

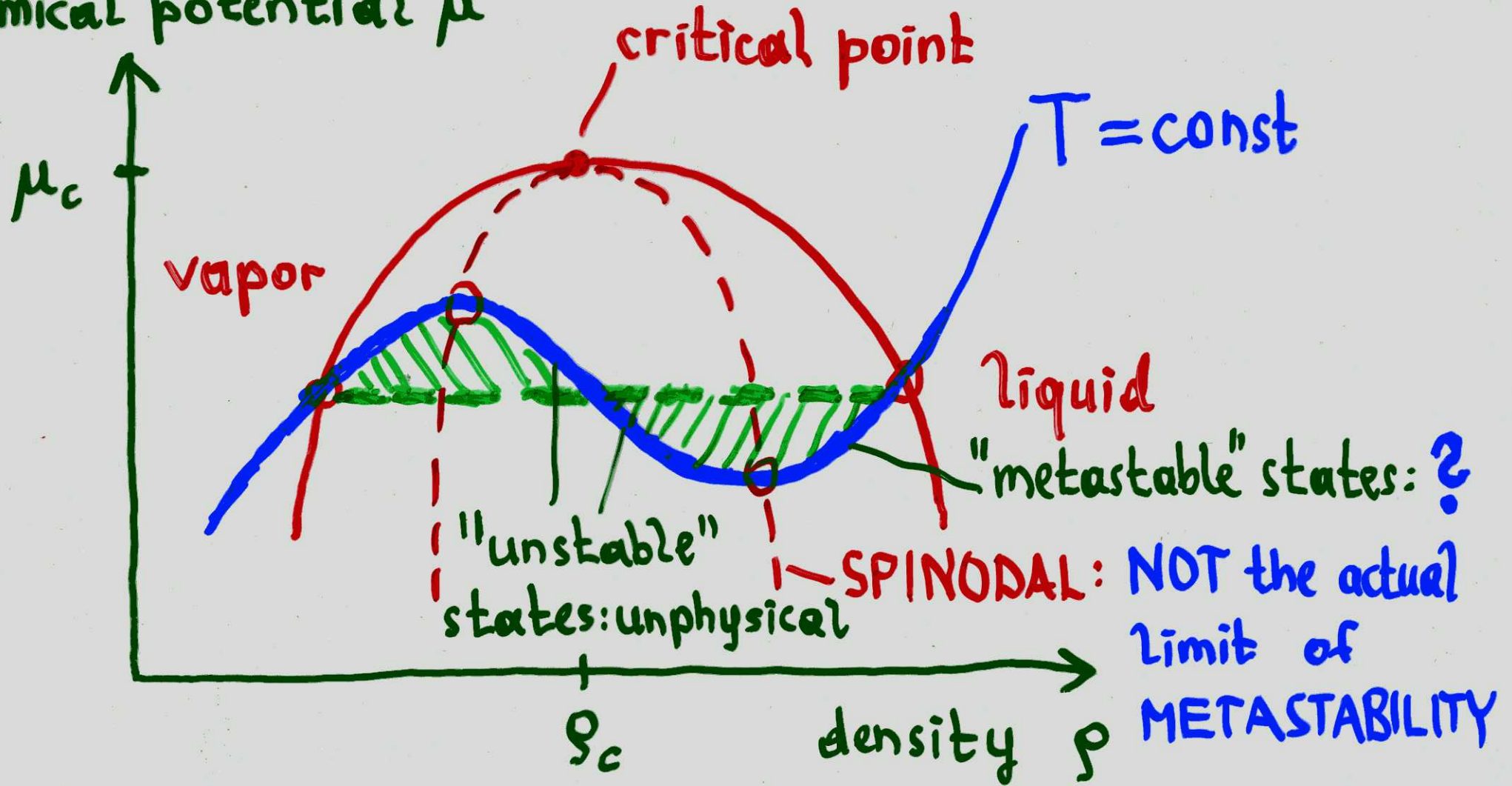
NUCLEATION PROCESSES AND THEIR STUDY BY SIMULATIONS

Kurt Binder

Coworkers: D. Stauffer, H. Müller-Krumbhaar,
H. Furukawa, D.W. Heermann, L.G. MacDowell,
M. Müller, P. Virnau, L. Yelash

van der Waals theory: MEAN FIELD!

chemical potential μ



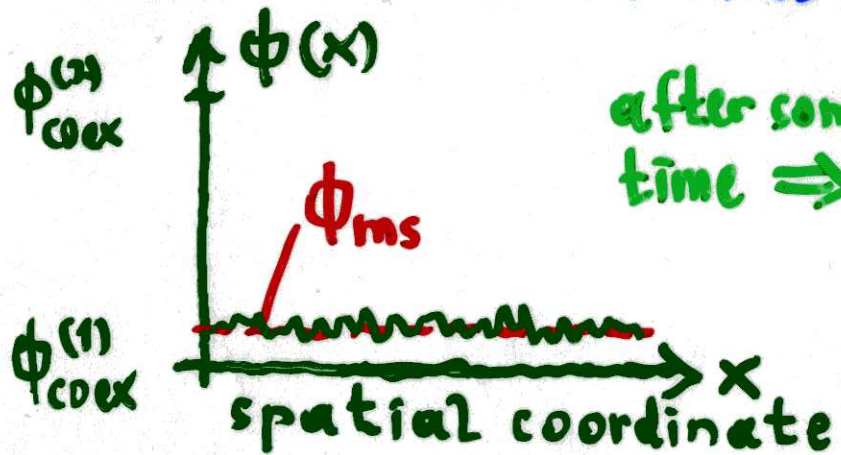
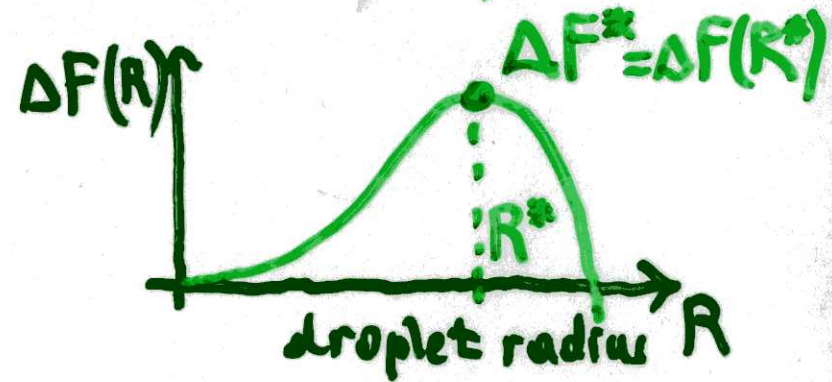
PHASE COEXISTENCE ?

Maxwell construction is ad hoc!

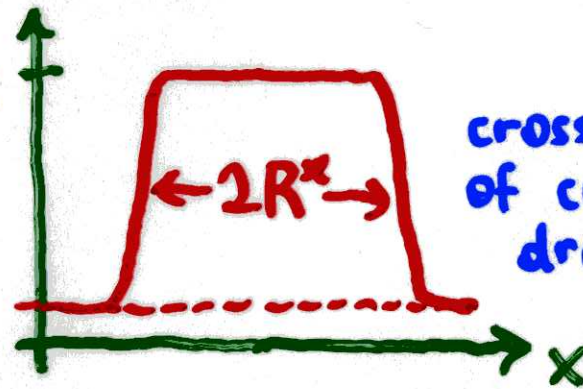
MECHANISMS for the INITIAL STAGES of PHASE SEPARATION KINETICS

(mean field theory: CAHN-HILLIARD 1959)

in between coexistence curve and spinodal;
NUCLEATION BARRIER must be overcome.
CRITICAL DROPLET must be formed



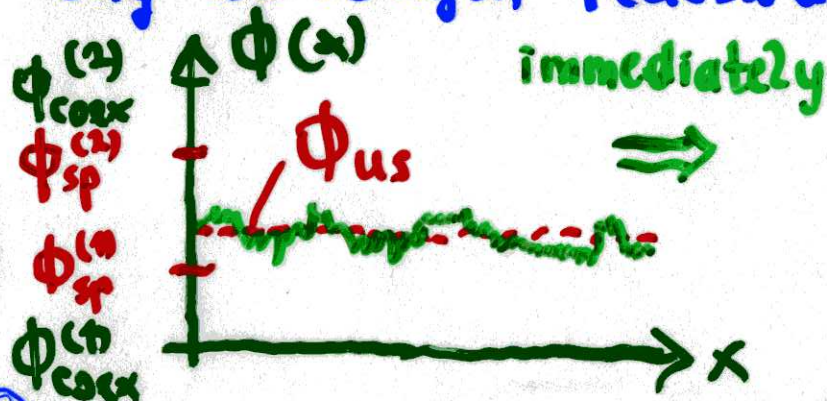
after some time \Rightarrow



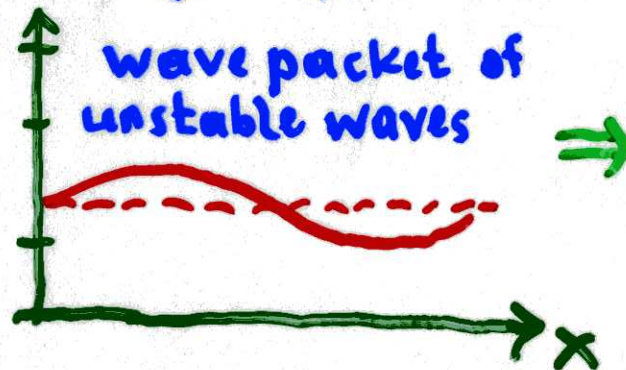
cross section of critical droplet \Rightarrow

droplet growth

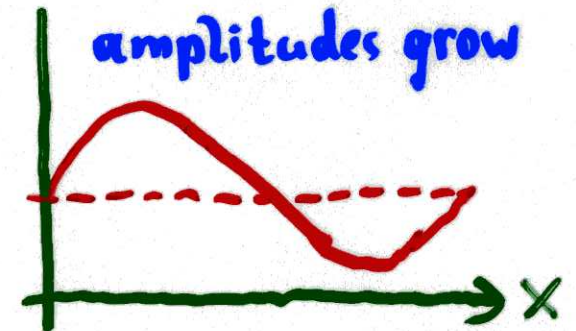
inside the spinodal region: $\phi_{sp}^{(1)} < \phi < \phi_{sp}^{(2)}$ **SPINODAL DECOMPOSITION**
 long wavelength fluctuations get spontaneously **AMPLIFIED**



immediately \Rightarrow



wave packet of unstable waves \Rightarrow



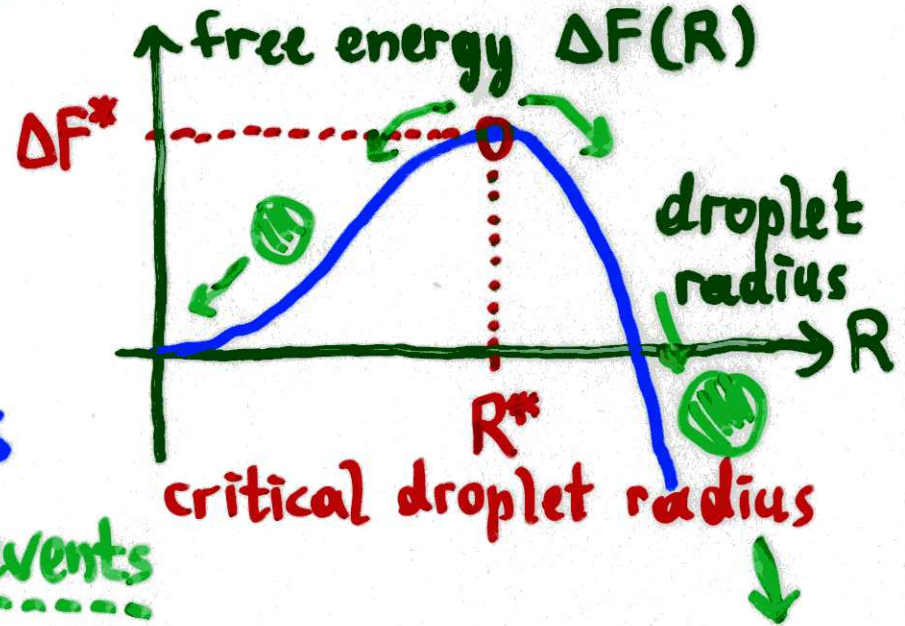
amplitudes grow

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

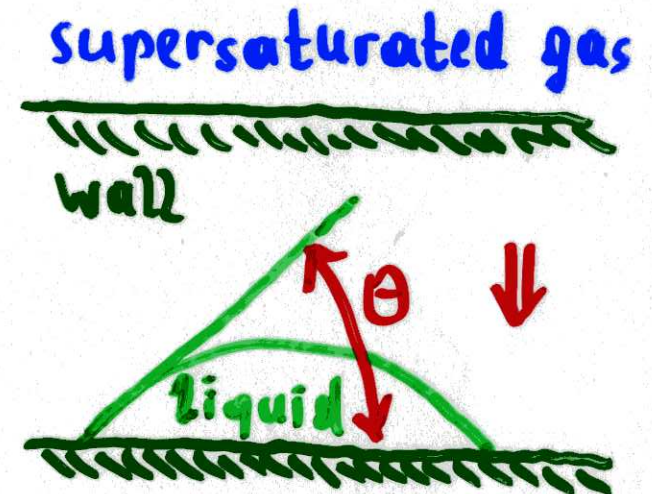
e.g. condensation of a liquid at a wall under INCOMPLETE WETTING conditions

$$\gamma_{wg} - \gamma_{wl} = \gamma_{gl} \cos \theta$$

$\theta =$ contact angle
YOUNG (1805)

- 3 interface tensions
- lower free energy barrier

$$\Delta F_{het}^* = \Delta F_{hom}^* f(\theta)$$



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

TURNBULL (1950)

CLASSICAL NUCLEATION THEORY

• estimate free energy barrier ΔF^* to form CRITICAL DROPLET (radius R^*)

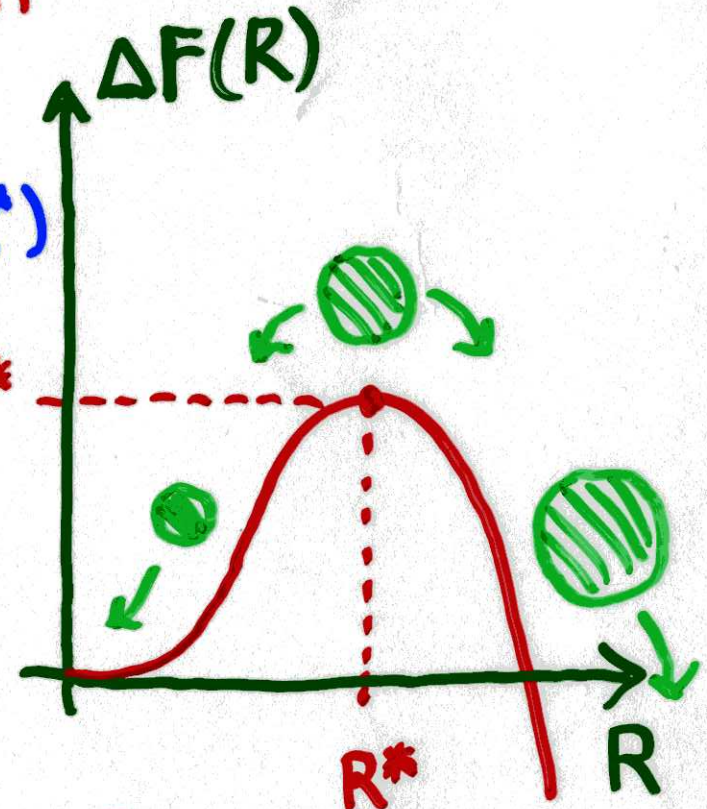
• spherical droplets

• macroscopic description: split $\Delta F(R)$ in BULK and SURFACE terms

$$\Delta F(R) = \Delta g \frac{4\pi R^3}{3} + \gamma_{v2} 4\pi R^2$$

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

SAME interfacial free energy as for a FLAT PLANAR INTERFACE

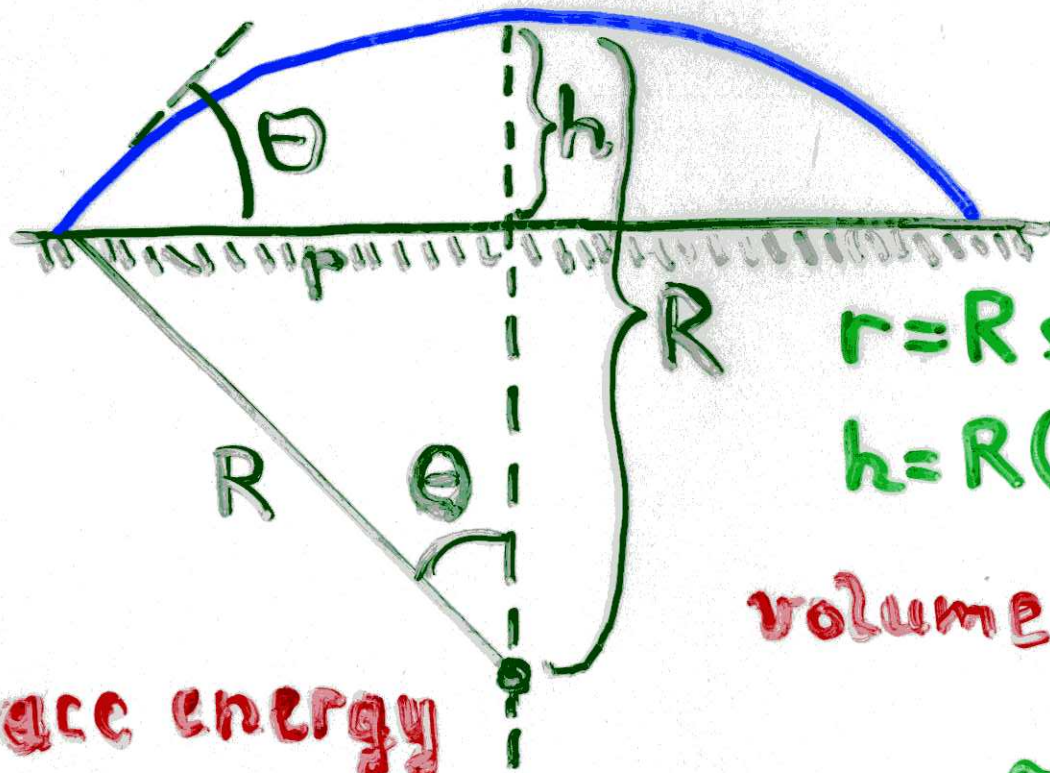


(near coexistence curve) $\delta\mu = \mu - \mu_{\text{coex}}$
chemical potential difference

$$\left. \frac{\partial(\Delta F(R))}{\partial R} \right|_{R^*} = 0 \Rightarrow R^* = \frac{2\gamma_{v2}}{(\rho_l - \rho_v)\delta\mu}, \quad \Delta F^* = \frac{16\pi}{3} \frac{\gamma_{v2}^3}{[(\rho_l - \rho_v)\delta\mu]^2}$$

nucleation rate J^* : # of crit. nuclei/cm³s : $J = \omega^* \exp[-\Delta F^*/k_B T]$

GEOMETRY OF SPHERE-CAP-SHAPED DROPLETS



$$r = R \sin \theta$$

$$h = R(1 - \cos \theta)$$

$$\text{volume } V_{\text{drop}} = \frac{\pi h}{6} (3r^2 + h^2)$$

surface energy

$$F_s = \gamma_{ve} \pi (r^2 + h^2)$$

$$+ \pi r^2 (\gamma_{ve} - \gamma_{wv}) \quad \downarrow \text{Young!}$$

$$F_s = \gamma_{ve} \pi [r^2(1 - \cos \theta) + h^2] = 4\pi \gamma_{ve} R^2 f(\theta)$$

$$\Rightarrow V_{\text{drop}} = \frac{\pi R^3}{3} \underbrace{(2 + \cos \theta)(1 - \cos \theta)^2}_{4f(\theta)}$$

4f(θ)

same factor

CLASSICAL THEORY OF HOMOGENEOUS NUCLEATION: VALIDITY?

$$\Delta F^* = \frac{16\pi}{3} \gamma_{gl}^3 / \underbrace{[(\rho_l - \rho_g) \delta \mu]^2}_{\rho - \rho_g}$$

• no knowledge on the existence of a SPINDAL (= limit of metastability) built in

NUCLEATION RATE (J): number of critical nuclei per second and cm^3

⇒ Arrhenius formula $J = \nu^* \exp(-\Delta F^*/k_B T)$

"attempt frequency": KINETICS of nucleation!

