Liquid interfaces in Ising fluids

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Supported by

Project No. P18592-TPH

Abstract

We study the thermodynamic properties and microscopic structure of liquid-liquid and liquid-vapor interfaces in Ising spin fluids by an integral equation (IE) approach. The coupled set of the Lovett-Mou-Buff-Wertheim equations for the inhomogeneous one-particle distribution functions and the Ornstein-Zernike equations for the bulk twoparticle correlation functions complimented by the closure relation are solved using a modified soft mean spherical approximation. The twoparticle inhomogeneous direct correlation functions are consistently constructed by nonlinear interpolation of the bulk ones corresponding to the coexisting phases. The density and magnetization profiles at the liquid-liquid and liquid-vapor interfaces are calculated in a wide range of temperatures including subcritical regions. The liquid-liquid adsorption coefficient and the liquid-vapor surface tension are evaluated as well. The influence of the external magnetic field on the structure of the liquid-vapor interfaces is also analyzed.

The Ising fluid model

The Hamiltonian of a 3-dimensional Ising fluid in an external magnetic field $B(\mathbf{r})$ reads

$$H = \sum_{i<j}^{N}\Big[\varphi(r_{ij}) - J(r_{ij})\,s_i s_j\Big] - \sum_{i=1}^{N} s_i B(\mathbf{r}_i),$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|, \qquad \mathbf{r} = (r_x, r_y, r_z), \qquad s_i = \pm 1.$$

Ferromagnetic exchange interaction and nonmagnetic repulsion are given by

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

The system can be mapped to a binary nonmagnetic mixture:

$$N^+: \quad s_i = +1, \qquad N^-: \quad s_i = -1, \qquad N^+ + N^- = N$$

$$H = \sum_{i<j}^{N^+}\phi_{++}(r_{ij}) + \sum_{i<j}^{N^-}\phi_{--}(r_{ij}) + \sum_{i,j=1}^{N^+,N^-}\phi_{+-}(r_{ij}) - \Psi$$

$$\phi_{++}(r) = \phi_{--}(r) = \varphi(r) - J(r), \qquad \phi_{+-}(r) = \phi_{-+}(r) = \varphi(r) + J(r)$$

$$\Psi = \sum_{i=1}^{N^+} B(\mathbf{r}_i) - \sum_{i=1}^{N^-} B(\mathbf{r}_i), \quad B(\mathbf{r}) \equiv B, \quad \Psi = BM, \quad M = \sum_{i=1}^{N} s_i = N^+ - N^-$$

Inhomogeneous IE approach

We consider a planar interface perpendicular to the z-axis,

$$\rho_\pm(\mathbf{r}) \equiv \rho_\pm(z), \qquad B(\mathbf{r}) \equiv B(z),$$

introducing cylindrical coordinates

$$\mathbf{r} = (\mathbf{s}, z), \qquad \mathbf{s} = (s, \psi), \qquad s_{12} = |\mathbf{s}_1 - \mathbf{s}_2|, \qquad r_{12} = [s_{12}^2 + (z_1 - z_2)^2]^{1/2},$$

such that the pair correlation functions can be written as $(\alpha, \beta = +, -)$:

$$h_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \equiv h_{\alpha\beta}(s_{12}, z_1, z_2), \qquad c_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \equiv c_{\alpha\beta}(s_{12}, z_1, z_2), \qquad g_{\alpha\beta} \equiv h_{\alpha\beta} + 1.$$

The one-particle density distribution fuctions ρ_α and the two-particle direct and total correlation functions $c_{\alpha\beta}$ and $h_{\alpha\beta}$ are connected via the LMBW (Lovett-Mou-Buff-Wertheim) equations,

$$\frac{\mathrm{d}\ln\rho_\alpha(z_1)}{\mathrm{d}z_1} = \frac{1}{k_\mathrm{B}T}\frac{\mathrm{d}B_\alpha(z_1)}{\mathrm{d}z_1} + 2\pi\sum_{\beta=+,-}\int_{-\infty}^{\infty}\mathrm{d}z_2\int_0^\infty s\mathrm{d}s\,c_{\alpha\beta}(s, z_1, z_2)\frac{\mathrm{d}\rho_\beta(z_2)}{\mathrm{d}z_2},$$

