KITP-UCSantaBarbara Aug-Sep ‘08

KATHOLIEKE UNIVERSITEIT LEUVEN

INSTITUUT VOOR THEORETISCHE FYSICA

Fluctuation-induced forces and wetting phenomena in colloid-polymer mixtures: Are renormalization group predictions measurable?

Y. Hennequin, D. G. A. L. Aarts, J. O. Indekeu, H. N. W. Lekkerkerker and D. Bonn, “*Fluctuation forces and wetting layers in colloid-polymer mixtures*”, Phys. Rev. Lett. **100**, 178305 (2008).

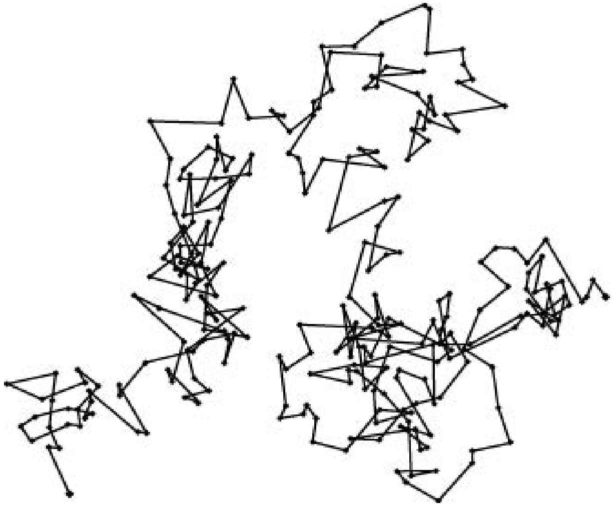
1. Colloidal suspension
2. Hard spheres + tunable attractions
3. Scales
4. Functions and variables
5. Walls and wetting
6. Free interface: capillary wave roughness
7. Unbinding from a wall: RG predictions vs experiment
8. Line tension

[1] H.N.W. Lekkerkerker, V.W.A. de Villeneuve, J.W.J. De Folter, M. Schmidt, Y. Hennequin, D. Bonn, J.O. Indekeu and D.G.A.L. Aarts, "*Life at Ultralow Interfacial Tension: wetting, waves and droplets in demixed colloid-polymer mixtures*", Eur. Phys. J. B (2008), to appear (www.itf.fys.kuleuven.ac.be/~joi/)
[2] Y. Vandecan and J.O. Indekeu, "*Theoretical study of the three-phase contact line and its tension in adsorbed colloid-polymer mixtures*", J. Chem. Phys. **128**, 104902 (2008).

1. Colloidal suspension

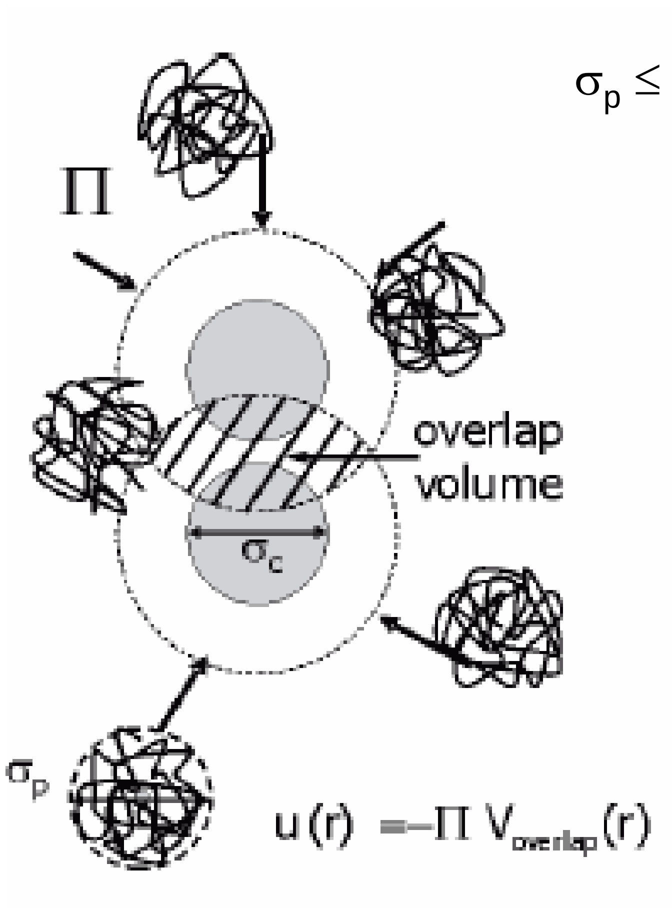
Brownian motion of a colloid:

