MONTE CARLO METHODS FOR ESTIMATING INTERFACIAL FREE ENERGIES AND LINE TENSIONS

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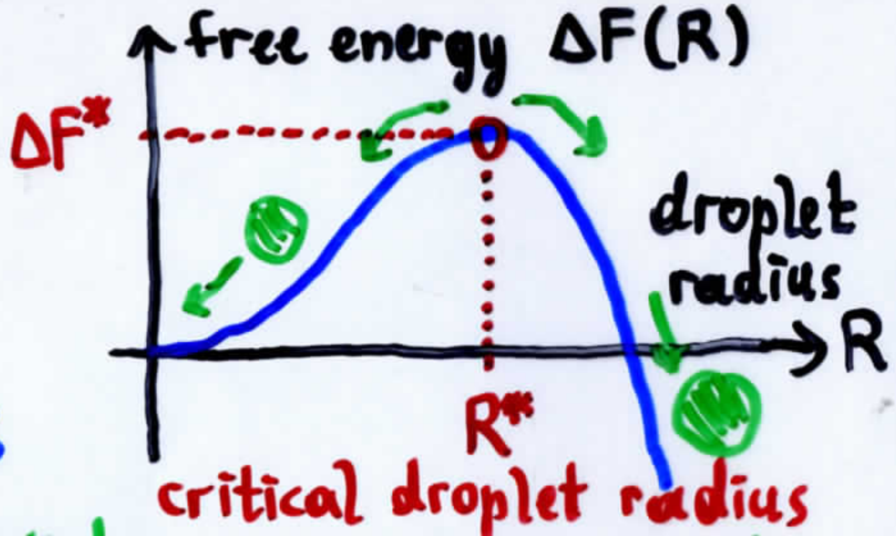
HOMOGENEOUS VERSUS HETEROGENEOUS NUCLEATION

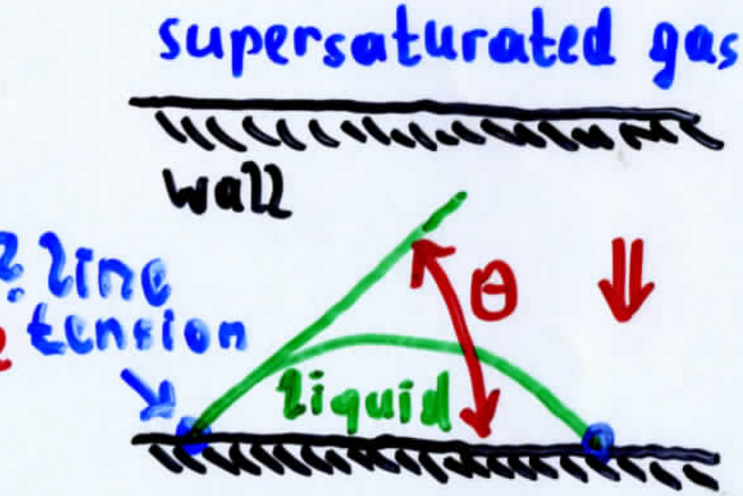


homogeneous nucleation:

a "droplet" of the new (stable) phase forms from the old (metastable) phase by SPONTANEOUS THERMAL FLUCTUATIONS

- high free energy barrier $\Delta F^* \Rightarrow$ rare events
- R^* nanoscopic : direct observation DIFFICULT

heterogeneous nucleation



e.g. condensation of a liquid at a wall under INCOMPLETE WETTING conditions

$$\boxed{\gamma_{wg} - \gamma_{wl} = \gamma_{gl} \cos\Theta}$$

Θ = contact angle
YOUNG (1805)

- 3 interface tensions
- lower free energy barrier

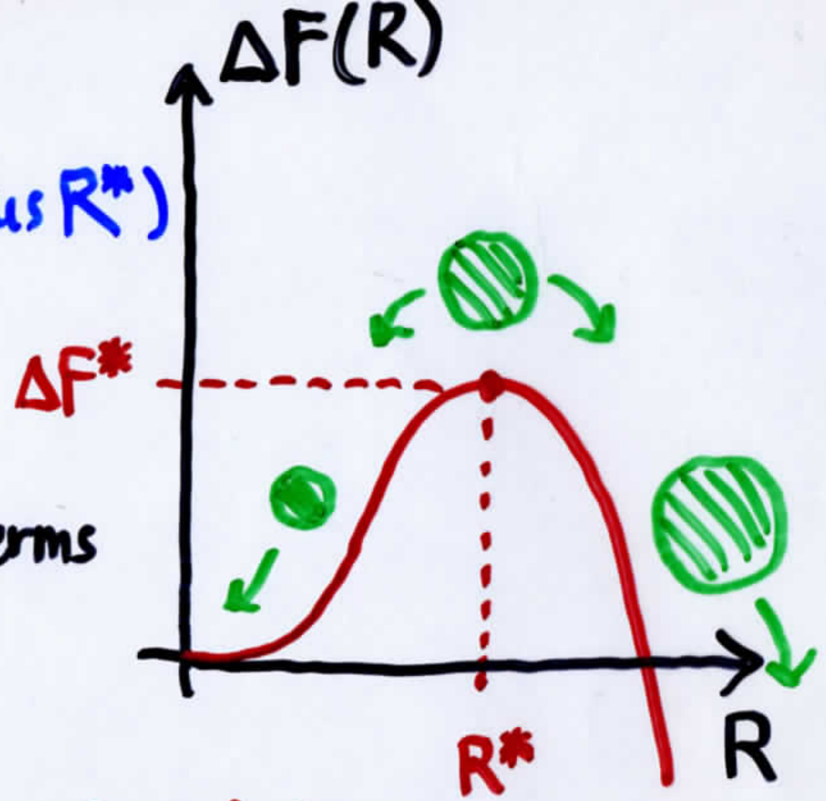
$$\Delta F^*_{het} = \Delta F^*_{hom}\, f(\Theta)$$

$$\boxed{f(\Theta) = (2+\cos\Theta)(1-\cos\Theta)^2/4}$$

TURNBULL (1950)

CLASSICAL NUCLEATION THEORY

- estimate free energy barrier ΔF^* to form CRITICAL DROPLET (radius R^*)
- spherical droplets
- macroscopic description: split $\Delta F(R)$ in BULK and SURFACE terms



$$\Delta F(R) = \Delta g \, 4\pi R^3/3 + \gamma_{vl} \, 4\pi R^2$$

$\Delta g = -(\rho_l - \rho_v)\,\delta\mu$

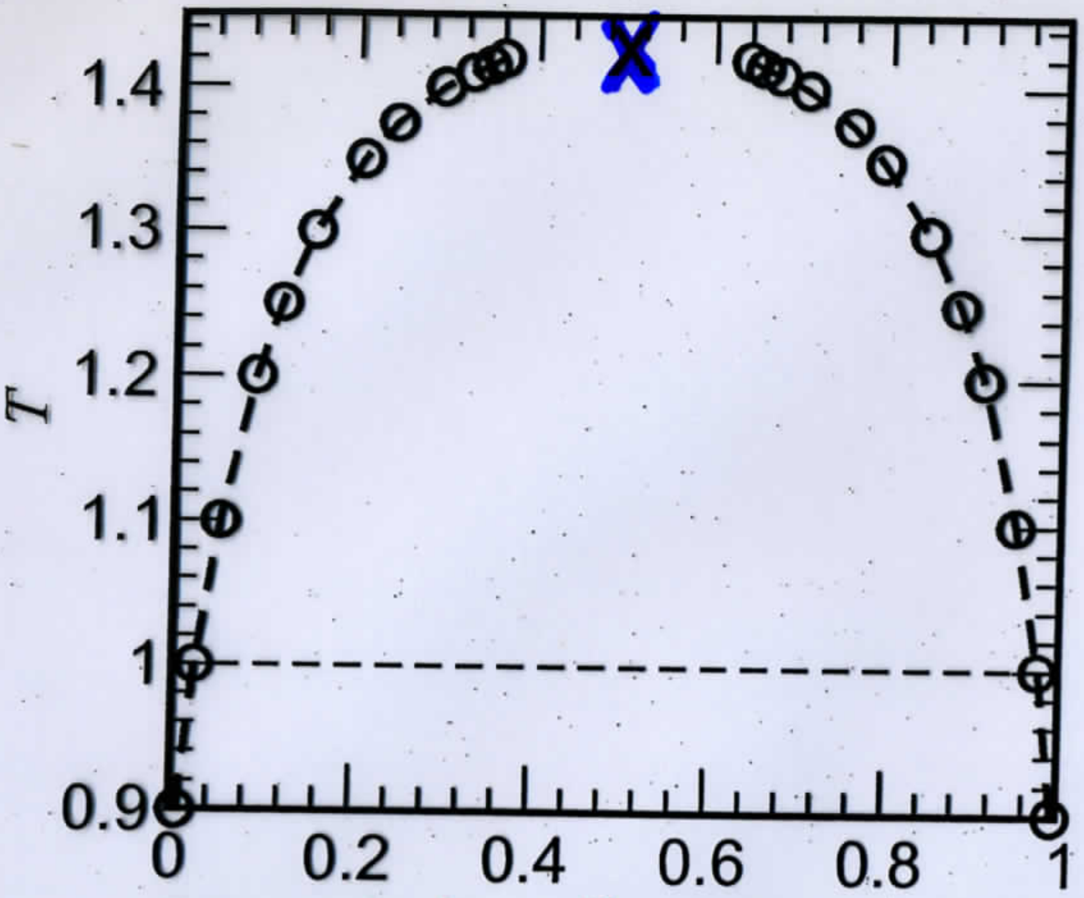
SAME interfacial free energy as for a FLAT PLANAR INTERFACE

(near coexistence curve) $\delta\mu = \mu - \mu_{coex}$ chemical potential difference

? Tolman correction

$$\left.\frac{\partial(\Delta F(R))}{\partial R}\right|_{R^*} = 0 \Rightarrow R^* = \frac{2\gamma_{vl}}{(\rho_l-\rho_v)\delta\mu}, \quad \Delta F^* = \frac{16\pi}{3}\frac{\gamma_{vl}^3}{[(\rho_l-\rho_v)\delta\mu]^2}$$

nucleation rate J^*: # of crit. nuclei/cm^3 & s : $J = \omega^* \exp[-\Delta F^*/k_BT]$



symmetrical binary Lennard-Jones mixture

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

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

LJ diameter

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

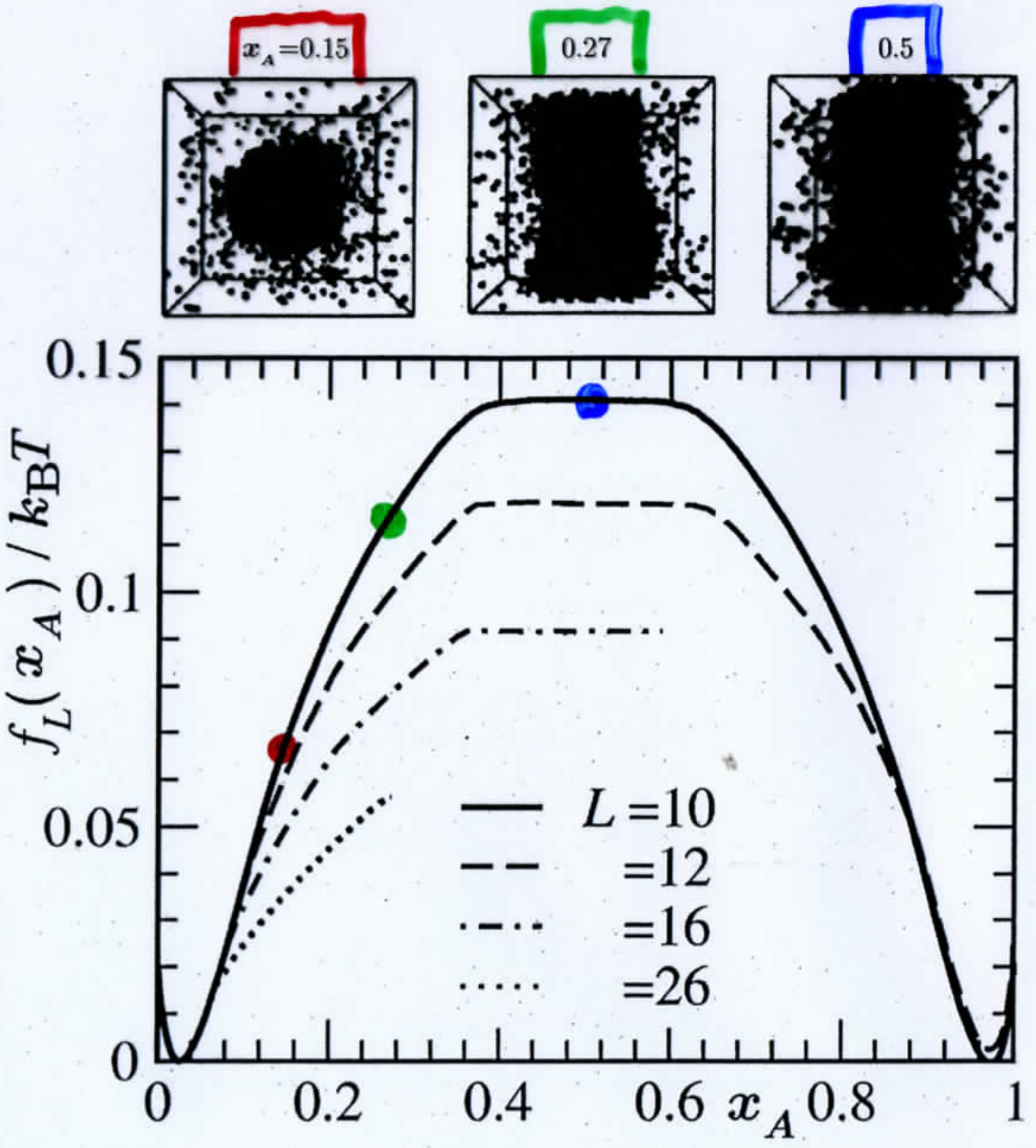
concentration $x_A = N_A/(N_A+N_B)$

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

$T_c = 1.4230 \pm 0.0005$
(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 $r_c = 2.5\sigma$



L×L×L cubic simulation box + periodic boundary conditions

effective free energy

$$f_L(x_A,T) \equiv -\frac{k_BT}{V} \ln \frac{P(x_A)}{P(x_A^{coex})}$$

$V=L^3$

$P(x_A)$ = probability to observe x_A in the semi-grandcanonical $\Delta\mu NVT$-ensemble

successive UMBRELLA SAMPLING

Dealing with all aspects of Monte-Carlo simulation of complex physical systems encountered in condensed-matter physics and statistical mechanics, this book provides an introduction to computer simulations in physics.