the IOZ (Inhomogeneous Ornstein-Zernike) equations,

$$h_{\alpha\beta}(s, z_1, z_2) = c_{\alpha\beta}(s, z_1, z_2) + \sum_{\gamma=+,-}\int\mathrm{d}\mathbf{s}'\int\mathrm{d}z_3\,c_{\alpha\gamma}(|\mathbf{s} - \mathbf{s}'|, z_1, z_3)\rho_\gamma(z_3)\,h_{\gamma\beta}(s', z_3, z_2),$$

and the closure relation,

$$g_{\alpha\beta}(s, z_1, z_2) = \exp\left[-\frac{\phi_{\alpha\beta}(r_{12})}{k_\mathrm{B}T} + h_{\alpha\beta}(s, z_1, z_2) - c_{\alpha\beta}(s, z_1, z_2) + b_{\alpha\beta}(s, z_1, z_2)\right],$$

where we use for the bridge function $b_{\alpha\beta}$ the MSMSA (Modified Soft Mean Spherical Approximation [2]), defined as

$$b_{\alpha\beta}(s, z_1, z_2) = \begin{cases} \ln[1 + \tau_{\alpha\beta}(s, z_1, z_2)] - \tau_{\alpha\beta}(s, z_1, z_2)\,, & \tau_{\alpha\beta}(s, z_1, z_2) > 0 \\ 0\,, & \tau_{\alpha\beta}(s, z_1, z_2) \leq 0 \end{cases},$$

with the renormalized indirect correlation function given by

$$\tau_{\alpha\beta}(s, z_1, z_2) = h_{\alpha\beta}(s, z_1, z_2) - c_{\alpha\beta}(s, z_1, z_2) - \frac{\phi_{\alpha\beta}(r_{12}) - \varphi(r_{12})}{k_\mathrm{B}T}\exp\left[-\frac{\varphi(r_{12})}{k_\mathrm{B}T}\right].$$

Interpolation of correlation functions

The inhomogeneous direct correlation functions $c_{\alpha\beta}(s, z_1, z_2)$ are consistently interpolated between the bulk functions $c_{\alpha\beta}^{\mathrm{blk}}(r)$ obtained within the homogeneous OZ-MSMSA approach:

$$c_{\alpha\beta}(s, z_1, z_2) = \frac{1}{2}\Big[c_{\alpha\beta}(r_{12}; \boldsymbol{\rho}(z_1)) + c_{\alpha\beta}(r_{12}; \boldsymbol{\rho}(z_2))\Big], \qquad \boldsymbol{\rho}(z) = \{\rho_+(z), \rho_-(z)\},$$

$$c_{\alpha\beta}(r; \boldsymbol{\rho}) = \sum_{k=0}^{2}\tilde{w}_k(\boldsymbol{\rho})c_{\alpha\beta}^{\mathrm{blk}}(r; \boldsymbol{\rho}^{(k)}), \qquad \boldsymbol{\rho}^{(1,2)} = (\rho_+^{(1,2)}, \rho_-^{(1,2)}), \qquad \rho_\pm^{(0)} \to +0,$$

$$\lim_{z\to-\infty}\rho_\pm(z) = \rho_\pm^{(1)}, \qquad \lim_{z\to+\infty}\rho_\pm(z) = \rho_\pm^{(2)},$$

$$w_1(\boldsymbol{\rho}) = \frac{\rho_+^{(0)}(\rho_- - \rho_-^{(2)}) + \rho_+^{(2)}(\rho_-^{(0)} - \rho_-) + \rho_+(\rho_-^{(2)} - \rho_-^{(0)})}{\rho_+^{(0)}(\rho_-^{(1)} - \rho_-^{(2)}) + \rho_+^{(1)}(\rho_-^{(2)} - \rho_-^{(0)}) + \rho_+^{(2)}(\rho_-^{(0)} - \rho_-^{(1)})},$$

$$w_2(\boldsymbol{\rho}) = \frac{\rho_+^{(0)}(\rho_-^{(1)} - \rho_-) + \rho_+^{(1)}(\rho_- - \rho_-^{(0)}) + \rho_+(\rho_-^{(0)} - \rho_-^{(1)})}{\rho_+^{(0)}(\rho_-^{(1)} - \rho_-^{(2)}) + \rho_+^{(1)}(\rho_-^{(2)} - \rho_-^{(0)}) + \rho_+^{(2)}(\rho_-^{(0)} - \rho_-^{(1)})},$$

$$w_0 = 1 - w_1 - w_2, \qquad w_{k'}(\boldsymbol{\rho}^{(k)}) = \delta_{k'k},$$

with the nonlinear interpolation weights

$$\tilde{w}_k = w_k + f_k w_k^2(1 - w_k)^2, \qquad k = 1, 2, \qquad \tilde{w}_0 = 1 - \tilde{w}_1 - \tilde{w}_2.$$