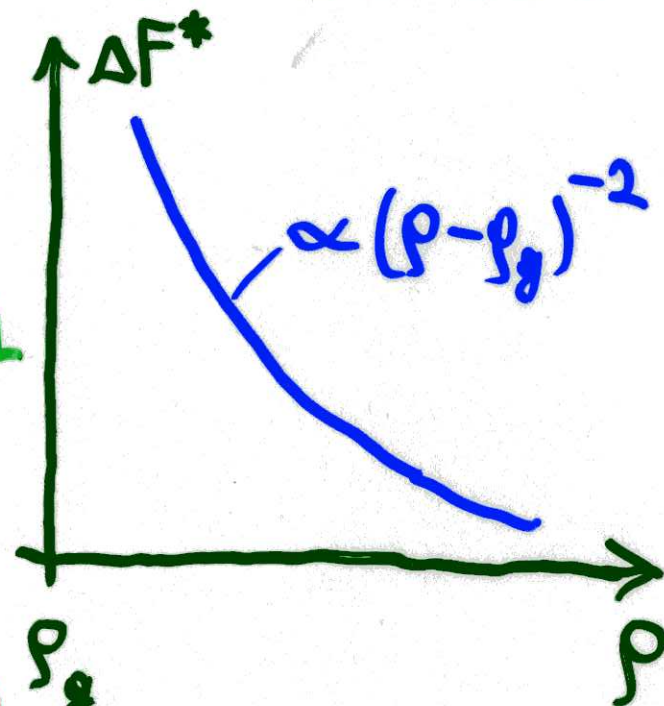
vapor-liquid nucleation: $\Delta F^* \approx 40 k_B T$ is of practical interest

⇒ 10% error of $\gamma_{gl} \rightarrow$ 30% error of $\Delta F^* \rightarrow$ error $\exp(\pm 10)$ in J

BUT SOME EXPERIMENTS INDICATE MUCH LARGER ERRORS ∇?

R^* is nanoscopic ⇒ $\approx 10^2$ molecules/critical droplet → Tolman length

CORRECTIONS? e.g. TOLMAN (1948) $\gamma_{gl}(R) = \gamma_{gl}(\infty) / [1 + 2\delta/R]$ (=?)



MONTE CARLO TEST of NUCLEATION BARRIERS:

ISING, LATTICE GAS MODEL

Furukawa and Binder 1982

nucleation barrier $\frac{\Delta F}{k_B T_c}$

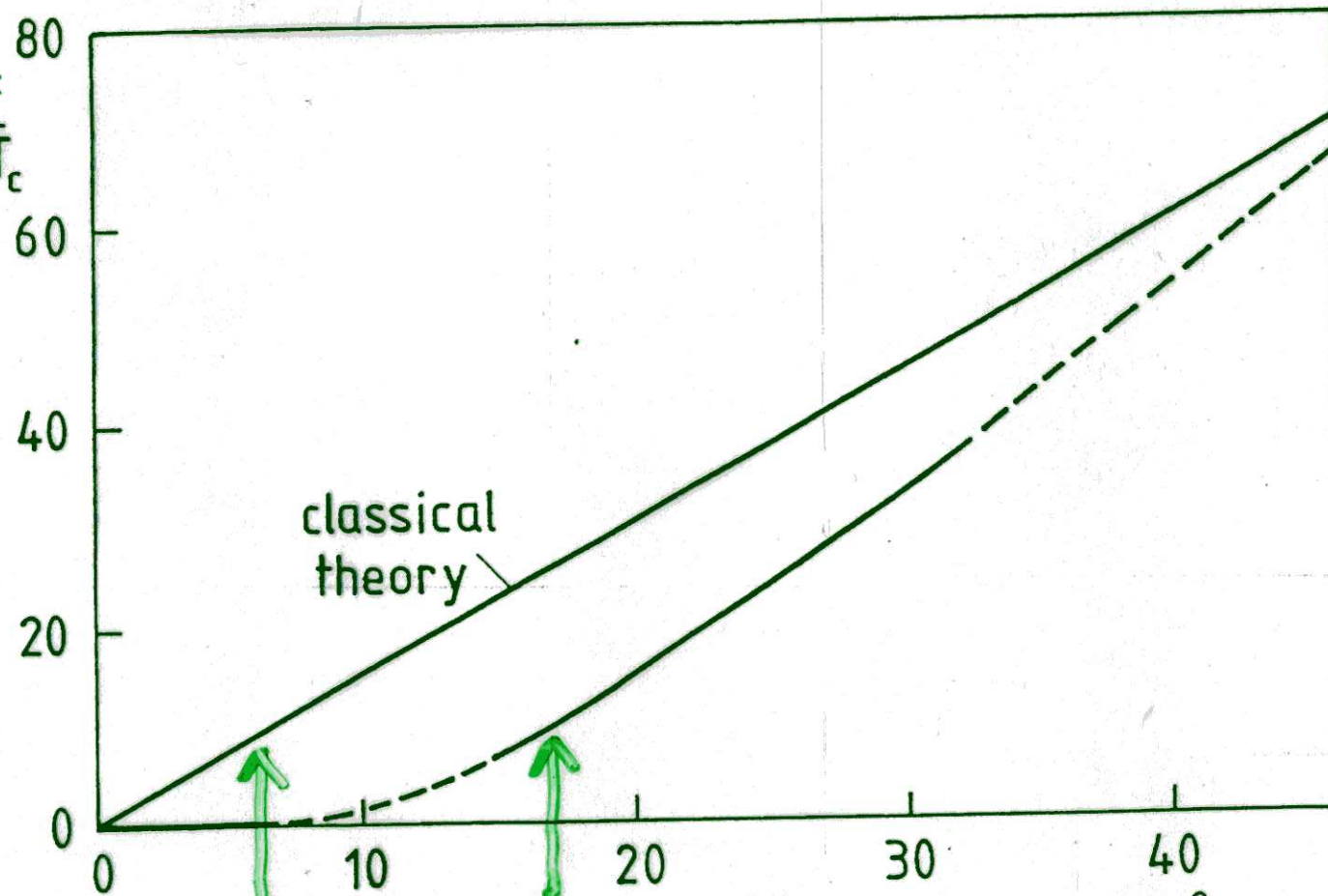
coexistence curve:

$$p_{\text{crit}} - p_{\text{gas}} \propto \left(1 - \frac{T}{T_c}\right)^\beta$$

classical theory:

$$\frac{\Delta F}{k_B T} \propto (p - p_{\text{gas}})^{-2}$$

classical theory



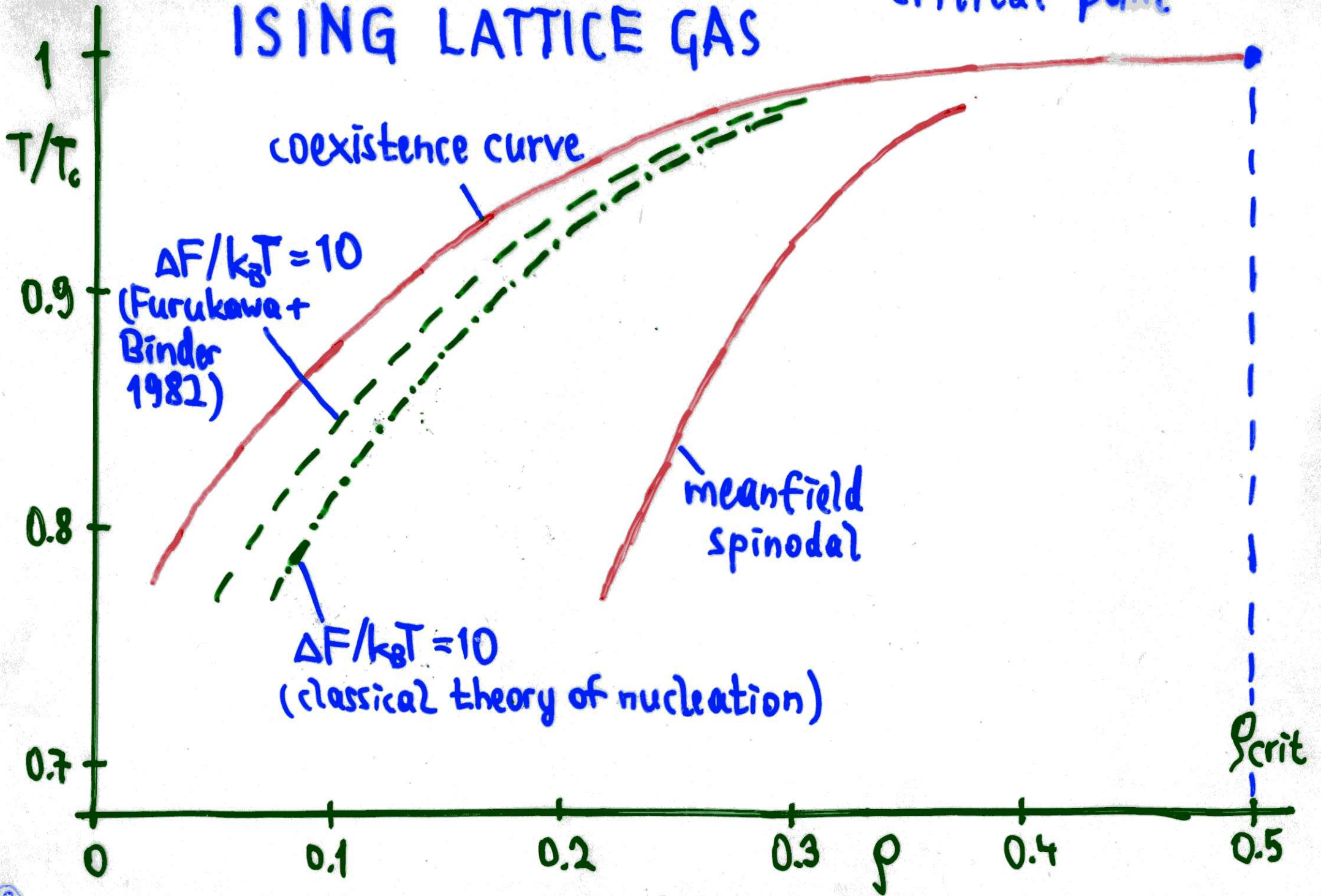
$$\frac{\Delta F}{k_B T_c} = 10$$

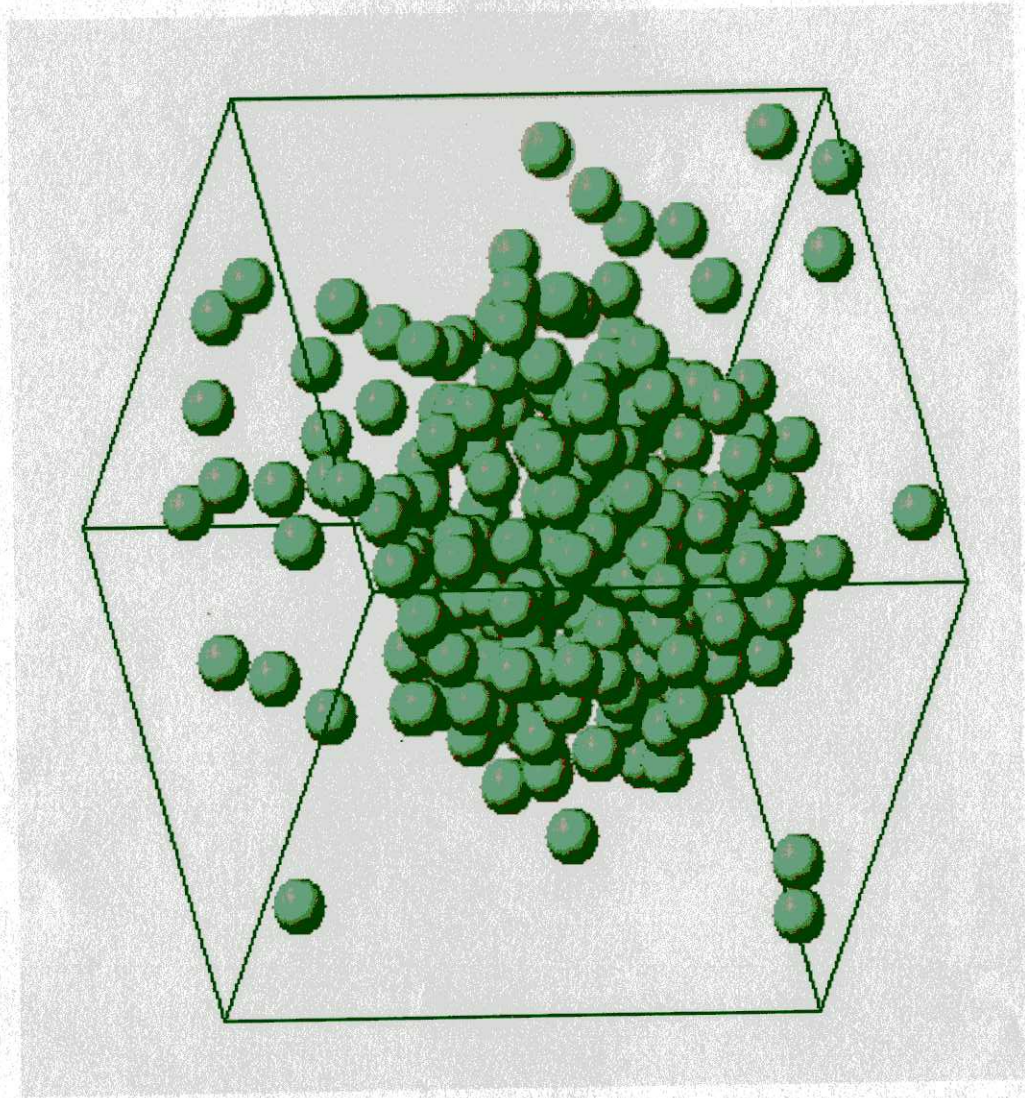
Monte Carlo

$$[2(p_1 - p_{\text{gas}}) / \Delta\rho\beta]^{-2}$$

ISING LATTICE GAS

critical point





M. Schröder, P. Virnau, K.B. (2009)

Surface free energy of liquid droplets in surrounding supersaturated vapor (Lennard-Jones fluid, $T = 0.68 T_c$)

capillarity approx.:
 $F_s(R) \approx 4\pi R^2 \gamma_{vl}$

$$\frac{F_s(R)}{k_B T}$$

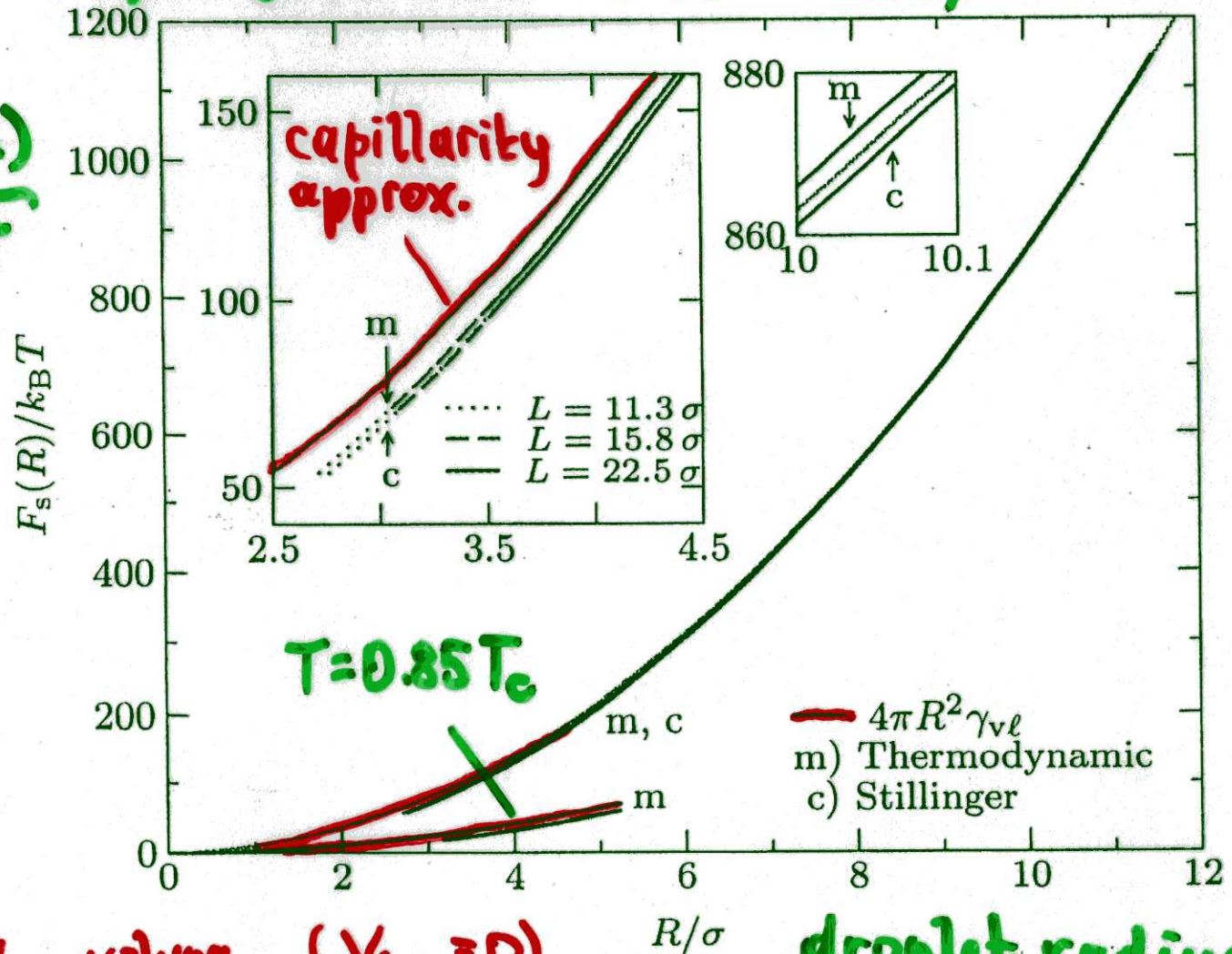
Stillinger
 CONNECTIVITY
 criterion:

distance $r < 1.5\sigma$
 \rightarrow two particles are connected

"thermodynamic"

method: $V = V_l + V_v$ volume ($V_{int} \approx 0$)
 $N = N_l + N_v$ particle number ($N_{int} \approx 0$)

$$\Rightarrow p = p_v' + (p_l' - p_v') (4\pi R^3 / 3V)$$



droplet radius

Test of Tolman's hypothesis

M. Schrader, P. Virnau, K.B. (2009)

$$\frac{\gamma_{vl}(R)}{\gamma_{vl}} \approx 1 - 2 \left(\frac{\delta}{R} \right) \quad R \rightarrow \infty$$