This third edition contains extensive new material describing numerous powerful new algorithms that have appeared since the previous edition. It highlights recent technical advances and key applications that these algorithms now make possible. With several new sections and a new chapter on the use of Monte-Carlo simulations of biological molecules, this edition expands the discussion of Monte-Carlo at the periphery of physics and beyond.

Throughout the book there are many applications, examples, recipes, case studies, and exercises to help the reader understand the material. It is ideal for graduate students and researchers, both in academia and industry, who want to learn techniques that have become a third tool of physical science, complementing experiment and analytical theory.

David P. Landau is the Distinguished Research Professor of Physics and founding Director of the Center for Simulational Physics at the University of Georgia.

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Landau & Binder

A Guide to Monte-Carlo Simulations in Statistical Physics

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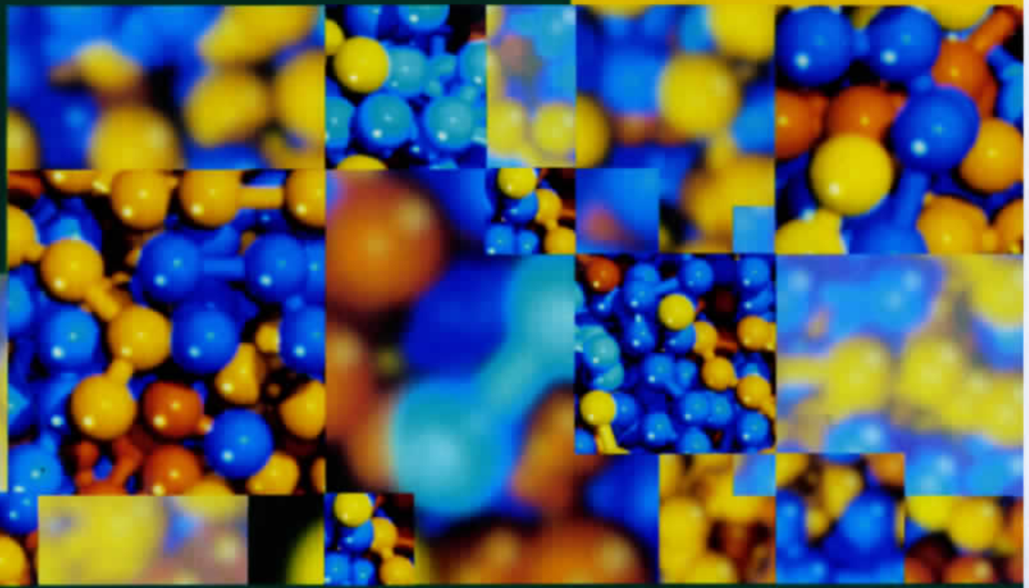


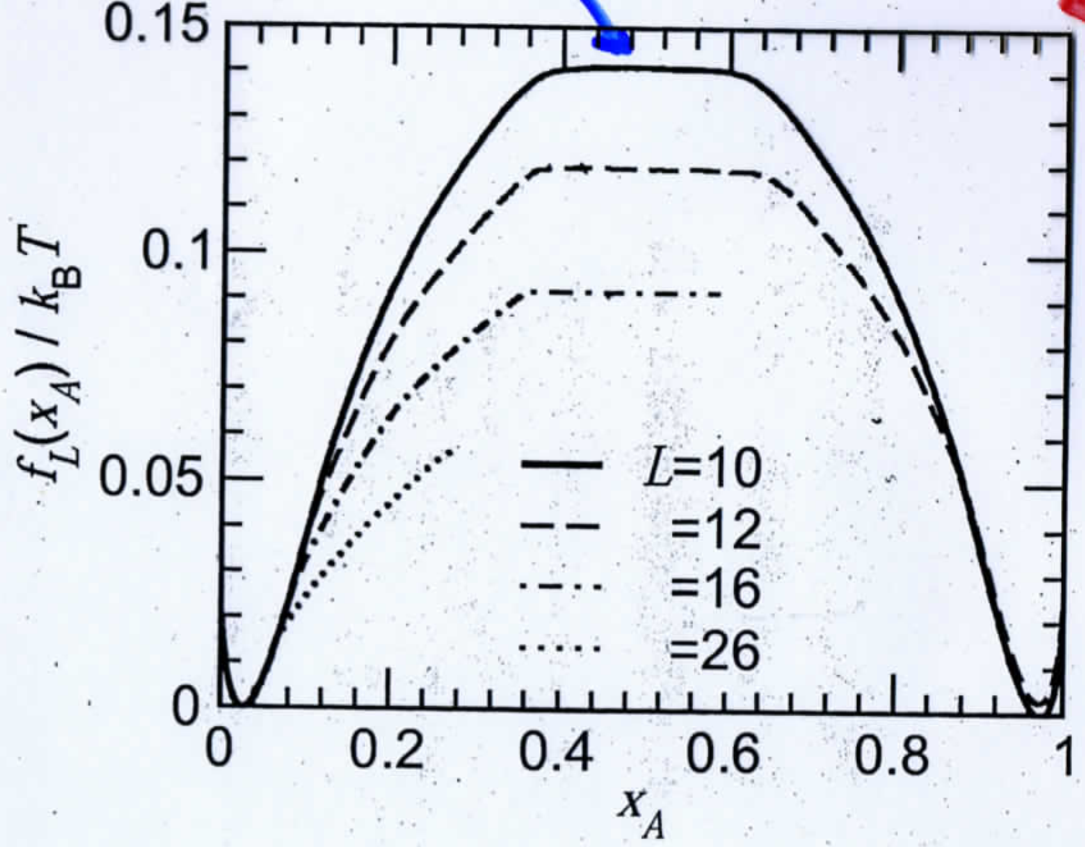
CAMBRIDGE

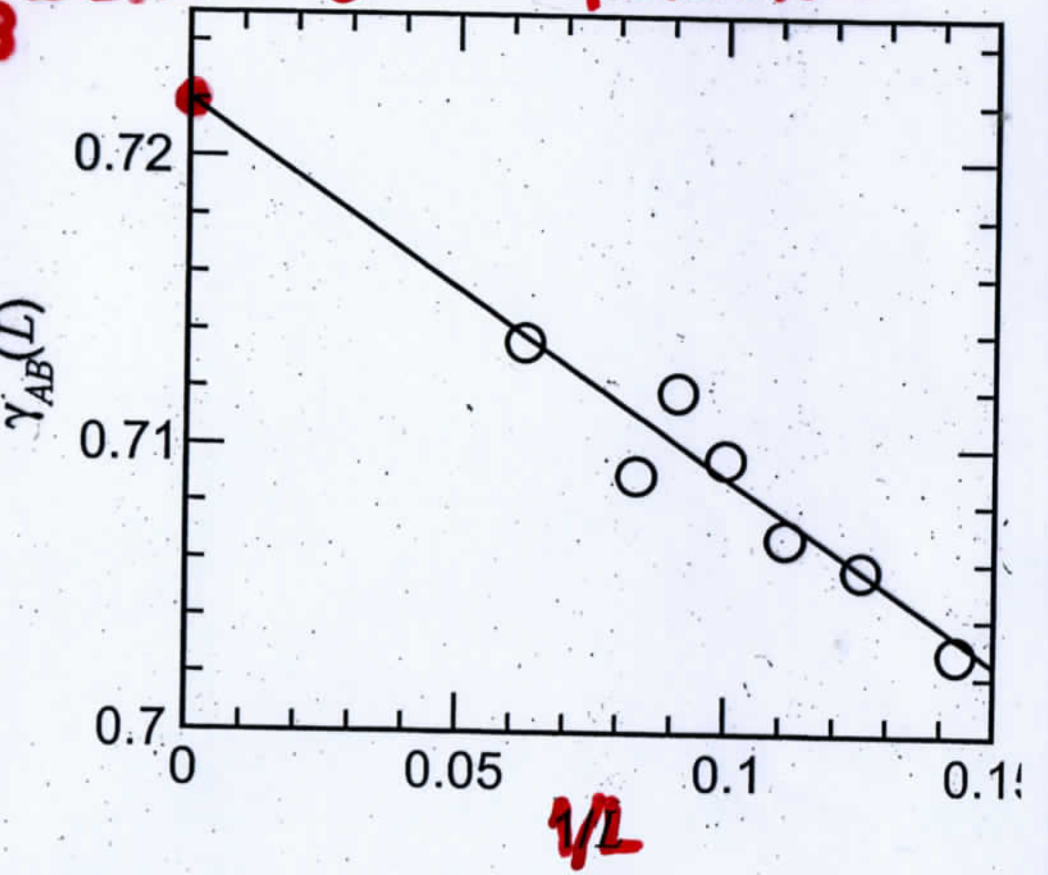
6

Estimation of the interfacial tension of flat INTERFACES (K.B., PR A 25, 1699 (1982))

"hump": SLAB configuration: 2 interfaces of area L^2

$\gamma_{AB} = 0.722$ (extrapolation)



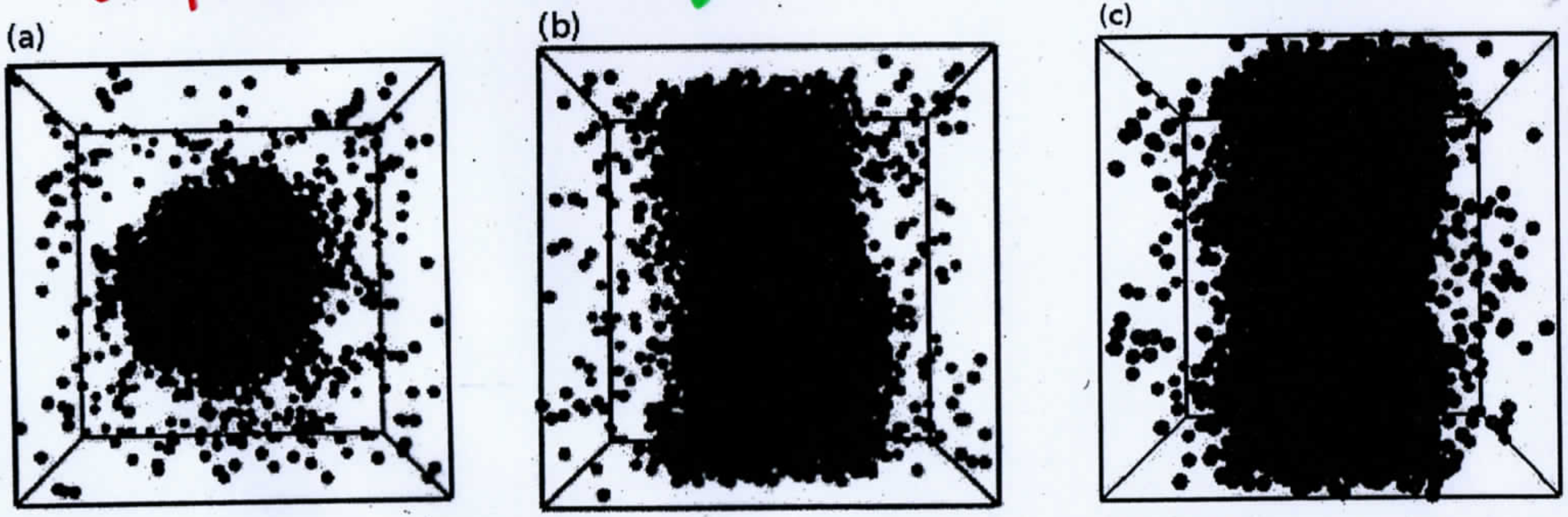


$\Rightarrow$ free energy density $f_L(x_A \approx 0.5) = 2\gamma_{AB}(L)/L$

$\gamma_{AB}(L)$ size-dependent (capillary waves constrained, etc.)

also the ascending/descending parts of the "free energy hump" are useful $\Rightarrow$ information on CURVATURE DEPENDENCE of SURFACE TENSION !

