Phase diagrams of Ising mixtures

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Mean Field Theory [1]

We describe a mixture of a van der Waals fluid and a ferromagnetic Ising fluid with mole fraction x and magnetization m at zero magnetic field in the framework of mean field theory. Setting $x = 1$ yields the mean field theory of the pure Ising fluid.

- Equations of state:

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

- Quadratic mixing rule:

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

- 3 parameters characterizing the mixture:

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

MC Simulation of phase transitions [2]

Potential between particles i and j of species a and b: Lennard-Jones + anisotropic Yukawa

$$u_{ij}(r) = \begin{cases} 4\varepsilon_{ab}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - R\varepsilon_{22}s_i s_j \frac{e^{-(r-\sigma)/\sigma}}{r/\sigma} & r < r_c \\ 0 & r > r_c \end{cases} \quad + \text{tail correction}$$

with spins $s_i = \pm 1$ for species 2, $s_i = 0$ for species 1

→ obtain 2D-histograms $H_i(S_1, S_2)$ from i-th simulation of length n_i at K_1^i, K_2^i
→ Multiple histogram reweighting:

$$P_{K_1K_2}(S_1,S_2) = \frac{\sum_{i=1}^{n} H_i(S_1,S_2)}{\sum_{j=1}^{n} n_j e^{(K_1^j - K_1)S_1 + (K_2^j - K_2)S_2 - C_j}}, \qquad e^{C_j} = \sum_{S_1,S_2} P_{K_1^j K_2^j}(S_1,S_2)$$

Pure fluid	Mixture

Grand Canonical Ensemble

- constant T, V, μ
- box size $L = 10\sigma \ldots 16\sigma$
- find shape of binodal near criticality, extrapolate tricritical point

$S_1 = E \quad K_1^j = -\beta_j$
$S_2 = N \quad K_2^j = \beta_j \mu_j$

Density of States MC [3]

- for high density/low temperature regions in pure fluid diagrams

Canonical Ensemble

- constant N, T, V
- $N = 150, 300, 500$, finite size scaling → find para-ferro phase transitions

$S_1 = E \quad K_1^j = -\beta_j$
$S_2 = M \quad K_2^j = \beta_j H = 0$

Semigrand Ensemble

- constant $N, T, p, \Delta\mu$
- $N = 300$
- find shape of binodal near criticality, extrapolate tricritical point
- reweighting at $p = const.$:

$S_1 = E + pV \quad K_1^j = -\beta_j$
$S_2 = N_2 \quad K_2^j = \beta_j \Delta\mu_j$

- reweighting at $T = const.$:

$S_1 = V \quad K_1^j = -\beta p_j$
$S_2 = N_2 \quad K_2^j = \beta \Delta\mu_j$

Isobaric-isothermal Ensemble

- constant N, T, p, x
- $N = 150, 300, 500$, finite size scaling → para-ferro transitions in mixtures

$S_1 = E + pV \quad K_1^j = -\beta_j$
$S_2 = M \quad K_2^j = \beta_j H = 0$

Gibbs Ensemble

- constant N, T, V, p
- $N = 500 \ldots 1000$
- not suitable for low temperatures
- does not work near criticality

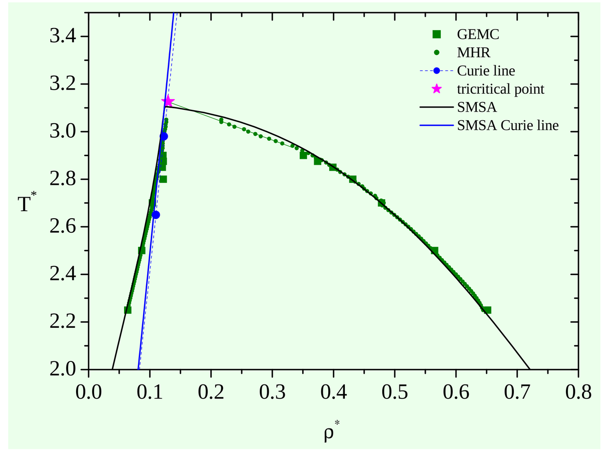
Results for pure Ising fluids

ideal Ising fluid:

- no nonmagnetic attraction: $\varepsilon_{22} = 0, R \to \infty, \varepsilon_m \equiv R\varepsilon_{22} = const.$
- soft-core repulsion:

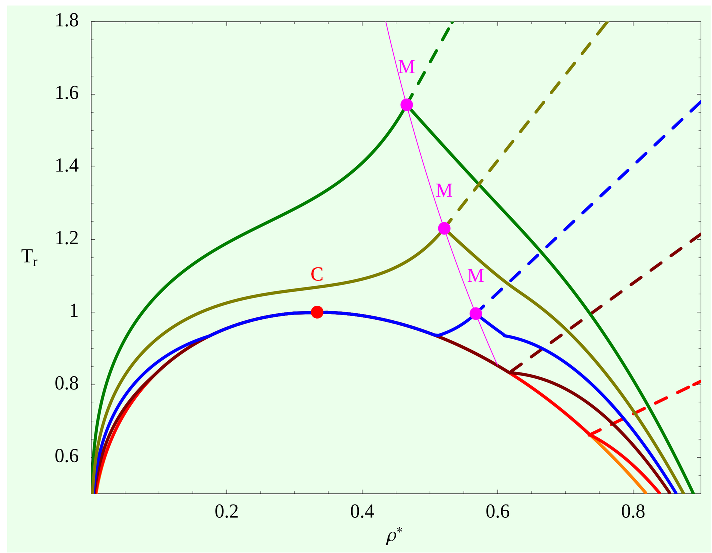
$$\varphi_{SC}(r) = \begin{cases} 4\varepsilon_{sc}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon_{sc} & r < \sqrt[6]{2}\sigma \\ 0 & r > \sqrt[6]{2}\sigma \end{cases}$$

- comparison with integral equation theory: Soft Mean Spherical Approximation (SMSA) [4]

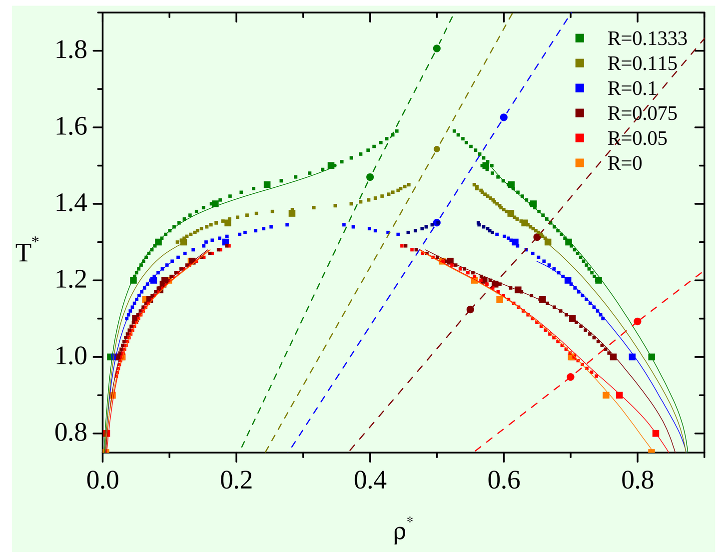


van der Waals Ising fluid:

Mean Field



Monte Carlo



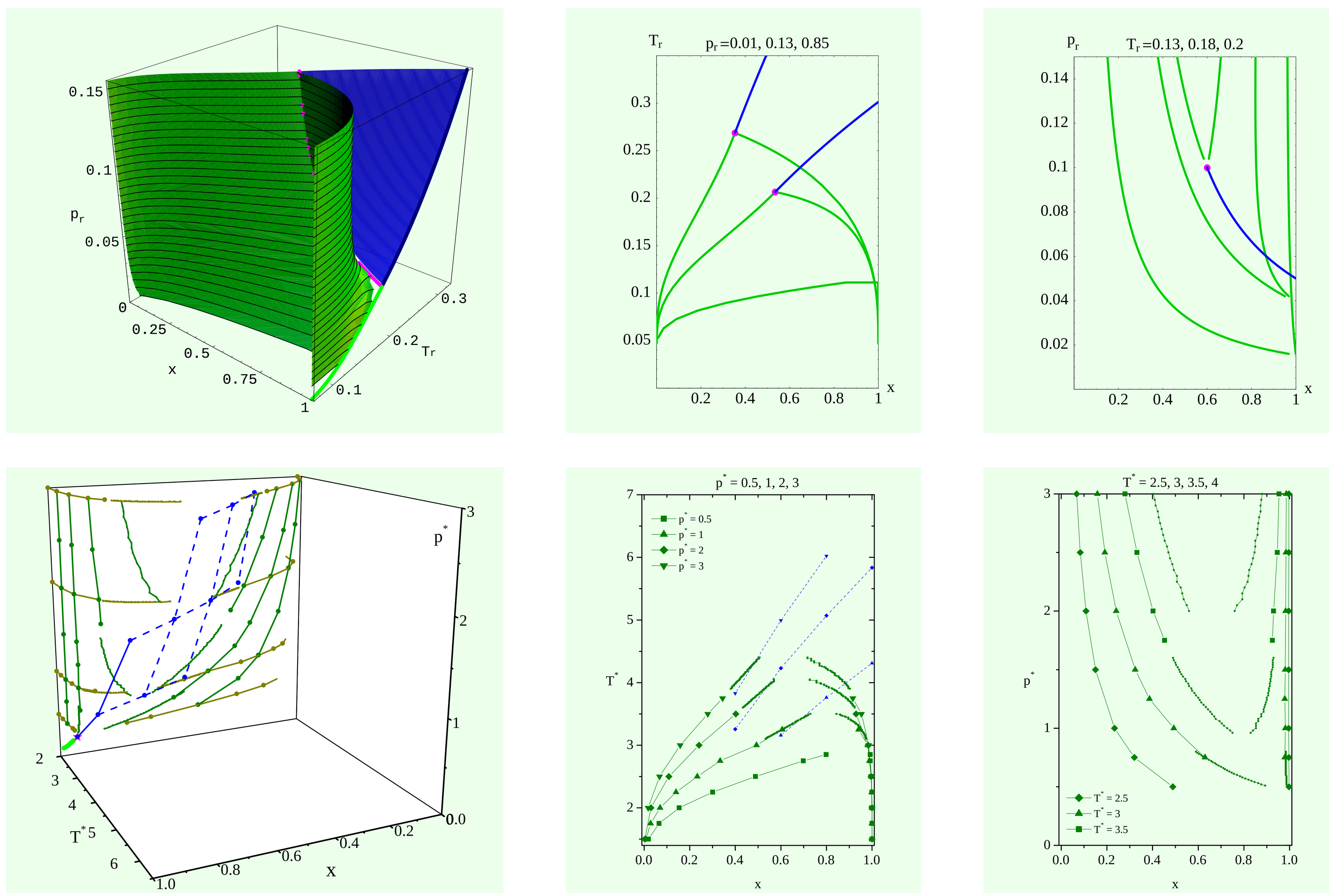
R_m = 0, 0.1333, 0.2, 0.26, 0.35, 0.5

C: Critical point
M: tricritical point
■ Gibbs Ensemble MC
• Multihistogram reweighting
– DOS MC
• magnetic phase transitions