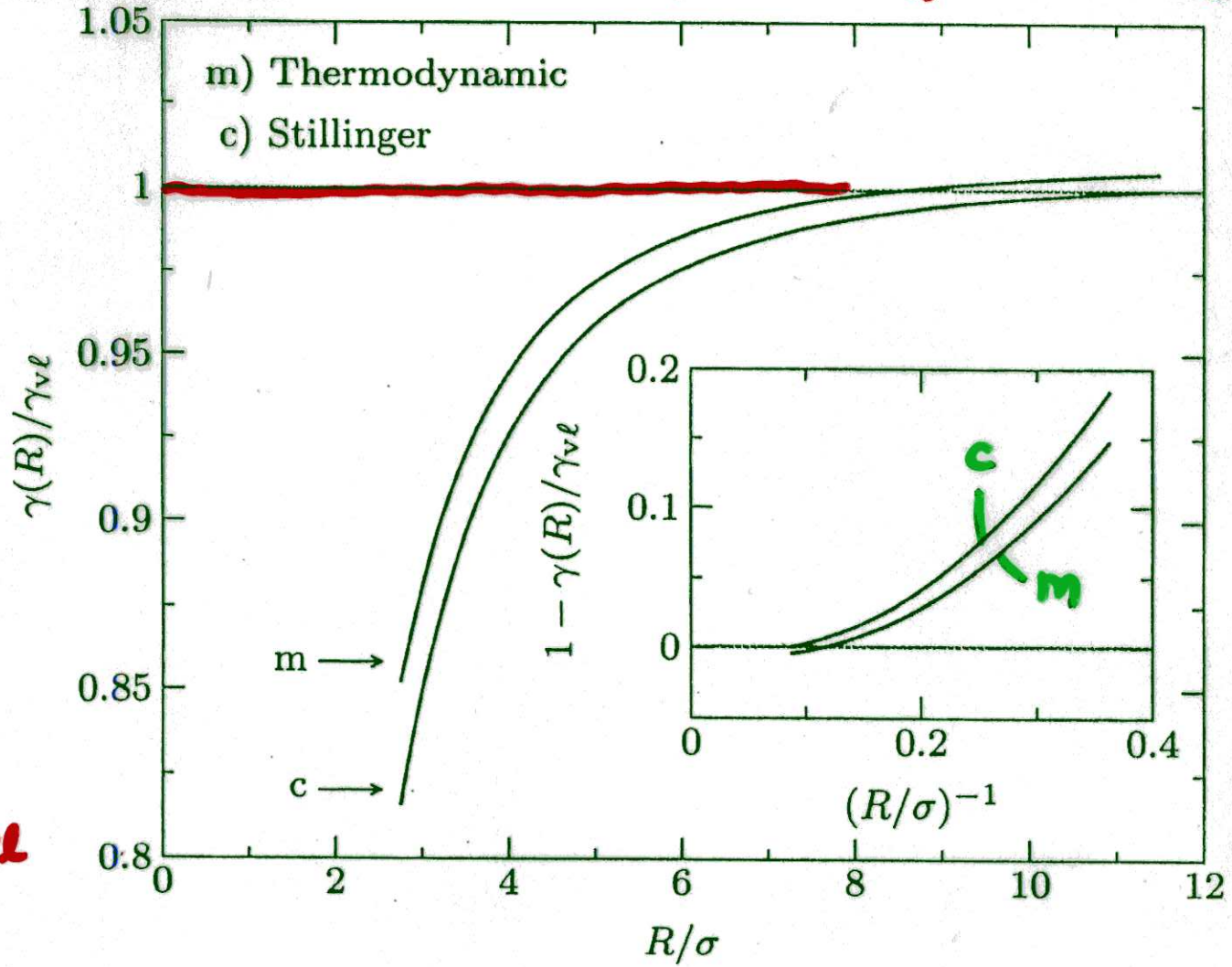
δ = Tolman length

$$\Rightarrow \delta = 0$$

(within our accuracy)

but for $R \leq 5\sigma$

$\gamma(R)$ is smaller than γ_{vl}
for flat interface
by $\geq 5\%$



$T = 0.68 T_c$ Lennard-Jones fluid

BUT: HUGE deviations between NUCLEATION EXPERIMENTS
for ARGON and CLASSICAL NUCLEATION THEORY $\nabla?$

10'

NUCLEATION KINETICS

Atomistic interpretation in terms of GROWTH and SHRINKING of CLUSTERS containing l ATOMS (molecules)

Volmer and Weber (1926), Becker and Döring (1935),



number of clusters of "size" l at time t per unit volume

$$\boxed{\bar{n}_l(t)} \quad \frac{d}{dt} \bar{n}_l(t) = -a_l \bar{n}_l - b_l \bar{n}_l + \underbrace{a_{l-1} \bar{n}_{l-1}}_{\text{gain from smaller clusters}} + \underbrace{b_{l+1} \bar{n}_{l+1}}_{\text{gain from larger clusters}}$$

hypothetical steady-state cluster concentration n_l : n_l^{ss}

$$d\bar{n}_l/dt = dn_l^{ss}/dt = 0 \Rightarrow a_{l-1} n_{l-1}^{ss} = b_l n_l^{ss}$$

NUCLEATION KINETICS

$$\frac{d}{dt} \bar{n}_l(t) = -a_l \bar{n}_l - b_l \bar{n}_l + a_{l-1} \bar{n}_{l-1} + b_{l+1} \bar{n}_{l+1}$$

differences \rightarrow differentials: $\bar{n}_{l+1} = \bar{n}_l + \frac{\partial \bar{n}_l}{\partial l} \cdot 1 + \frac{1}{2} \frac{\partial^2 \bar{n}_l}{\partial l^2} + \dots$

\Rightarrow CONTINUITY EQUATION for the CURRENT J_l in the (one-dimensional) "cluster-size space" $\{l\}$

$$\frac{\partial \bar{n}_l}{\partial t} + \frac{\partial J_l}{\partial l} = 0, \text{ "current" } J_l = \underbrace{-a_l \frac{\partial \bar{n}_l(t)}{\partial l}}_{\text{"diffusion term"}} + \underbrace{\left(a_l \frac{\partial \ln n_l}{\partial l} \right) \bar{n}_l(t)}_{\text{"drift velocity"}}$$

$$b_l = a_{l-1} n_{l-1} / n_l \text{ used } \rightarrow$$

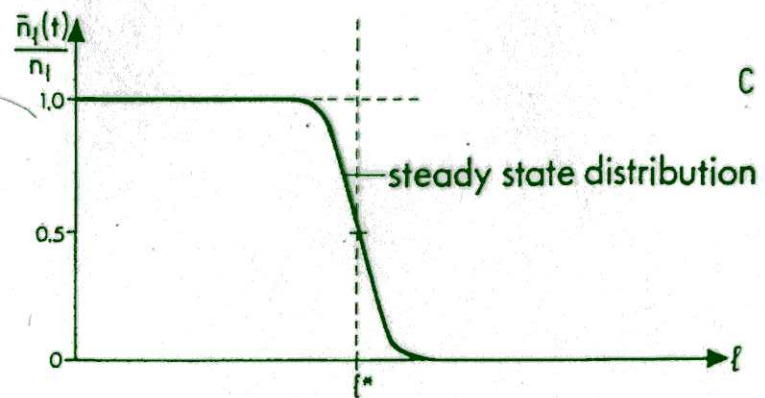
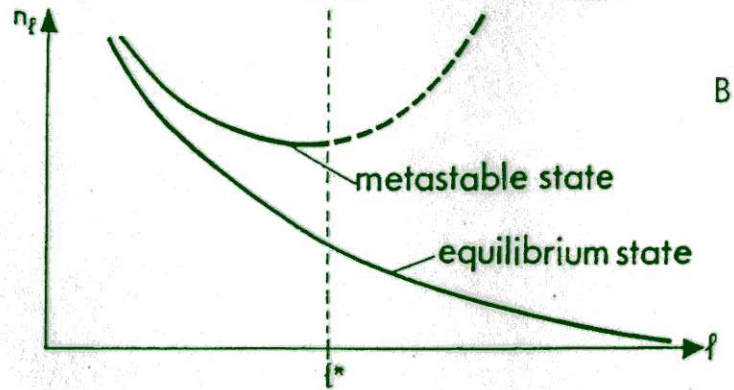
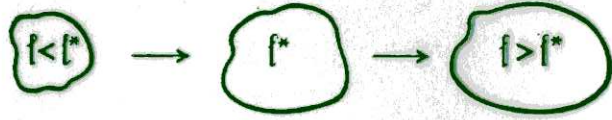
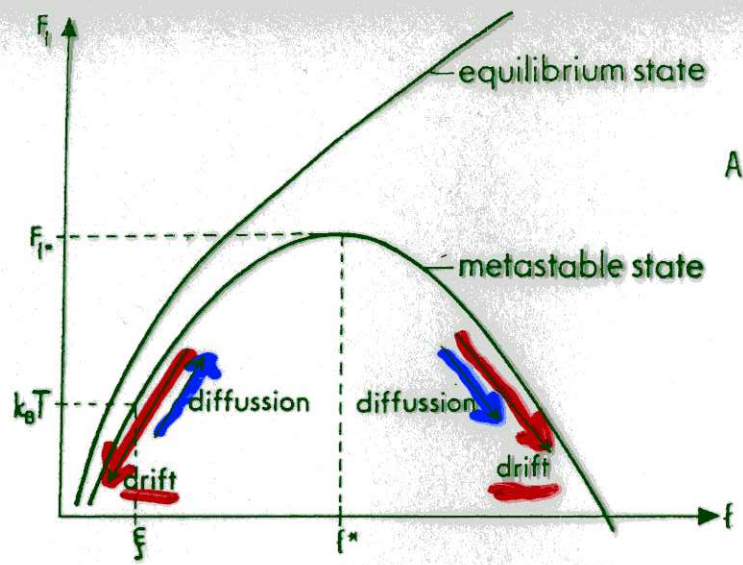
"diffusion term" "drift velocity"

neglect depletion of monomers ($l=1$) \Rightarrow

STEADY STATE solution $J_l(t) = J$ INDEPENDENT of l

$$\frac{\bar{n}_l(t)}{n_l} = J \int_l^{\infty} (a_l n_l)^{-1} dl$$

$$J = \left[\int_0^{\infty} (a_l n_l)^{-1} dl \right]^{-1}$$



diffusion

current $J_l = -a_l \frac{\partial \bar{n}_l(t)}{\partial l}$

$+ (a_l \frac{\partial \ln n_l}{\partial l}) \bar{n}_l(t)$

"drift velocity"

corresponds to $F(R)$

$n_l \equiv \exp(-F_l/k_B T)$

$n_l \equiv$ hypothetical cluster concentration "in equilibrium" with rate constants a_l, b_l

DYNAMICS OF NUCLEATION

Nucleation rate $J = \left[\int_0^{\infty} (a_l n_l)^{-1} dl \right]^{-1}$

$n_l = \exp(-F_l/k_B T)$

if $F_{l^*} \gg k_B T$: expand F_l quadratically

at l^* : $F_l \approx F_{l^*} - \frac{1}{2} g (l - l^*)^2 + \dots$

$a_l \approx a_{l^*} = \text{const}$

$\Rightarrow J = a_{l^*} \sqrt{g} \exp[-F(l^*)/k_B T]$

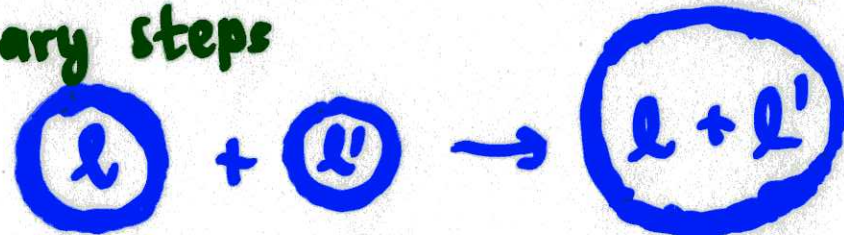
kinetic factor

ZELDOVICH (1942) factor

FURTHER CORRECTIONS (e.g. BINDER + STAUFFER 1976)

(i) "CLUSTER REACTIONS" in arbitrary steps

"cluster reaction matrix" $W(l, l')$

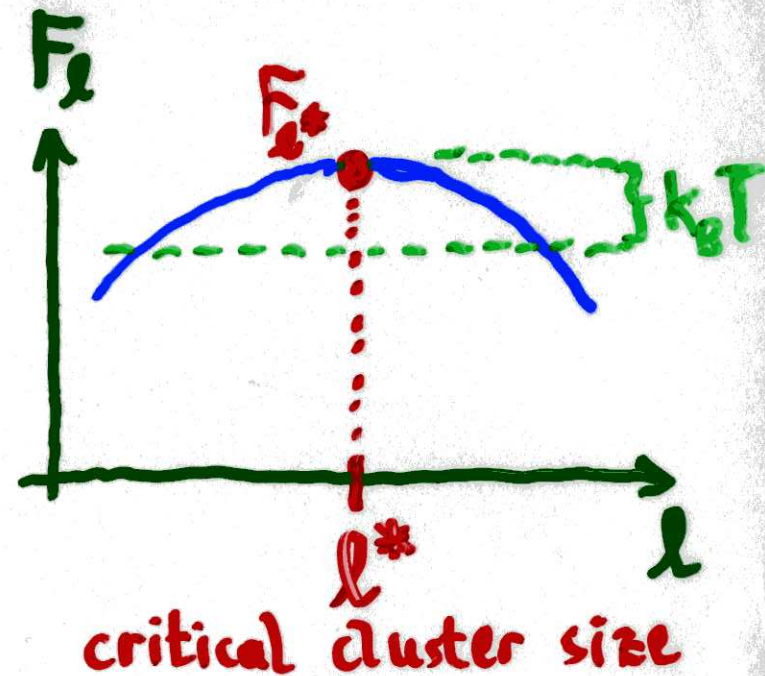


$\Rightarrow a_l$ gets replaced by a

"cluster reaction rate"

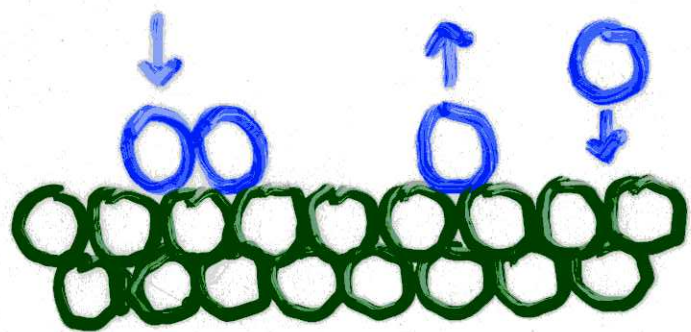
$R_l = \sum_{l'} [W(l, l')/n_l] l'^2$

important near T_c



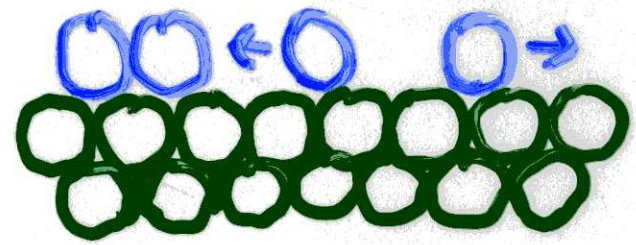
Adsorption of monolayers at crystal

surfaces from the gas: KINETIC ISING MODELS



evaporation/
condensation

surface diffusion



preferred sites: regular lattice \rightarrow LATTICE GAS MODEL

phonons of crystal substrate: heat bath \rightarrow

MARKOVIAN MASTER EQUATION: MONTE CARLO!

$$\frac{dP(\vec{x}, t)}{dt} = - \sum_{\vec{x}'} W(\vec{x} \rightarrow \vec{x}') P(\vec{x}, t) + \sum_{\vec{x}'} W(\vec{x}' \rightarrow \vec{x}) P(\vec{x}', t)$$

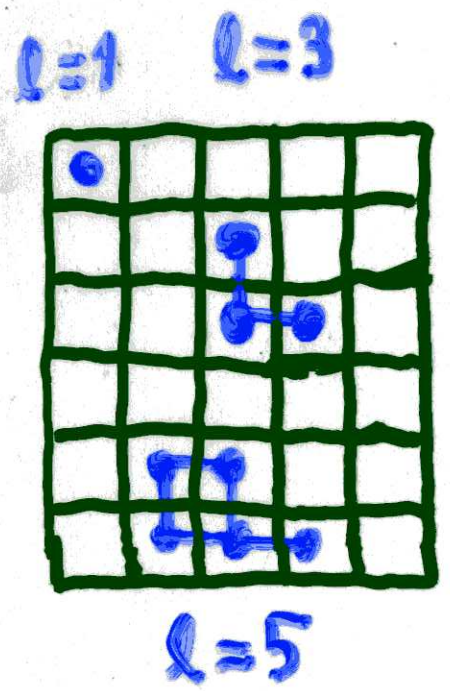
\vec{x}' - microstates \vec{x}' - transition probab.

Lattice gas \leftrightarrow Ising ferromagnet (density $\rho \leftrightarrow$ magnetization m)

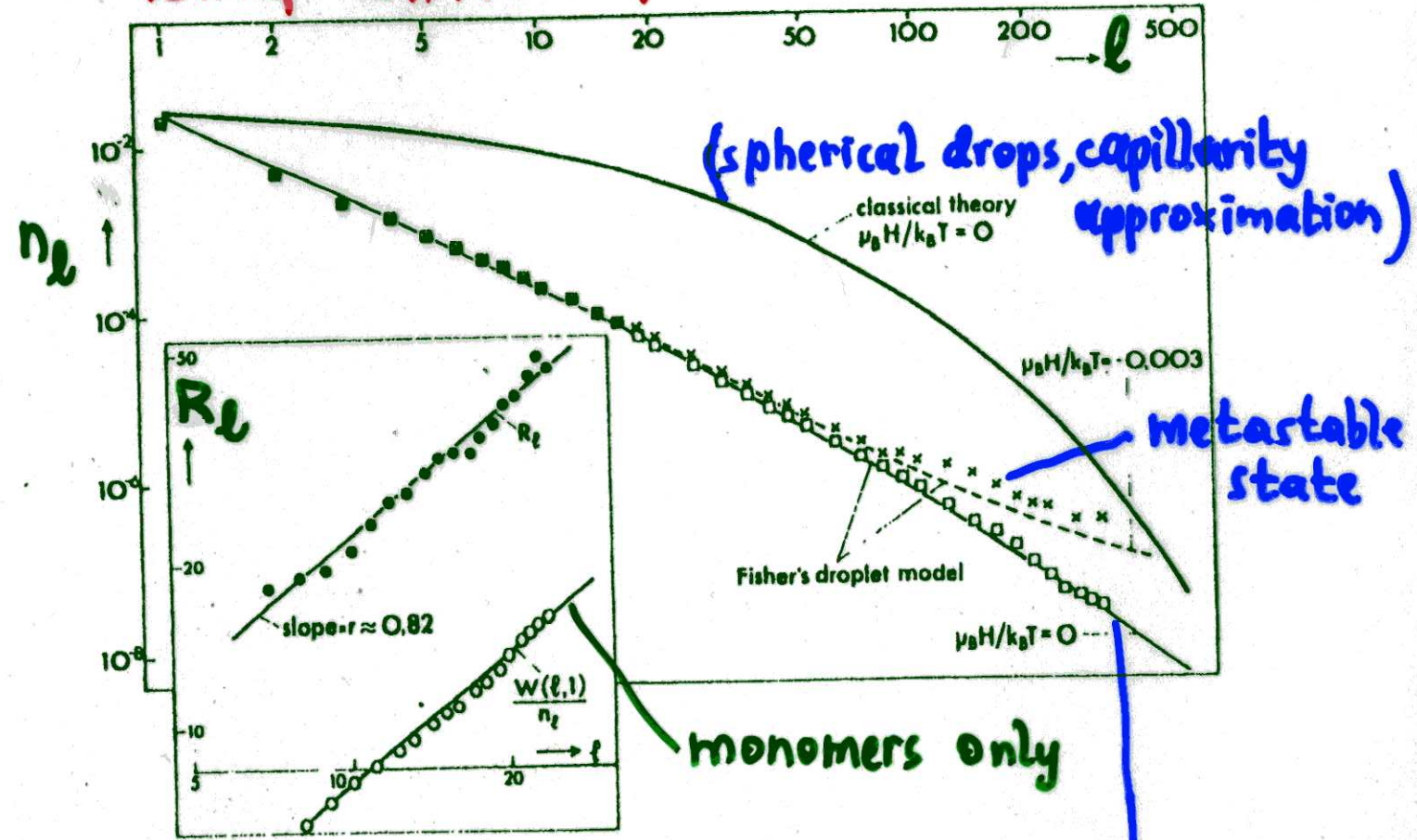
evaporation/condensation: single spin flip model

surface diffusion: spin-exchange kinetic Ising model

"CLUSTERS"



