Colloidal stability

Important practical questions:

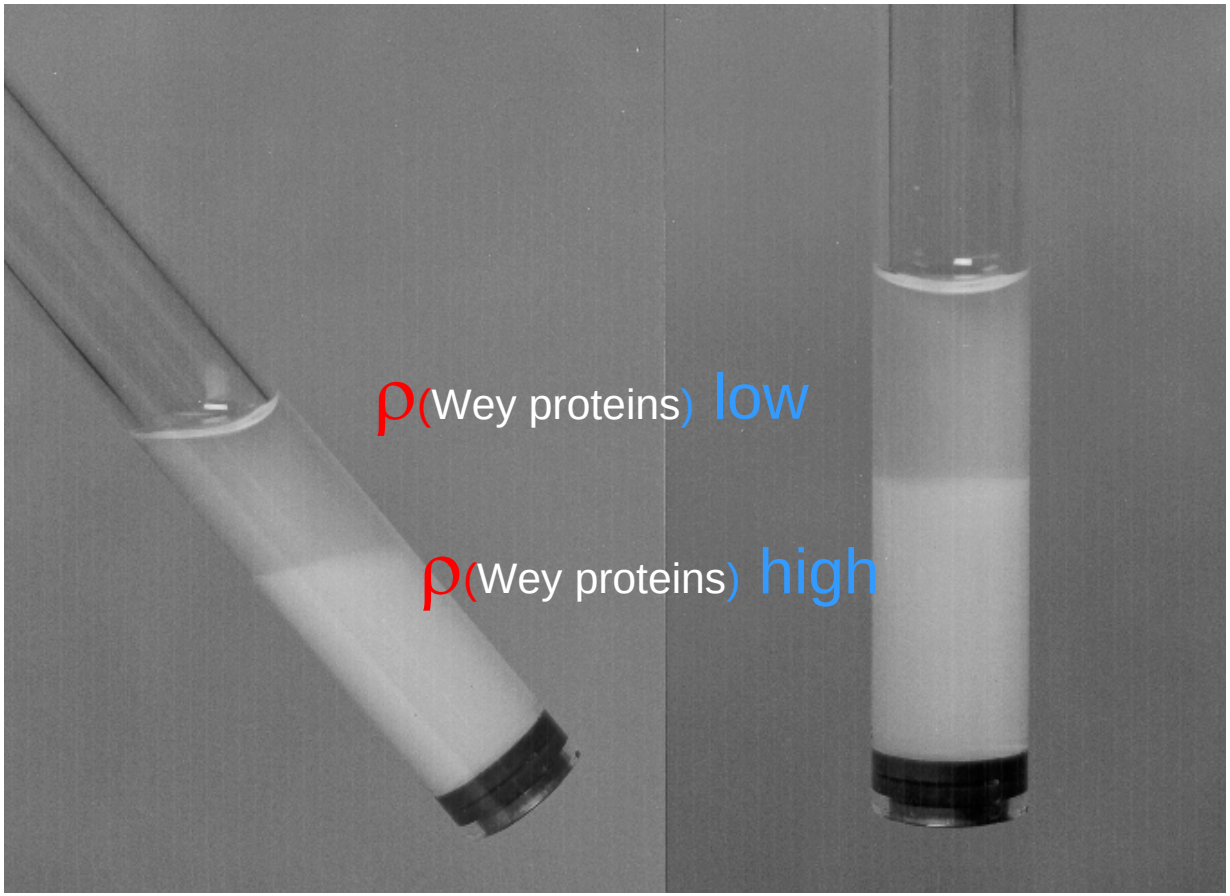
- Does dispersion change when T, P or ... is changed?
- If T, P or ... is changed and the dispersion phase separates, what are then the final products?
- How fast does the phase separation take place?

Examples:

- Food processing
- Protein crystal growing
- Rain makers
- Cataract (grauer Star)
- Synthesis of monodisperse colloidal particles
- Percipitation of $CaCO_3$

Dutch example: Cheese

Depletion of Wey proteins by Extracellular Poly-Saccharides

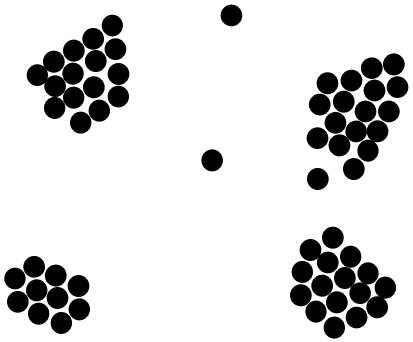


Phase separation:

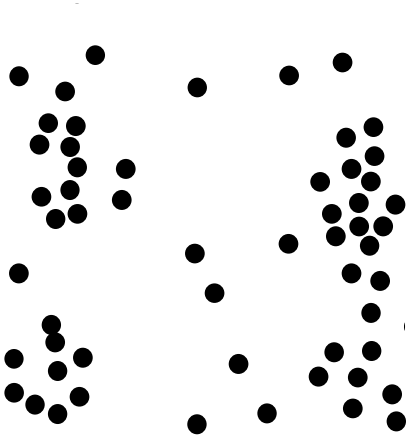
System with concentration ρ_0 decomposes in to a phase with a higher concentration ρ_+ and a phase with a lower concentration ρ_-

Two types of phase separation, two types of kinetics :

Liquid-solid or Gas-Solid



Gas-liquid



Molecular systems hard to study:

- Phase separation is too fast
- Particles are too small to be observed with a microscope
- No control on/knowledge of the interaction potential

Use Colloids:

- Mesoscopic Brownian particles dispersed in solvent instead of molecules dispersed in vacuum ➔ consider Π instead of ***P***.

Advantages:

- Potential can be tuned by choice of particles and solvent
- Dynamics is slow
- Particles are detectable by microscopy and light scattering

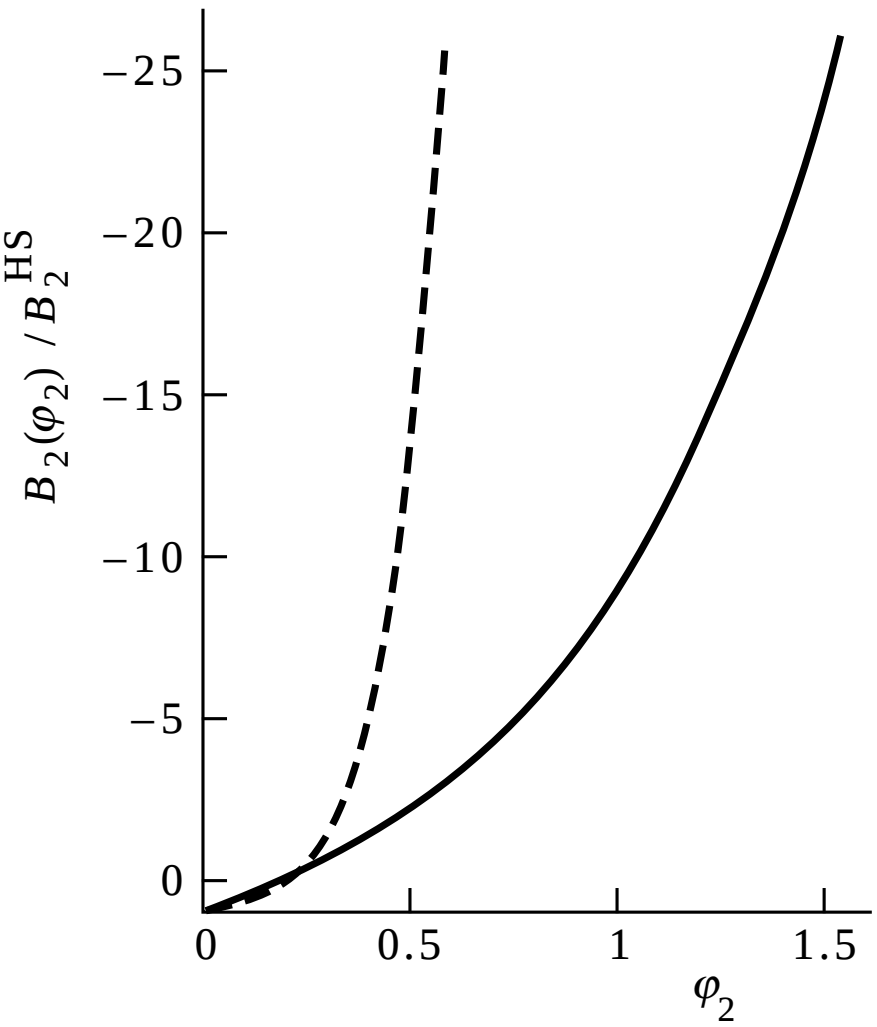
Simple estimation of spinodal

When B_2 becomes sufficiently negative demixing takes place

$$\frac{\partial(\Pi_c v_c / kT)}{\partial \phi} = 1 + 2(B_2 / v_c)\phi + \ldots$$

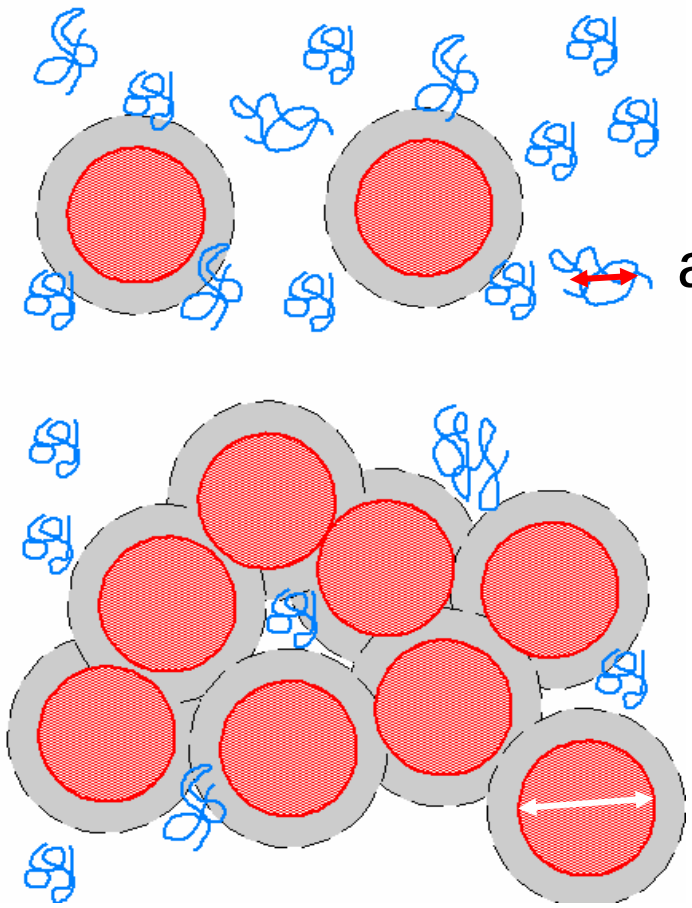
Estimation spinodal:

$$\boxed{\phi_{spinodal} = \frac{-v_c}{2B_2}}$$



Colloid Dispersion with mediated by depletion forces

$q=a_{FOS}/R$



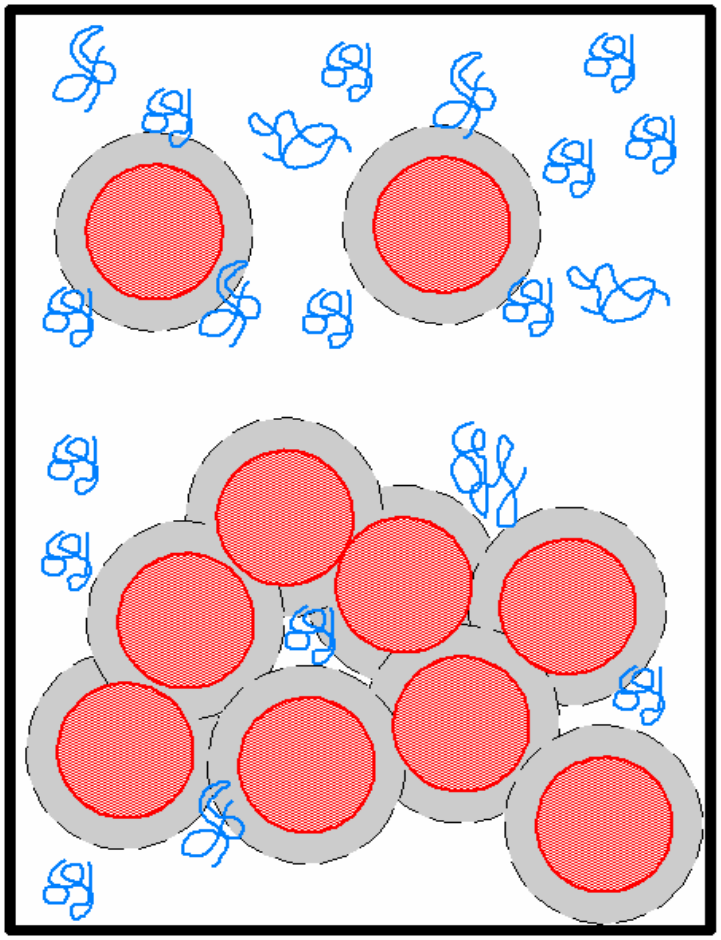
Second virial coefficient

B_2 can be computed from depletion potential:

$$B_2 = 2\pi \int_0^{\infty} r^2 \left[1 - e^{\frac{-\omega(r)}{kT}} \right] \mathrm{d}r$$

$$\omega(r) = \begin{cases} \infty & for \;\; r < \sigma \\ -\Pi_p V_{overlap}(r) & for \;\; \sigma < r < \sigma + 2\delta \\ 0 & for \;\; r > \sigma + 2\delta \end{cases}$$

