

UNCONVENTIONAL FIRST ORDER PHASE TRANSITIONS

are "dogmas" of statistical mechanics VIOLATED?

COWORKERS

Escapetransition: A. Milchev, V. Yamakov

H.-P. Hsu, A. M. Skvortsov, L. Klushin

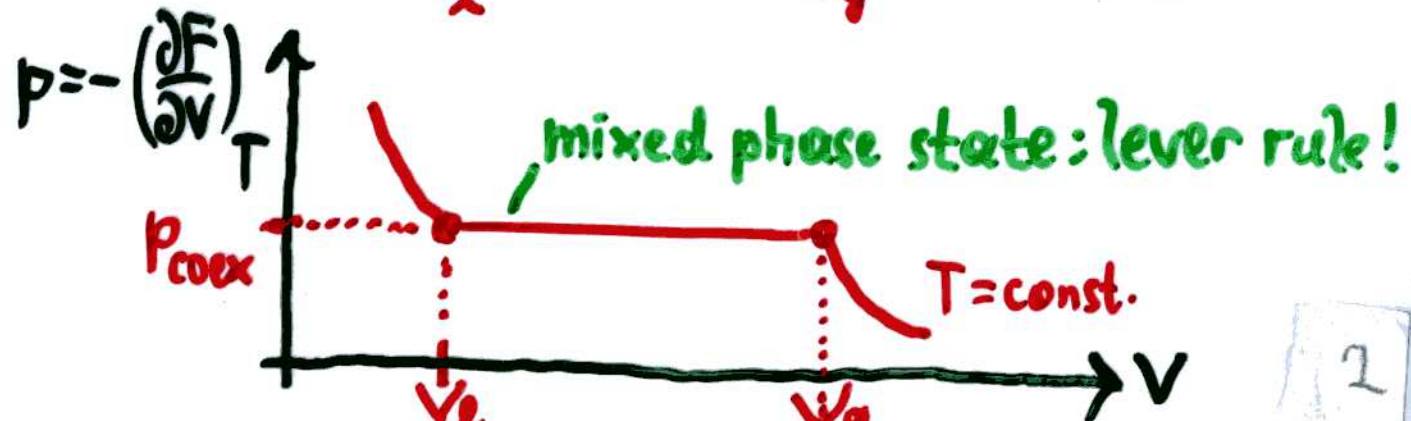
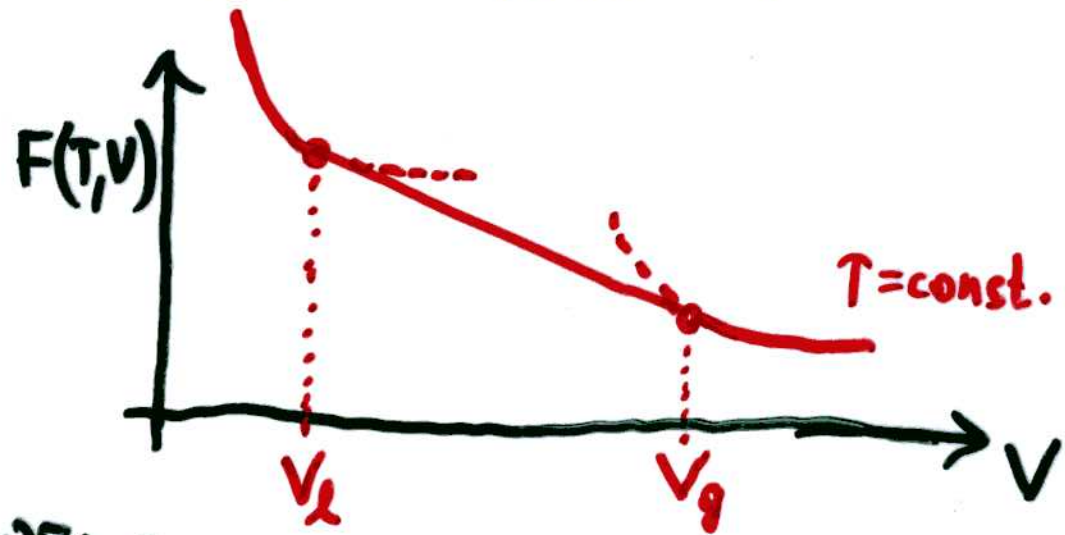
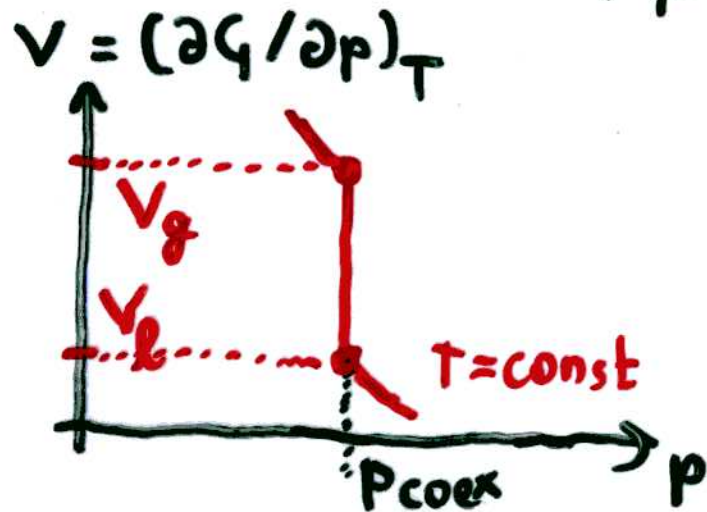
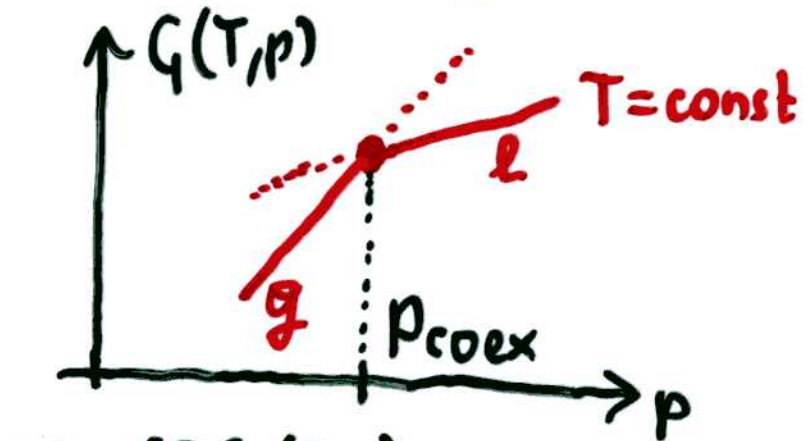
Droplet evaporation-condensation

transition: L. G. MacDowell, P. Virnau, M. Müller

FIRST ORDER PHASE TRANSITIONS

- EXTENSIVE thermodynamical variables JUMP
- DIFFERENT STATISTICAL ENSEMBLES are EQUIVALENT
(THERMODYNAMIC LIMIT ! LEGENDRE TRANSFORMATIONS !)

e.g. vapor-liquid transition $F(T,V) = G(T,p) - pV$



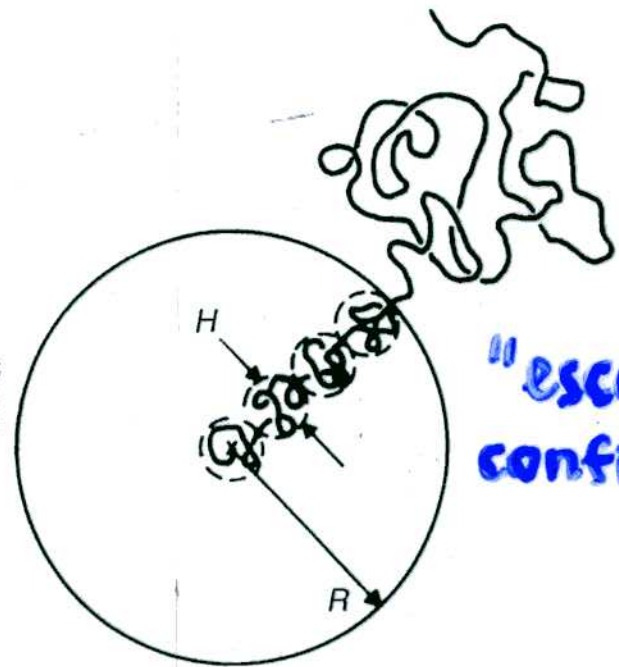
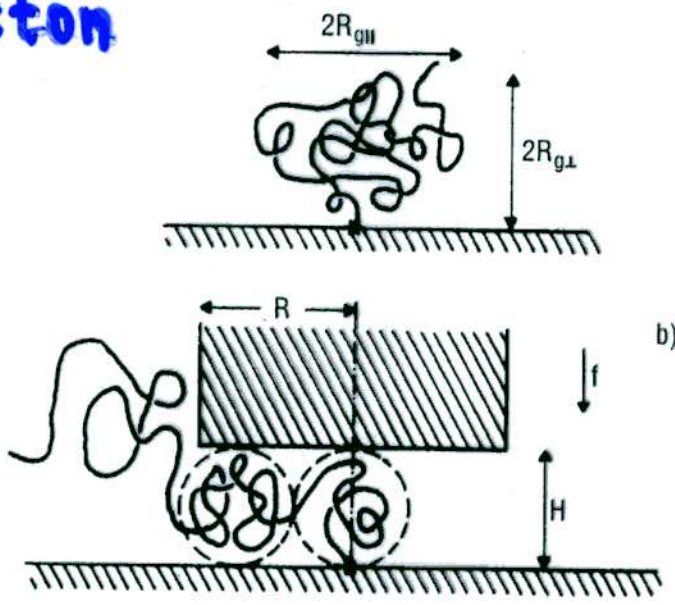
ESCAPE TRANSITION of a compressed "polymer mushroom"

Subramanian et al. 1995

flexible polymer chain, N monomers,
 $N \rightarrow \infty$, endgrafted at repulsive flat
 substrate surface

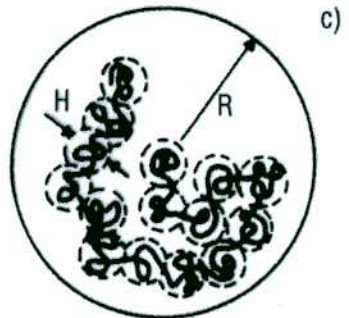
good solvent: $R_{g||} \propto R_{g\perp} \propto R_{bulk} \propto N^\nu$
 $\nu \approx 0.588$

