \frac{1}{1-x}}}}\right) \quad (18)$$

where $A(x) = \alpha(x,0)/R_m + \frac{3}{2}x^2$, $B(x) = A'(x)/2$ and $C(x) = B'(x)$.
In the limit of infinite pressure, the concentration x_∞ on the tricritical line is given by

$$x_\infty = \frac{4\Lambda + R_m(1+\zeta)}{4\Lambda + 3R_m(1+\zeta)} \quad (19)$$

and there is no tricritical point with $x < x_\infty$. For some parameter values however, (19) becomes negative, in which case the tricritical line takes on a maximum pressure value and ends in a critical end point on a first order surface.

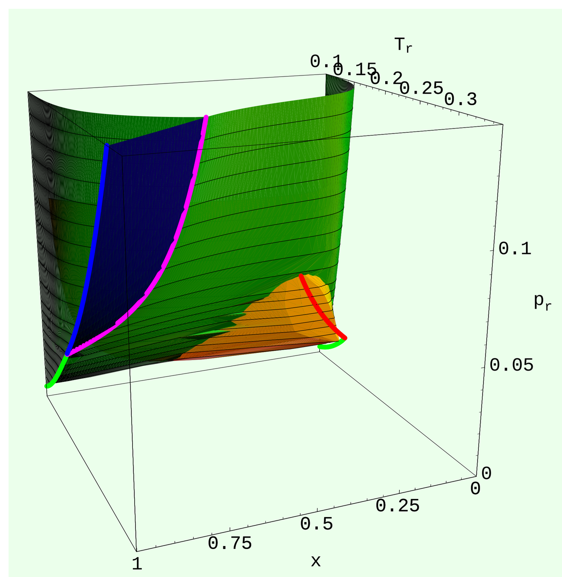


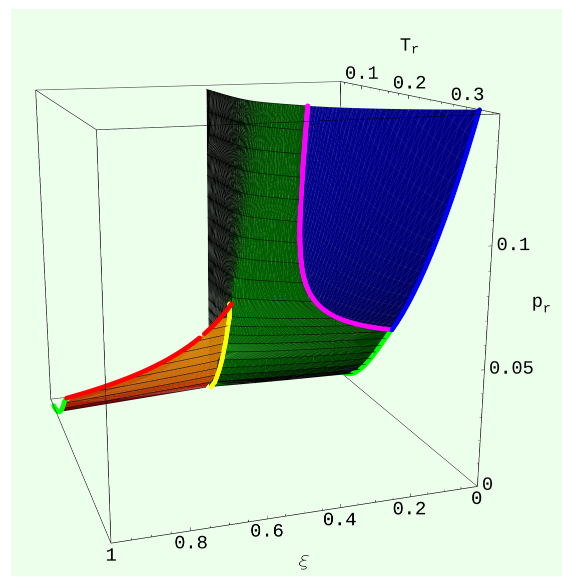


Phase diagrams I

green: first order surface (magnetic-nonmagnetic)
orange: first order surface (nonmagnetic-nonmagnetic)
light green: liquid-vapour curves
red: critical line
purple: tricritical line
yellow: three-phase line

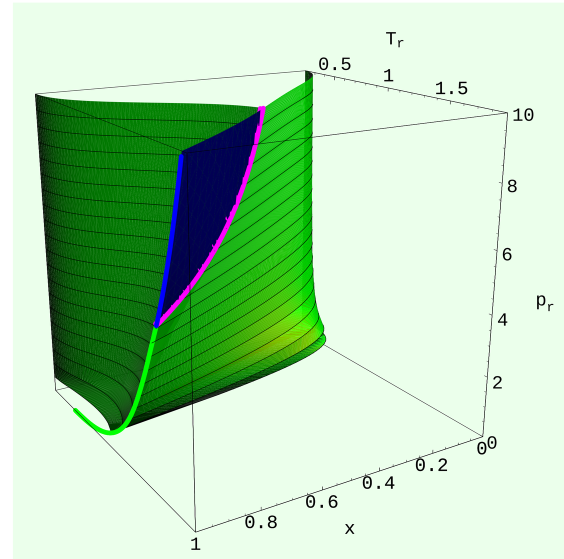
$\zeta = -1$, $\Lambda = 1$, $R_m = \infty$, $a_{11}/a_m = 0.5$:
Ideal Ising fluid plus van der Waals fluid