"dance driven by random collisions with atoms according to the kinetic theory of heat" (Thirion, Delsaux, Carbonelle, s.j.; 1874); proof of the existence of atoms (Perrin 1910, Einstein 1905)

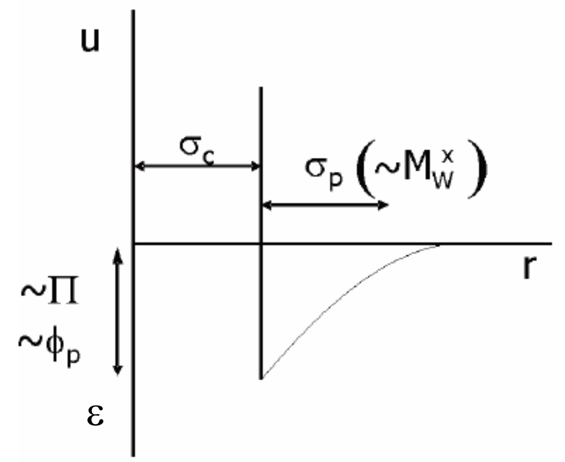


"Levitation by agitation": $Pe = (m_c - m_f) g R_c / kT < 1$

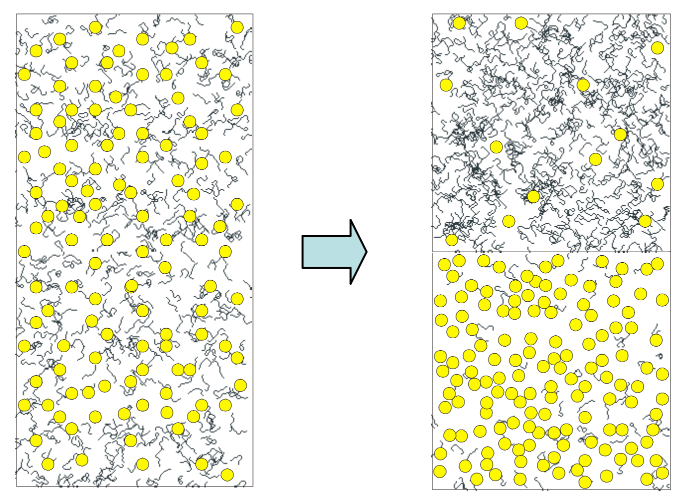
2. Hard spheres + tunable attractions



$\sigma_p \leq \sigma_c \approx 0.1\ \mu m$



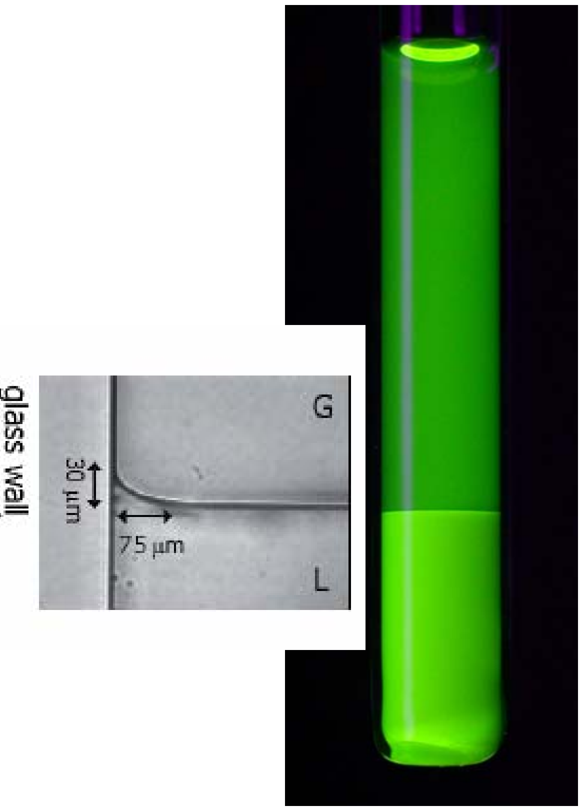
$\varepsilon / kT \approx 1$



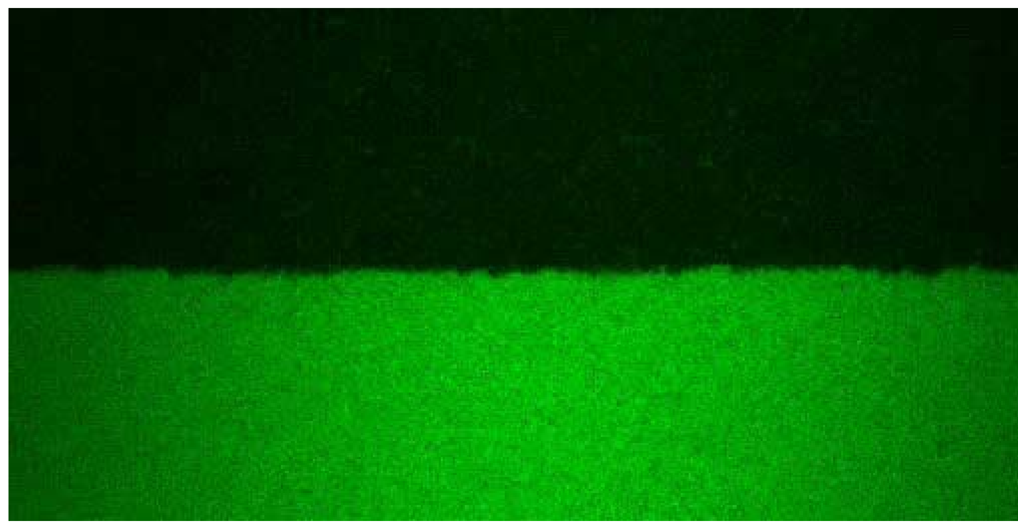