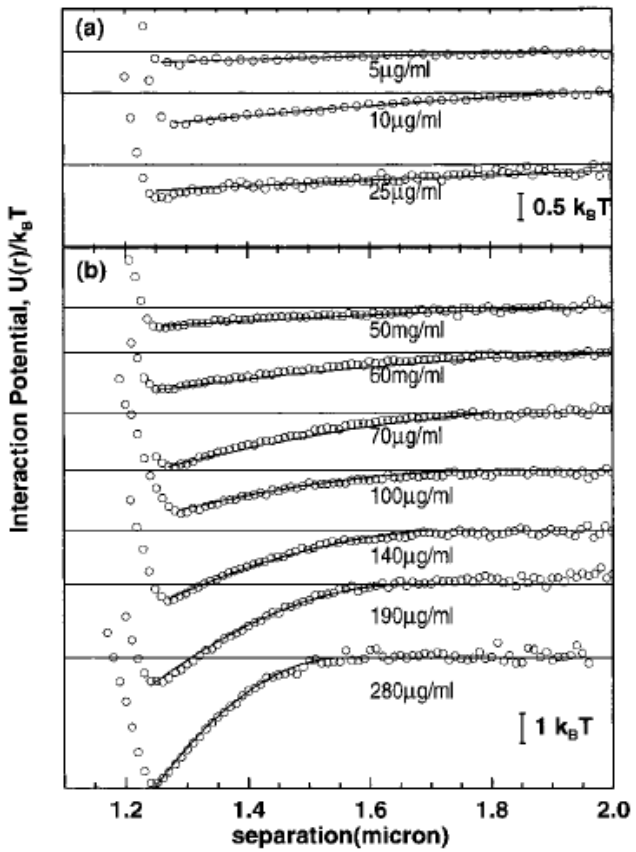
$$B_2 = 4V_{HS} + 2\pi \int_{\sigma}^{\sigma+2\delta} r^2 \left[1 - \exp\left(\frac{\Pi_p V_{ov}(r)}{kT} \right) \right] \mathrm{d}r$$



Macromolecules **2000,** *33,* 177−186

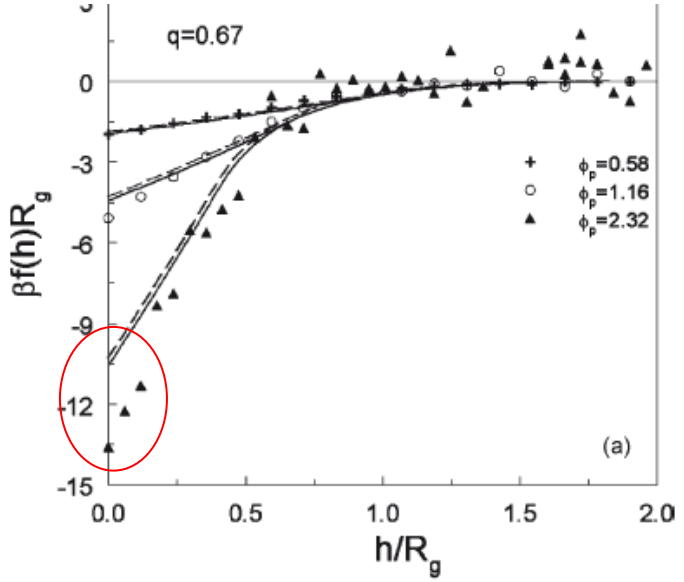
Attractions between Hard Colloidal Spheres in Semiflexible Polymer Solutions

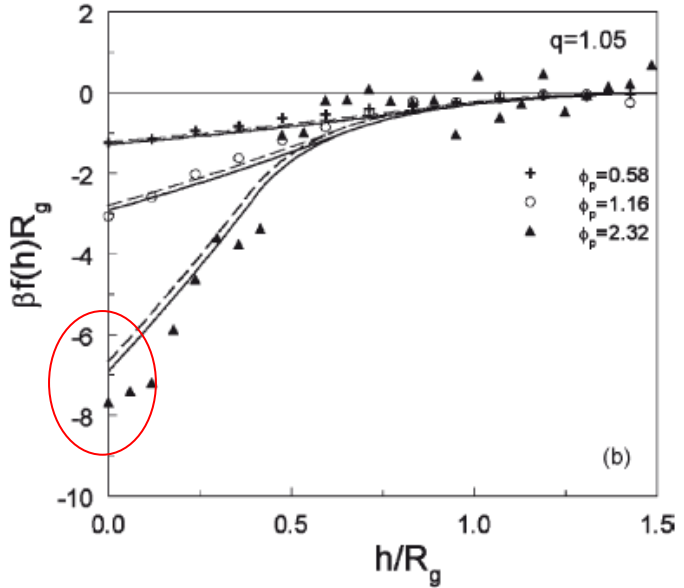
Ritu Verma, J. C. Crocker, T. C. Lubensky, and A. G. Yodh*



Pair interaction and phase separation in mixtures of colloids and excluded volume polymers

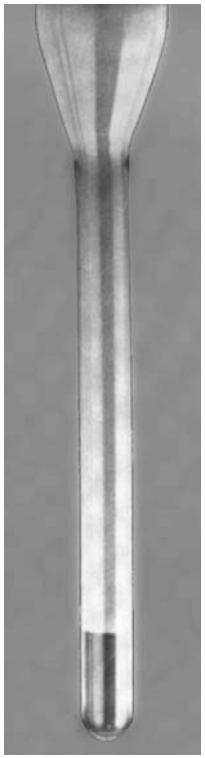
R. Tuinier,*[a] D. G. A. L. Aarts,[b] H. H. Wensink[b] and H. N. W. Lekkerkerker[b]



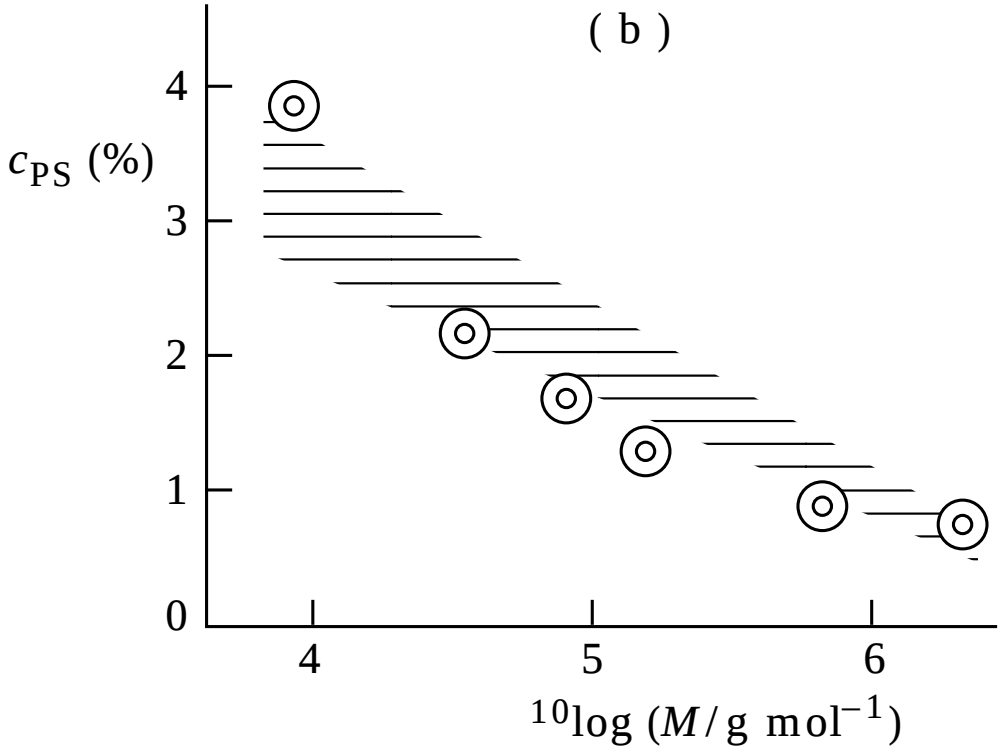


Demixing concentrations estimated from B_2

- De Hek and Vrij, 1980:
- 1 wt% HS-like silica a=46 nm
- mixed with PS in CHX

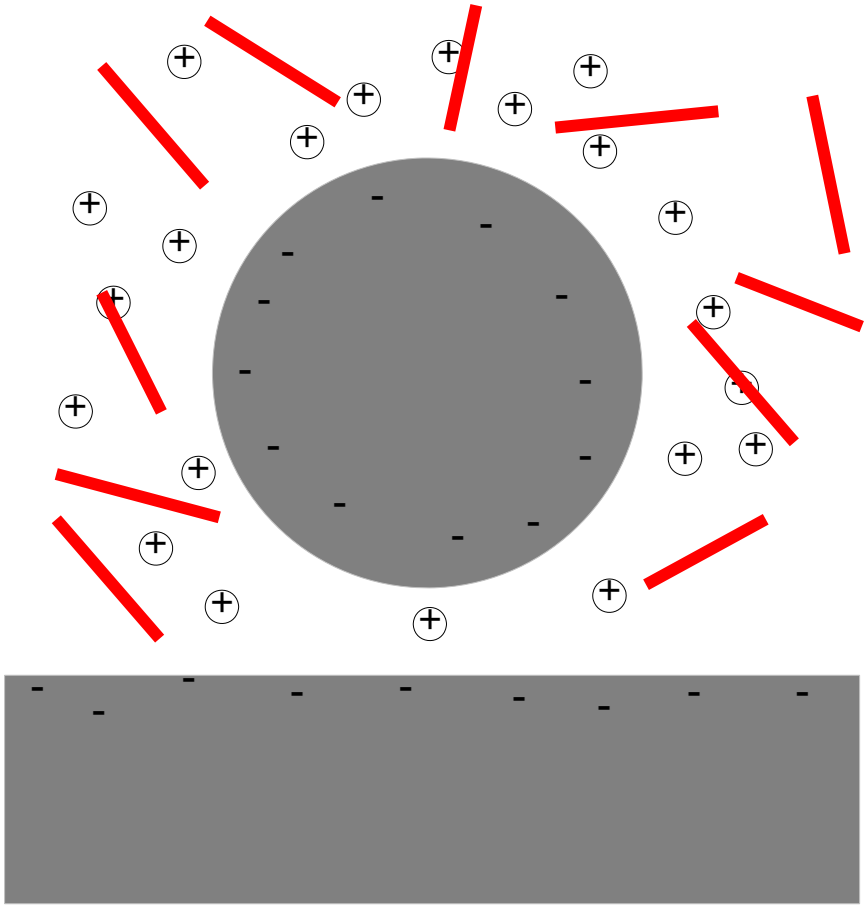


(a)

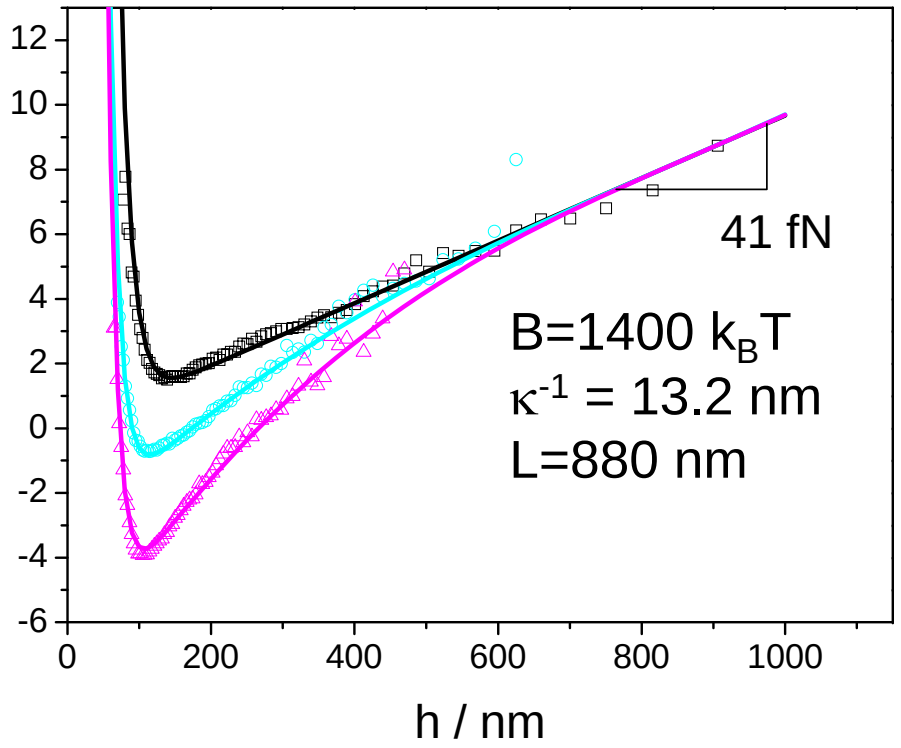


Sphere Rod Mixtures

R = 3 μm
c_{TRIS} = 1.2 mM
κ^{-1} = 12.4 nm



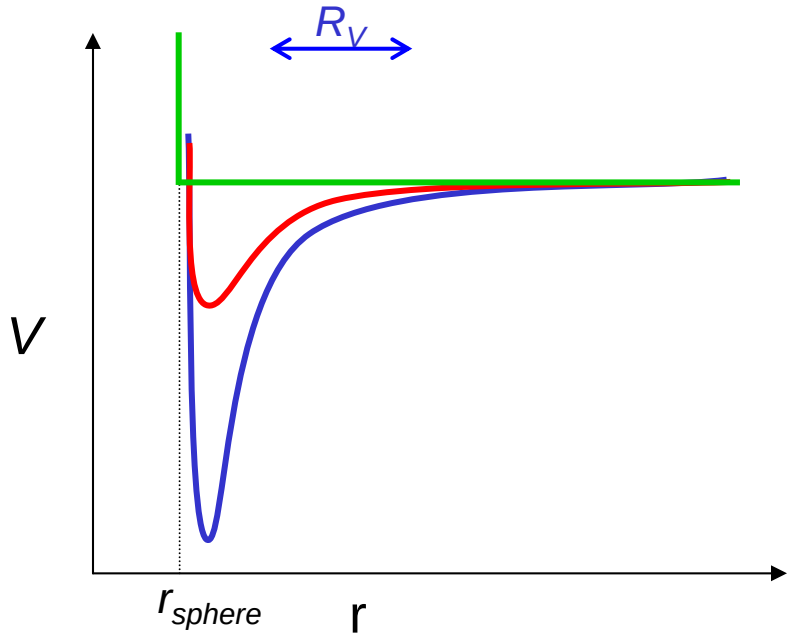
$$\frac{\Delta\phi(h)}{k_BT} = B\exp\{-\kappa h\} + \frac{G_{eff}h}{k_BT} + \frac{\phi_{depl}}{k_BT}$$