Droplet concentration n_l in the $d=2$ ISING LATTICE GAS near T_c



cluster reaction rate

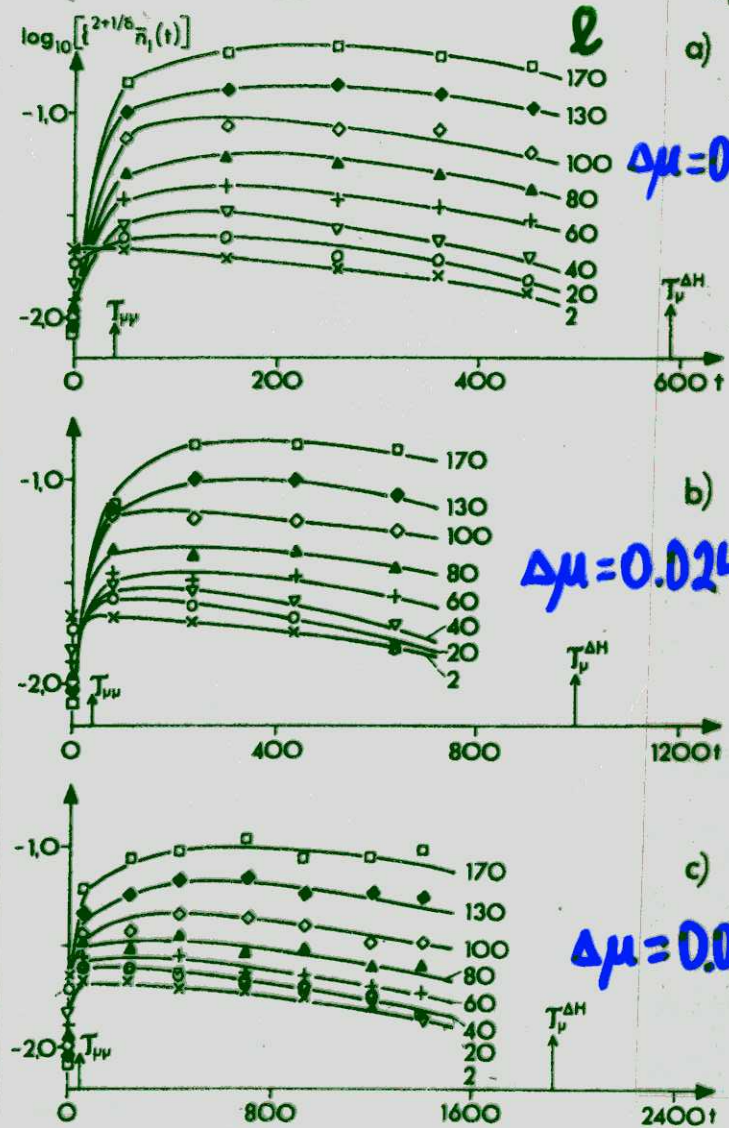
$$J/k_B T_c \approx 0.44$$

$$J/k_B T = 0.46$$

Binder & Müller-Krumbhaar 1974

Monte Carlo test of nucleation theory

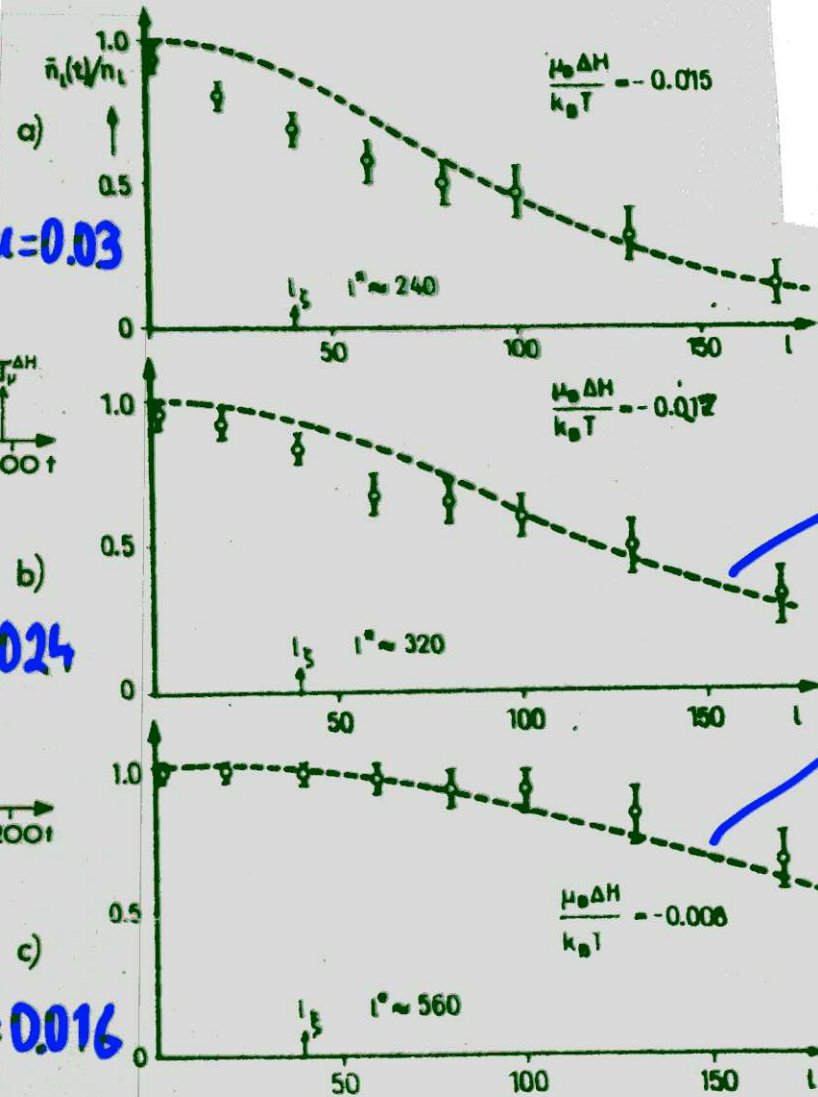
cluster concentrations



flat regions \Rightarrow estimates of "steady state"

CLUSTER CONCENTRATION

ISING LATTICE
GAS $T \approx 0.96 T_c$
 $d=2$

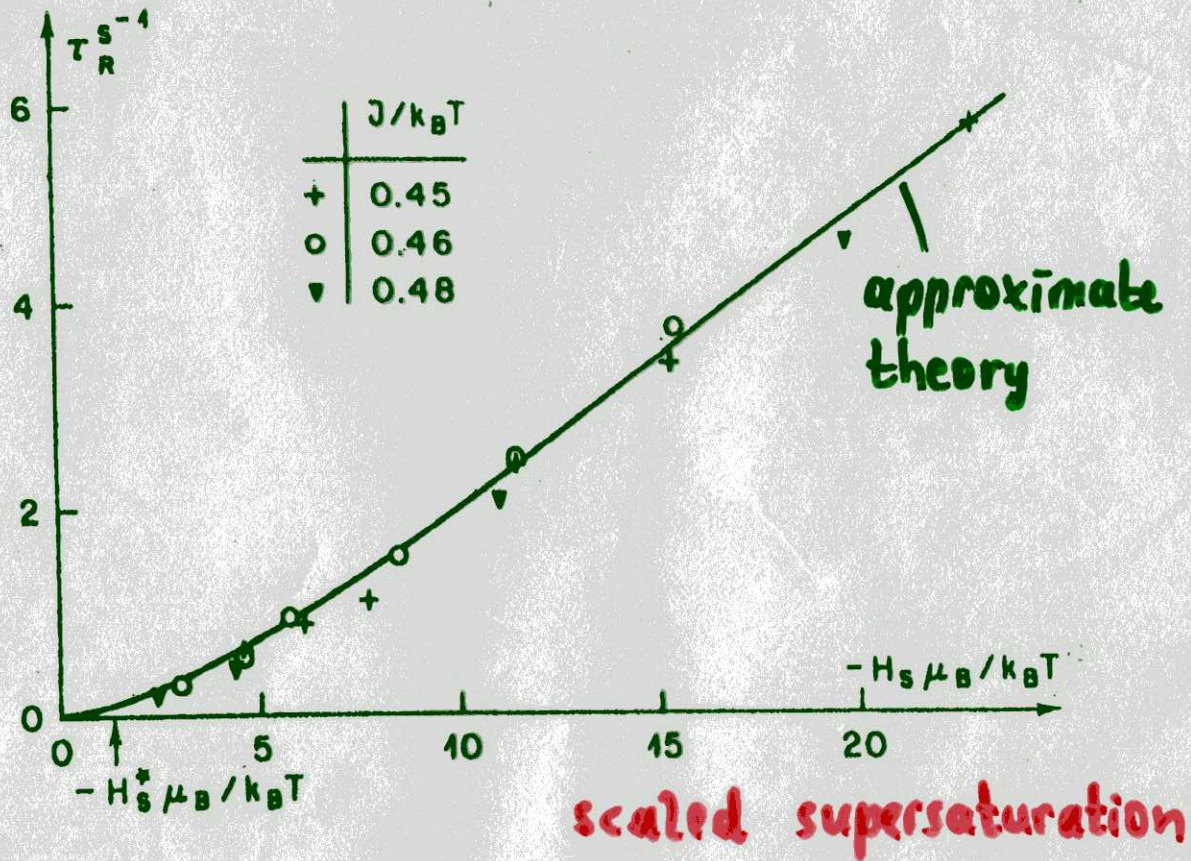


Theory using Monte Carlo estimates for R_l, n_l

$$\frac{\bar{n}_l(t)}{n_l} = \int_0^{\infty} (R_l n_l)^{-1} dl$$

Monte Carlo "time"

Scaled inverse lifetime of metastable states in the $d=2$ LATTICE GAS near T_0



BINDER & MÜLLER-KRUMBHAAR (1974)

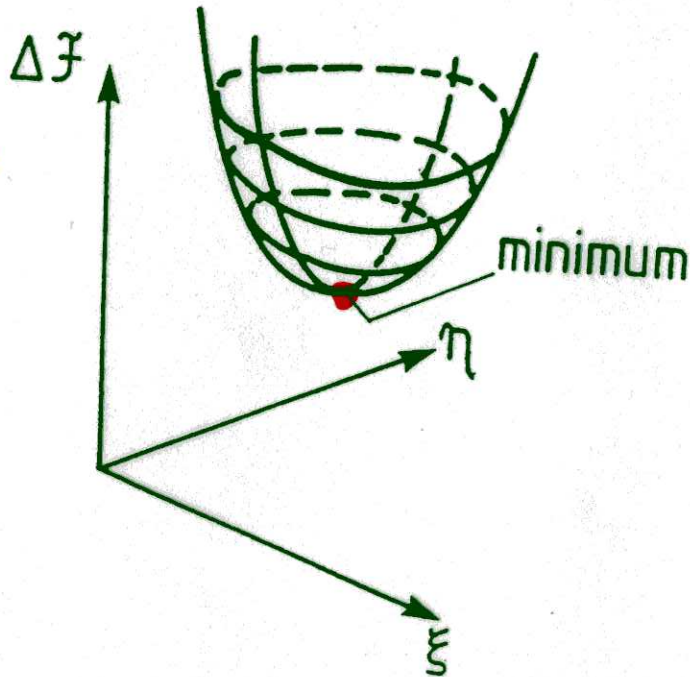
NUCLEATION DYNAMICS

(ii) include more cluster properties than simply the cluster size
 (fluctuations in cluster shape, etc.) $\Rightarrow l \rightarrow \vec{l}$

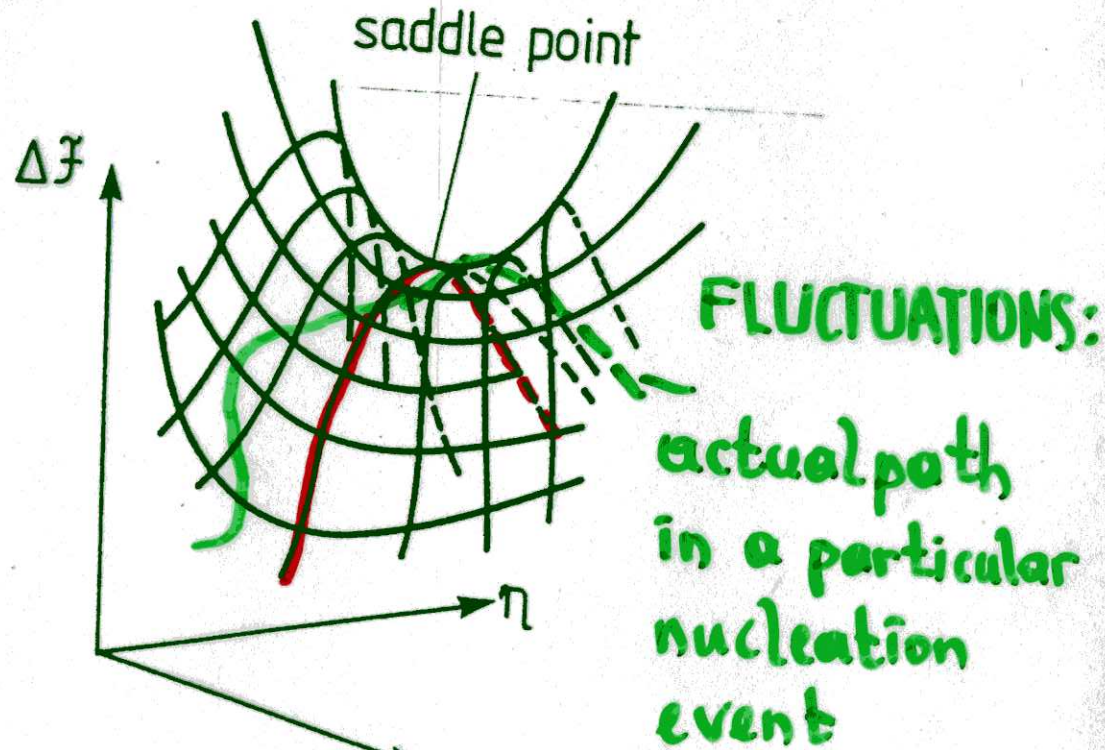
\Rightarrow steady state nucleation \longleftrightarrow currents in electrodynamics

$$\nabla \cdot \vec{j}(\vec{l}) = 0; \quad \vec{E}(\vec{l}) = -\nabla\phi; \quad \phi = -\bar{n}(\vec{l})/n(\vec{l}); \quad \nabla \times \vec{E}(\vec{l}) = 0$$

stable or metastable state



phase space coordinates



DENSITY FUNCTIONAL THEORIES OF NUCLEATION

- calculate ΔF^* , interfacial free energy, droplet density profile, etc., on a unique footing!
- suitable also for small nucleation barriers (near SPINODAL)

simplest version: ∇^2 THEORY vd Waals, Cahn Hilliard, Ginzburg Landau

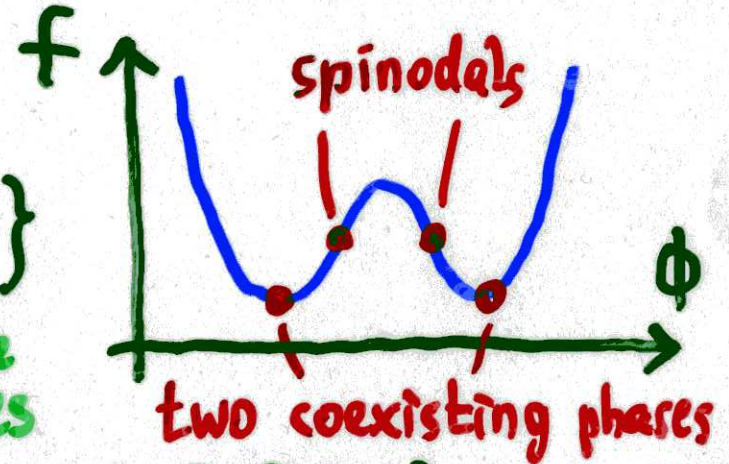
$\phi(\vec{x})$ = order parameter field

FREE ENERGY FUNCTIONAL

$$\mathcal{F}\{\phi(\vec{x})\} = \int d^3x \left\{ f[\phi(\vec{x})] + r^2 k_B T [\nabla\phi(\vec{x})]^2 \right\}$$

(course-grained) free energy density

interaction range between molecules



STATISTICAL MECHANICS: VARIATIONAL PRINCIPLE!

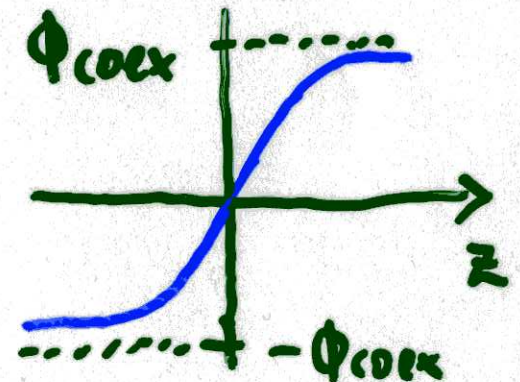
$$\mathcal{F}\{\phi(\vec{x})\} \rightarrow \text{Min}$$

\Rightarrow Ginzburg-Landau differential equation

homogeneous solution ($\nabla\phi \equiv 0$) \Rightarrow equilibrium

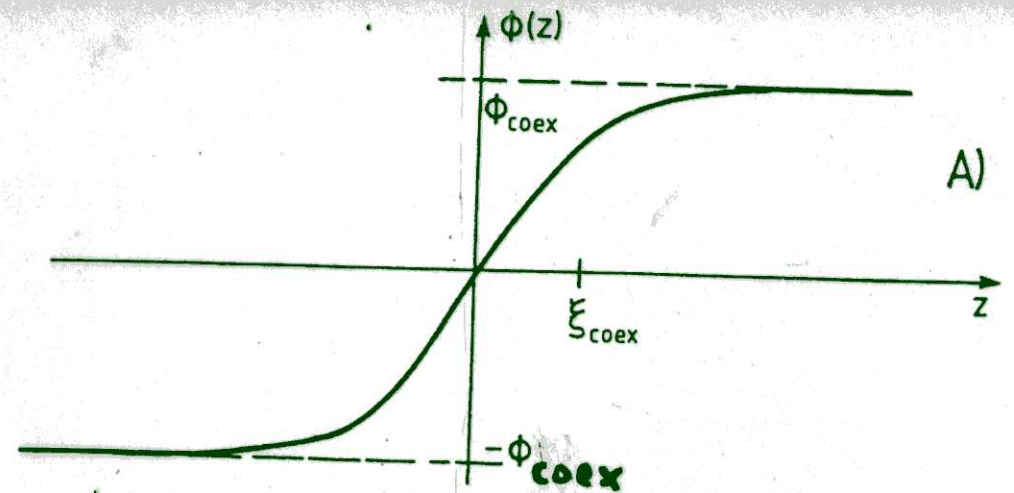
inhomogeneous solution VIA BOUNDARY CONDITIONS!

e.g. $\phi(z \rightarrow -\infty) = -\phi_{\text{coex}}$, $\phi(z \rightarrow +\infty) = +\phi_{\text{coex}}$