Depletion attraction (Asakura-Oosawa-Vrij)

3. Scales

Interfacial tension $\gamma = \varepsilon / \sigma^2$; 10nN/m for colloids, 10mN/m for molecular fluids

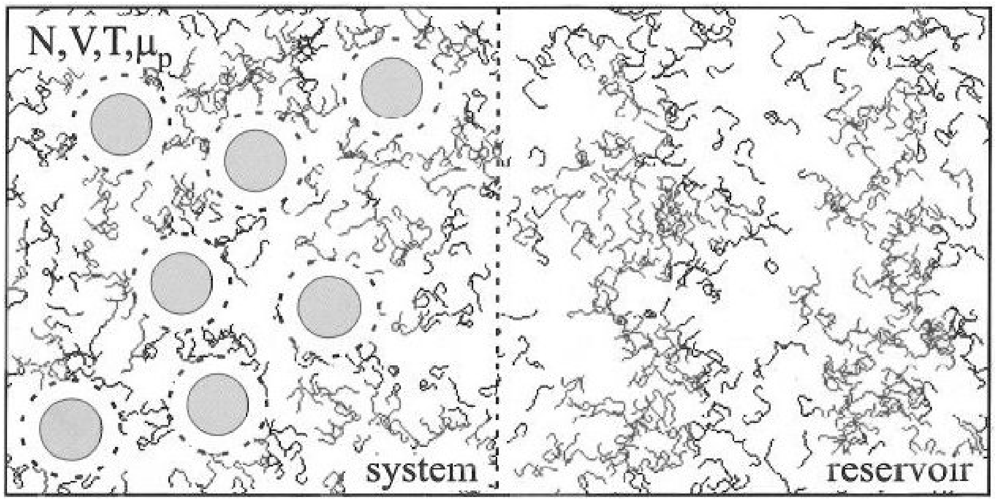


Thermal agitation of the interface: $L_T = (kT / \gamma)^{1/2} \approx \sigma$;
0.1µm for colloids, 0.1nm for molecular fluids



Capillary length $L_{cap} = (\gamma / g\Delta\rho)^{1/2}$; µm for colloids, mm for molecular fluids

4. Functions and variables



Semi-grand canonical potential

$\Omega \approx F(T,V,N_c) - kT\ N_p(\mu_p)$,

ideal polymers ($\Pi = n_p^r\ kT$)