droplet cylinder slab

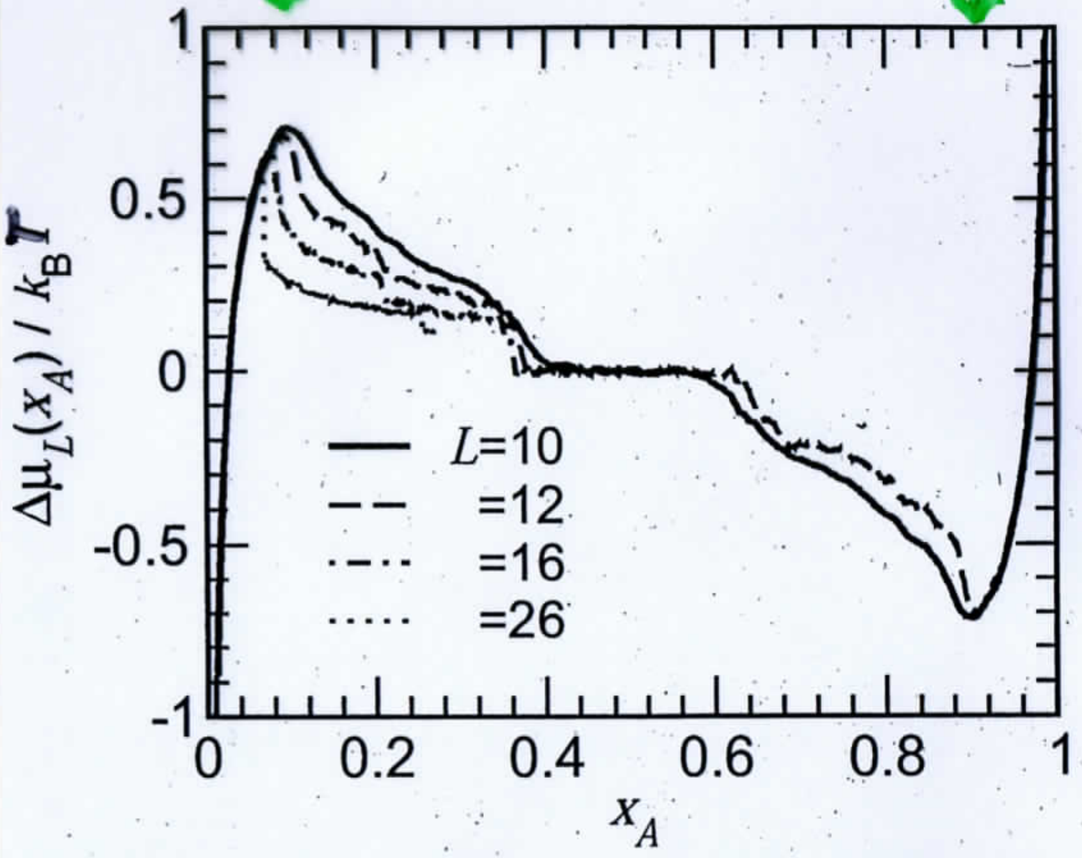


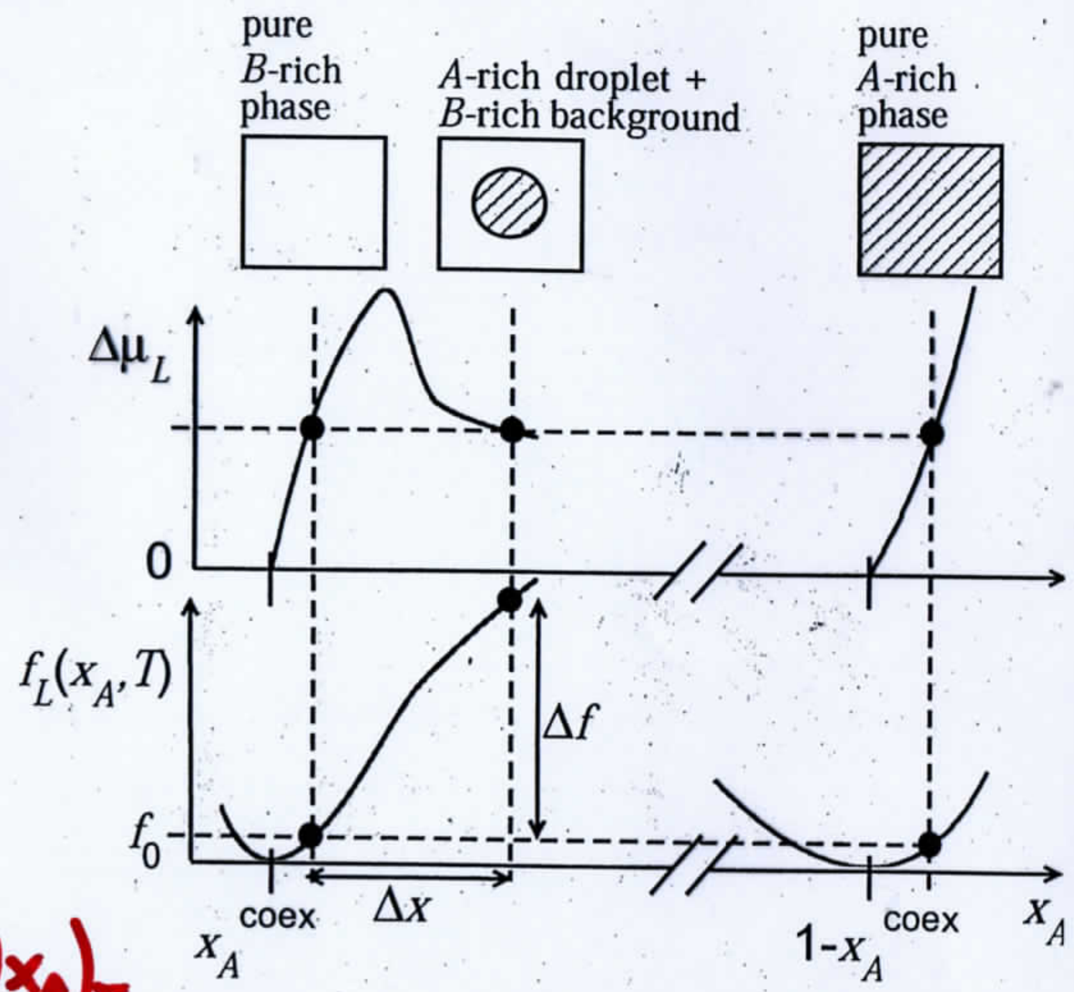
now accurate sampling of $f_L(x_A, T)$ is possible

M.H. Kalos + K.B. (1980) : DROPLET evaporation/condensation transition

H. Furukawa + K.B. (1982)

droplet evaporation/condensation transition





effective chemical potential difference $\Delta\mu_L(x_A) \equiv (\partial f_L(x_A)/\partial x_A)_T$

NO metastable or unstable STATES: FULL EQUILIBRIUM OF A FINITE SYSTEM: states with the same $\Delta\mu_L$ can COEXIST

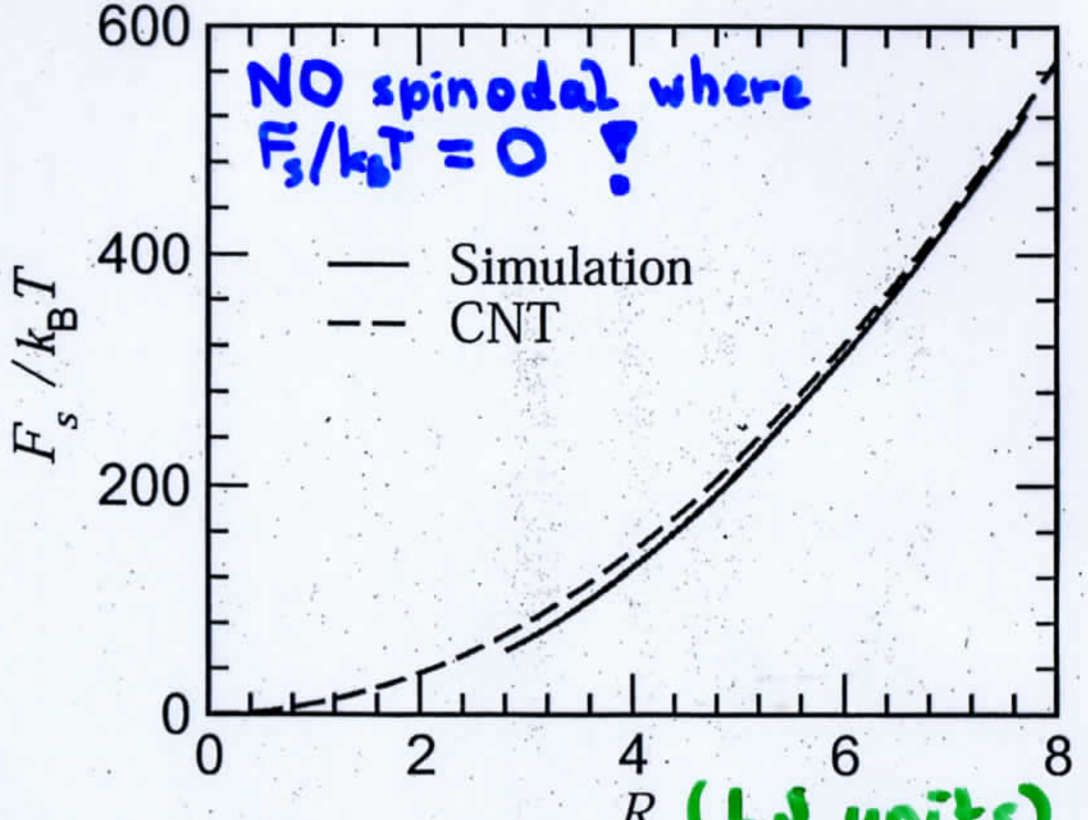
$V\Delta f = 4\pi R^2 \gamma_{AB}(R)$ $\qquad$ $\Delta x = (1-2x_A^{coex})(4\pi R^3/3L^3)$

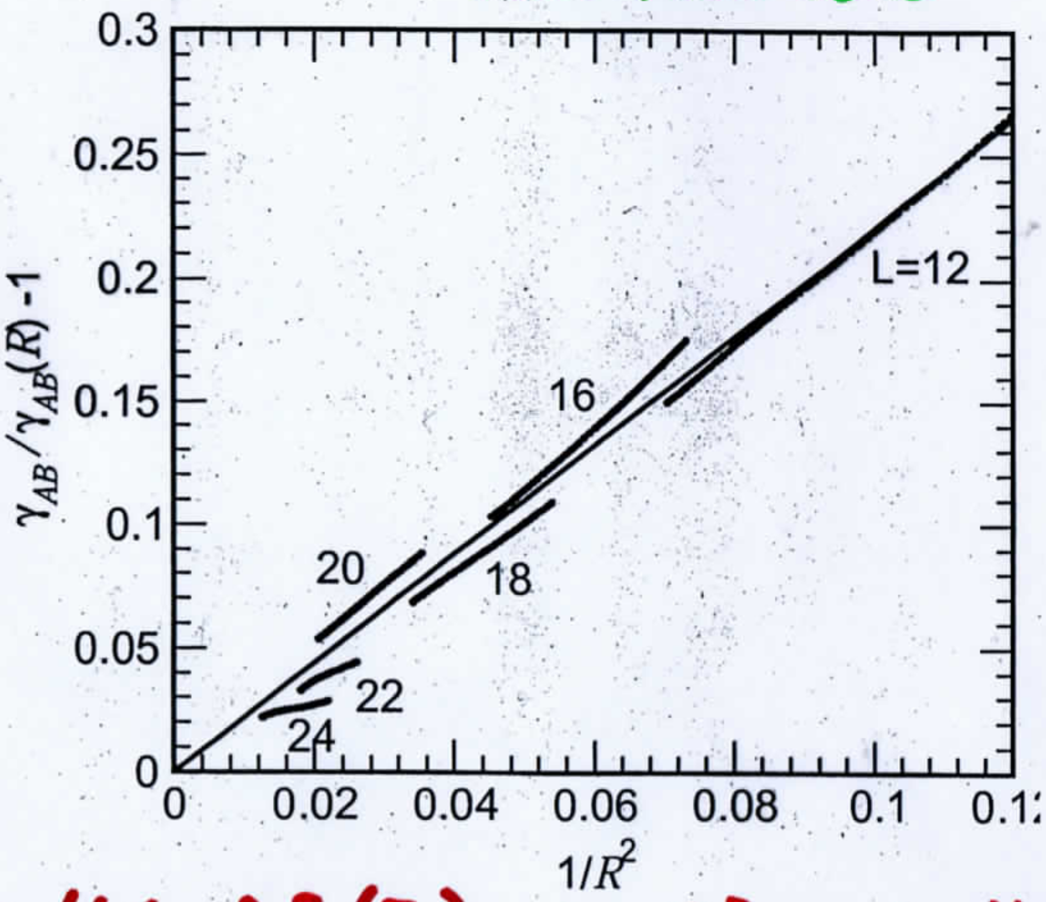
Droplet free energy $F_s(R)/k_BT$ of binary LJ mixture at $T=1$

classical nucleation theory (CNT) : $F_s(R)/k_BT \approx 4\pi R^2 \gamma_{AB}$

flat interface

nucleation barrier $\Delta F^* = F_s(R^*)/3$





TOLMAN (1949) : $\gamma(R) = \gamma(\infty)/(1+2\delta/R)$ δ = Tolman length

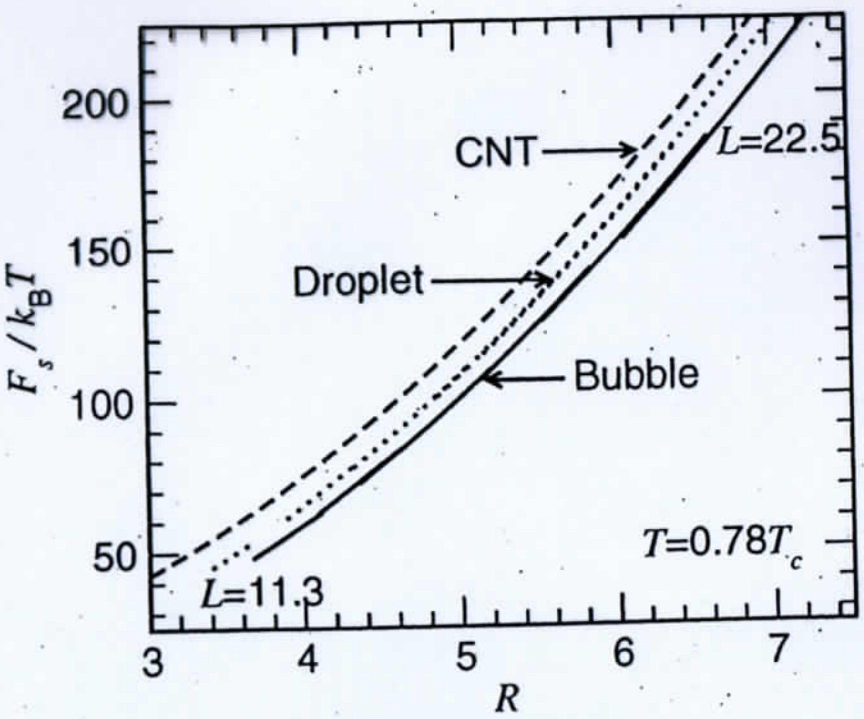
(Tolman assumed δ is positive, constant, and of order σ)

M.P.A. Fisher + Wortis (1984) : $\delta \equiv 0$ in symmetric systems (droplet $\leftrightarrow$ bubble)

10 $\gamma_{AB}(R) = \gamma_{AB}(\infty)/[1+2(\ell_s/R)^2]$ $\ell_s \approx 1.05$