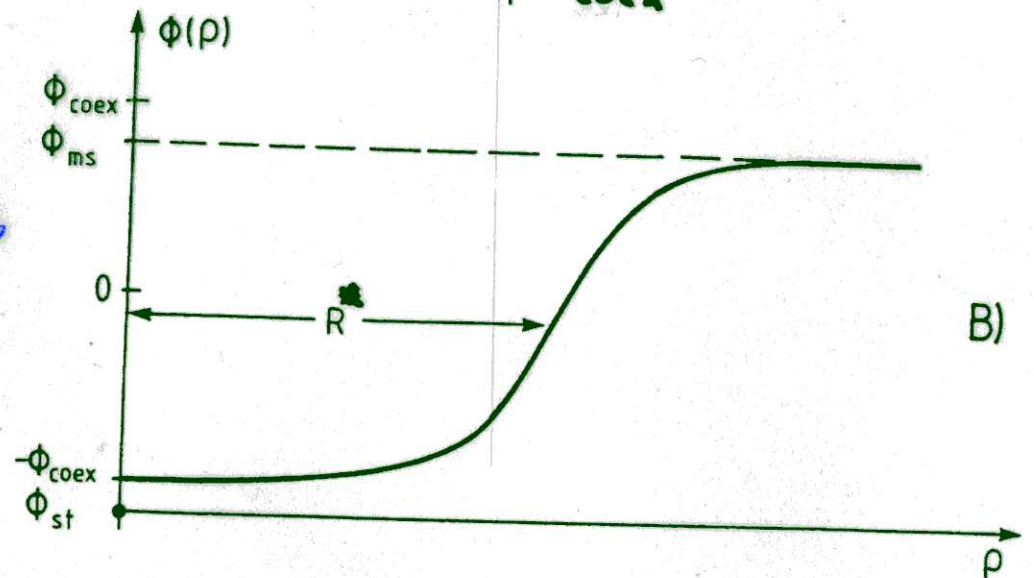


ORDER PARAMETER PROFILES

across flat planar interface

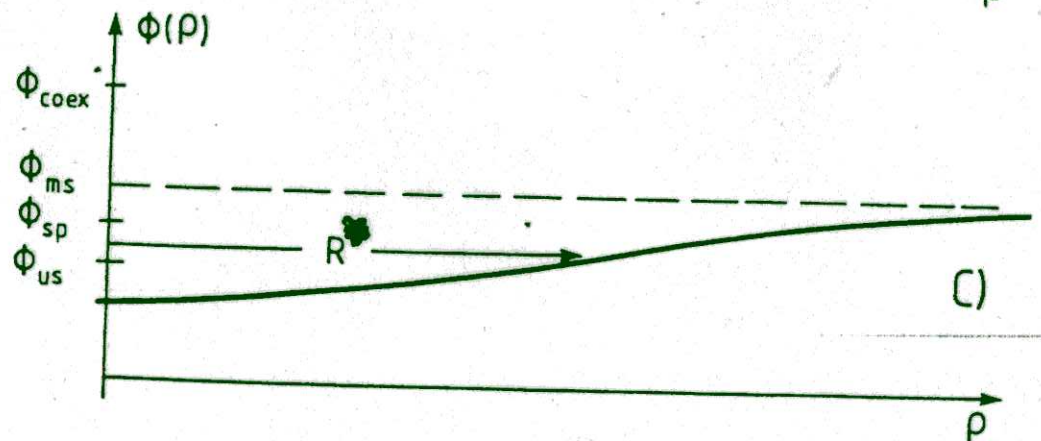


radial profile across critical droplet near coexistence curve



droplet near spinodal

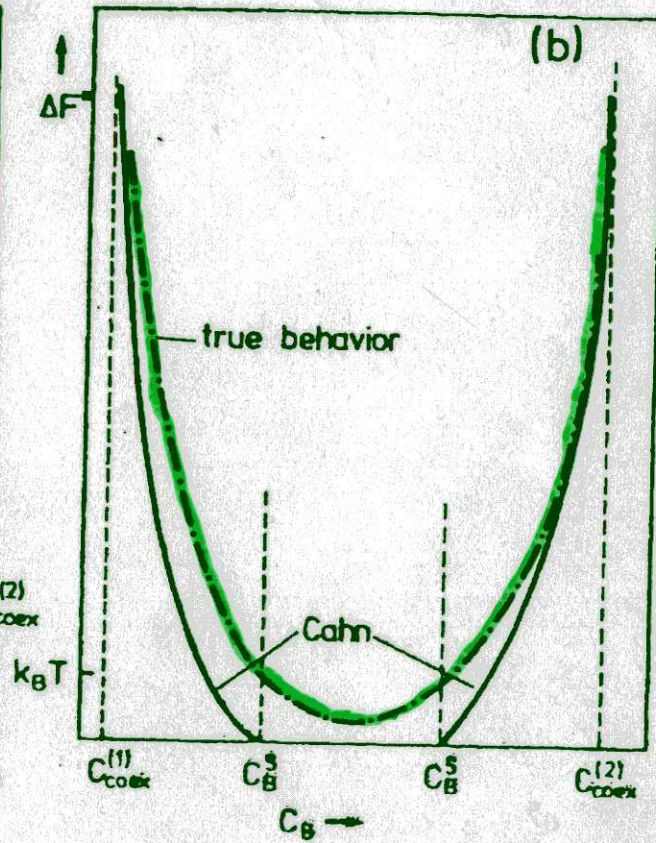
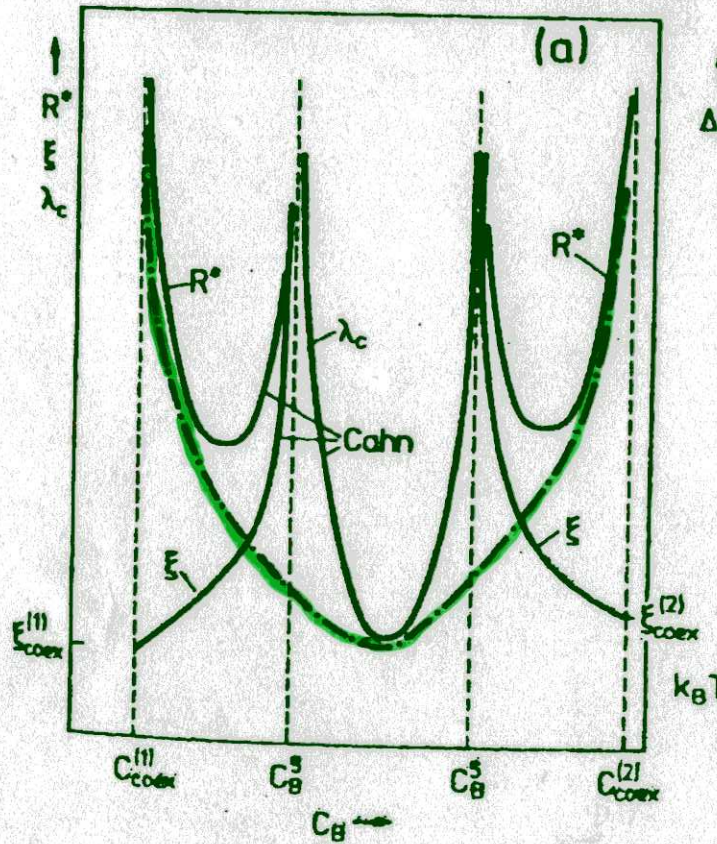
$R^3 \rightarrow \infty$ near spinodal!



Cahn-Hilliard theory

characteristic lengths

free energy barrier



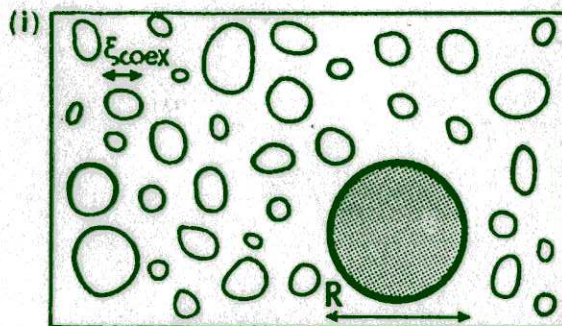
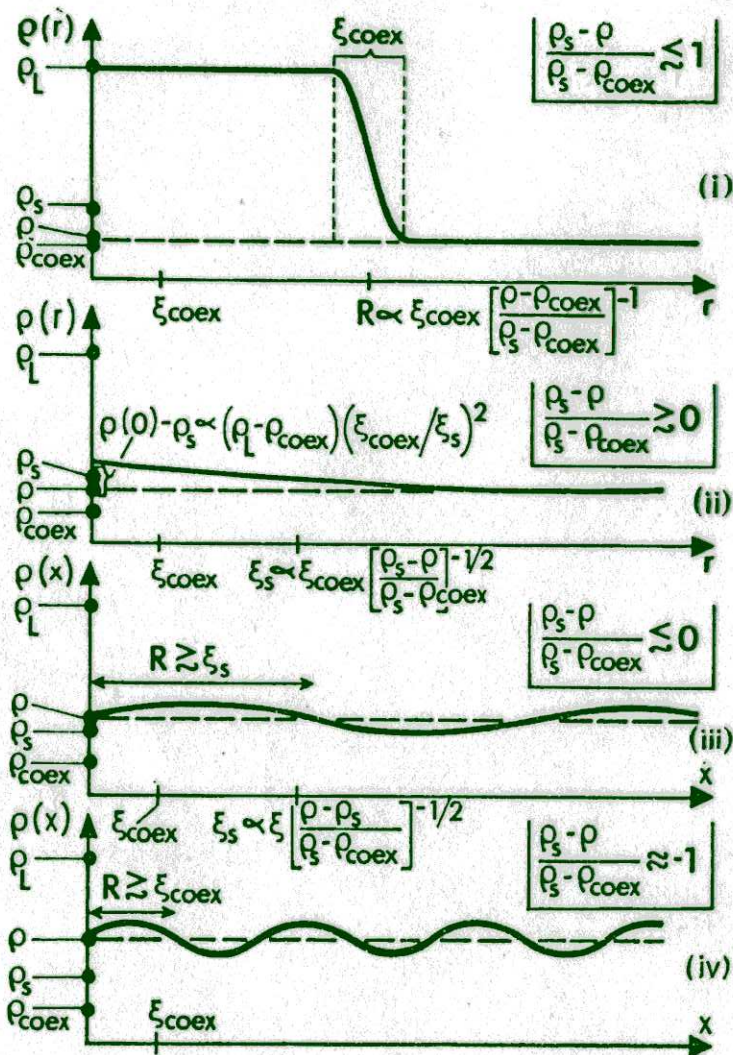
Cahn-Hilliard theory

Fig. 2

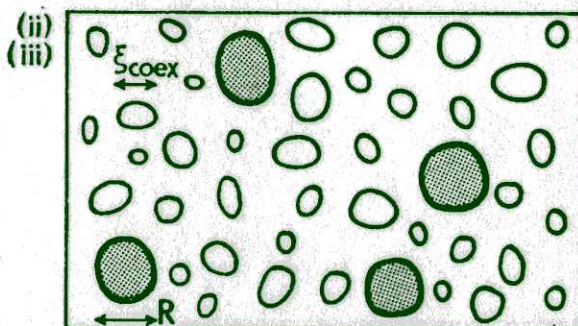
true behavior

nucleation

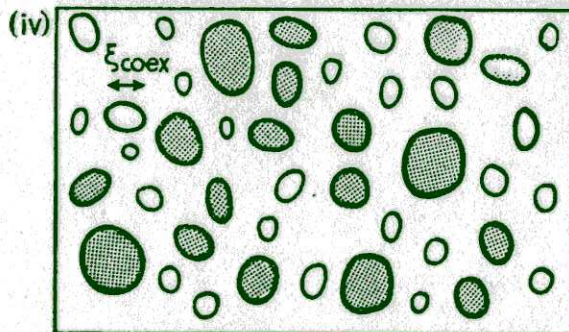
spinodal decomposition



near coexistence curve



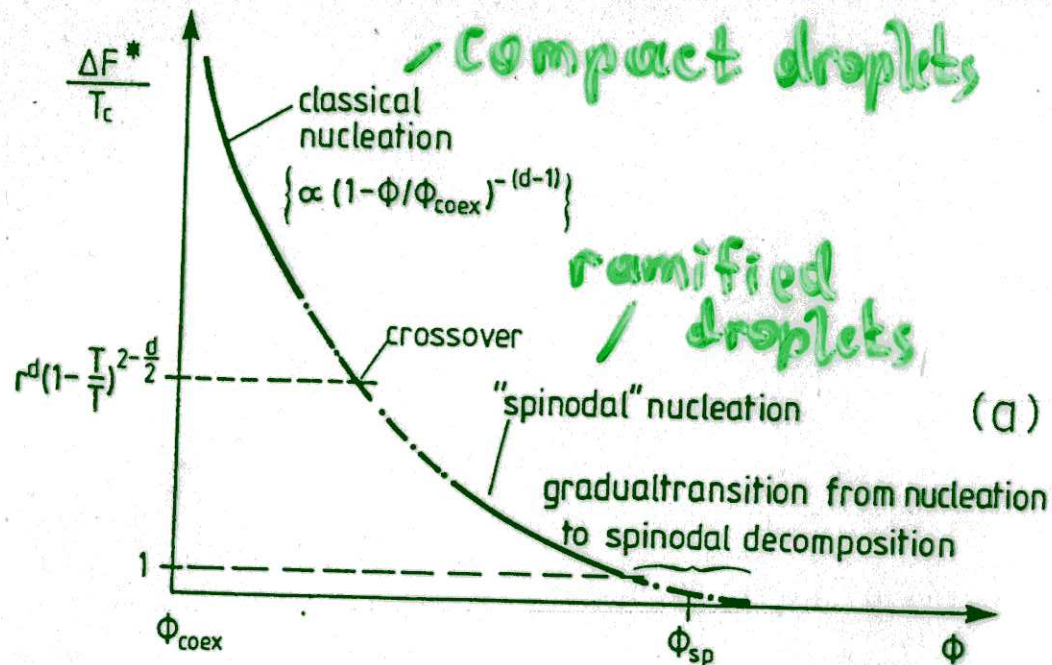
near spinodal



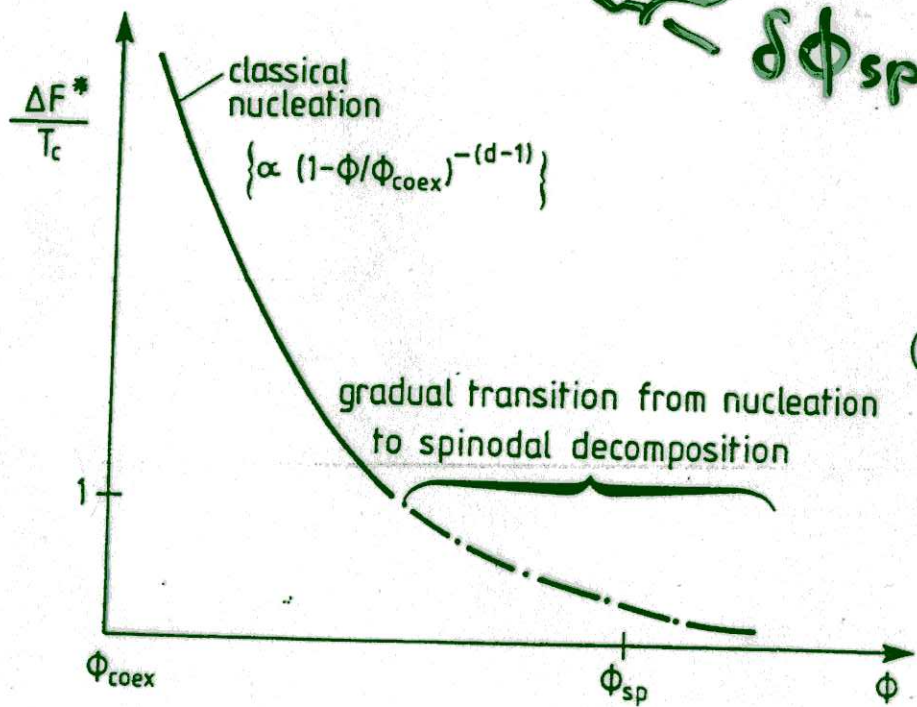
inside the spinodal

GINZBURG CRITERION

for nucleation barriers



(a) large range r of interactions



(b)

short range r of interactions

$$\delta\phi_{\text{sp}}/\phi_{\text{sp}} \propto \left[r^d \left(1 - \frac{T}{T_c}\right)^{\frac{4-d}{2}} \right]^{-\frac{2}{6-d}}$$

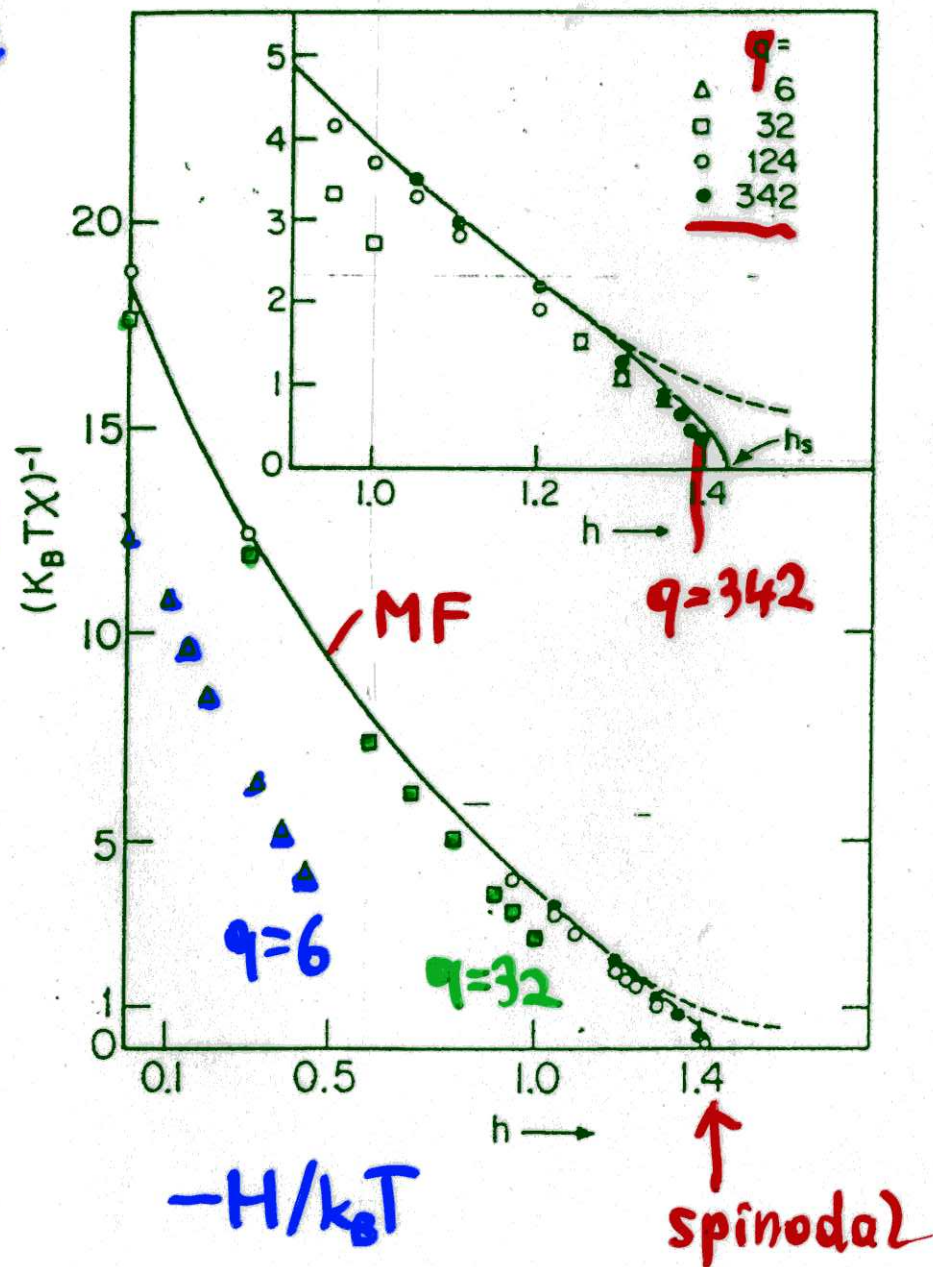
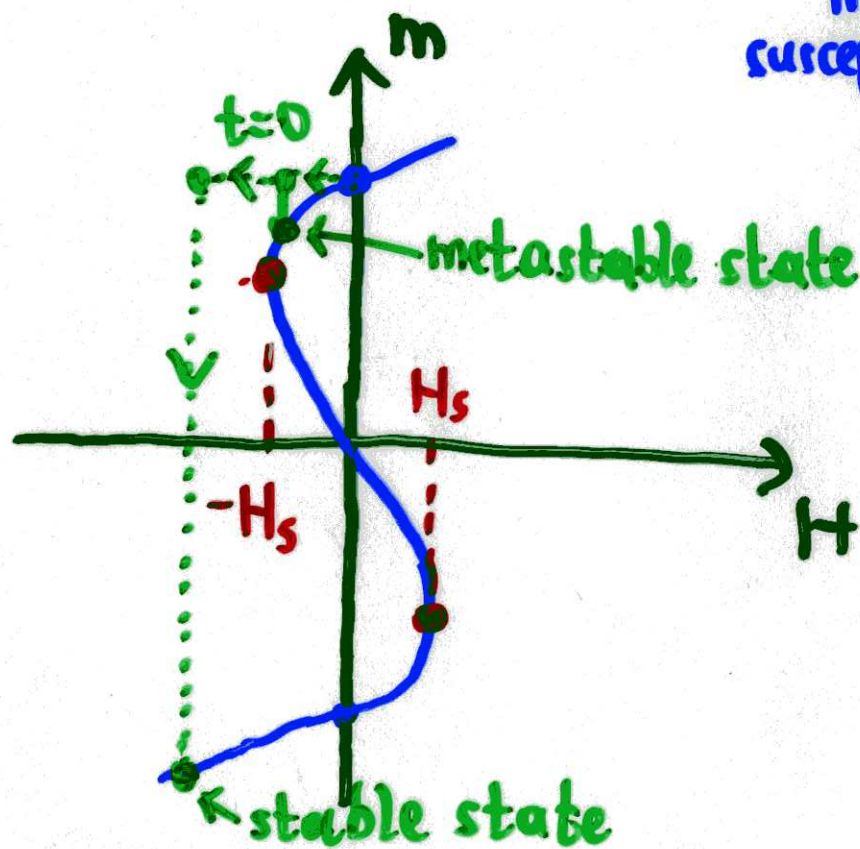
$$\propto \left[r^3 \left(1 - \frac{T}{T_c}\right)^{1/2} \right]^{-2/3} \quad (d=3)$$

