CONTACT ANGLES, WETTING TRANSITIONS, AND MACROSCOPIC INTERFACIAL FLUCTUATIONS

Kurt Binder (J.G.U. Mainz)

in collaboration with

E.V. Albano (La Plata), S.K. Das (Bangalore), A. Statt, P. Virnau, A. Winkler, D. Winter (J.G.U. Mainz)

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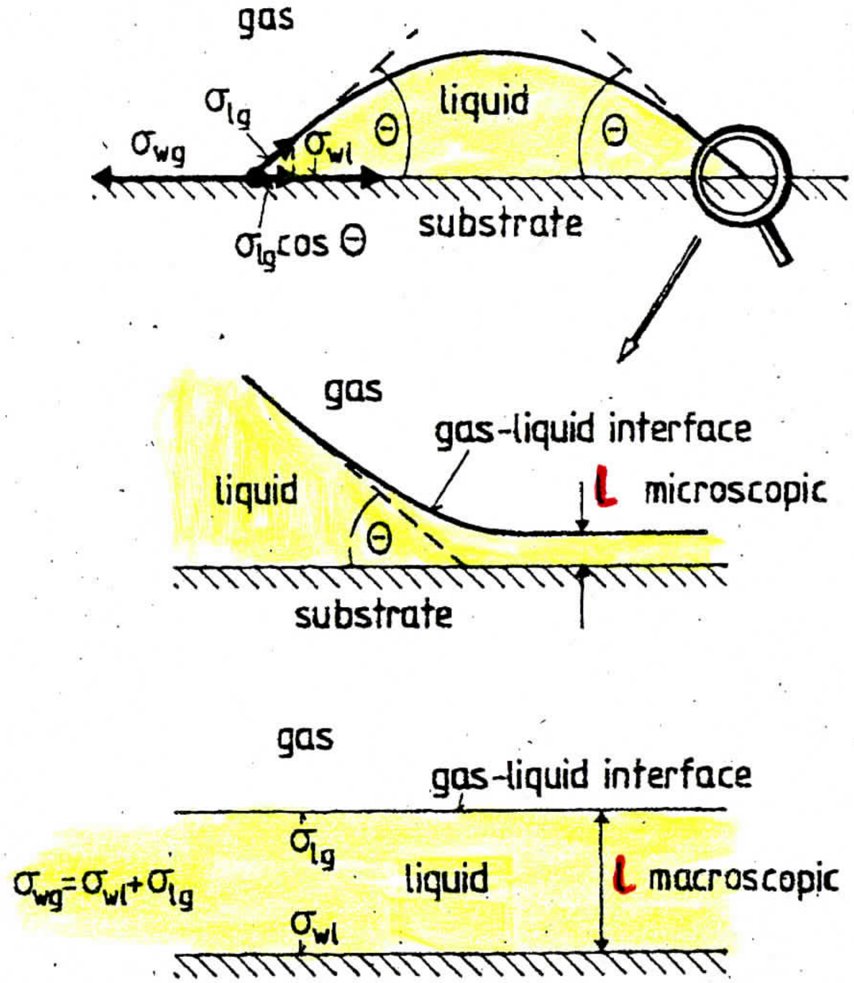
vapor ↔ liquid transition of a fluid:

saturated gas exposed to a wall



partial (incomplete) wetting:

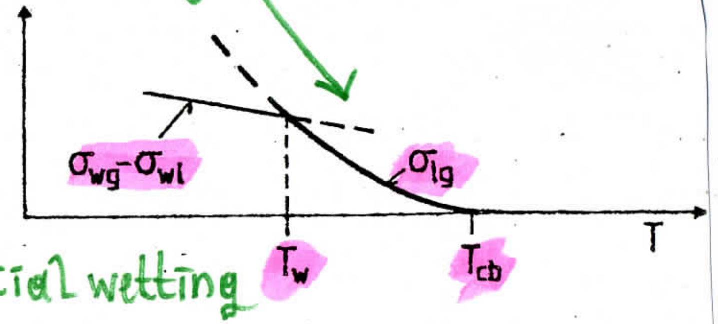
MACROSCOPIC DROPLET can coexist with the gas

CONTACT ANGLE Θ : Young (1805)

$$\sigma_{wg}(T) - \sigma_{wl}(T) = \sigma_{lg}(T)\cos\Theta$$

$\cos\Theta \to 1$: wetting transition

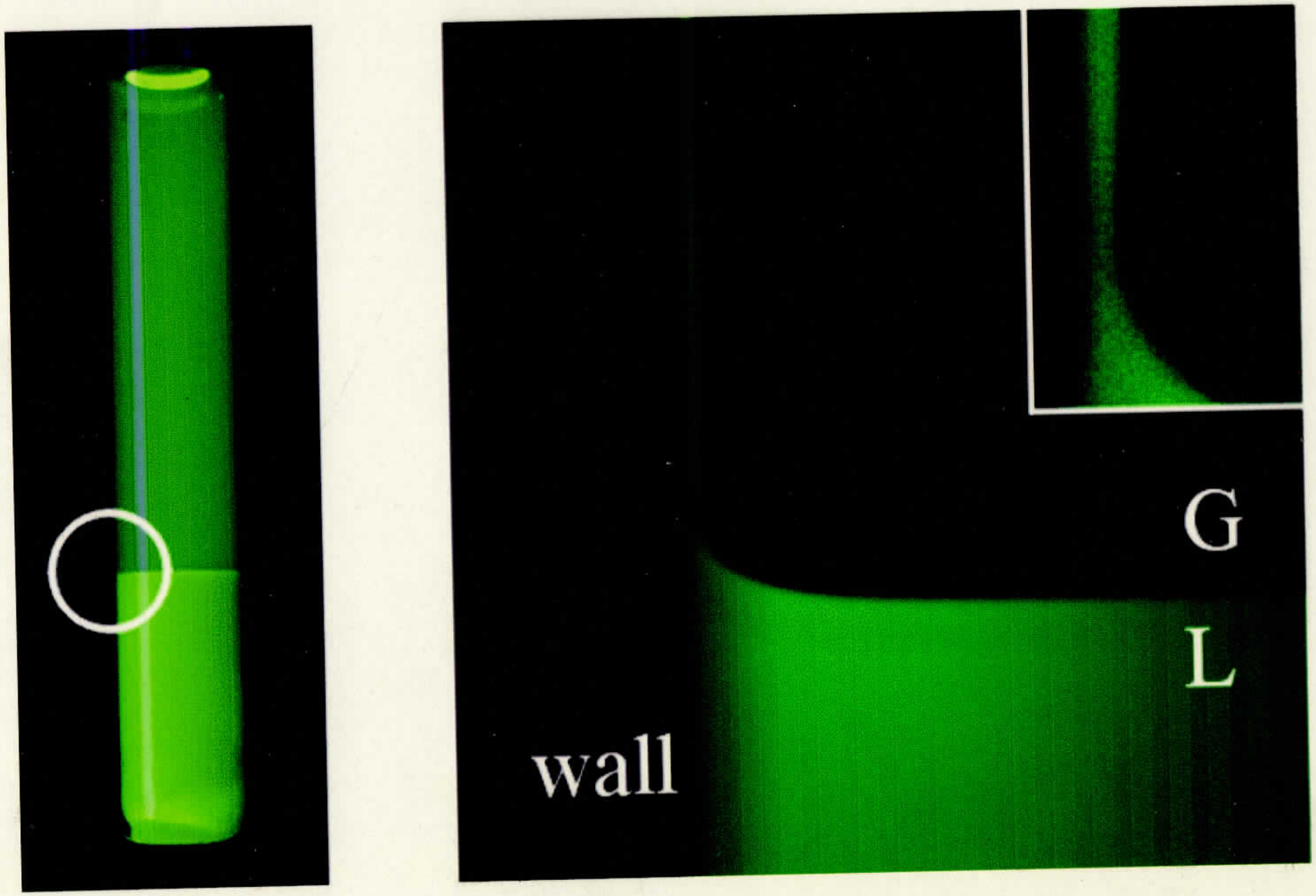
complete wetting $(T>T_w)$



$T<T_w$: partial wetting

Colloid-Polymer Mixture in Confinement

experiment using laser scanning microscopy [Aarts and Lekkerkerker, J. Phys.: Condens. Matter **16**, S4231 (2004)]



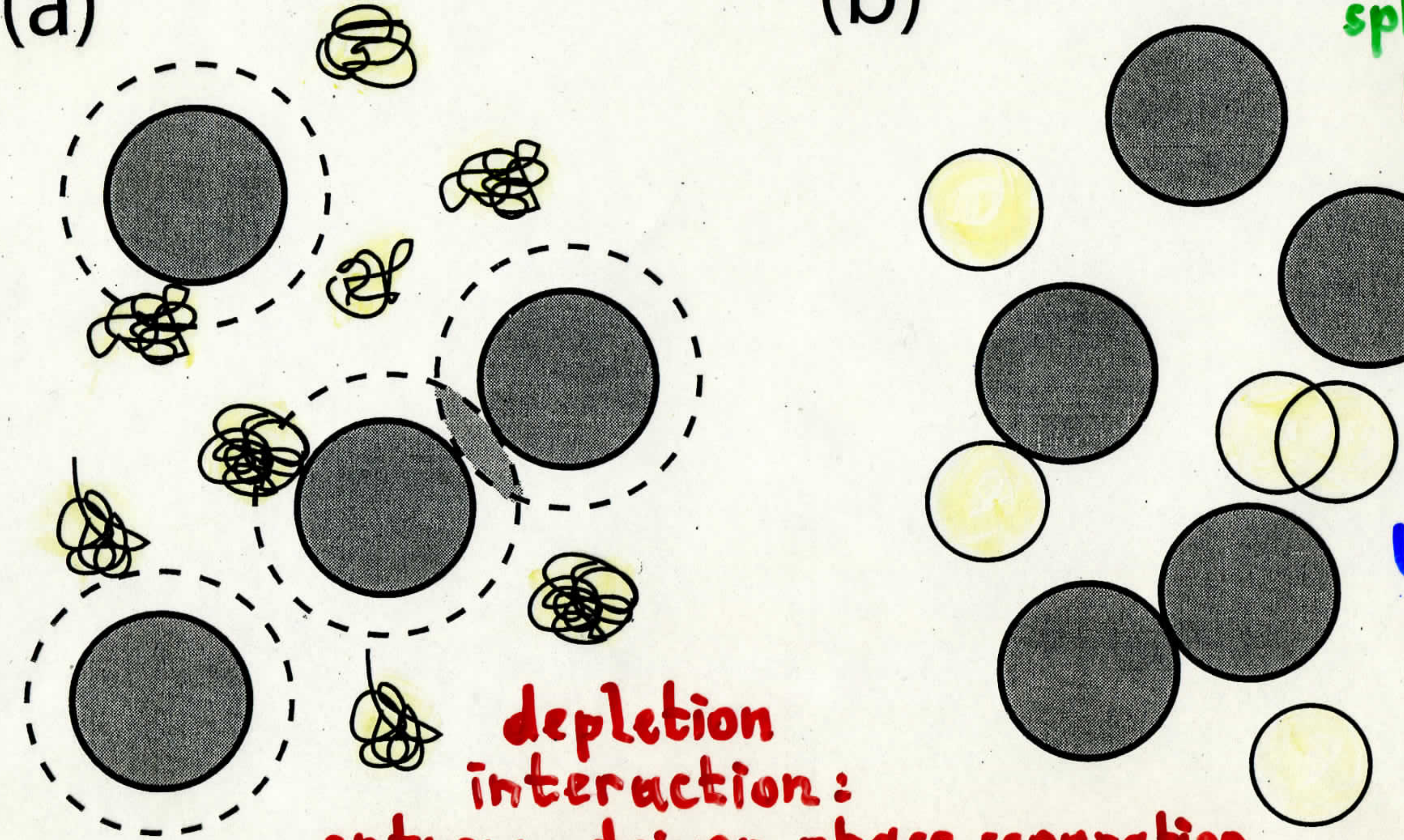
COLLOID-POLYMER MIXTURES

ASAKURA-OOSAWA MODEL

colloids: hard spheres, $R_c = 1$

polymers: soft spheres R_p

(a) (b)

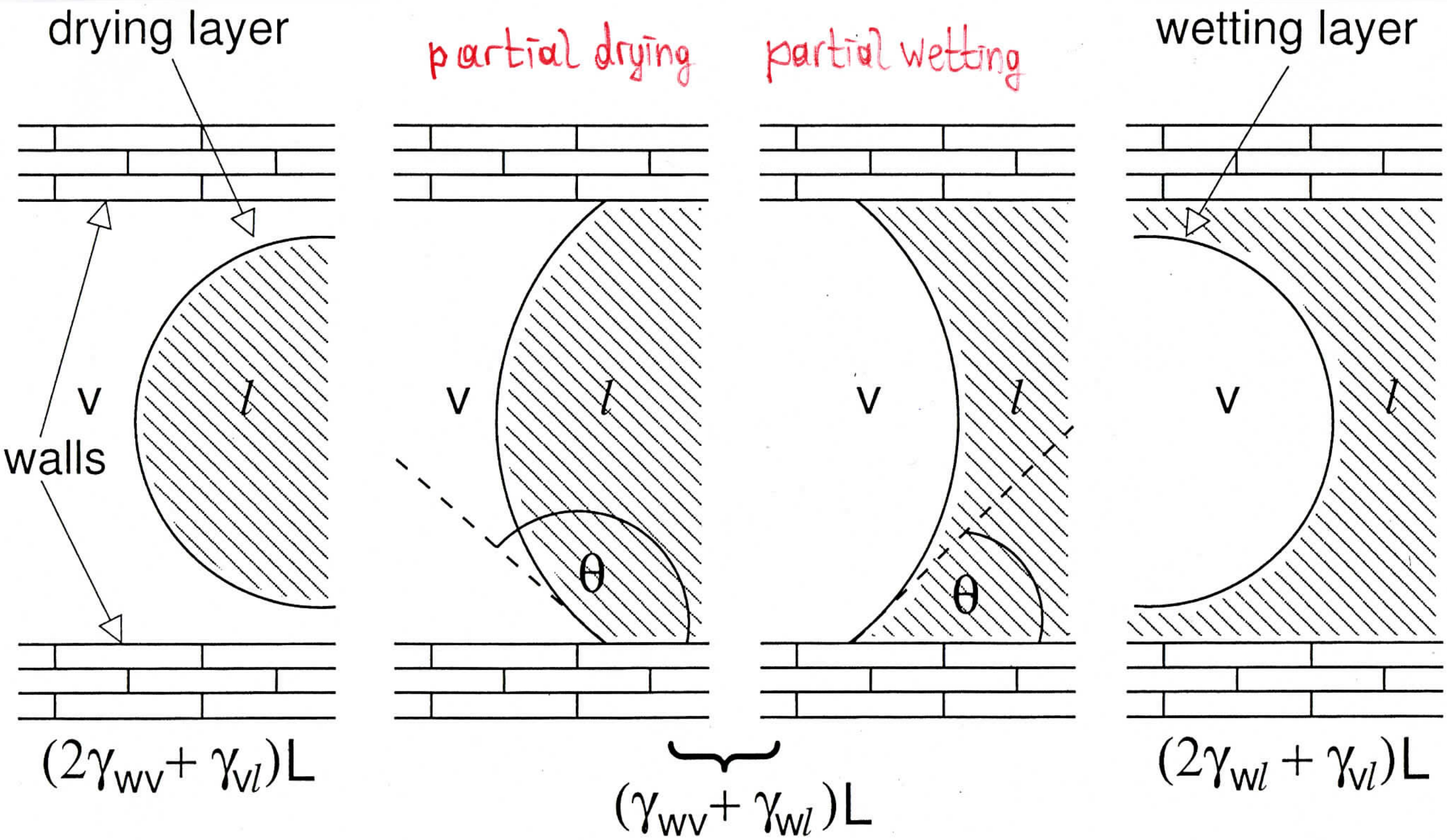


$U_{pp}(r) = 0$

depletion interaction: entropy-driven phase separation

Simulation of macroscopically large ("SEMI-INFINITE") system IMPOSSIBLE ! ⇒ study NANOSCOPIC SLIT PORE with SYMMETRIC walls ?

