On the Evaporation/Condensation phase transition

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Abstract:
We study the mixed phases of phase separated 2d Ising and Potts models at low temperature. We describe in the Evaporation/Condensation(E/C) phase transition.

* with Hager, Janke, Nußbaumer

1) Introduction:

- metastability - homogeneous nucleation: of droplets is an important physical process applicable e.g. to nuclear reactions, heavy ion collisions , ...
- discontinuous behavior at a first order phase transition in

- field theories with broken Z(2) symmetry

- field theories with temperature T driven 1'st order p.t.'s

$$\eta \ \propto \ T \ , \ \mu \ , \ H \ , \ldots$$

$$\Psi \ \propto \ E \ , \ N \ , \ M \ , \ldots$$

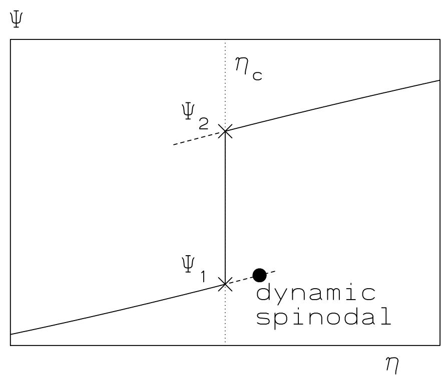
$$\frac{F_1}{V} = \frac{F_2}{V} \qquad \textbf{2 phase coexistence}$$

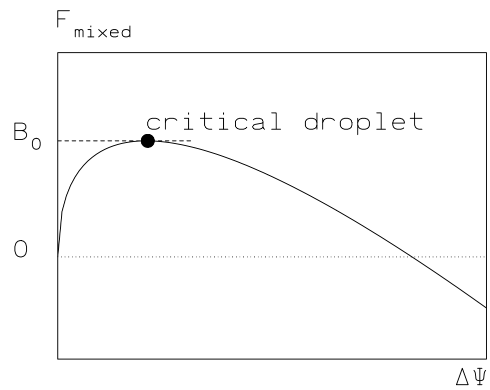
$$\sigma \neq 0 \qquad \textbf{surface tension}$$

$$\Delta\eta > 0 \qquad \textbf{supersaturation}$$

- classical nucleation theory

- calculates the surface tension σ summing over fluctuations expanded in spherical harmonics, Langer and Fishers droplet theory





- obtains an exponentially large lifetime for the metastable state

$$\tau_{LIFE} = A(\Delta\eta)\ e^{+B_0(\Delta\eta)}$$

- parametrizes a single droplet in an infinitely large mixed phase

$$\Delta\Psi = \Psi_2 - \Psi \quad \text{mixture concentration}$$

$$\Delta\Psi_{GAP} = \Psi_2 - \Psi_1$$

$$\Omega(\Delta\Psi) = V\frac{\Delta\Psi}{\Delta\Psi_{gap}}$$

$$F_{mixed}(\Delta\Psi) = \sigma\sqrt{4\pi\Omega(\Delta\Psi)} - V\Delta\eta\Delta\Psi$$

D=2 !

$$B_0(\Delta\eta) = \frac{\pi\sigma^2}{\Delta\Psi_{GAP}\Delta\eta} \quad \text{nucleation barrier}$$

$$R_0(\Delta\eta) = \frac{\sigma}{\Delta\Psi_{GAP}\Delta\eta} \quad \text{critical radius}$$

- **fluctuation corrections**

- dynamic spinodal behavior seen in field switching computer experiments Rickvold, Tomita, Miyashita, Sides, 1994 Rickvold, Novotny, many papers Stauffer et al., 1998 at large supersaturation $\Delta\eta$

- capillary waves, translational dof's, Tolman corrections, Gibbs Thomson corrections in effective theory calculations