The bulk direct correlation functions fulfill homogeneous OZ equations + MSMSA closure:

$$h_{\alpha\beta}(r) = c_{\alpha\beta}^{\mathrm{blk}}(r; \boldsymbol{\rho}^{(k)}) + \sum_{\gamma=+,-}\rho_\gamma^{(k)}\int c_{\alpha\gamma}^{\mathrm{blk}}(|\mathbf{r} - \mathbf{r}'|; \boldsymbol{\rho}^{(k)})\,h_{\gamma\beta}(r')\mathrm{d}\mathbf{r}'$$

LMBW-OZ-MSMSA reformulation

The LMBW equations now take the form

$$\frac{\mathrm{d}\ln\rho_\alpha(z_1)}{\mathrm{d}z_1} = \frac{1}{k_\mathrm{B}T}\frac{\mathrm{d}B_\alpha(z_1)}{\mathrm{d}z_1} + \frac{1}{2}\sum_{\beta=+,-}\int_{-\infty}^{\infty}\frac{\mathrm{d}\rho_\beta(z_2)}{\mathrm{d}z_2}\sum_{k=0}^{2}[\tilde{w}_k(\boldsymbol{\rho}(z_1)) + \tilde{w}_k(\boldsymbol{\rho}(z_2))]\,c_{\alpha\beta}^{\mathrm{blk}}(|z_1 - z_2|; \boldsymbol{\rho}^{(k)})\mathrm{d}z_2$$

with

$$c_{\alpha\beta}^{\mathrm{blk}}(|z_1 - z_2|; \boldsymbol{\rho}^{(k)}) = 2\pi\int_0^\infty s\mathrm{d}s\,c_{\alpha\beta}^{\mathrm{blk}}(r_{12}; \boldsymbol{\rho}^{(k)}).$$

The densities $\boldsymbol{\rho}^{(1,2)}$ of coexisting bulk phases at T are determined by equilibrium conditions:

$$\begin{aligned} P\big(\rho_+^{(1)}, \rho_-^{(1)}, T\big) &= P\big(\rho_+^{(2)}, \rho_-^{(2)}, T\big), \\ \mu_+\big(\rho_+^{(1)}, \rho_-^{(1)}, T\big) &= \mu_+\big(\rho_+^{(2)}, \rho_-^{(2)}, T\big) \equiv \mu_+^{\mathrm{eq}}, \\ \mu_-\big(\rho_+^{(1)}, \rho_-^{(1)}, T\big) &= \mu_-\big(\rho_+^{(2)}, \rho_-^{(2)}, T\big) \equiv \mu_-^{\mathrm{eq}}, \end{aligned}$$

in combination with the external field constraint [2]

$$\mu_-^{\mathrm{eq}} - \mu_+^{\mathrm{eq}} = 2B,$$

where

$$\begin{aligned} P(\rho_+, \rho_-, T) &= \rho k_\mathrm{B}T - \frac{2\pi}{3}\sum_{\alpha,\beta}^{+,-}\rho_\alpha\rho_\beta\int_0^\infty\frac{\mathrm{d}\phi_{\alpha\beta}}{\mathrm{d}r}g_{\alpha\beta}(r)r^3\mathrm{d}r, \\ \mu_\alpha(\rho_+, \rho_-, T) &= k_\mathrm{B}T(\ln\rho_\alpha + 3\ln\Lambda_\alpha) \\ &\quad + k_\mathrm{B}T\sum_{\beta=+,-}\rho_\beta\int_0^\infty\Big[\frac{1}{2}h_{\alpha\beta}^2(r) - c_{\alpha\beta}(r) - \frac{1}{2}h_{\alpha\beta}(r)c_{\alpha\beta}(r) + b_{\alpha\beta}(r)g_{\alpha\beta}(r) \\ &\qquad - \frac{h_{\alpha\beta}(r)}{\tau_{\alpha\beta}(r)}\int_0^{\tau_{\alpha\beta}(r)}b_{\alpha\beta}(\tau')\mathrm{d}\tau'\Big]4\pi r^2\mathrm{d}r. \end{aligned}$$