Results for the ideal Ising mixture

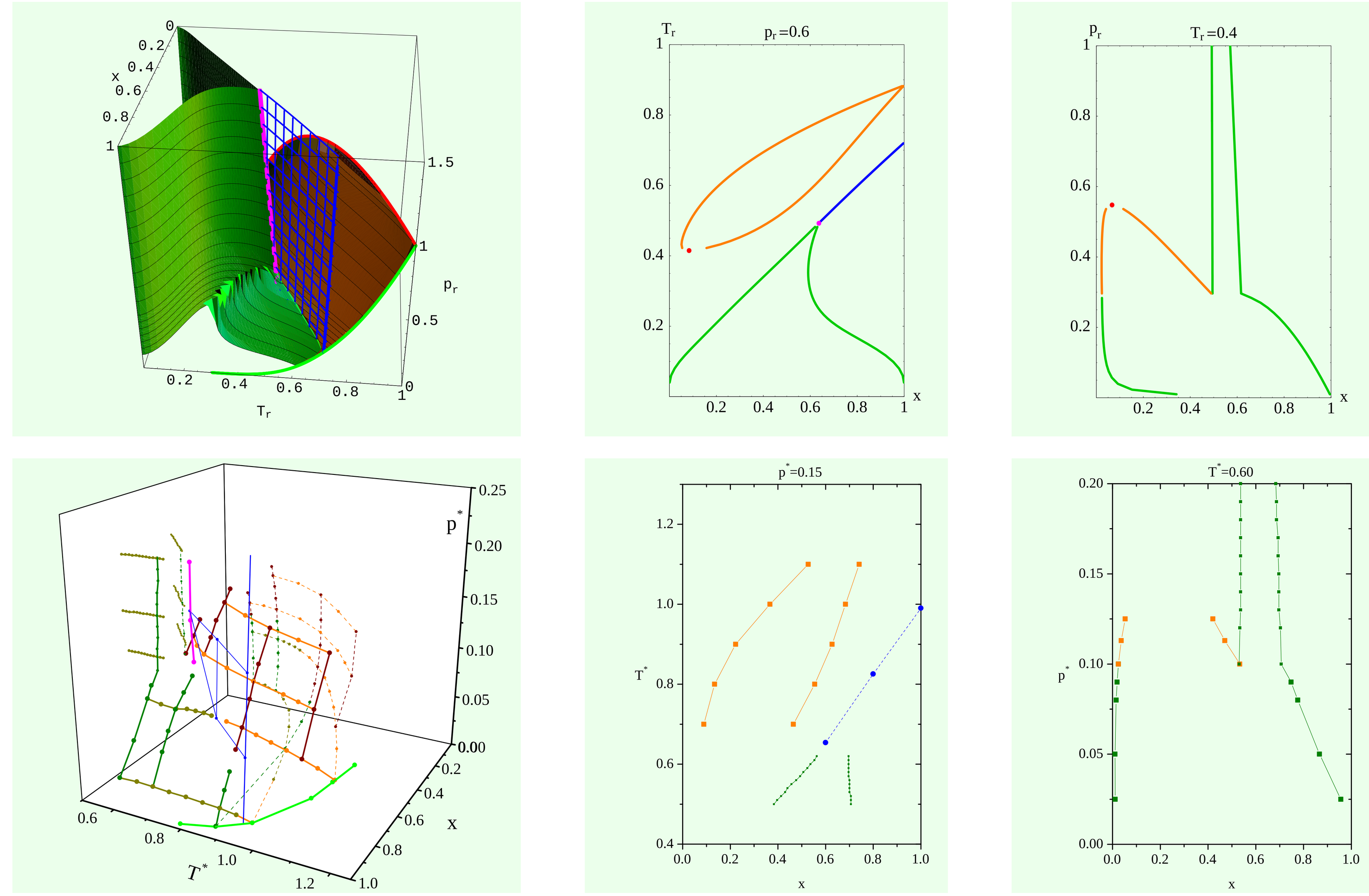
green: 1st order surface (magnetic - nonmagnetic)
orange: 1st order surface (nonmagnetic - nonmagnetic)
light green: liquid-vapour curve
red: critical line
cyan: magnetic critical line
purple: tricritical line
blue: surface of magnetic phase transitions

