

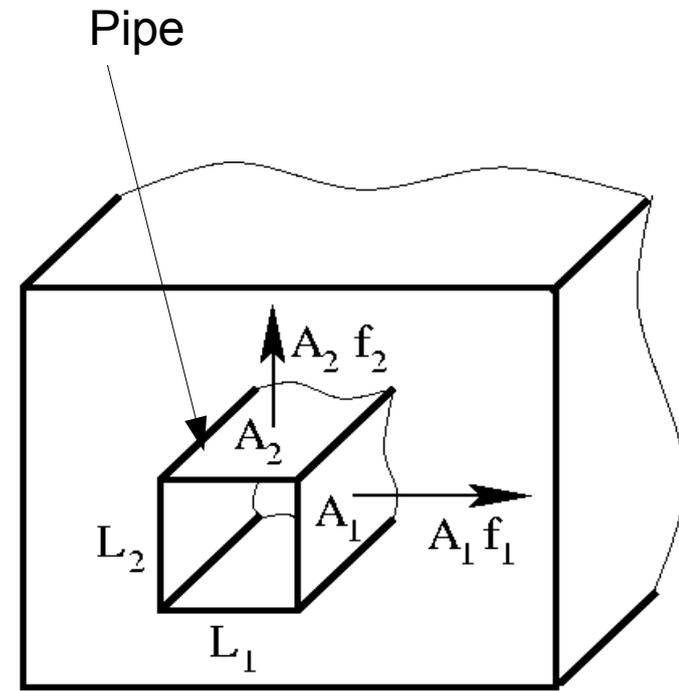
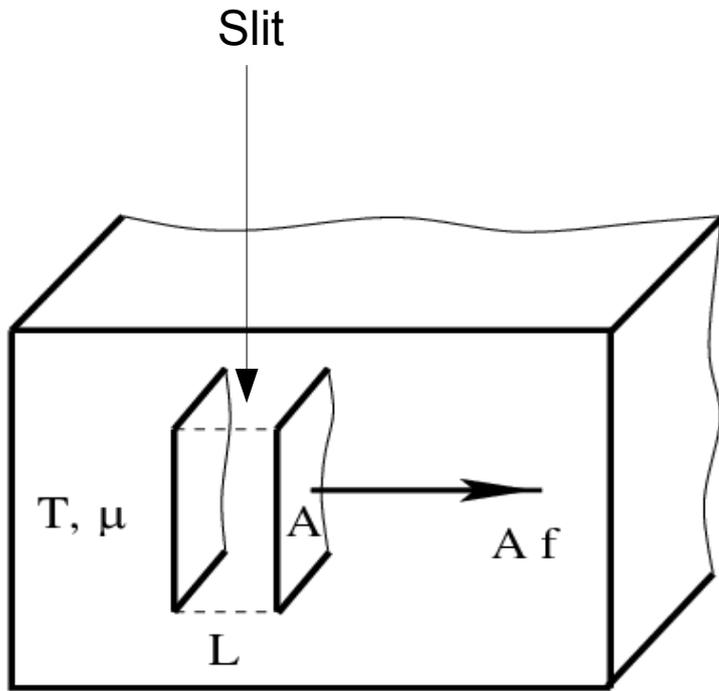
# Effects of confinement on phase equilibria in nonisotropic and nonuniform fluids

A. Ciach and M. Tasinkevych

- Confinement
- Capillary condensation and Kelvin equation
- Lyotropic liquid crystals
- Slit – role of elasticity
- Pipe – role of domain walls

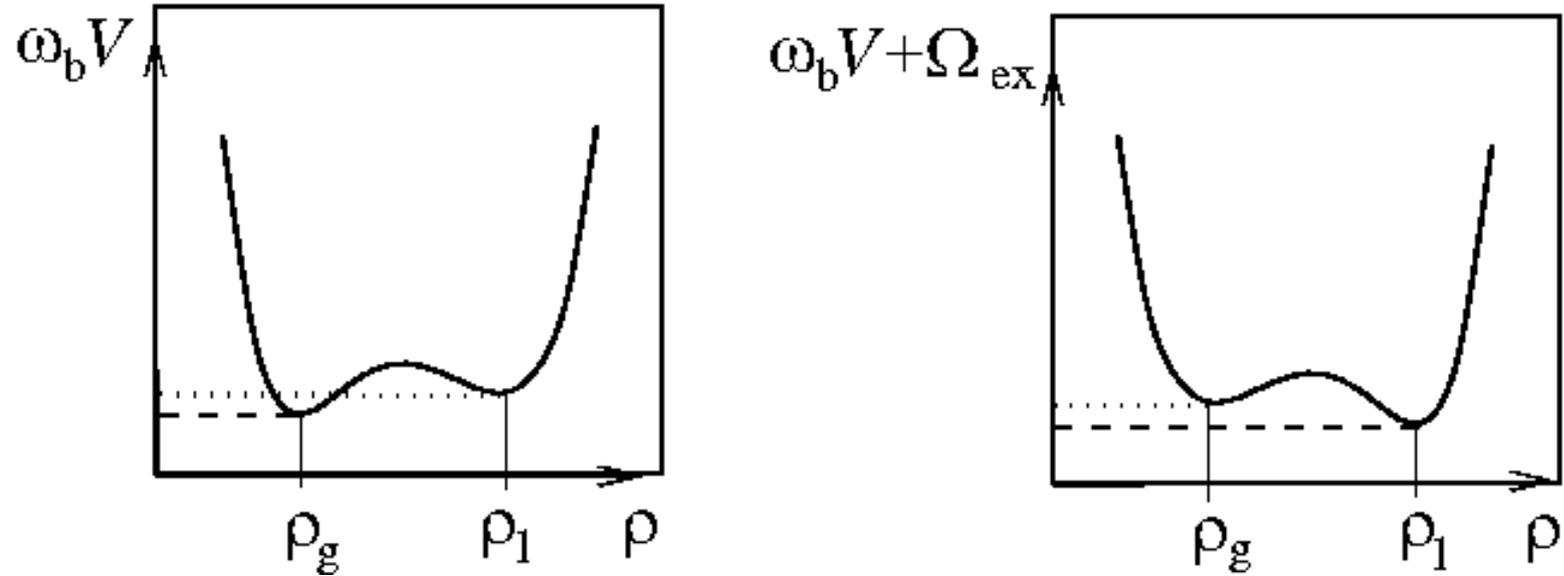
# Confinement

$$\Omega = \omega_b V + \Omega_{ex}$$



Question: dependence of  $\Omega_{ex}$  on the size and shape of a container in nonuniform phases

