

# Surface Phase Transitions: different wetting scenarios

As an example: the wetting transition

## wetting of a solid substrate by a liquid drop

phases in equilibrium: liquid (l) and vapour (v)  
substrate phase: solid (s)

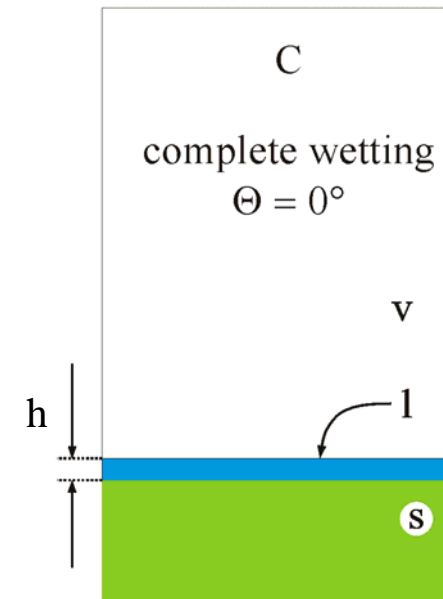
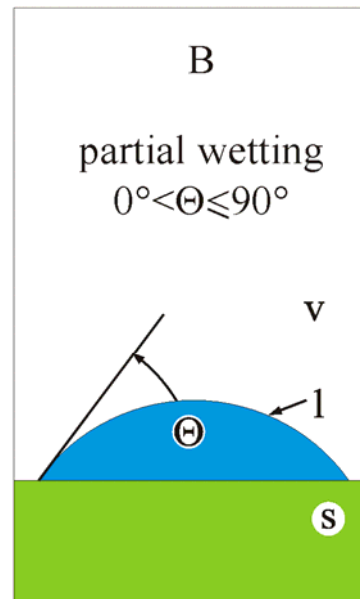
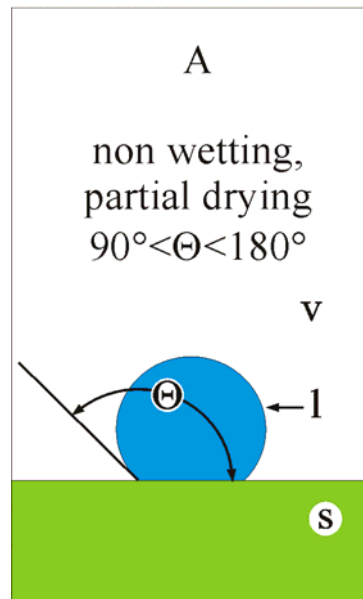
Configurations of particular interest here:

Reviews:

S. Dietrich, in *Phase Transitions and Critical Phenomena*, eds. C. Domb, J. Lebowitz, Vol. 12 (Academic Press, London, 1987).

M. Schick, in *Liquids at Interfaces, Les Houches Session XLVIII*, eds. J. Charvolin, J. F. Joanny, J. Zinn-Justin (North-Holland, Amsterdam, 1990).

D. Bonn, D. Ross, *Rep. Prog. Phys.* **64**, 1085 (2001).



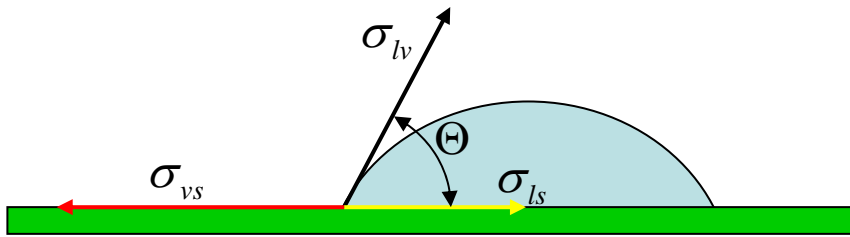
Problems:

How does transformation from B to C occur?

What is the value of the film thickness  $h$ ?

On what does  $h$  depend on?