cylindrical piston
 of radius R
 compresses
 mushroom with
 force f to
 height H



"escaped" configuration

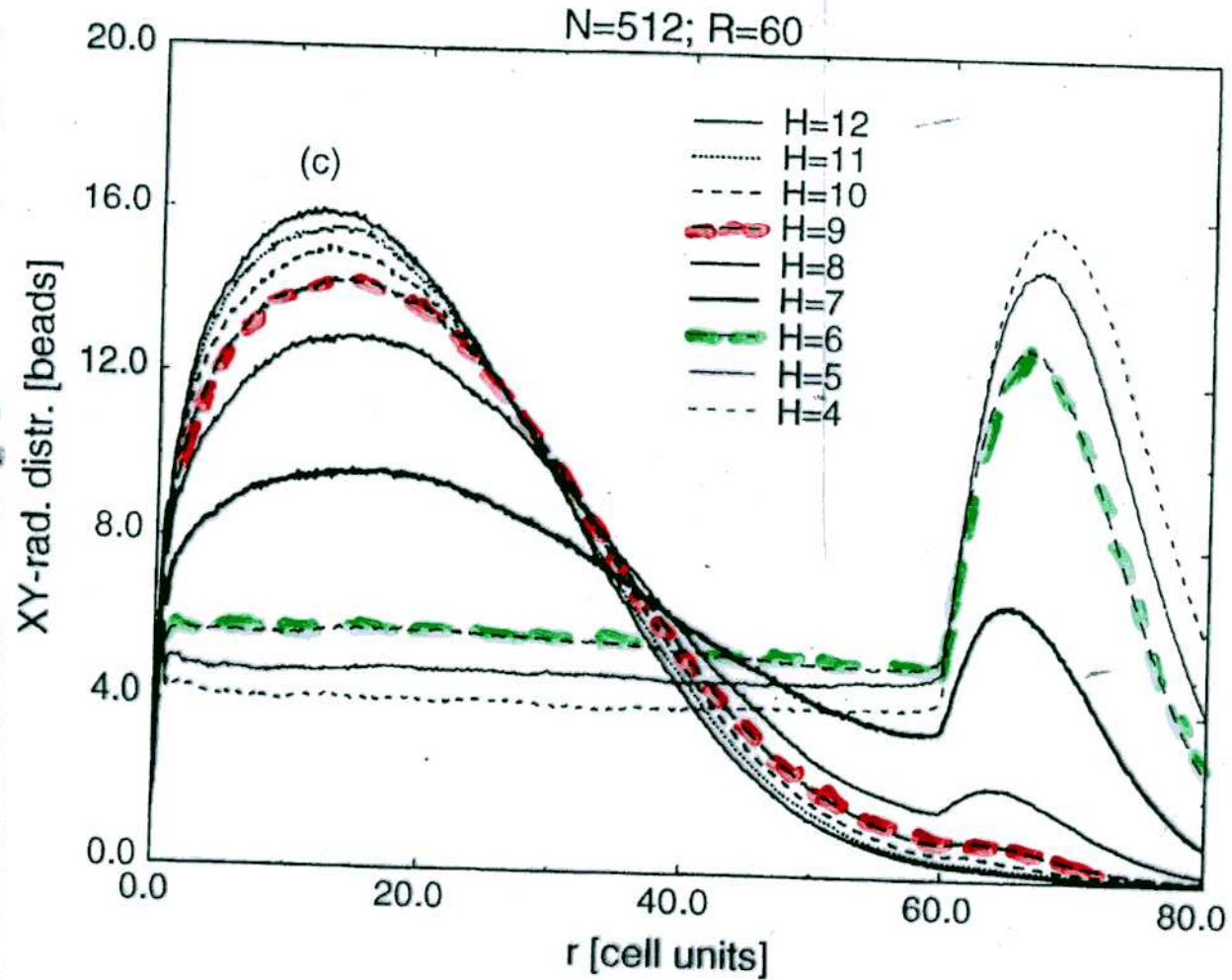
"imprisoned" configuration



Monte Carlo study of a bead-spring model

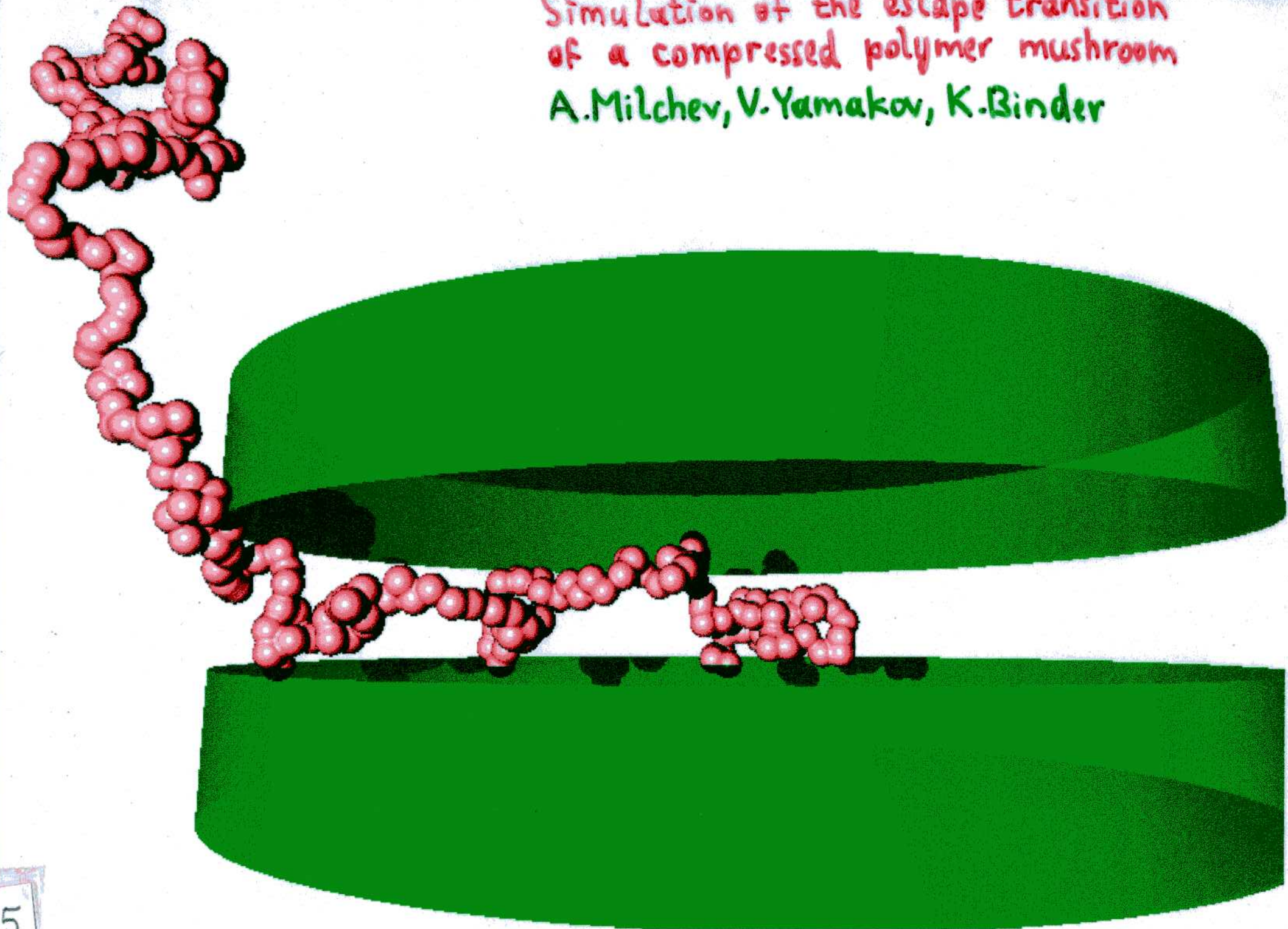
A. Milchev, V. Yamakov, K.B. 1999

radial density
distribution
of the monomers
of the compressed
mushroom

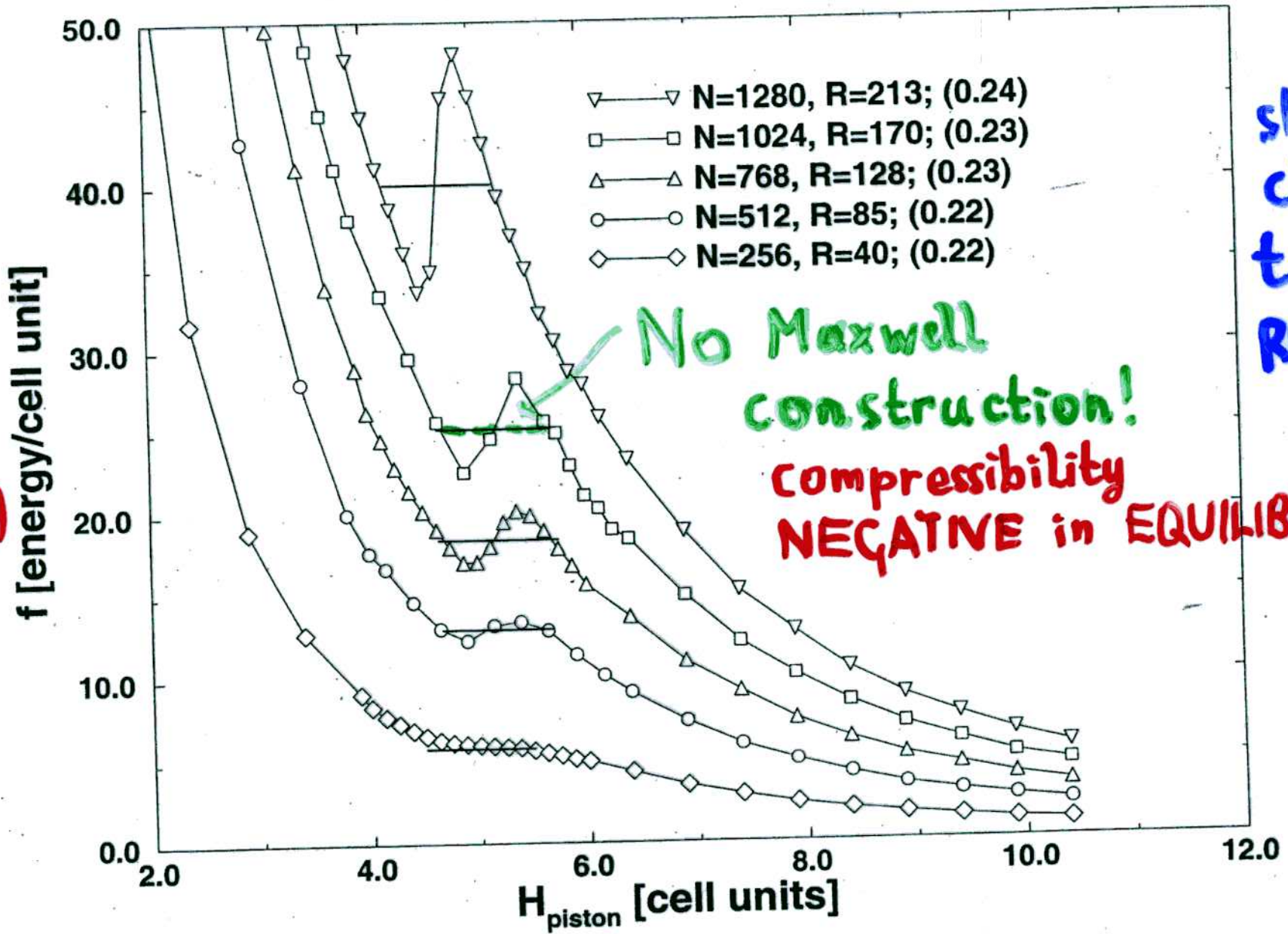


length unit = maximal spring extension

Simulation of the escape transition
of a compressed polymer mushroom
A. Milchev, V. Yamakov, K. Binder



A. Milchev, V. Yamakov, K.B. 1999



force on piston (observed)

No Maxwell construction!

compressibility NEGATIVE in EQUILIBRIUM!