# Capillary condensation in simple fluids



$$d\Omega_{ex} = 2\sigma dA + f(L) A dL$$

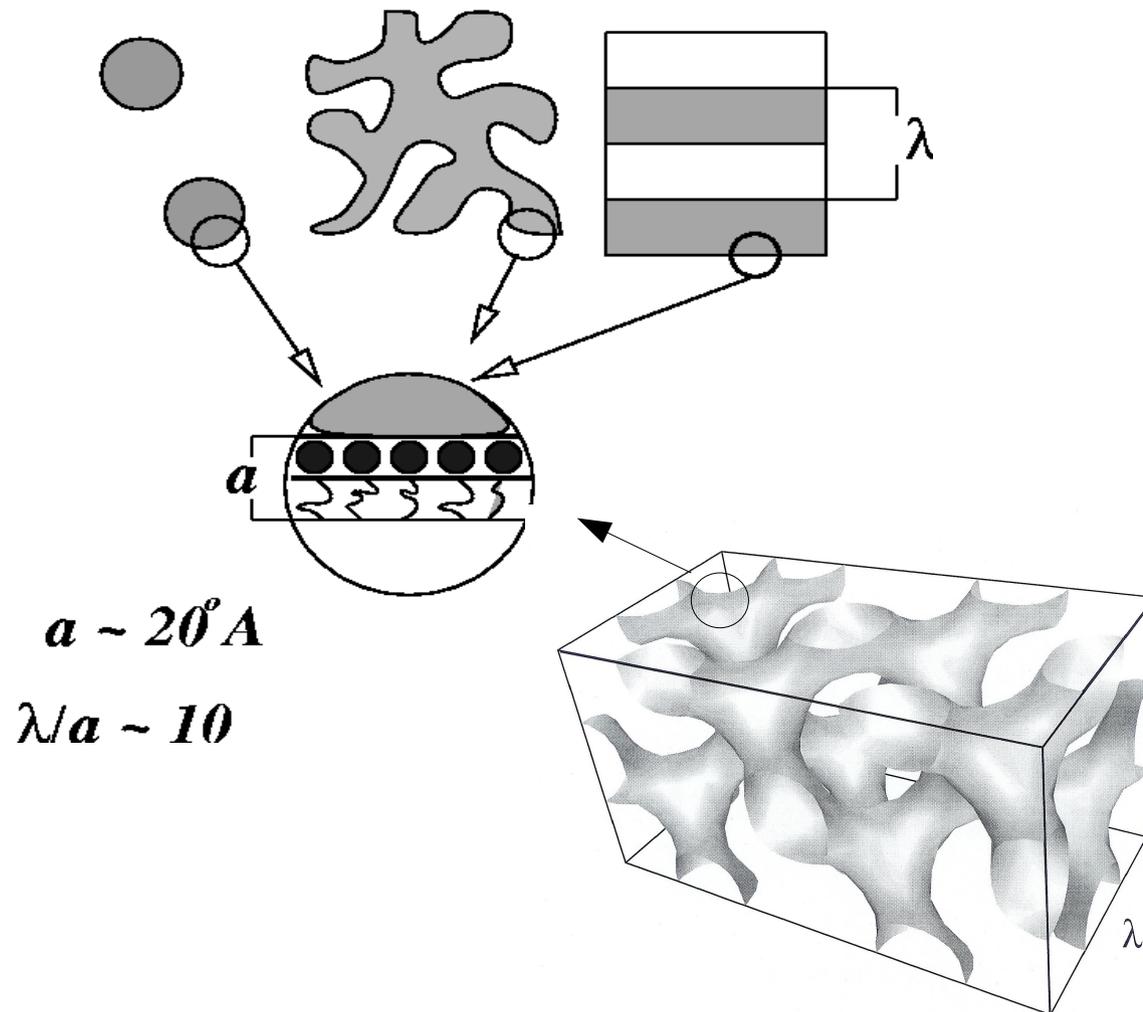
Kelvin equation, obtained for  $L$  such that  $f(L)$  is negligible:

$$\Delta\mu = \frac{\Delta\sigma}{\Delta\rho L}$$

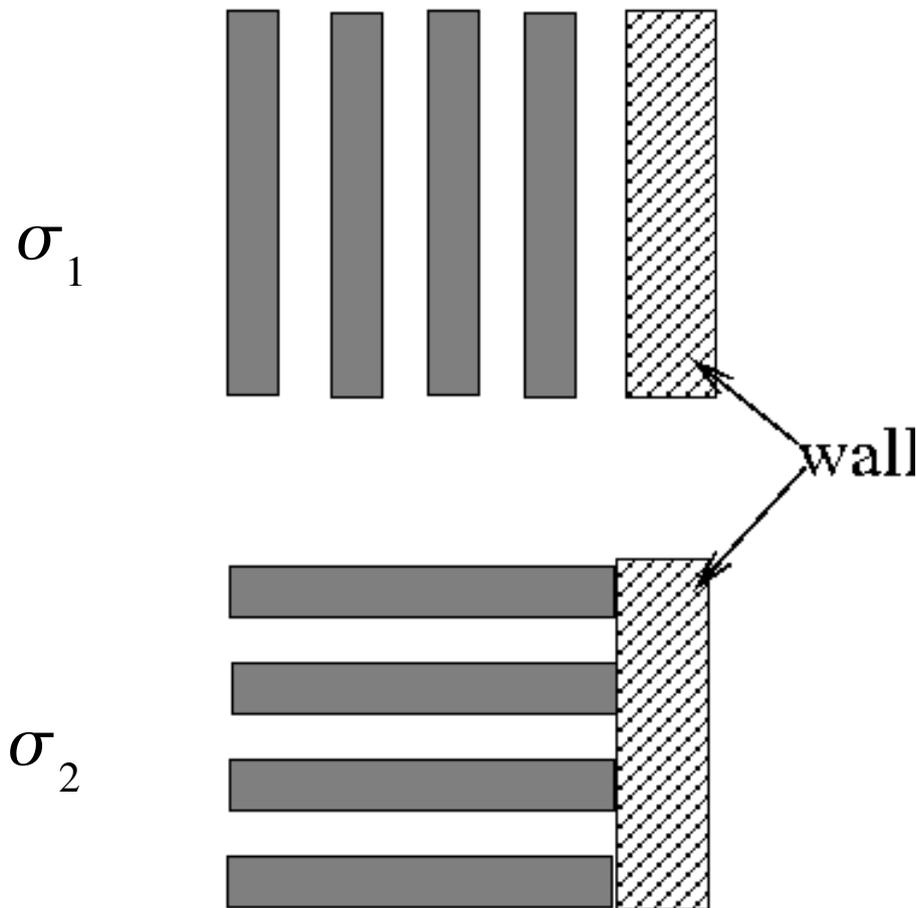
# Lyotropic liquid crystals

There are many metastable phases with different morphology

## TYPICAL STRUCTURES



Wall-fluid surface tension  $\sigma$  depends on the orientation of the wall.