If we introduce the independent one-fluid quantities

$$\mu = (\mu_+ + \mu_-)/2, \qquad \Delta\mu = (\mu_- - \mu_+)/2, \qquad \rho = \rho_+ + \rho_-, \qquad m = (\rho_+ - \rho_-)/\rho,$$

and solve the external field constraint with respect to m, $m = m(\rho, T, B)$, we can rewrite the equilibrium conditions like in a simple liquid:

$$\begin{aligned} P(\rho^{(1)}, B, T) &= P(\rho^{(2)}, B, T), \\ \mu(\rho^{(1)}, B, T) &= \mu(\rho^{(2)}, B, T), \\ m^{(1,2)} &= m(\rho^{(1,2)}, T, B). \end{aligned}$$

Consistency conditions

The LMBW equations require two independent integration constants:

$$\rho(z)|_{z=0} = \rho_0 \in]\rho^{(1)}, \rho^{(2)}[, \qquad m(z)|_{z=0} = m_0.$$

The consistency conditions for the liquid-vapor interface are

$$\lim_{z\to-\infty}\rho(z) = \rho^{(1)}, \qquad \lim_{z\to+\infty}\rho(z) = \rho^{(2)}, \qquad \lim_{z\to\mp\infty}m(z) = m^{(1,2)} = m(\rho^{(1,2)}, T, B),$$

where $\rho^{(1,2)}$ and $m^{(1,2)}$ are bulk values obtained within the homogeneous OZ-SMSA approach. Only 3 of the 4 conditions can be fulfilled by adjusting f_1, f_2 and m_0, but one can achieve complete consistency by a modified interpolation scheme with coarse-grained densities:

$$\overline{\rho}_\pm(z) = \frac{1}{D}\int_{z-D/2}^{z+D/2}\rho_\pm(z')\,\mathrm{d}z',$$

with a grain diameter $D \sim \sigma$, which is adjusted together with f_1, f_2, m_0

Liquid-liquid interfaces

$$B = 0, \quad \rho^{(1)} = \rho^{(2)} = \rho, \quad m^{(1)} = -m^{(2)}, \qquad \begin{array}{l} T \geq T_\lambda(\rho) : \rho(z) = const, m(z) = 0 \\ T < T_\lambda(\rho) : \rho(z) \neq const, m(z) \neq 0 \end{array}$$

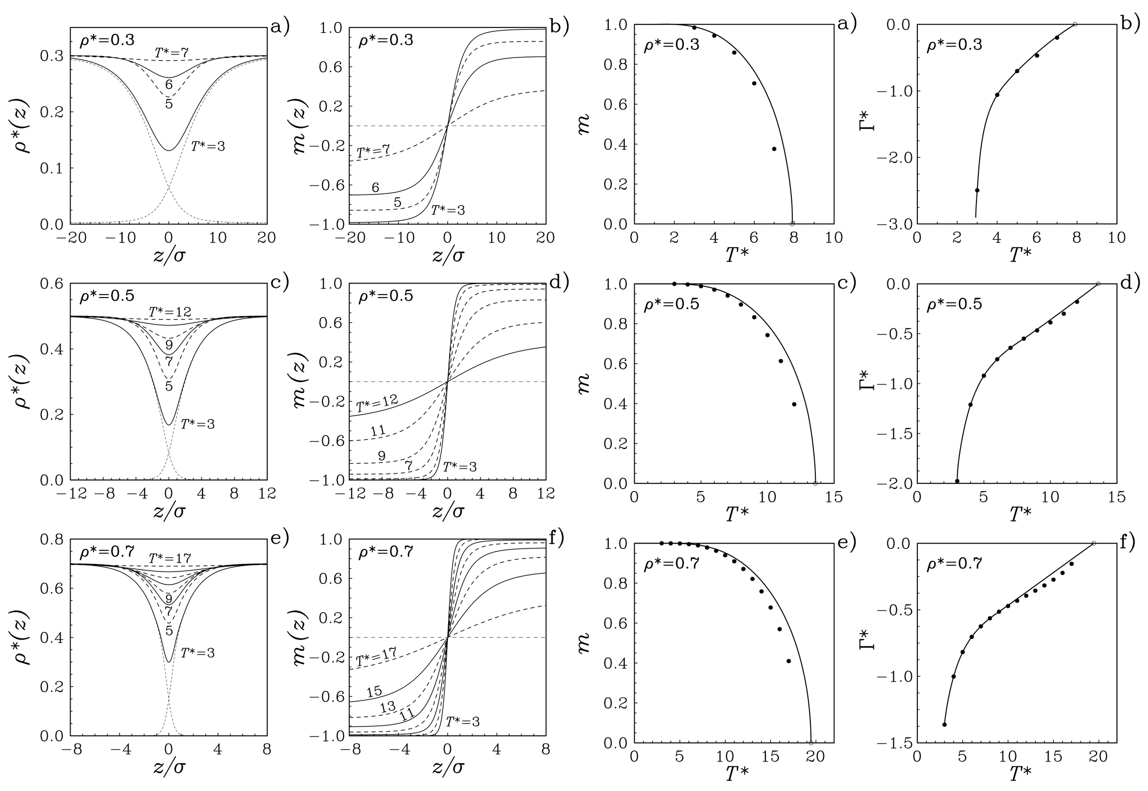
Symmetries:

$$\rho_+(-z) = \rho_-(z), \qquad \rho_-(-z) = \rho_+(z), \qquad \rho(-z) = \rho(z), \qquad m(-z) = -m(z)$$

Interpolation scheme:

$$m_0 = 0, \qquad \rho_0 : \lim_{z\to\pm\infty}\rho(z) = \rho, \qquad f_1 = f_2 = f : \lim_{z\to\mp\infty}m(z) = m^{(1,2)}, \qquad D = \sigma$$

Gibbs absorption coefficient: $\Gamma = \int_{-\infty}^{\infty}(\rho(z) - \rho_{\mathrm{blk}})\mathrm{d}z, \qquad \rho_{\mathrm{blk}} \equiv \rho$



full circles: linear interpolation ($f = 0$); **open circles:** critical points; **solid curves:** nonlinear interpolation

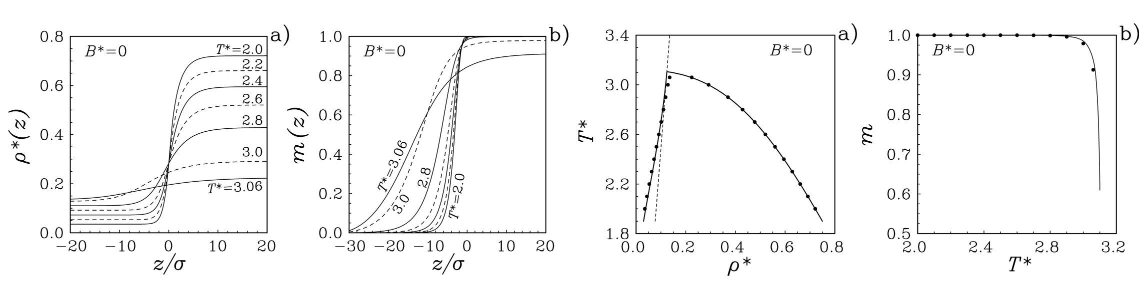
Liquid-vapor interfaces

$$\begin{array}{llll} T \geq T_\mathrm{c}(B) : & \rho(z) = const, & m(z) = const & \\ T < T_\mathrm{c}(B) : & \rho(z) \neq const, & \rho^{(1)} \neq \rho^{(2)}, \quad m(z) \neq const, & m^{(1)} \neq m^{(2)} \end{array}$$

Interpolation scheme:

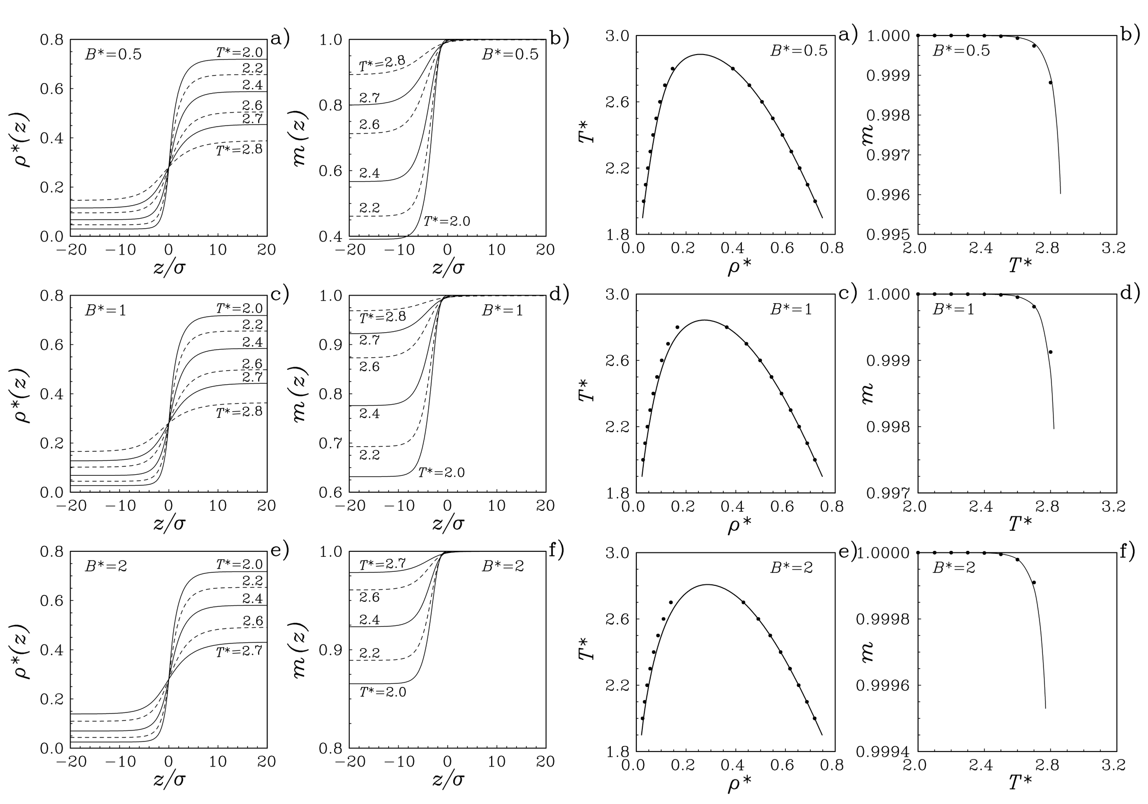
$$m_0 : \lim_{z\to-\infty}m(z) = m^{(1)}, \qquad f_2 : \lim_{z\to+\infty}\rho(z) = \rho^{(2)}, \quad f_1 = 0, \qquad D = \sigma$$

Zero field case:

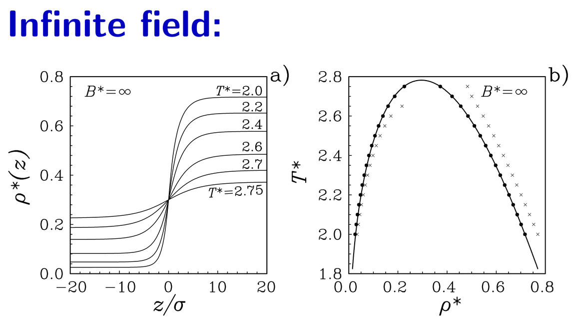


circles: inhomogeneous LMBW-OZ-MSMSA theory; **solid curves:** homogeneous OZ-MSMSA theory

Nonzero field:



Infinite field:

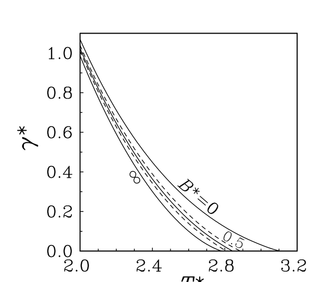


circles: asymptotic values of LMBW-OZ-MSMSA density profiles
solid curve: bulk OZ-MSMSA densities
crosses: asymptotic values obtained using another (linear) interpolation scheme (Iatsevitch and Forstmann)

Surface tension:

$$\gamma = \frac{\pi k_\mathrm{B}T}{2}\sum_{\alpha,\beta}\int\int\int\rho'_\alpha(z_1)\rho'_\beta(z_2)s^3c_{\alpha\beta}(s, z_1, z_2)\,\mathrm{d}z_1\mathrm{d}z_2\mathrm{d}s$$

$$T < T_\mathrm{c}(B): \quad \gamma(T) > 0, \qquad T \geq T_\mathrm{c}(B): \quad \gamma = 0$$



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