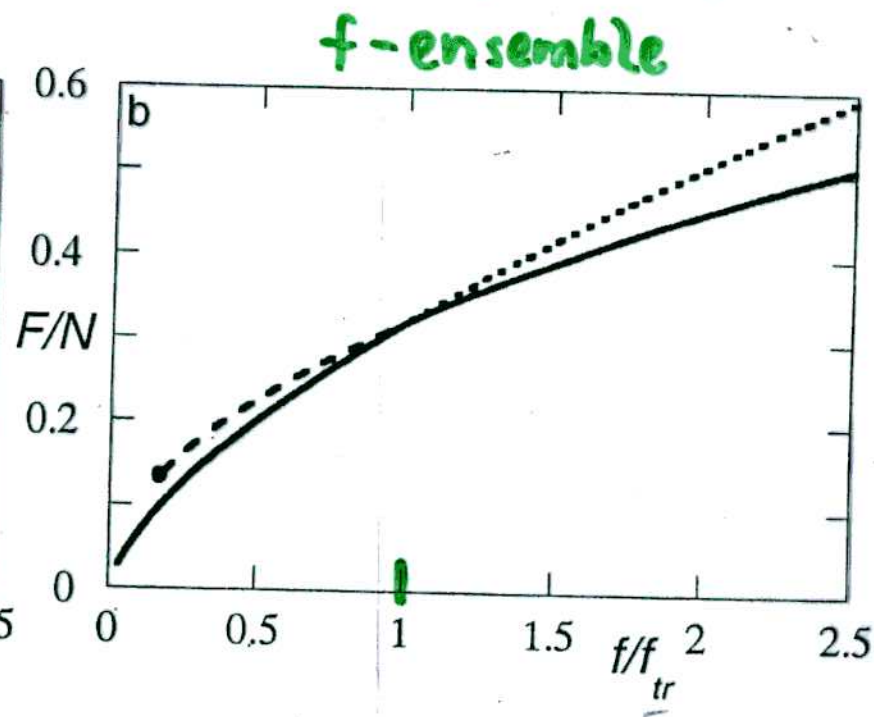
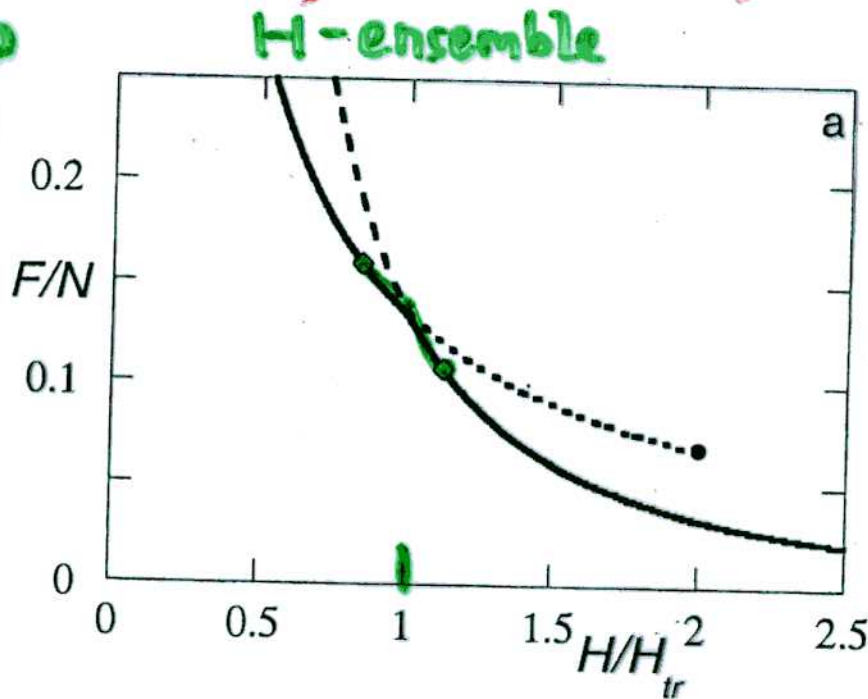
short chains: transition ROUNDED

piston height: control variable

exact partition functions for the escape of Gaussian chains

A.M. Skvortsov, L.I. Klushin, F.A.M. Leermakers (2006)

$N \rightarrow \infty$
 $R \rightarrow \infty$
 R/N fixed



$$Z(H, N, R) = \exp(-F/k_B T) = Z_{\text{coil}} + Z_{\text{flower}} =$$

$$= \text{erf}\left(\frac{R}{2R_g}\right) \exp\left[-\left(\frac{\pi R_g}{H}\right)^2\right] + \exp\left(-\frac{\pi R}{H}\right) \left[1 - \text{erf}\left(\frac{R}{2R_g} - \frac{\pi R_g}{H}\right)\right]$$

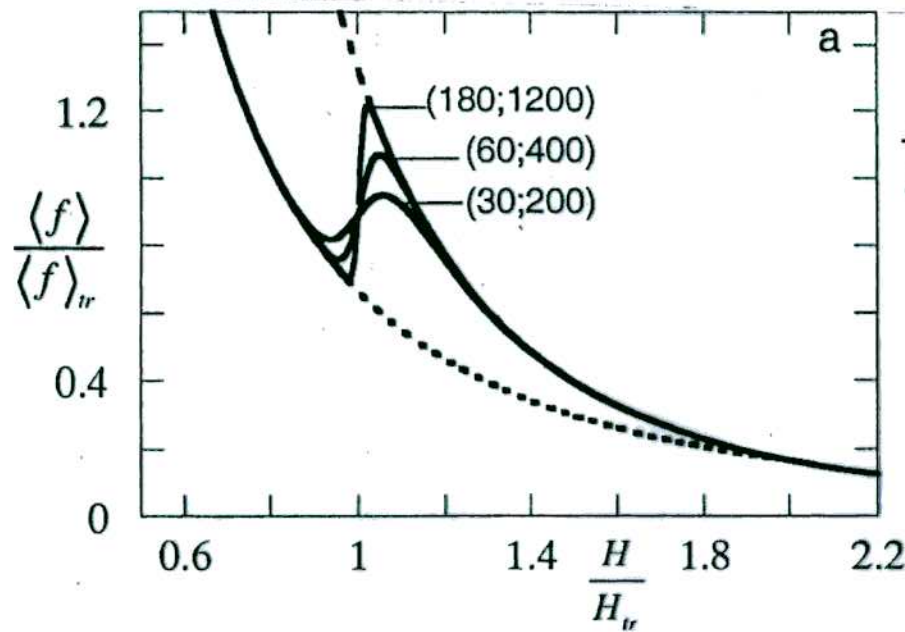
$$F(H, R, N) \approx \begin{cases} \frac{\pi R}{H} - \ln 2 & \text{for } H < H_{tr} \text{ flower} \\ \pi^2 R_g^2 / H^2 & \text{for } H > H_{tr} \text{ coil} \end{cases}$$

$$H_{tr} = \frac{\pi R_g^2}{R} = \frac{\pi N a^2}{6R}$$

escape transition of Gaussian chains: approach to the thermodynamic limit

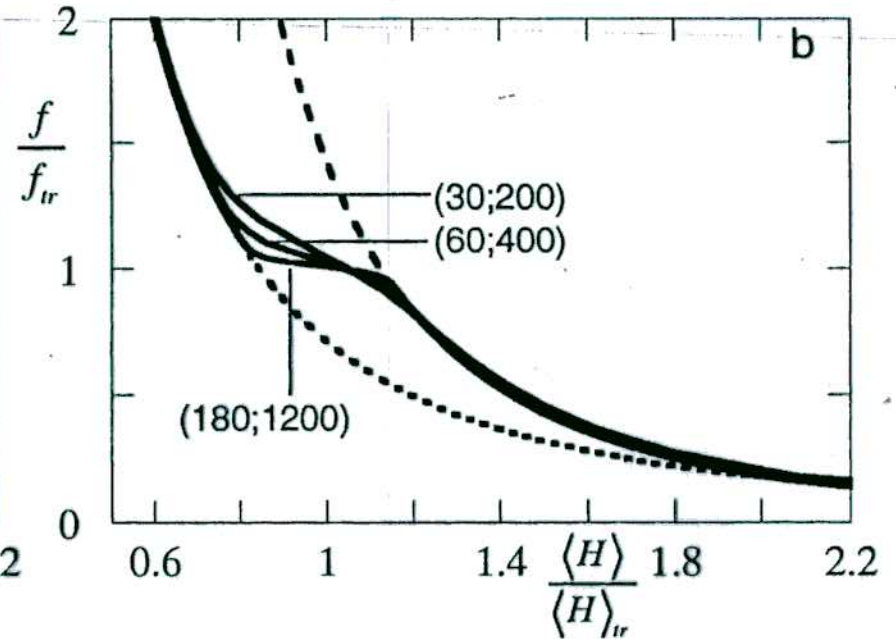
A.M. Skvortsov, L.I. Klushin, F.A.M. Leermakers (2006)

$(R/a; N)$



H-ensemble

$\frac{3^3}{25} < \frac{H}{H_{tr}} < \frac{3^2}{2^3}$: ensembles inequivalent also for $N \rightarrow \infty$

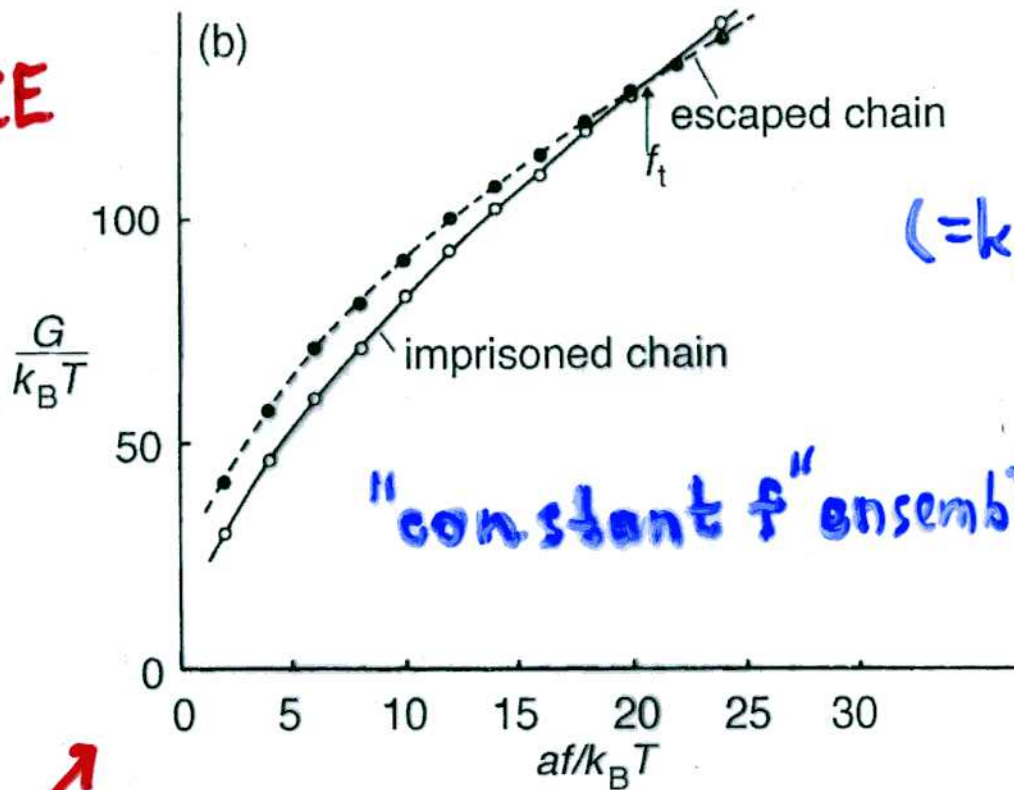


f-ensemble

$$\langle H \rangle = \begin{cases} (\pi R/f)^{1/2} & f < f_{tr} \\ \left(\frac{\pi^2 N a^2}{3f} \right)^{1/3} & f > f_{tr} \end{cases}$$

$$f_{tr} = \frac{9R^3}{\pi N^2 a^4}$$

INEQUIVALENCE
 between
 "constant f "
 and
 "constant H "
 ensemble



$$F_{imp} = c k_B T N \left(\frac{a}{H}\right)^{1/\nu}$$

($= k_B T \times$ number of "blobs")

$$F_{esc} = c' k_B T \frac{R}{H}$$

$$G(T, f) = F(T, H) + fH$$

"constant f " ensemble

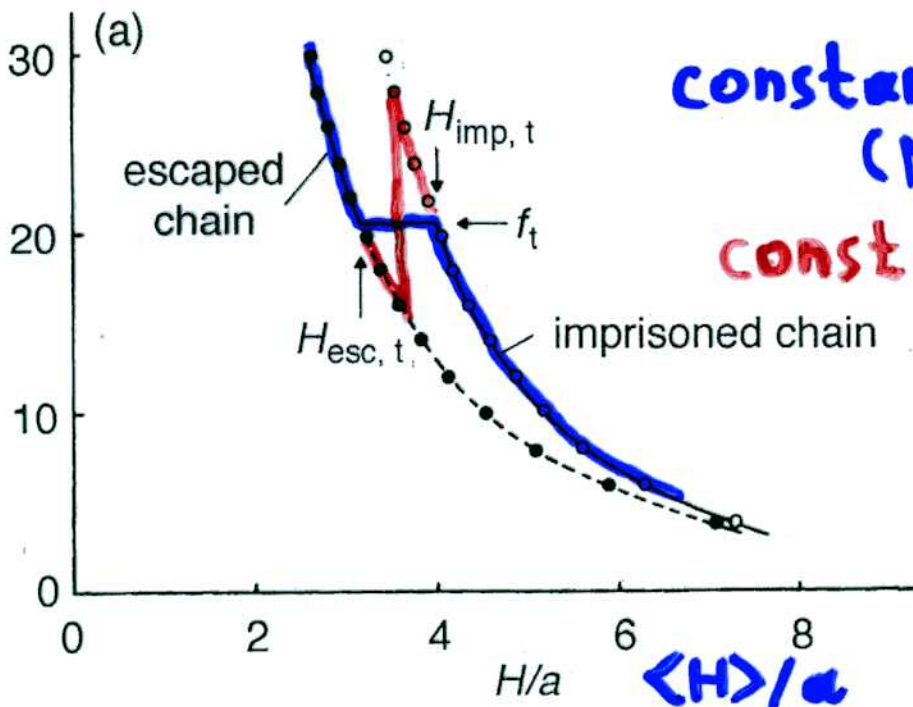
SCALING THEORY
 (approximate!)