SPINODALS exist in the MEAN FIELD LIMIT

evidence from the Ising ferromagnet
at $T/T_c^{MF} = 4/9$ where in $d=3$

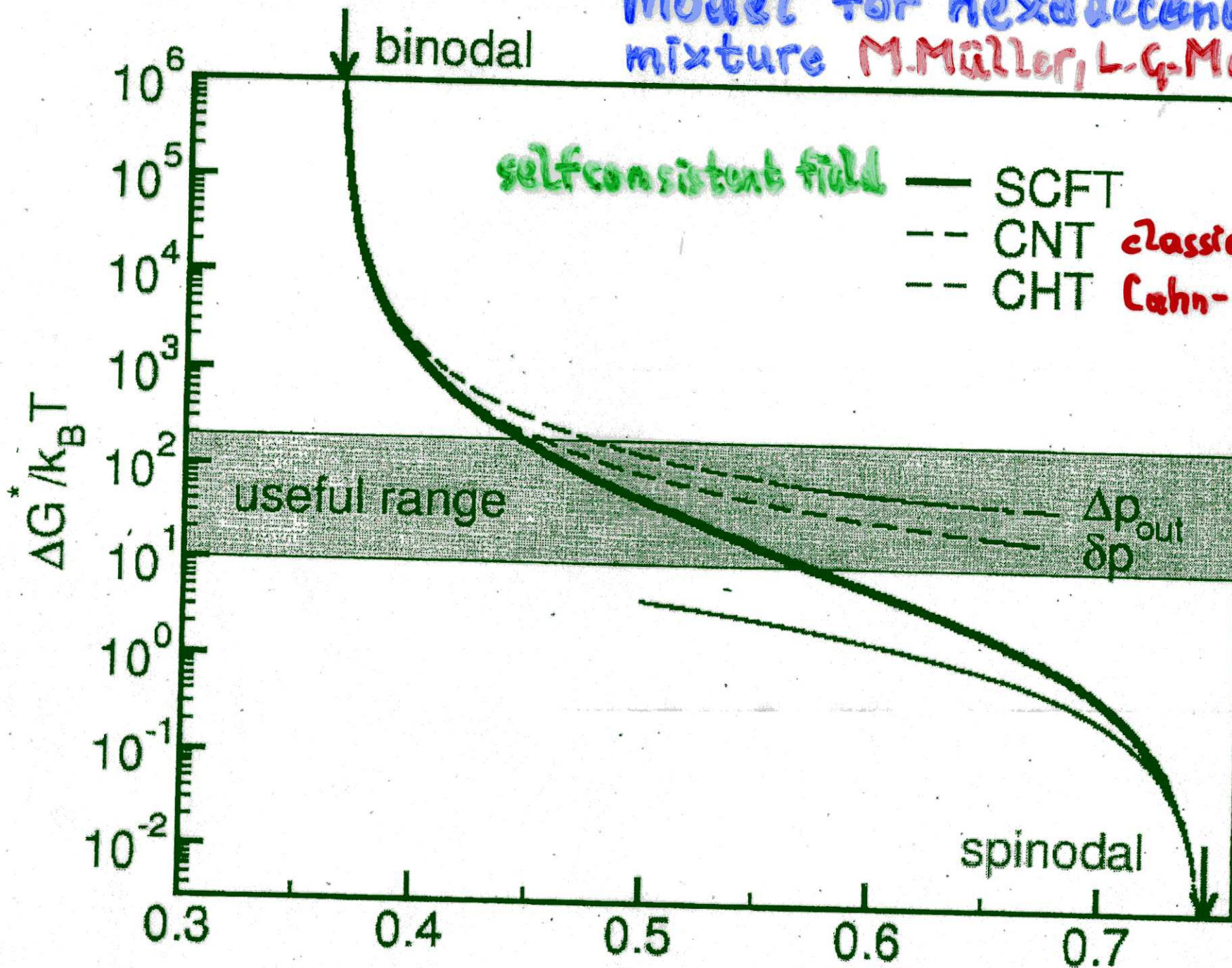
each spin interacts with q neighbors

HEERMANN et al. (1982)



model for hexadecane-CO₂ mixture M. Müller, L-G. MacDowell,

F. Virnau, K.B. (2002)



selfconsistent field

— SCFT

-- CNT

-.- CHT

classical nucleation

Cahn-Hilliard

theory

useful range

$\frac{\Delta p_{out}}{\delta p}$

spinodal

$\rho \epsilon^3/k_B T = 0.1, k_B T/\epsilon = 0.75$

x mole fraction of CO₂

SIMULATION GEOMETRY : NVT ensemble

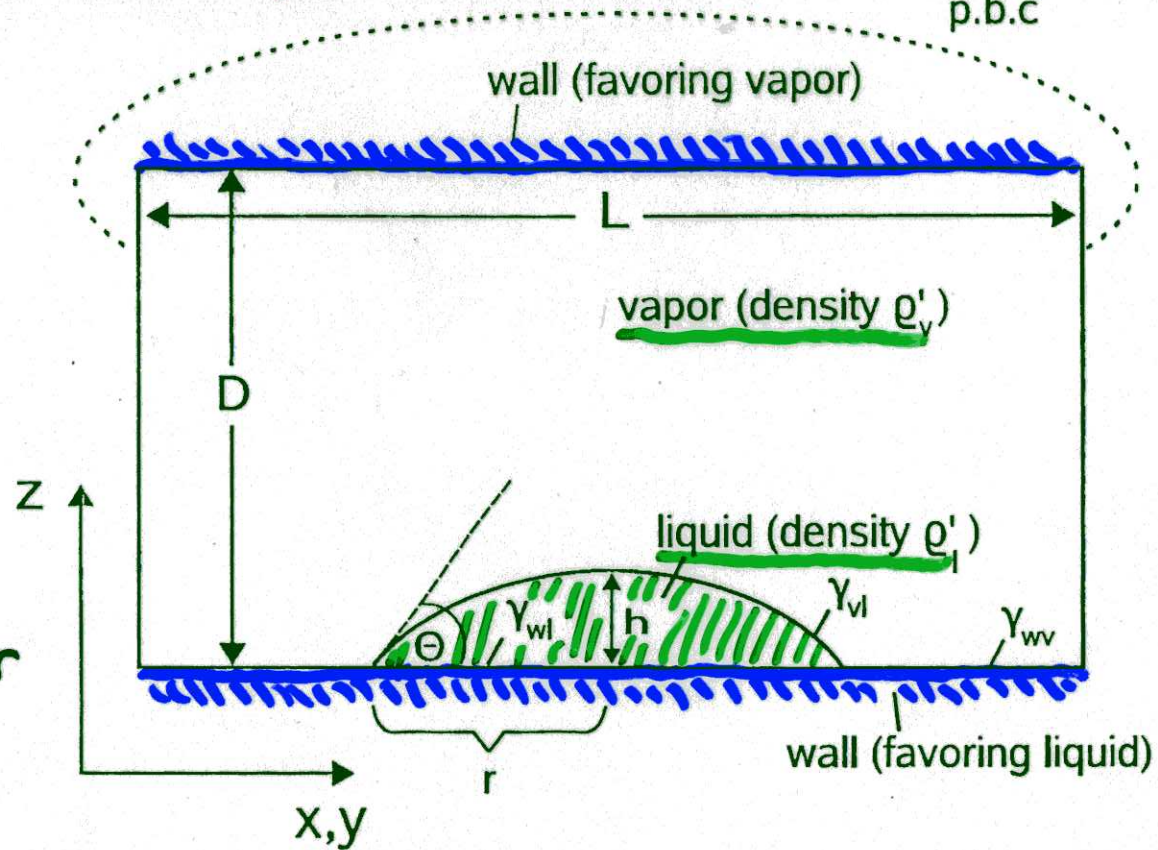
p.b.c

interfacial
tensions:

γ_{vl} vapor-liq.

γ_{wl} wall-liq.

γ_{wv} wall-vapor



$$V = L^2 D$$

density

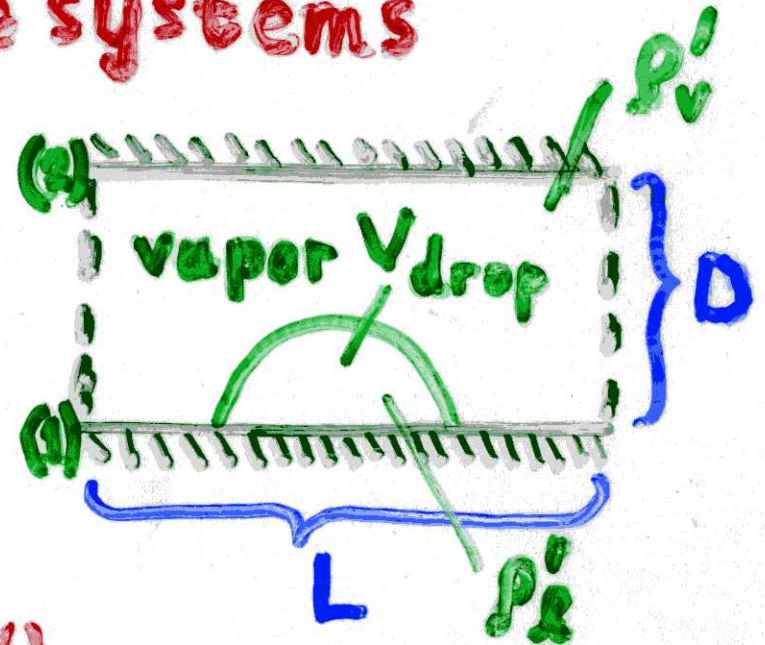
$$\rho = N/V$$

- $T < T_c$: vapor-liquid coexistence for $\rho_v < \rho < \rho_l$
 - finite system; incomplete wetting of lower wall
- coexisting densities
- ⇒ STABLE WALL-ATTACHED DROPLET OF FINITE SIZE
- $\rho_v' > \rho_v$; $\rho_l' > \rho_l$ (finite size effects!)

LEVER RULE for finite systems

$$V = L^2 D = V_v + V_{\text{drop}}, \quad V_{\text{int}} \equiv 0$$

$$N = N_v + N_{\text{drop}}, \quad N_{\text{int}} \equiv 0$$



$$\Rightarrow \rho = \frac{N}{V} = \rho'_v + (\rho'_d - \rho'_v) (V_{\text{drop}}/V)$$

$$\rho'_d = N_{\text{drop}}/V_{\text{drop}}$$

additivity of subsystems

$$g(p) = g(p'_v) + (\gamma_{vw}^{(1)} + \gamma_{vw}^{(2)})/D + V_{\text{drop}} [g(p'_d) - g(p'_v)]/V$$

$$+ F_s(R, \Theta)/V$$

=====

external walls

$\equiv 0$ (lattice gas)

$$N'_v = N_v + \rho'_v V_{\text{drop}}$$

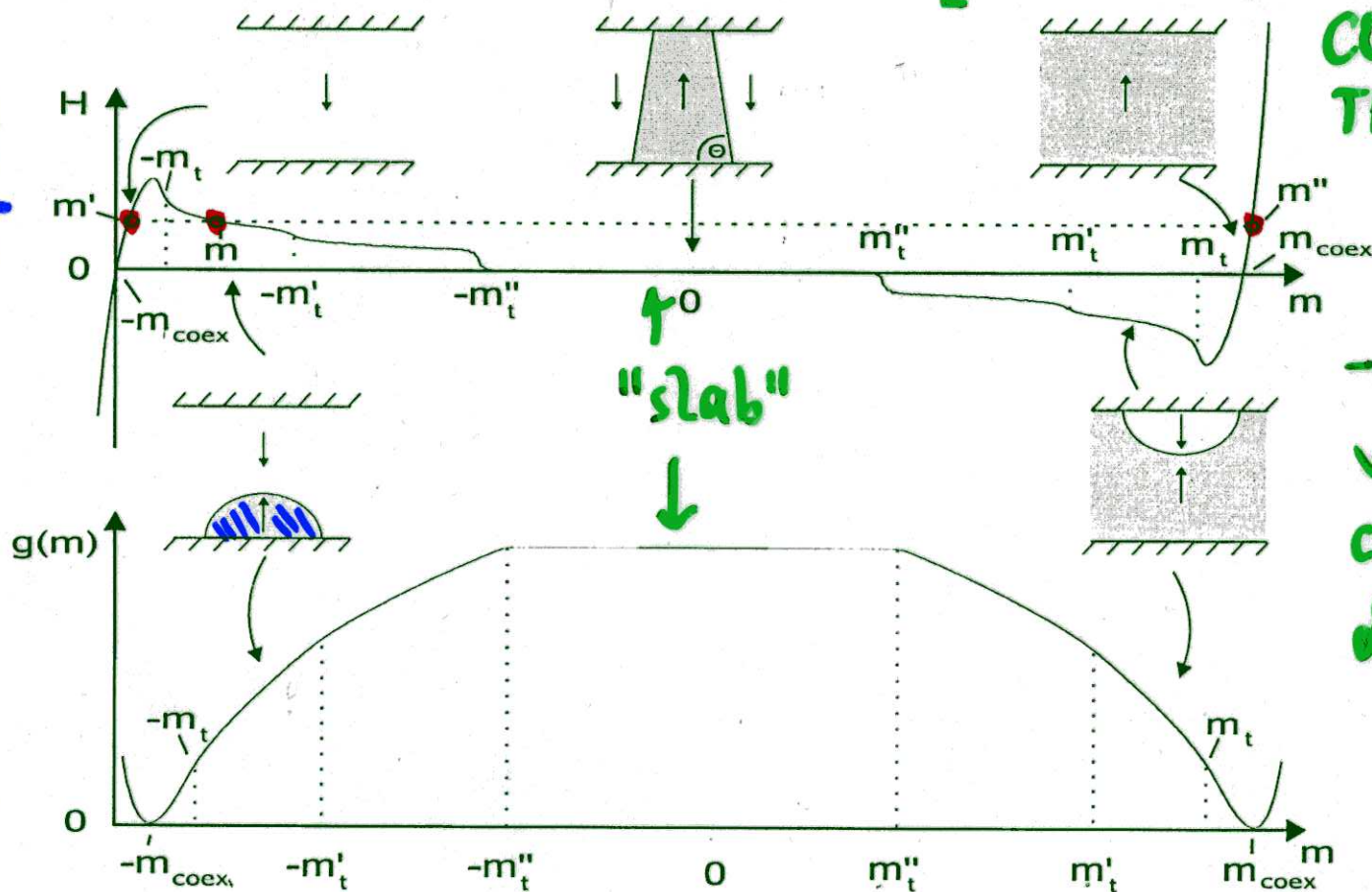
$$\rho'_v = N'_v/V$$

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

$-m < m < -m_{t, \text{coex}}$: vapor; $-m_t < m < -m'_t$: vapor + sphere-cap droplet

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

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



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

density $g(m)$
of the
thermodynamic
potential

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

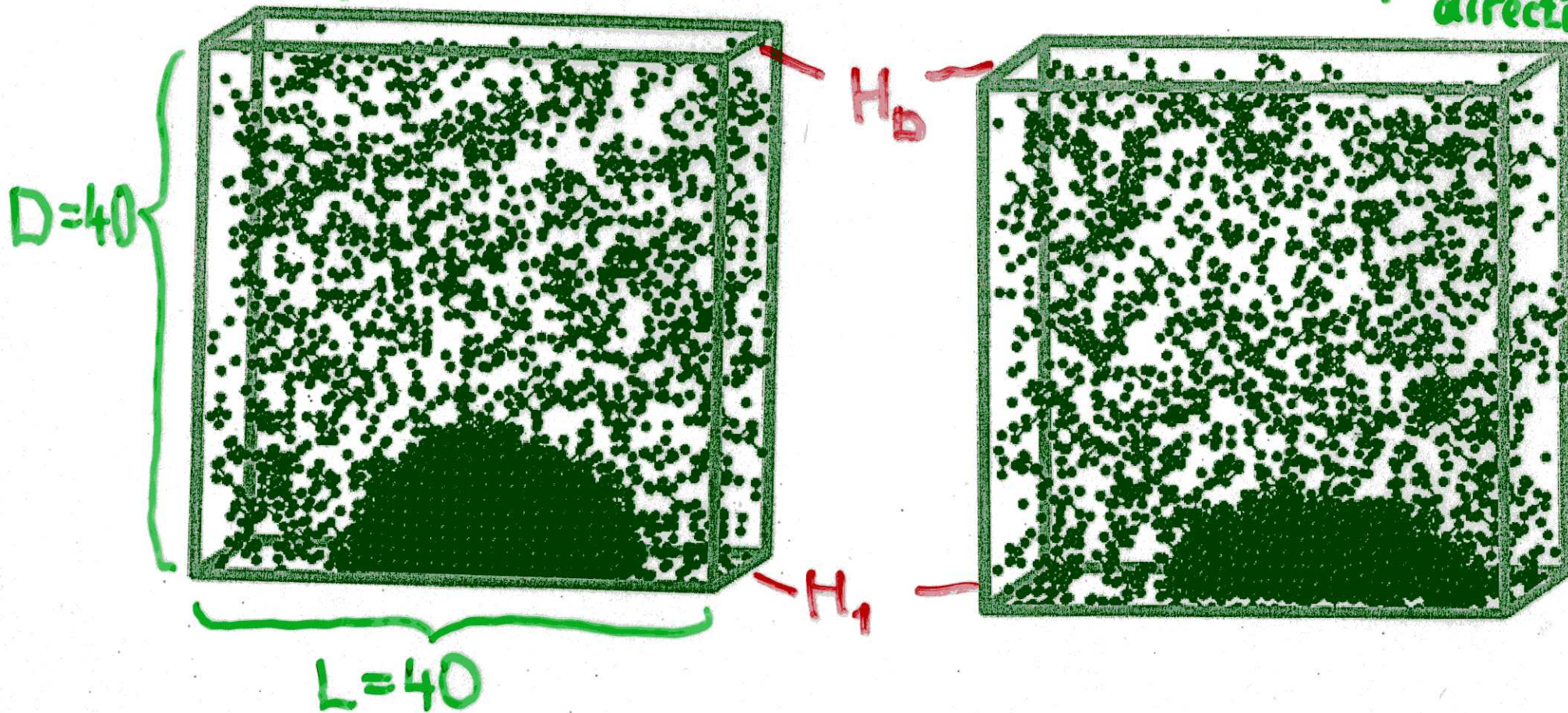
transitions at $\pm m_t, \pm m'_t, \pm m''_t$ sharp only for $L \rightarrow \infty$

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: $H_D = -H_L$

$H_L = 0 = \text{contact angle } \Theta = 90^\circ$

$$H_L = 0.4 J$$

$$\Rightarrow \Theta \approx 56^\circ$$

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

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

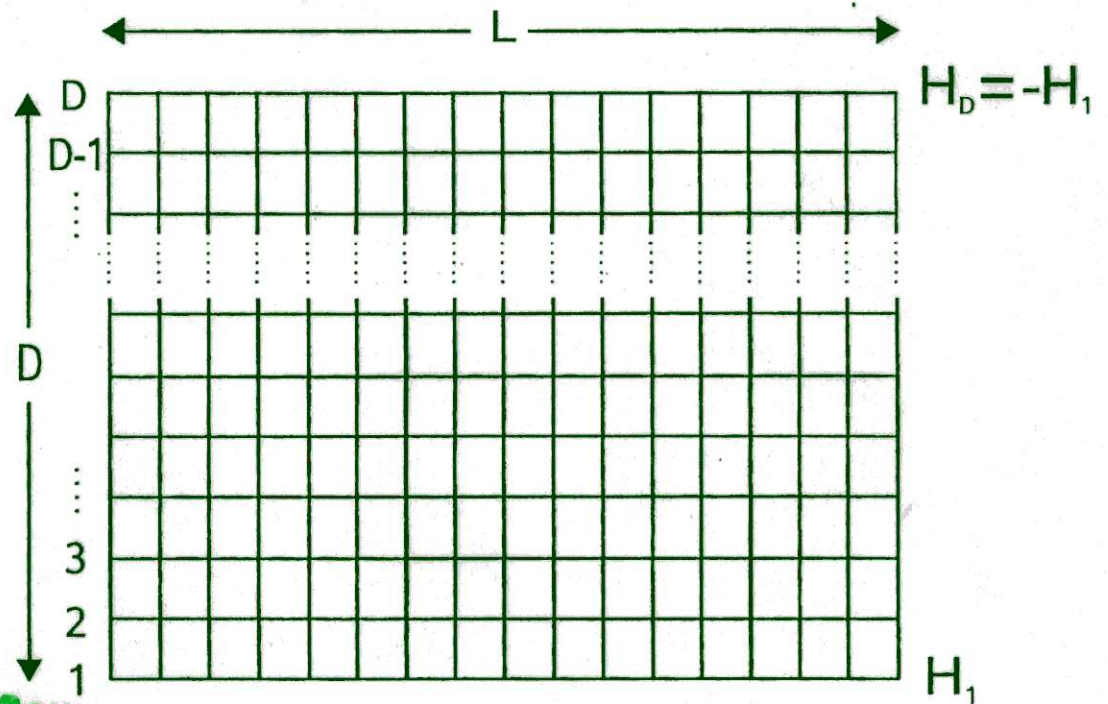
$$\rho = (1 + \langle S_i \rangle_T) / 2$$

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

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

m_{coex} = spontaneous magnetization

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



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

Phase coexistence in finite Ising systems

"bulk" = p.b.c in all 3 directions,
no walls (full spherical droplet rather than sphere cap!)