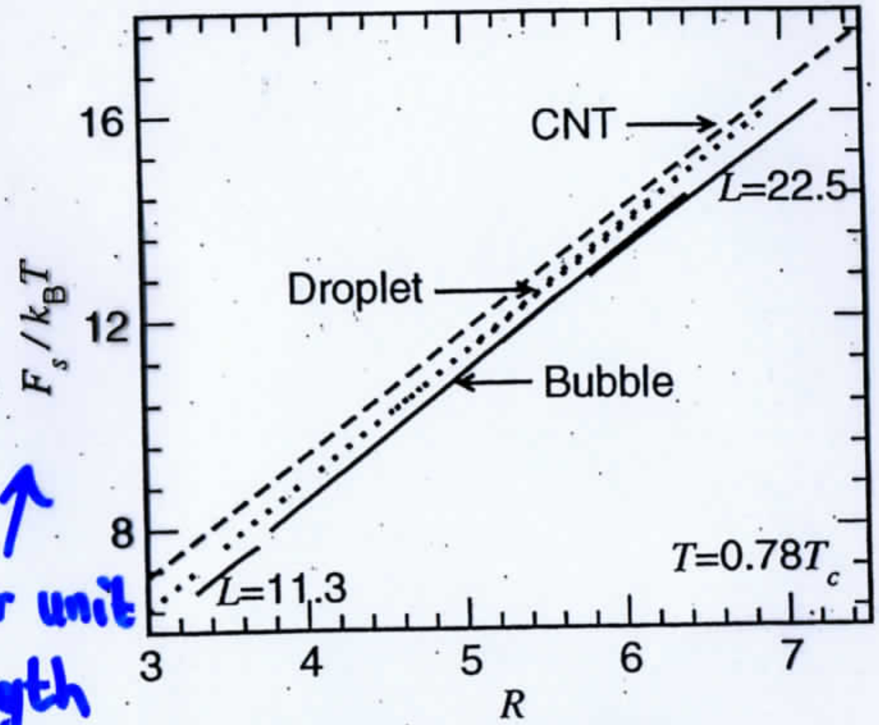
VAPOR-LIQUID TRANSITION of SIMPLE LENNARD-JONES FLUID

NO SYMMETRY BETWEEN DROPLETS and BUBBLES !



SPHERES

per unit length of the cylinder



CYLINDERS

<u>hypothesis</u>:

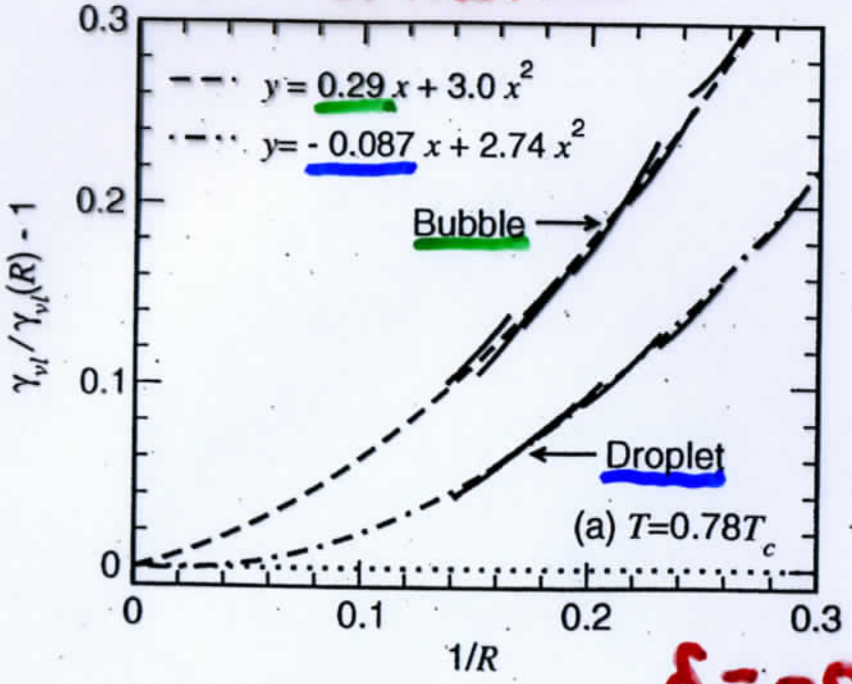
$\gamma_{vl}(\infty)/\gamma_{vl}(R) = 1 + 2\delta/R + 2(\ell_s/R)^2$ spherical droplet

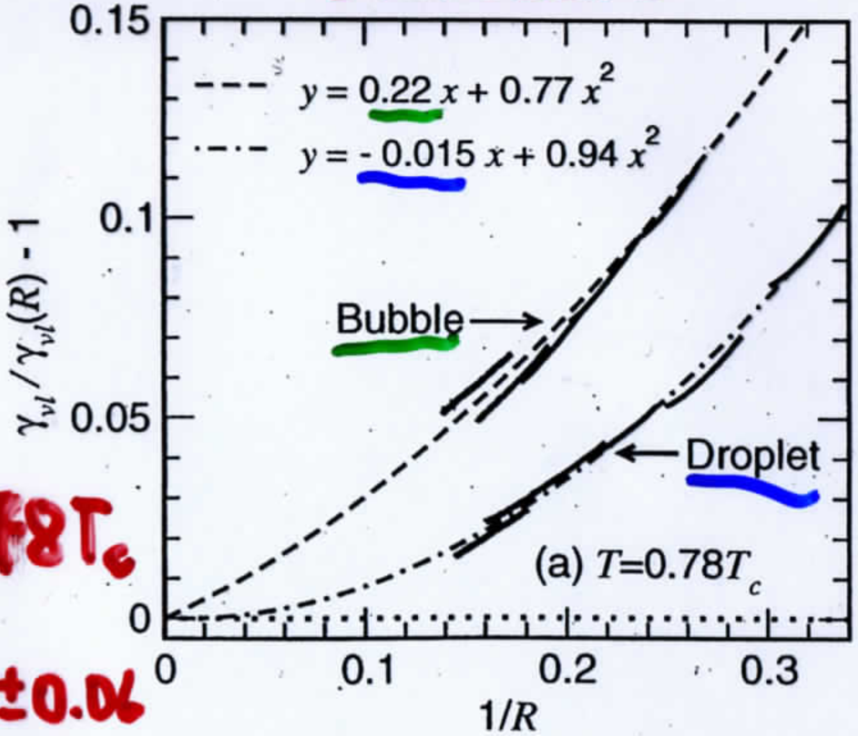
$\gamma_{vl}(\infty)/\gamma_{vl}(R) = 1 - 2\delta/R + 2(\ell_s/R)^2$ spherical bubble

$\gamma_{vl}(\infty)/\gamma_{vl}(R) = 1 + \delta/R + 2(\ell_s/R)^2$ cylindrical drop

$\gamma_{vl}(\infty)/\gamma_{vl}(R) = 1 - \delta/R + 2(\ell_s/R)^2$ cylindrical bubble