$$\frac{a \langle f \rangle}{k_B T}$$

$$\frac{af}{k_B T}$$

$$cN = 512$$

$$c'R/a = 208$$



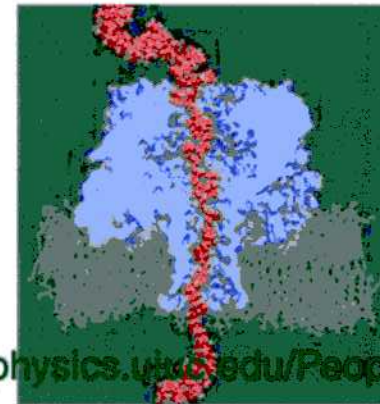
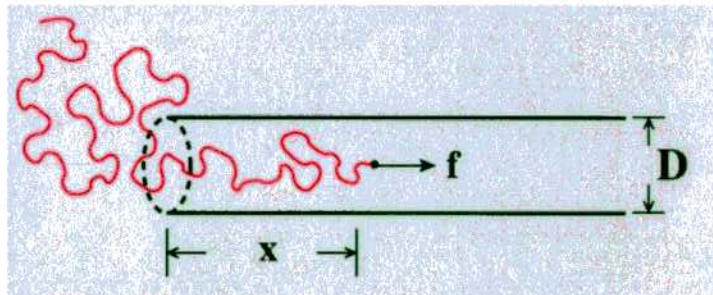
constant f ensemble
 ($N \rightarrow \infty$)

constant H ensemble
 ($N \rightarrow \infty$)

$$H_{tr} \propto \left(\frac{Na}{R}\right)^{\nu/(1-\nu)}$$

Motivations

- The **confinement**, **escape**, & **drag** problems of polymer chains confined in a finite cylindrical tube



<http://www.physics.uva.edu/People/Aksimentiev>

- Polymer translocation through pores in a membrane
- DNA confined in artificial nanochannels

- **2d escape** problem \Rightarrow **3d escape** & **drag** problems
Landau theory approach, Monte Carlo simulations

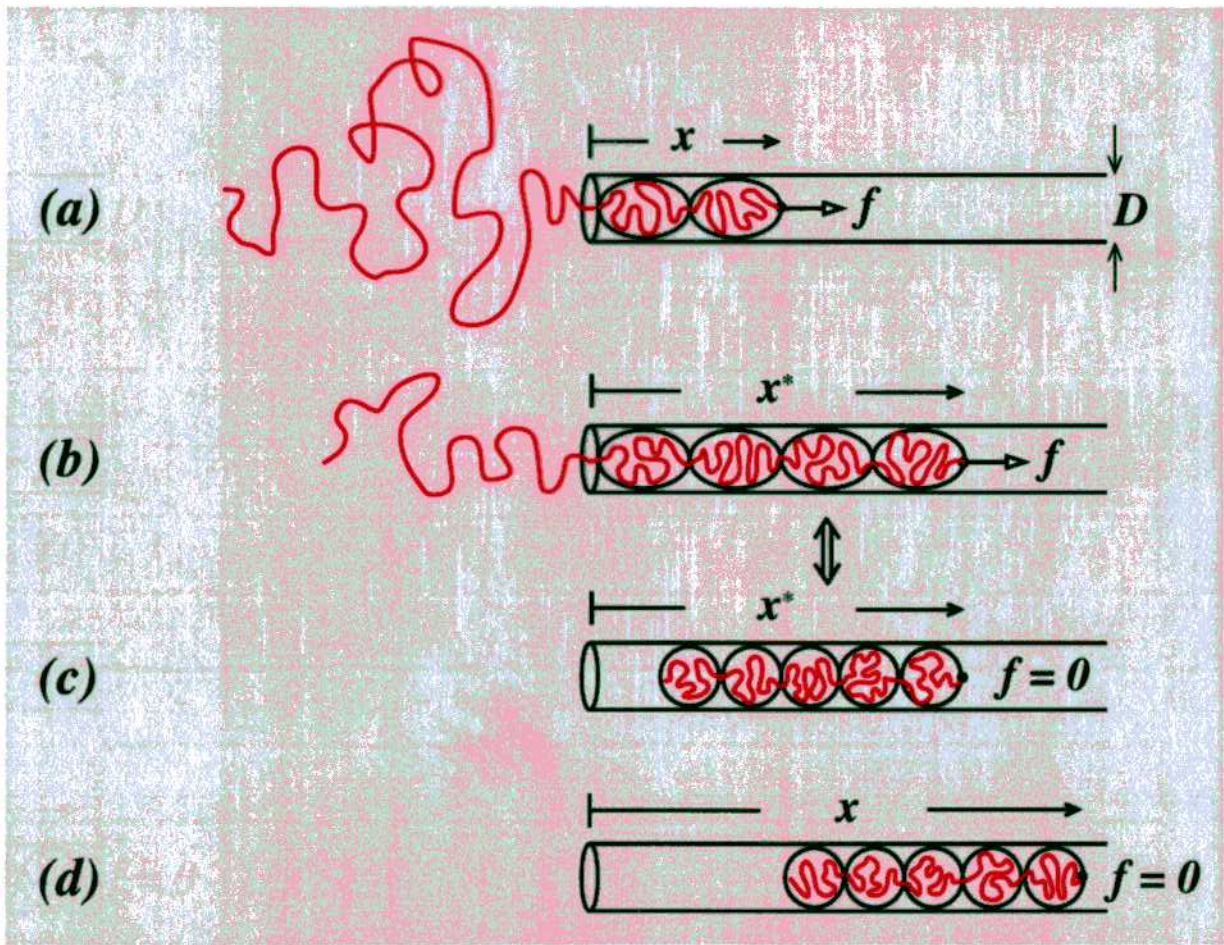
"What is the order of the 2d polymer escape transition ?"

Phys. Rev. E 76, 021108 (2007). a Weak First-Order Transition!

3d escape: Macromolecules 41, 5890 (2008)

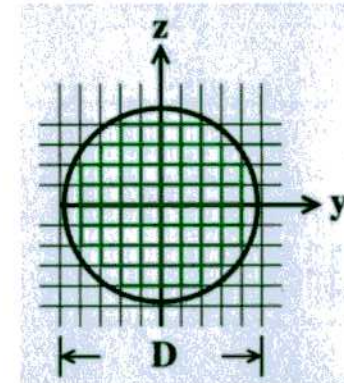
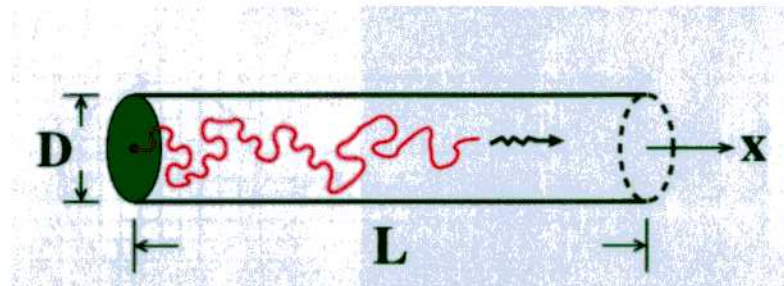
Flower state \Leftrightarrow imprisoned state

Dragging a polymer chain into a nanotube in a quasi-equilibrium process



Simulations

- Model: grafted **biased/unbiased** SAWs on a simple cubic lattice



Monomers are forbidden to sit on

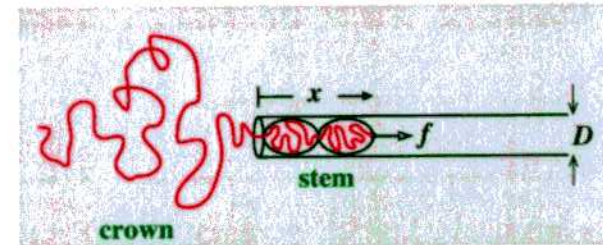
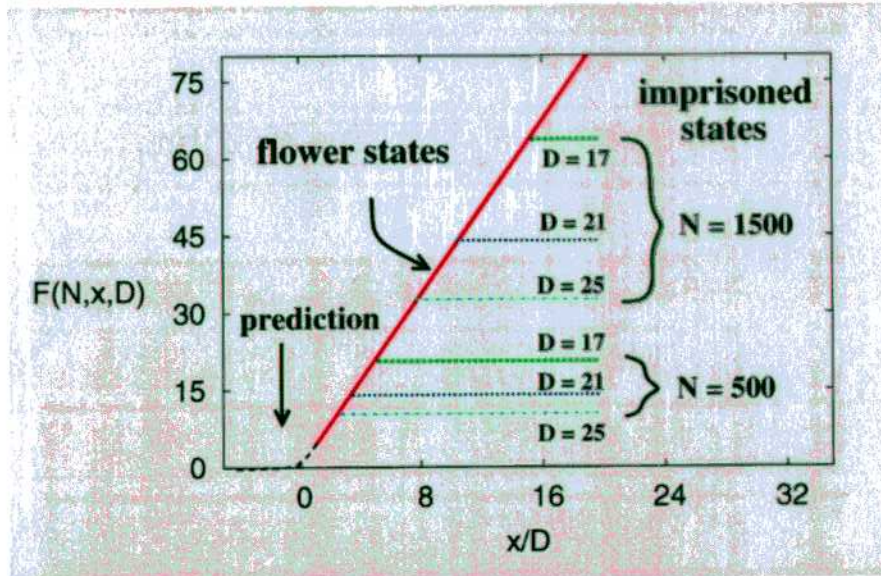
$$\{1 \leq x \leq L, y^2 + z^2 = D^2/4\} \text{ \& \} \{x = 0, y^2 + z^2 = D^2/4\}$$

- Algorithm: **Pruned-Enriched Rosenbluth Method** with k -step Markovian anticipation

Grassberger, Phys. Rev. E 56, 3682 (1997)

Hsu & Grassberger, Eur. Phys. J. B 36, 209 (2003)

Free energy $F(N, x, D)$



- Scaling:

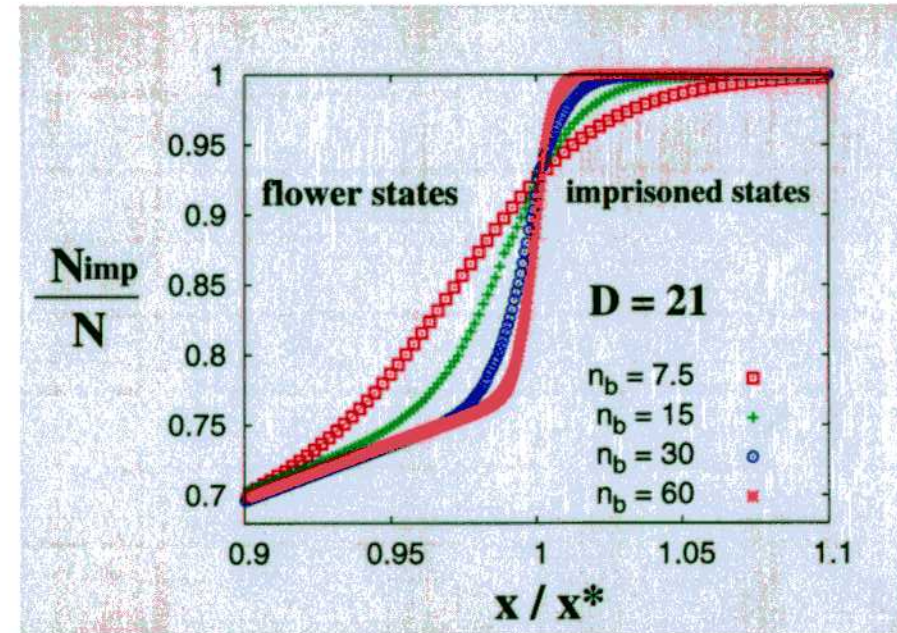
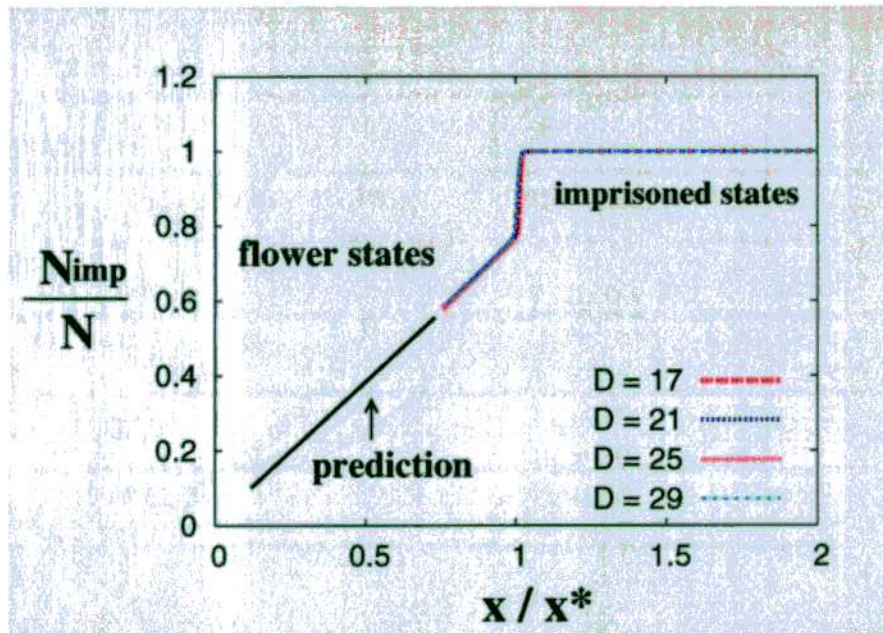
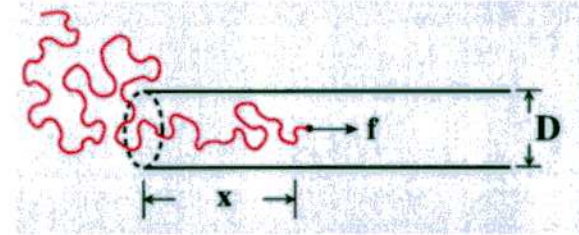
$$F(N, x, D) = \begin{cases} F_{\text{imp}} = 5.33(8)ND^{-1/\nu}, & \text{imprisoned state} \\ F_{\text{fl}} = 4.23(6)x/D, & \text{flower state} \end{cases}$$

- Transition point:

$$F_{\text{imp}} = F_{\text{fl}} \Rightarrow x^* \sim 1.26(4)ND^{1-1/\nu}$$

of imprisoned monomers

- At the transition point $x/x^* = 1$
 flower states ($\frac{N_{\text{imp}}}{N} \approx 3/4$)
 \Leftrightarrow imprisoned states ($\frac{N_{\text{imp}}}{N} \approx 1$)
- Finite-size rounding



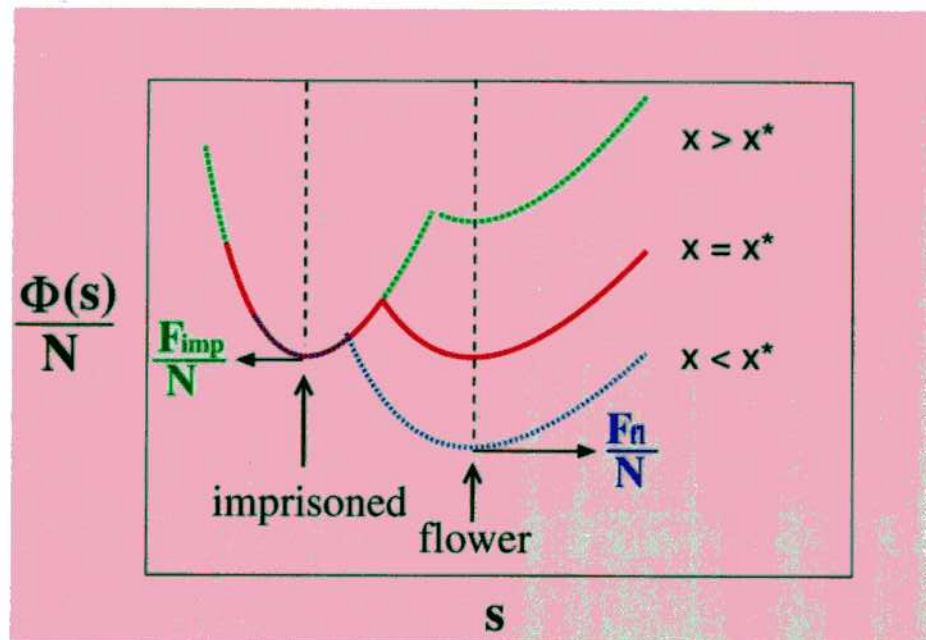
$$x^* \approx 1.26ND^{1-1/\nu}$$

Theoretical predictions

Landau theory approach

- Partition sum: $Z = \exp(-F) = \int ds \exp(-\Phi(s))$

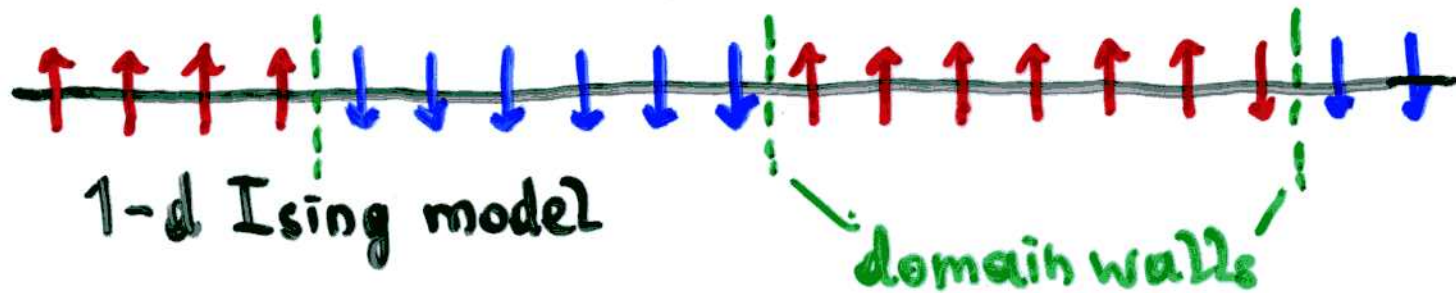
F : free energy, $\Phi(s)$: Landau free energy function



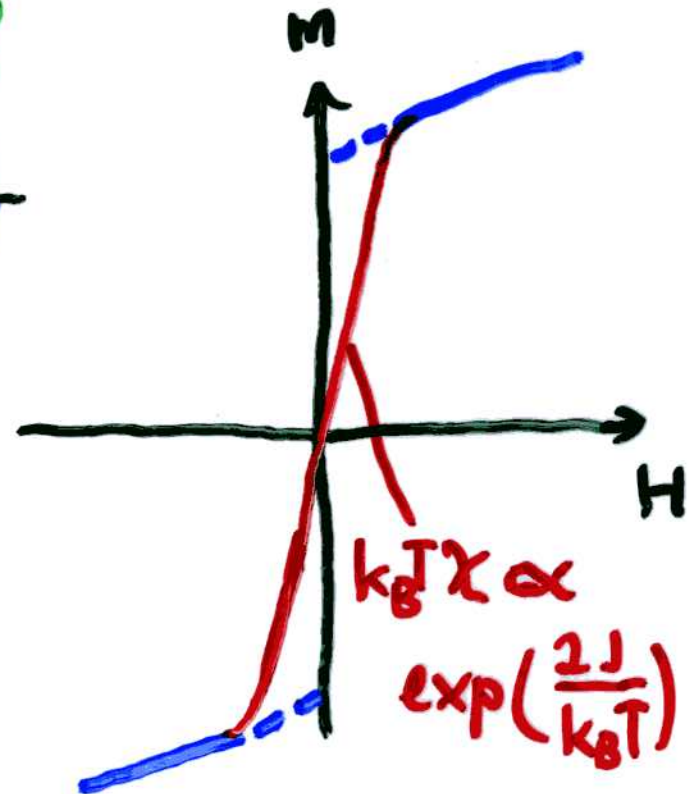
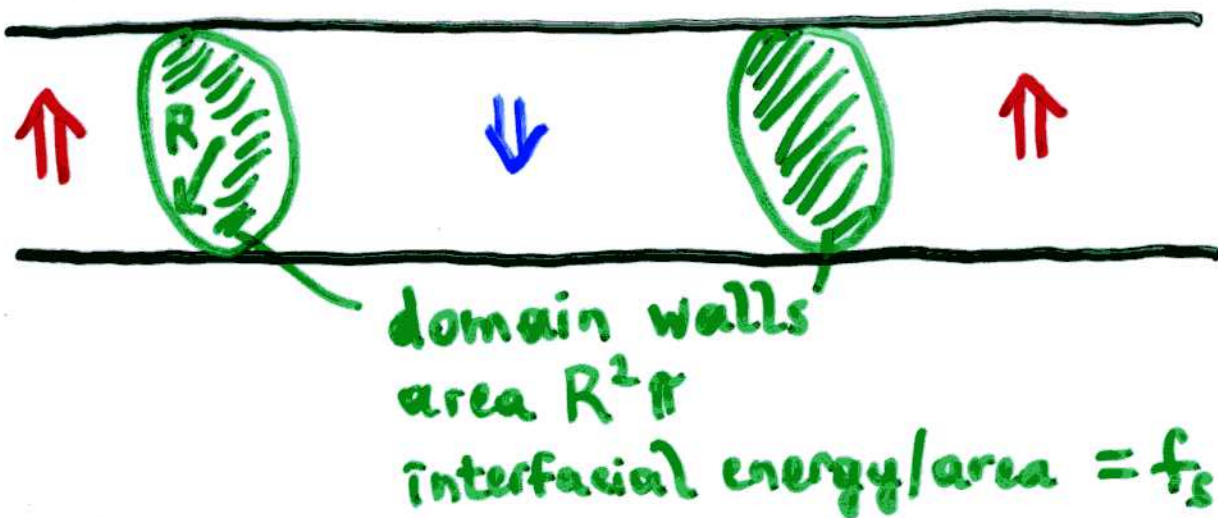
s : order parameter

$$s = \begin{cases} r/N_{\text{imp}}, \text{ imprisoned} \\ (N_{\text{imp}} = N) \\ x/N_{\text{imp}}, \text{ flower} \end{cases}$$

Absence of 1st-order phase transitions in (quasi)-one-dimensional systems with short-range forces
 relation to phase coexistence!



cylinder of radius R



$$k_B T \chi \propto \exp\left(\frac{R^2 \pi f_s}{k_B T}\right)$$

⇒ transition is rounded, if phase coexistence is possible

Landau free energy $\Phi(s)$

- Theoretical predictions:

$$\Phi(s) = \begin{cases} \Phi_{\text{imp}}(s) = ND^{-1/\nu} A(u^{-\alpha} + Bu^{\delta} + C) & , s \leq x/N \\ \Phi_{\text{fl}}(s) = xA(u^{-\alpha-1} + Bu^{\delta-1} + Cu^{-1})/D & , s \geq x/N \end{cases}$$

$$\alpha = \frac{1}{3\nu-1}, \delta = \frac{1}{1-\nu}, u = sD^{-1+1/\nu}, \nu = 0.588$$