Note:

$$\lim_{L \rightarrow \infty} g(m) = 0, \quad -m_{\text{coex}} < m < +m_{\text{coex}}$$

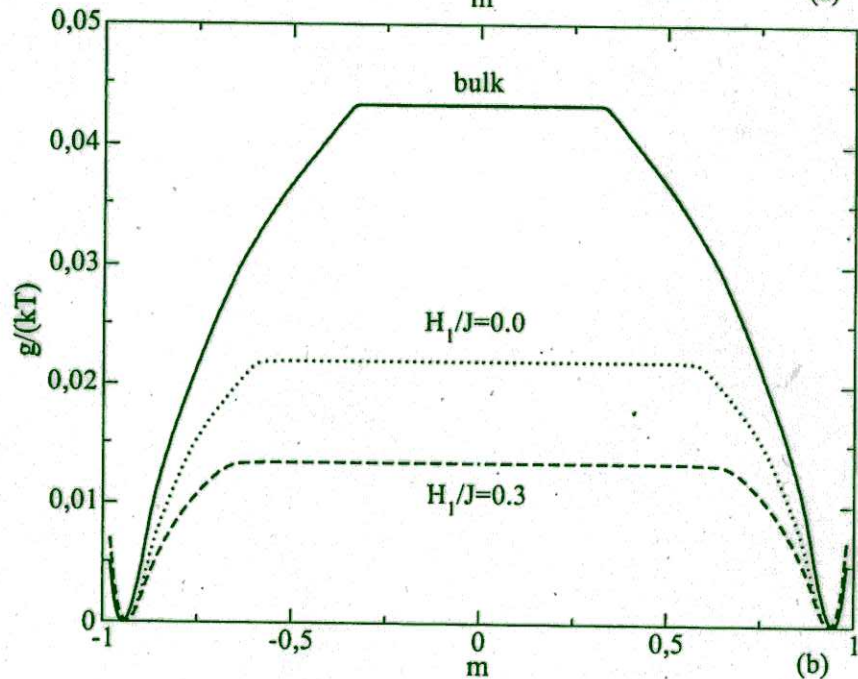
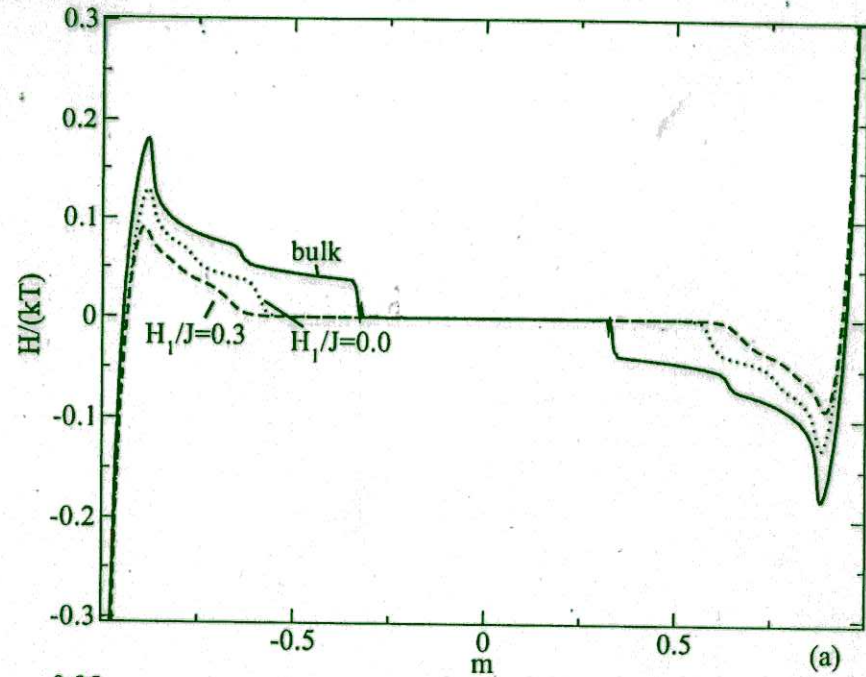
but

$$\lim_{L \rightarrow \infty} G(m) = \infty, \quad -m_{\text{coex}} < m < +m_{\text{coex}}$$

$$G(m) = L^2 D g(m)$$

surface effects !

$$L=D=20, \quad k_B T/J=3.0$$



ESTIMATION OF THE CONTACT ANGLE: ISING MODEL

use YOUNG's equation!

Hasenbusch + Pinn (1993)

$L \rightarrow \infty$, 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):

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

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

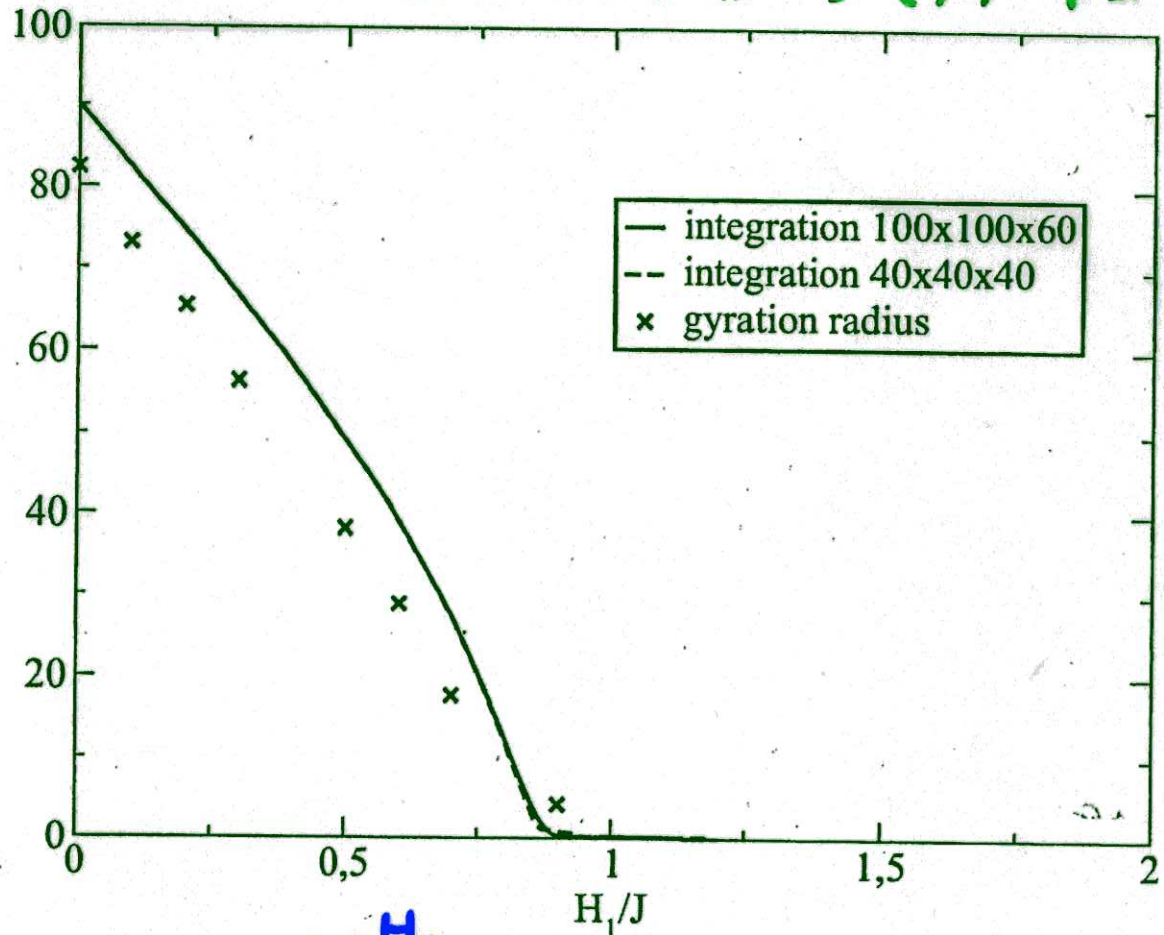
Ising symmetry:

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

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

$$m_1 = -(\partial f_s(T, H, H_1) / \partial H_1)_T \Rightarrow \cos \theta = \left\{ \int_0^{H_1} [m_D(H'_1) - m_1(H'_1)] dH'_1 \right\} / \gamma_{ve}$$

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



Estimation of the chemical potential of a lattice gas in a simulation at constant density:

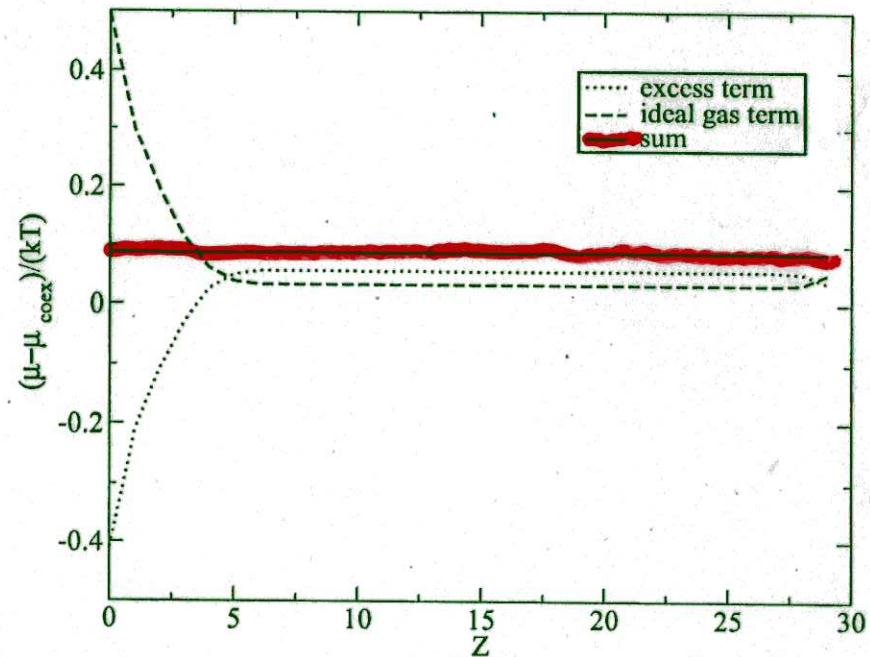
ADAPTATION OF WIDOM'S PARTICLE INSERTION METHOD TO THE LATTICE: VIRTUAL SPIN FLIPS

$\Delta E_{M \pm 2}$ = energy to flip a spin from the magnetization M to $M \pm 2$

$$H = \frac{k_B T}{2} \ln \left(\frac{2V}{V-M-2} \right) \quad \text{ideal gas term}$$

$$+ \frac{k_B T}{2} \ln \left(\frac{1}{V} \sum_{M_{\pm}} \exp(-\Delta E_{M \pm 2} / k_B T) \right) \quad \text{excess term}$$

$\sum_{M_{\pm}}$ = sum over all lattice sites with $S_i = -1$



↑ wall

Chemical potential strictly constant in inhomogeneous system

Chemical potential as function of the density of the lattice gas IN THE BULK

$$k_B T / J = 3.0$$

$L \rightarrow \infty$:

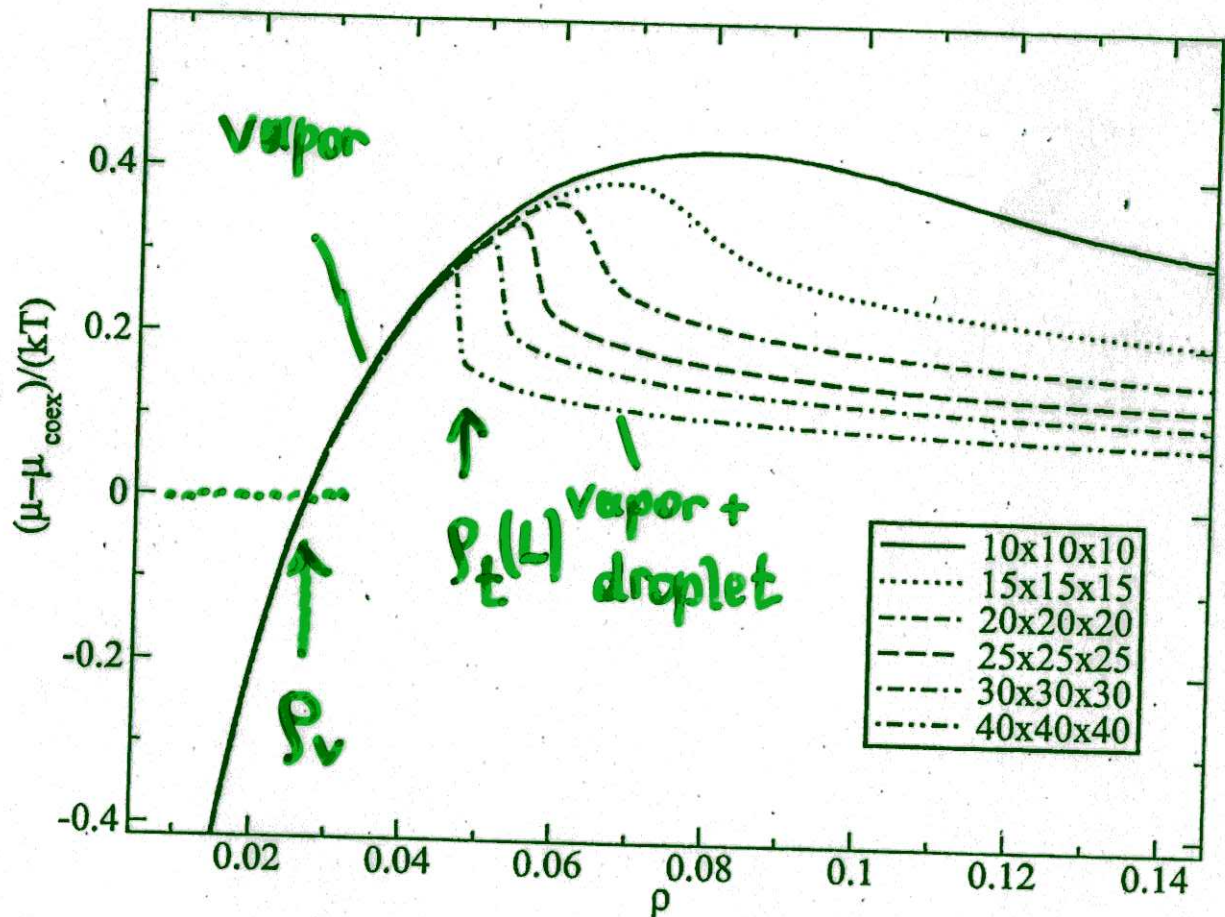
droplet-evaporation
condensation transition
becomes sharp

BUT

$$\rho_t(L) \xrightarrow{L \rightarrow \infty} \rho_v$$

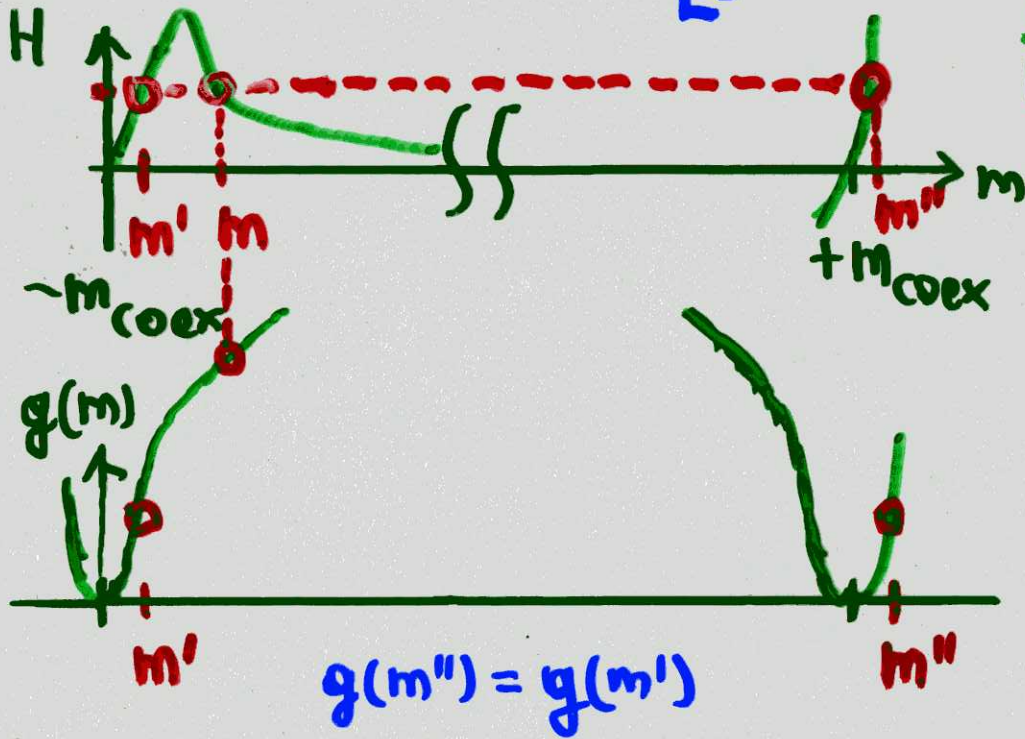
$$\rho_v < \rho < \rho_t(L):$$

$\mu(\rho)$ independent
of L !