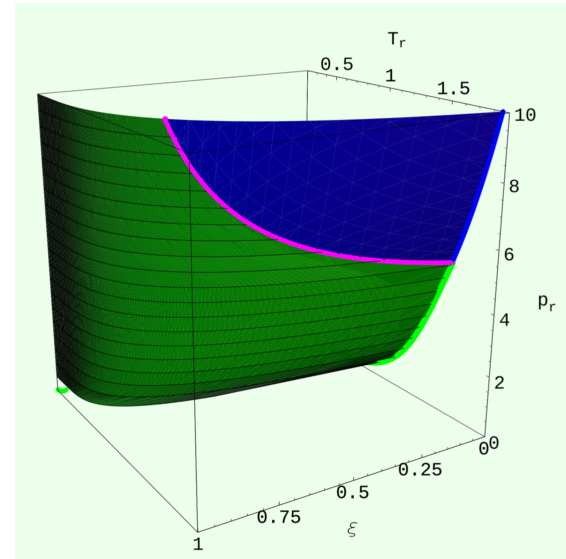




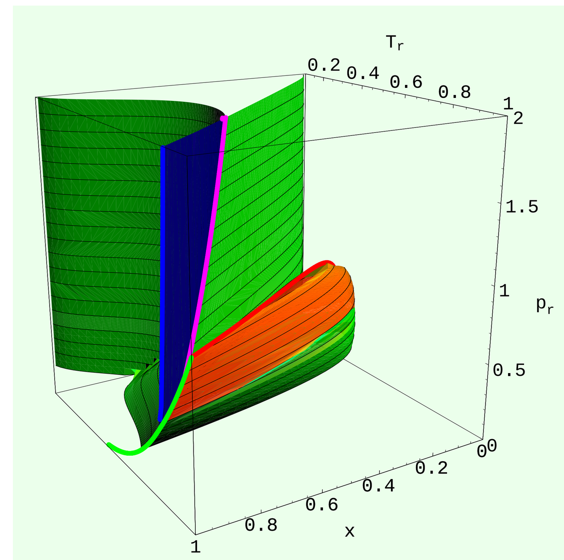
Phase diagrams II

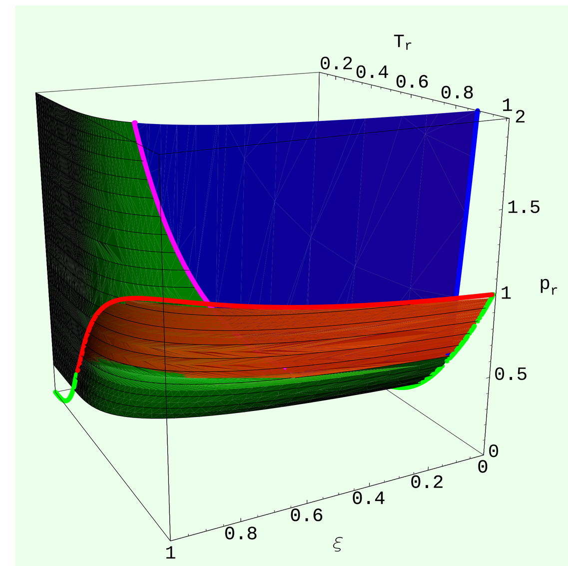
$\zeta = 0.5$, $\Lambda = -0.05$, $R_m = 0.5$:





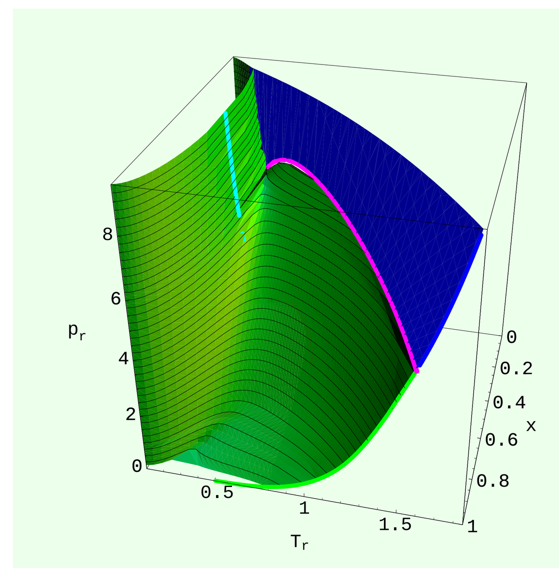
$\zeta = 0.5$, $\Lambda = -0.05$, $R_m = 0.2$:
Critical and tricritical line

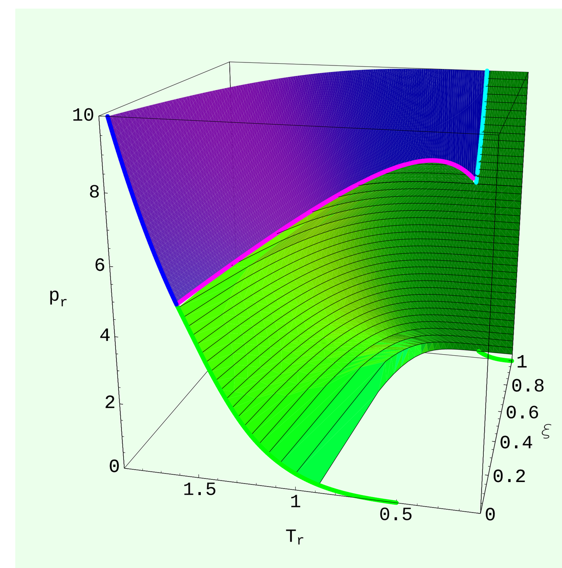




$\zeta = 0.5$, $\Lambda = -0.25$, $R_m = 0.5$:
Line of consolute points in the magnetic regime

cyan: magnetic critical line





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.
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References

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[2] P. C. Hemmer and D. Imbro, Phys. Rev. A **16**, 1977.
[3] A. Z. Panagiotopoulos, Mol. Phys. **61**, 1987.