A, B, C : coefficients

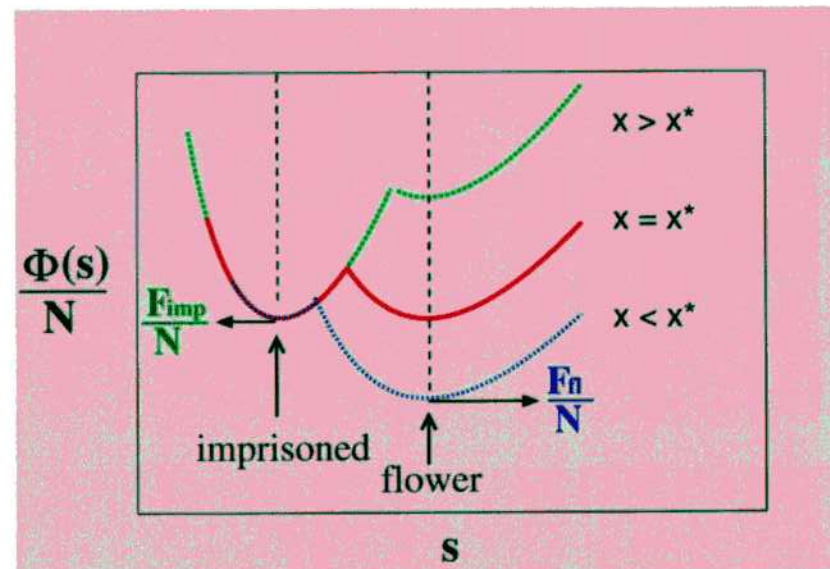
- MC results:

$$\Phi(s = S_{\text{imp}}) = F_{\text{imp}},$$

$$\Phi(s = S_{\text{fl}}) = F_{\text{fl}}$$

$$\Rightarrow A = 1.48, B = 0.67,$$

$$C = 1.98$$



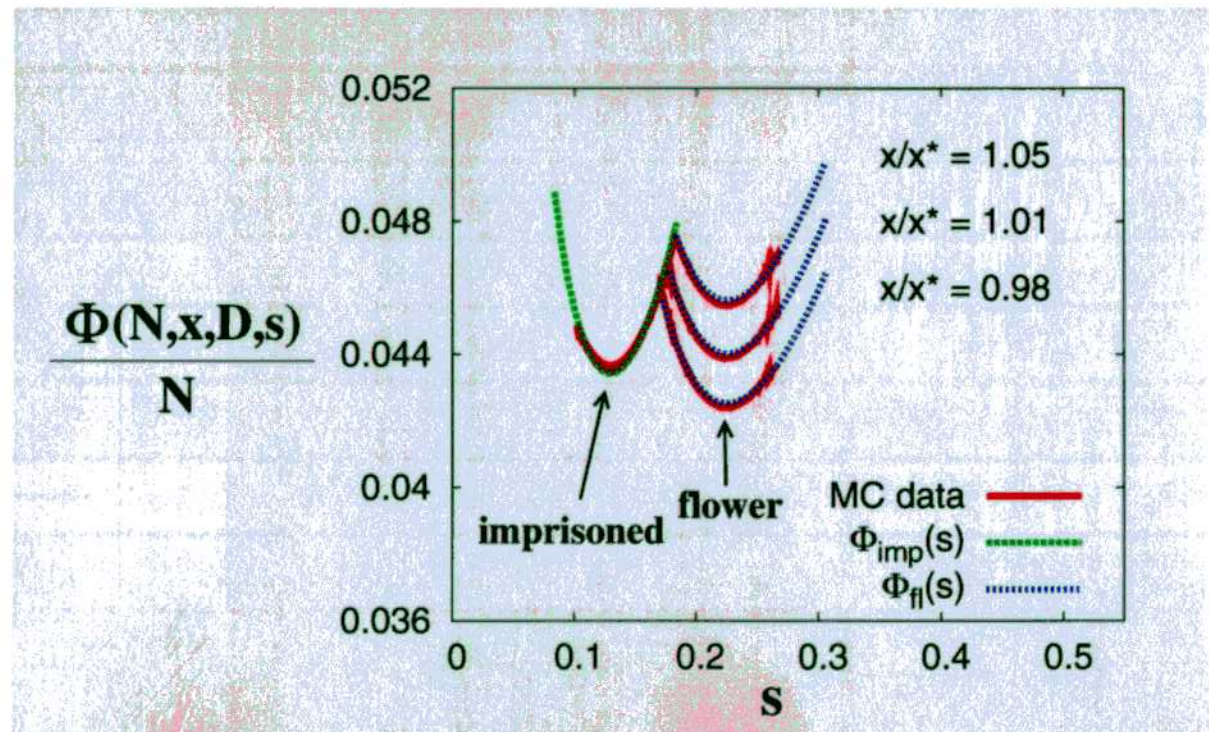
$$x^* \approx 1.26ND^{1-1/\nu}$$

$\Phi(N, x, D = 17, s)$

- Landau free energy: $\Phi(N, x, D, s) = -\ln \left(\frac{P(N, x, D, s)}{Z_0(N)} \right)$

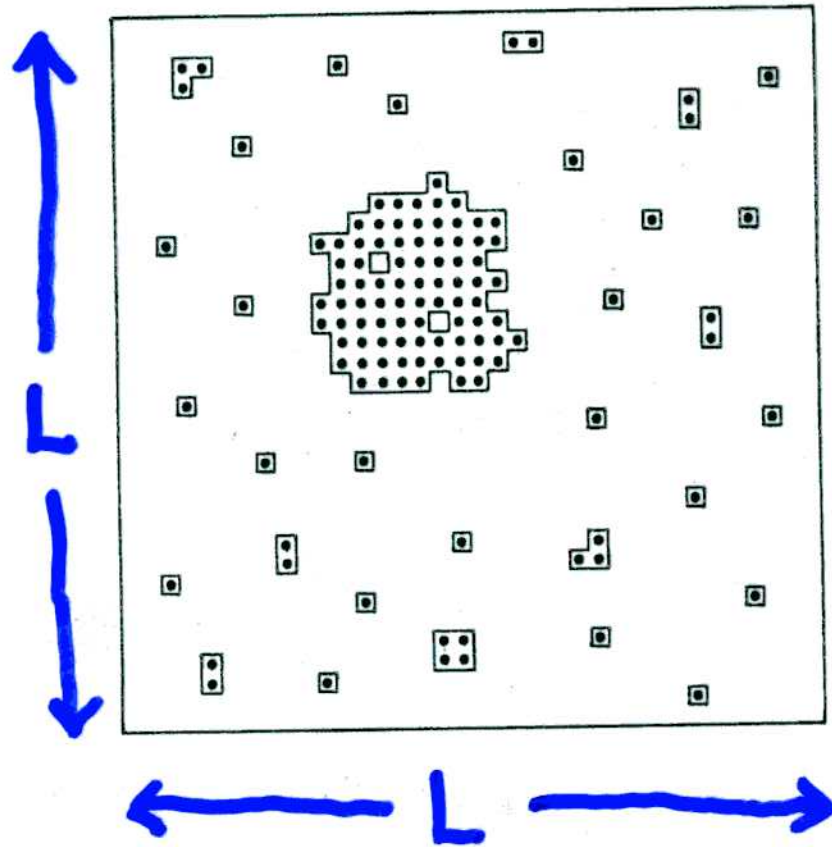
$P(N, x, D, s)$: accumulated histogram of s

$Z_0(N)$: Partition sum of a free random coil

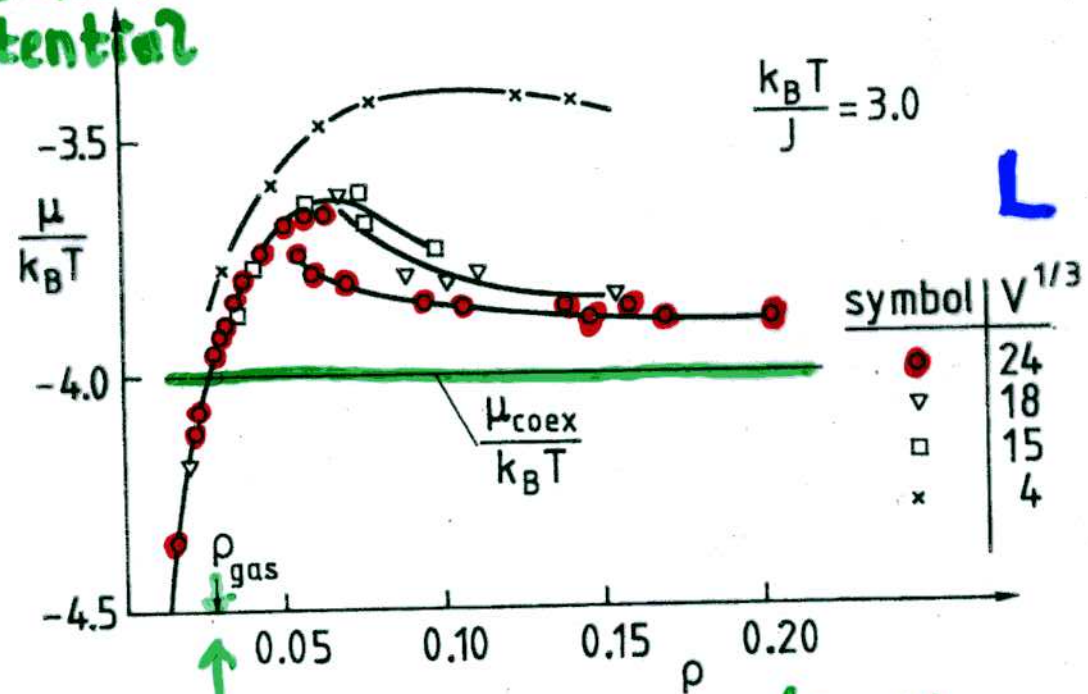


EQUILIBRIUM BETWEEN DROPLET AND SURROUNDING SUPERSATURATED GAS

$d=3$ lattice gas model



chemical potential



coexistence for infinite volume

density

periodic boundary conditions

H. Furukawa + K.B.
1982

LENNARD-JONES FLUID ($d=3$ dimensions)