- constraint partition function/effective potential field theory calculations

$$V_{eff}(\Psi) = -\ln[\sum_{conf.} e^{-\beta H} \delta(\Psi - \Psi_{conf.})]$$

- e.g. Morel et. al. in the 90-ties used large Q series expansion in the Potts model to obtain

$$-\ln \mathrm{Z_i}(T - T_c) = \mathrm{const} + E_i(T - T_c) + \frac{C_i}{2}(T - T_c)^2 + \ldots$$

$$i = \mathrm{ordered, disordered}$$

and performed a change of variables $T - T_c \to E - E_i$ via inverse Laplace transformation to obtain

$$P(E - E_i) = \ln \mathrm{Z_i}(E - E_i)$$

for the mixed phase

- a true constraint partition function singularity is suggested: the homogeneous vapor condenses into a mixed phase configuration with a drop
- the E/C evaporation/condensation phase transition is described in the recent literature
- 2000

  Droplets in the coexistence region of the 2d Ising model, Pleimling, Selke
- 2001

  Crossing the coexistence line at constant magnetization, Pleimling, Hueller
- 2002

  2D crystal shapes, droplet condensation and exponential slowing down in simulations of first order phase transitions, Hager, Neuhaus

  On the formation/dissolution of equilibrium droplets, Biskup, Chayes, Kotecky
- 2003

  The droplet evaporation/condensation phase transition in finite volumes ,Virnau, MacDowell, Mueller, Binder

  Comment on the theory of evaporation/condensation transition of equilibrium droplets in finite volumes, Biskup, Chayes, Kotecky

  Reply to the comment by Biskup, Chayes and Kotecky, Binder

  Critical region for droplet formation in the 2d Ising model, Biskup, Chayes and Kotecky

  Proof of the Gibbs Thomson formula in the droplet formation regime, Biskup, Chayes, Kotecky

2) Gibbs Thomson corrected effective Droplet Theory for the C/E phase transition in 2D

study the phase coexistence of homogeneous supersaturated vapor with a mixed phase configuration of vapor and a drop

- supersaturated vapor

$$F_{vapor} = c_2 L^2 \Delta\psi^2$$

- Gibbs Thomson corrected droplet free energy in the one droplet sector

Krishnamachari, McLean, Cooper, Sethna, PRB 54 8899 1996

spins in vicinity of a curved surface have increased/reduced effective coordination number, pending on the surface curvature

Gibbs Thomsom shift:

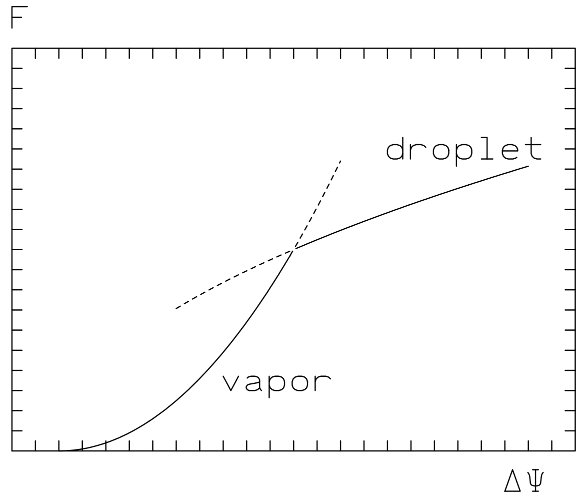
$$\begin{array}{lrl} \text{majority phase in} & V - \Omega : & \psi_2 \rightarrow \psi_2 - \Delta\psi_{GT} \\ \text{minority phase in} & \Omega : & \psi_1 \rightarrow \psi_1 - \Delta\psi_{GT} \end{array}$$

mixture concentration:

$$\psi L^2 = (L^2 - \Omega)(\psi_2 - \Delta\psi_{GT}) + \Omega(\psi_1 - \Delta\psi_{GT})$$

minority droplet mass:

$$\Omega = L^2 [\frac{\Delta\psi - \Delta\psi_{GT}}{\Delta\psi_{GAP}}]$$



the droplet free energy

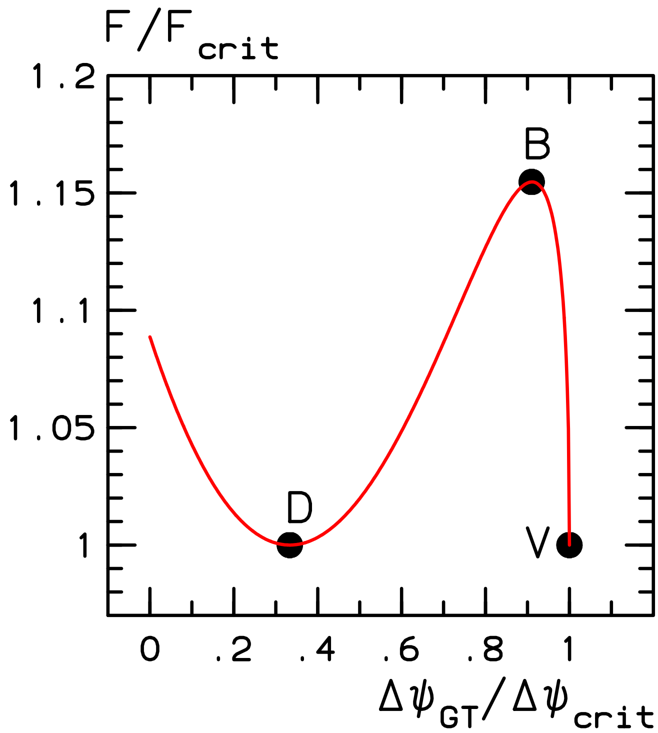
$$F_D(\Delta\psi, \Delta\psi_{GT}) = \sigma L \sqrt{4\pi \frac{\Delta\psi - \Delta\psi_{GT}}{\Delta\psi_{GAP}} + L^2 c_2 {\Delta\psi_{GT}}^2}$$

is minimized with respect to $\Delta\psi_{GT}$, this yields at $\Delta\psi$ a downward free energy correction

$$F_D = F_D^0 - \frac{\text{const}}{\partial\Omega}$$

and a pressure balance for symmetric and asymmetric GT effects

$$c_2^1 \Delta\psi_{GT}^1 = c_2^2 \Delta\psi_{GT}^2$$



F/F crit
1.2
1.15
1.1
1.05
1
B
D
V
0
.2
.4
.6
.8
1
Δψ GT/Δψ crit

- $F_D = F_{vapor}$ **results at coexistence (cxc)**

- transition location

$$\frac{\Delta\psi_{cxc}}{\Delta\psi_{GAP}} = \frac{3}{2}\gamma L^{-2/3}$$

$$\gamma = [\frac{\pi\ \sigma^2}{c_2^2 \Delta\psi_{GAP}^4}]^{1/3}$$

- Gibbs Thomson shift

$$\Delta\psi_{GT,cxc} = \frac{1}{3}\Delta\psi_{cxc}$$

- GAP in Ω

$$\frac{\Delta\Omega_{cxc}}{V} = \frac{2}{3}\frac{\Delta\psi_{cxc}}{\Delta\psi_{GAP}}$$

- INVARIANT Q at coexistence

$$Q = \frac{3}{2} = \frac{\frac{\Delta\psi_{cxc}}{\Delta\psi_{GAP}}}{\frac{\Delta\Omega_{cxc}}{V}}$$

- RADIUS at coexistence

$$R_{cxc} = \sqrt{\frac{\gamma}{\pi}} L^{2/3}$$

- CRITICAL DROPLET RADIUS (crit) at coexistence (cxc)

$$R_{crit} = \sqrt{\frac{\gamma(2-\sqrt{3})}{2\pi}} L^{2/3} = 0.36\ldots\ R_{cxc}$$