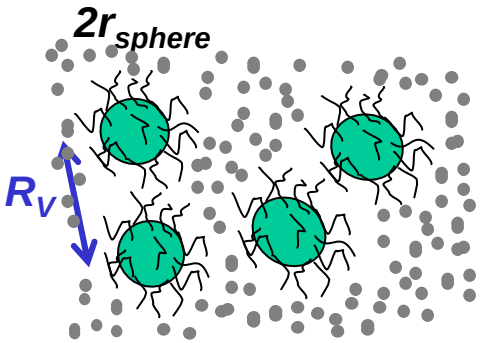


$$\frac{\phi_{depl}}{k_BT} = -\frac{\pi}{3}c\frac{N_A}{M_{fd}}RL^2\left(1-\frac{h}{L}\right)^3$$

Mao, Cates, Lekkerkerker JCP '97

Example: *stearyl alcohol-coated silica in cyclohexane*
Tunable attraction, hard core repulsion

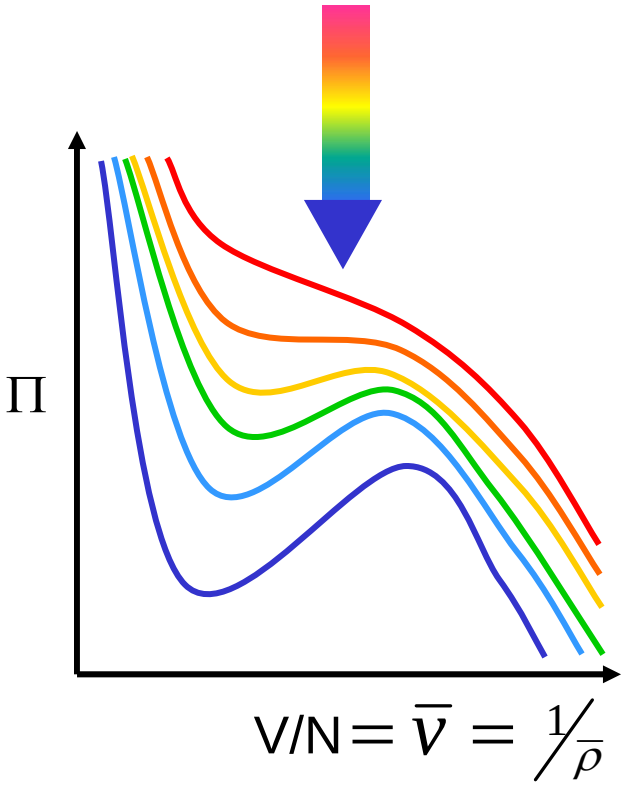


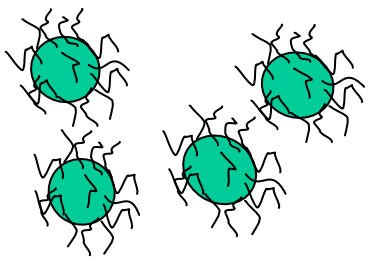


Potential of colloidal particles similar to non-ideal gas➔ van der Waals-like behavior of osmotic pressure Π.

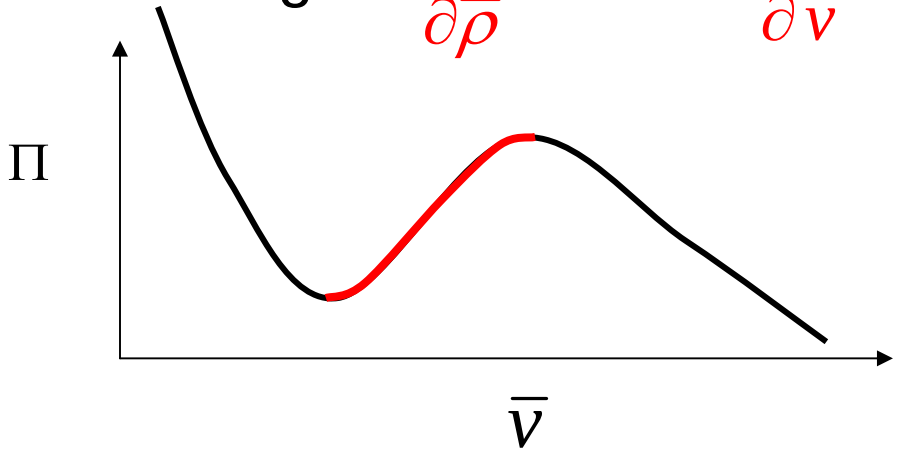
Unstable region

Temperature quench



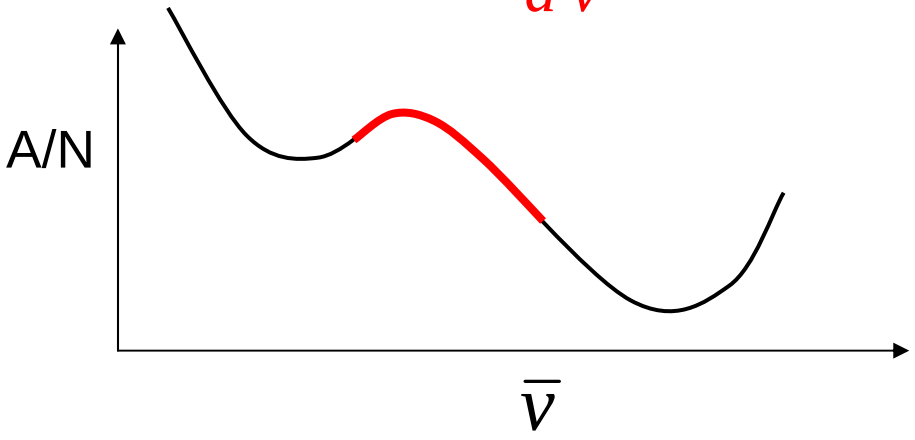


Unstable region: $\frac{\partial \Pi}{\partial \bar{\rho}} < 0$ or $\frac{\partial \Pi}{\partial \bar{v}} > 0$

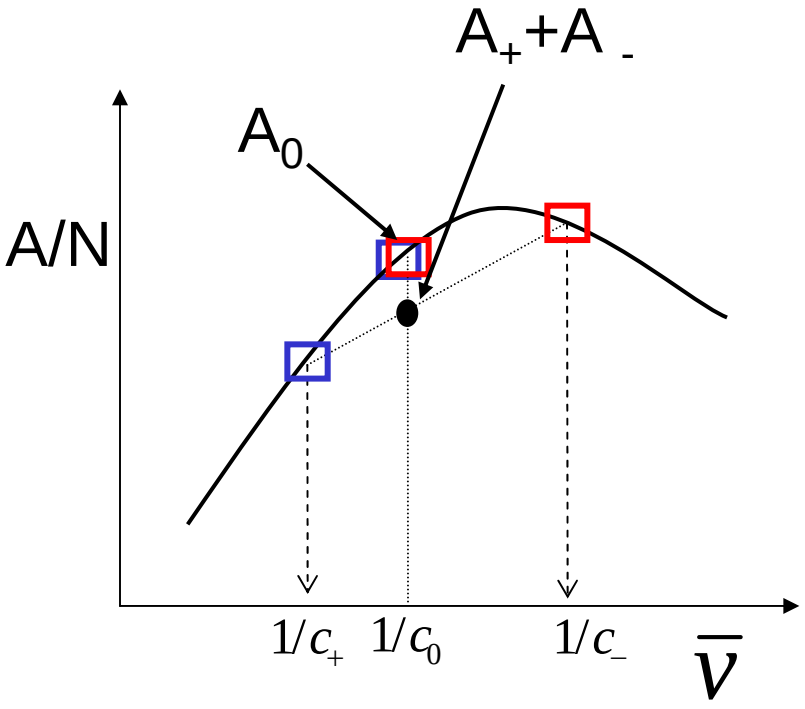


Connection to free energy: $\Pi = -\partial A / \partial V \big|_N$

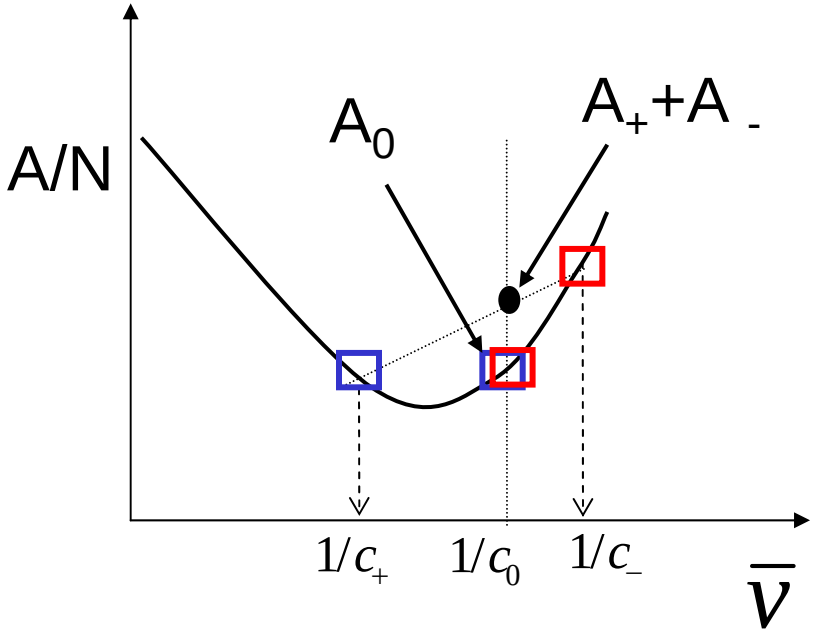
Unstable region: $\frac{d^2(A/N)}{d\bar{v}^2} < 0$