SPHERES | **CYLINDERS**





$T = .78\,T_c$

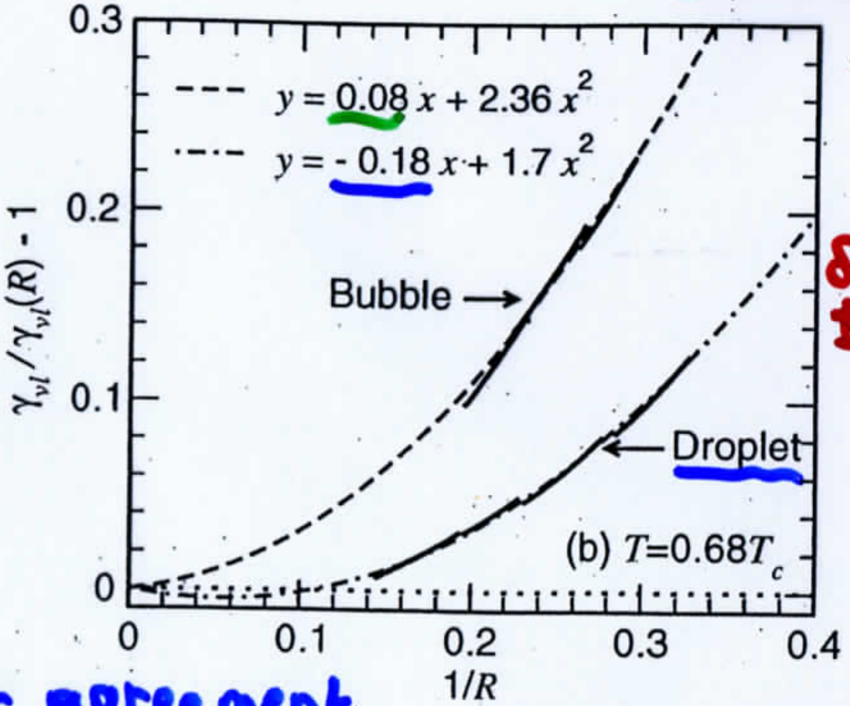
↓

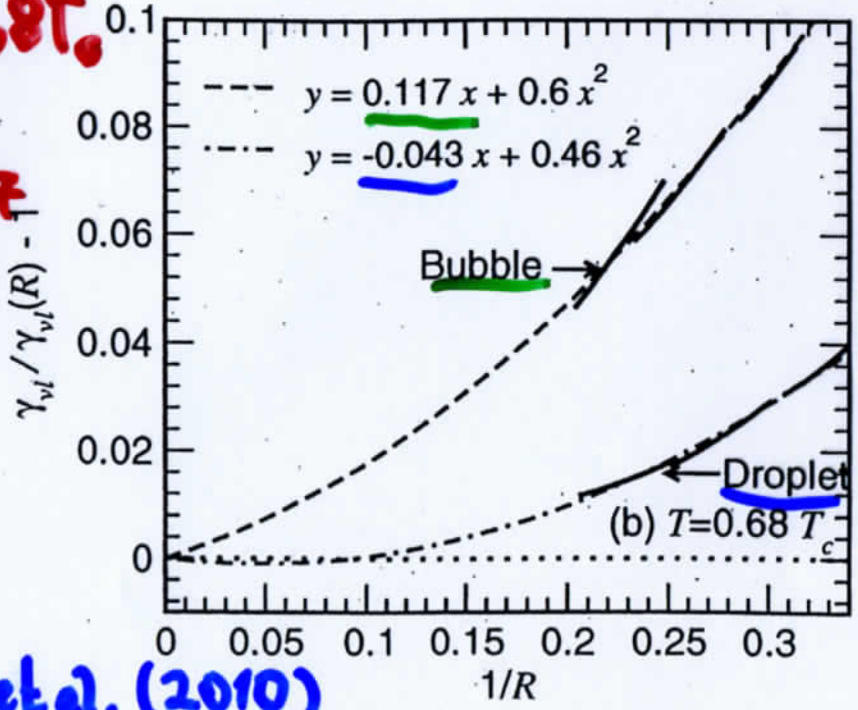
$\delta = -0.11 \pm 0.06$

$T = .68\,T_c$

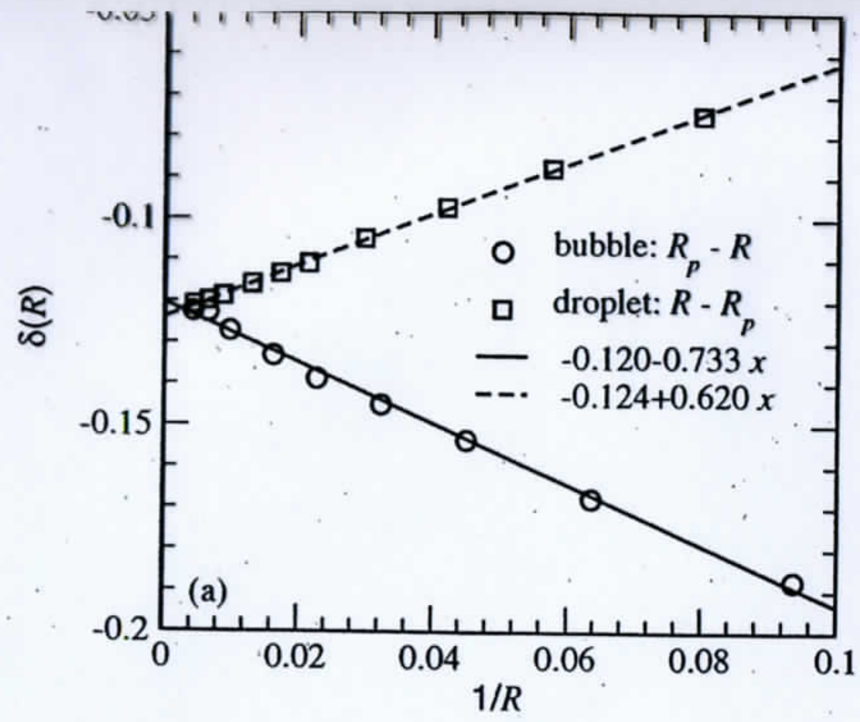
↓

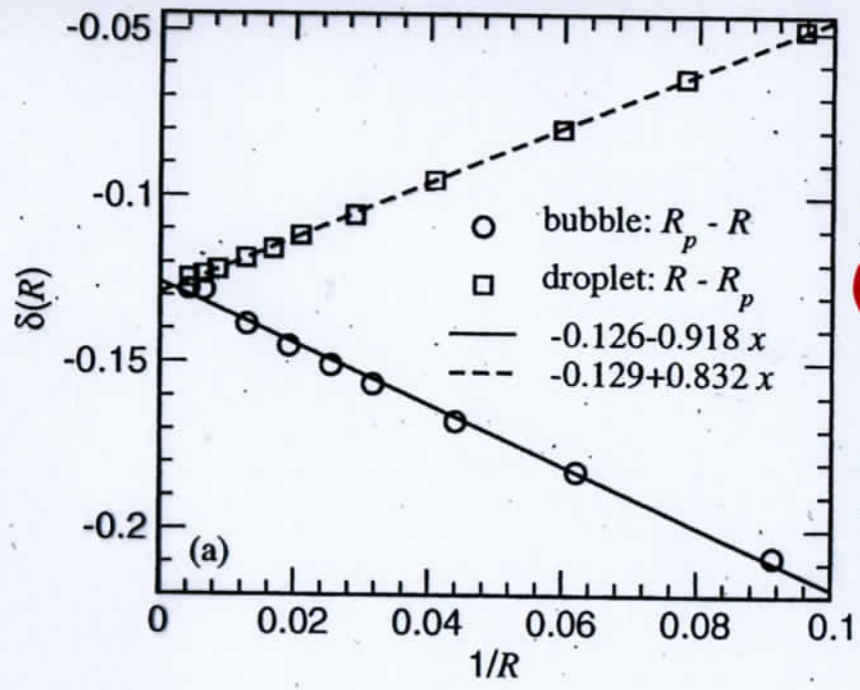
$\delta = -0.07$
± 0.04





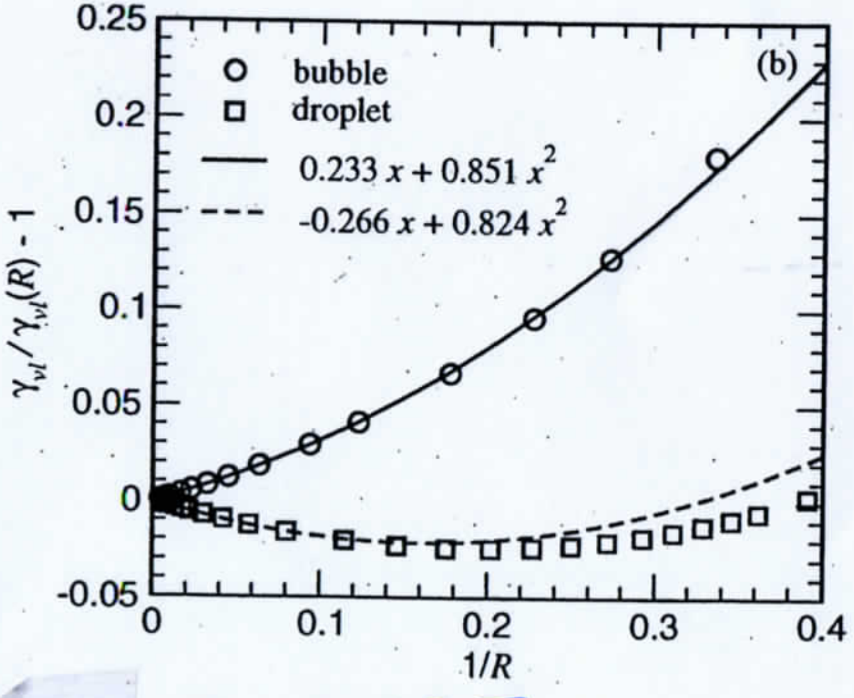
fair agreement
with BLOKHUIS et al. (2009) + JACKSON et al. (2010)

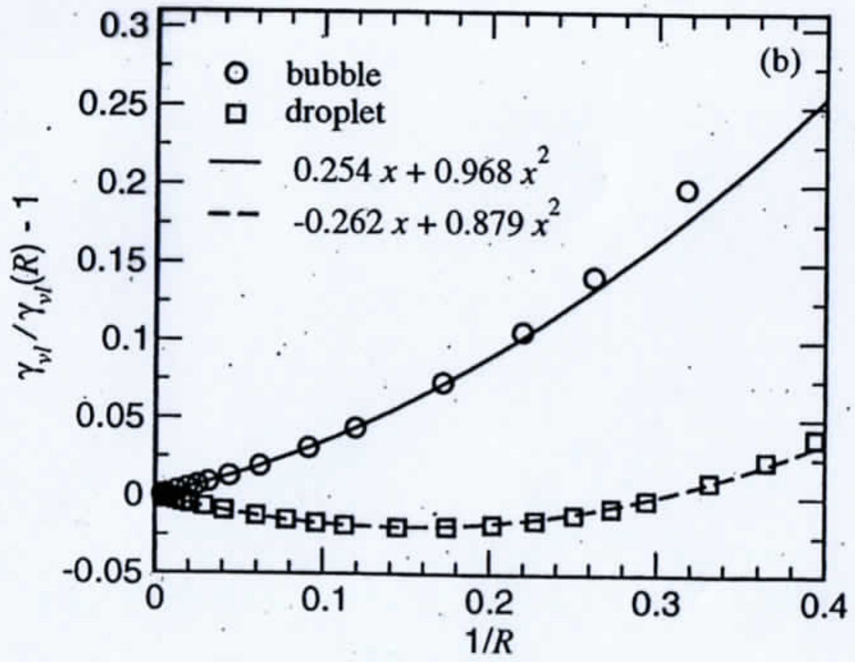




density functional theory (M.Oettel 2010)

R-dependent Tolman length





$$\frac{\gamma_{vl}}{\gamma_{vl}(R)} - 1$$

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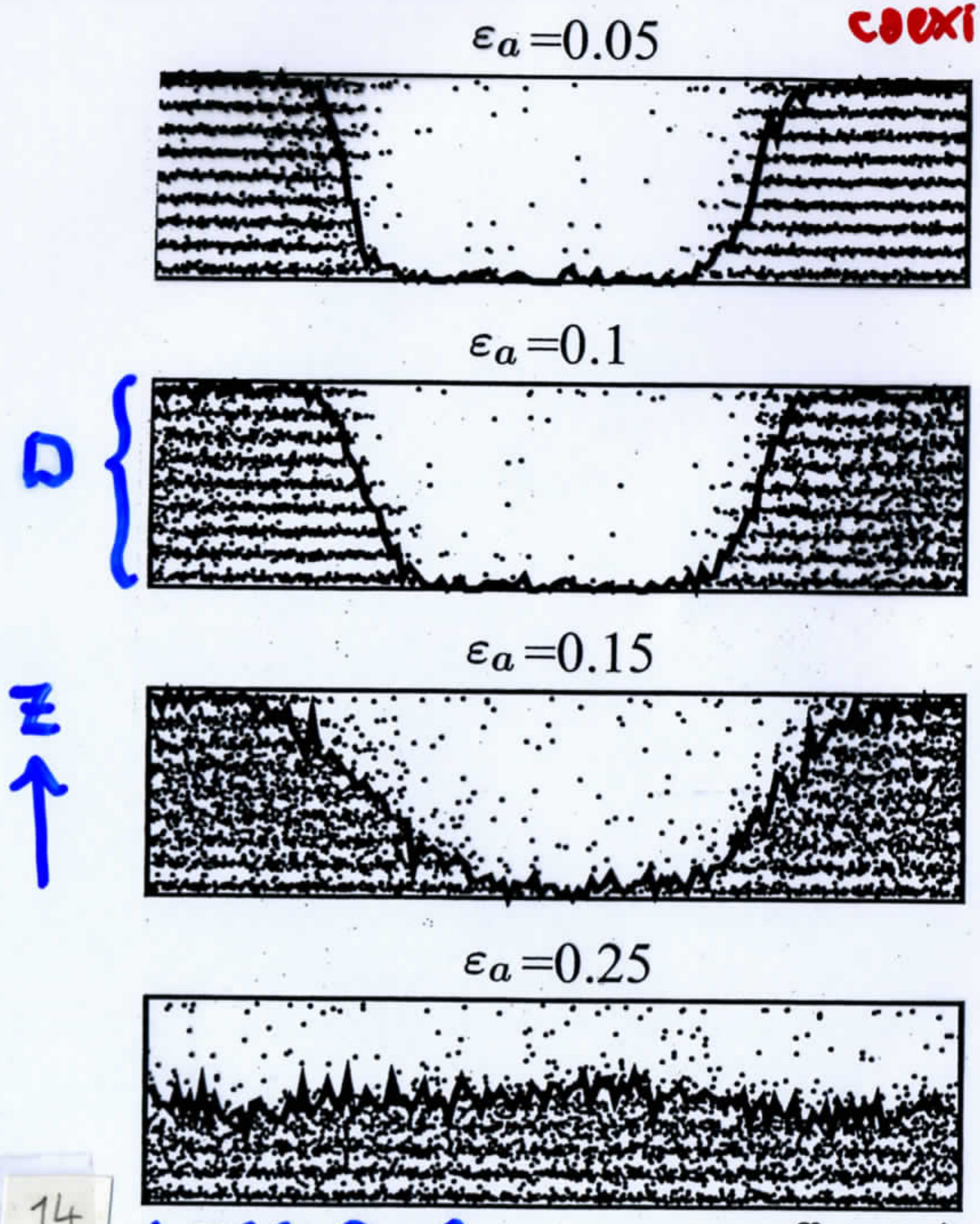
$T \approx 0.68\, T_c$

$T = 0.78\, T_c$

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

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



$L = 32$, $D = 8$

wall potentials:

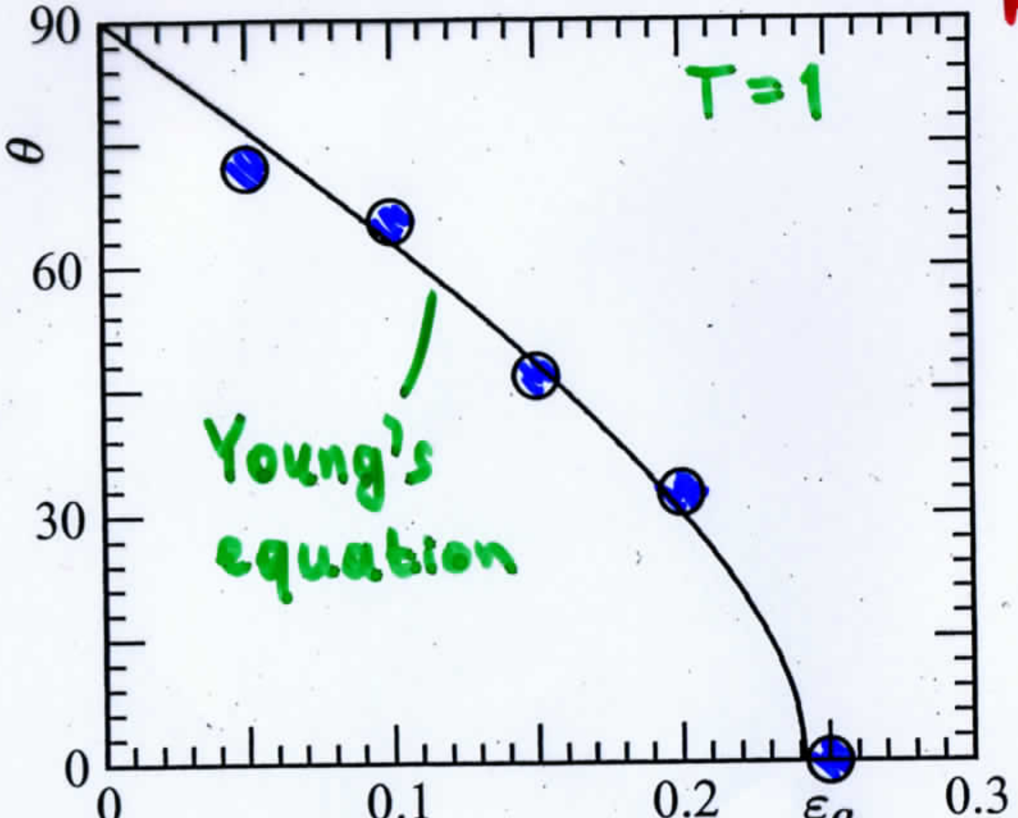
$$U_A(z) = \frac{2\pi\rho}{3}\left\{\varepsilon_r\left[\left(\frac{\sigma}{z+\sigma/2}\right)^9 + \left(\frac{\sigma}{D+\frac{\sigma}{2}-z}\right)^9\right] - \varepsilon_a\left(\frac{\sigma}{z+\sigma/2}\right)^3\right\}$$

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

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



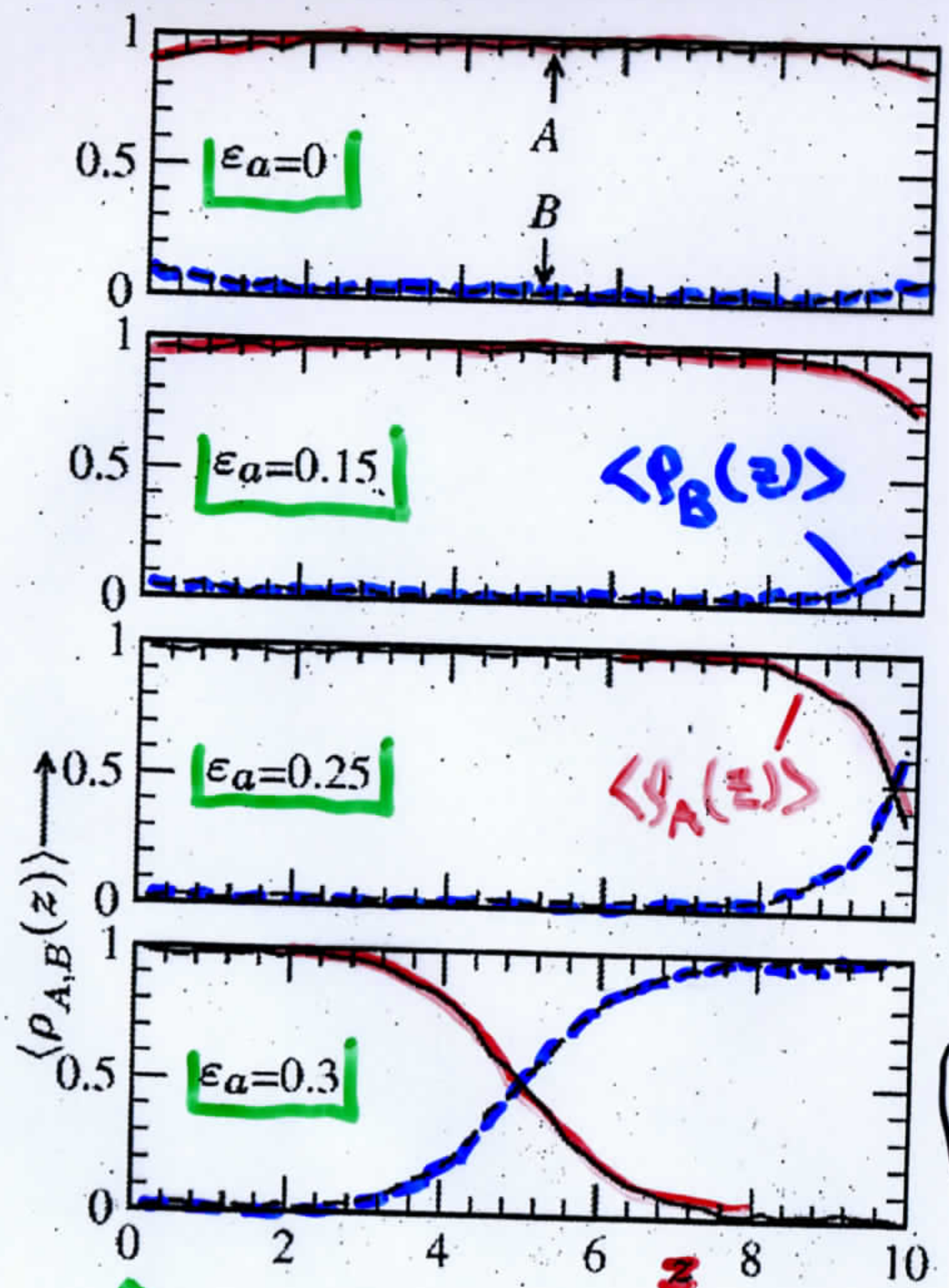
- observations from flat but inclined interfaces in nano-films