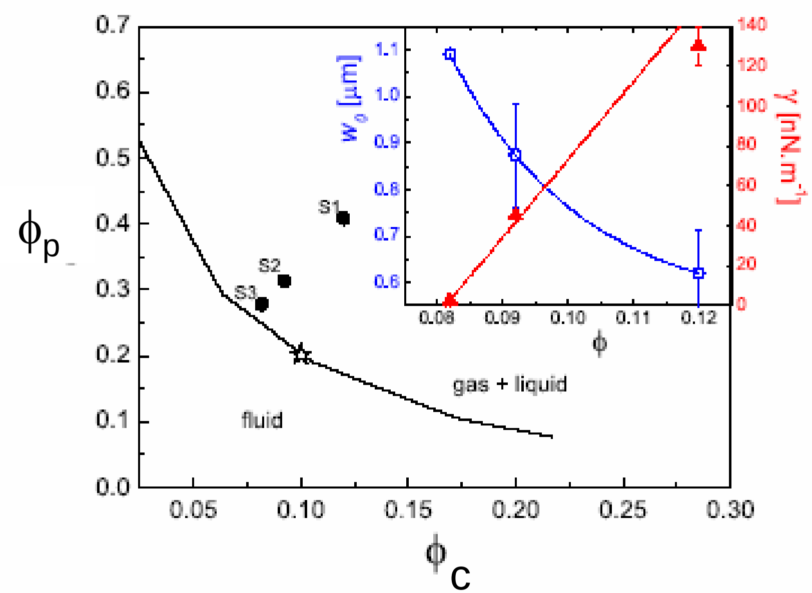
$N_p = n_p^r\ \alpha\ V$

Free volume $\alpha\ V \approx\ V - N_c(4/3)\pi(R_c + \Delta)^3$

R_g

$\alpha(\phi_c, \Delta/R_c) < 1 - \phi_c;\ \ \phi_p = \alpha\ \phi_p^r$

Excluded-volume-interacting polymers...

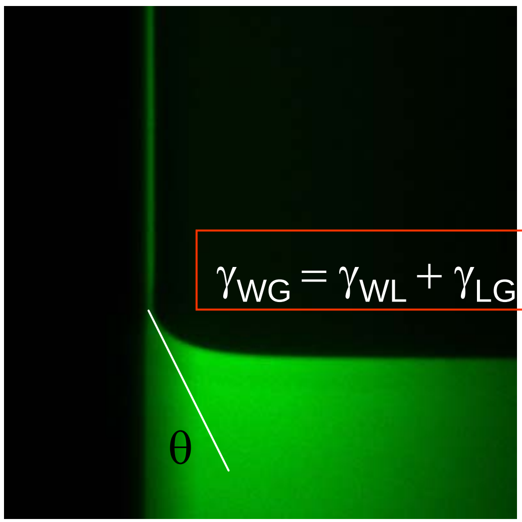


5. Walls and wetting

Cahn-Landau theory

$$\gamma[\rho] = \int_0^\infty dz \left(f(\rho) - \mu_c \rho(z) + p_c + m(\rho)\left(\frac{d\rho}{dz}\right)^2 \right)$$

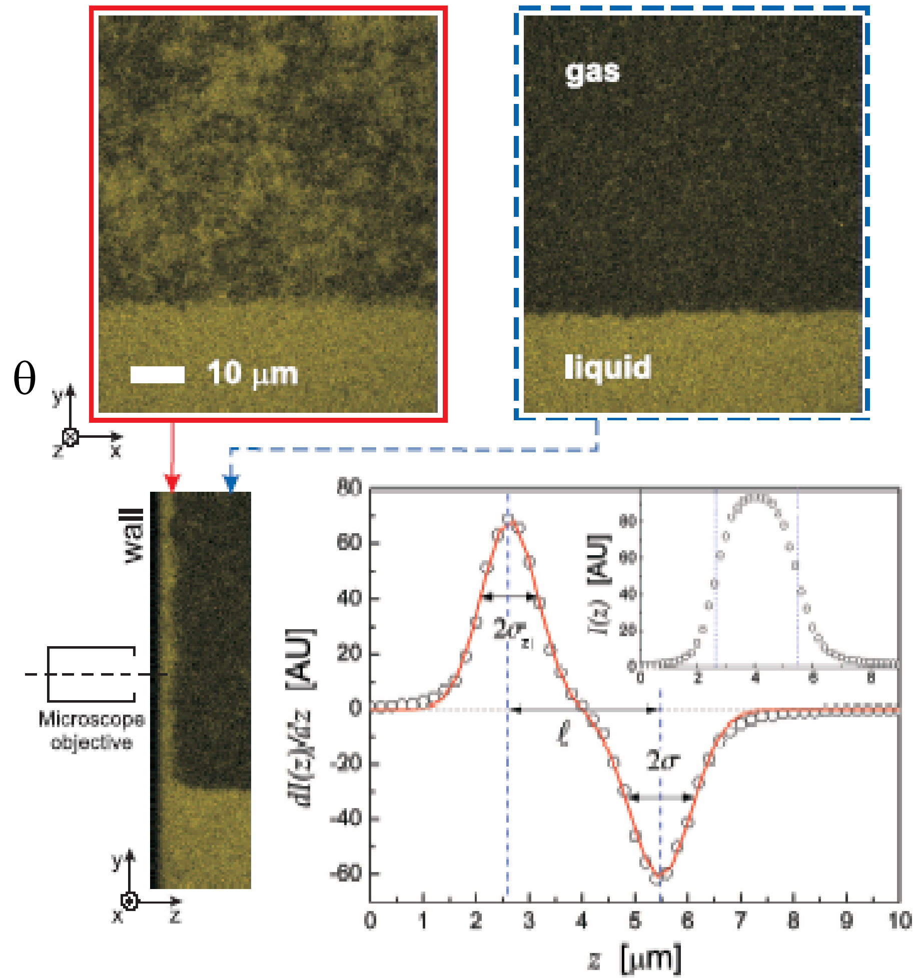
$$- h_1 \rho_1 - \frac{1}{2} g \rho_1^2, \qquad \rho = \phi_c$$