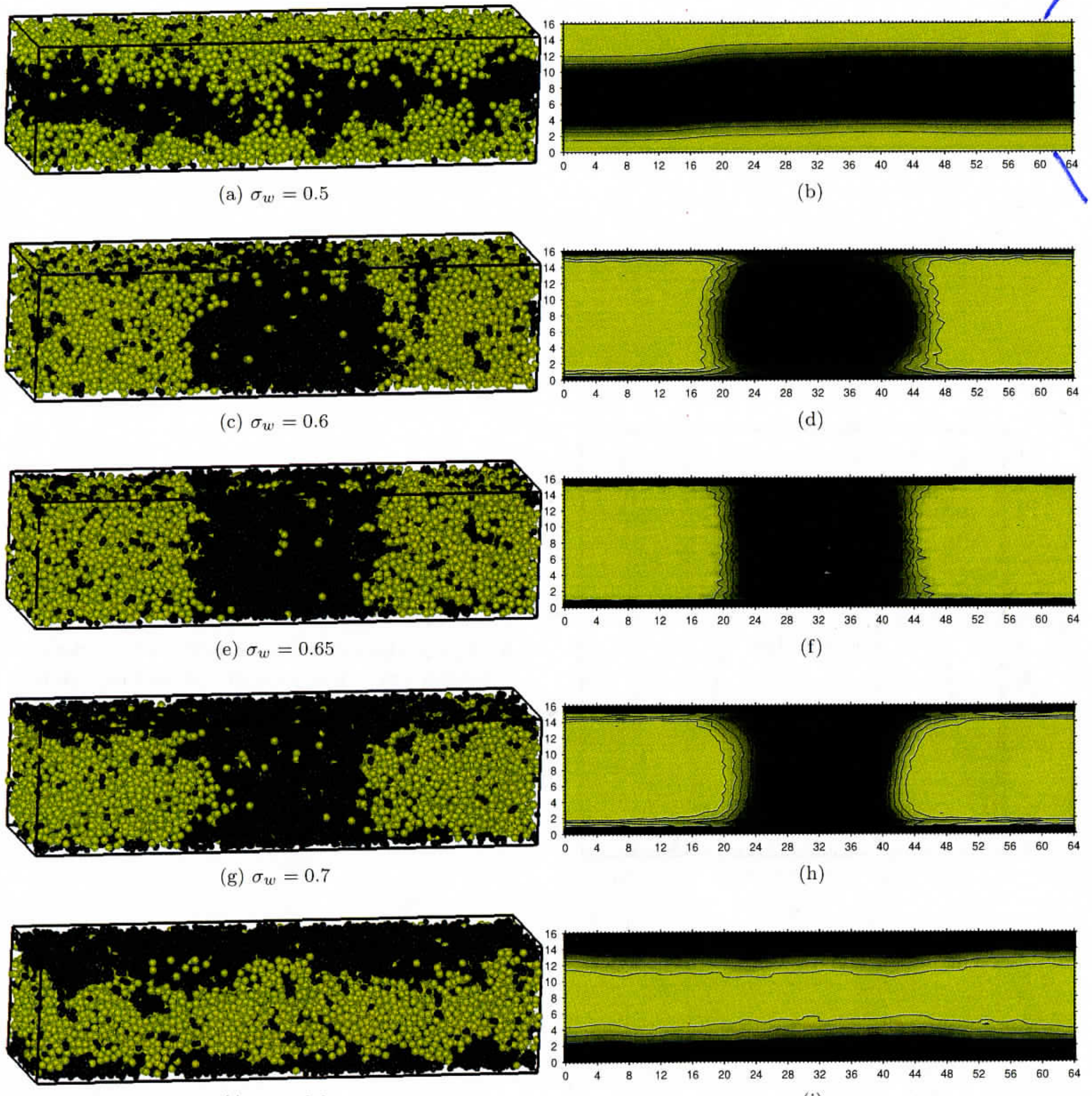
HOWEVER : INTERFACES not SHARP but DIFFUSE



Colloid-polymer mixture in a planar slitpore

- colloids
- polymers

ASAKURA-OOSAWA model



wall

wall

(a) $\sigma_w = 0.5$ (b)

(c) $\sigma_w = 0.6$ (d)

(e) $\sigma_w = 0.65$ (f)

(g) $\sigma_w = 0.7$ (h)

(i) $\sigma_w = 0.8$ (j)

range σ_w of WCA potential at walls varied:

complete DRYING ($\cos\Theta = -1$)

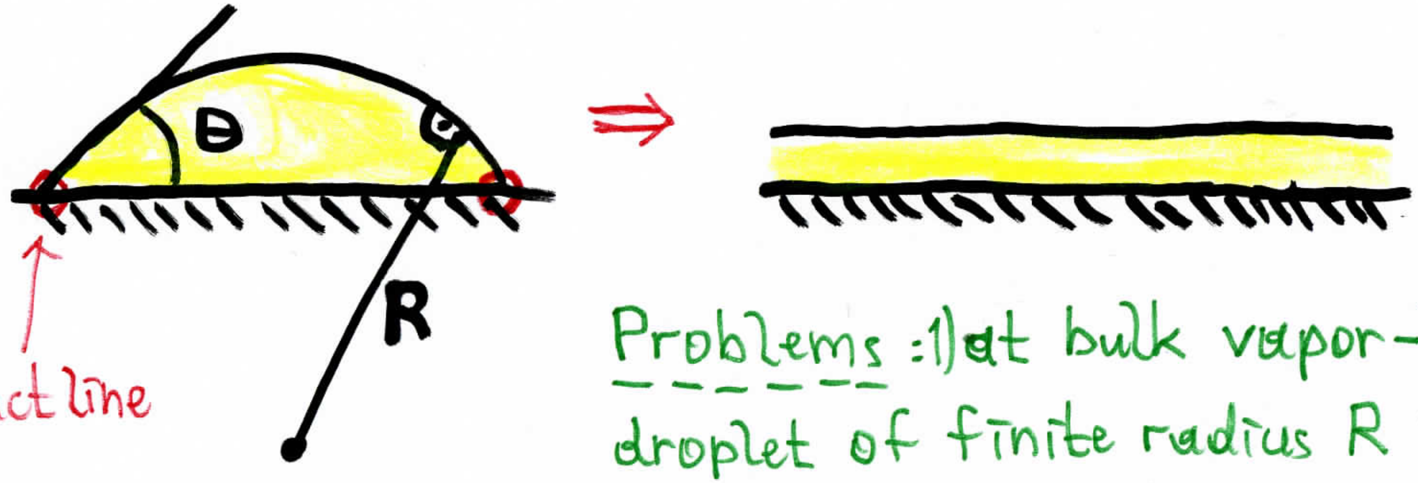
partial DRYING

"neutral" walls: $\Theta = 90°$

partial wetting

complete wetting ($\cos\Theta = +1$)

? Can we study wetting transition by simulating how the contact angle vanishes for wall-attached droplets?



Problems: 1) at bulk vapor-liquid coexistence droplet of finite radius R is UNSTABLE (equilibrium only for enhanced pressure [Laplace!])

2) Young's equation needs VAPOR-LIQUID surface tension for a MACROSCOPIC PLANAR INTERFACE ⇒ CURVATURE CORRECTIONS TO INTERFACIAL TENSION?
TOLMAN'S LENGTH?

3) Corrections to Young's equation due to the LINE TENSION of the wall-vapor-liquid contact line?

⇒ Do not attempt to "measure" the contact angle directly

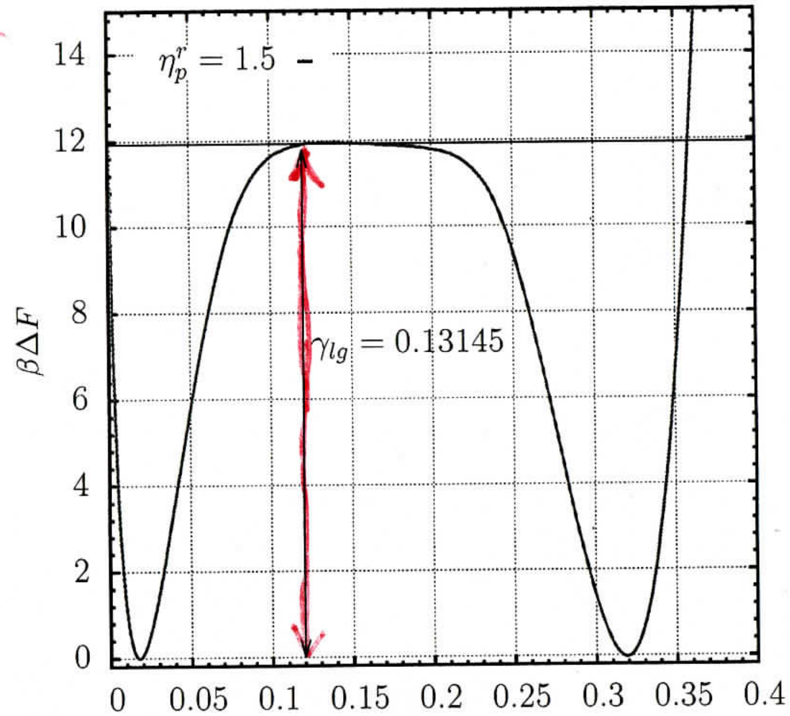
⇒ rather infer Θ from Young's equation, infer the necessary INTERFACIAL TENSIONS FROM SUITABLE SIMULATIONS

estimation of the "gas" – "liquid" interface free energy

$L_z \times L \times L$ geometry, $L_z > L$, periodic boundary conditions in all directions

free energy

$\beta \Delta F(\eta_c)$



"gas"

"liquid"

colloid packing fraction η_c

(i) vary colloid chemical potential, find gas-liquid coexistence from the EQUAL WEIGHT RULE $\Rightarrow \mu_c^{coex}$

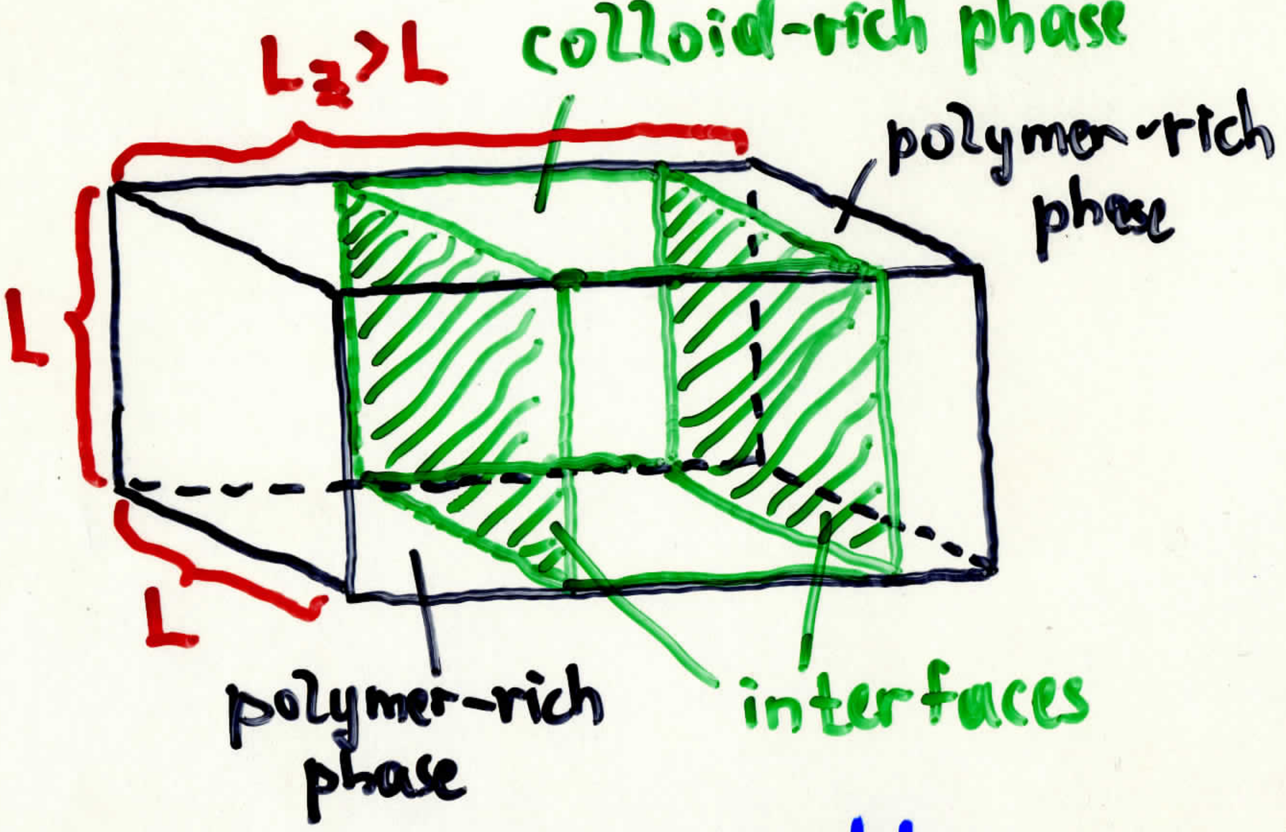
(trivial for Ising model: coexistence between phases of opposite spontaneous magnetization $\pm m_{coex}$ occurs for $H=0$)

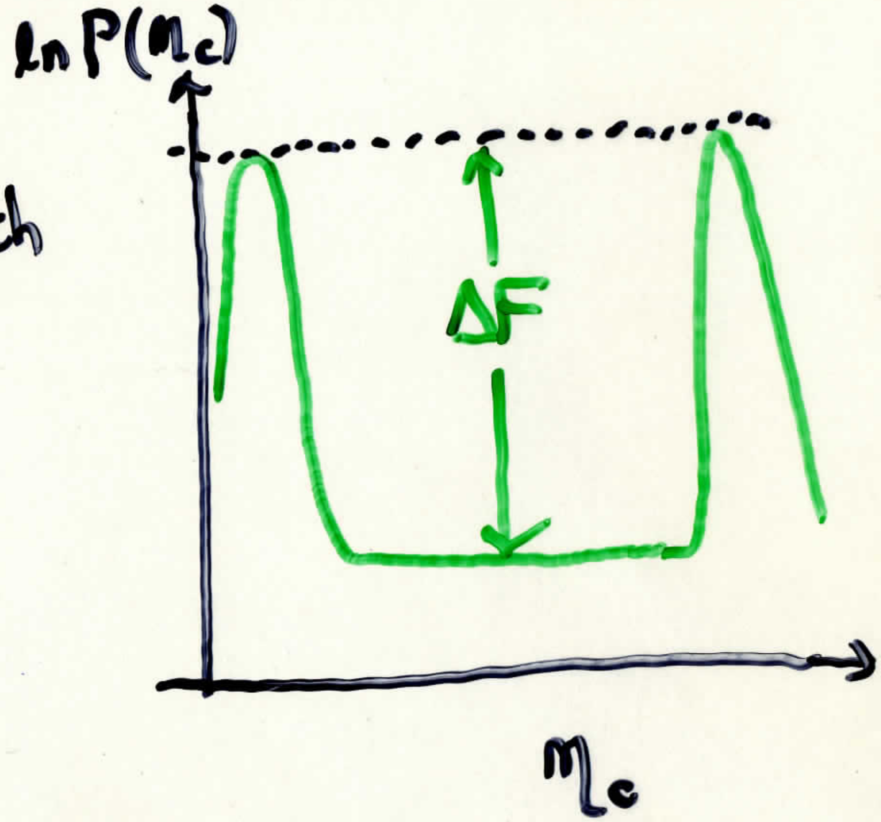
(ii) sample the probability distribution of the order parameter $P(\eta_c)$ ($P(m)$ in the Ising magnet)

(iii) interpret $-\log P(\eta_c)$ as effective free energy $\beta \Delta F(\eta_c)$