- NUCLEATION BARRIER (nucl) at coexistence (cxc)

$$\frac{B_{nucl}}{L^2 c_2 \Delta\psi_{cxc}^2} = 0.154701\ldots$$

as a function of the supersaturation $\Delta\eta_{cxc} = 2c_2\Delta\psi_{cxc}$ one finds

$$B_{nucl} = 1.044231\ldots \frac{\pi\sigma^2}{\Delta\psi_{GAP}\Delta\eta_{cxc}}$$

$$R_{crit} = 1.098076\ldots \frac{\sigma}{\Delta\psi_{GAP}\Delta\eta_{cxc}}$$

$\longrightarrow$ in 2D, for drops right at C/E coexistence, fluctuation corrections of few percent to classical nucleation theory

$\longrightarrow$ on finite systems the droplet radius R is bounded through

$$R_{cxc} \leq R \leq \mathcal{O}(L^2)$$

$\longrightarrow$ there exists a length scale

$$\xi(R) = [\pi/\gamma]^{3/4} R^{3/2},$$

which for drops with radius R limits the validity of classical nucleation theory to the $L < \xi(R)$ region

3) Theories studied in numerical Simulations:

- 2D Ising

$$Z = \sum_{conf.} e^{-\beta H}$$

$$H = H_I - hM := - \sum_{<i,j>} s_i s_j - h \sum_i s_i$$

$\beta = 0.7$ or $t/t_c = 0.63$ with $\sigma_{0,1} = 0.89643...$

$$\frac{\Delta\Psi_{GAP}}{2} = m_0 = 0.99016... \quad \text{Onsager}$$

