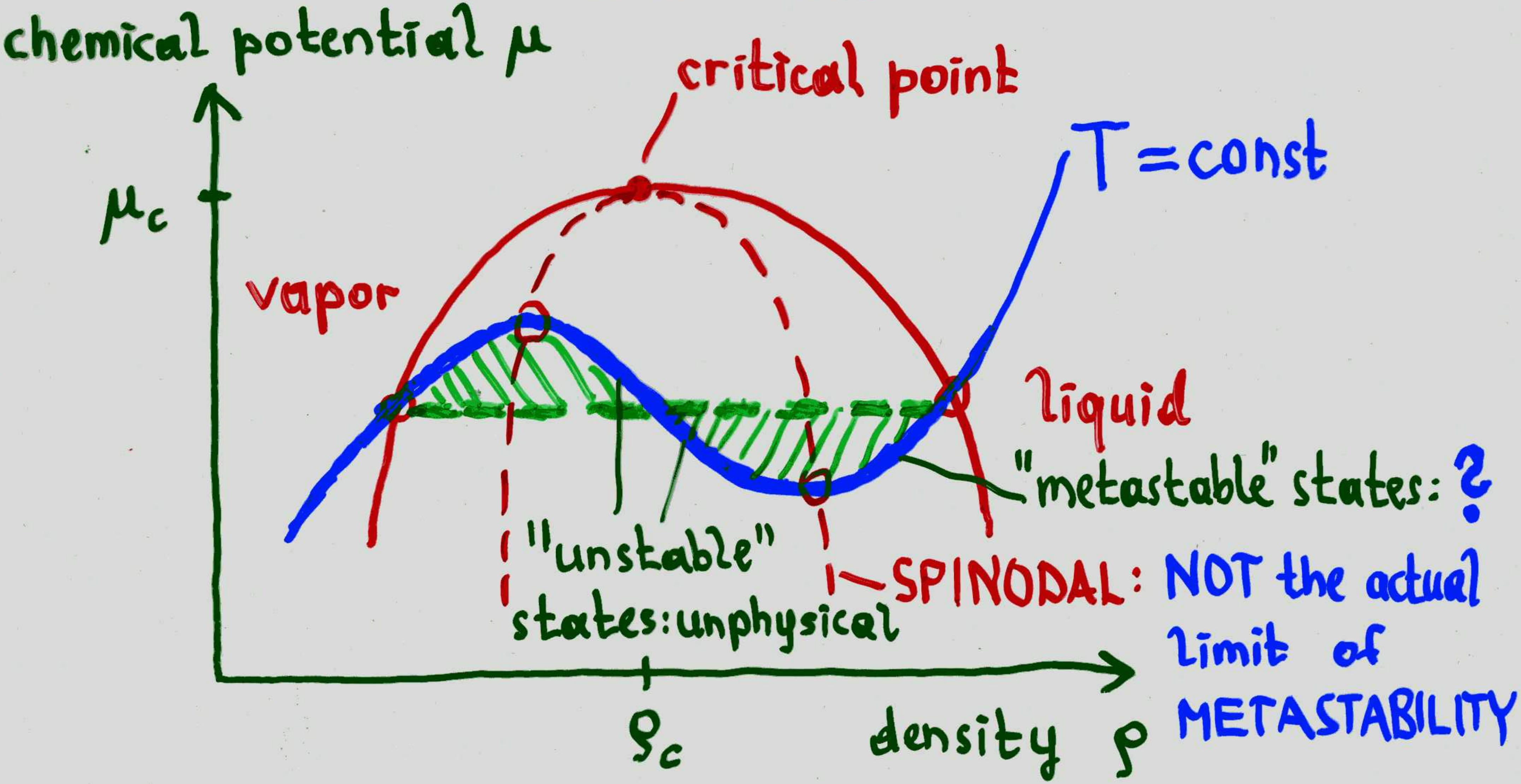
NUCLEATION PROCESSES AND THEIR STUDY BY SIMULATIONS

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!