$$\gamma_{WG} = \gamma_{WL} + \gamma_{LG} \cos\theta$$

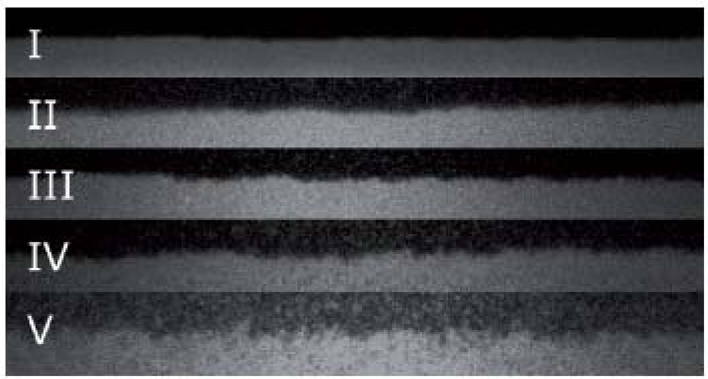
350μm

Laser scanning confocal microscopy



First-order wetting transition is predicted; complete wetting is observed

6. Free interface: capillary wave roughness



$\longleftarrow$ L_x $\longrightarrow$

$\uparrow$ $L_T = (kT/\gamma)^{1/2}$ "fluctuate with moderation"

$\longrightarrow$ $L_{cap} = (\gamma/g\Delta\rho)^{1/2}$ "stay horizontal"

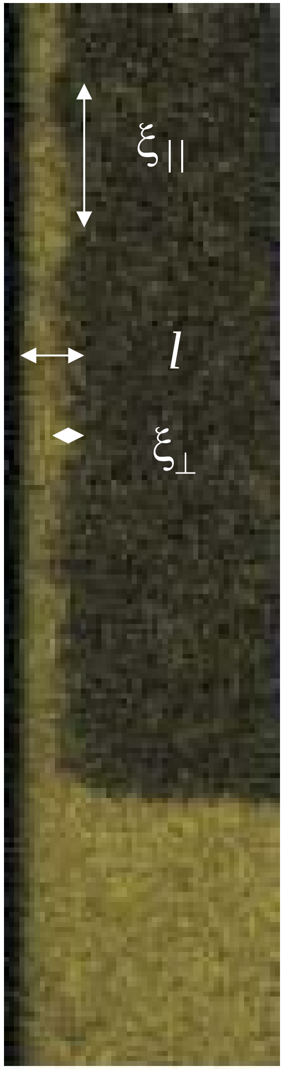
$\langle h(x,y)^2 \rangle \propto L_T^2 \log [\, ((2\pi/R_c)^2+(1/L_{cap})^2)/((2\pi/L_x)^2+(1/L_{cap})^2)]$

Without gravity: $\langle h(x,y)^2 \rangle \propto L_T^2 \log [L_x/R_c] \longrightarrow \infty$

Thermal wandering in space dimension d: $\langle h(x,y)^2 \rangle \propto L_x^{2\zeta}$; $\zeta = (3-d)/2$