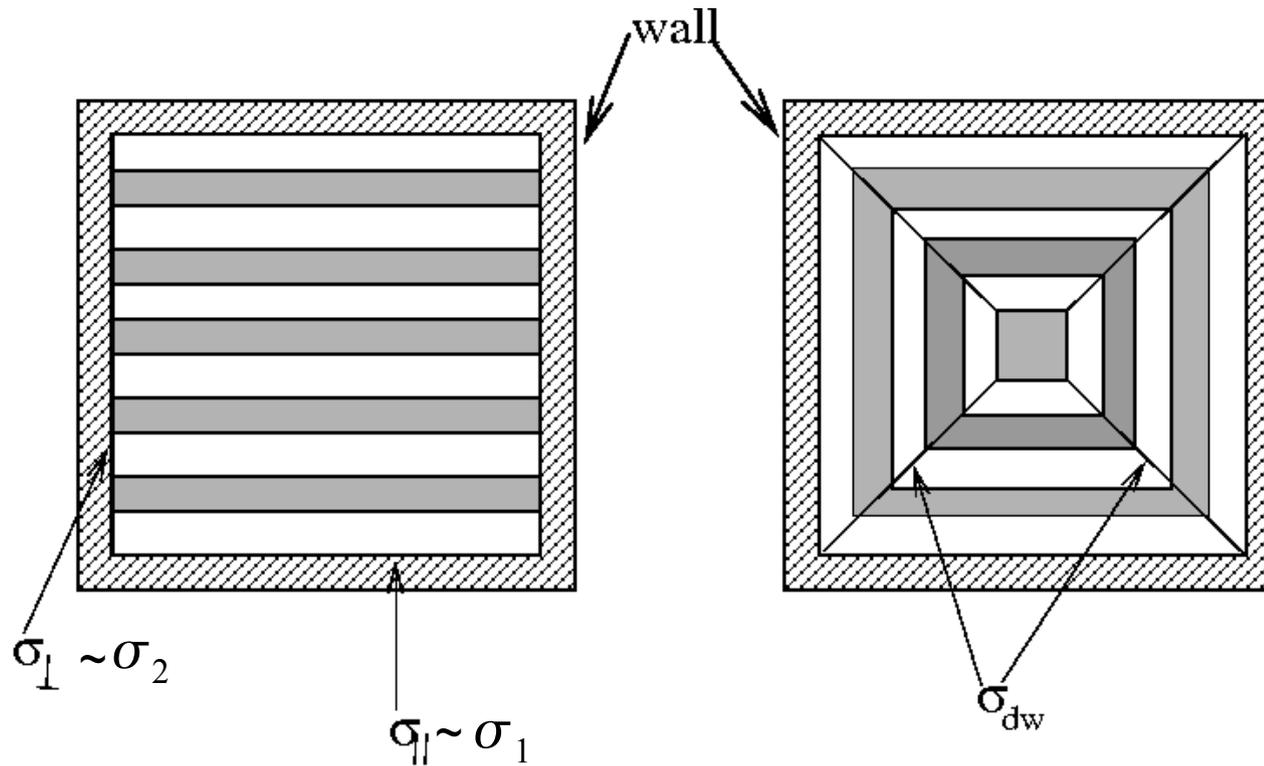


except from neutral or weakly hydrophilic walls, and small  $\lambda/a$ ,

$$\sigma_1 < \sigma_2$$

In slits  $\Omega$  depends on  $L/\lambda$  in the case of the parallel orientation.

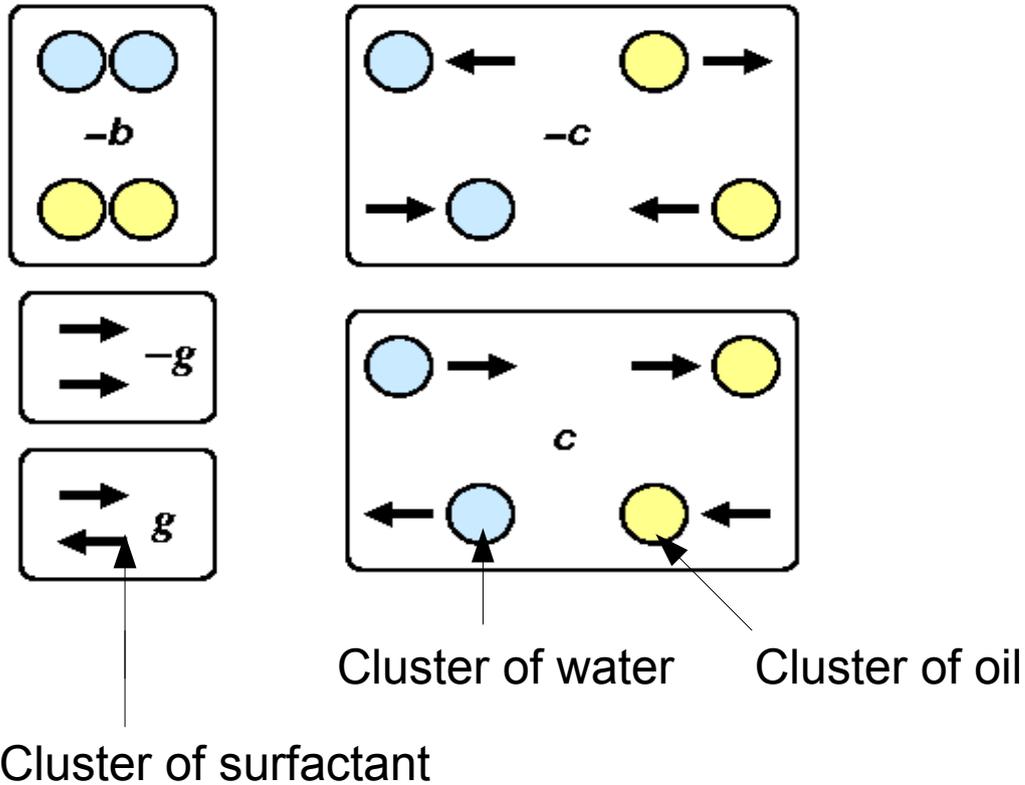
# Frustration in a pipe for any value of $L$