$$F_D = \sqrt{(W/\pi) 4\pi\Omega}$$

$$\sigma = \sqrt{W/\pi} = 0.90358...$$

Rottman, Wortis, 1984 Wulff, 1901

$$F_{\text{vapor}} = c_2 \, V \, (m - m_0)^2 \, + ... \qquad c_2 = 18.125...$$

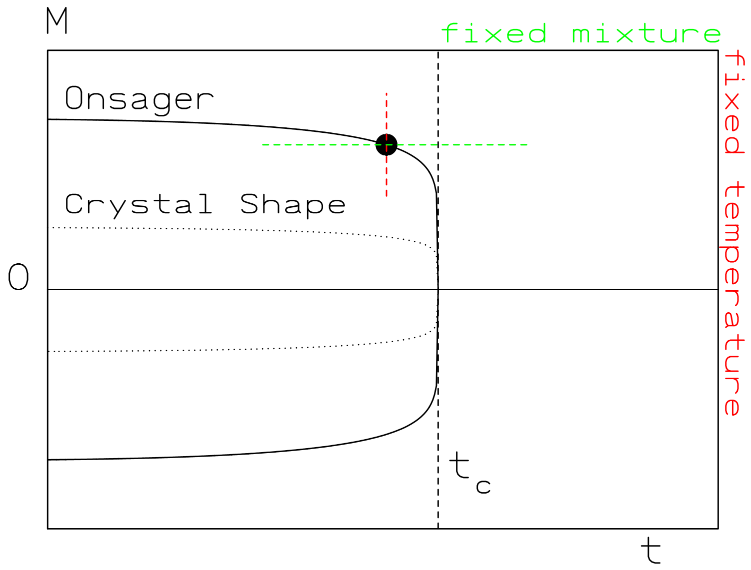
LT expansion: Campostrini, 2001

- 2D q=256 state Potts

$$H = - \sum_{<i,j>} \delta_{q_i, q_j}$$

$$\beta_c = 1/k_b t_c = \ln(17) = 2.833213...$$

$$e_o = -1.984838... \quad e_d = -0.140161...$$



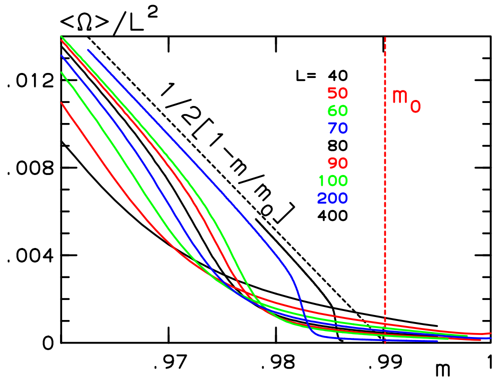
$$\Delta\psi_{GAP} = 1.844676...$$

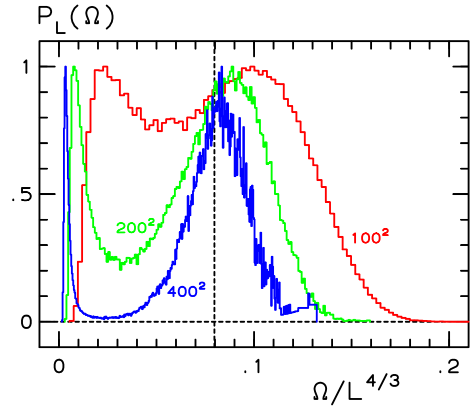
$$\sigma_{0,1} = 0.951694...$$

no Wulff construction avaiable, and in vicinity of e_d at β_c

$$F_{\text{vapor}} = c_2 \, V \, (e - e_d)^2 \; + ... \qquad c_2 = 2.657648...$$

large Q expansion: SACLAY





4) Numerical Results:

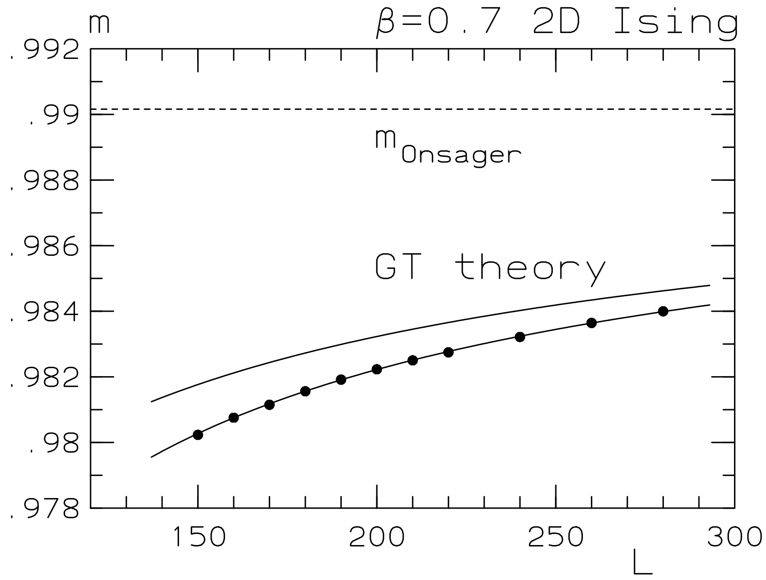
- algorithms: Muca-Ω, MGME-Ω, Kawasaki, N-fold way
- measure the masses Ω_i of all droplets and sort them with respect to their value, e.g. in the Ising model

$$\Omega_0 \qquad \text{majority droplet}$$

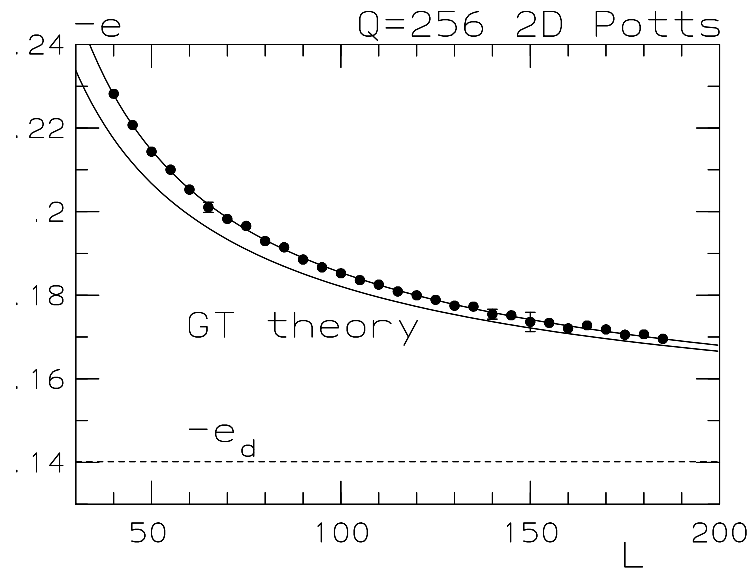
$$\Omega \qquad \text{largest minority droplet}$$

