INTERFACES BETWEEN COEXISTING PHASES: WHAT CAN WE LEARN FROM MONTE CARLO SIMULATIONS?

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in collaboration with

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Numerical Calculations of Spin Correlation Functions
and Magnetization Curves of Ferromagnets

The static correlation functions and the magnetization curves of finite (125—1000 spins) Ising- and Heisenberg-ferromagnets are calculated using a Monte-Carlo-method for all temperatures. We assume $S=\infty$, a simple cubic lattice and nearest neighbours interactions. Various theoretical assumptions concerning the correlation functions and the magnetization may be examined by means of the calculated results. Magnetization curves for superparamagnetic systems were computed also.

... and CONGRATULATIONS to your 80th birthday!
symmetrical polymer mixture

\[ N = 32 \]

Snapshot of coarse-grained interface

$L=64$
Capillary wave theory:

\[ H_{CW} \approx \frac{\gamma}{2} \int_{0}^{L} \| \nabla h(x, y) \|^{2} \, dx \, dy \]

\[ h(\vec{r}) = \sum_{\vec{q}} h(\vec{q}) \exp(i\vec{q}\cdot\vec{r}) \]

\[ \Rightarrow H_{CW} = \frac{\gamma}{2} \sum_{\vec{q}} q^{2} |h(\vec{q})|^{2} \]

In 3D: \[ W_{CW}^{2} \propto \ln L \]

\[ \text{equipartition: } \frac{\gamma}{2} q^{2} \langle |h(\vec{q})|^{2} \rangle = \frac{4}{2} k_{B} T \]
VARIATION of the MEAN SQUARE INTERFACE WIDTH $W^2$ WITH THE LATERAL SIZE $L$

$$s_L^2 = \frac{1}{2\pi} \int_0^{2\pi} \frac{\ln(L/B_0)}{s_L^2} \, dq$$

CONVOLUTION APPROXIMATION

intrinsic profile (width $W_0$)

Gaussian distribution

$$P_L(h) = \frac{1}{(2\pi s_L^2)^{1/2}} \exp\left(-\frac{h^2}{2s_L^2}\right)$$

$$\Rightarrow W^2 = W_0^2 + \frac{1}{48\pi} \ln \frac{L}{B_0}$$

**One cannot determine the two parameters $W_0, B_0$ separately!**
ORDER PARAMETER PROFILE across an INTERFACE of area $L \times L$

Interfacial width depends on interfacial area

$\epsilon_{AA} = \epsilon_{BB} = -\epsilon_{AB} = k_B T \epsilon$

$W_L^2 \propto \ln L$

$\epsilon = 0.03 \ (T/T_c = 0.48)$

Strongly segregated polymer mixture

A. Werner et al. (1999)

"state of
the art":

\[ L_\text{z} = 150\sigma \]

\[ S = 50\sigma \]

LJ fluid,

\[ r_c = 36 \]

\[ \varphi_v \delta^3 = 0.118 \]

\[ \varphi_e \delta^3 = 0.540 \]

separating capillary wave broadening from the "intrinsic width" is an ILL-POSED PROBLEM:

"The representation of a l-v-interface by a two-dimensional manifold renders only an incomplete picture of this inherently three-dimensional object."
van der Waals equation

Landau theory

Order parameter \( \psi = \frac{1}{2} \left( \frac{\rho}{\rho_c} - 1 \right) \)

Free energy density

\[
\Delta f_{\text{Landau}}(\rho, T) = \frac{9}{2} k_B T \rho_c \left[ \frac{1}{2} \left( \frac{T}{T_c} - 1 \right) \psi^2 + \frac{1}{4} \psi^4 \right]
\]

Description of interfaces:

Ginzburg-Landau free energy functional

\[
\Delta F[\psi(\mathbf{x})] = \int d^3 x \left[ \Delta f_{\text{Landau}}(\psi) + \frac{R^2}{2d} (\nabla \psi)^2 \right]
\]

\( R = \) interaction range

\( d = \) dimensionality

\( \Delta F[\psi(\mathbf{x})] \rightarrow \) Minimum

Inhomogeneous solution:

\( \psi(z \to \pm \infty) = \pm \psi_{\text{coex}} \)
Ginzburg-Landau Mean Field Theory of Interfaces

\[ \phi = \frac{\psi}{\psi_{\text{coex}}} \quad \xi = \frac{z}{\xi} \]

\[ \delta A F(\psi(z))/\delta \psi(z) = 0 \Rightarrow \text{Ginzburg-Landau equation} \]

\[ \phi - \phi^3 = 2 \frac{d^2 \phi}{dz^2} \Rightarrow \phi(z) = \tanh(z/2) \]

\[ \psi_{\text{coex}} = (1 - T/T_c)^{1/2} \]

\[ \frac{F_{\text{int}}}{k_B T A} = \frac{1}{3} \phi_{\text{coex}}^4 \xi \propto (1 - T/T_c)^{3/2} \]

Interfacial area

Mean field critical behavior

Main problem: \[ \frac{\Delta \mu}{k_B T} = \frac{\partial (A F)}{\partial \psi} \propto \phi - \phi^3 \] is Mean Field Artefact!
Computer simulation yields "numerically exact" results for FINITE SYSTEMS only (cf. critical phenomena: finite size scaling).

M.E. FISHER et al.

Finite size effects important also for PHASE COEXISTENCE

FLUID of point particles interacting with LJ potential

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + C \right], \quad r \leq r_c \]

\[ r_c = 2^{1/6} \sigma, \quad C = 12\sigma / 16\varepsilon \]

\( \sigma = 1 \) unit of length

\( V = (L \times L \times L) \), periodic b.c.

grandcanonical \( \mu V T \) ensemble

\[ \mathcal{P}_{\mu V T}(N), \quad F(N,V,T) = -k_B T \ln \mathcal{P}_{\mu V T}(N) + N\mu + \text{const} \]
TWO-PHASE COEXISTENCE WITHIN THE FINITE L x L x L BOX

\[ \frac{\Delta f}{\Delta L} (\rho \approx \rho_c) = \frac{2 \omega}{L} \]

SNAPSHOT PICTURES

spherical droplet + surrounding vapor

cylindrical droplet + vapor

slab-like liquid domain: 2 L x L interfaces

free energy excess per particle due to the 2 interfaces:
\textbf{\(d = 2\) ISING MODEL: interfacial tension EXACTLY KNOWN from ONSAGER's transfer matrix solution (1944)}

\(\Rightarrow\) TEST the method where \(\chi\) is estimated from this free energy excess due to "liquid slabs" in finite \(L \times L\) boxes

\(\Rightarrow\) LARGE FINITE SIZE EFFECTS! slight curvature

\(? WHERE\ DO\ THESE\ SIZE ? \) EFFECTS COME FROM

\[\frac{1}{L}\]

\[k_B T / J = 2 : \text{correlation length} \sim \text{lattice spacing}\]

PRL \textbf{112}, 126701 (2014)
**ISING MODEL:**
- **Antiperiodic boundary conditions possible**
- **Periodic boundary conditions** (pbc): \( S(x, z + L_z) = S(x, z) \); \( S(x \pm L_x, z) = S(x, z) \)
  
  \Rightarrow \text{number of interfaces EVEN } = 0 \text{ or } 2

- **Antiperiodic boundary conditions** (apbc): \( S(x, z + L_x) = -S(x, z) \)
  
  \Rightarrow \text{number of interfaces ODD } = 1

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**GRANDCANONICAL ENSEMBLE** of the lattice gas: phase coexistence \( \cong \) no magnetic field in the **ISING MODEL**
- **apbc**: interface position NOT fixed
- **pbc**: no interfaces in equilibrium

**CANONICAL ENSEMBLE** of the lattice gas at critical density \( 1/2 \cong \) magnetization = 0 in the Ising model
- **apbc**: average interface position FIXED at \( L_x/2 \)
- **pbc**: two interfaces, average distance \( L_x/2 \)
SIZE-DEPENDENCE of the effective interface excess free energy \( \gamma_{L_1 L_2} \)

DIFFERENT boundary conditions and ensembles (APBC, PBC) (canonical=c; grandcanonical=gc)

DIFFERENT temperatures

(factor \( k_B T \) is divided out)