(Ising model surface tension inferred from $-\log P(m)$ in K.B, Phys. Rev. A 25, 1699 (1982))

estimation of the interface free energy





periodic boundary conditions

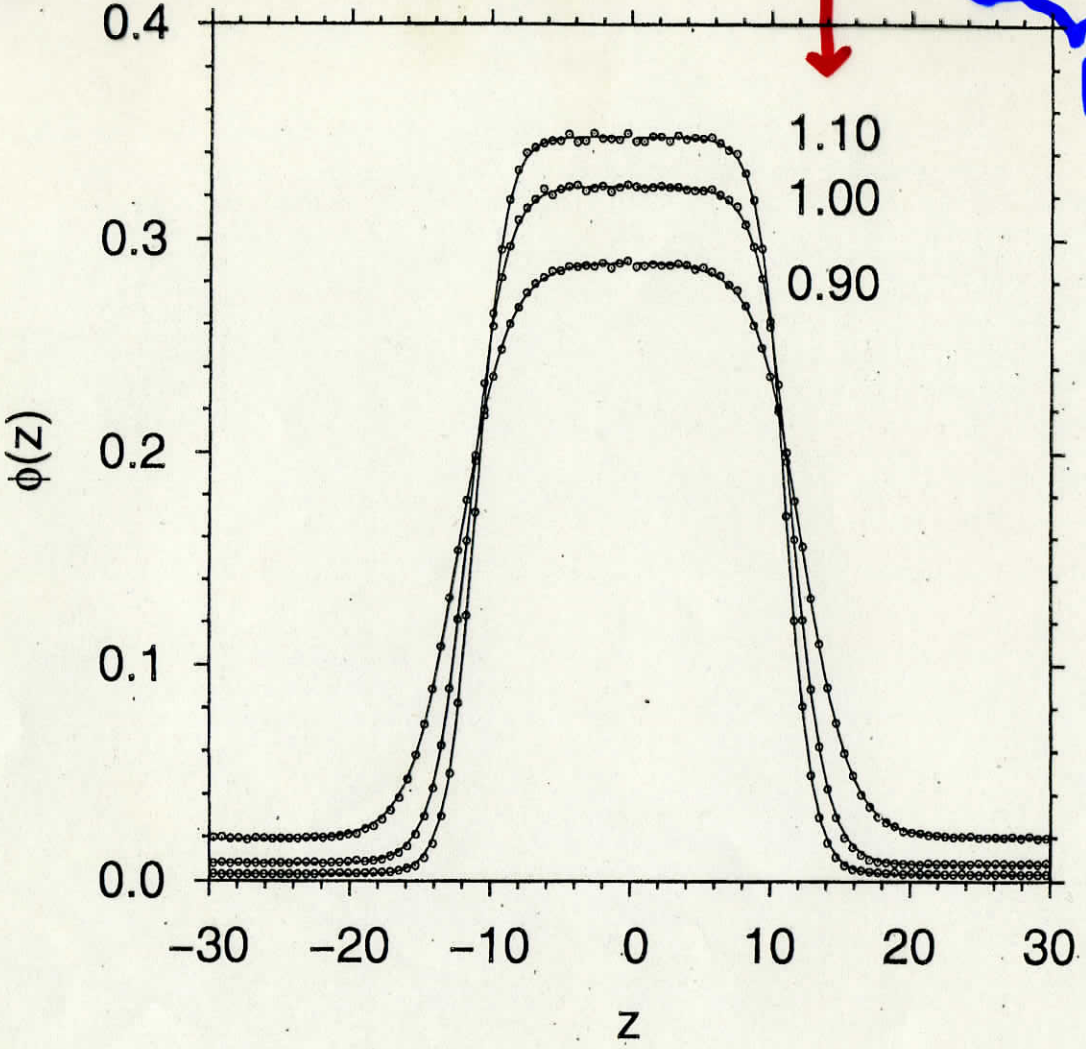
ΔF independent of colloid volume fraction η_c for non-interacting interfaces

$$\Delta F = 2L^2 f_{int}/k_BT$$

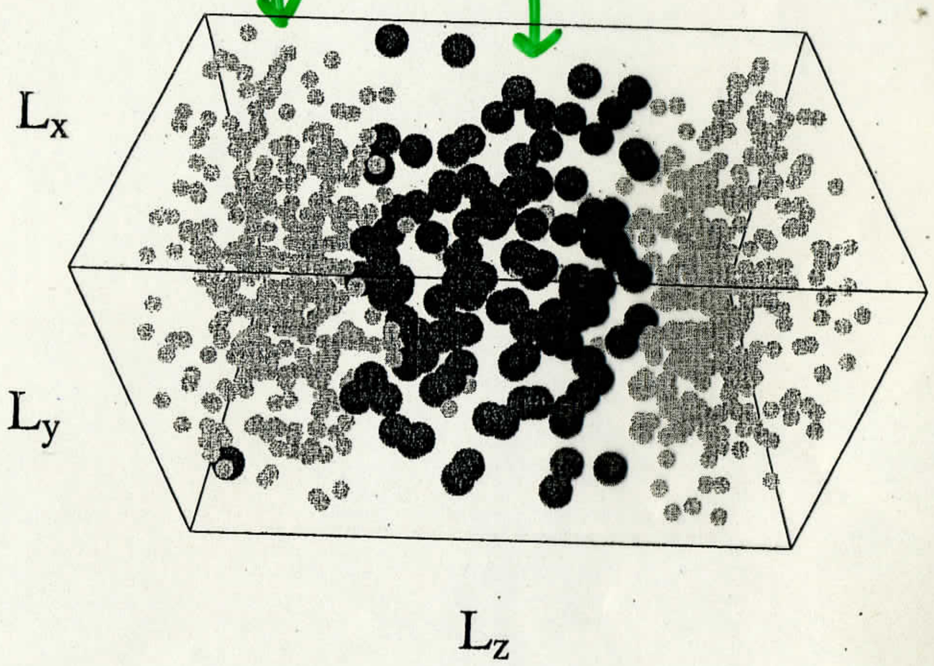
2 $L \times L$ interfaces

colloid density profile

$$\eta_p^r = \underbrace{\exp\left(\frac{\mu_p}{k_BT}\right)}_{\text{polymer fugacity}}\left(\frac{4\pi R_p^3}{3}\right) = \text{"polymer reservoir packing fraction"}$$



polymers colloids



LATTICE GAS (ISING MODEL)

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j - H \sum_i S_i - H_1 \sum_{i \in n=1} S_i - H_D \sum_{i \in n=D} S_i \ , \quad S_i = \pm 1$$

local density: $\rho_i = (1+S_i)/2 = \begin{cases} 1 \\ 0 \end{cases}$

magnetic field $H \leftrightarrow$ chemical potential difference

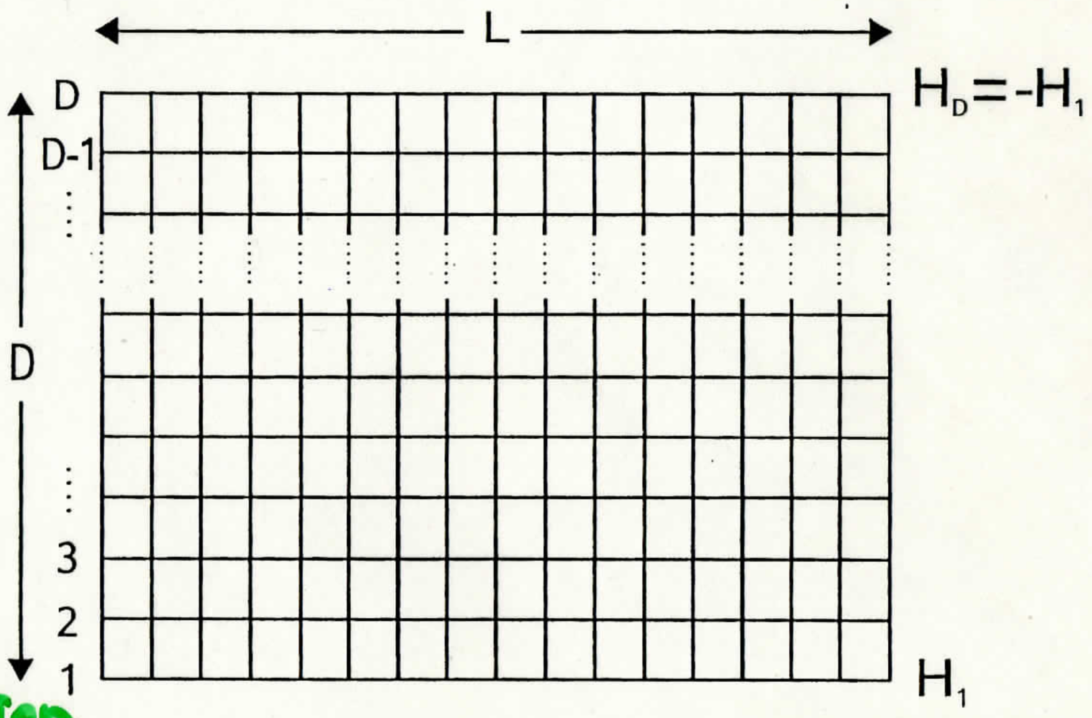
$2H = \mu - \mu_{coex}$

$\rho = (1 + \langle S_i \rangle_T)/2$

$\rho_v = (1 - m_{coex})/2$

$\rho_e = (1 + m_{coex})/2$

m_{coex} = spontaneous magnetization



units: $J \equiv 1$, lattice spacing $= 1$

no planes $n = 0$, $n = D+1$: "missing neighbors"

ESTIMATION of wall free energies and the CONTACT ANGLE for the ISING MODEL using YOUNG's EQUATION

$$\gamma_{v\ell}\cos\Theta = f_{w+}(T,H=0,H_1) - f_{w-}(T,H=0,H_1) \equiv \Delta f_{1D}$$

sign of spontaneous magnetization

ISING SYMMETRY: $f_{w-}(T,0,-H_1) = f_{w+}(T,0,H_1)$ $\Longrightarrow$ $H_1=0$ implies $\Theta = 90^\circ$

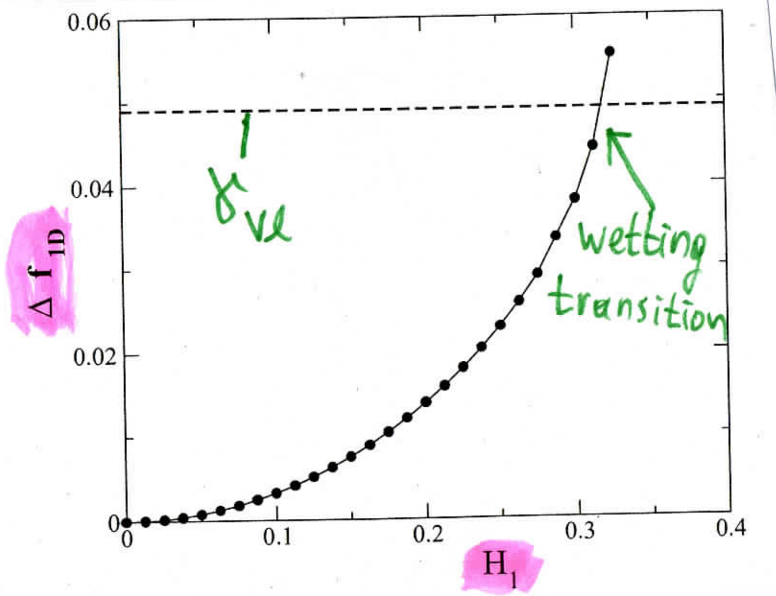
surface thermodynamics: $m_1 = -(\partial f_w(T,0,H_1)/\partial H_1)_T$

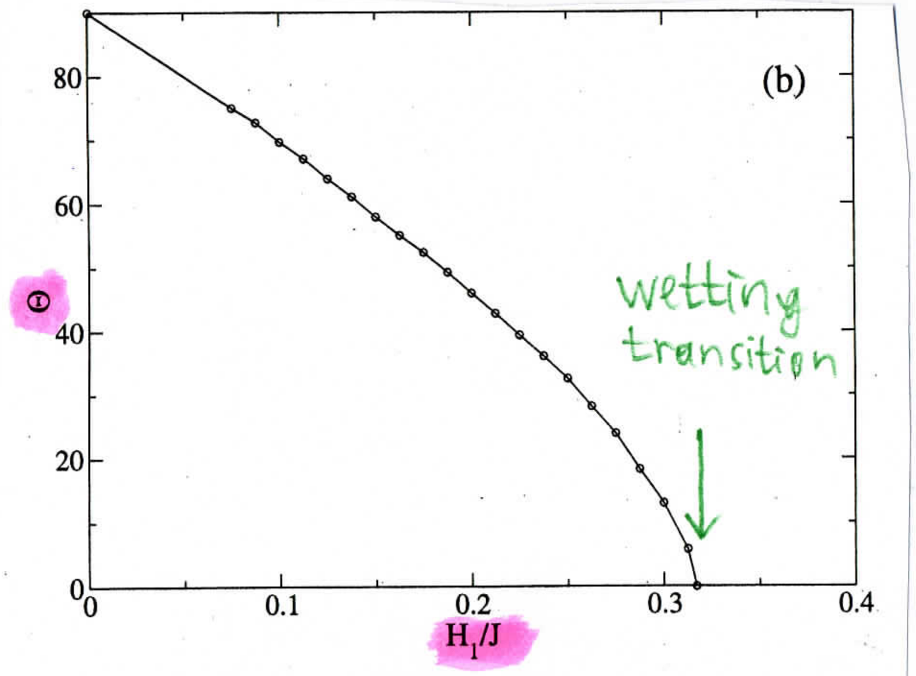
$\Rightarrow$ $\Delta f_{1D} = f_{w+}(T,0,H_1) - f_{w+}(T,0,H_D=-H_1)$

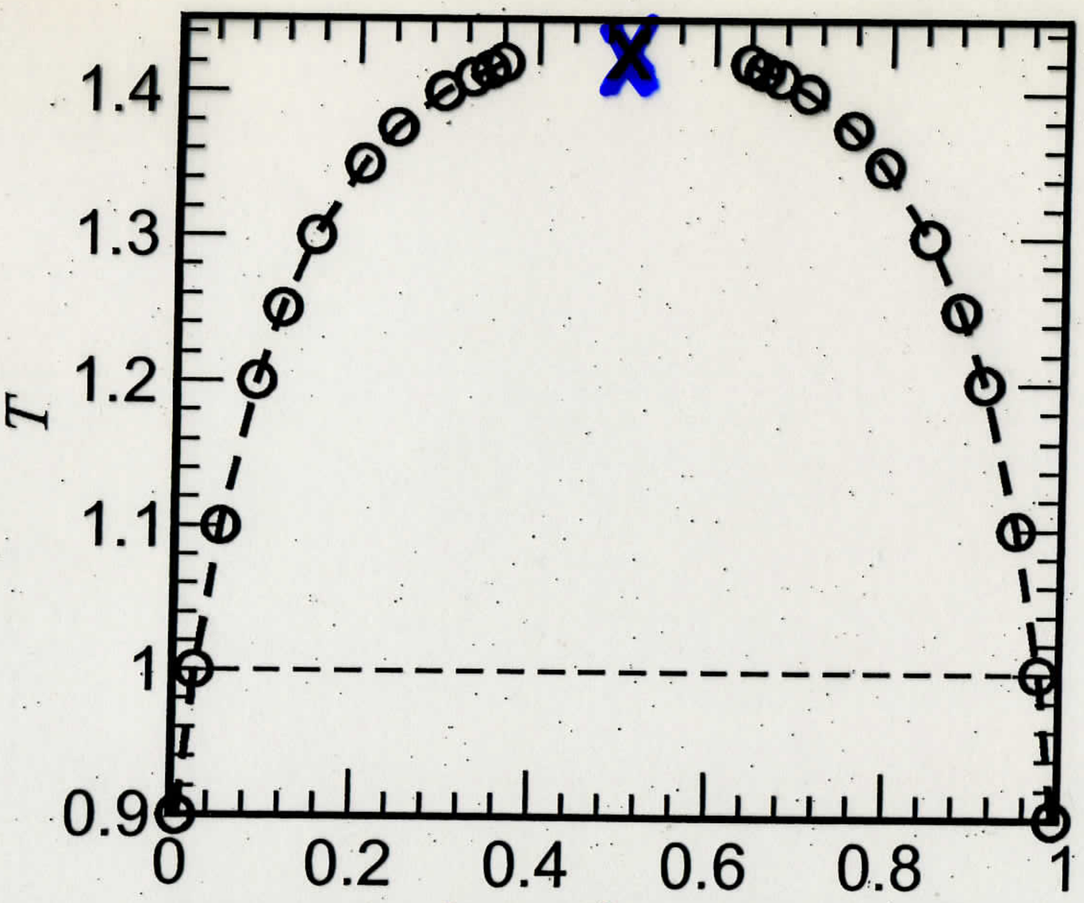
thermodynamic integration

$$\Delta f_{1D} = \int_0^{H_1} [m_D(-H_1') - m_1(H_1')]\,dH_1'$$

Young's equation







concentration $x_A = N_A/(N_A+N_B)$

symmetrical binary Lennard-Jones mixture

symmetric around $x_A^c = \frac{1}{2}$

density $\rho^* = \rho\sigma^3 = 1$

LJ diameter

$\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma = 1$

energy parameters: $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon = 1$, $\varepsilon_{AB} = \frac{1}{2}$

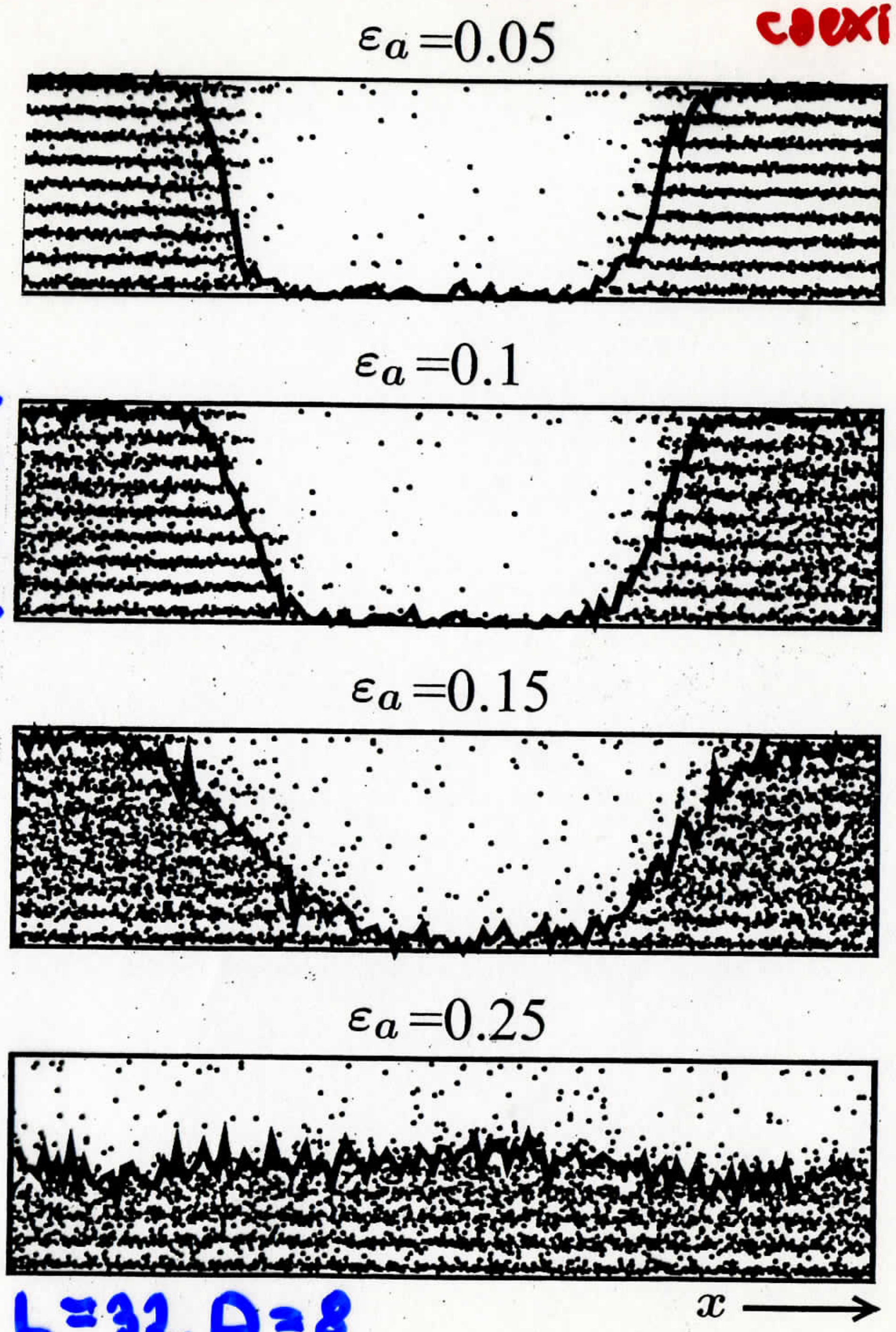
$T_c = 1.4130 \pm 0.0005$
(finite size scaling)

$$\phi_{LJ}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right]$$

truncated + shifted at $r_c = 2.5\sigma$

BINARY LJ MIXTURE between ANTISYMMETRIC WALLS: phase coexistence at $x_A = 0.5$ (FIXED!)