Also favourable <u>time</u> scales for direct visualization: $\tau = (\eta/\gamma) L_{cap}$;
seconds for colloids, 10μs for molecular fluids

7. Unbinding from a wall: RG predictions vs experiment



$\langle h(x,y)^2 \rangle = (1/2\pi)\, L_T^2 \log(\xi_{||} / R_c)$

wetting parameter $\omega = kT/4\pi\gamma\xi^2 \approx 0.8$, Ising model

RG theory for wetting with short-range forces in d=3

D.S. Fisher and D.A. Huse, Phys. Rev. B **32**, 247 (1985);

R. Lipowsky and M.E. Fisher, Phys. Rev. B **36**, 2126 (1987).

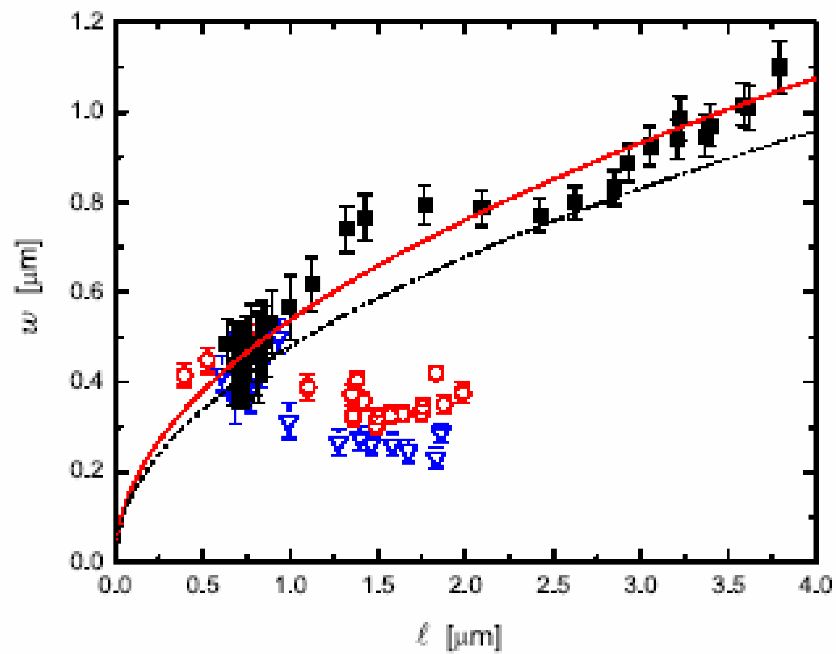
T. Kerle, J. Klein, and K. Binder, PRL **77**, 1318 (1996); Eur. Phys. J. B **7**, 401 (1999).

$l/\xi = F(\omega) \log(\xi_{||}/\xi)$

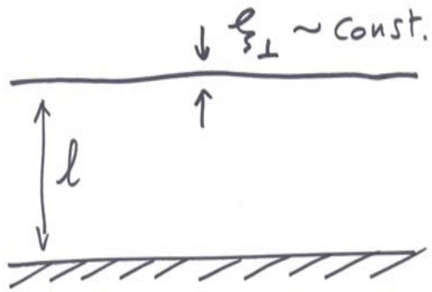
$\xi_\perp^2 = f(\omega)\, L_T\, l$

Expt. $\xi_\perp^2 = 0.29\ \mu m\ l$

Theory $\xi_\perp^2 = 0.23\ \mu m\ l$



Mean-field regime: $\xi_\perp$ remains constant* while l *and* $\xi_{||}$ diverge



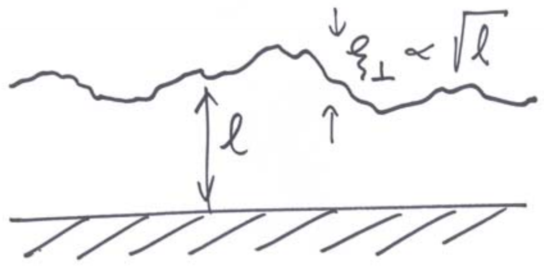
e.g., systems with van der Waals forces in d=3

* or diverges logarithmically

All fluctuation regimes: $\xi_\perp \propto l$

d < d_u, regardless of short- or long-range forces, critical or complete wetting, and including membranes