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

obtained from thermodynamic integration of systems with walls (NO PHASE COEXISTENCE) in the semi-grandcanonical ensemble (incomplete wetting conditions)

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

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



wall attracts A

wall attracts B

Density profiles across the film (D = 10)

(semi-grandcanonical ensemble)

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

$\Rightarrow$

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

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

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

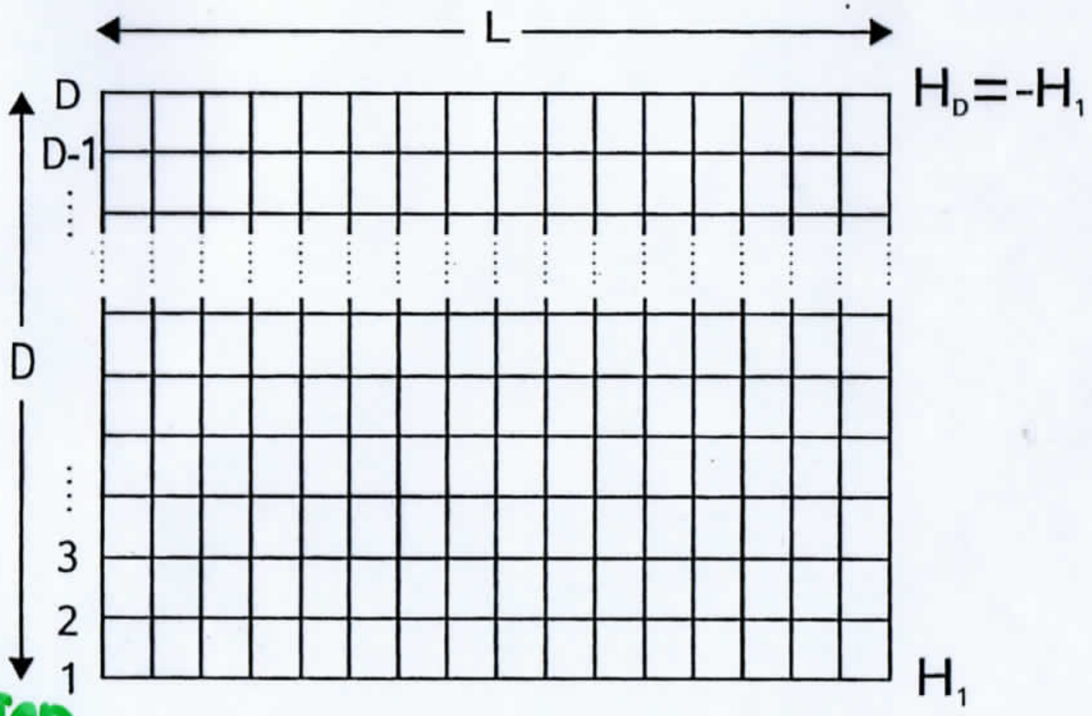
$2H = \mu - \mu_{coex}$

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

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

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

m_{coex} = spontaneous magnetization



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

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

ESTIMATION OF THE CONTACT ANGLE: ISING MODEL

use YOUNG's equation!

Hasenbusch + Pinn (1993)

$L \to \infty$, large D:

$$f(T,H,H_1,H_D,D) = f_b(T,H) + \frac{1}{D} f_s(T,H,H_1) + \frac{1}{D} f_s(T,H,H_D)$$

Young (1805):

$$\gamma_{v\ell} \cos\theta = f_s^{(+)}(T,0,H_1) - f_s^{(-)}(\ldots)$$

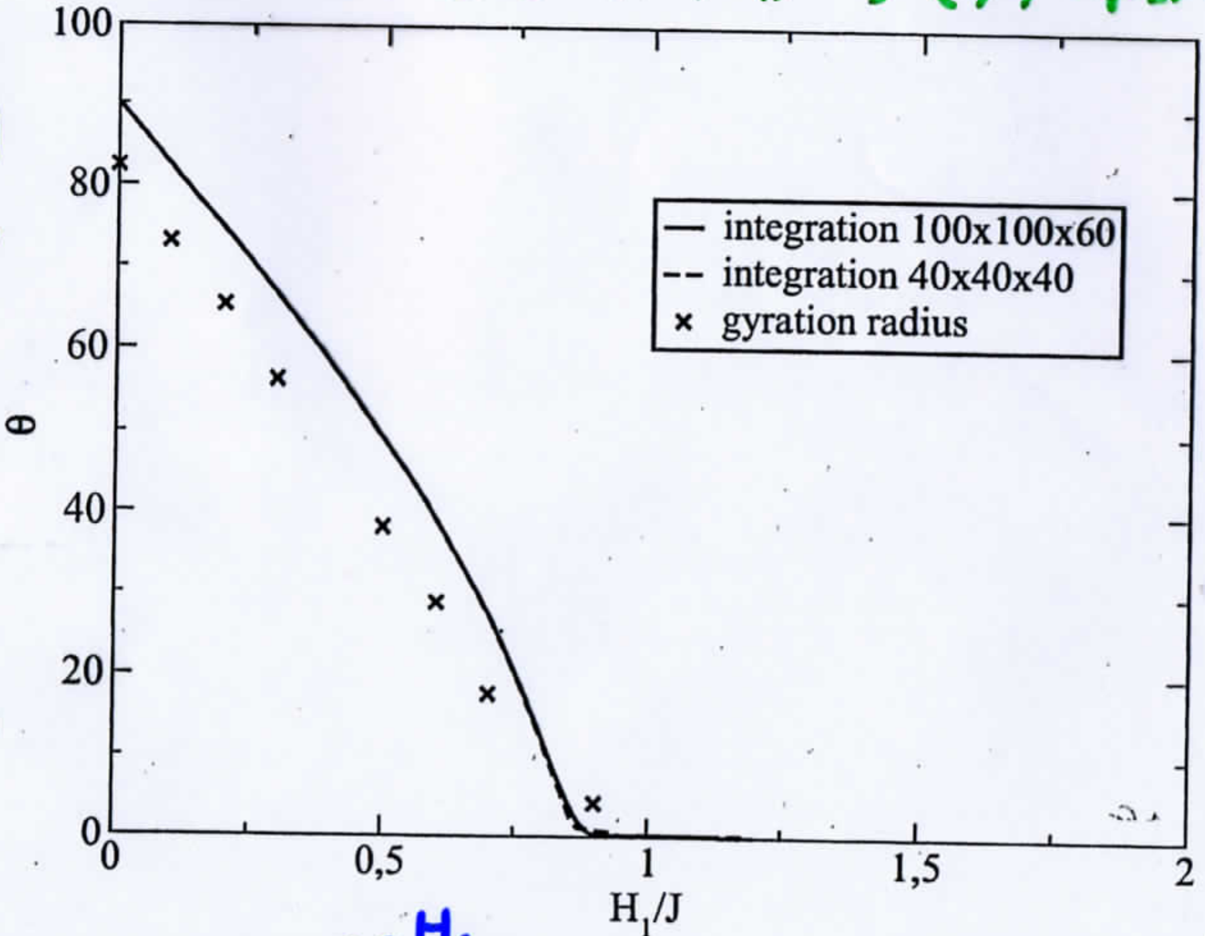
$(+)$, $(-)$: sign of spont. magn.

Ising symmetry:

$$f_s^{(-)}(T,0,H_1) = f_s^{(+)}(T,0,-H_1)$$

$$\{S_i\}, H, H_1 \leftrightarrow \{-S_i\}, -H, -H_1$$

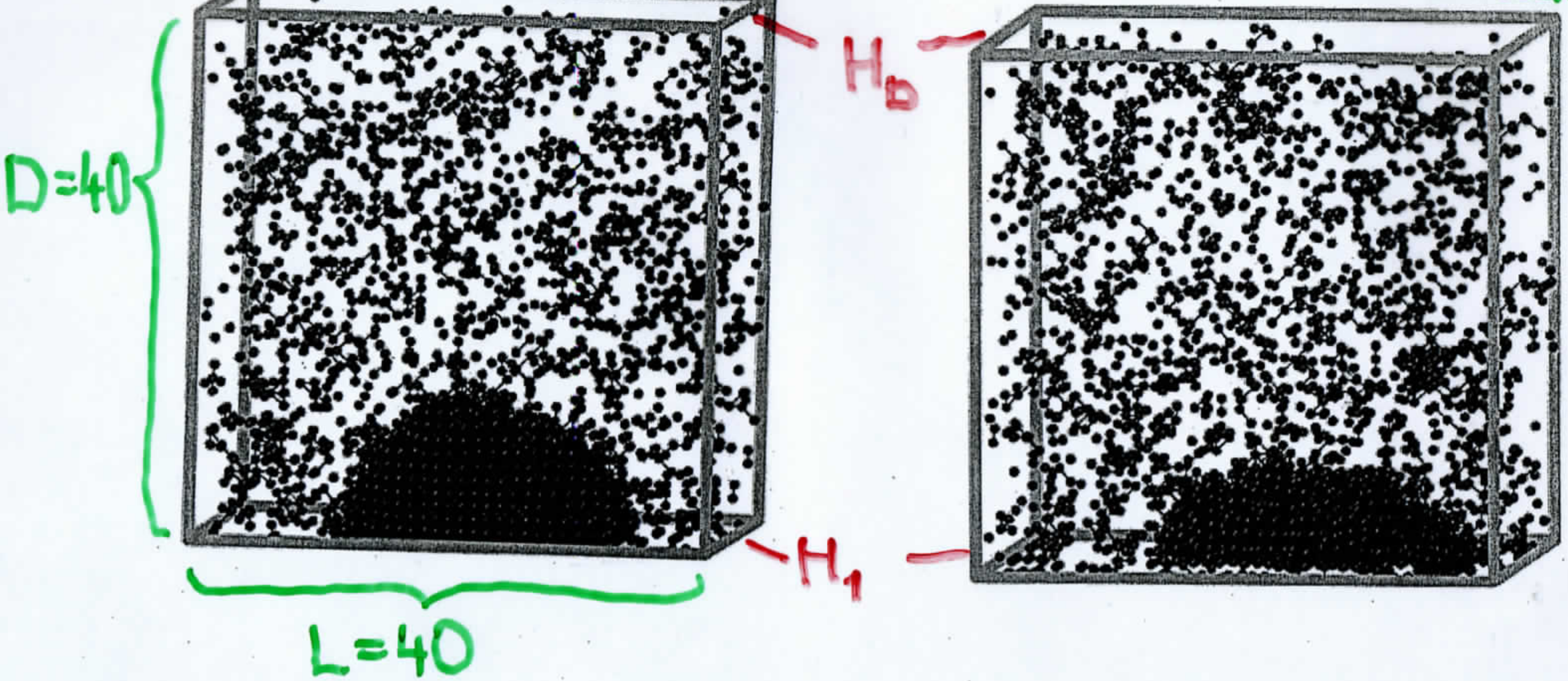
$$\cos\theta = [f_s^{(+)}(T,0,H_1) - f_s^{(+)}(T,0,-H_1)]/\gamma_{v\ell}(T)$$



$$m_1 = -(\partial f_s(T,H,H_1)/\partial H_1)_T \Rightarrow \cos\theta = \{\int_0^{H_1} [m_D(H_1') - m_1(H_1')]\, dH_1'\}/\gamma_{v\ell}$$

Lattice gas model $k_B T/J = 3.0$ $(k_B T_c/J \approx 4.51)$

$L \times L \times D$ geometry, two free $L \times L$ surfaces; pbc in x,y directions



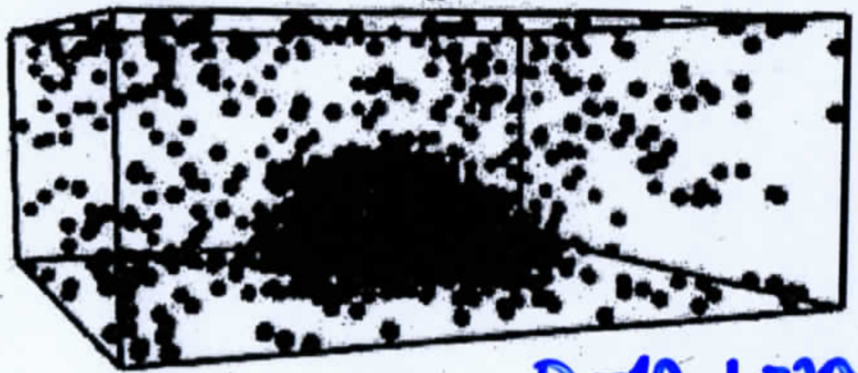
surface fields: $H_D = -H_1$ $H_1 = 0.4\,J$