Monte Carlo estimation of the surface free energy of droplets IN THE BULK

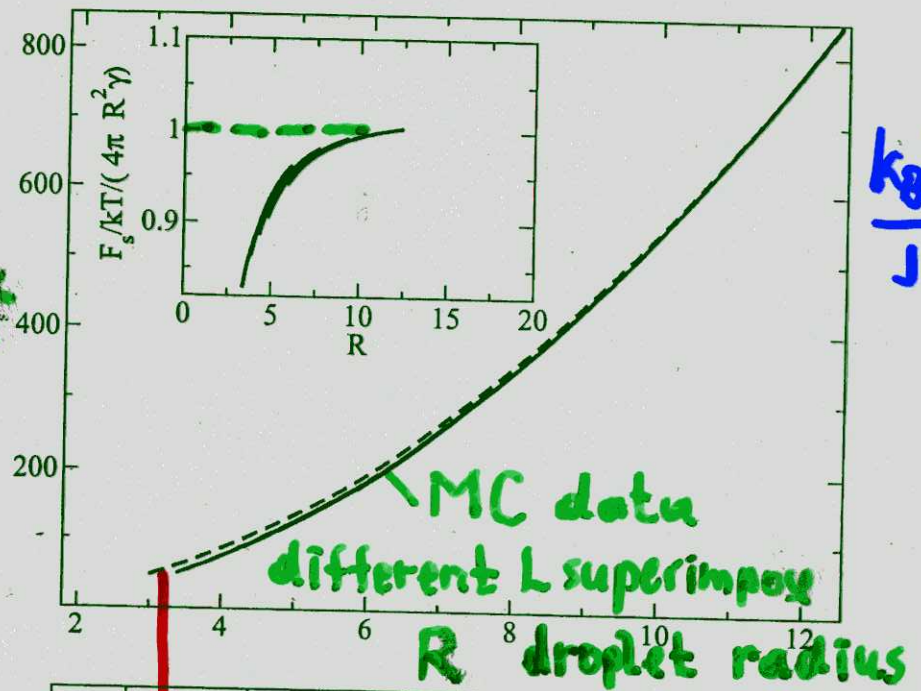
$$g(m) = g(m') + \frac{F_s/k_B T}{L^3}$$



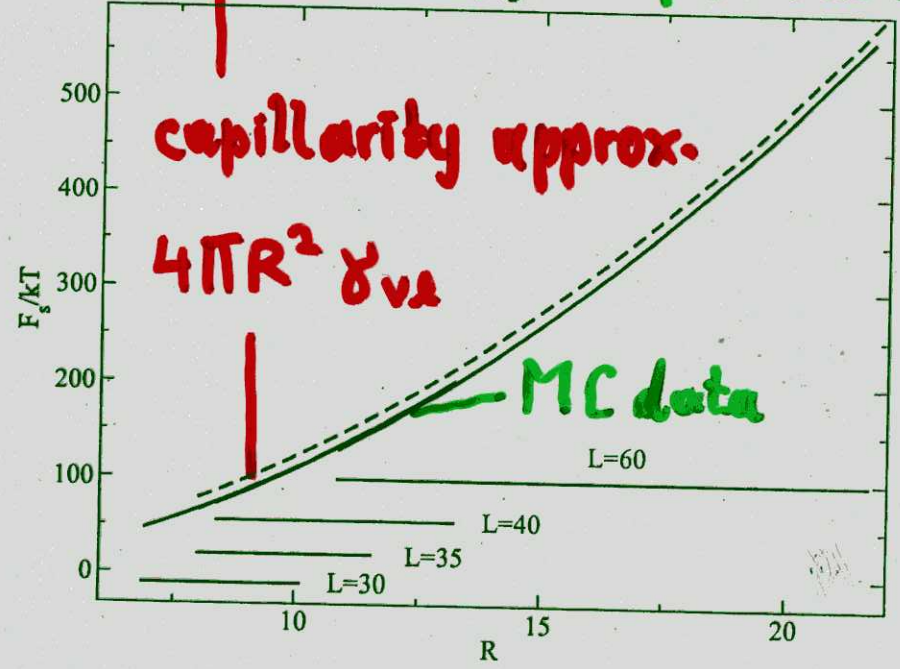
$$m'' - m' = 2m_{coex} \frac{4\pi R^3/3}{L^3}$$

magnetization excess due to droplet: LEVER RULE!

$\frac{F_s}{k_B T}$

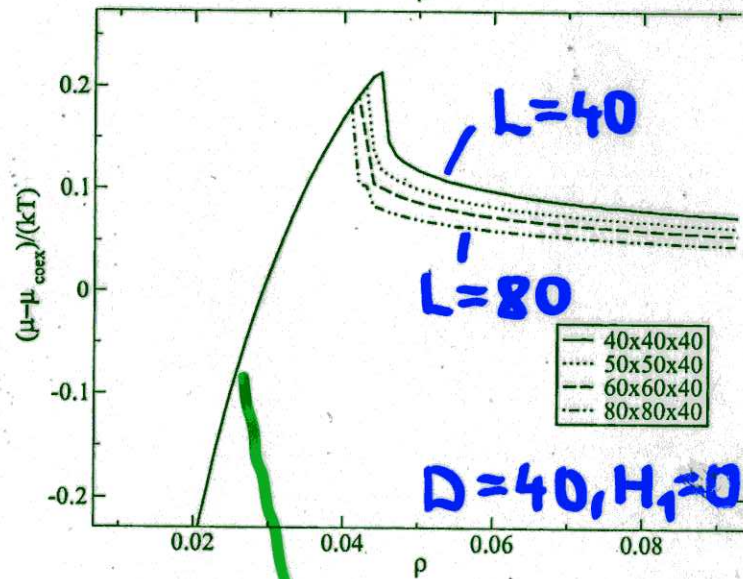
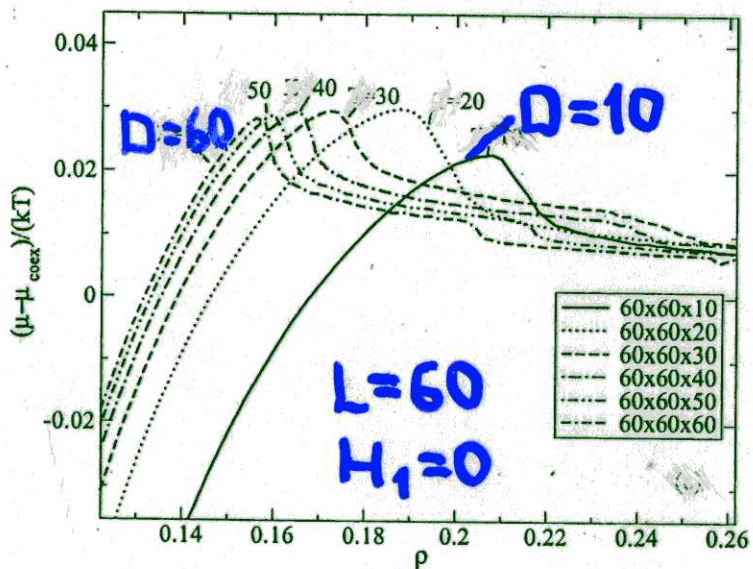
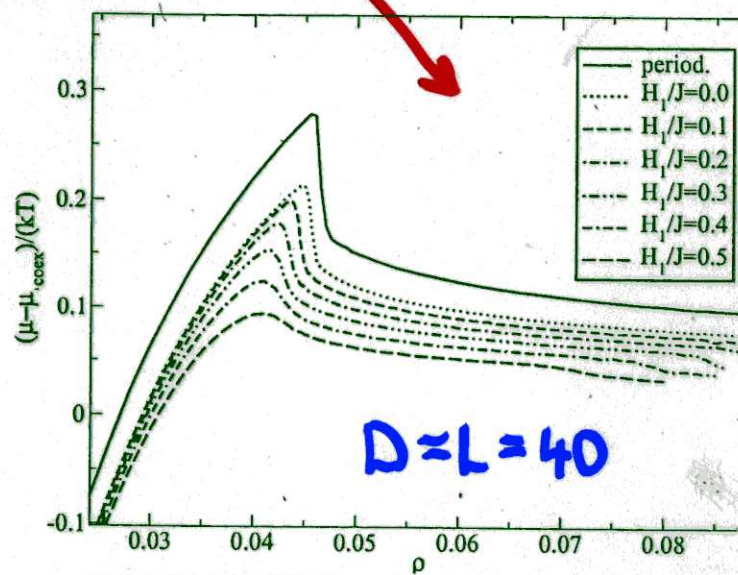
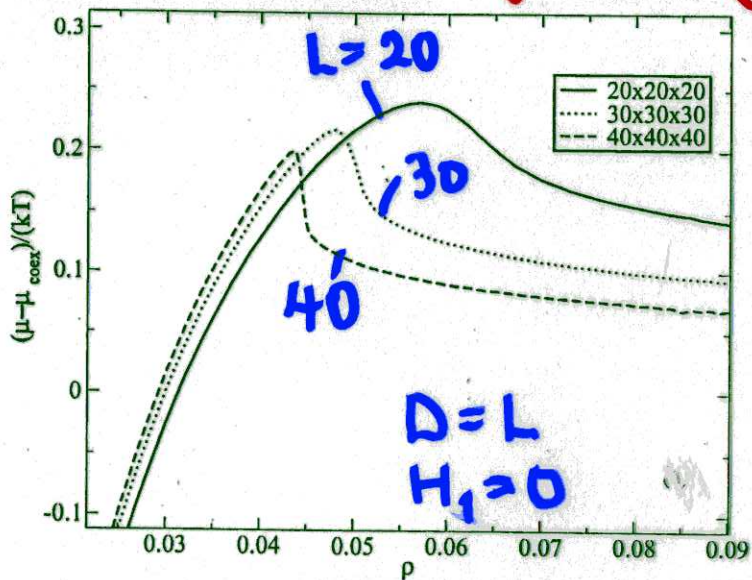


$$\frac{k_B T}{J} = 3.0$$



$$\frac{k_B T}{J} = 4.0$$

excess chemical potential $(\mu - \mu_{\text{coex}})/k_B T$ versus density ρ in different $L \times L \times D$ systems (for various H_1)



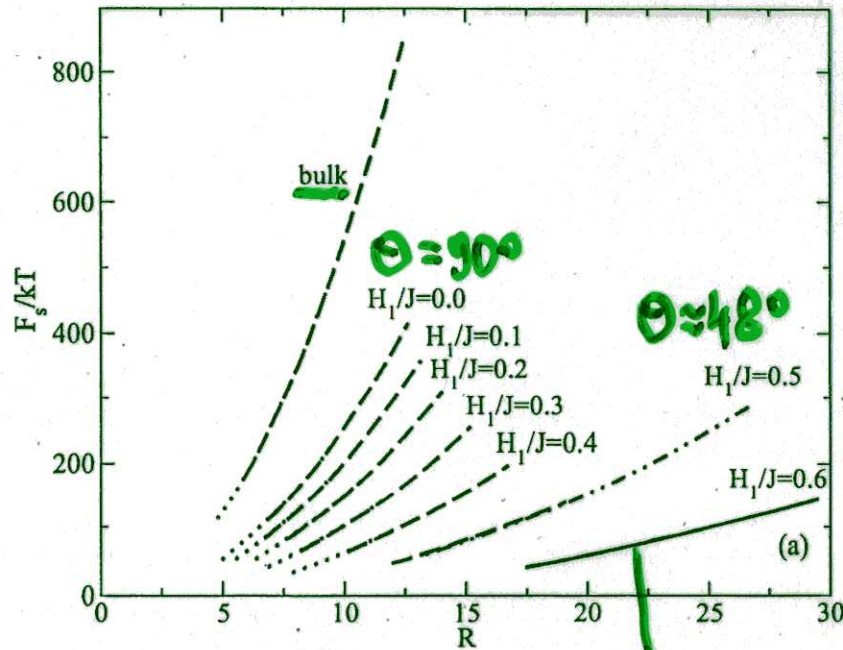
vapor branch:
 INDEPENDENT of L as it should be

Surface excess free energy of wall-attached droplets

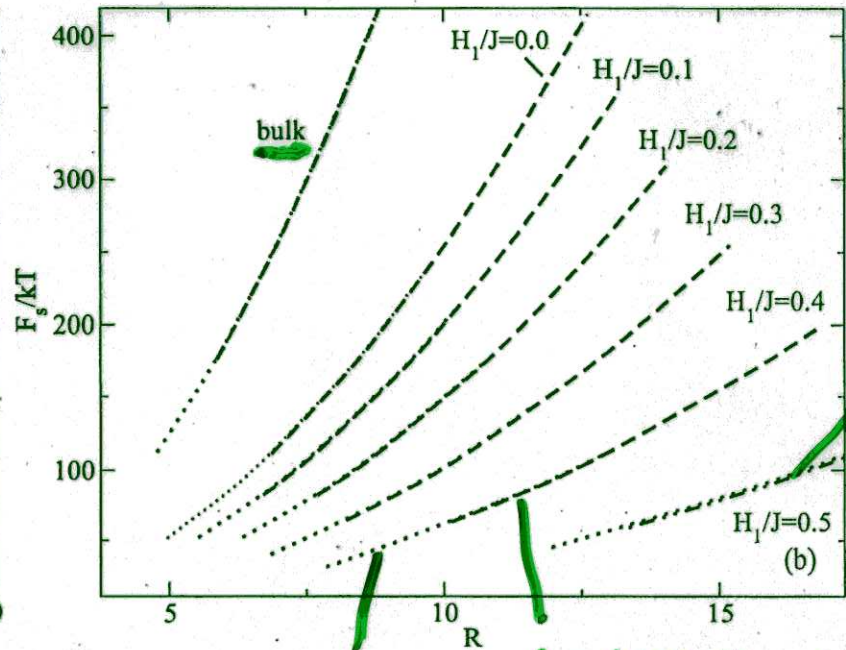
$F_s(R, \theta) / k_B T$ vs. droplet radius R

lever rule: $\rho = \rho'_v + (\rho'_s - \rho'_v)(V_{\text{drop}} / V)$

$V = L^2 D$



$L=50$



$L=30, D=30$
 $L=40, D=40$

ρ, ρ'_v, ρ'_s MEASURED
in the simulation

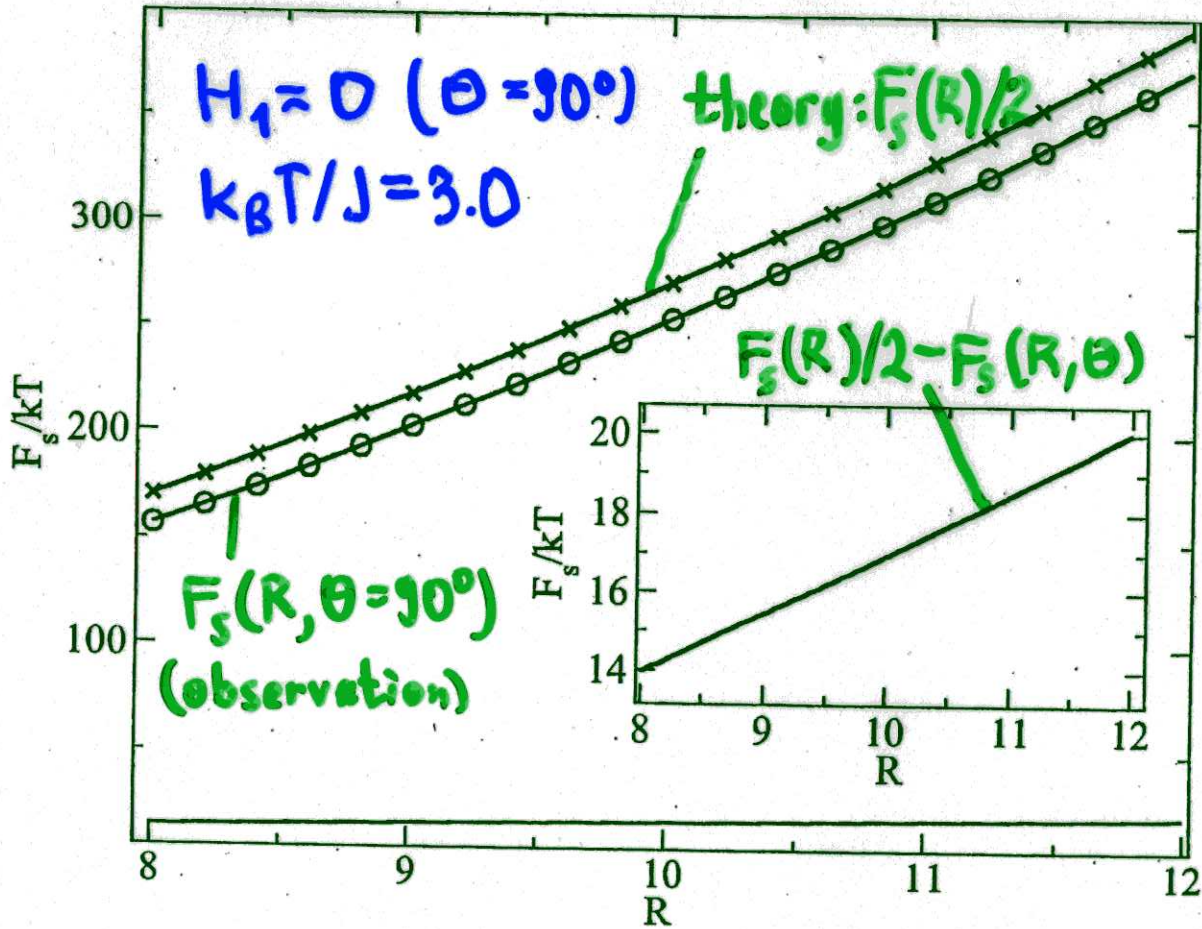
different linear dimensions yield identical results for $F_s(R, \theta) / k_B T$, as it should be

$\Rightarrow V_{\text{drop}}$

μ measured $\Rightarrow R = \gamma_{v,s} / (m_{\text{coex}} H)$

$g(g)$ measured $\Rightarrow F_s$

SURFACE FREE ENERGY versus DROPLET RADIUS



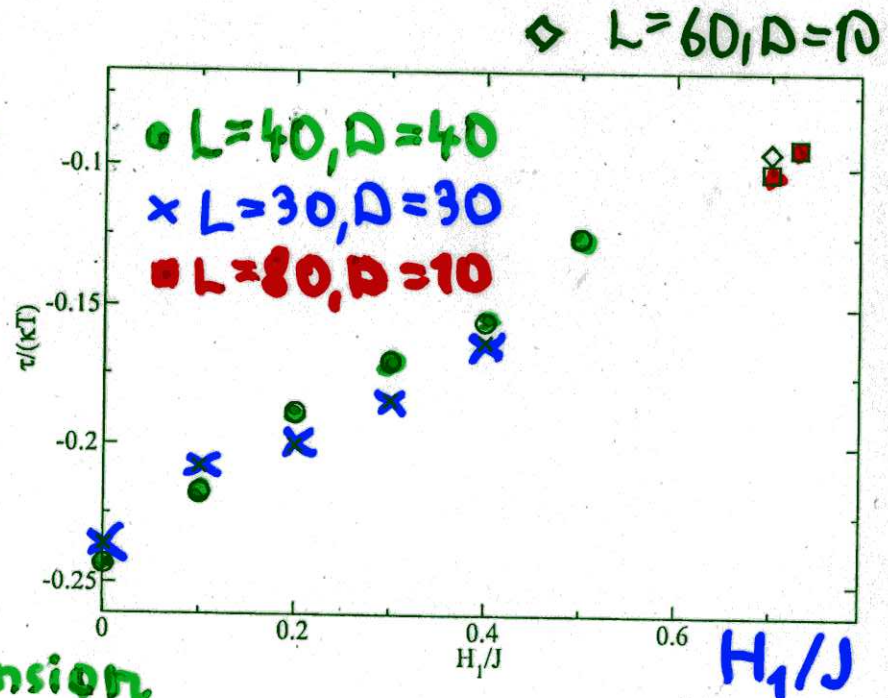
Linear variation with R:
EVIDENCE for
LINE TENSION contribution

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

$$F_s(R, \theta) = 4\pi R^2 \gamma_{ve} f(\theta) + 2\pi R \underbrace{\sin \theta}_{F} \underbrace{\tau}_{\text{line tension}}$$

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

line tension.



CONCLUSIONS

- The CLASSICAL THEORY of homogeneous nucleation is accurate for high free energy barriers ΔF_{hom}^*
- For small droplets (e.g. $R \leq 56$ in L₁-fluid) deviations occur since $F_s(R) < 4\pi R^2 \gamma_{v2}$. These deviations CANNOT be described by a TOLMAN LENGTH
- The SPINODAL is a MEAN FIELD CONCEPT. Cahn-Hilliard theory of NUCLEATION near spinodals almost never has any application. Rather a gradual transition to SPINODAL DECOMPOSITION occurs
- In FINITE SYSTEMS a "SPINODAL" (defined from the maximum of $\mu = \mu(p, T)$ as function of density p) is well-defined (droplet evaporation/condensation transition). The descending part of $\mu(p, T)$ vs. p yields information on $F_s(R)$