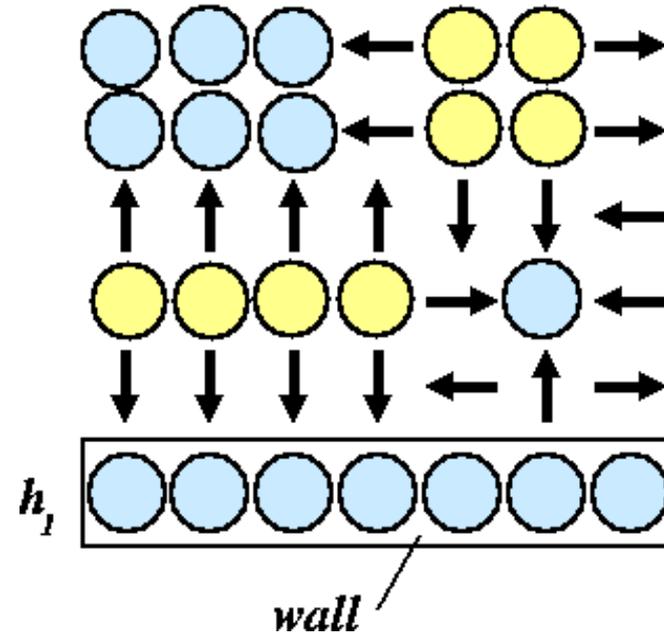
Stable structure depends on surface energies and on  $L/\lambda$

# Generic model for oil-water-surfactant mixtures

## Pair interactions



## Typical configuration



## Mean-field approximation

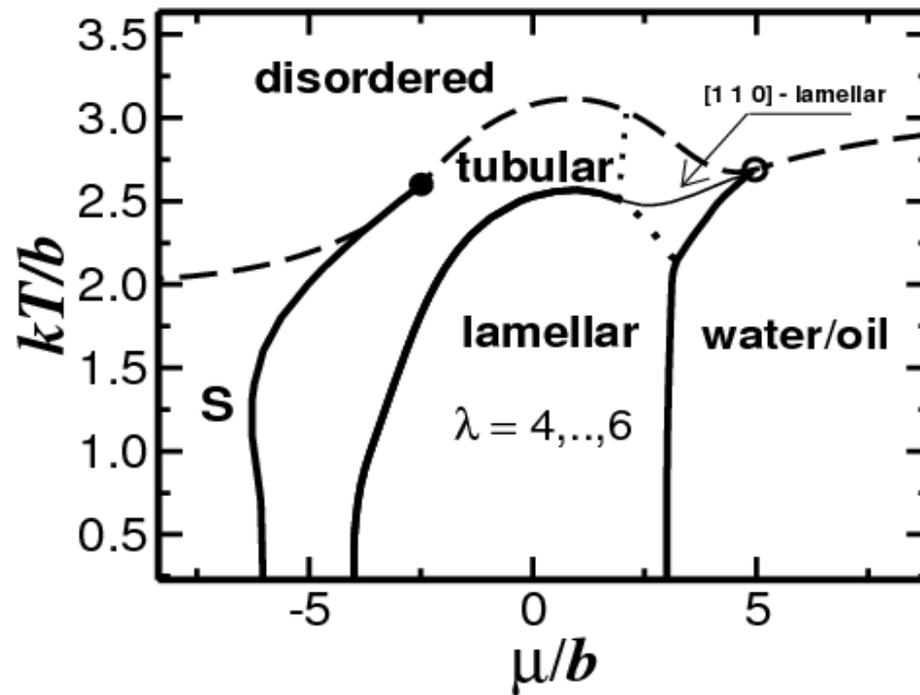
$$\Omega[\{\rho_i(\mathbf{r})\}] = H_{MF}[\{\rho_i(\mathbf{r})\}] + kT \sum_r \rho_i(\mathbf{r}) \log \rho_i(\mathbf{r})$$

$$H_{MF}[\{\rho_i(\mathbf{r})\}] = \frac{1}{2} \sum_{r_1} \sum_{r_2} \rho_i(\mathbf{r}_1) u_{ij}(\mathbf{r}_1 - \mathbf{r}_2) \rho_j(\mathbf{r}_2) \\ - \mu \sum_r (\rho_1(\mathbf{r}) + \rho_2(\mathbf{r})) + \sum_r h_i(\mathbf{r}) \rho_i(\mathbf{r})$$

Stable (metastable) phases correspond to a global (local) minimum of  $\Omega$ . At the phase coexistence  $\Omega$  assumes the same value at two minima, corresponding to different density profiles.

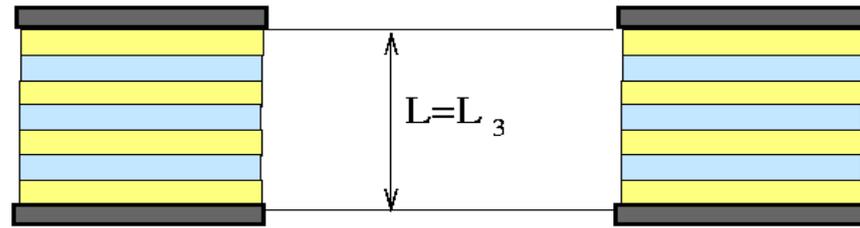
$\mu$  is the difference between chemical potentials of water and surfactant,  $h_i$  is the surface field.

Phase diagram in the CHS model for  $c/b = 2.5$ ,  $g/b = 1$   
in the mean-field approximation

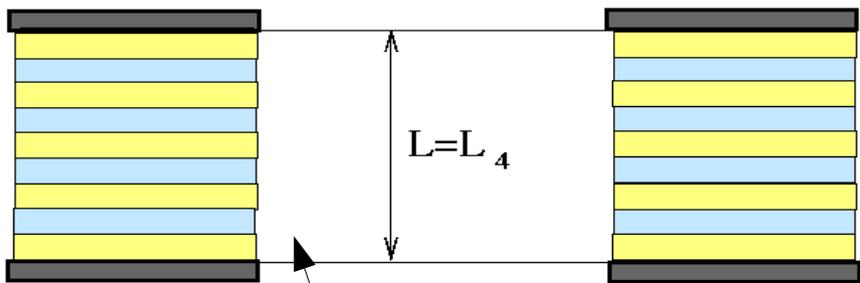
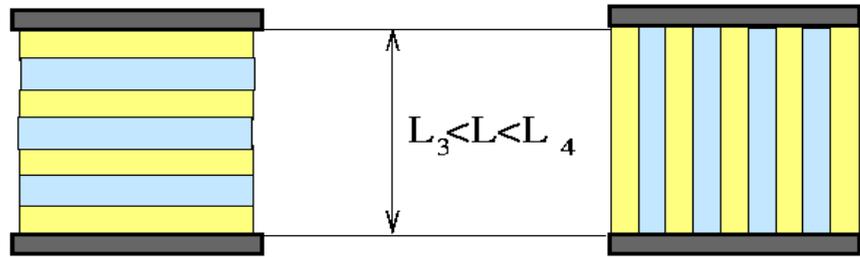