DIFFERENT \( L \)

\[
\text{APBC, gc: translational invariance of the spin configuration in z-direction}
\]

\[
\Rightarrow \text{entropy } \ln(L_z)
\]

\[
\Rightarrow \gamma_{L_1 L_2} \text{ gets correction } -\frac{1}{L} \ln(L_z) \text{ in } d=2
\]

\[
\text{APBC, c: } \gamma_{L_1 L_2} \text{ gets correction } -\gamma_{1} \frac{4}{L} \ln(L_z) \text{ with } \gamma_{1}=\frac{4}{2}: \text{DOMAIN BREATHING}
\]
BOLTZMANN: $S = k \log W$ \hspace{1cm} \text{ENTROPY}

$W =$ number of configurations of the system in a thermodynamic state $(E, V, N)$
DOMAIN BREATHING

fluctuations of the bulk order parameter in the two domains are coupled with fluctuations of the interface position. 

→ can be generalized to PBC (c) case

\[ \rho(z) \]

$\text{domain volume } L^{d-1} S \text{ can fluctuate when } S \text{ fluctuates}$

density fluctuations depend on domain volume

$d=2$ Ising model, APBC
$L=60, L_z=120, m=0$ (conserved magnetization)
Size-dependence of the effective interface excess free energy $\gamma_{L_1L_2}$ for the case of PBC and the canonical ensemble.

\[ d = 2 \]

The scaling variable $L^{-1}\ln(L)$ has correction $-X_l \frac{1}{L} \ln(L_{1/2})$ with $X_l = \frac{3}{4}$.

Translational entropy (1) + domain breathing $\frac{3}{2}$, but 2 interfaces.
CAPILLARY WAVE EFFECTS

\[ d = 2 : L_w^2 = \frac{1}{2} \frac{L}{\kappa} \]

\[ \Rightarrow \text{additional logarithmic correction to } \chi_{\perp z} \]

\[ + \frac{1}{2} \frac{\ln L}{L} \]

**Interpretation:**

In the counting of states where the interface can be put in the system (for the translational entropy) one should *normalize \( L_z \) NOT BY THE LATTICE SPACING BUT RATHER BY \( W_L \)

In each "cell" of size \( L \times W_L \) the interface "fits"
Extension to $d=3$ dimensions:
straightforward for translational entropy and domain breathing

$k_B T/J = 3.0$
Ising model

EFFECTIVE
SIZE-DEPENDENT
INTERFACE TENSION

$\Rightarrow$ corrections to $\kappa_{L_1L_2}$ of order $\frac{1}{L^2} \times_1 \ln(L_2)$
$\times_1 = \begin{cases} \frac{1}{2} & 3/4 \\ 1 \end{cases}$
FINITE SIZE CORRECTIONS to the interface free energy

\[ \chi^*_{L_1 L_2} = \chi^*_\infty - x_1 \frac{1}{L_d} \ln(L_z) + x_{11} \frac{1}{L_d} \ln(L) + \frac{C}{L_{d-1}} \]

<table>
<thead>
<tr>
<th>dimensionality</th>
<th>BC/ensemble</th>
<th>( x_1 )</th>
<th>( x_{11} )</th>
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<td>apbc/gc</td>
<td>1</td>
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</tr>
</tbody>
</table>

C non-universal

\{ \text{UNIVERSAL CONSTANTS} \}

⇒ RECIPE: correct for the LOGARITHMIC effects

define \( \tilde{\chi}^*_{L_1 L_2} = \chi^*_{L_1 L_2} + x_1 \frac{1}{L_d} \ln(L_z) + x_{11} \frac{1}{L_d} \ln(L) = \chi^*_\infty + \frac{C}{L_{d-1}} \)

⇒ plot \( \tilde{\chi}^*_{L_1 L_2} \) versus \( \frac{1}{L_d} \): should yield straight line (apart from higher order corrections)
\( d = 3 \) Ising model, \( k_B T = 3.0 \)

\( \gamma_{00} = 0.434 \pm 0.001 \) good accuracy!

\[ \gamma_{L_1L_2} \]

RECIPe: plot \( \gamma_{L_1L_2} \) vs. \( 1/L^2 \); fit function:

\[ \gamma_{L_1L_2} = \gamma_{00} + \frac{C_1}{L} + \frac{C_2}{L^2} \]

When logarithmic corrections are taken care of, the remaining nonuniversal correction in \( d = 3 \) is of order \( 1/L^2 \) AND NO \( 1/L \) TERM EXISTS

\[ \text{constant } C_1 \text{ should NOT DEPEND on } L_2 \]

\[ \text{IS NOT } \{ \text{ should not } \} \text{ be present} \]
LJ fluid $r_c/\sigma = 2$, $T/T_c = 0.78$, $d=3$, Monte Carlo

$\gamma_\infty = 0.374 \pm 0.001$ good accuracy reached!