Phase separation?**Minimize Free Energy**



$A_0 > A_+ + A_-$

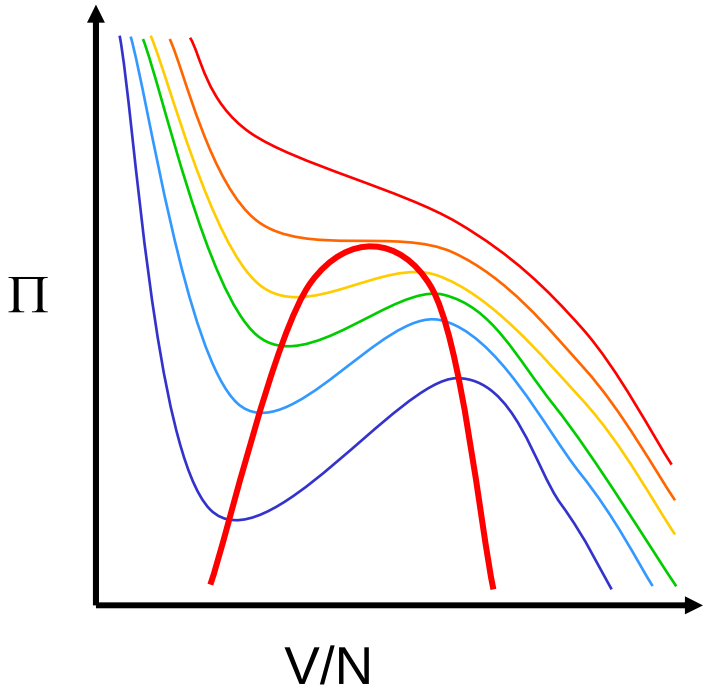


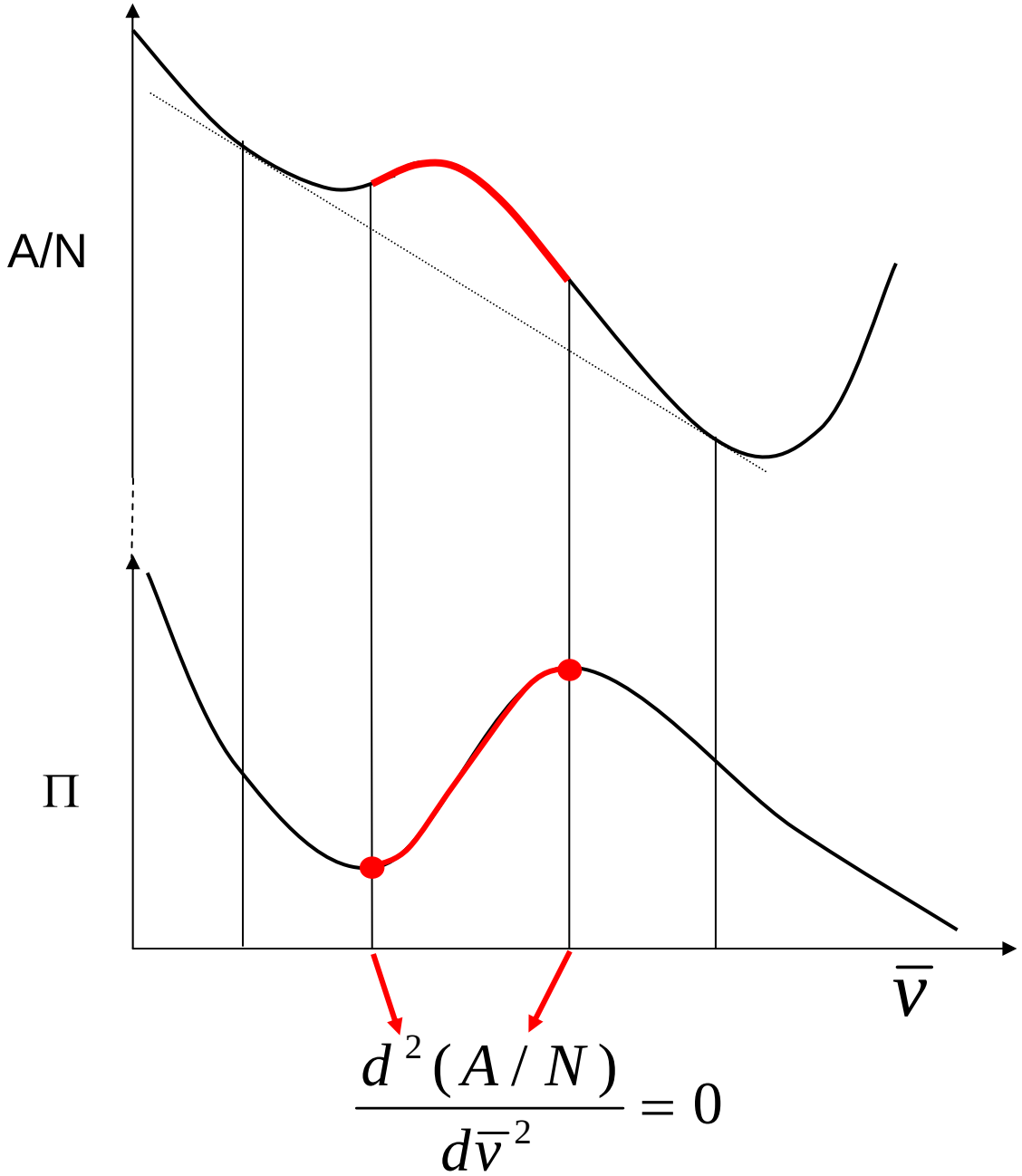
$A_0 < A_+ + A_-$

Concave, $\frac{d^2(A/N)}{d\bar{\nu}^2} < 0$ **:** YES

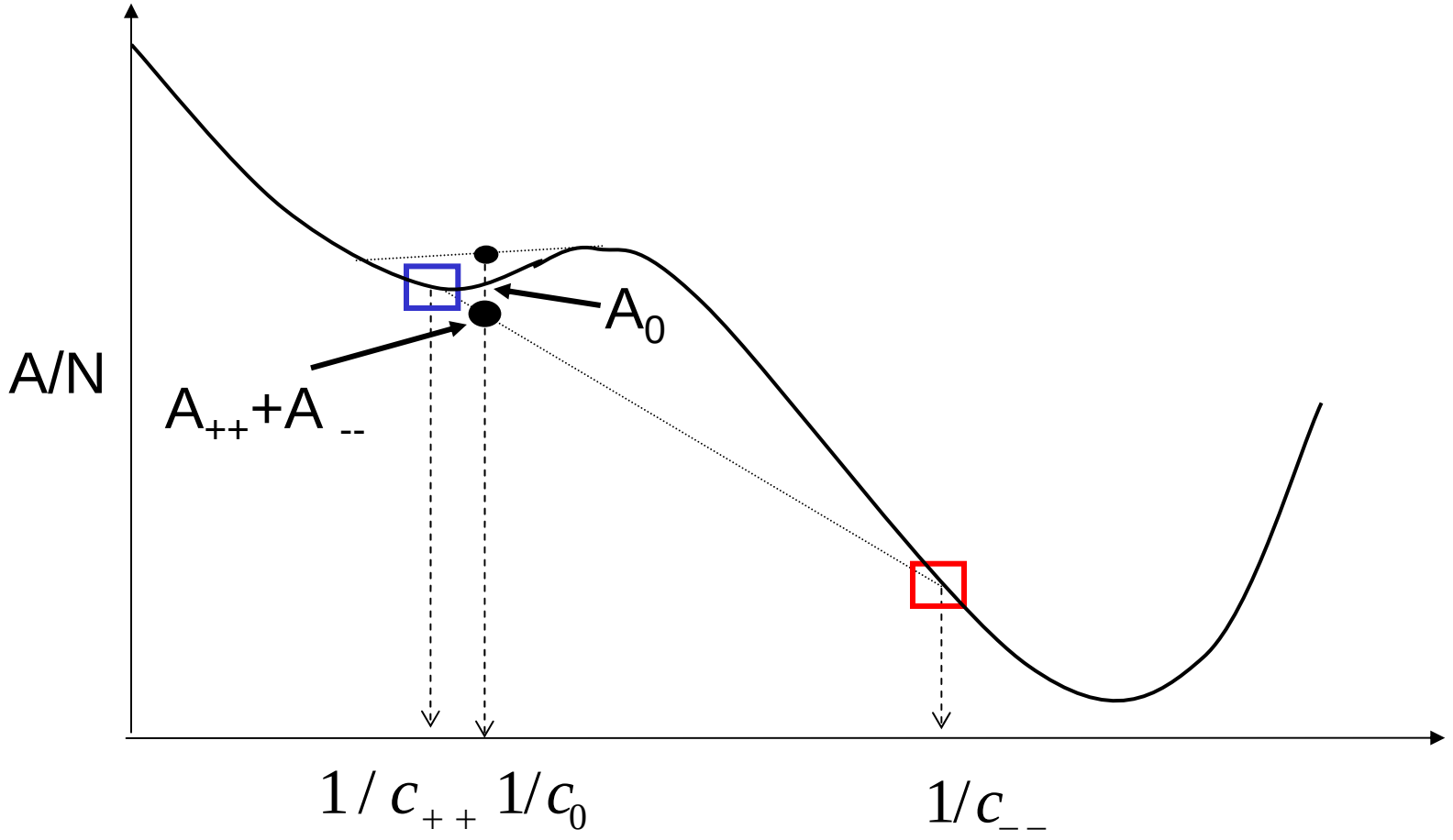
Convex, $\frac{d^2(A/N)}{d\bar{\nu}^2} > 0$**:** NO

Spinodal





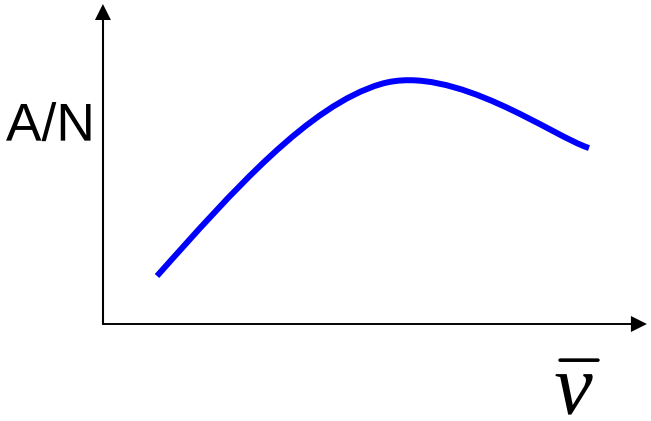
Meta-stable region



$A_{++}+A_{--}<A_0$

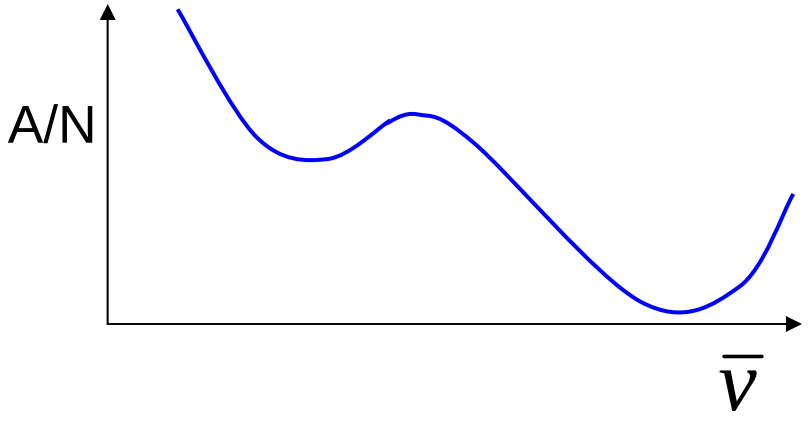
Lower free energy for big fluctuations
But small probability

Unstable:
Spinodal decomposition



- Small fluctuations grow
- Instantaneous start of phase separation
- Phase separation starts throughout the sample

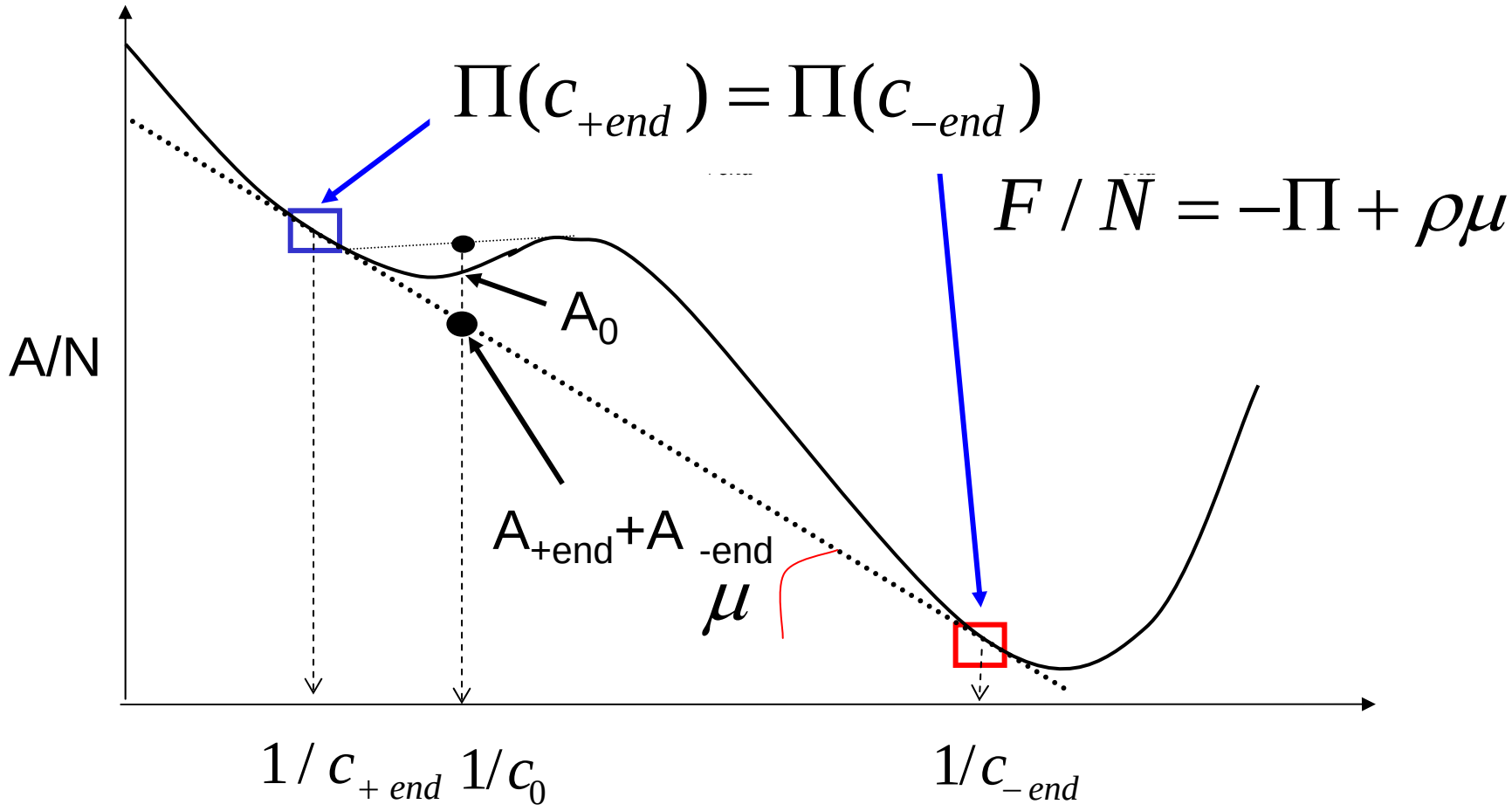
Meta-stable:
Nucleation and growth



- Only big fluctuations grow
- Induction time before phase separation
- Phase separation only local

Where does the phase separtion end up?