Structures in a slit **far from the phase transition** to the uniform phase.  
 Left column: large  $\lambda/a$ , any kind of walls, and small  $\lambda/a$ , hydrophilic walls;  
 right column: small  $\lambda/a$ , weakly hydrophilic walls

Small  $B$ :  
 elastic behavior



Large  $B$ :  
 switch of orientation for weakly hydrophilic walls,  
 or perpendicular orientation for neutral walls



Experimentally verified for water – surfactant and block – copolymer systems.

In the parallel orientation elastic response to compression or expansion with respect to the bulk structure.

Solvation force (disjoining pressure) decays algebraically as a function of  $L$ .  
Stress is not released for large  $L$ , if  $L$  is incommensurate with  $\lambda$ .

Modulus of elasticity  $B$  is a decreasing function of  $\lambda$

$$\frac{\Omega_{ex}}{A} = 2\sigma_1 + \frac{B}{2L_N} (L - L_N)^2$$

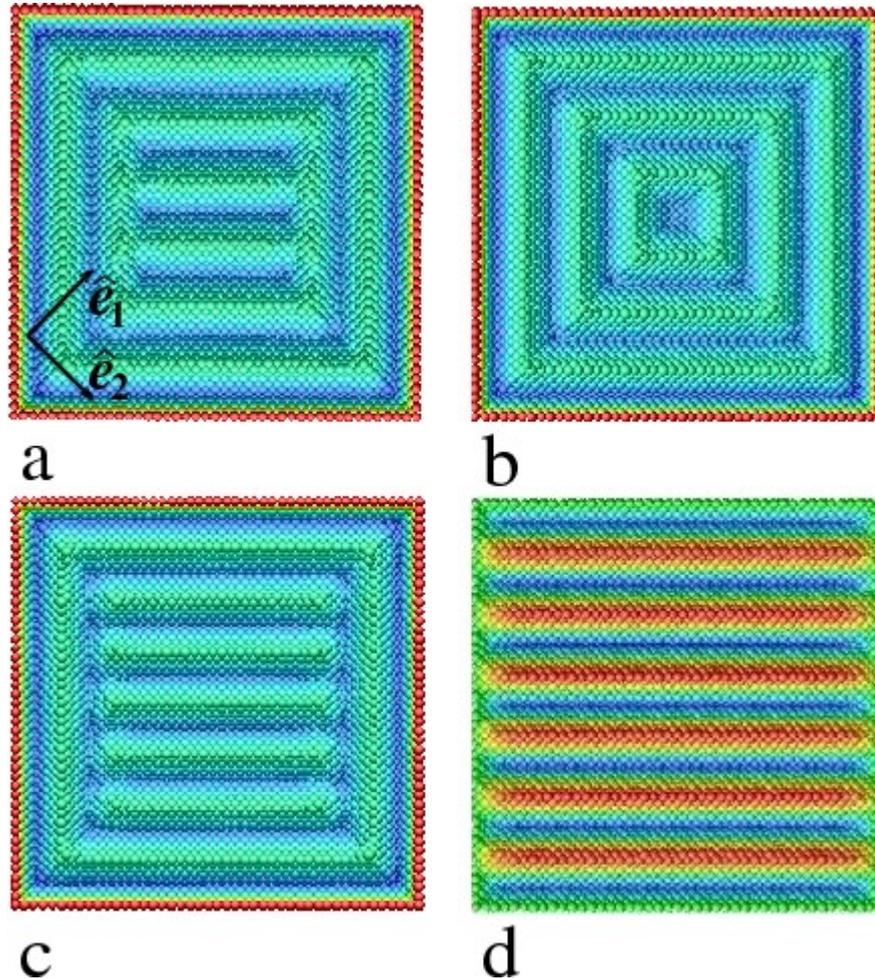
In the perpendicular orientation no stress is present for  $N > 5$

$$\frac{\Omega_{ex}}{A} = 2\sigma_2$$

$L_N$  - equilibrium width for  $N$  confined layers

$B$  shows a good semiquantitative agreement with experiments for  $\lambda \sim 10a$

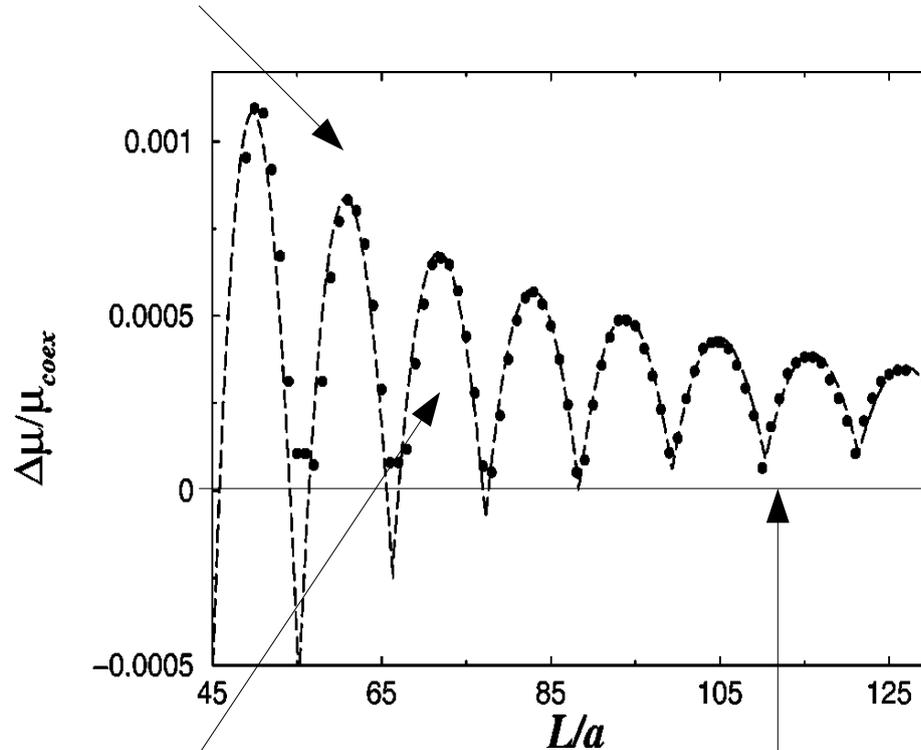
Structures in a pipe **far from the phase transition** to the uniform phase.  
a-c hydrophilic walls ( $L/d=82, 84, 90$  resp.) , no stress in the case c.  
d - neutral walls