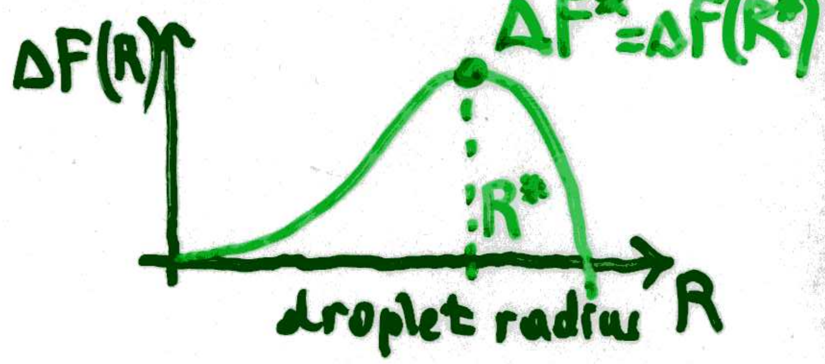


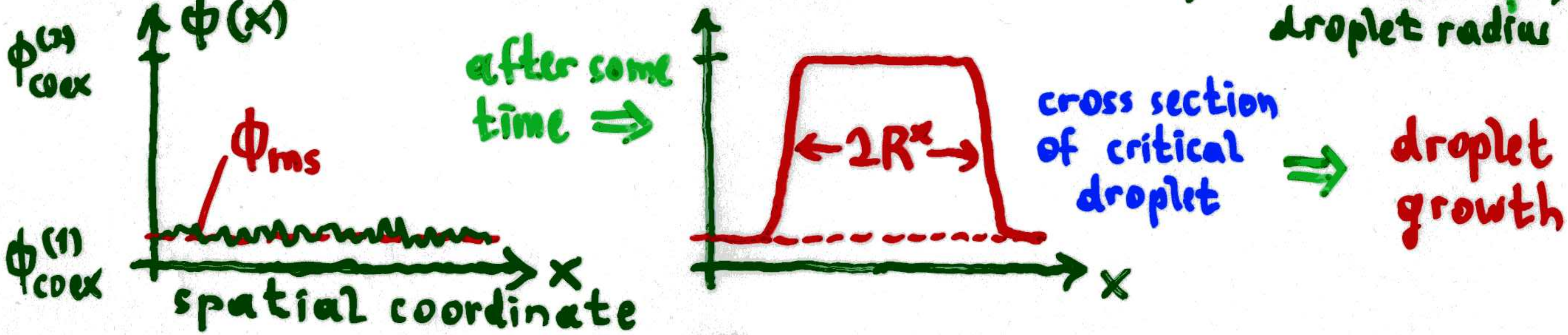
PHASE COEXISTENCE ?

Maxwell construction is ad hoc!

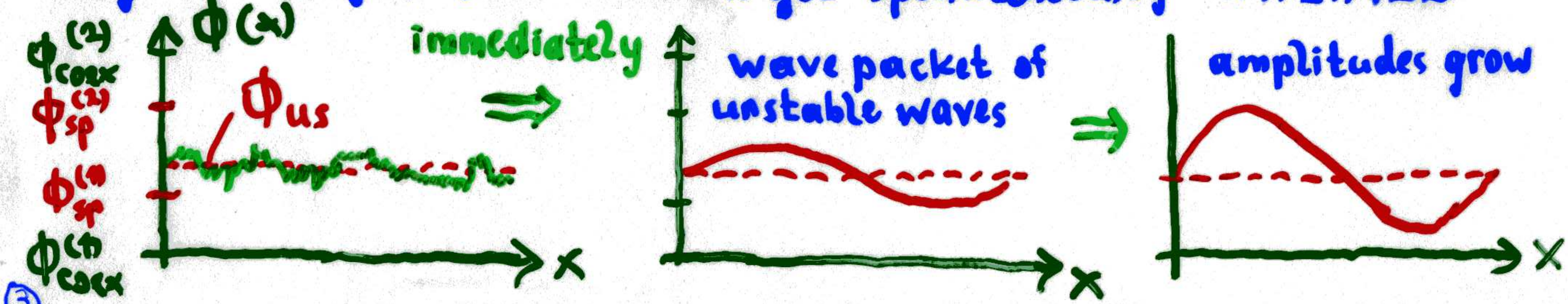
MECHANISMS for the INITIAL STAGES of PHASE SEPARATION KINETICS (mean field theory: CAHN-HILLIARD 1959)

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

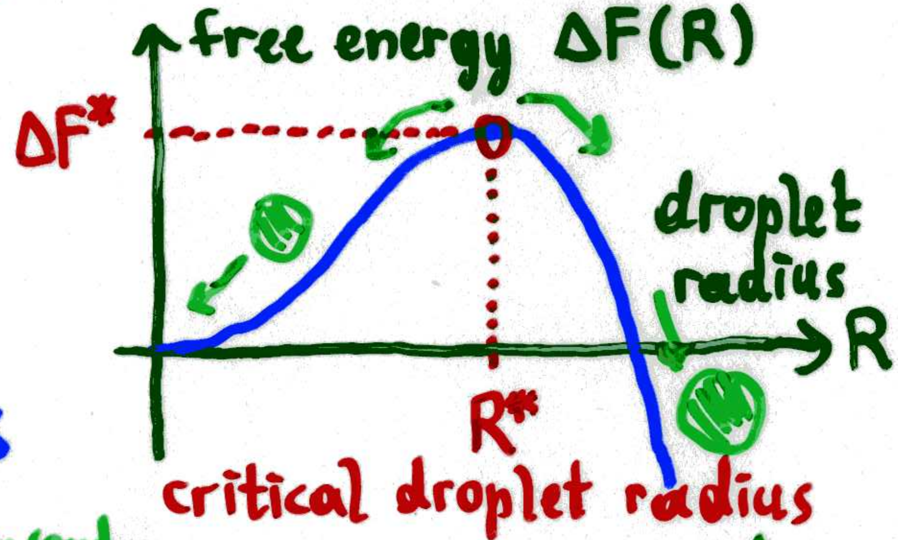




inside the spinodal region: $\phi_{sp}^{(1)} < \phi < \phi_{sp}^{(2)}$ **SPINODAL DECOMPOSITION**
long wavelength fluctuations get spontaneously **AMPLIFIED**