allows "measurement" of CONTACT ANGLE Θ $\quad L \times L \times D$ geometry



D

z

$L = 32, D = 8$

wall potentials:

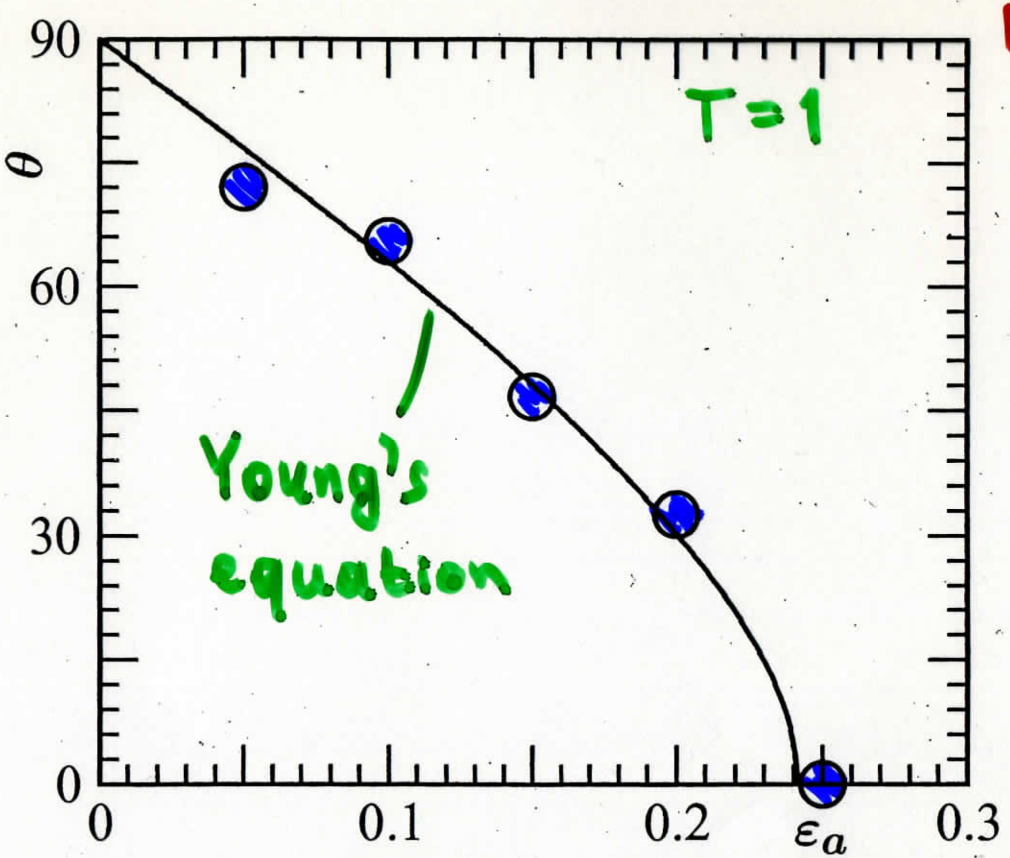
$$U_A(z) = \frac{2\pi\rho}{3}\left\{\varepsilon_r\left[\left(\frac{\sigma}{z+\sigma/2}\right)^9 + \left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^9\right] - \varepsilon_a\left(\frac{\sigma}{z+\sigma/2}\right)^3\right\}$$

$$U_B(z) = \frac{2\pi\rho}{3}\left\{\varepsilon_r\left[\left(\frac{\sigma}{z+\frac{\sigma}{2}}\right)^9 + \left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^9\right] - \varepsilon_a\left(\frac{\sigma}{D+\sigma/2-z}\right)^3\right\}$$

one wall attracts only A, the other wall only B, with the same strength

← complete wetting (resp. interface "unbinding from walls) has occurred

CONTACT ANGLE vs. STRENGTH of attractive part of wall potential for the binary LJ mixture



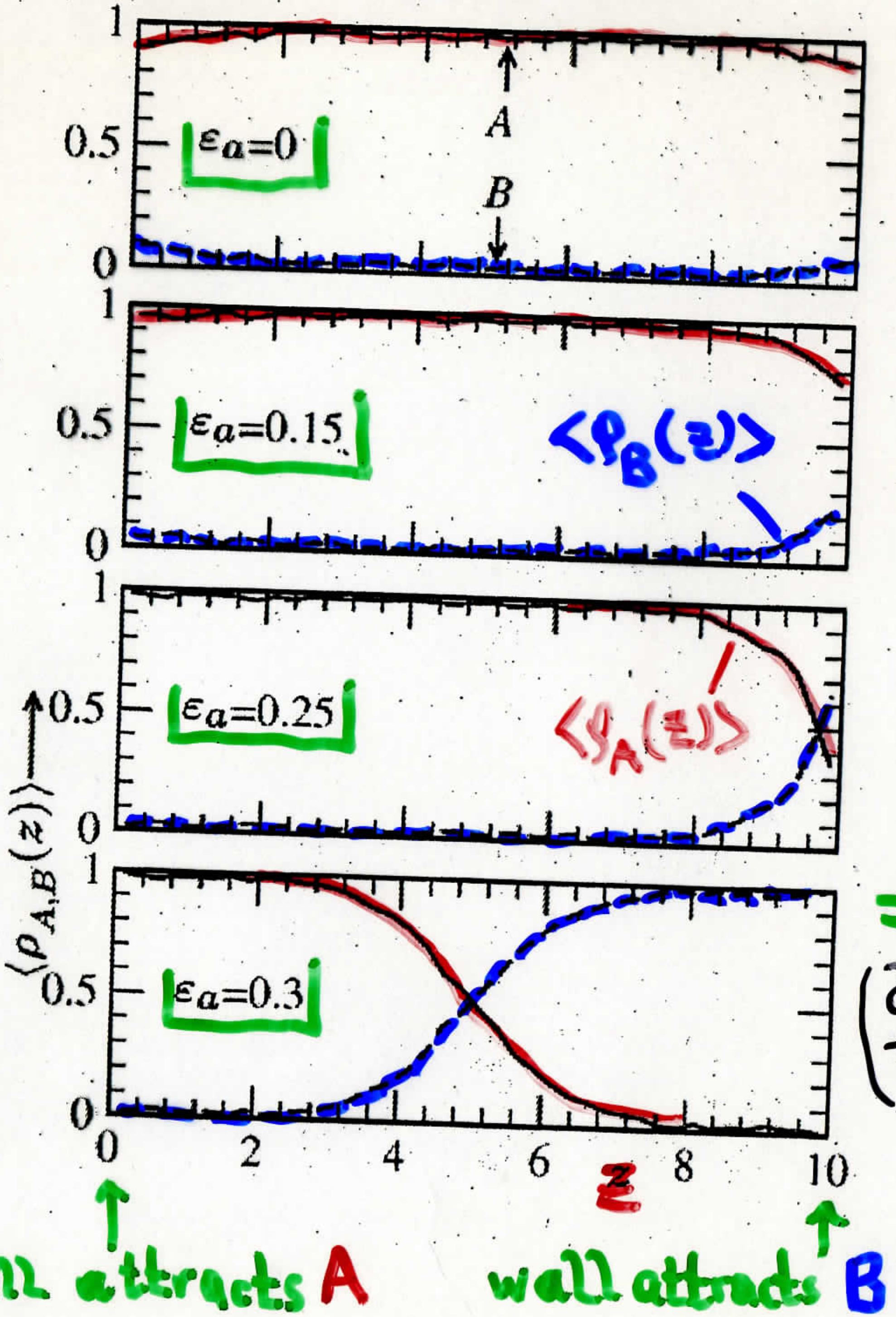
$\bullet$ observations from flat but inclined interfaces in nano-films

— $\cos\Theta = (\gamma_{WA} - \gamma_{WB})/\gamma_{AB}$

$\underbrace{\gamma_{WA} - \gamma_{WB}}$ obtained from thermodynamic integration of systems with walls (NO PHASE COEXISTENCE) in the semi-grandcanonical ensemble (incomplete wetting conditions)

$$\gamma_{WA} - \gamma_{WB} = f_s^{(z=0)}(\varepsilon_a)\Big|_{A\text{-rich phase}} - f_s^{(z=0)}(\varepsilon_a)\Big|_{B\text{-rich phase}} =$$

$$= \frac{2\pi\rho}{3}\int_0^{\varepsilon_a} d\varepsilon'_a \int_0^D dz\left[\langle\rho_A(\varepsilon'_a, z)\rangle_{A\text{-rich}}\left(\frac{\sigma}{z+\frac{\sigma}{2}}\right)^3 - \langle\rho_B(\varepsilon'_a, z)\rangle_{A\text{-rich}}\left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^3\right]$$



Density profiles across the film (D = 10)

(semi-grandcanonical ensemble)

$$F = -k_B T \ln \int d\vec{X} \exp\Big\{-\beta \mathcal{H}_b(\vec{X}) - \beta \mathcal{H}_w^r(\vec{X}) + \beta \varepsilon_a L^2 \frac{2\pi\rho}{3} \times \Big[\int_0^D \rho_A(z)\left(\frac{\sigma}{z+\frac{\sigma}{2}}\right)^3 dz + \int_0^D \rho_B(z)\left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^3 dz\Big]$$

$\Rightarrow$

$$\left(\frac{\partial f_s^{(z=0)}}{\partial \varepsilon_a}\right)_T = \frac{2\pi\rho}{3}\int_0^D \langle \rho_A(z) \rangle \left(\frac{\sigma}{z+\sigma/2}\right)^3 dz$$

$$\left(\frac{\partial f_s^{(z=D)}}{\partial \varepsilon_a}\right)_T = \frac{2\pi\rho}{3}\int_0^D \langle \rho_B(z) \rangle \left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^3 dz$$

ASYMMETRIC SYSTEMS: obtain excess free energies due to walls from ENSEMBLE SWITCH METHOD

$$\mathcal{H}(\vec{X}) = (1-\kappa)\,\mathcal{H}_1(\vec{X}) + \kappa\,\mathcal{H}_2(\vec{X})$$

$\kappa \in [0,1]$ discretized $\{\kappa_i,\ i=1,2,\dots,100\}$

"microstate"   systems WITHOUT walls   system WITH two equivalent walls

SAME PARTICLE NUMBER, SAME LINEAR DIMENSIONS

Monte Carlo sampling includes "SWITCHES" $\kappa_i \rightleftarrows \kappa_{i+1}, \kappa_{i-1} \Rightarrow$ free-energy differences $k_BT\,[\ln P(i) - \ln P(i\pm1)]$