Concentrations of lowest energy: Equality of chemical potential



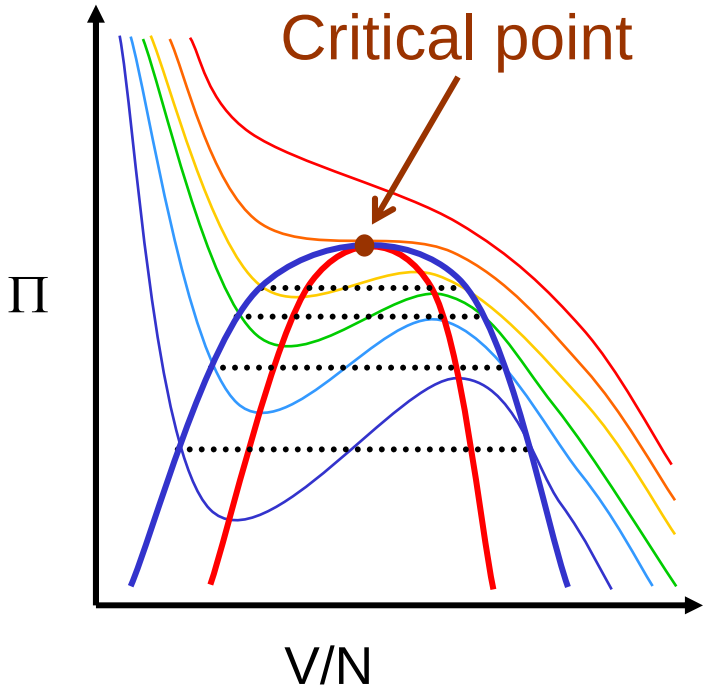
..... The line of minimum energy

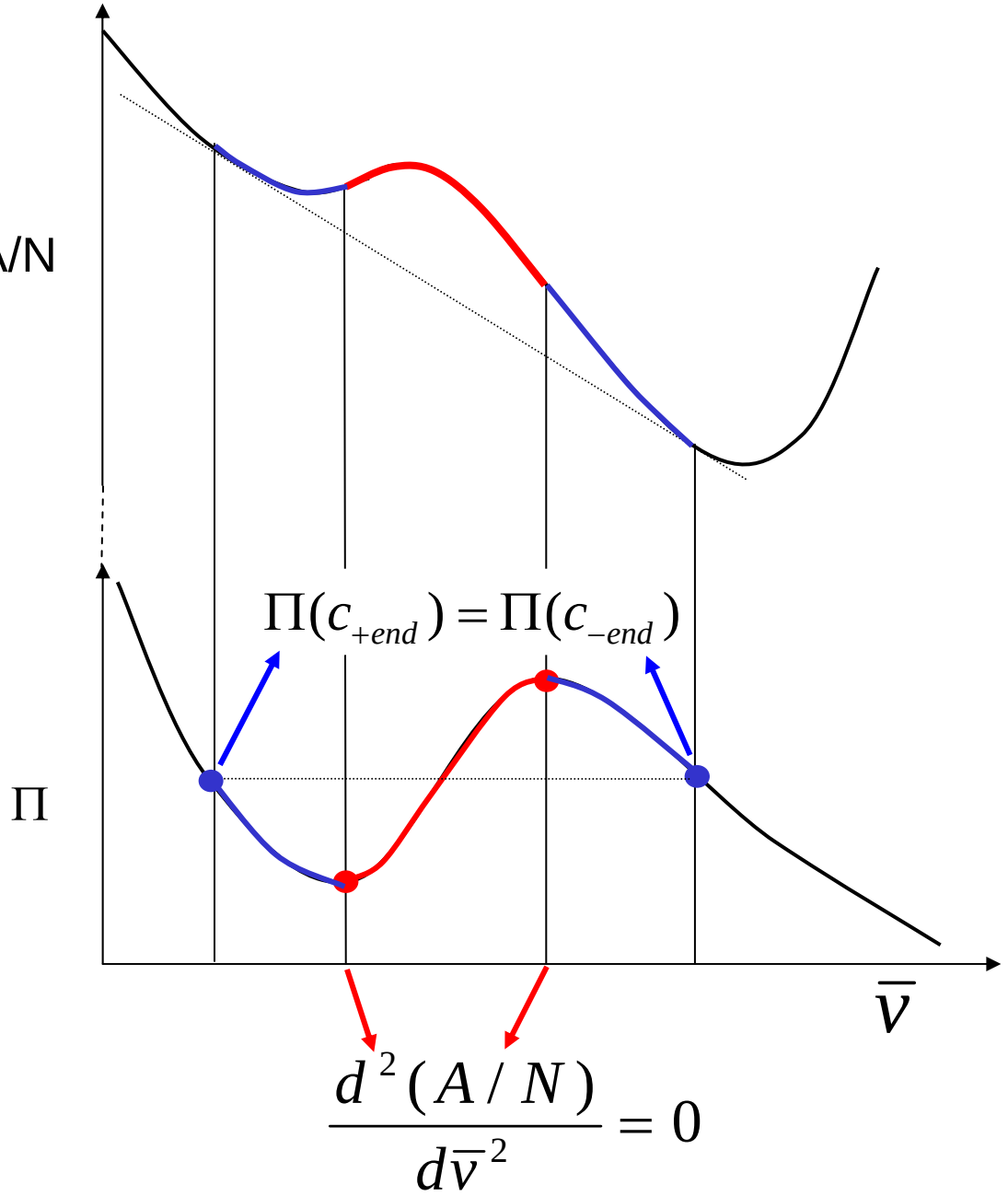
We found the binodal points
(which depend on T or …)