$H_1 = 0$: contact angle $\Theta = 90°$ $\Rightarrow \Theta \approx 56°$

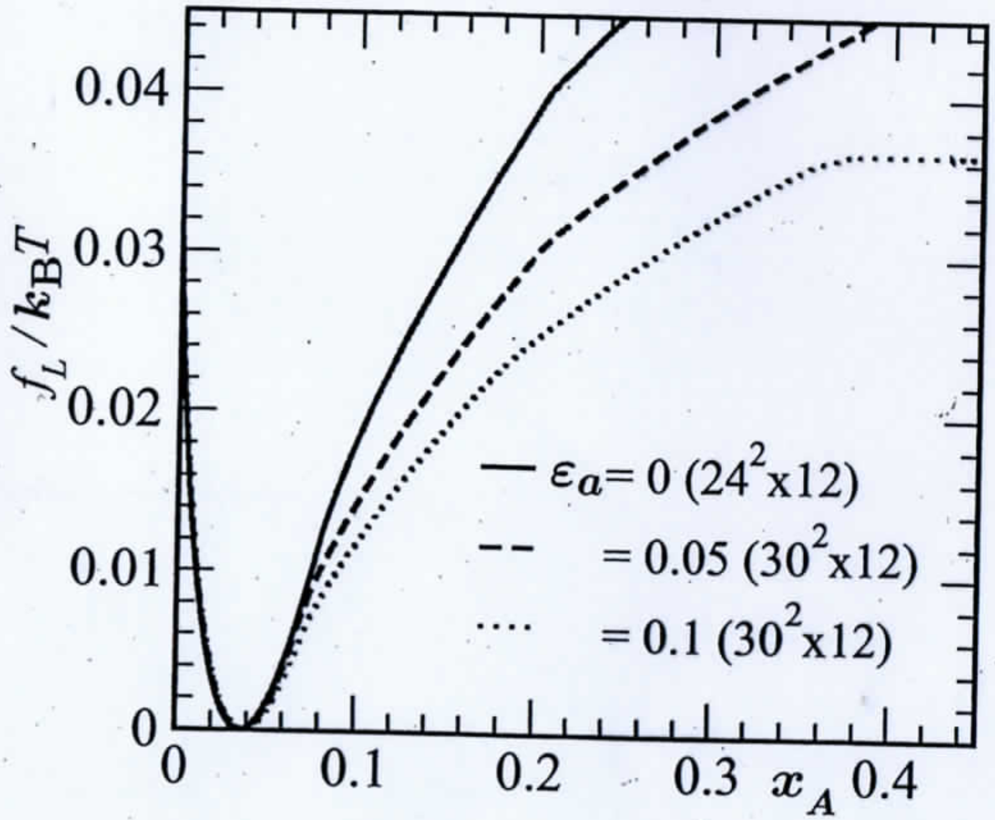
Wall-attached droplets in the binary Lennard-Jones mixture

$\varepsilon_a = 0: \Theta = 90°$

$\varepsilon_a = 0.05$ $\Theta \approx 77°$



effective free energy in the presence of walls



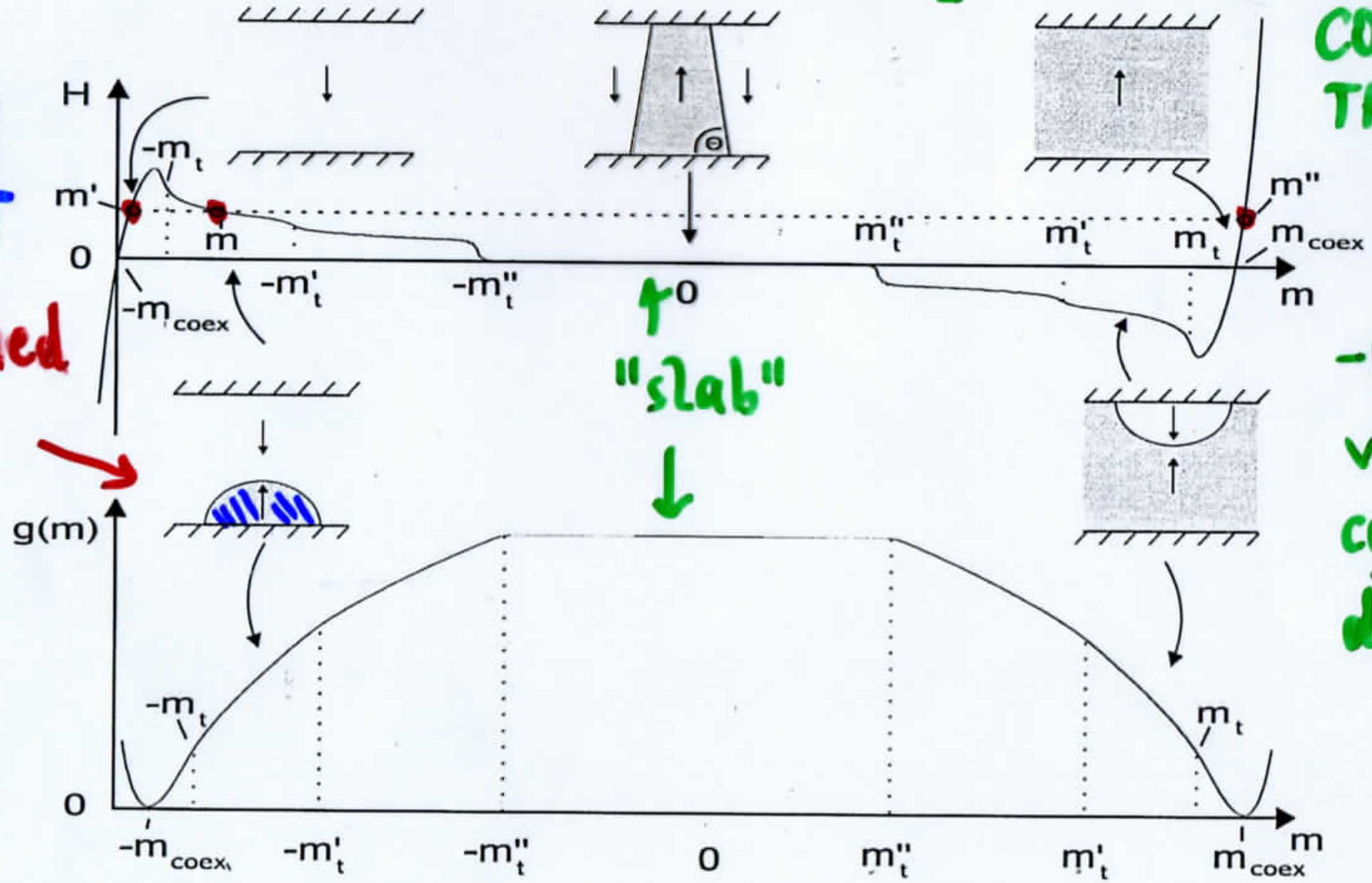
PHASE COEXISTENCE IN FINITE L×L×D ISING SYSTEMS: GENERAL CONSIDERATIONS

$-m_{coex} < m < -m_t$: vapor; $-m_t < m < -m'_t$: vapor + sphere-cap droplet

$m = -m_t$: DROPLET EVAPORATION-CONDENSATION TRANSITION

$$H(m) = \left(\frac{\partial g(m)}{\partial m}\right)_T$$

wall-attached droplet



$\downarrow 0$

"slab"

$-m'_t < m < -m''_t$: vapor + cylinder-cap droplet

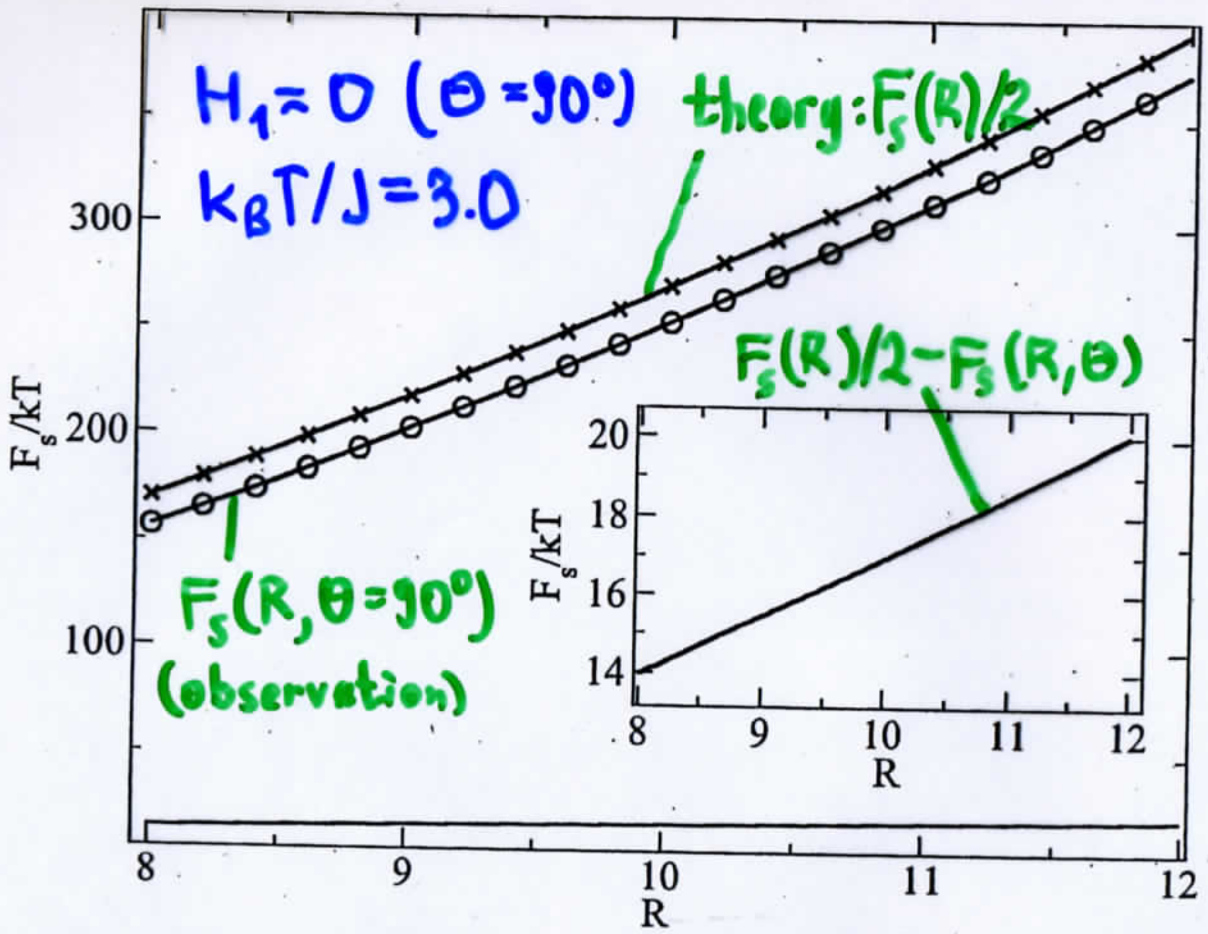
density $g(m)$ of the thermodynamic potential

$g(m = m_{coex}) = g(m = -m_{coex}) = 0$

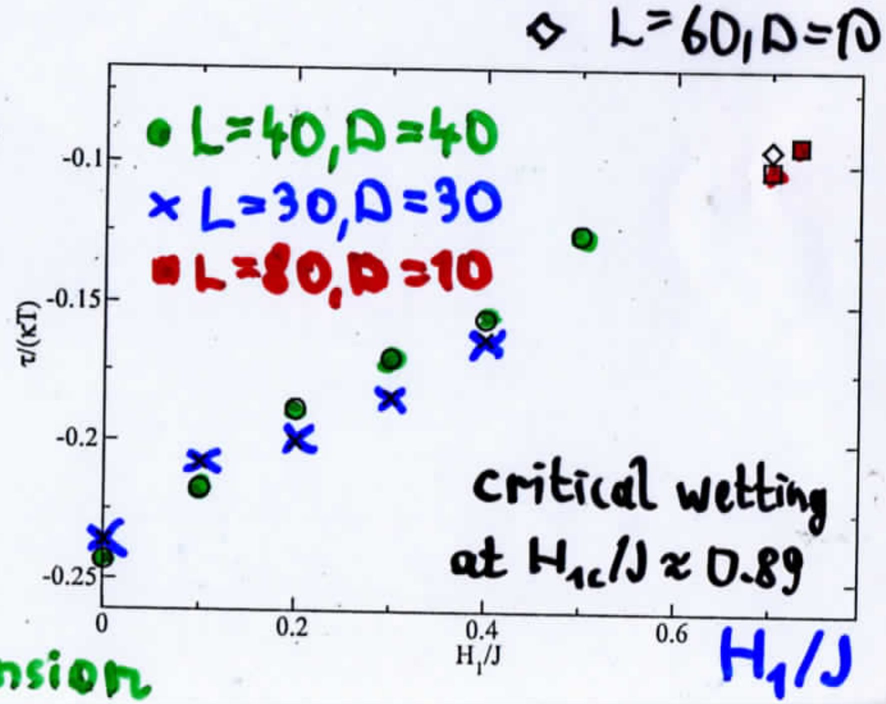
transitions at $\pm m_t$, $\pm m'_t$, $\pm m''_t$ sharp only for $L \to \infty$

SURFACE FREE ENERGY versus DROPLET RADIUS

(wall-attached droplets)