+ WANG-LANDAU SAMPLING

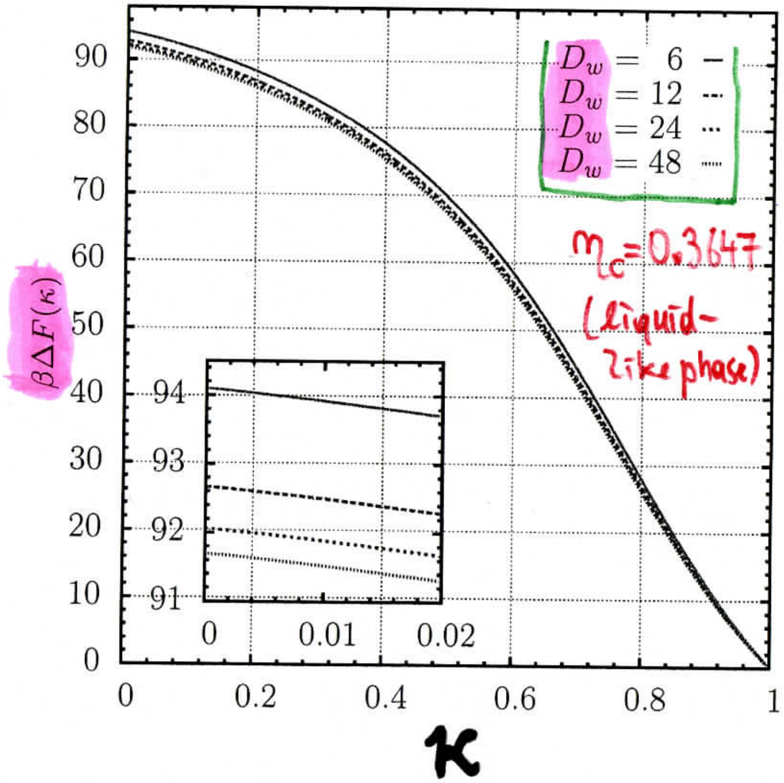
AO-model

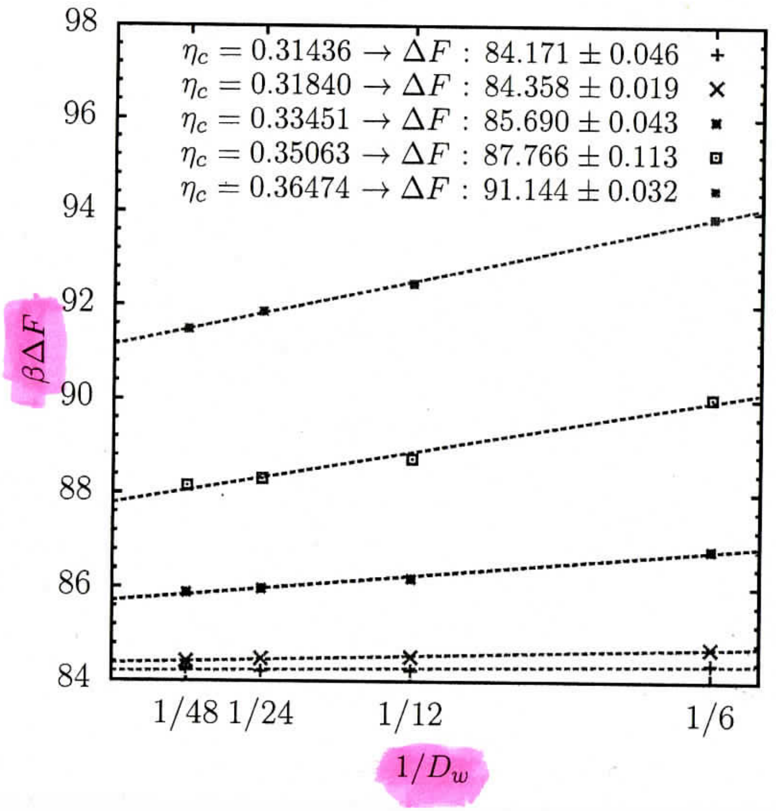
$L \times L \times D_w$

$L = 6.735$

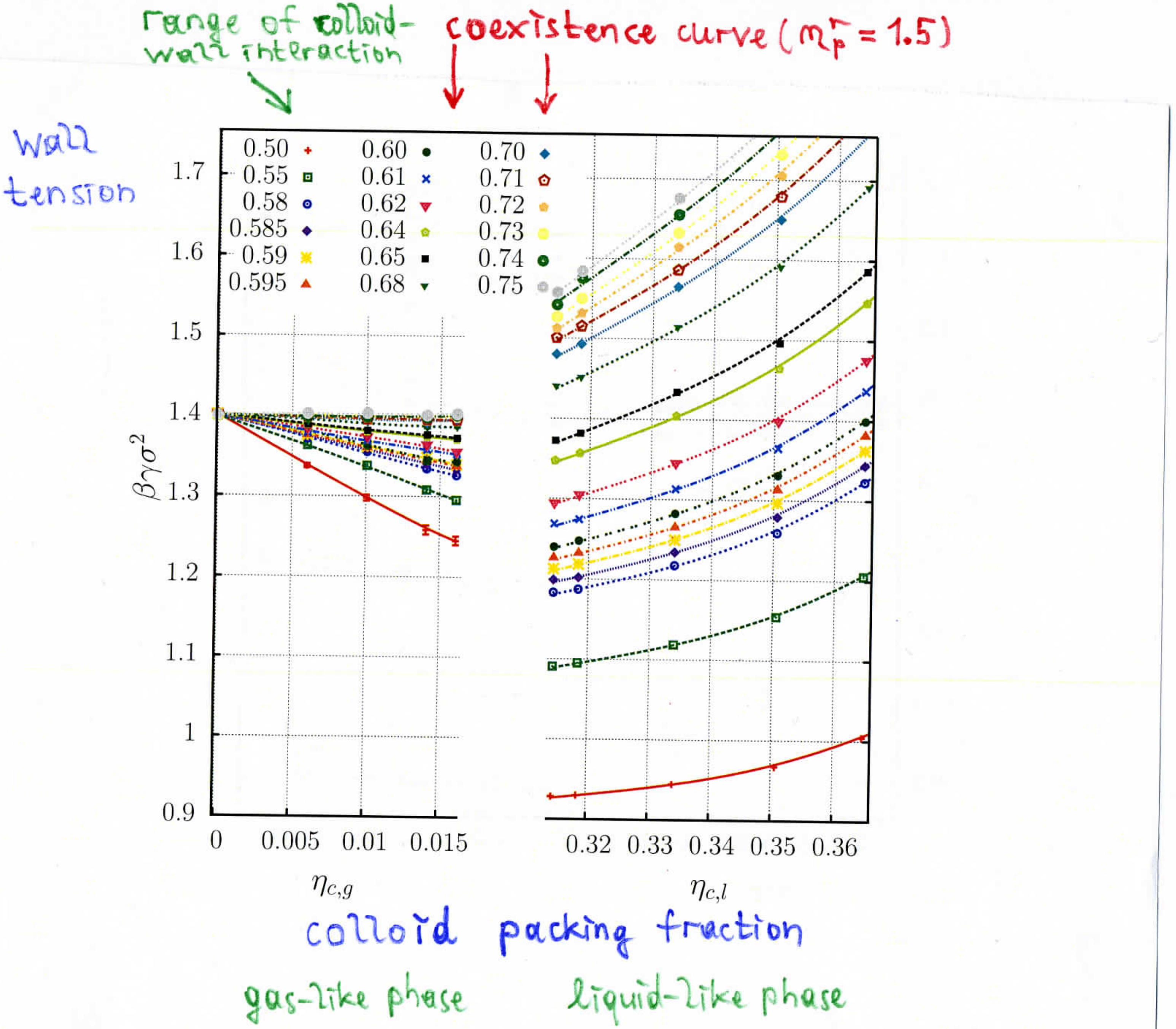
(length unit = colloid diameter)

$\sigma_w = 0.5$





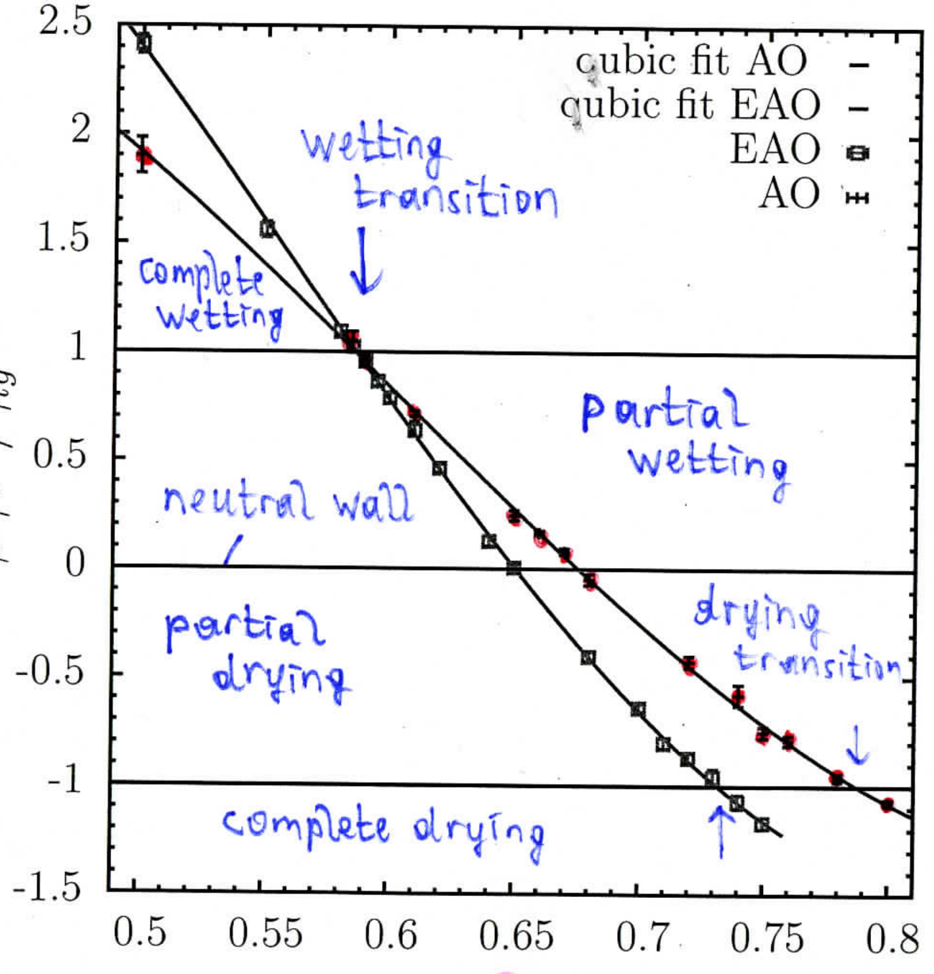
WALL TENSION OF THE AO-MODEL FOR COLLOID-POLYMER MIXTURES



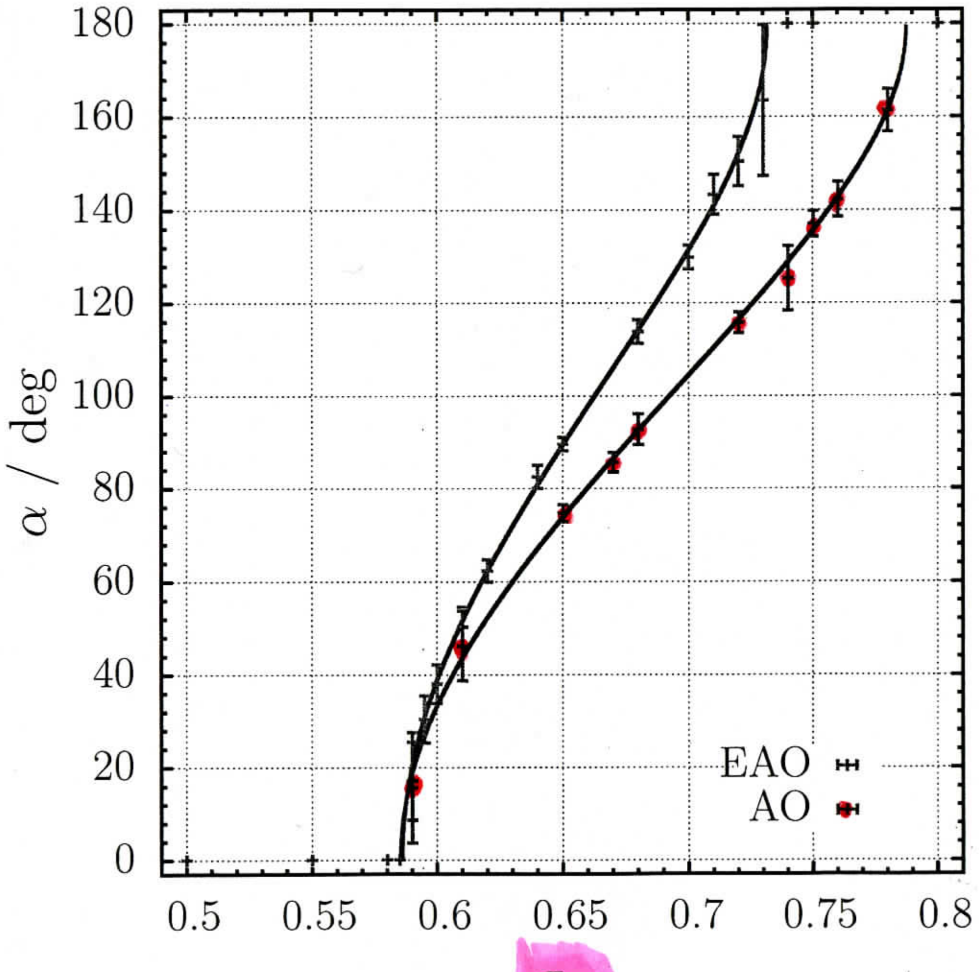
WETTING PHASE DIAGRAMS FOR TWO MODELS OF COLLOID-POLYMER MIXTURES

$\frac{\sigma_{wg} - \sigma_{wl}}{\sigma_{lg}}$ ($= \cos\Theta$, if partial wetting/drying)

contact angle



range of wall-colloid σ_w repulsion



CRITICAL WETTING IN THE ISING MODEL

review of the analytic theory : SEMI-INFINITE SYSTEM

- temperature T less than bulk critical temperature T_{cb}
- small positive bulk field $H \to 0^+$: positive spontaneous magnetization in the bulk
- negative surface field $-|H_1|$ which controls the wetting transition (which occurs at $T_w(H_1) < T_{cb}$

$\Rightarrow$ singular surface excess free energy

$$f_s^{(sing)}/k_BT = |t|^{2-\alpha_s} \tilde{F}_s(H|t|^{-\Delta_s}) , \quad t = 1 - T/T_w(H_1) \to 0$$

reminiscent of well-known scaling at the bulk transition ($\tau = 1 - T/T_{cb} \to 0$)

$$f_b^{(sing)}/k_BT = |\tau|^{2-\alpha_b} \tilde{F}_b(H|\tau|^{-\Delta_b}) , \quad \Delta_b = \gamma_b + \beta_b , \quad \langle m \rangle \propto \tau^{\beta_b}$$

$$\chi = (\partial \langle m \rangle / \partial H)_{H=0}^{H=0} \propto \tau^{-\gamma_b}$$

criticality $\Leftrightarrow$ emergence of long range critical correlations

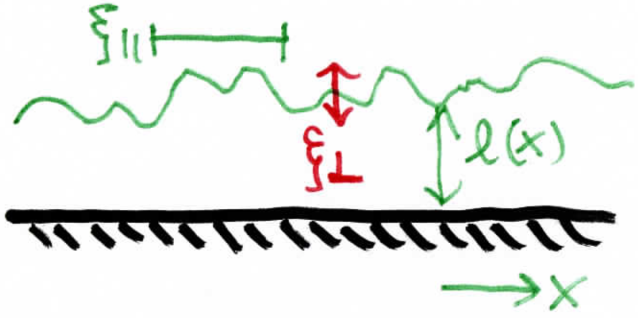
bulk: $G(r) = \langle S_0 S_r \rangle - \langle S_0 \rangle \langle S_r \rangle = r^{-(d-2+\eta)} g_b(r/\xi_b)$ $\quad d$ = dimensionality

correlation length $\xi_b = \tau^{-\nu_b} \tilde{\xi}_b(H|\tau|^{-\Delta_b})$

scaling : $\gamma_b = \nu_b(2-\eta_b)$ $\quad$ "hyperscaling" : $d\nu_b = 2 - \alpha_b = \gamma_b + 2\beta_b$

$$\Delta_b = \frac{\nu_b}{2}[d+2-\eta_b]$$

CRITICAL WETTING: correlations of interfacial height fluctuations



$\delta\ell(x) = \ell(x) - \langle \ell \rangle \qquad G(x) = \langle \delta\ell(0)\,\delta\ell(x) \rangle$

$G(x) = x^{-(d-3+\eta_{\parallel})}\,\tilde{G}(x/\xi_{\parallel}) \qquad \xi_{\parallel} = t^{-\nu_{\parallel}}\,\tilde{\xi}_{\parallel}(H|t|^{-\Delta_s})$

scaling as in the bulk: $\Delta_s = \frac{\nu_{\parallel}}{2}\left[d-1+2-\eta_{\parallel}\right]$

One important distinction: capillary wave Hamiltonian $\Rightarrow \eta_{\parallel} = 0,\ \Delta_s = \frac{\nu_{\parallel}}{2}(d+1)$

$\Rightarrow$ only ONE independent critical exponent

(hyperscaling for interfacial phenomena: $(d-1)\nu_{\parallel} = 2 - \alpha_s$)

<u>$d=2$ dimensions</u>: all exponents for critical wetting known and satisfy scaling

$\nu_{\parallel} = 2 \qquad \alpha_s = 0 \qquad \Delta_s = 3$

surface excess {magnetization $\quad m_s = -\left(\frac{\partial f_s^{(sing)}}{\partial H}\right)_T \propto t^{2-\alpha_s-\Delta_s} \equiv t^{\beta_s} \Rightarrow \beta_s = -1$

{susceptibility $\quad \chi_s = -\left(\frac{\partial^2 f_s}{\partial H^2}\right)_T \propto t^{2-\alpha_s-2\Delta_s} \equiv t^{-\gamma_s} \Rightarrow \gamma_s = 4$

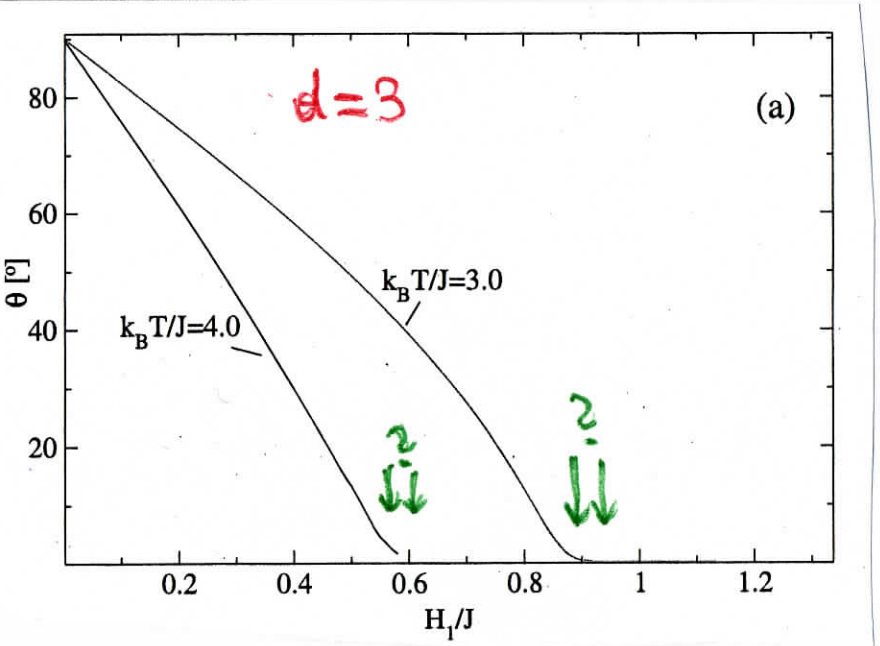
$\beta_s = -1$ means $\langle \ell \rangle \propto t^{-1}$

capillary wave Hamiltonian $\Rightarrow \left.\begin{array}{l} \xi_{\perp} \propto \xi_{\parallel}^{1/2} \\ \xi_{\perp} \propto t^{-\nu_{\perp}} \end{array}\right\} \nu_{\perp} = 1$

HOW SHALL ONE STUDY CRITICAL WETTING BY SIMULATIONS ?

? Thermodynamic integration ?