+ other droplets

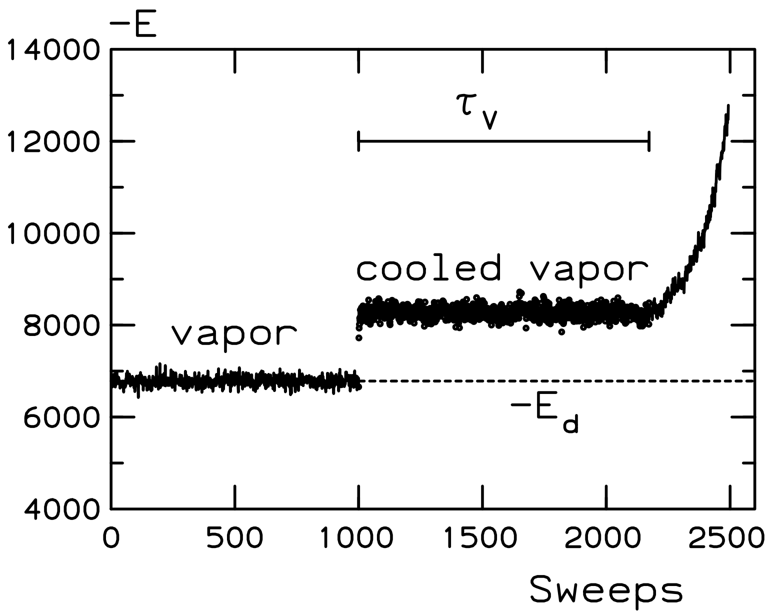
- when the mixture concentration is varied over the coexistence line - from the vapor to the droplet nucleated phase - expect Ω/V to be a percolation order parameter, this can be done and yields interesting finite size effects



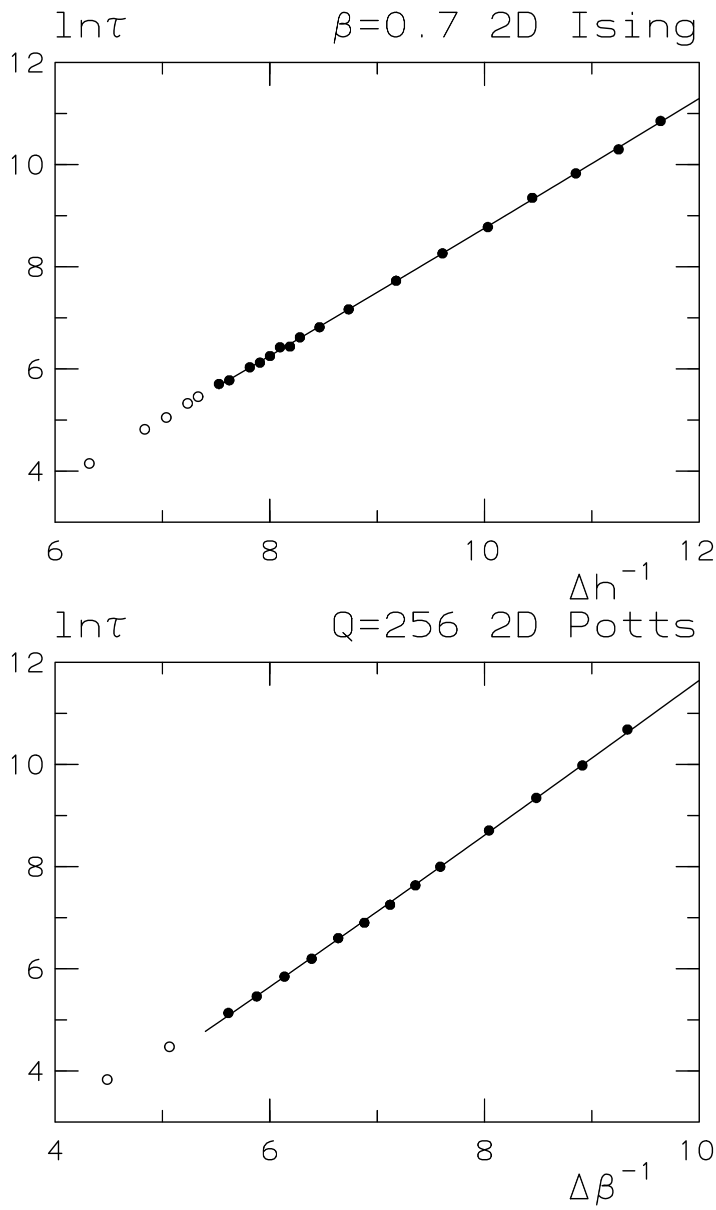
m
β=0.7 2D Ising
.992
.99
.988
.986
.984
.982
.98
.978
m_Onsager
GT theory
150
200
250
300
L