# Surface Phase Transitions: Cahn's argument



Cahn's argument:

J. W. Cahn, J. Chem. Phys. **66** (1977) 3667

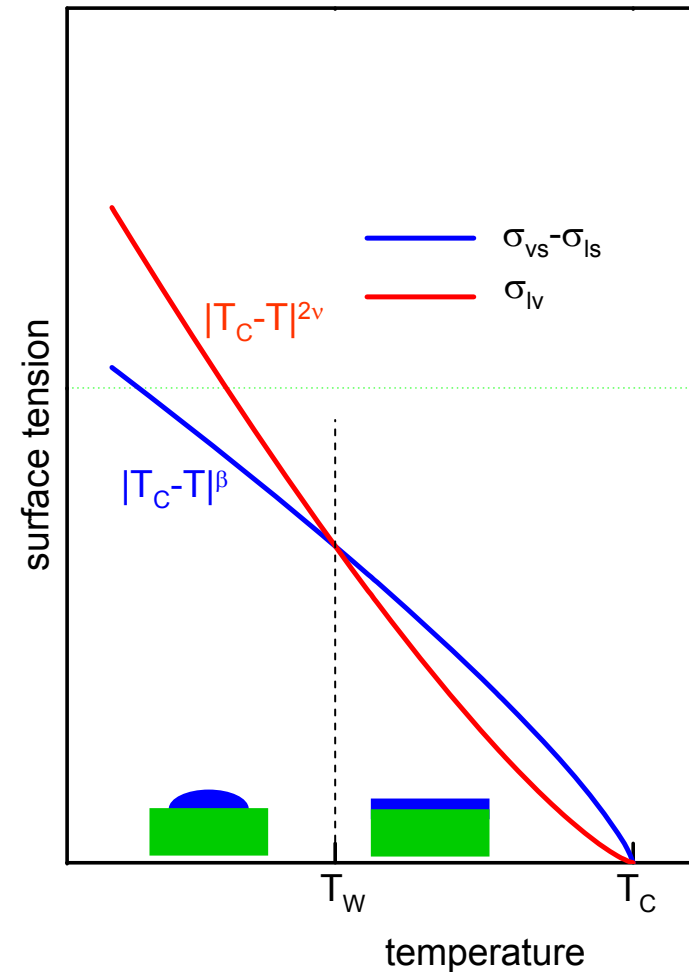
Young-Dupree-equation: 
$$\cos \Theta = \frac{\sigma_{vs} - \sigma_{ls}}{\sigma_{lv}}$$

Temperature dependence close to the critical point:

$$\sigma_{vs} - \sigma_{ls} \propto |T_C - T|^{\beta_1} \quad \text{with} \quad \beta_1 \approx 0.8$$

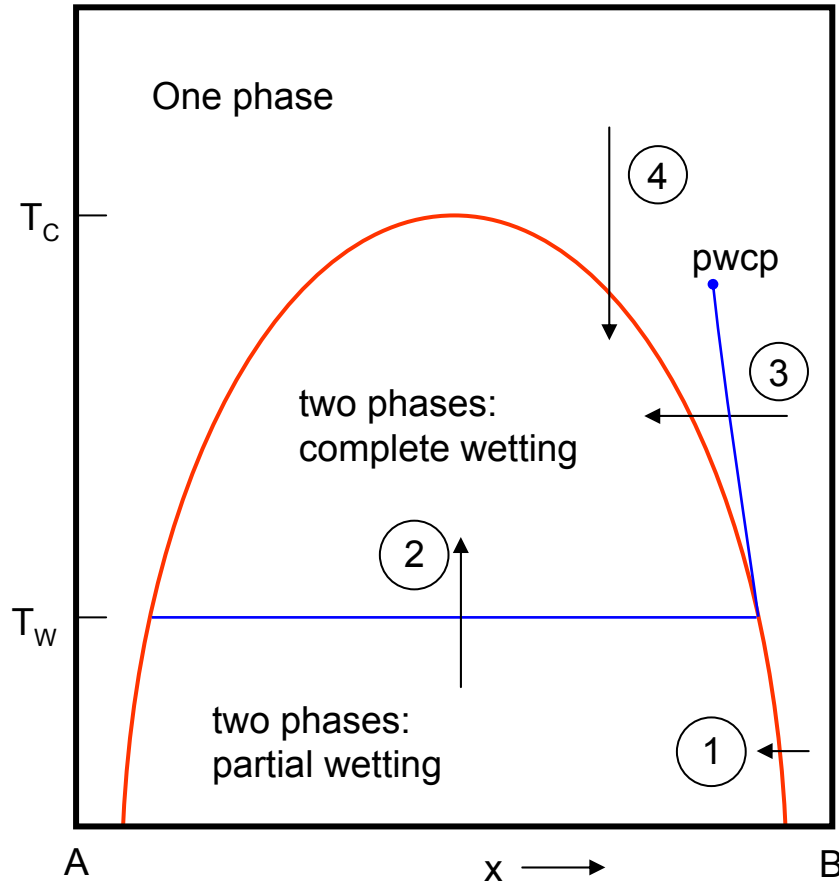
$$\sigma_{lv} \propto |T_C - T|^{2\nu} \quad \text{with} \quad \nu \approx 0.63$$

At the wetting temperature  $T_w < T_C$  the cosine in the Young-Dupree-equation is one, and  $\Theta$  becomes zero. Below  $T_w$  we have partial wetting, above  $T_w$  we have complete wetting.