$f_s^{(sing)} \propto t^{2-\alpha_s} \Rightarrow$ nontrivial to find where $\Theta \to 0$?
(finite size rounding, critical slowing down...)



bulk critical phenomena:

the method of choice is FINITE SIZE SCALING

all linear dimensions $= L$, periodic boundary conditions, $H=0$

probability distribution of the magnetization

$$P_L(m) = \xi_b^{\beta_b/\nu_b}\,\tilde{P}_b\left(L/\xi_b,\, m\,\xi_b^{\beta_b/\nu_b}\right)$$

$$\Rightarrow k_BT\chi_b' = L^d\left(\langle m^2\rangle - \langle |m|\rangle^2\right) = L^{\underbrace{d-2\beta_b/\nu_b}_{\gamma_b/\nu_b}}\,\tilde{\chi}_b(L/\xi_b)$$

GENERALIZATION TO WETTING TRANSITION FOR A $L\times M$ GEOMETRY WITH ANTISYMMETRIC SURFACE FIELDS

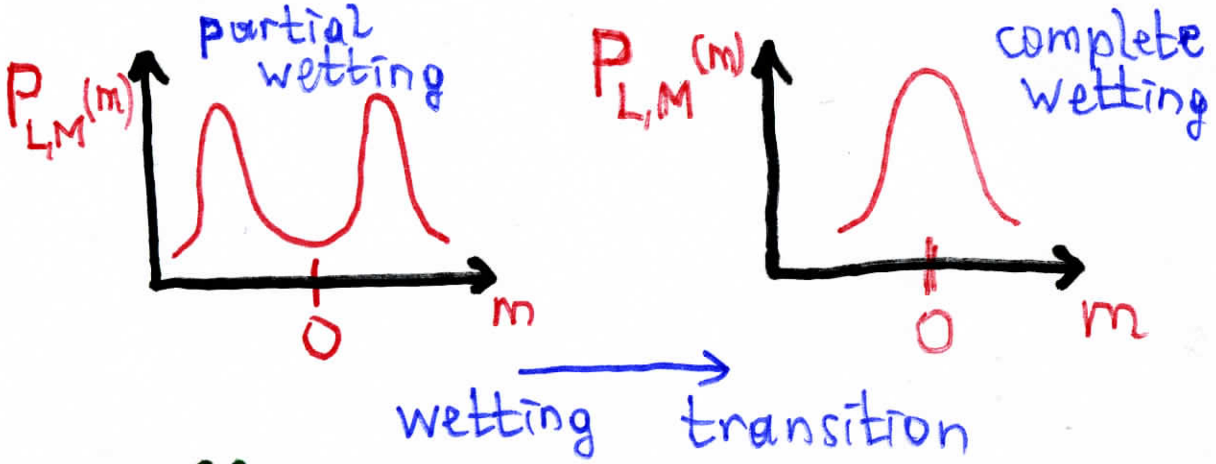
$$P_{LM}(m) = \xi_{\parallel}^{\beta/\nu_{\parallel}}\,\tilde{P}\left(L^{\nu_{\parallel}/\nu_{\perp}}/M,\, M/\xi_{\parallel},\, m\,\xi_{\parallel}^{\beta/\nu_{\parallel}}\right)$$

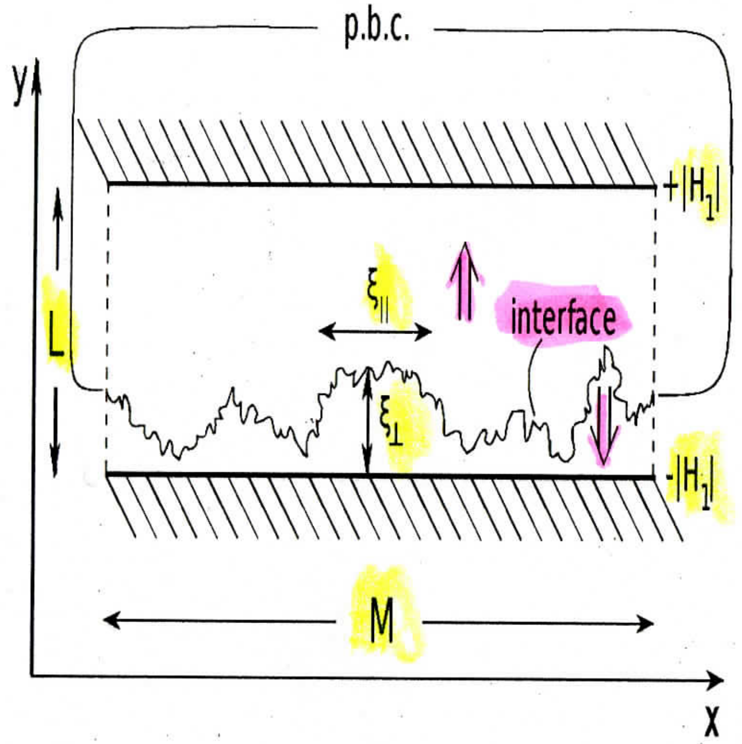
FINITE SIZE SCALING FOR CRITICAL WETTING

$$P_{L,M}(m) = \xi_{\parallel}^{\beta/\nu_{\parallel}} \tilde{P}\left(L^{\nu_{\parallel}/\nu_{\perp}}/M,\ M/\xi_{\parallel},\ m\xi_{\parallel}^{\beta/\nu_{\parallel}}\right)$$

$H=0$ + antisymmetric surface fields:

like a bulk transition!





$L^{\nu_{\parallel}/\nu_{\perp}}/M = c$ generalized aspect ratio

$$\int_{-1}^{+1} P_{L,M}(m)\,dm = 1, \quad \langle |m| \rangle = \int_{-1}^{+1} dm\,|m|\,P_{L,M}(m) = \xi_{\parallel}^{-\beta/\nu_{\parallel}}\, \tilde{m}\left(L^{\nu_{\parallel}/\nu_{\perp}}/M, \frac{M}{\xi_{\parallel}}\right)$$

$$\langle m^{2k} \rangle = \xi_{\parallel}^{-2k\beta/\nu_{\parallel}}\, \tilde{m}_{2k}\left(L^{\nu_{\parallel}/\nu_{\perp}}/M,\ M/\xi_{\parallel}\right) \qquad k = 1, 2, \ldots$$

FINITE SIZE SCALING FOR CRITICAL WETTING (ctd.)

$$\langle m^{2k}\rangle = \xi_{\parallel}^{-2k\beta/\nu_{\parallel}}\,\tilde{m}_{2k}(c, M/\xi_{\parallel})$$

$c = L^{\nu_{\parallel}/\nu_{\perp}}/M = \text{const.}$

generalized aspect ratio

susceptibility $k_B T\chi' = LM(\langle m^2\rangle - \langle |m|\rangle^2)$

$d=2$ dimensions

$$\Rightarrow k_B T\chi' = LM\,\xi_{\parallel}^{-2k\beta/\nu_{\parallel}}\,\tilde{\chi}(c, M/\xi_{\parallel}) \quad , k=1$$

$$k_B T\chi' = M^{1+\nu_{\perp}/\nu_{\parallel}-2\beta/\nu_{\parallel}}\,\tilde{\tilde{\chi}}(c, M/\xi_{\parallel})$$

$\tilde{\chi}, \tilde{\tilde{\chi}}$ = scaling functions

critical wetting transition: $\xi_{\parallel}\to\infty$, $M/\xi_{\parallel}\to 0$

$$\underset{\sim\sim}{k_B T\chi'} \propto M^{1+\nu_{\perp}/\nu_{\parallel}-2\beta/\nu_{\parallel}} = \underset{\sim\sim\sim\sim}{M^{3/2-2\beta/\nu_{\parallel}}} \qquad \begin{pmatrix}\nu_{\perp}/\nu_{\parallel} = 1/2\\ \text{in } d=2\end{pmatrix}$$

using finite size scaling for the surface excess susceptibility of the semi-infinite system:

$$\underline{\chi_s} = t^{-4}\,\tilde{\chi}_s(M/\xi_{\parallel}) \propto \xi_{\parallel}^{2}\,\tilde{\chi}_s(M/\xi_{\parallel}) \propto \underline{M^2} \quad \text{for } T=T_w \ (t=0)$$

$(\gamma_s = 4)$

singularity of χ' due to χ_s: $k_B T\chi'\big|_{t=0} = k_B T\chi_s\big|_{t=0}/L = k_B T_w\chi_s\big|_{t=0}/(M^{1/2}c^{-1/2})$

$$\Rightarrow \underset{\sim\sim\sim\sim}{k_B T\chi'\big|_{t=0} \propto M^{3/2}} \Rightarrow \beta/\nu_{\parallel} = 0\ , \text{ i.e. } \boxed{\beta = 0}$$

$$k_B T\chi'\big|_{t=0} \propto M^{\gamma/\nu_{\parallel}} \Rightarrow \underline{\gamma = 3}$$

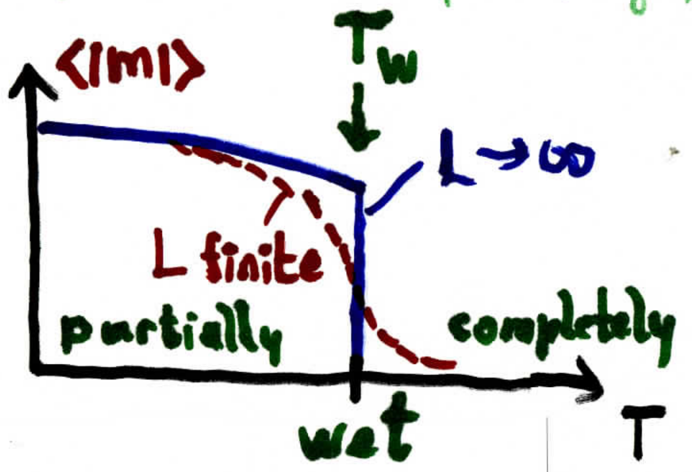
VARIATION OF THE GENERALIZED ASPECT RATIO

$$c = L^{\nu_{\parallel}/\nu_{\perp}}/M \quad \left(= L^2/M \text{ in } d=2\right)$$

self similar distribution changes from single peak (small c) to double peak (large c)

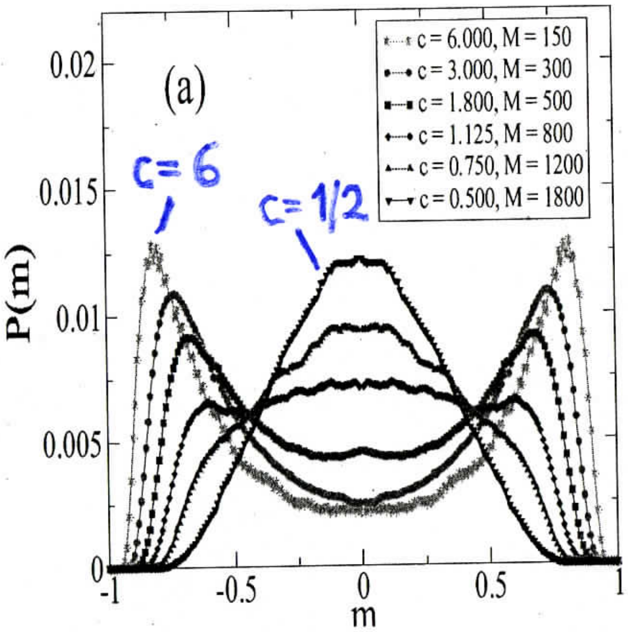
NEVER a 3-delta-function structure appears:

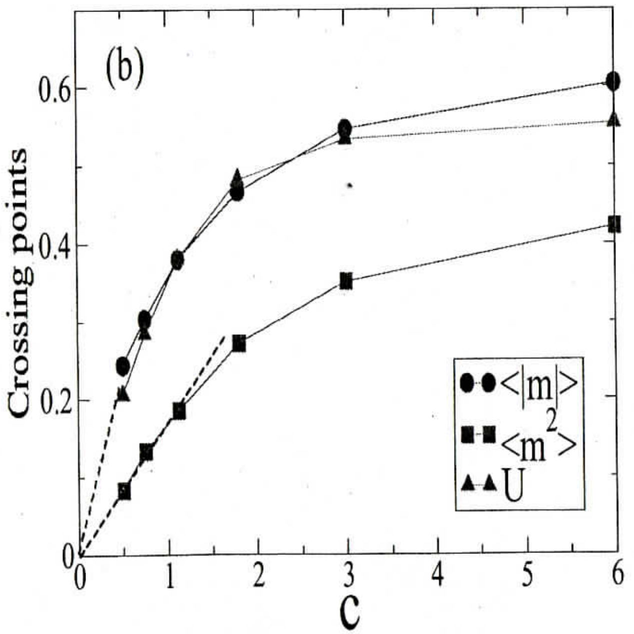
$\beta = 0$ does NOT mean FIRST-ORDER TRANSITION



$H_1/J = 0.7$

$T = T_w$, $L = 30$





CRITICAL WETTING LIKE A BULK TRANSITION IF THERMODYNAMIC LIMIT IS APPROACHED AT CONSTANT GENERALIZED ASPECT RATIO!

$d=2: \nu_{\parallel}=2, \nu_{\perp}=1, \Delta_s=3 \Rightarrow \beta=0, \gamma=3$

SCALING HOLDS: $\gamma+\beta=\Delta_s=3$

anisotropic bulk hyperscaling in $d=2$ holds: $(d-1)\nu_{\parallel}+\nu_{\perp}=2\beta+\gamma=3$

$\Rightarrow$ **recipes to locate critical wetting transitions**

extrapolation of susceptibility peak locations

e.g. $k_B T \chi' = L^{\gamma/\nu_\perp} \tilde{\chi}'(c, L/\xi_\perp)$

$\Rightarrow \chi_{max} \propto L^3, \; T_w/T_{max}-1 \propto L^{-1/\nu_\perp} = L^{-1}$

moments and cumulants intersect at T_w (where $M/\xi_{\parallel} \to 0$)

$\langle |m| \rangle = \tilde{m}(c, M/\xi_{\parallel}) \qquad \langle m^{2k} \rangle = \tilde{m}_{2k}(c, M/\xi_{\parallel})$

$U_{L,M} = 1 - \langle m^4 \rangle / [3\langle m^2 \rangle^2] = \tilde{U}(c, M/\xi_{\parallel})$

intersection values depend on $c = L^{\nu_{\parallel}/\nu_\perp}/M$ ($=L^2/M$ in $d=2$)

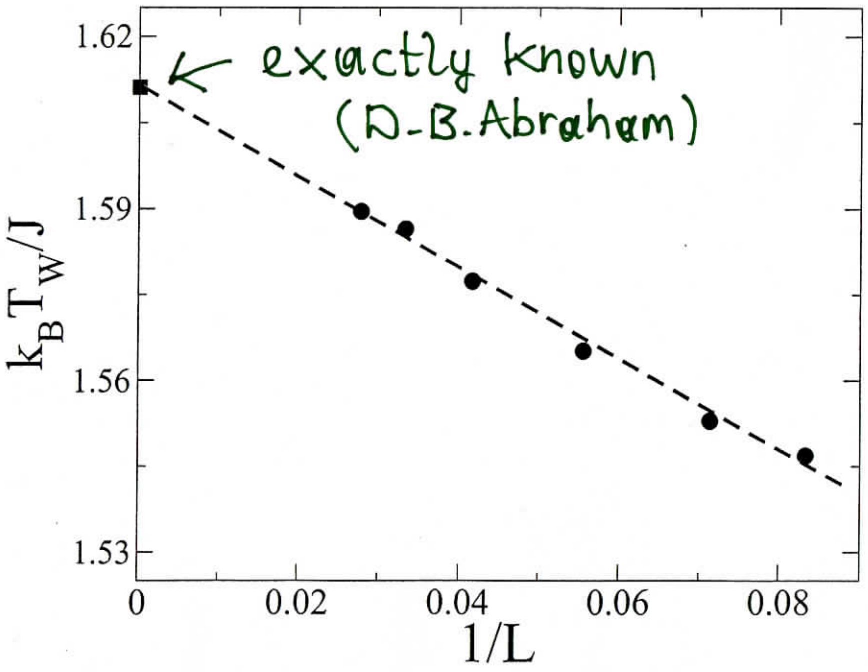
MONTE CARLO TEST

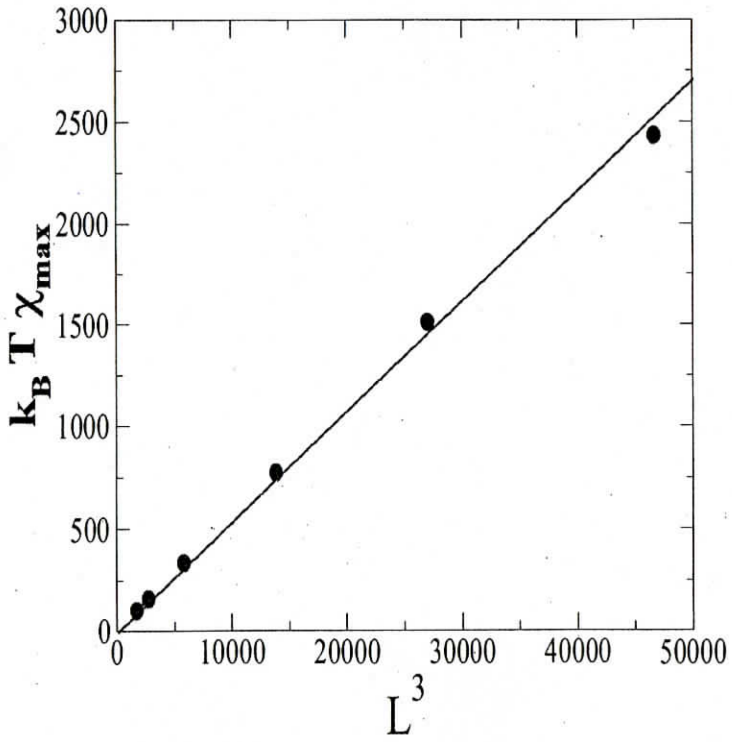
of the finite size scaling theory for CRITICAL WETTING