![Graph showing interfacial tension vs inverse interfacial area $L^2$.](image)

- Local moves: $L_2 = 26.94$, $\gamma_\infty = 0.3735$, $C_2 = 1.22$, $C_1 = 0.000$
- Local moves: $L_2 = 17.96$, $\gamma_\infty = 0.3745$, $C_2 = 1.13$, $C_1 = 0.000$
- Nonlocal moves: $L_2 = 26.94$, $\gamma_\infty = 0.3744$, $C_2 = 1.12$, $C_1 = 0.000$
- Nonlocal moves: $L_2 = 17.96$, $\gamma_\infty = 0.3745$, $C_2 = 1.10$, $C_1 = 0.000$

$c_1 = 0$ enforced

Recipe: $\gamma_{L_1 L_2} = \gamma_{L_1 L_2} + \frac{3}{4} \frac{1}{L^2} \ln(L_2) - \frac{1}{2} \frac{1}{L^2} \ln(L) = \gamma_\infty + \frac{c_2}{L^2}$
Ising/lattice gas model
$k_B T/J = 3.0 \quad \phi = 0.1$
$(T/T_c \approx 0.665)$

Lennard-Jones fluid
$T/T_c = 0.68 \quad \phi = 0.16^{-3}$

DROPLET - VAPOR COEXISTENCE

$\Rightarrow$ INTERFACE TENSION OF CURVED INTERFACES
SURFACE TENSION OF SPHERICAL DROPLETS & BUBBLES

$$\gamma_{ve}(T,R) = \frac{\gamma_{ve}(T,\infty)}{\left\{1 + 2\delta(T)/R + 2[\ell(T)/R]^2\right\}}, \quad R \to \infty$$

interface tension of PLANAR INTERFACE

TOLMAN LENGTH

TOLMAN'S HYPOTHESES (1949):

(i) $\delta(T) > 0$ for droplets

(ii) $|\delta(T)| \approx \delta$ molecular diameter

(iii) $|\ell(T)| \ll |\delta(T)|$

controversial until very recently!
\[ \Delta F = 2\pi R_e \chi(R_e) \]

\[ d = 2 \text{ Ising model} \]

\[ k_B T/J = 2.0 \]

Correct for translational entropy:

\[ \Delta F = 2\pi R_e \chi(R_e) - 2k_B T \ln L \]
 Leading correction due to capillary waves: TOLMAN's analysis inapplicable

\[ \gamma (R_e) = \gamma_\infty + \frac{5}{4\pi} \frac{\ln R_e}{R_e} \]

\[ \uparrow \]

analog to flat interfaces: \[ + \frac{1}{2} \ln \frac{L}{L} \]

universal constant \( \frac{5}{4\pi} \) known from quantum field theory

CONCLUSIONS

- Analytical theory of interfaces not on firm ground.

- Mean field theory (van der Waals, Ginzburg-Landau, density functional theory...) all based on free energy $f(T,p)$ of homogeneous states inside two-phase coexistence region that do not exist for $T$ well below $T_c$.

  (Note: for $T \rightarrow T_c$, we can consider a length scale $l$ such that $\xi \ll l \ll \xi_f$. A coarse-grained free-energy density of subsystems of scale $l$ does exist and have Ginzburg-Landau shape but somewhat depend on $l$, $f_x(T,p)$.)

  Basis for renormalization group theory of critical phenomena.

- Long wavelength fluctuations of interfaces are well described by capillary wave theory; crossover to bulk fluctuations on small scales is not well understood; theories yield "intrinsic profile", not seen in simulations.

- Analysis of finite size effects on two-phase coexistence in simulations allow accurate estimations of interfacial free energies. Fluctuation effects (capillary wave effects, translational entropy, etc.) need careful consideration.

- Curvature corrections can be described by Tolman's length in $d=3$, but not in $d=2$. 