Close to the phase transition to the uniform phase the case b corresponds to the equilibrium structure for all  $L$  and for all kinds of surfaces

# Lamellar phase in a slit **close** to the bulk phase transition

uniform



lamellar

transition in the bulk

**Capillary lamellarization** in slits with hydrophilic walls. Sequence of lamellar-uniform phase transitions

Modified Kelvin equation

$$\Delta\mu = \frac{\Delta\sigma}{\Delta\rho L} + \frac{B(L - L_N)}{2\Delta\rho L L_N}$$

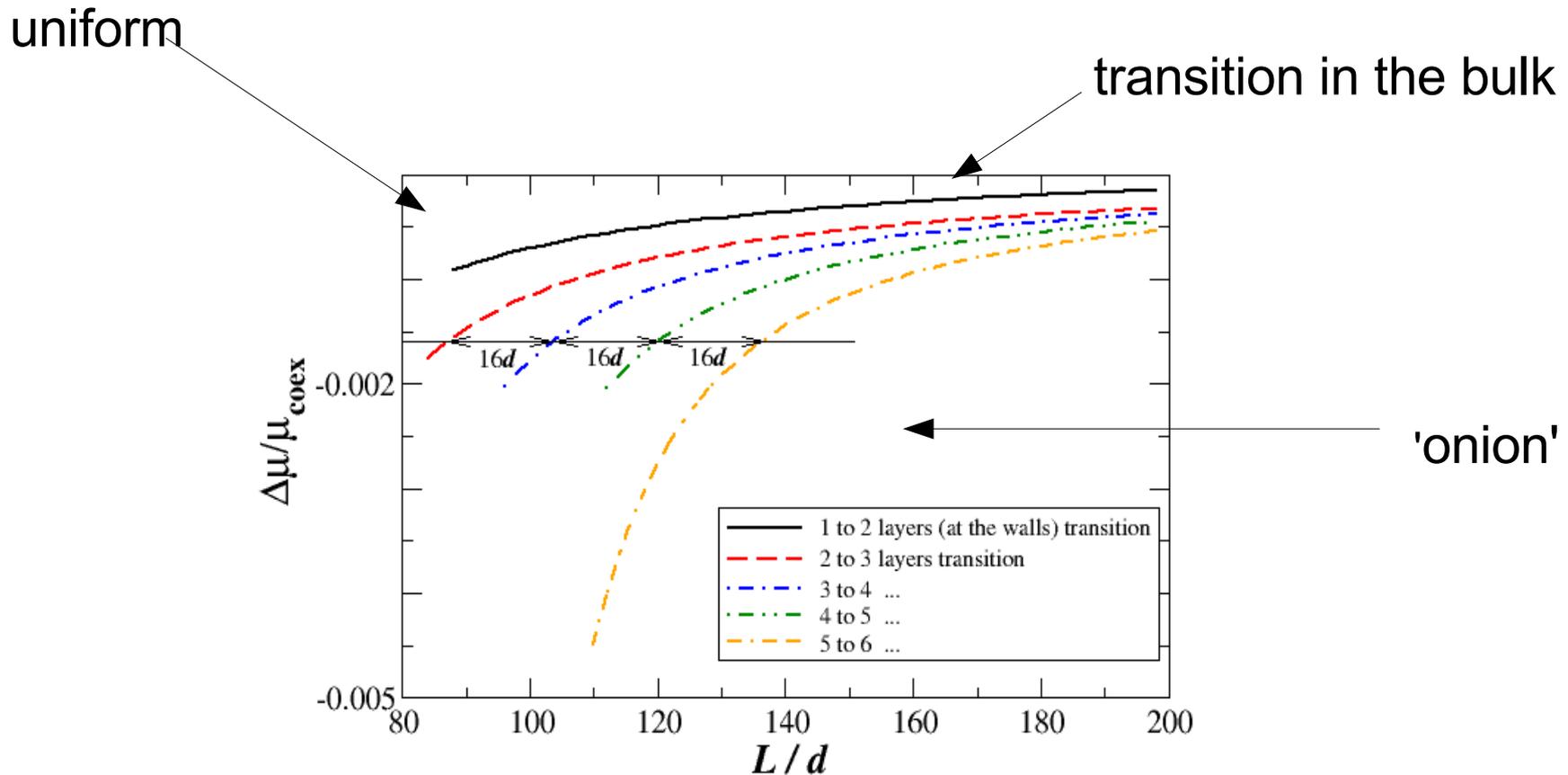
Symbols - results obtained in the generic model (for  $c/b=2.4$ ,  $g/b=0.15$ ).  
Line - modified Kelvin equation with phenomenological parameters obtained by independent calculations.