<u>linear</u> variation with R:
EVIDENCE for
LINE TENSION contribution



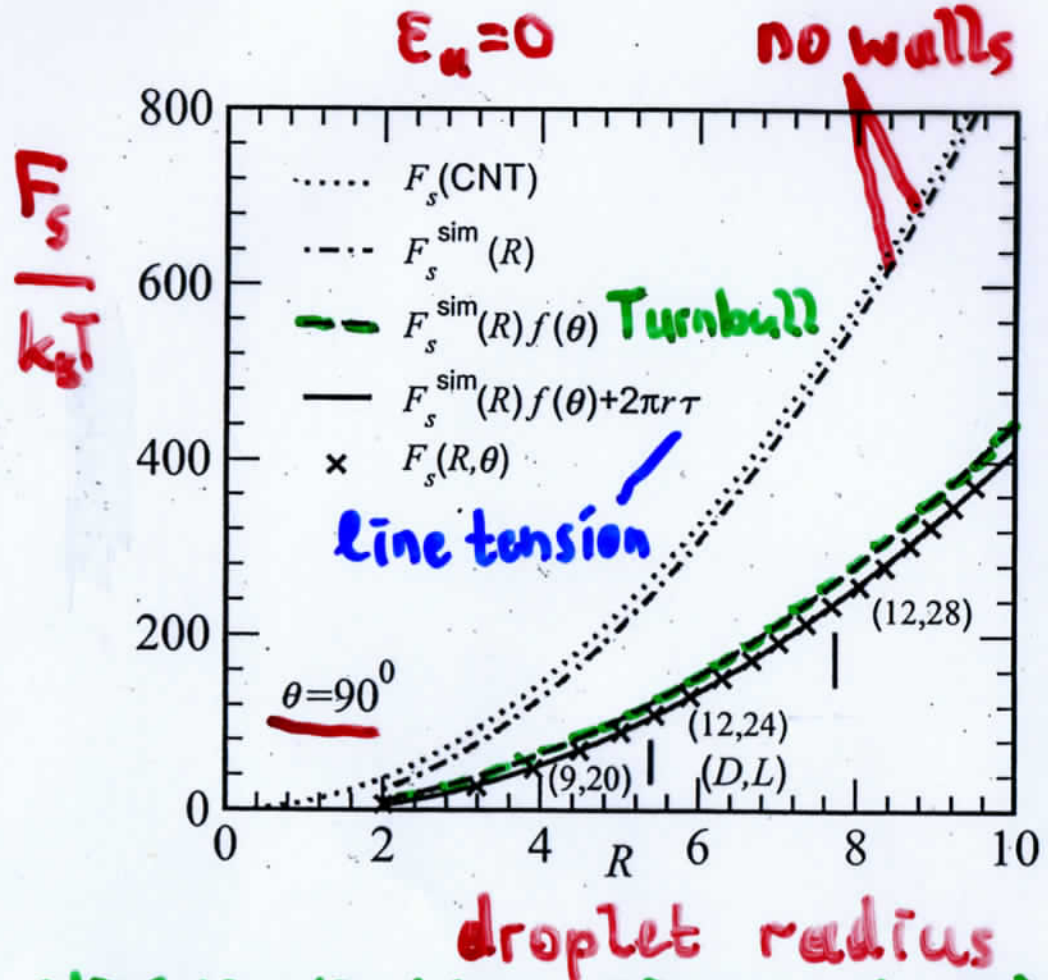
Classical theory including line tension (GRETZ 1966, NAVASCUEZ + TARANZONA 1981):

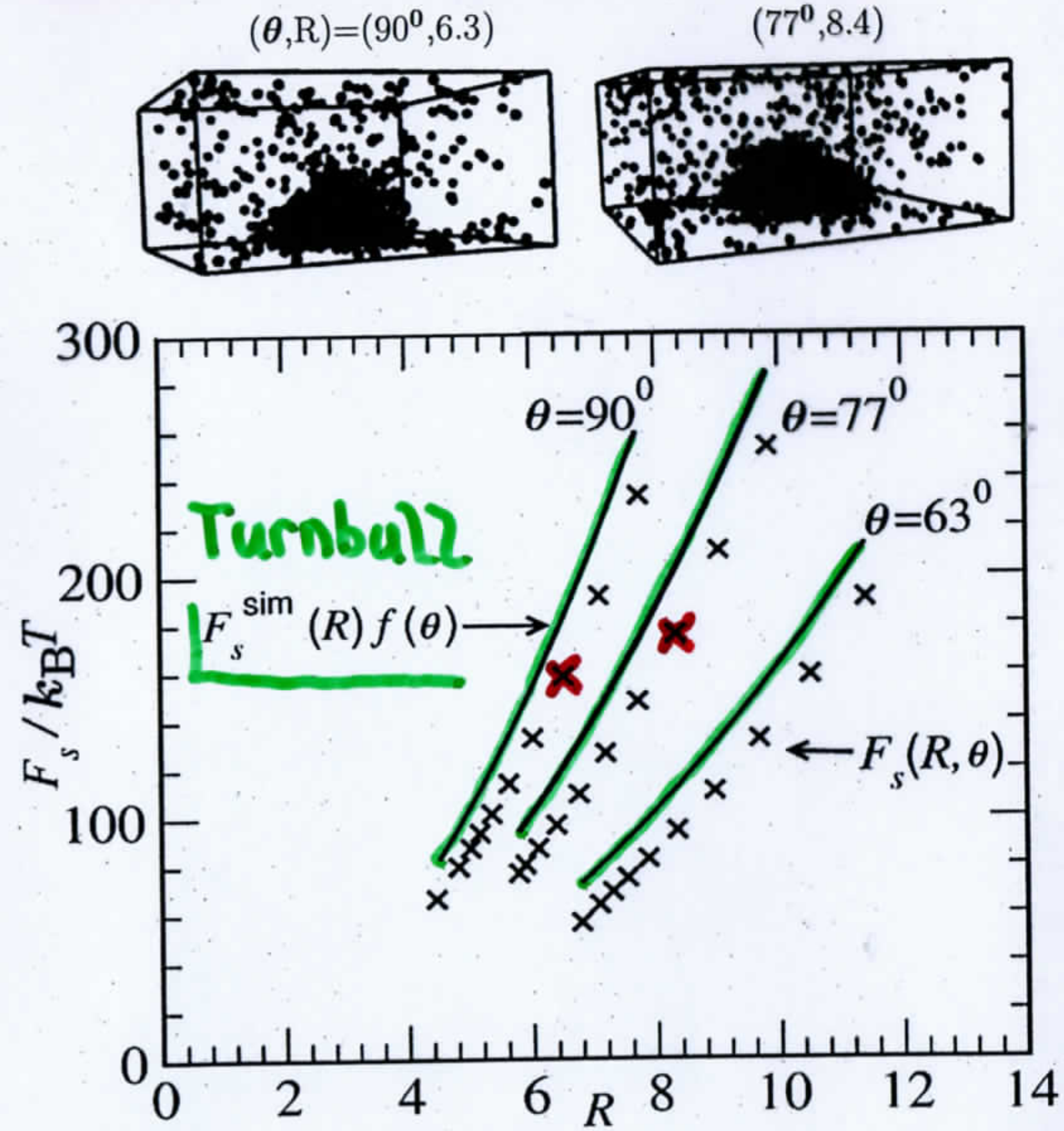
$$F_s(R,\Theta) = 4\pi R^{*2} \gamma_{vl} f(\Theta) + 2\pi \underbrace{R^* \sin\Theta}_{r} \underline{\tau}$$

$$f(\Theta) = (2 + \cos\Theta)(1 - \cos\Theta)^2/4$$

line tension

surface free energy of wall-attached droplets for the binary Lennard-Jones mixture

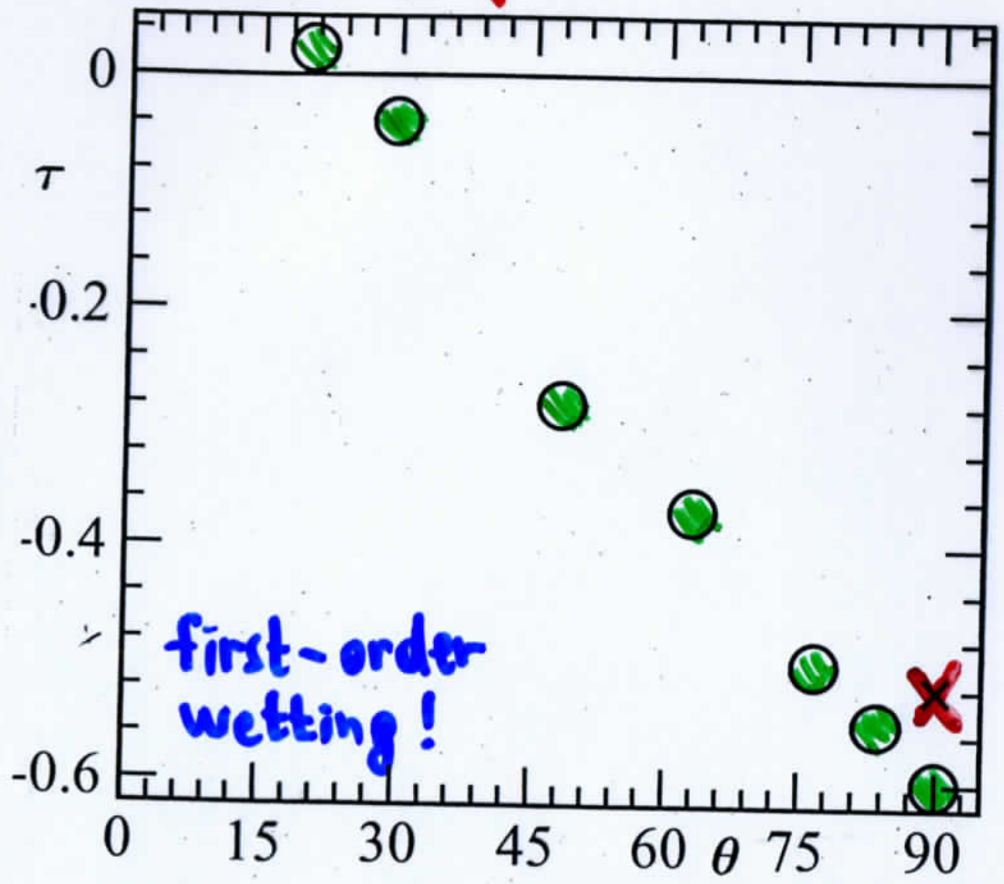


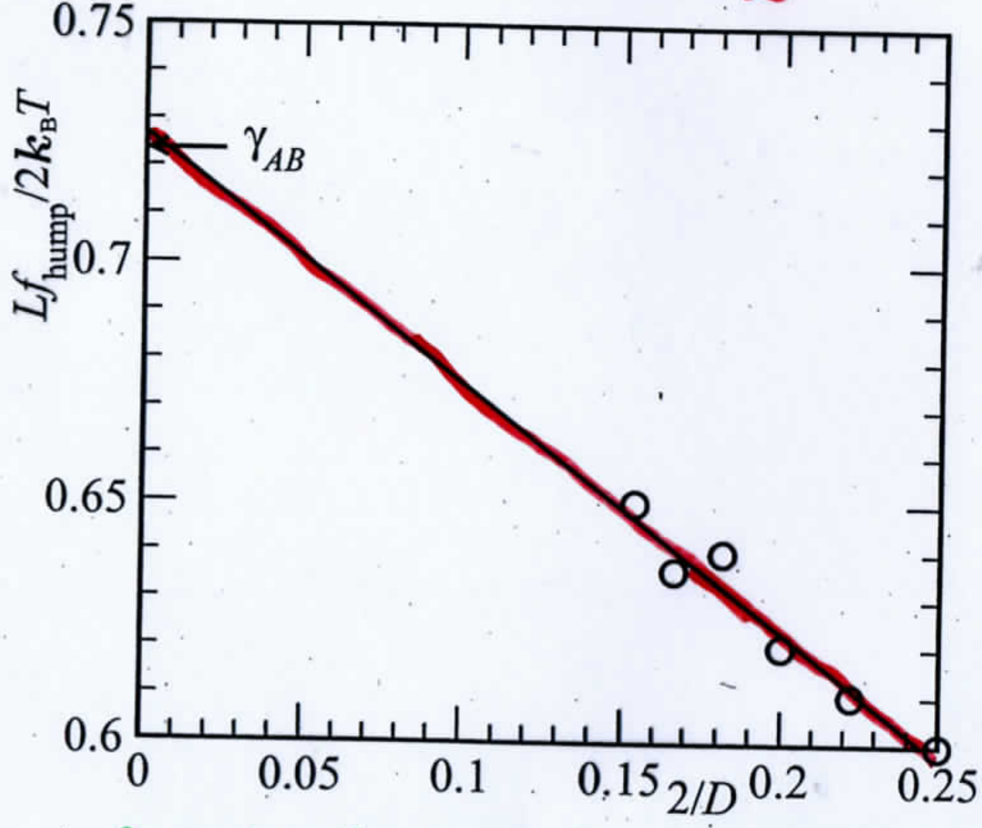


NEGATIVE LINE TENSION ⇒
Turnbull's formula $F_s(R)f(\theta)$ overestimates actual surface free energy cost even if the (KNOWN) curvature correction is included

Line tension of the binary Lennard-Jones mixture versus contact angle

$$Lf_{hump}/2k_BT = \gamma_{AB} + \tau \frac{2}{D}$$

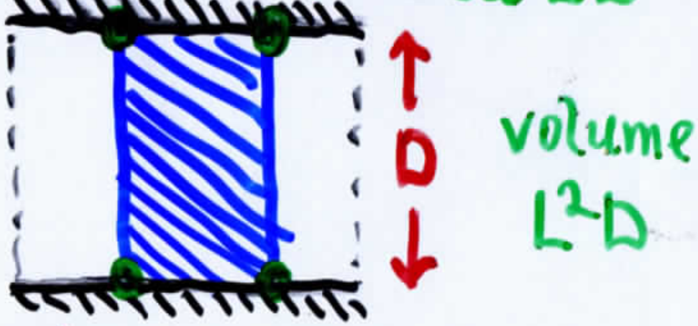




● extracted from the free energy of wall-attached droplets

✕ finite-size analysis of slab configurations

2 interfaces of area LD



4 3-phase contact lines

CONCLUSIONS

- method developed for the study of sessile wall-attached droplets in full equilibrium
- no "cluster criterion" needed to identify droplets → also bubbles accessible
- no "bias potential" needed to stabilize droplets
- chemical potential of gas coexisting with droplet and droplet volume and droplet surface (+line) energy "measured"
- Tolman Length ≈ -0.16 ; quadratic correction more important
- applications: 3-dim lattice gas model, binary LJ mixture
  - contact angle $\Theta(H_1)$ easy to determine
  - classical prediction $F_s(R,\Theta) = F_s(R)(2+\cos\Theta)(1-\cos\Theta)^2/4$ is accurate, if line tension correction is applied
  - still difficult: T near T_c ; H_1 near wetting transition