ideal Ising fluid + SC fluid

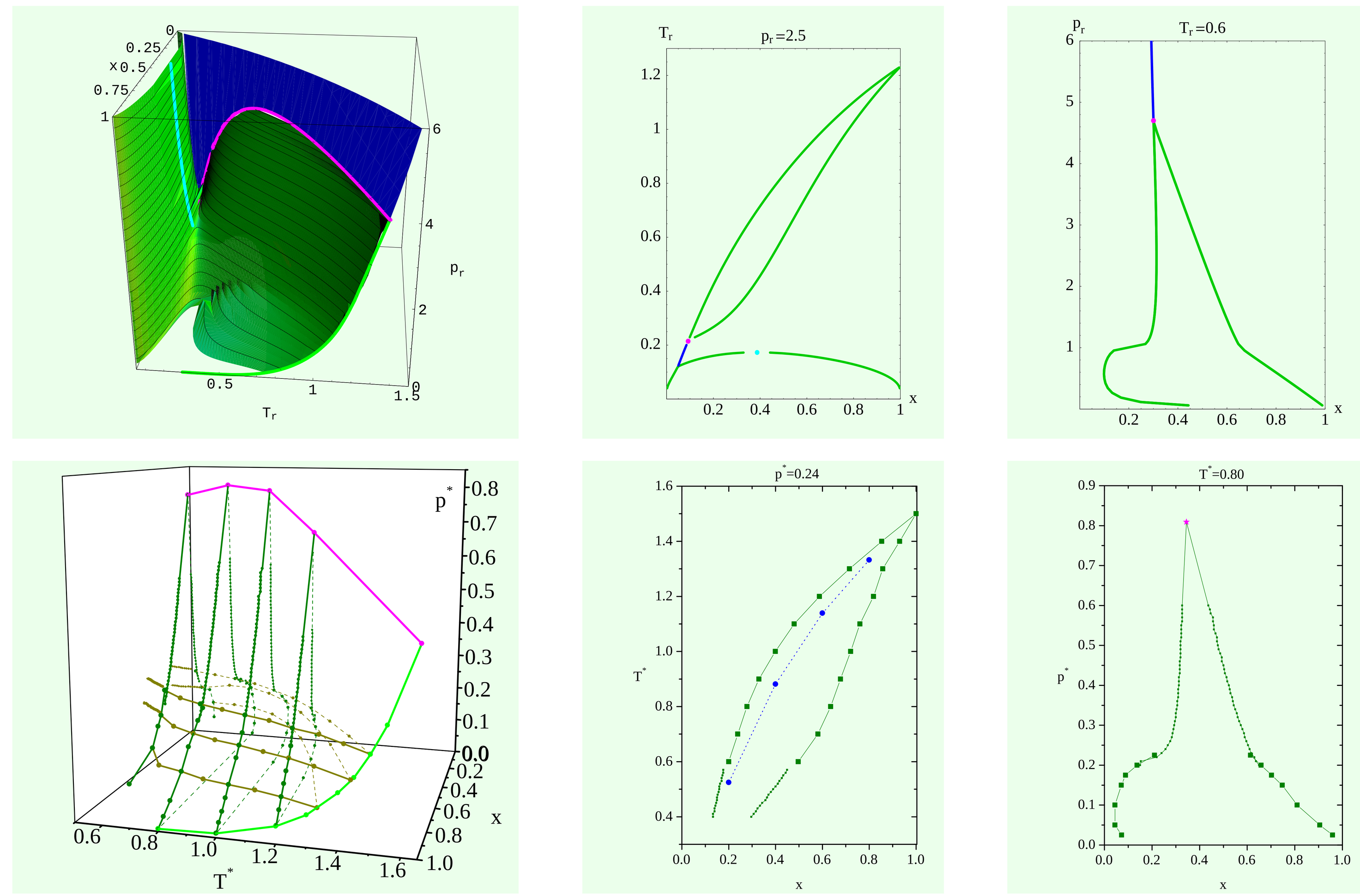


Results for Ising mixtures

$\zeta = 0.5, \Lambda = -0.05, R_m = 0.15$



$\zeta = 0.5, \Lambda = -0.25, R_m = 0.4$



Summary

While in ordinary binary fluid mixtures tricritical points occur only under special circumstances, mixtures with a magnetic fluid component show a line of tricritical points, that has either the character of a consolute point line or a plait point line. These topologies of the phase diagrams calculated in mean field theory were verified with Monte Carlo simulations at certain parameter values. (Grant: FWF P15247)

References

[1] W. Fenz and R. Folk, Phys. Rev. E **67**, 021507 (2003)
[2] W. Fenz, R. Folk, Cond. Matt. Phys. **6**, 675 (2003)
[3] F. G. Wang and D. P. Landau, Phys. Rev. Lett. **86**, 2050 (2001)
[4] I. P. Omelyan, I. M. Mryglod, R. Folk, W. Fenz, submitted to Phys. Rev. E