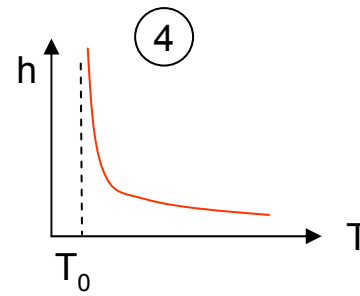


# Surface Phase Transitions: different paths towards complete wetting

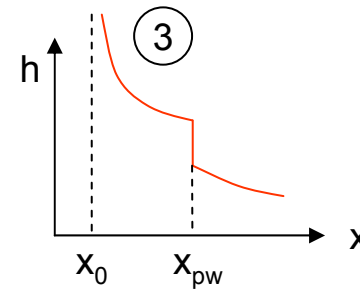
e. g.: first order wetting in two-component systems



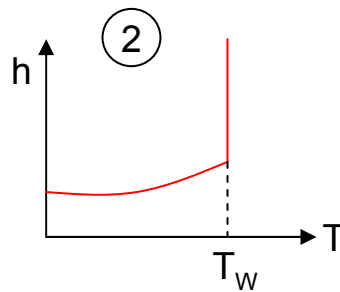
Order parameter: excess-surface-density or (with some simplifications) film thickness  $h$



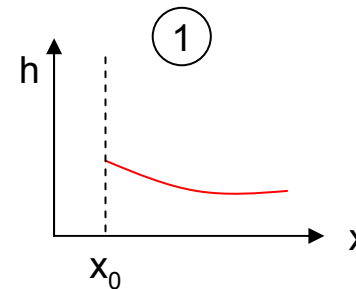
complete wetting:  
 $h$  shows a characteristic divergence



complete wetting with  
prewetting transition



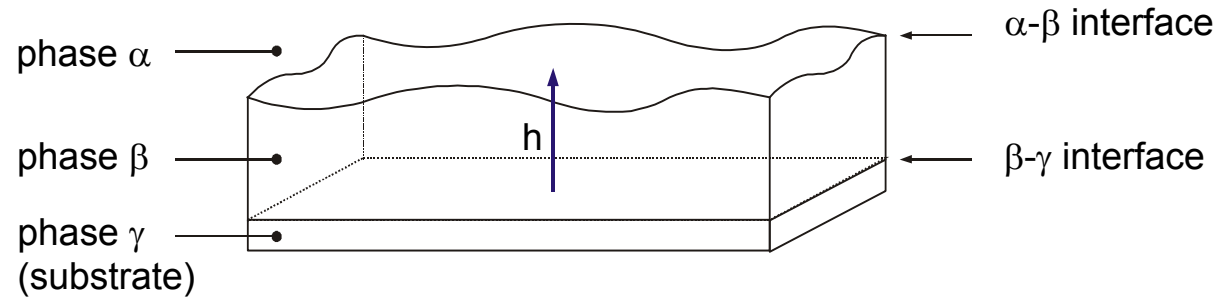
$h$  jumps discontinuously  
to macroscopic values



$h$  finite and  
microscopic

# Surface Phase Transitions and intermolecular interactions

Relevant for the description of wetting phenomena: Effective interface potential:  $\Omega_s(h, T, \mu)$



Contributions to  $\Omega_s$ :

$$\Omega_s(h; T, \mu) = h\Delta\mu$$

← deviation from coexistence

$$+\sigma_{\alpha\beta} + \sigma_{\beta\gamma}$$

← interfacial energies

$$+\omega(h)$$

← thin film correction

$\omega(h)$  depends on the intermolecular interactions in the film and between film and the adjoining bulk phases

$$\frac{\partial \Omega_s}{\partial h} = 0$$

leads to the equilibrium film thickness

Type of intermolecular interactions:

a) Long range  
e. g. Van der Waals  
(algebraically decaying)

b) Short range  
e. g. screened Coulomb  
(exponentially decaying)

$$h = \left( \frac{2H}{\Delta\mu} \right)^{\frac{1}{3}}$$

$$h = \xi \ln \left( \frac{\Phi}{\Delta\mu} \right)$$

Measure h as function of  $\Delta T$  which can be related to  $\Delta\mu$ ,