−e
Q=256 2D Potts
.24
.22
.2
.18
.16
.14
GT theory
−e_d
50
100
150
200
L



−E
14000
12000
10000
8000
6000
4000
0
500
1000
1500
2000
2500
Sweeps
τ_v
cooled vapor
vapor
$-E_d$



lnτ
β=0.7 2D Ising
12
10
8
6
4
6
8
10
12
Δh⁻¹
lnτ
Q=256 2D Potts
12
10
8
6
4
4
6
8
10
Δβ⁻¹

fit results

Ising:

$$m_{cxc}(L) = m_{Onsager} - \frac{0.235(4)}{L^{2/3}} - \frac{1.2(1)}{L^{4/3}}$$

compare 0.235(4) to 0.236970... !

on the line $h(L) = 2c_2 \Delta m_{cxc,theor}(L)$

$$\tau_{LIFE}(h) \;=\; 0.078(4)\,\frac{1}{h}\,e^{1.050(5)B_0/h}$$

compare 1.050(5) to 1.044231... !

flux factor $\frac{1}{\Delta\eta}$ corresponds to random walk in Gibbs Thomson shift with local update

Potts:

$$e_{cxc}(L) = e_d - \frac{0.913(7)}{L^{2/3}} - \frac{1.3(2)}{L^{4/3}}$$

compare 0.913(7) to 0.903452... !

$$\tau_{LIFE}(\Delta\beta) \;=\; 0.097(5)\,\frac{1}{\Delta\beta}\,e^{1.055(5)B_0/\Delta\beta}$$

compare 1.055(5) to 1.044231... !

5) Conclusion

- the data are in support of the theory , which is a theory of the equilibrium mixed phase at its boundary the coexistence line
- the coexistence line is the locus of the E/C phase transition, which on finite L^D systems

- describes a minimal sized droplet of radius $R_{cxc} = \text{const } L^{D/D+1}$, which can coexist with the vapor

- there is also a minimal critical droplet with a critical radius $R_{crit} = \text{const}' \ L^{D/D+1}$ of about one third in size in 2D with a nucleation barrier close to the classical one. The theory predicts a maximum 4.5 percent upward correction to B_{nucl} relative to the classical result.

- it is important to include the Gibbs Thomson effect into the quantitative description - the GT effect is also theoretically quite elegant: it combines quadratic fluctuations - Ginzburg Landau theory for magnets - with the interface tension, which in is a non-perturbative quantity

- in other words, potentially singular $\partial\Omega^{-1}$ curvature free energy corrections to minute droplets are bounded at the E/C phase transition

- one does not have all this in Van der Waals theory
- finally it is suggested, that the crossover - or transition - from single to many droplet nucleation as observed in non-equilibrium field switching experiments (dynamic spinodal point), is related to the the existence of the scale $\xi(R)$ and we are currently investigating this possibility. We also conjecture that many droplet nucleation can be described by catastrophic statistics of the Weibull, Gumpel ,... kind.