Marginal regime: $\xi_\perp \propto \sqrt{l}$



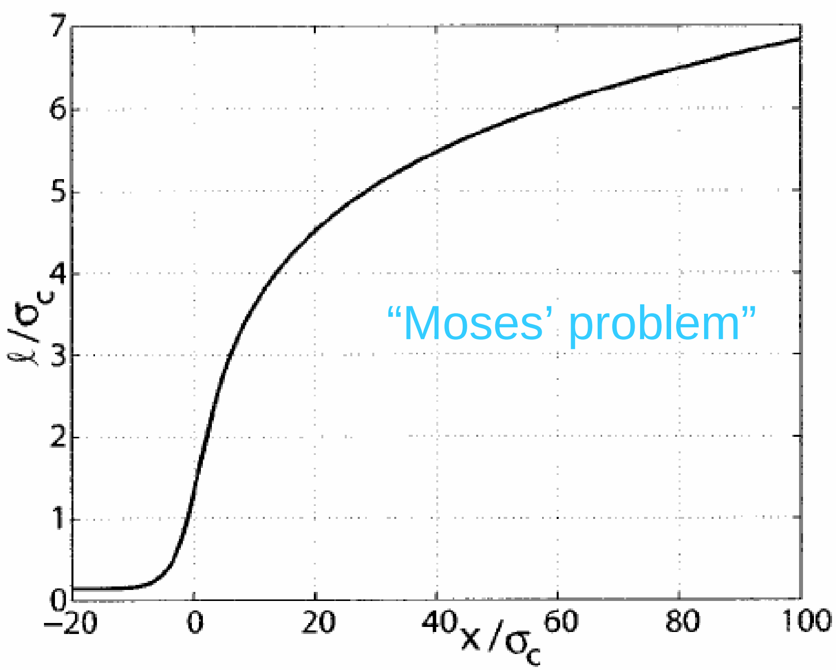
short-range forces and $d = d_u = 3$,
regardless of critical or complete wetting

8. Line tension

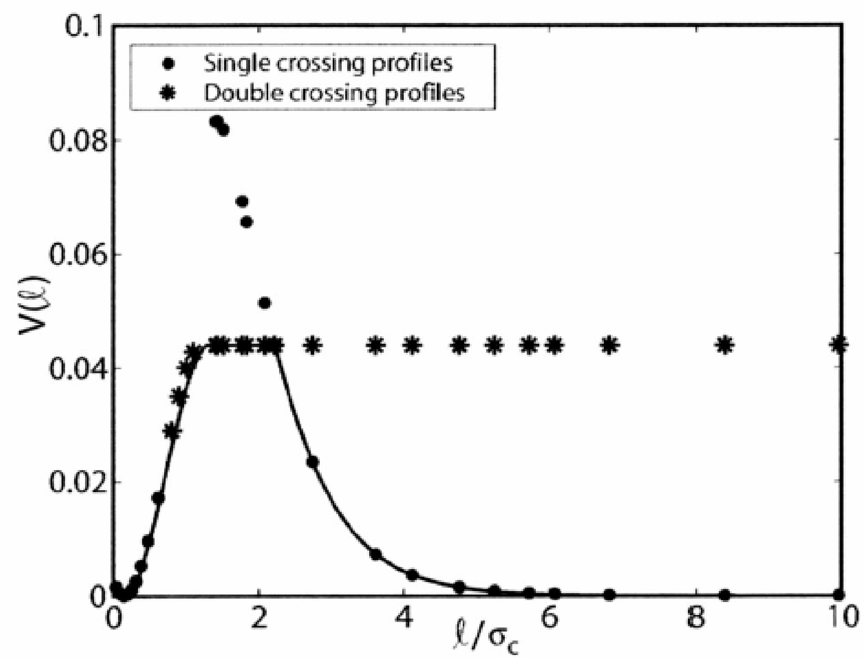
$$\tau[\ell] = \int_{-\infty}^{\infty} dx \left[\gamma_{LG} \left(\sqrt{1 + \left(\frac{d\ell}{dx} \right)^2} - 1 \right) + V(\ell(x)) + c(x) \right],$$

$$\tau = (2\gamma_{LG})^{1/2} \xi \int_{\ell_1}^{\infty} d\tilde{\ell} [V(\tilde{\ell})^{1/2} - E^{1/2}],$$

Typically $\tau \approx \gamma\xi$; 10^{-13} N for colloids, 10^{-11} N for molecular fluids



Interface displacement at first-order wetting



Interface potential