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

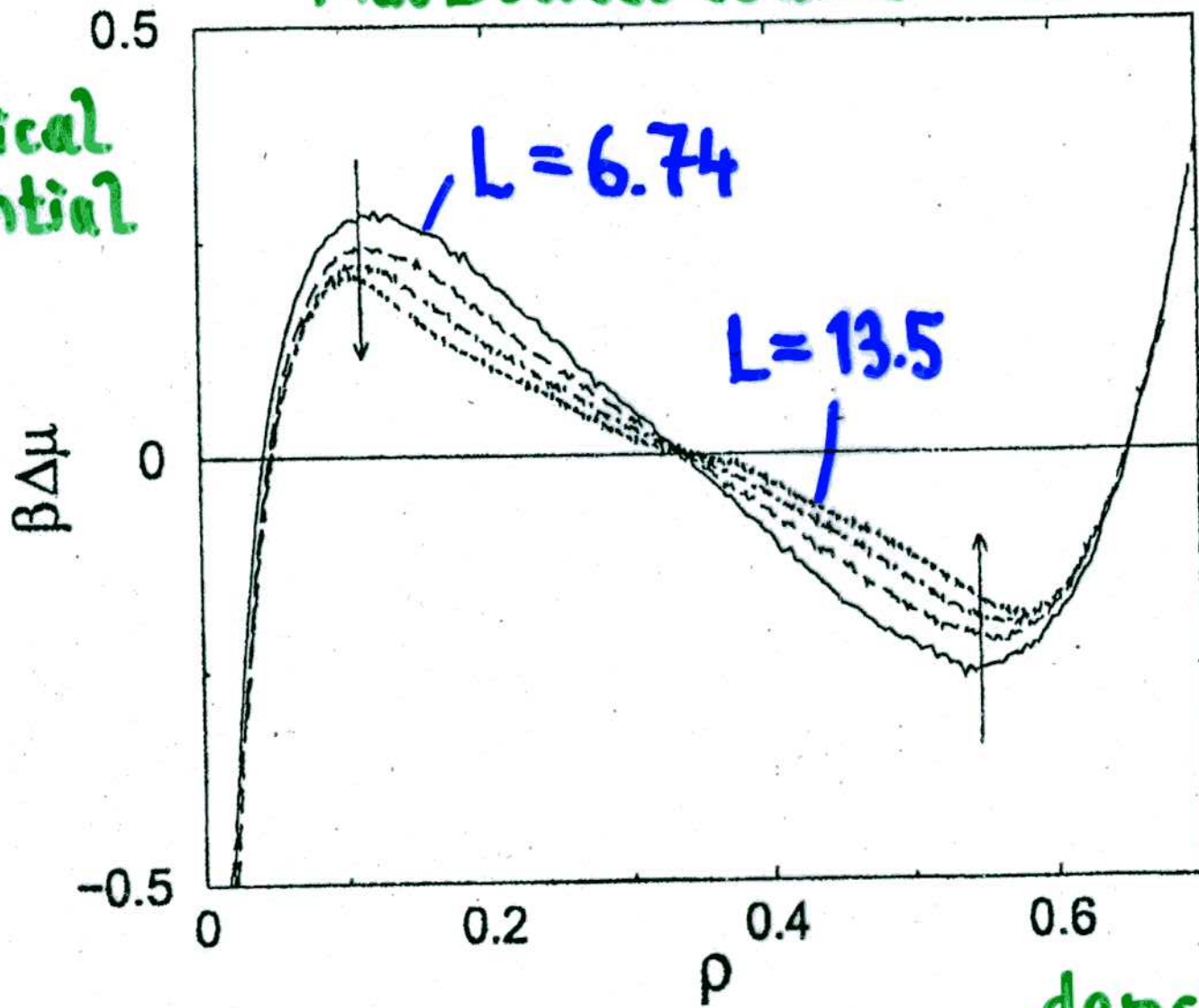
MacDowell et al. (2004)

$$\epsilon = 1$$

$$\sigma = 1$$

$$\Rightarrow T_c \approx 1$$

chemical potential



$$T = 0.854$$

← bulk
two-phase
coexistence

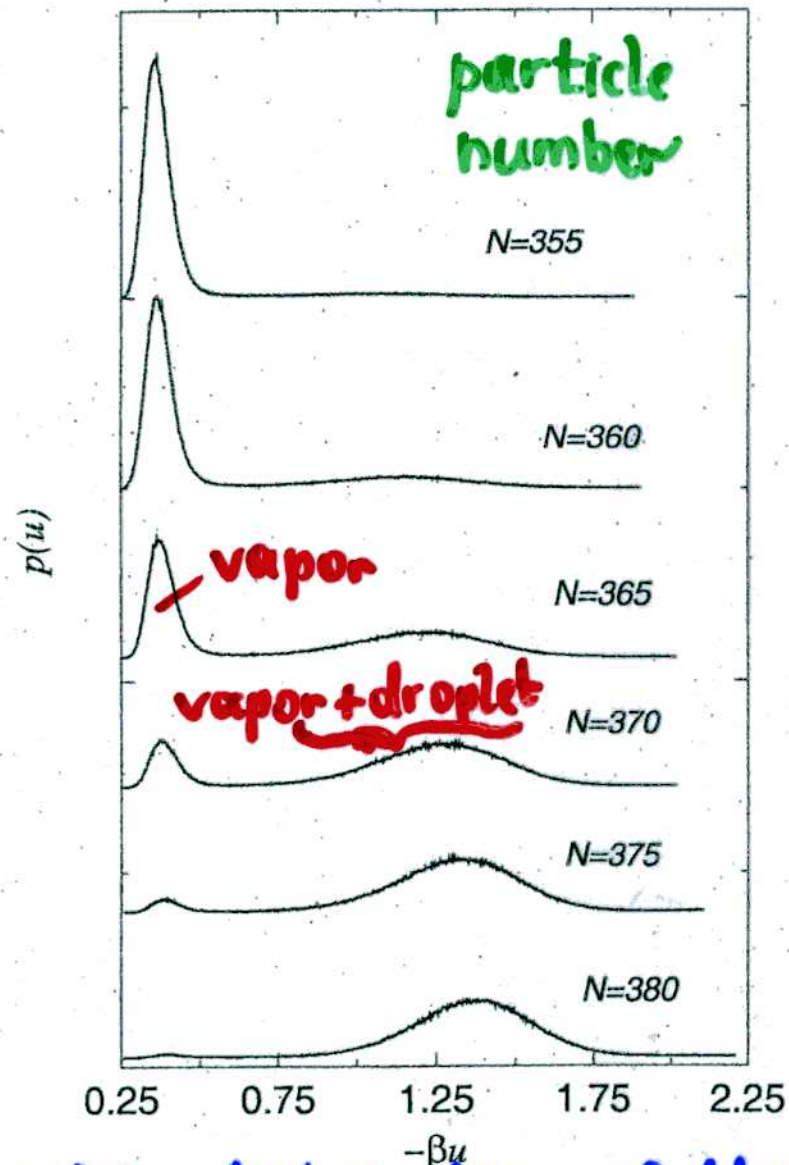
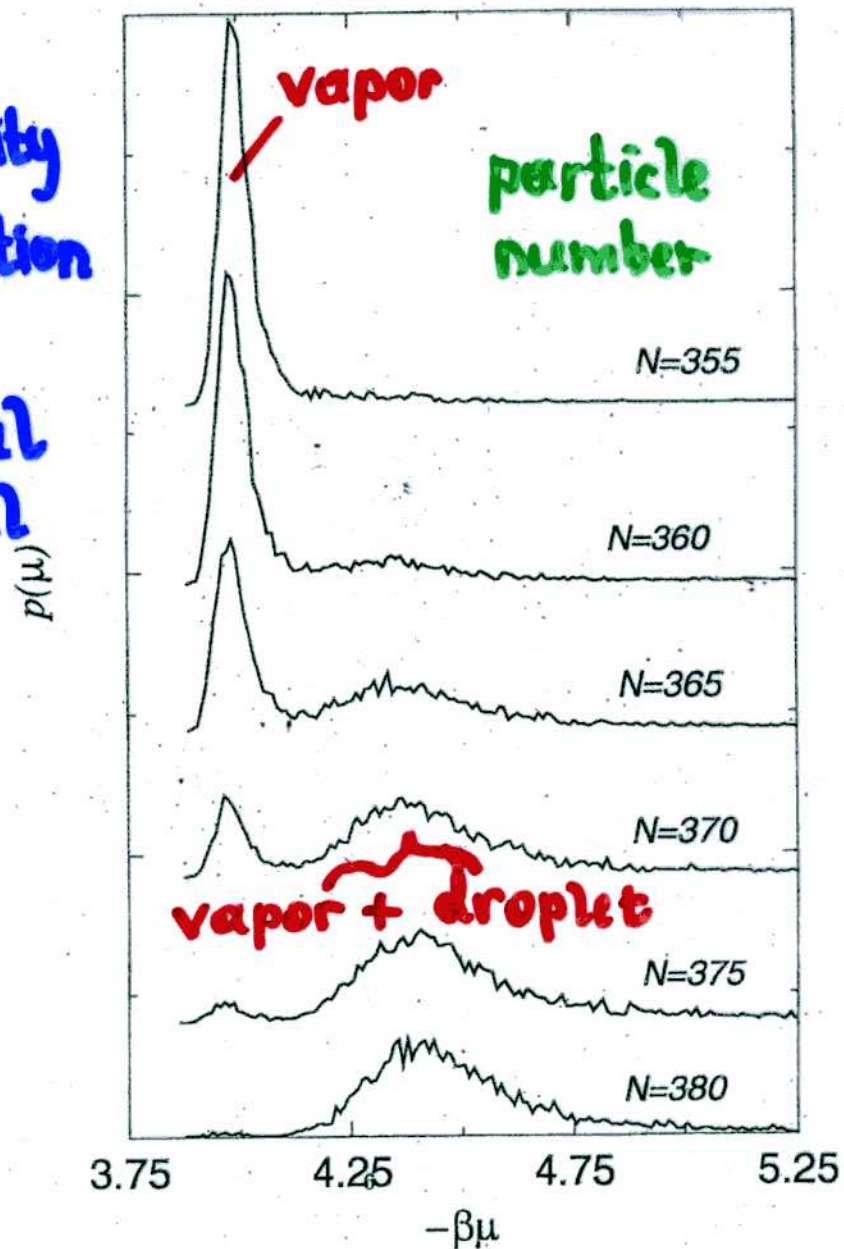
EQUILIBRIUM!

LENNARD JONES FLUID

$d=3$ $T=0.68$

$L=22.5\sigma$

probability distribution of the chemical potential

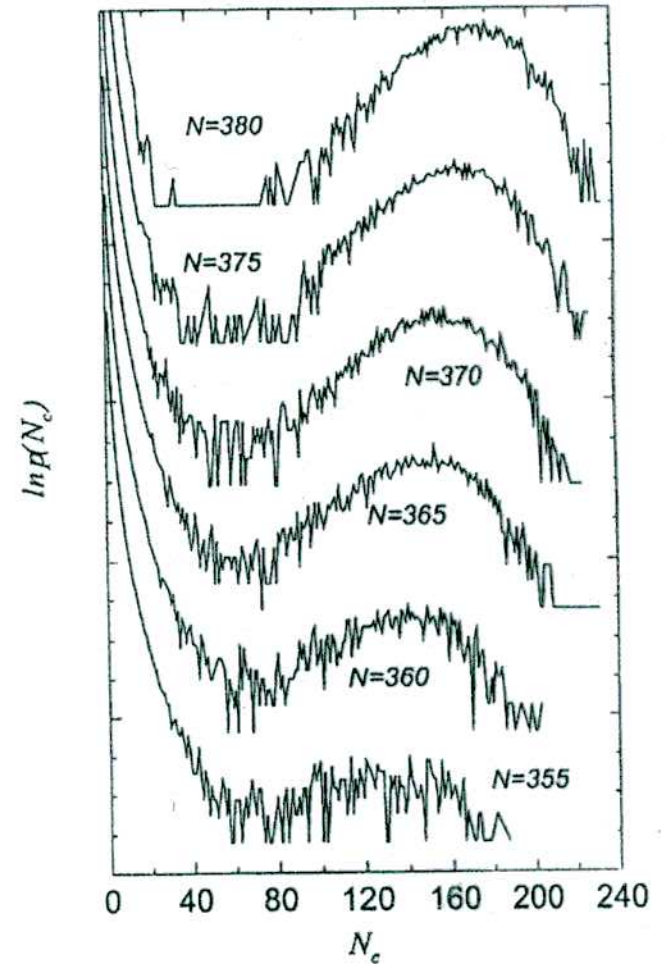
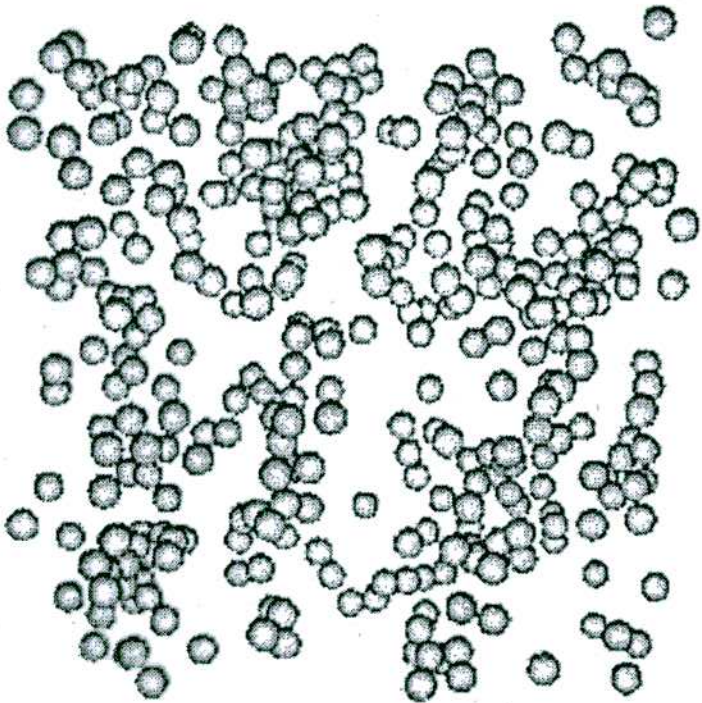
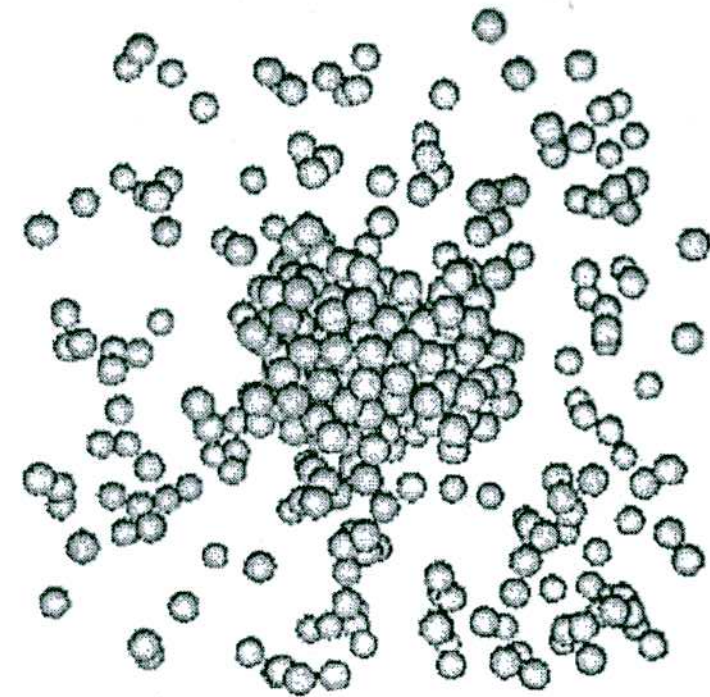