# Lamellar phase in a pipe **close** to the bulk phase transition

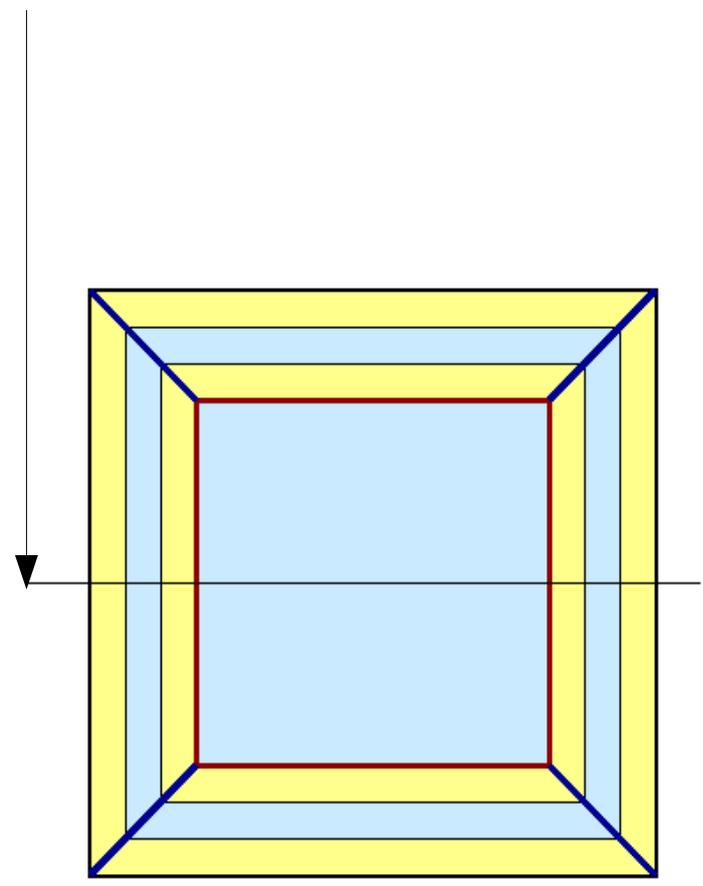
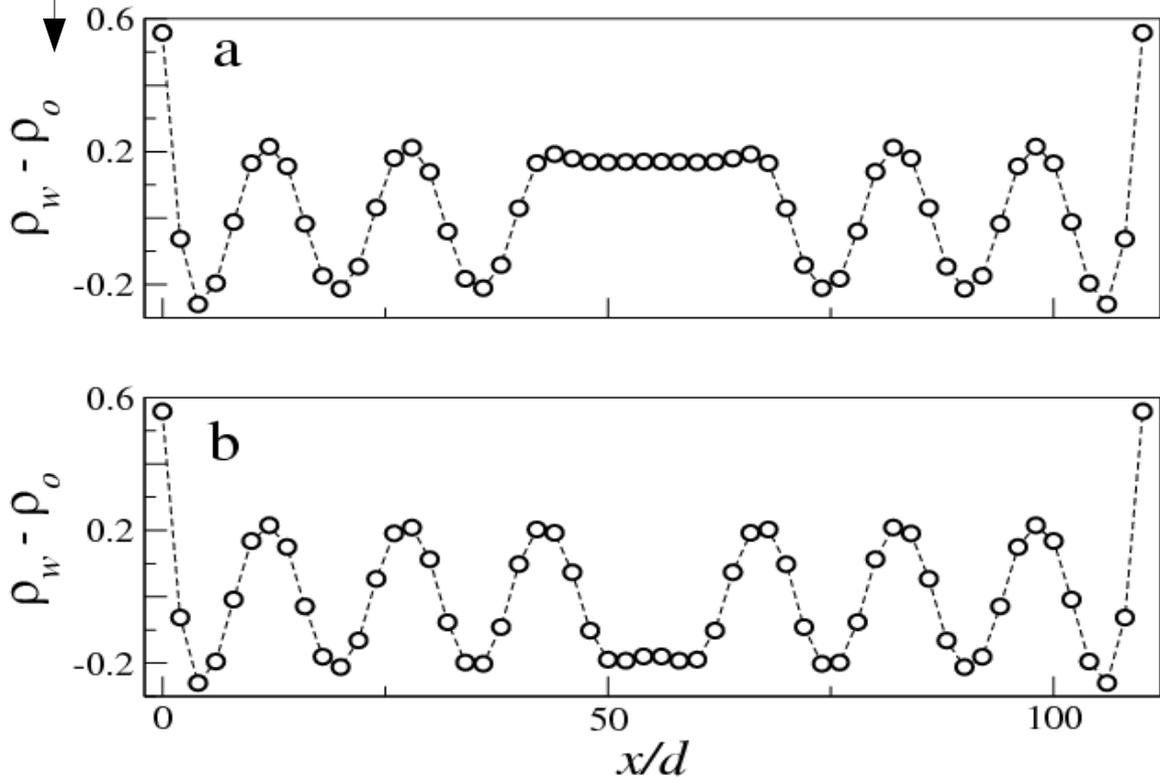
## **Capillary delamellarization** in pipes with arbitrary walls.

The number of lamellar rings at the walls decreases, when the bulk transition to the uniform phase is approached.

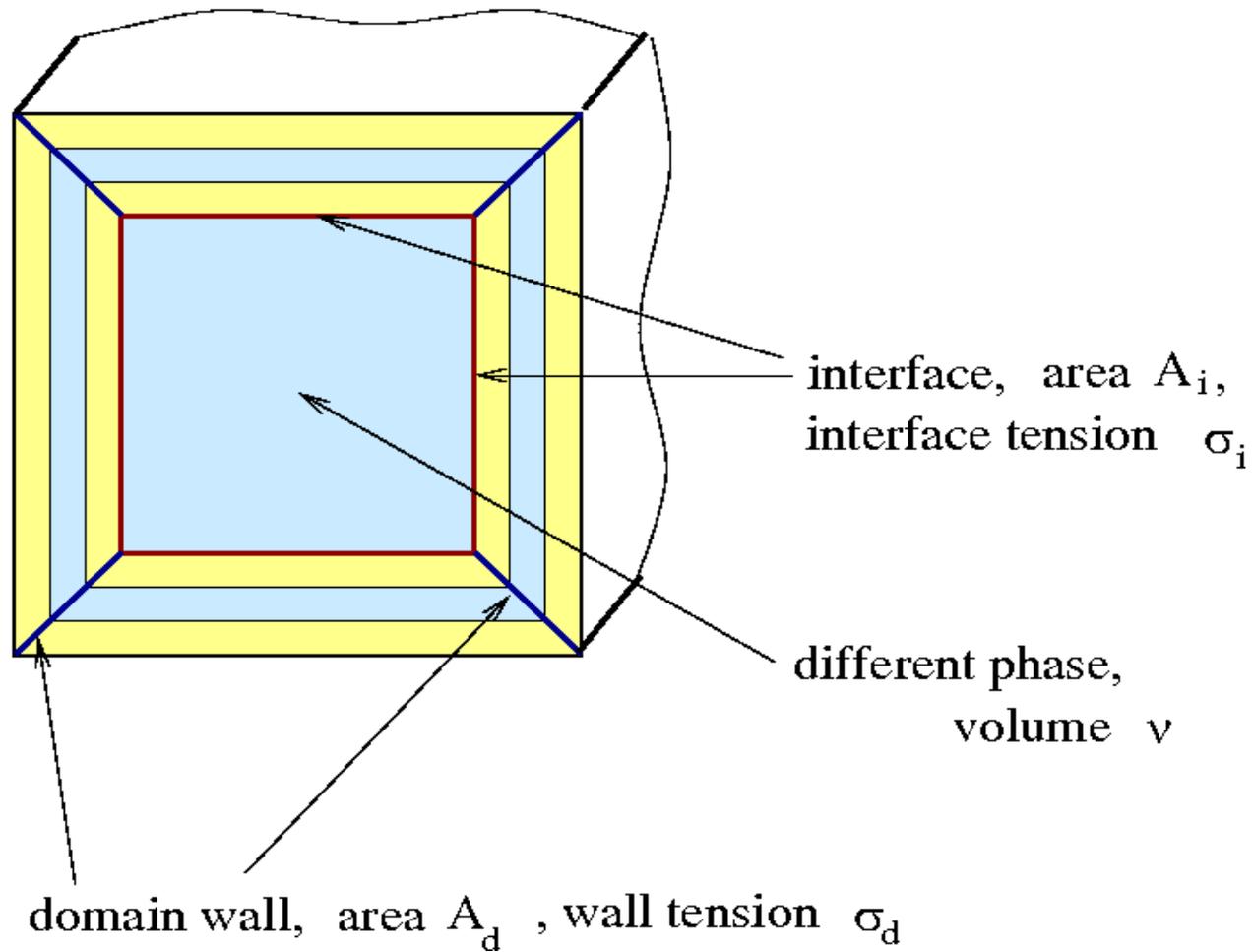
The center is occupied by the uniform phase.