susceptibility extrapolation

$$T_w / T_{max} - 1 \propto L^{-1}$$

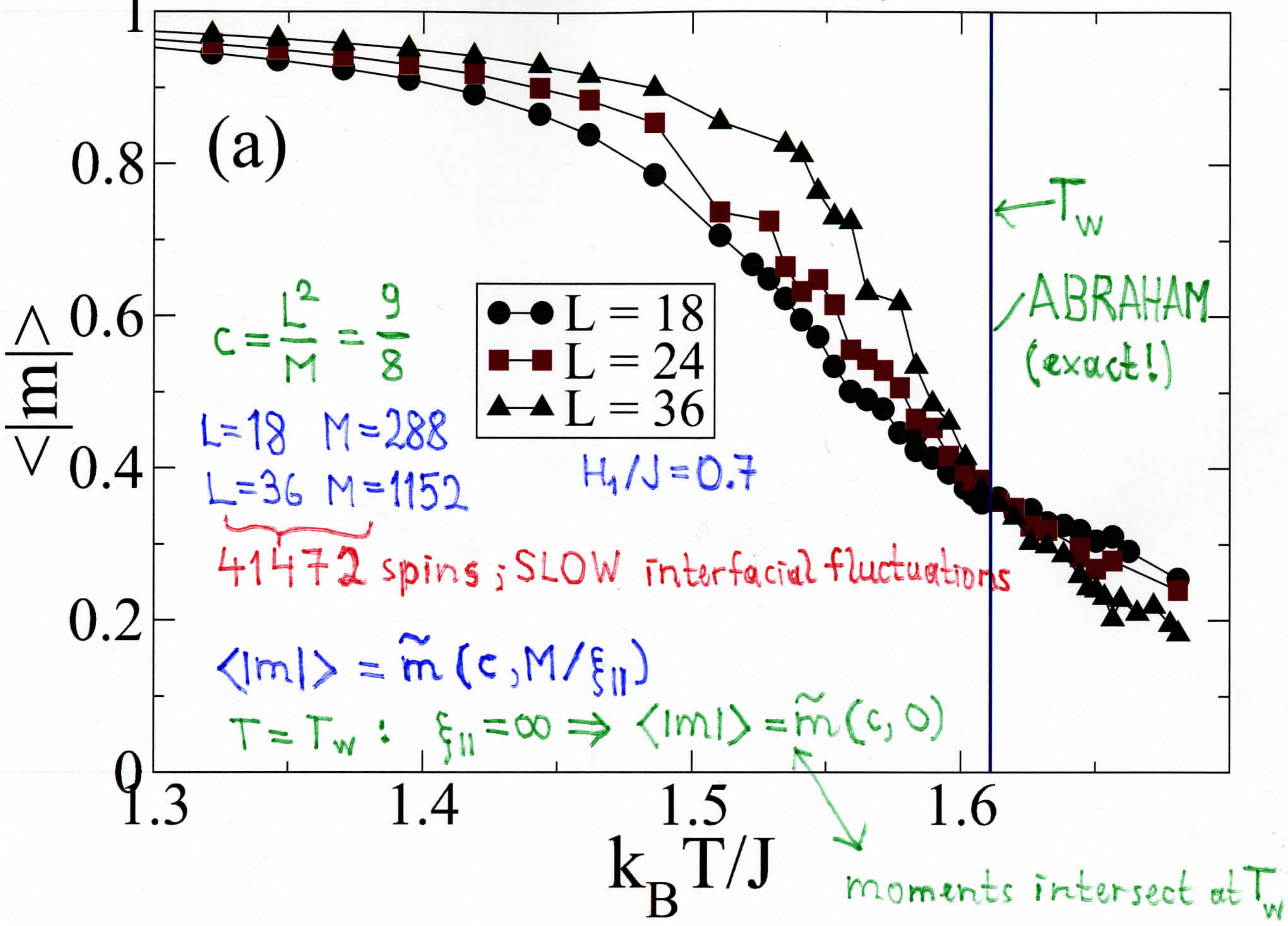
$$\chi_{max} \propto L^3$$



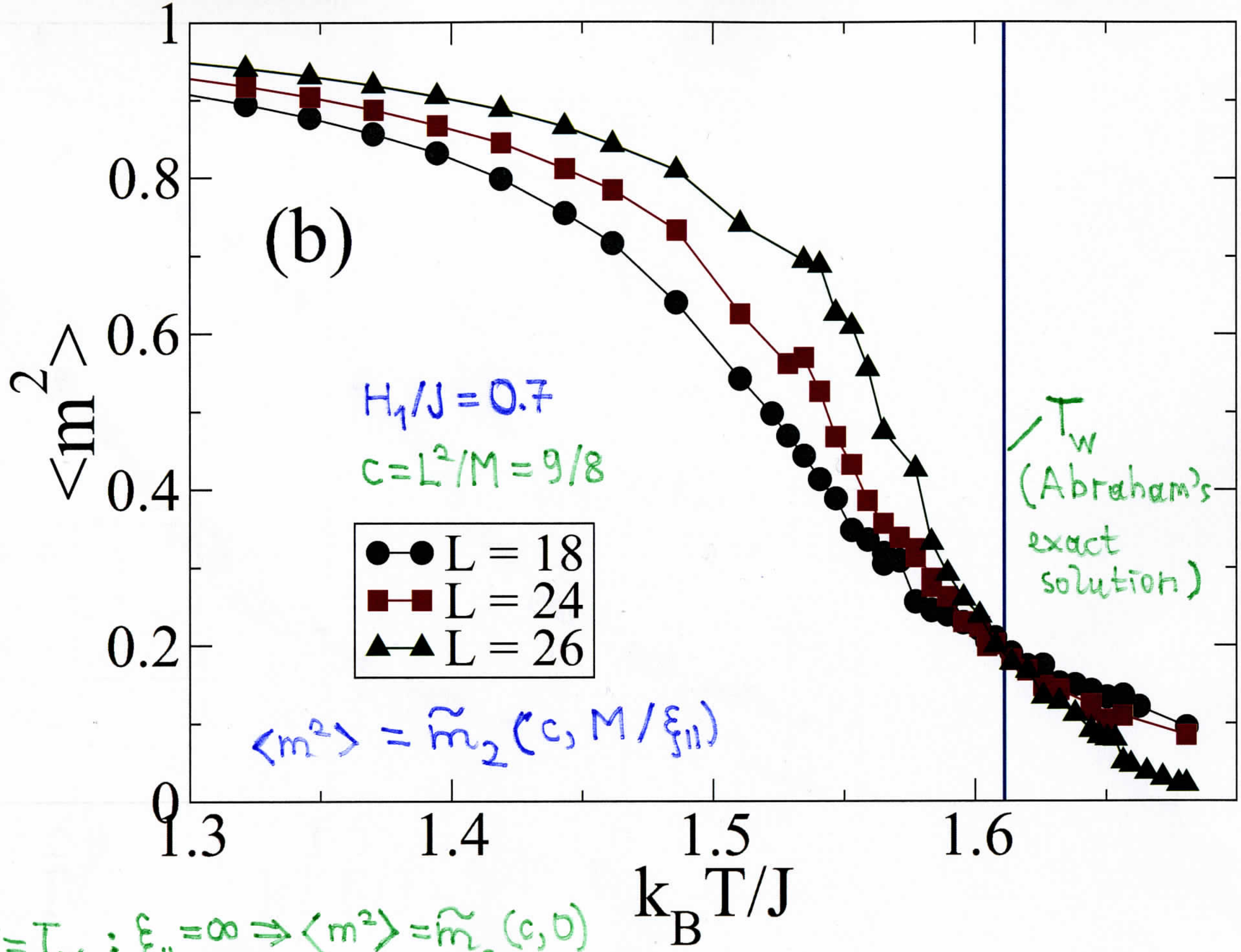


$c = L^2 / M = 9/8$

MONTE CARLO TEST (ctd)

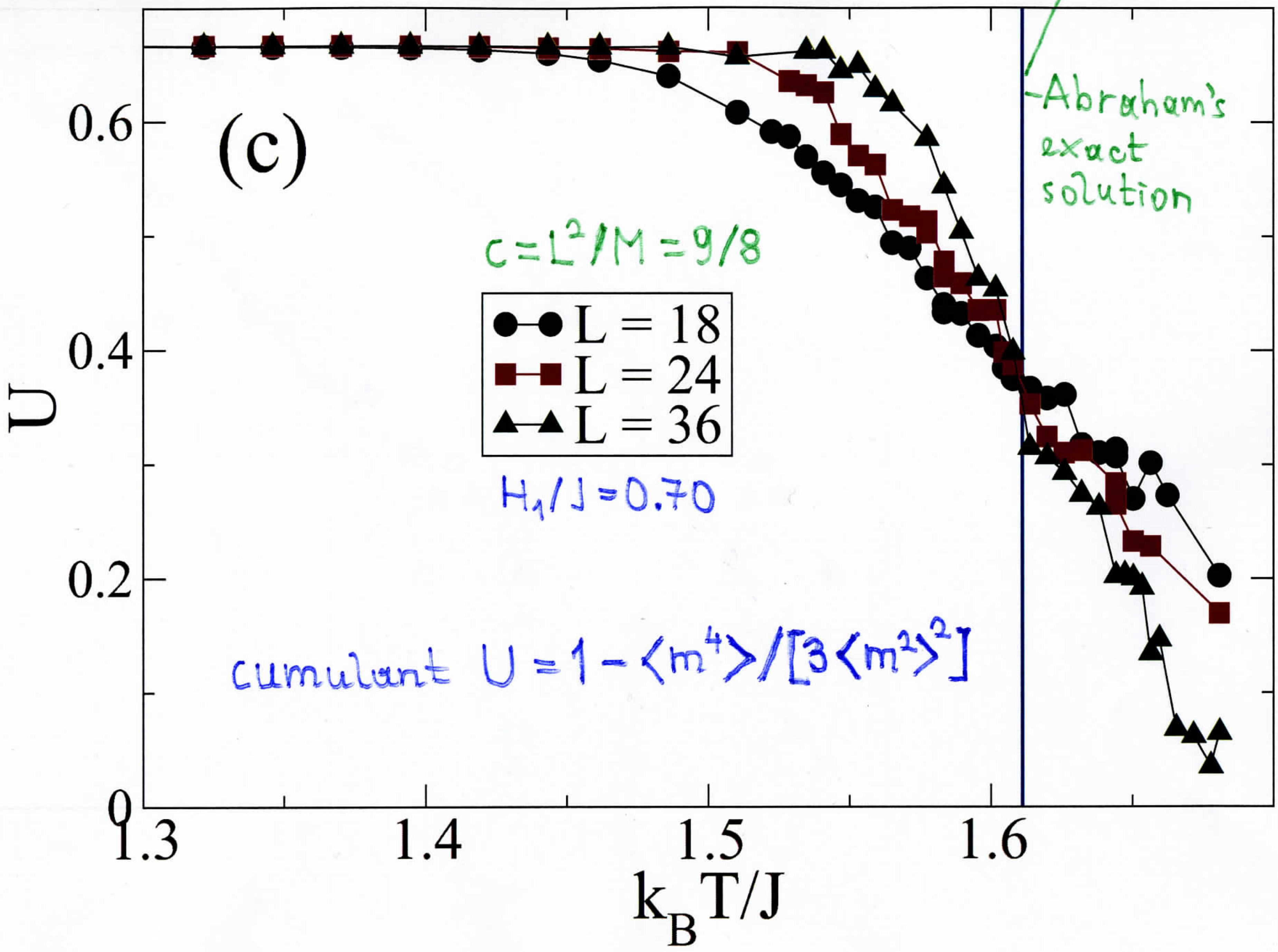


MONTE CARLO TEST: second moments intersect at T_w

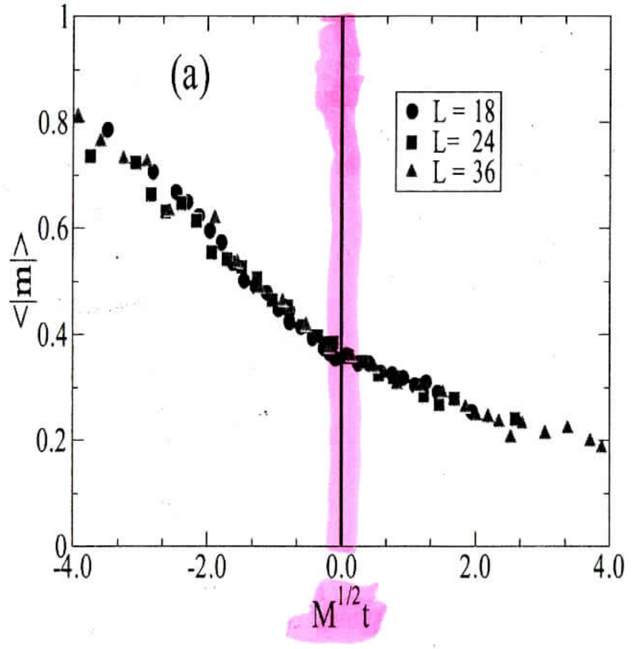


$T = T_w$: $\xi_{\parallel} = \infty \Rightarrow \langle m^2 \rangle = \tilde{m}_2(c, 0)$

MONTE CARLO TEST : cumulants intersect at T_w



MONTE CARLO TEST: "data collapse" on scaling functions



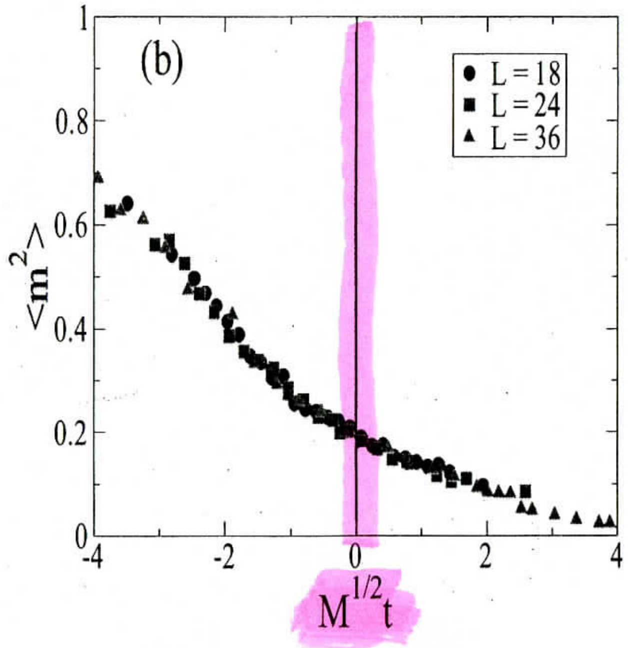
$$\langle |m| \rangle = \tilde{m}\,(c, \underbrace{M/\xi_{\parallel}}_{\propto\, \underbrace{M t^2}_{=\,(M^{1/2}t)^2}})$$

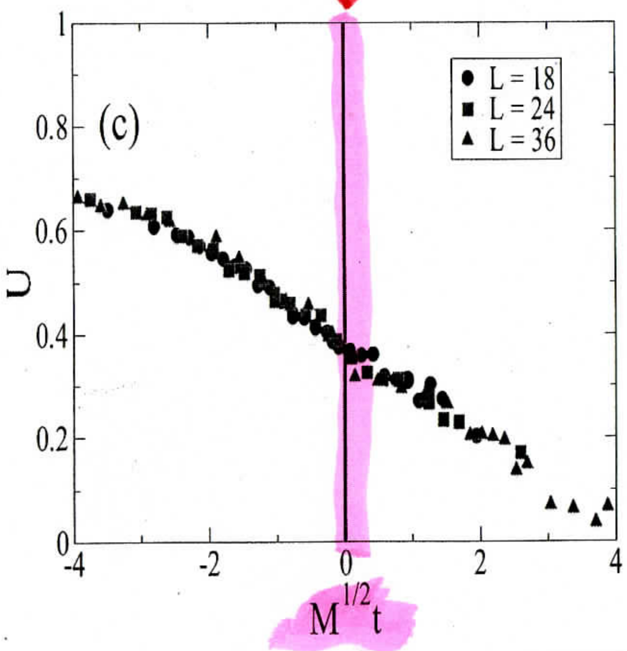
$t = 1 - T/T_W$

NO ADJUSTABLE PARAMETER WHATSOEVER!