probability distribution of the internal energy / particle

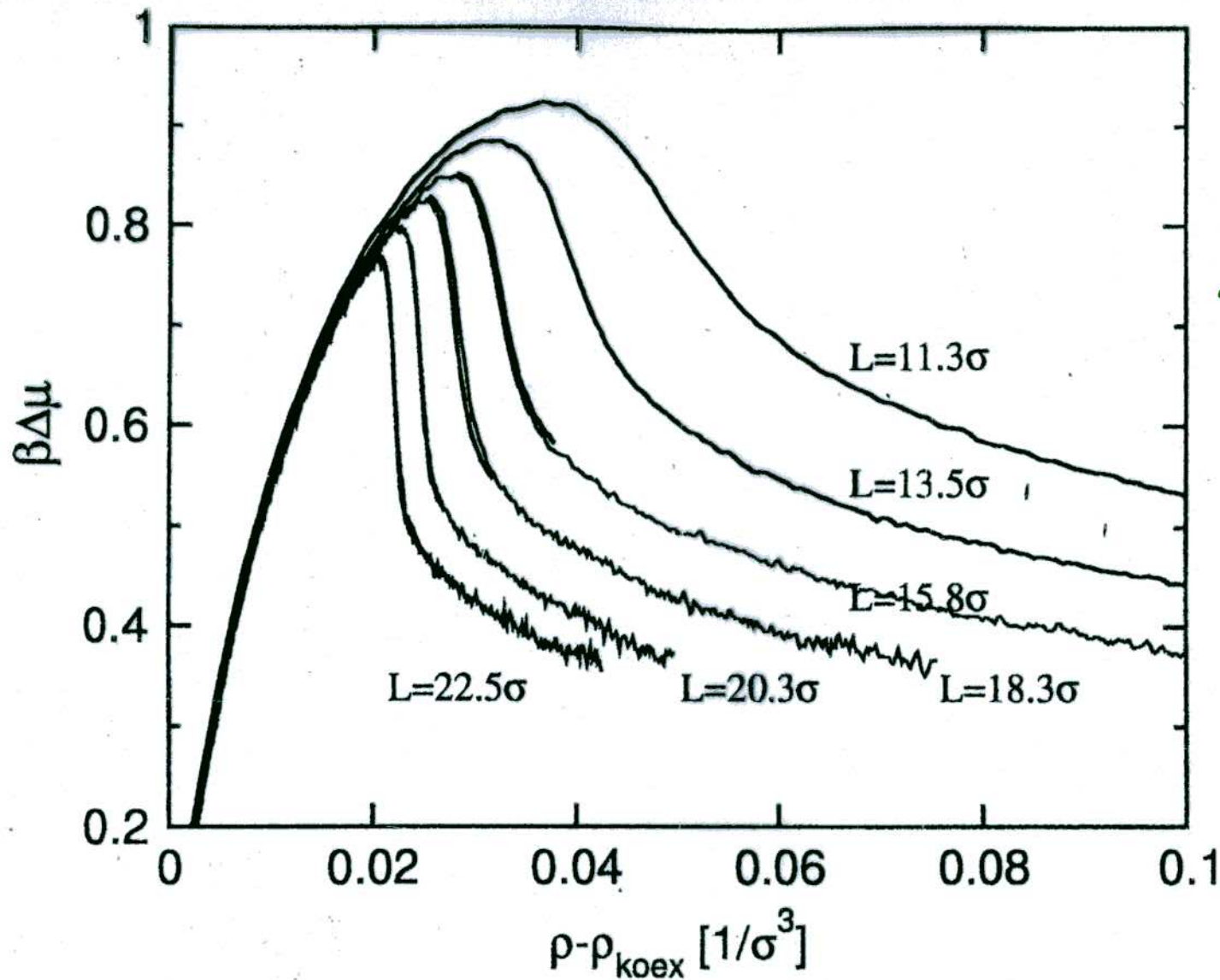
Lennard-Jones fluid

$$T = 0.68 \epsilon$$

$$L = 22.56$$



probability distribution of finding
a state with N_c atoms/cluster



Lennard-Jones
fluid

$T \approx 0.68 T_c$

$L \times L \times L$ boxes
+ p.b.c.

DROPLET EVAPORATION-CONDENSATION TRANSITION
P. Virnau, L. G. MacDowell, M. Müller, K. B. (2004)

PHENOMENOLOGICAL THEORY OF THE DROPLET EVAPORATION-CONDENSATION TRANSITION

K.B., Physica A 319, 99 (2003)

scaled field

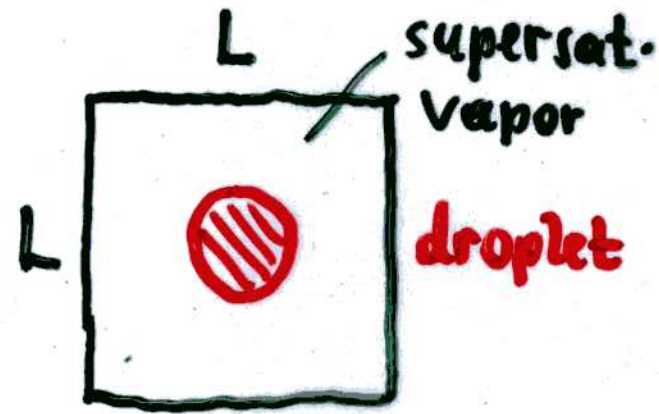
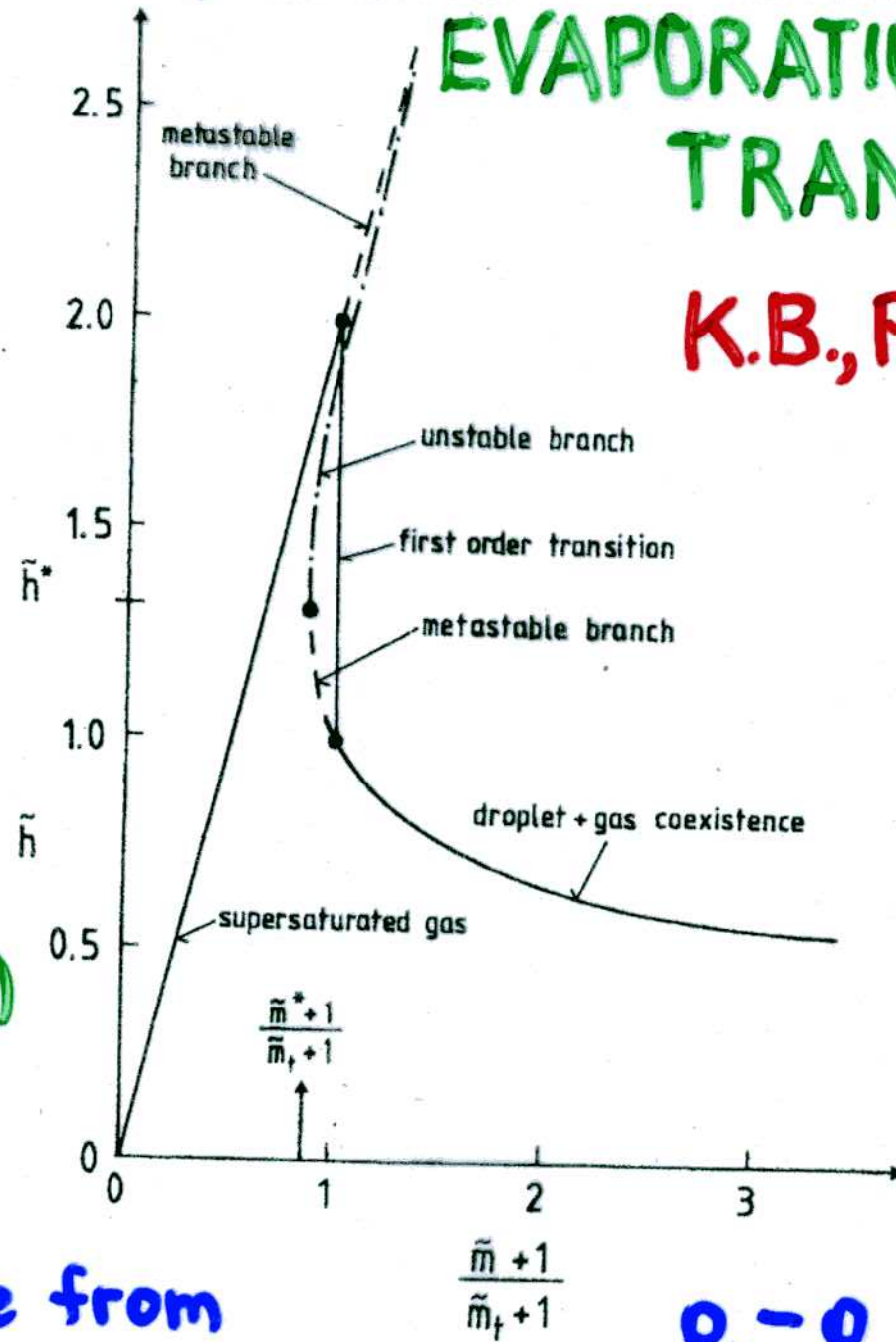
$$\tilde{h} = \Delta\mu / \Delta\mu_t$$

$$\Delta\mu_t \propto L^{-d/(d+1)}$$

$$d=3: \Delta\mu_t \propto L^{-3/4}$$

rigorous results:
Biskup et al. (2002)
d=2 Ising model

scaled distance from coexistence curve



balance free energies!

$$\rho_t - \rho_{coex} \propto L^{-\frac{d}{d+1}}$$

CONCLUSIONS

- Are basic theorems of statistical mechanics VIOLATED for these UNCONVENTIONAL 1st order transitions?
- NO, conditions necessary for the theorems to hold do not apply!
- theorems require that PHASES between which transitions occur are homogeneous on macroscopic scales
- interfaces and phase coexistence must be possible
- For the transitions considered here at least one of the two phases is an essentially inhomogeneous state!
- interfaces between the phases + phase coexistence not possible
⇒ no double-tangent construction, no convexity properties, ...