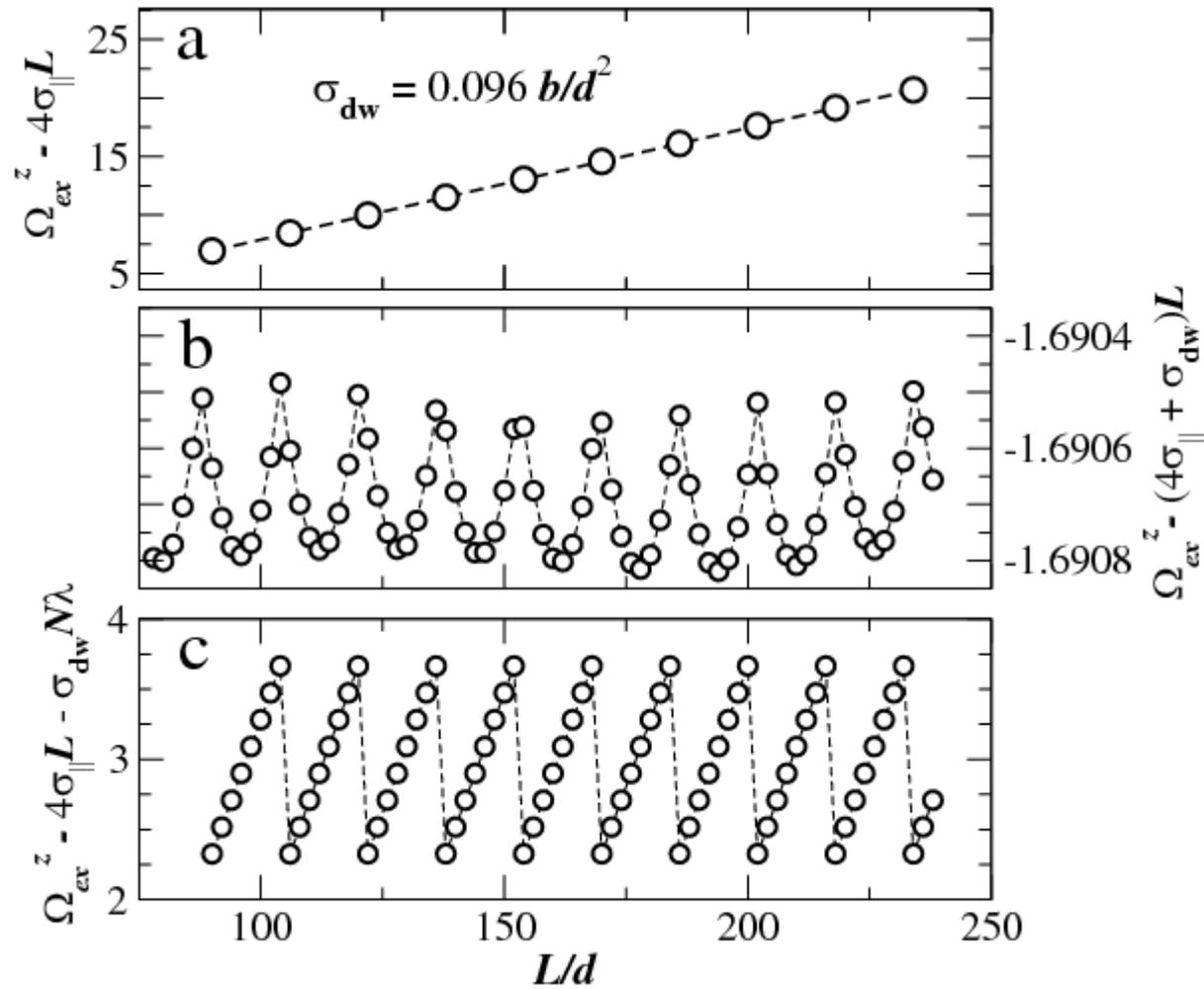
# Water-oil density difference across the center of the pipe



Two coexisting onion structures at the delamellarization transition are shown



$$\begin{aligned}
 d\Omega_{ex} = & 2\sigma_1 dA_1 + f_1 A_1 dL_1 + 2\sigma_2 dA_2 + f_2 A_2 dL_2 \\
 & + 4\sigma_d dA_d + 4\sigma_i dA_i + \Delta\omega_b dv
 \end{aligned}$$



$$\Omega_{ex}^z = \Omega_{ex} / L_z = 4\sigma_1 L + \sigma_{dw} L + \Delta\omega_b (L - N\lambda)^2 + \delta$$

$$\sigma_{dw} L = \sigma_{dw} N\lambda + 4\sigma_i (L - N\lambda)$$



Surface energy of all domain walls and interfaces per area of one external wall

Our findings show that **mechanical** and **structural** effects of confinement strongly influence phase equilibria between uniform and nonuniform phases.

A phase **metastable** in the bulk may occupy a part of the confined space.

**Elastic** properties influence phase equilibria in slits.

In pipes **domains** with **different orientations** of the symmetry elements of the periodic phase that meet at domain walls are favorable compared to a single domain.

Elastic energy is negligible compared to surface energies associated with a domain-wall and interface tension.

The above effects are associated with **additional positive contributions** to the thermodynamic potential. The phenomenological parameters are not independent of each other, and result from interaction potentials. They can be calculated for model systems within statistical mechanics, as we did for the generic model of effective interactions.