HOMOGENEOUS VERSUS HETEROGENEOUS NUCLEATION

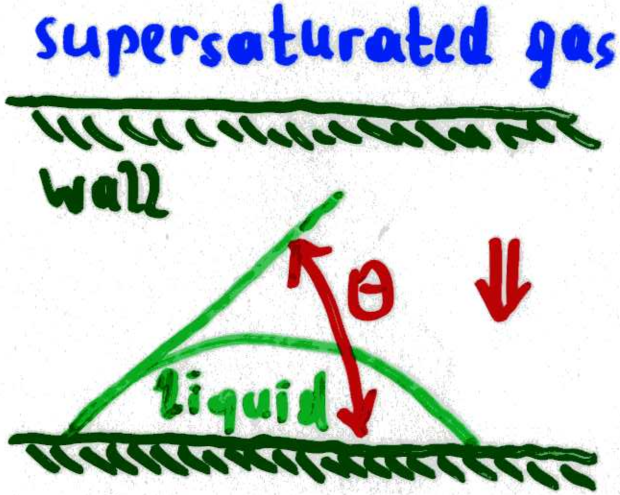


homogeneous nucleation:

a "droplet" of the new (stable) phase forms from the old (metastable) phase by SPONTANEOUS THERMAL FLUCTUATIONS

- high free energy barrier ΔF^* ⇒ rare events
- R^* nanoscopic: direct observation DIFFICULT

heterogeneous nucleation



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

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

Θ = contact angle
YOUNG (1805)

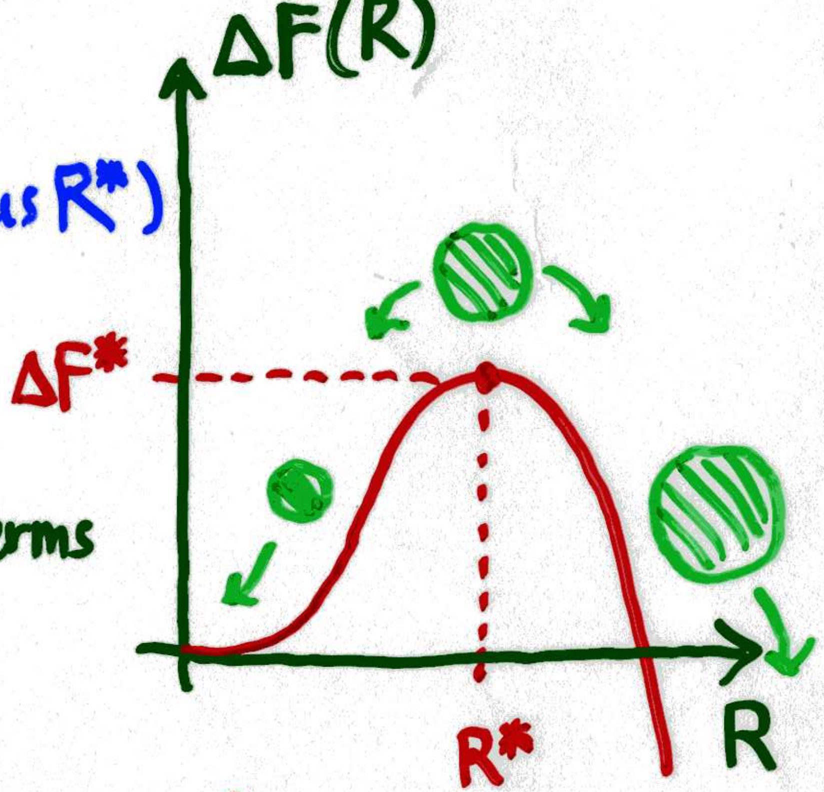
- 3 interface tensions
- lower free energy barrier

$$\Delta F^*_{het} = \Delta F^*_{hom} \, f(\Theta)$$

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

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

$$\Delta F(R) = \Delta g \, 4\pi R^3/3 + \gamma_{vl} \, 4\pi R^2$$

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

SAME interfacial free energy as for a FLAT PLANAR INTERFACE

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

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

 nucleation rate J^*: # of crit. nuclei/cm³ & s : $J = \omega^* \exp[-\Delta F^*/k_BT]$