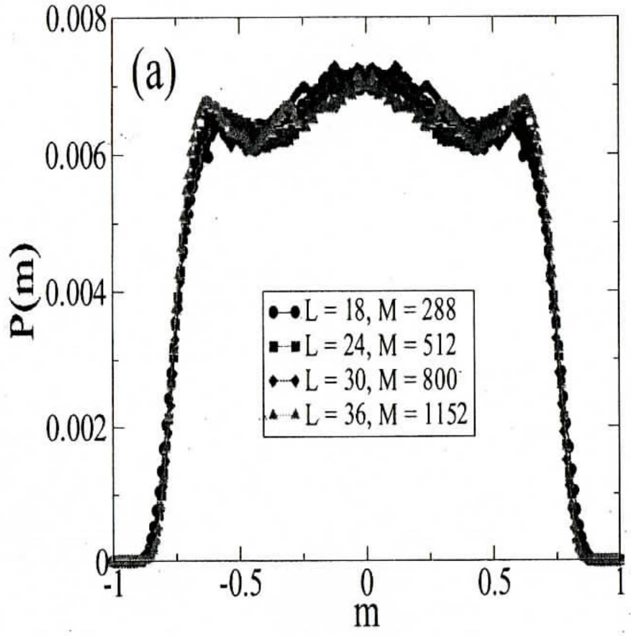
$H_1/J = 0.70 \qquad c = L^2/M = 9/8$

D. B. Abraham





$T = T_W$



APPLICATION: WETTING IN THE BLUME-CAPEL MODEL

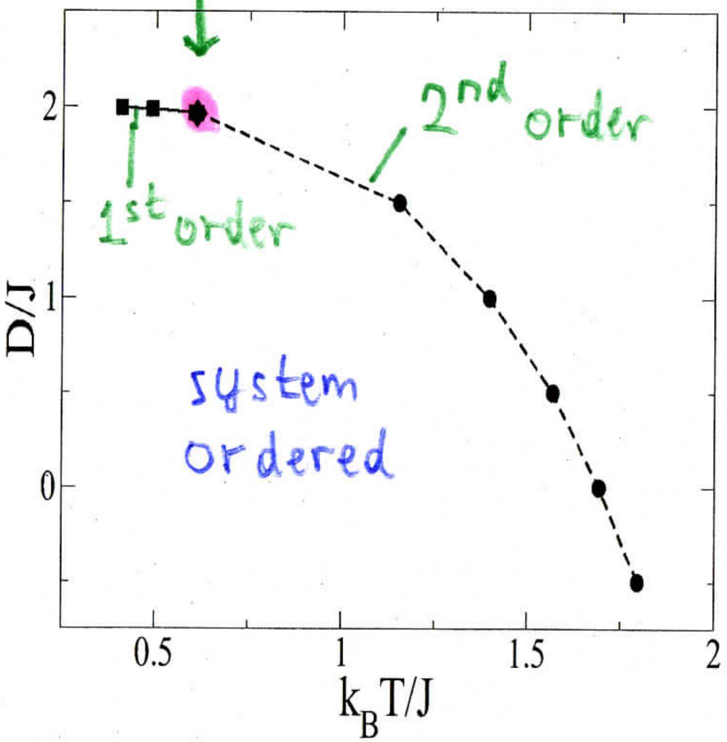
$$\mathcal{H} = -J\sum_{\langle i,j\rangle} S_i S_j + D\sum_i S_i^2 - H\sum_i S_i - H_1 \sum_{i\in \text{row}1} S_i - H_L \sum_{i \in \text{row} L} S_i$$

$S_i = 0, \pm 1$

$D/J \to -\infty$: ISING MODEL

BULK PHASE DIAGRAM

tricritical point



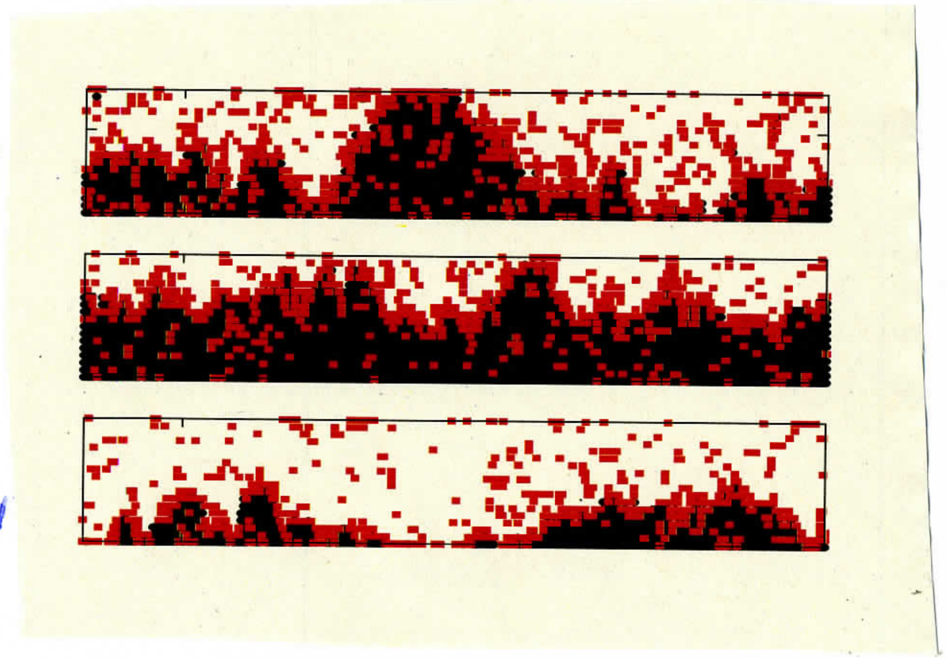
VACANCIES: interfacial wetting

W. SELKE et al. (1983/84)

T>T_W

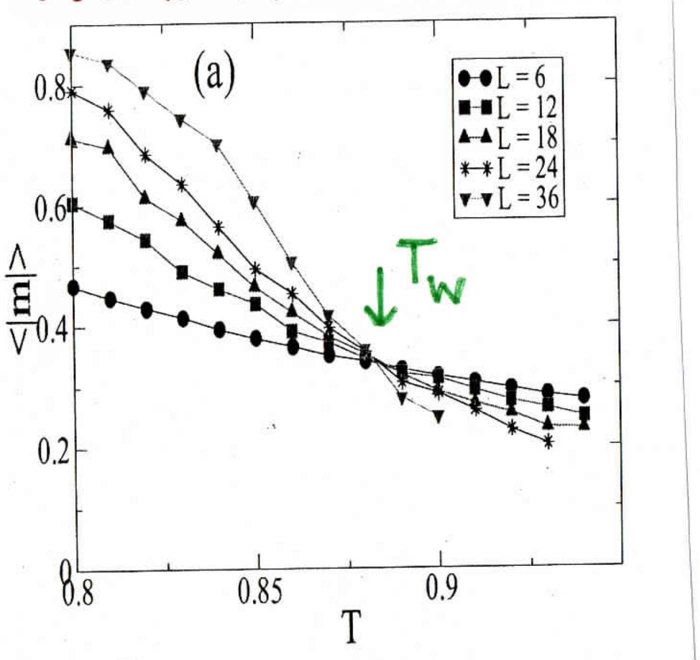
T≈T_W

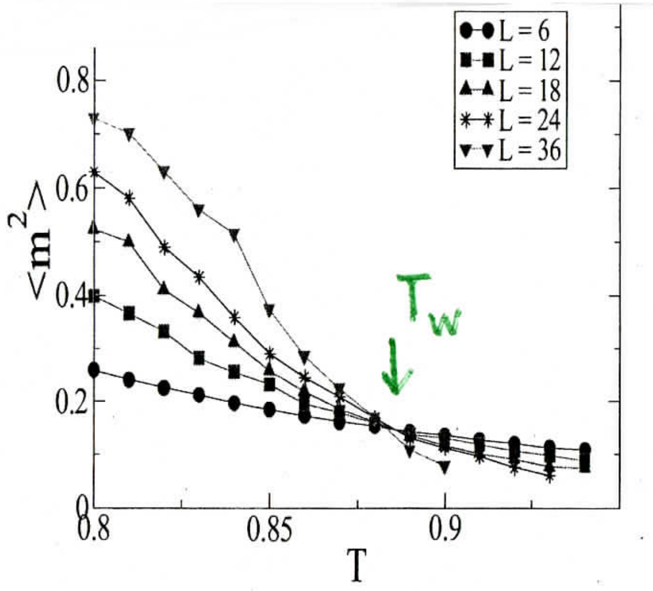
T<T_W



$D/J = 1.5 \quad H_1/J = 0.7 \quad L = 18$

FINITE SIZE SCALING WORKS ALSO FOR WETTING TRANSITIONS IN THE BLUME-CAPEL MODEL





$D/J = 1.75$

$H_1/J = 0.85$

$\Rightarrow$

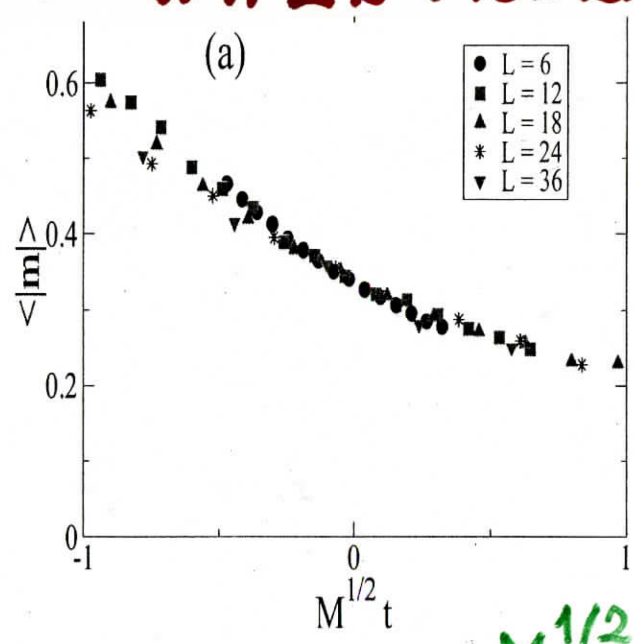
$\frac{k_B T_W}{J} = 0.883 \pm 0.005$

(L, M)

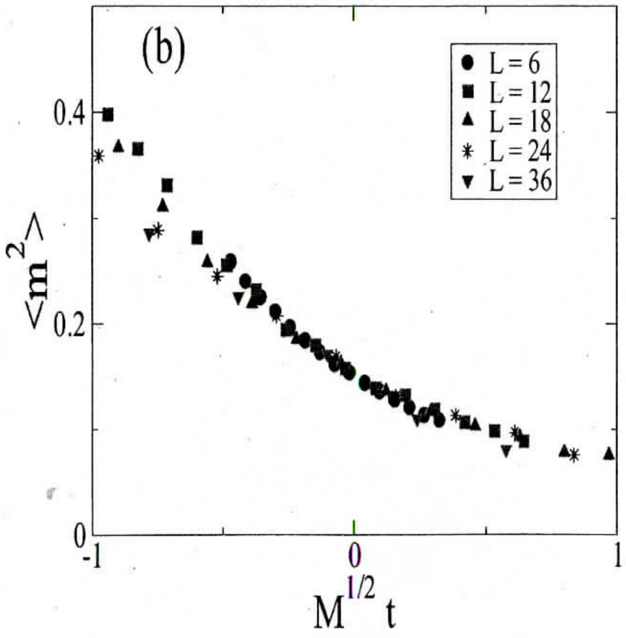
$(6, 32)$

$\dots$

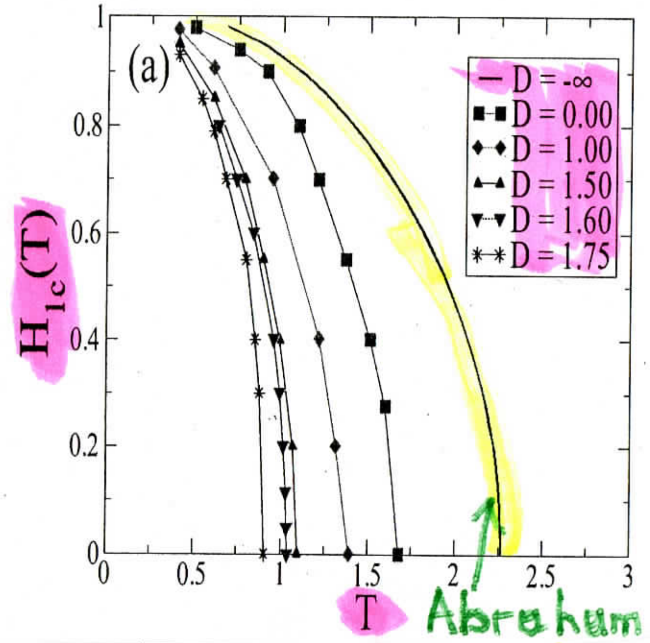
$(36, 1152)$

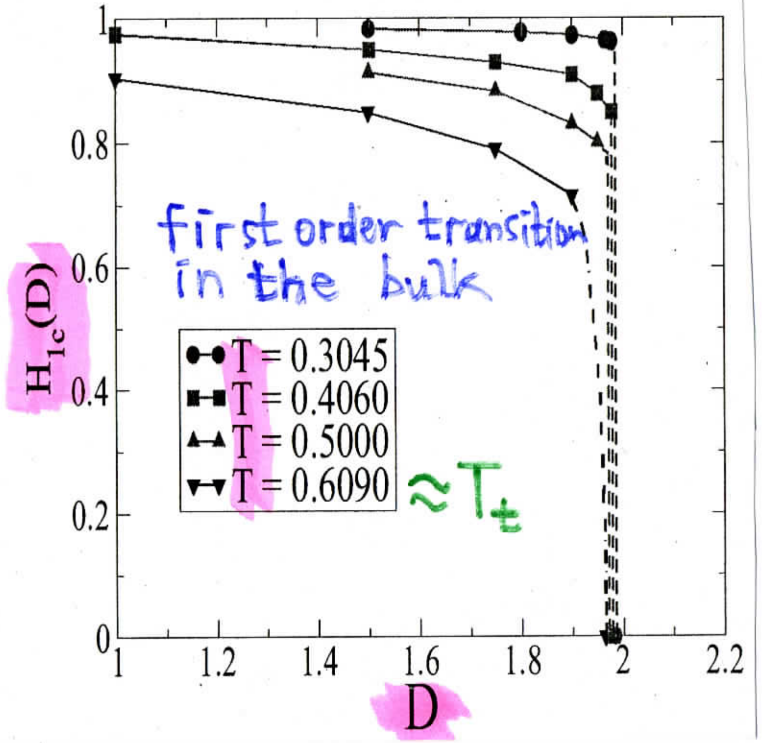


$\rightarrow M^{1/2}(1 - T/T_W)$

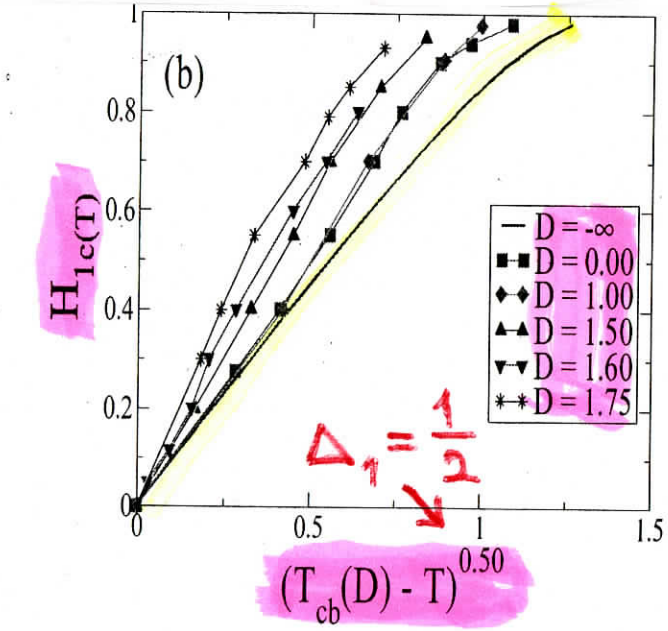


WETTING PHASE DIAGRAMS for the two-dimensional BLUME-CAPEL MODEL





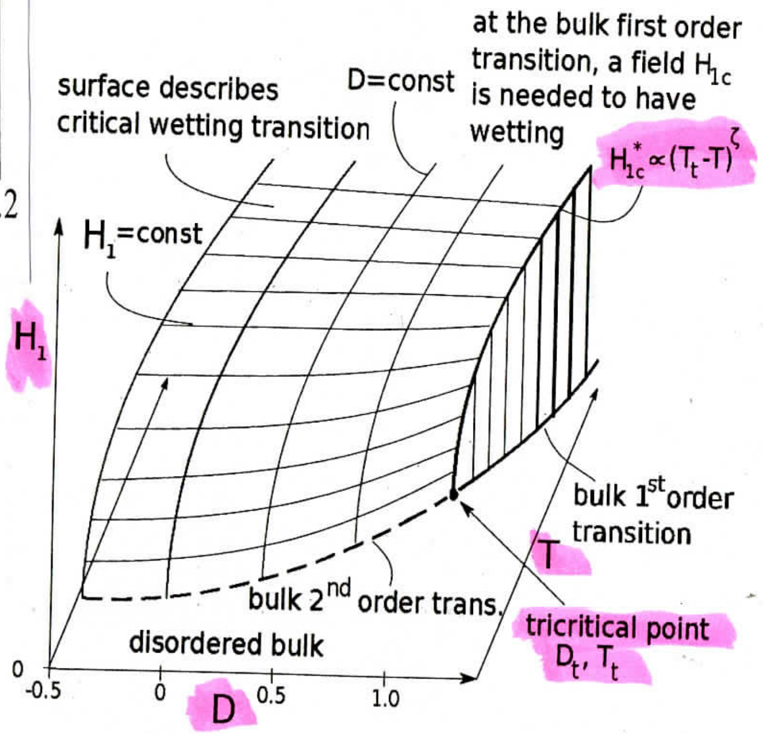
global wetting phase diagram



$H_{1c}(T, D)$ = inverse function of $T_W(H_1, D)$

near bulk critical point

$H_{1c}(T, D) \propto (T_{cb}(D) - T)^{\Delta_1}$



CONCLUSIONS

- Thermodynamic Integration methods for the study of FIRST ORDER WETTING TRANSITIONS have been developed, including OFF-LATTICE SYSTEMS lacking any symmetry between coexisting phases (e.g. AO model)
- FINITE SIZE SCALING methods for the study of CRITICAL WETTING have been developed
  - TEST for $d=2$ ISING MODEL

    open problem: $d=3$ since $\xi_\perp \propto \ln|t|$ rather than $|t|^{-\nu_\perp}$
  - APPLICATION to the $d=2$ BLUME-CAPEL MODEL

    open problem: clarification of critical wetting at the bulk TRICRITICAL POINT

THANK YOU

FOR YOUR ATTENTION