Spinodal

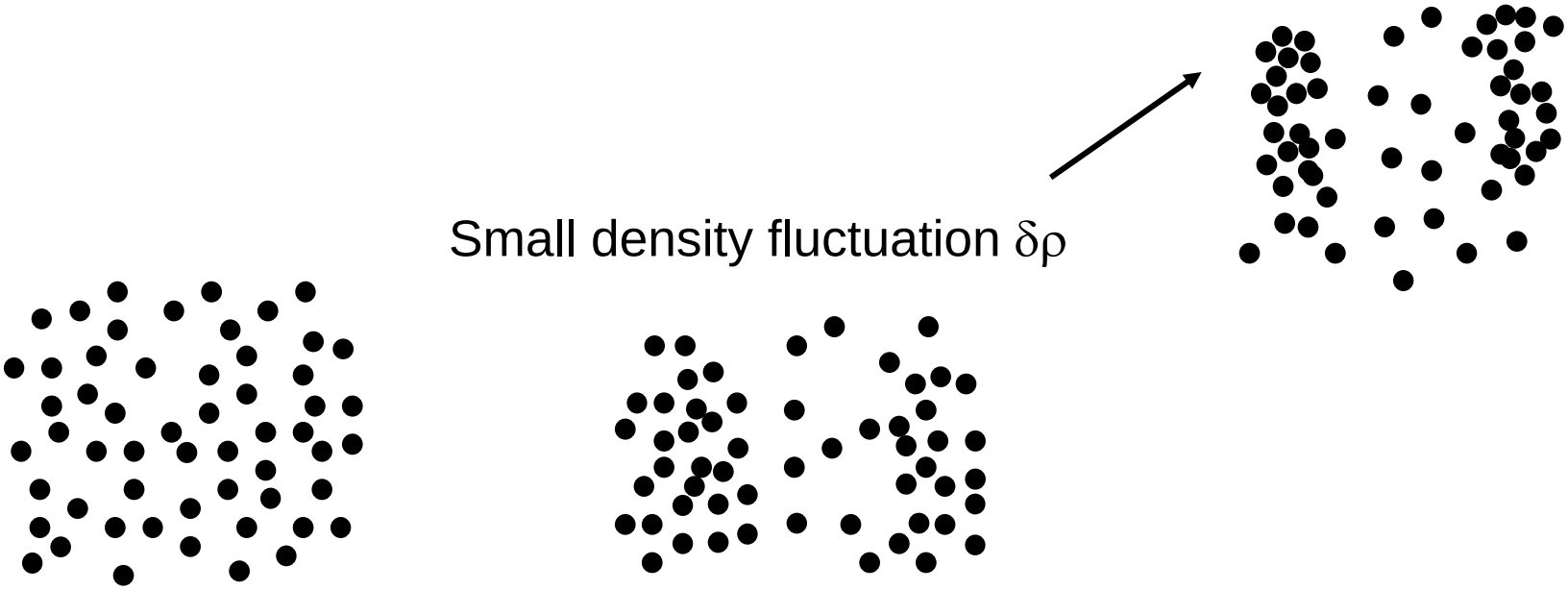
and

Binodal

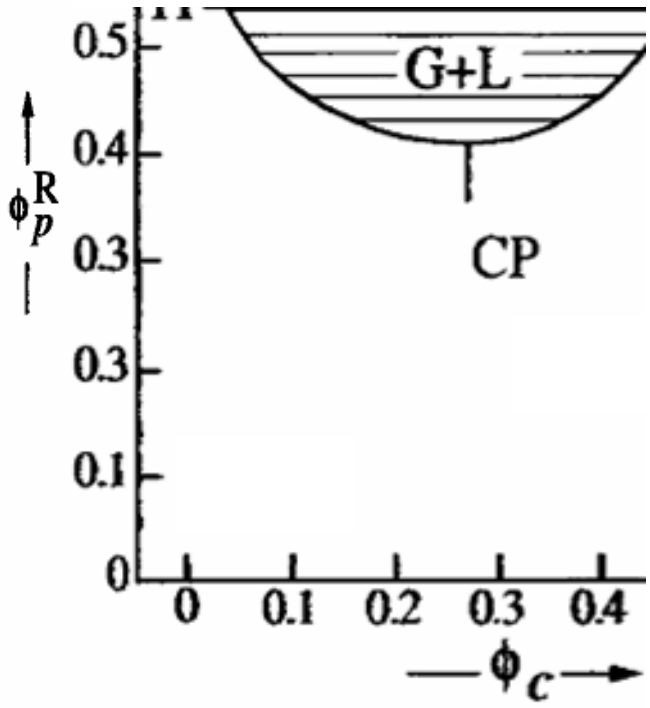




Attractive potential between particles

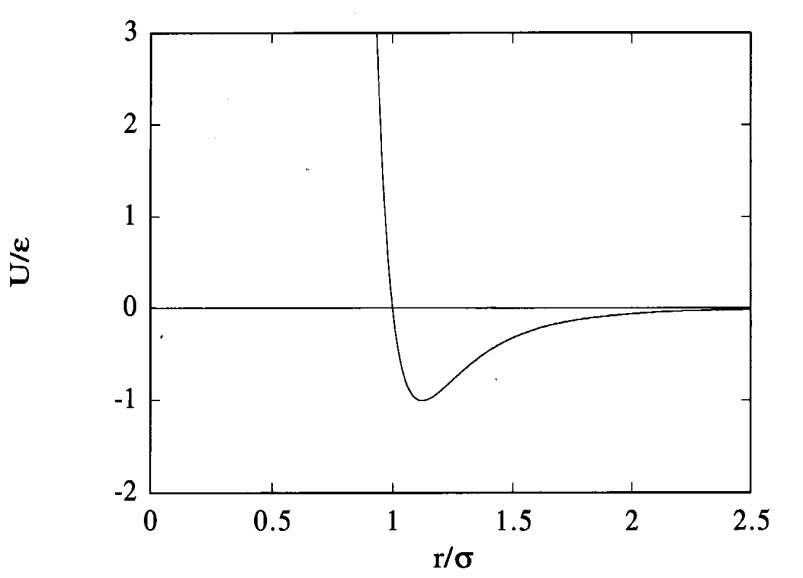


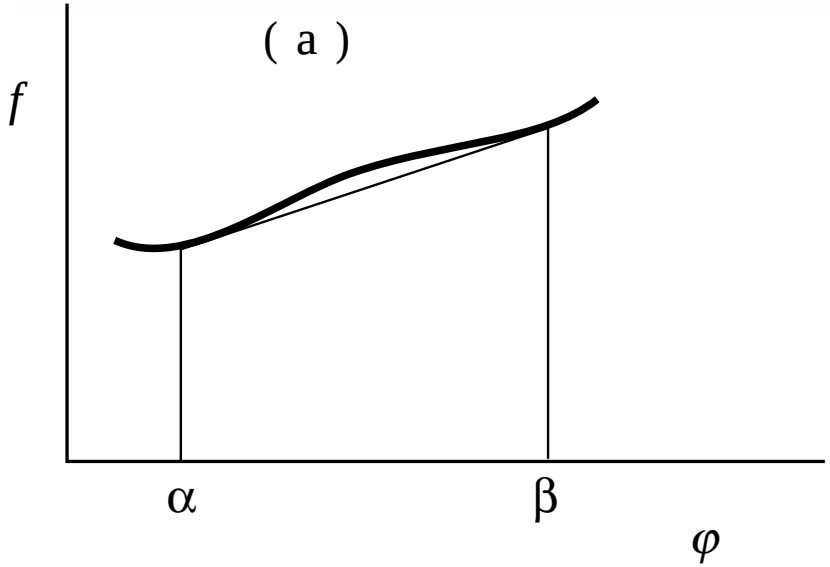
gas-liquid



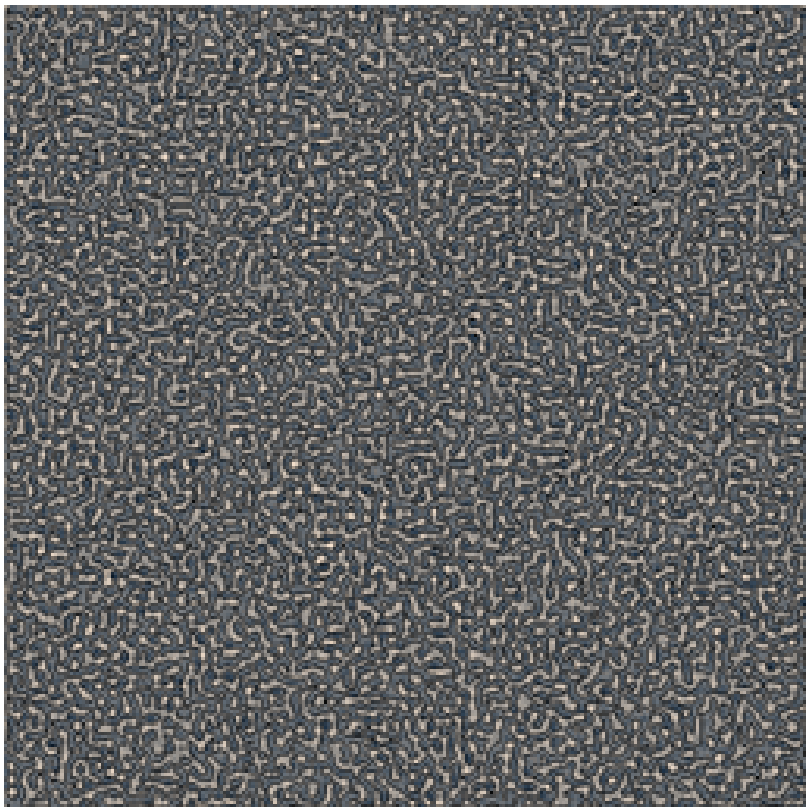
polymer concentration
≈ inversed temperature!

Lennard-Jones



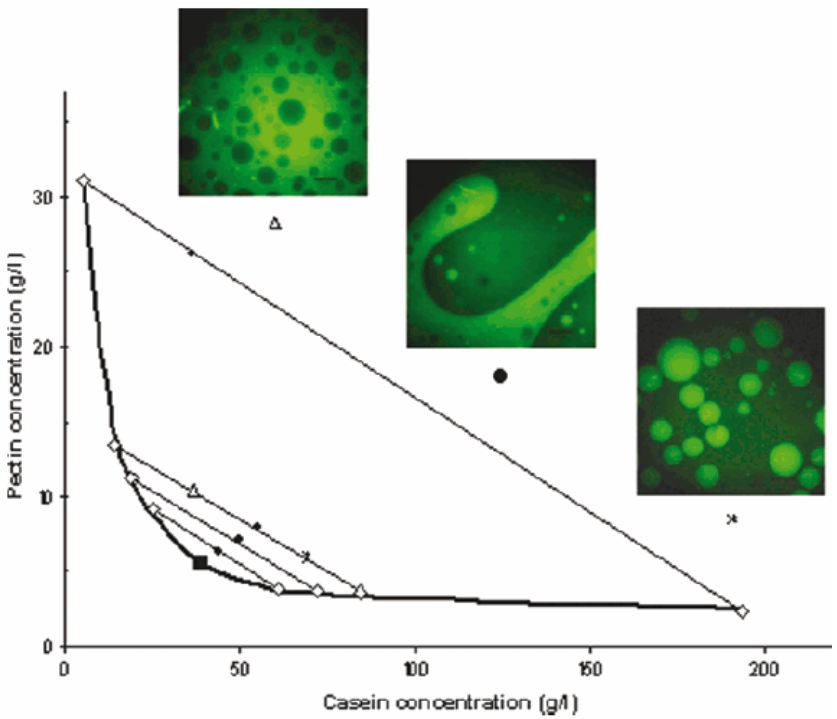


Simulation of the **spinodal** decomposition followed by domain coarsening



Cates and Wagner, Nov. 2000

End states after demixing…



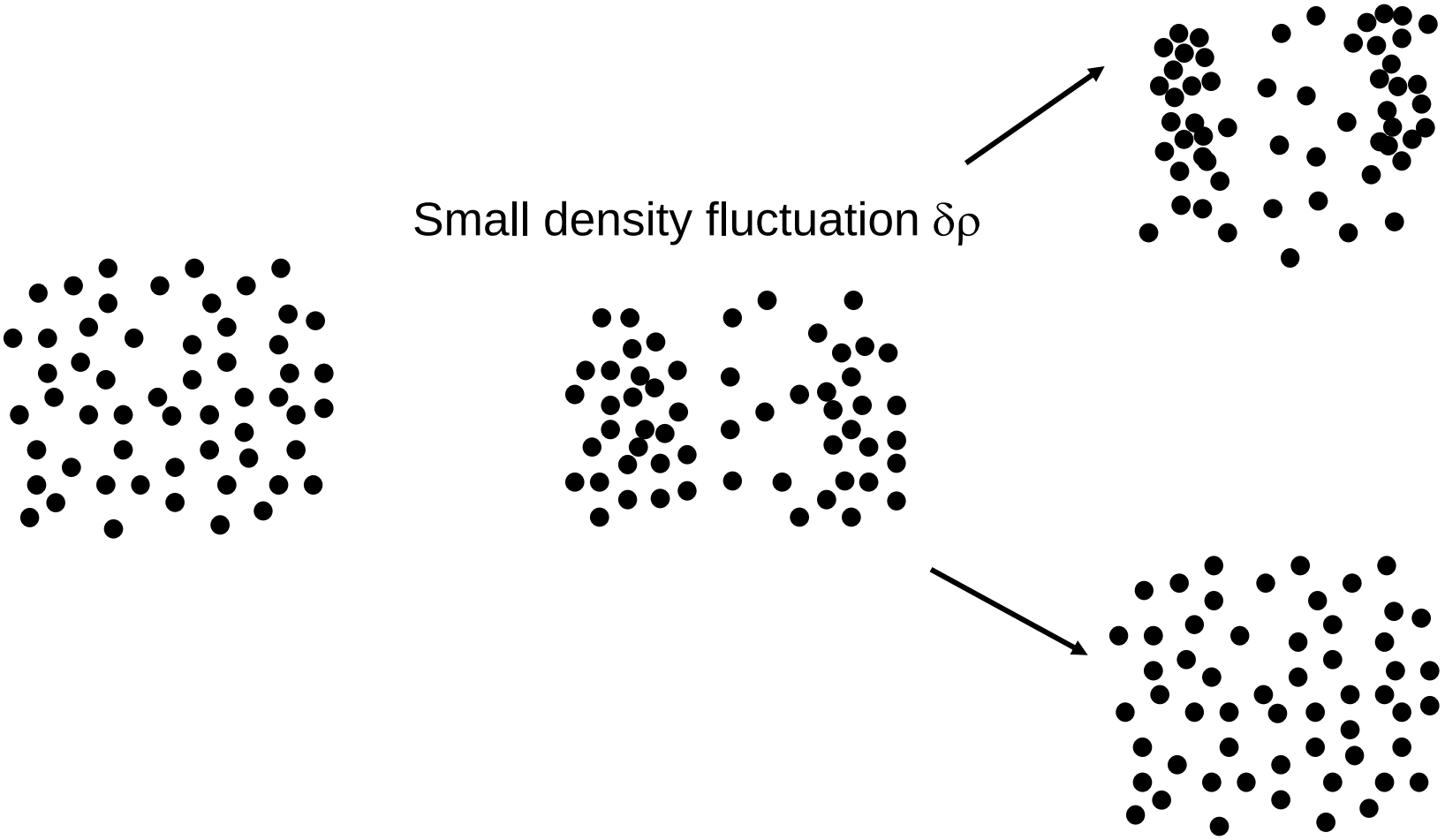
Biomacromolecules **2007**, *8*, 3345−3354

Thermodynamic Incompatibility and Complex Formation in Pectin/Caseinate Mixtures

Camila F. Rediguieri,† Osvaldo de Freitas,† M. Paul Lettinga,‡ and Remco Tuinier*,‡

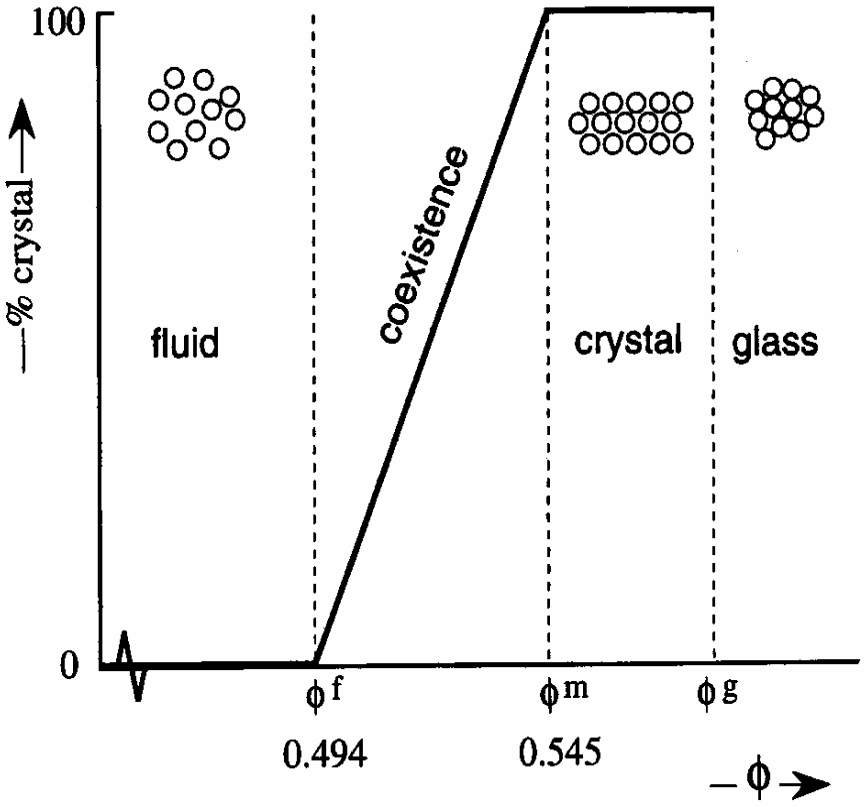
Attractive potential between particles

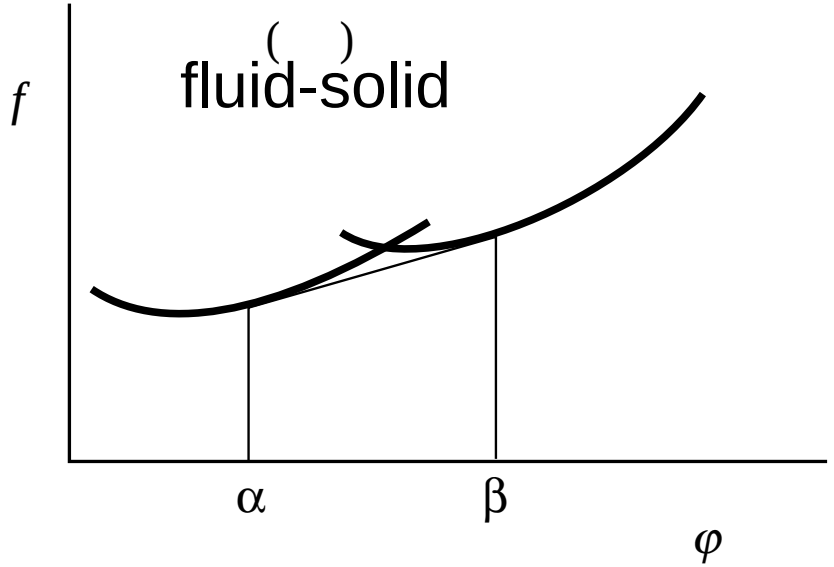
Small density fluctuation $\delta\rho$



Hard sphere

Fluid-solid

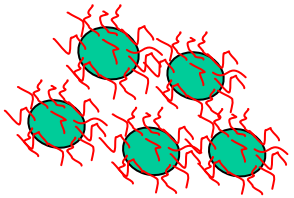




No attraction, so:

1) very simple phase diagram.
2) use equation of state for fluid and FCC crystal

Colloidal hard spheres

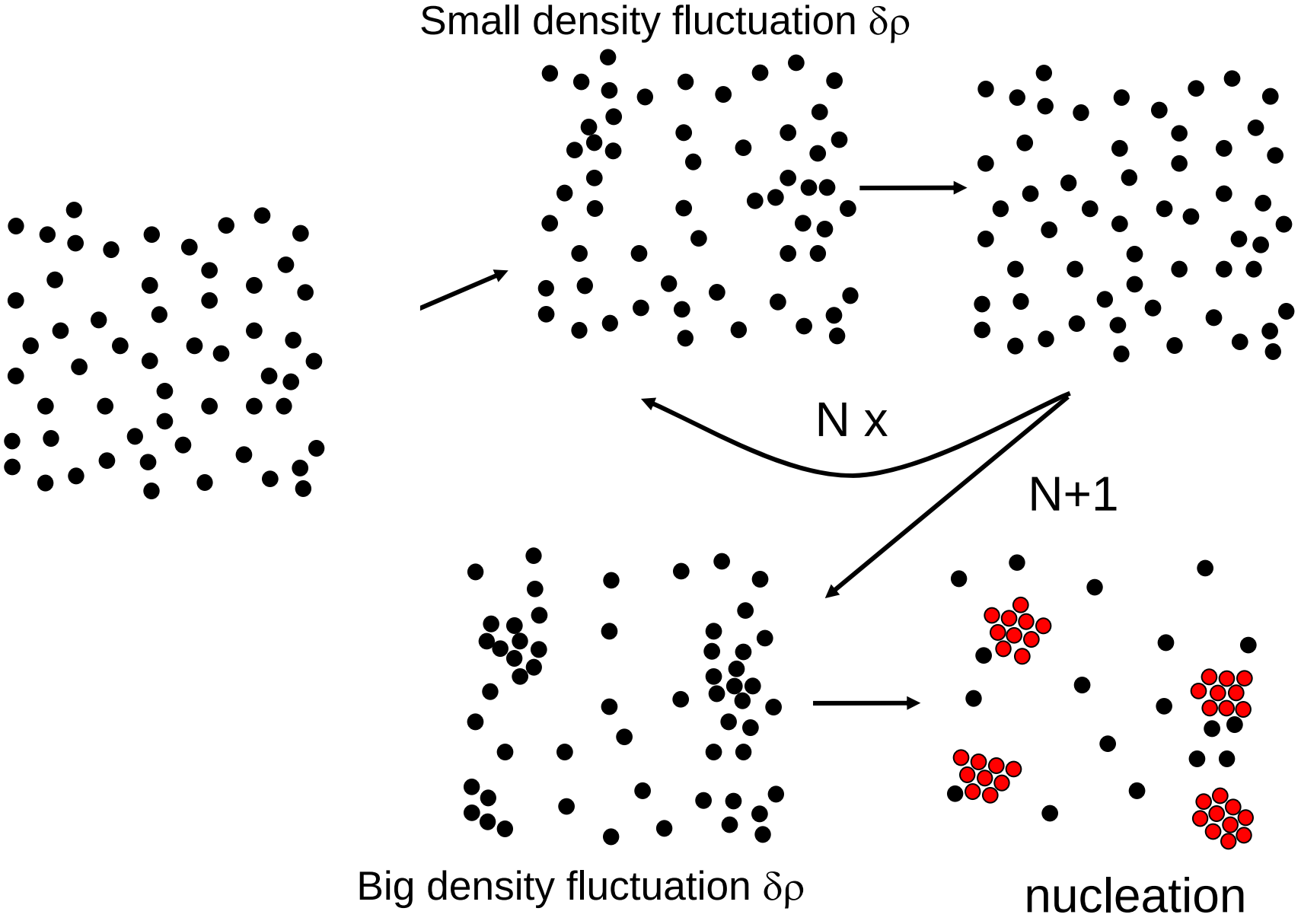


Glass (see Zorn)

heterogeneous

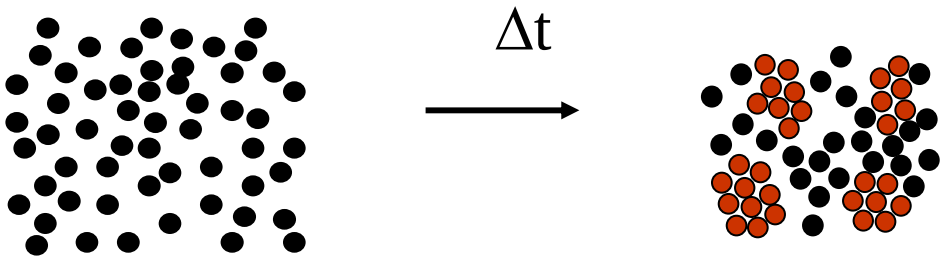
homogeneous

Shallow quench

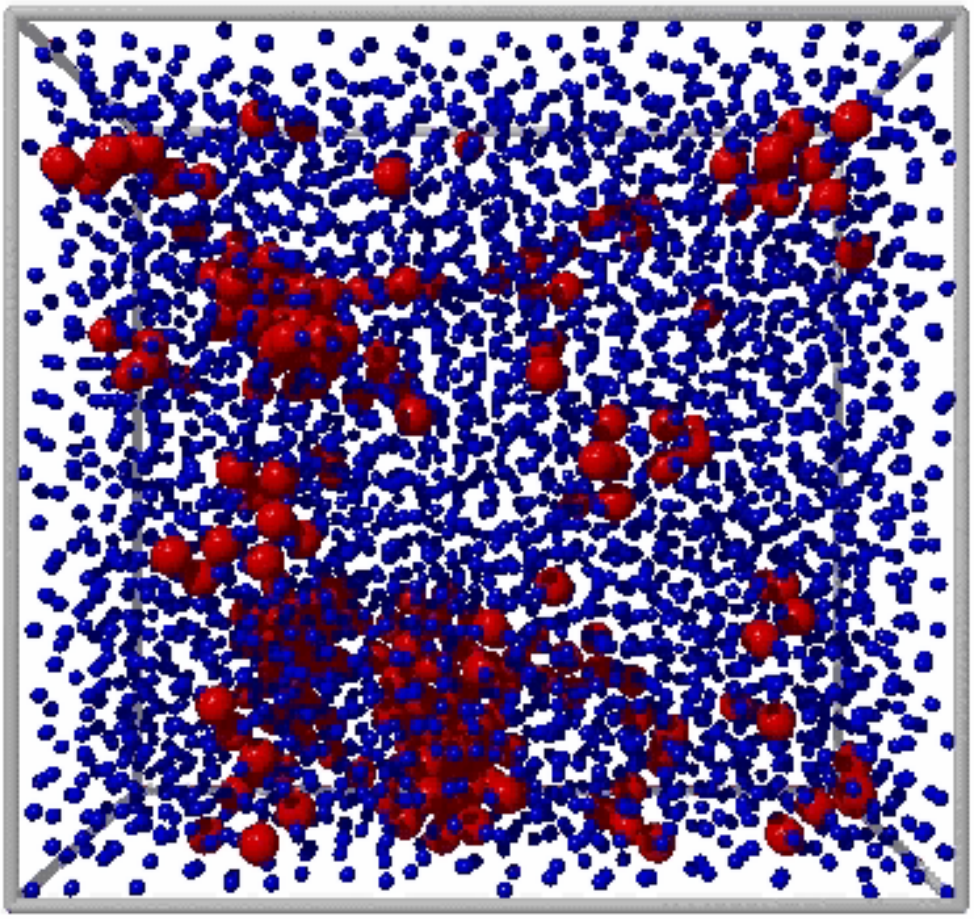


Very deep quench

nucleation

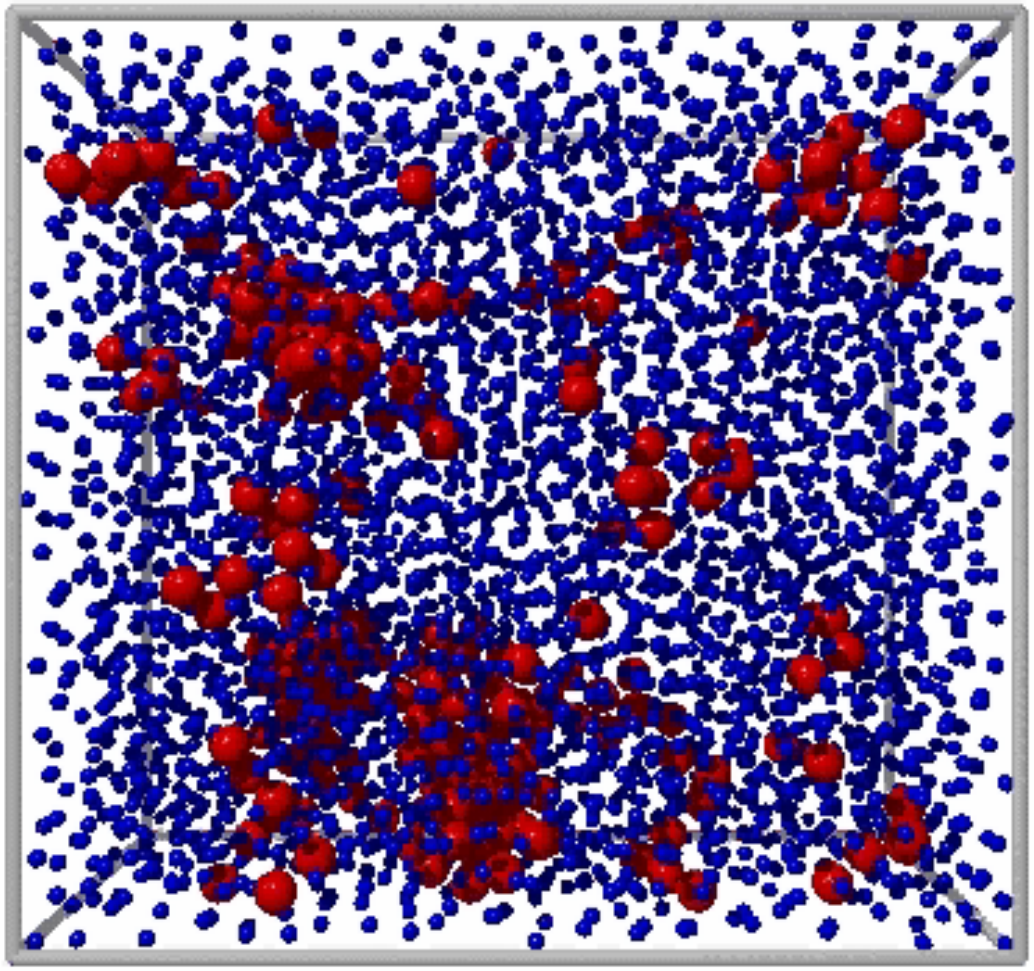


Concentrated hard spheres, initial stage: *nuclei dissolve*



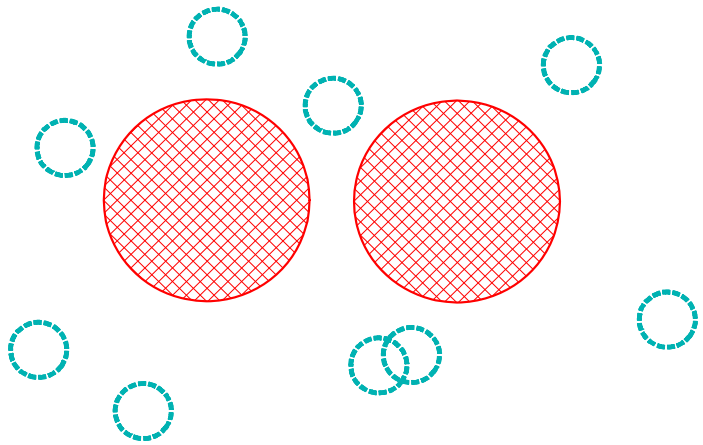
Gasser *et al*, Science **292,** April 2001

Full picture:



Gasser *et al*, Science **292,** April 2001

Hard spheres +freely overlapping spheres

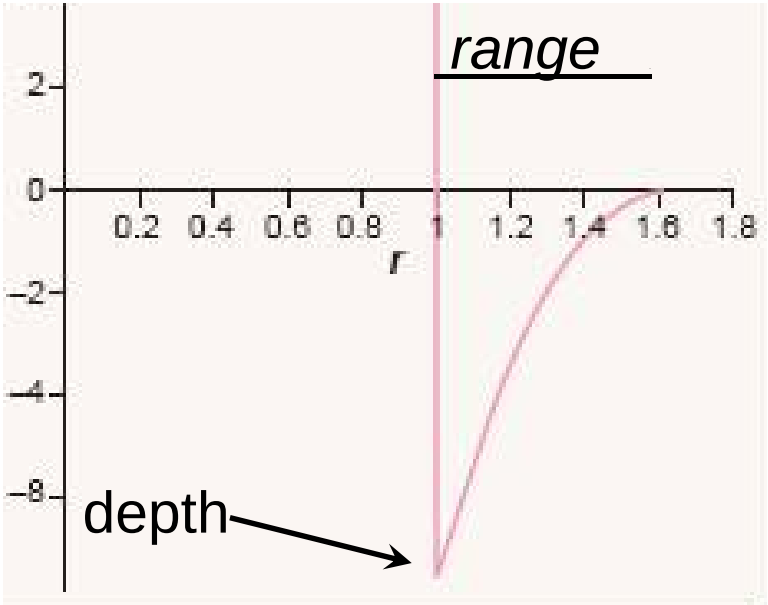


Depletion potential:

$$W_{dep}(r) = -\Pi V_{overlap}(r)$$

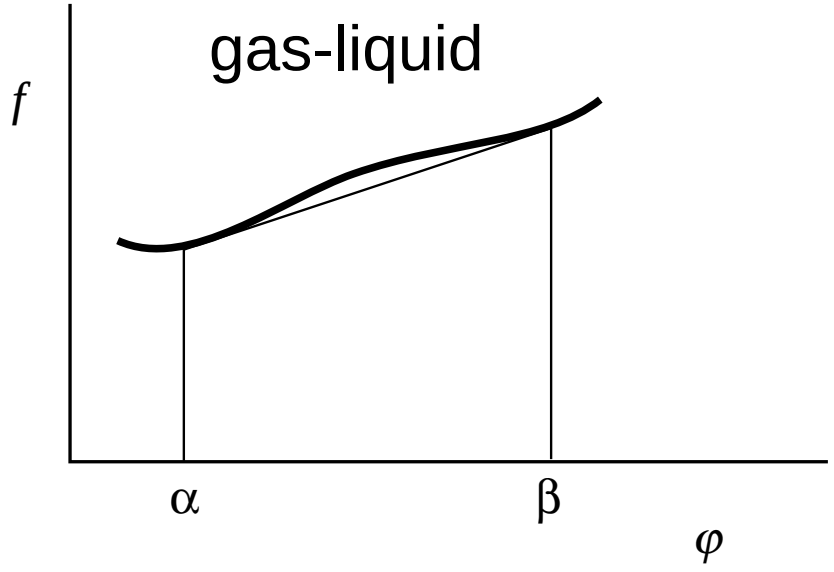
larger chains → longer range of *W*

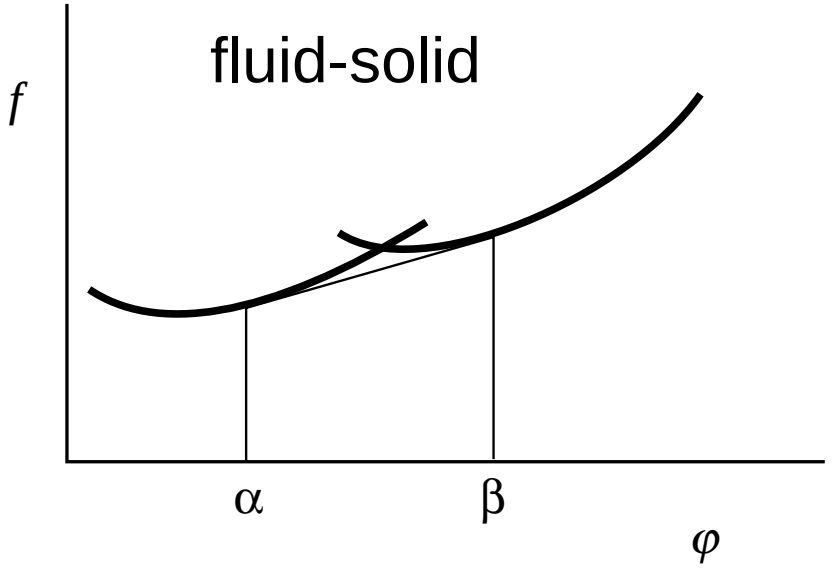
more chains → depth,
more attractive *W*

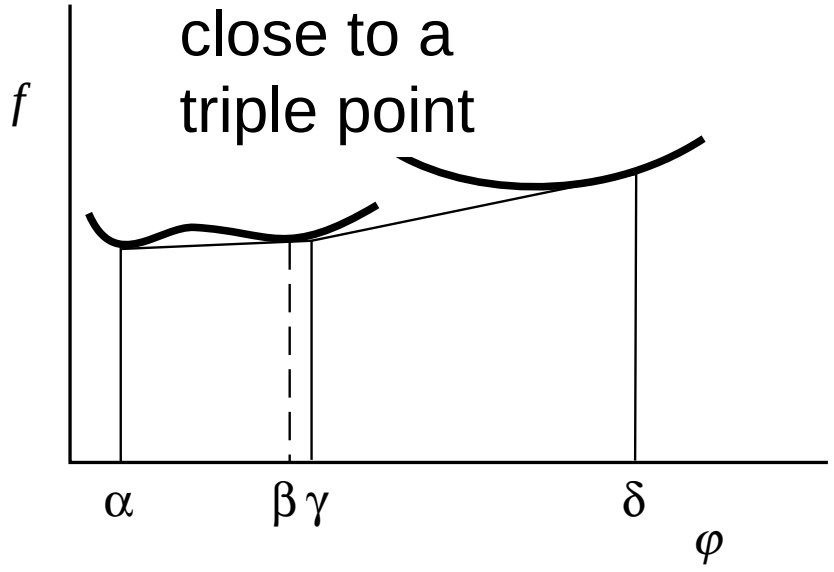


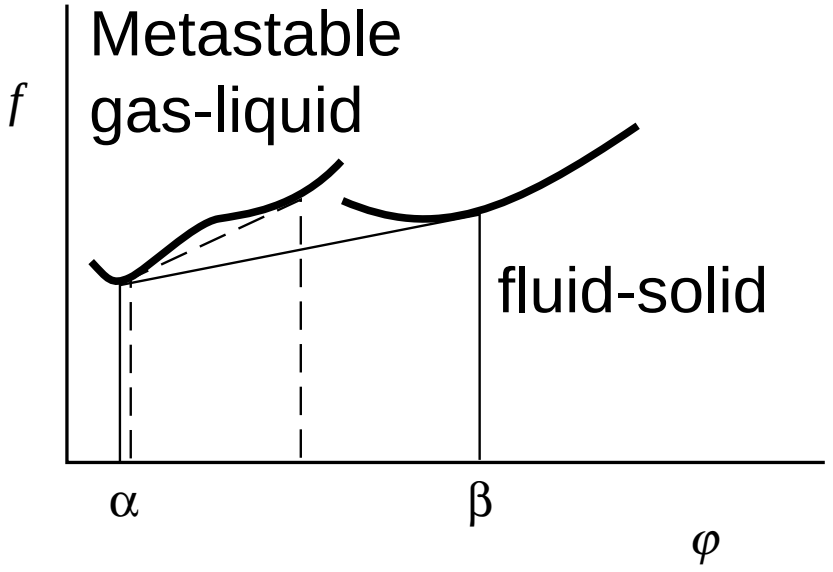
at c=c*, a_{HS}/a_{FOS}=5/3, W_{min}= –2.5 kT

Phase behaviour from *f*



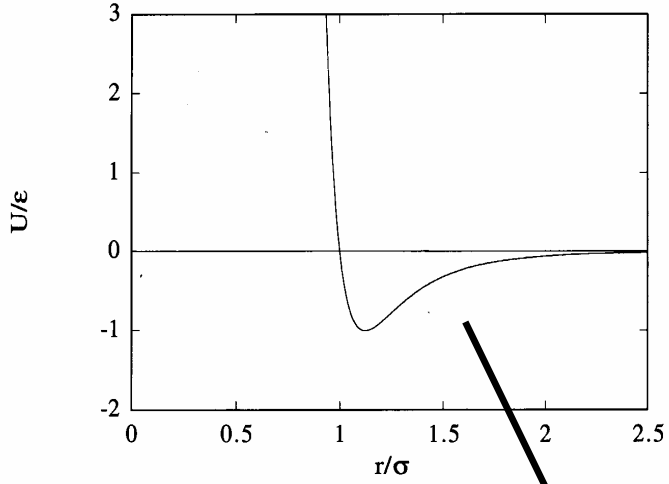


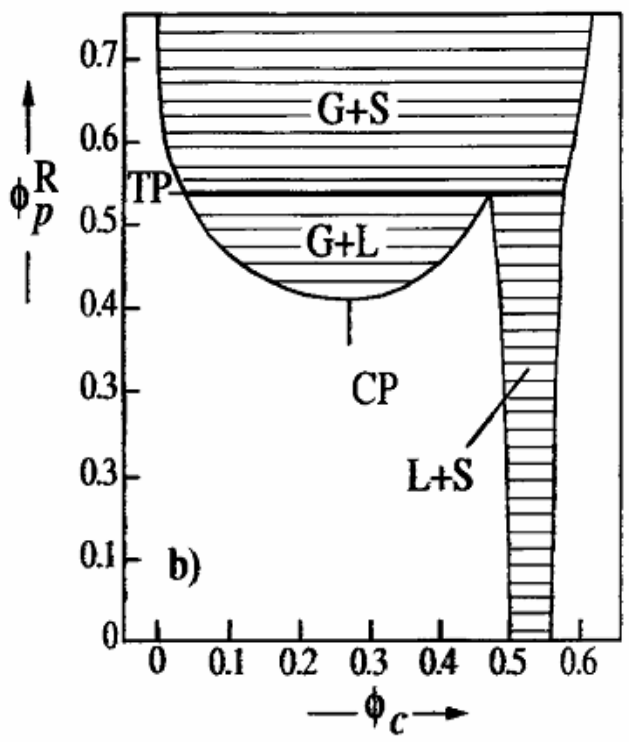


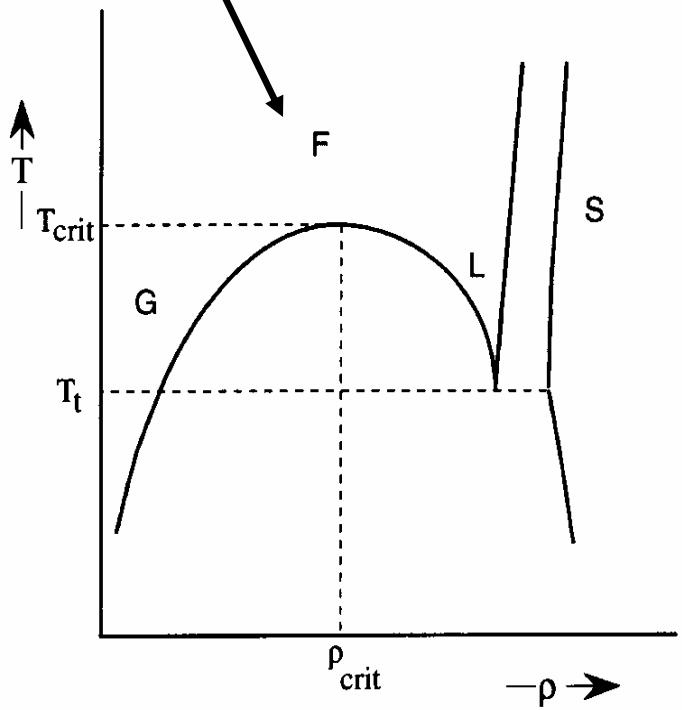


Compare to atomic/molecular fluids with Lennard-Jones interaction:

Lennard-Jones intera



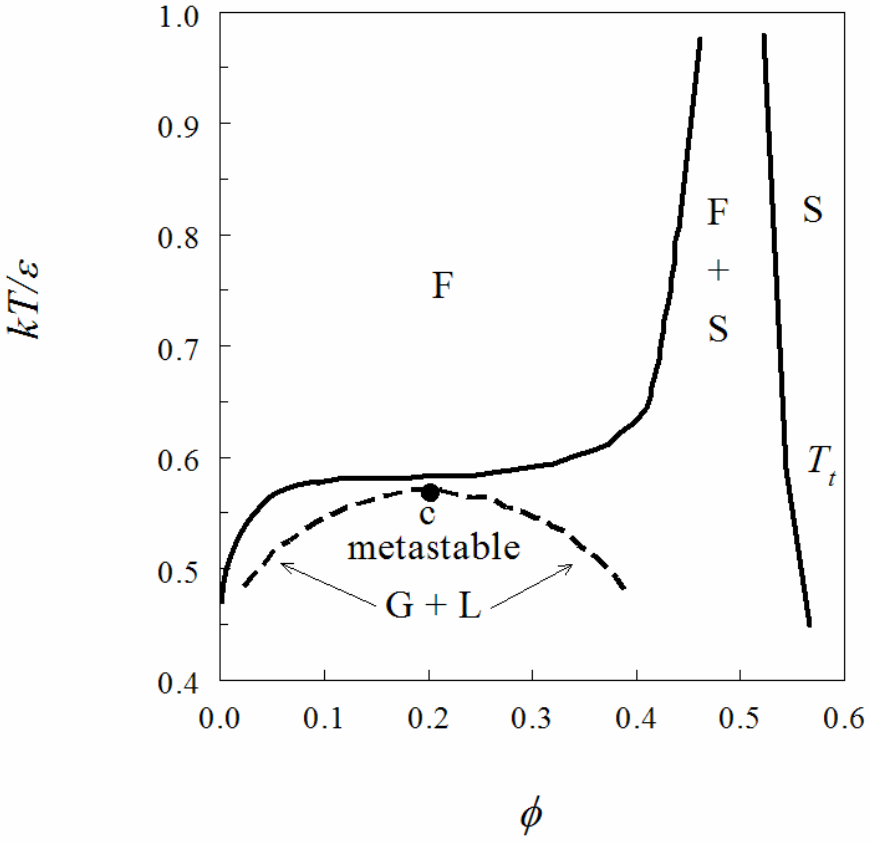




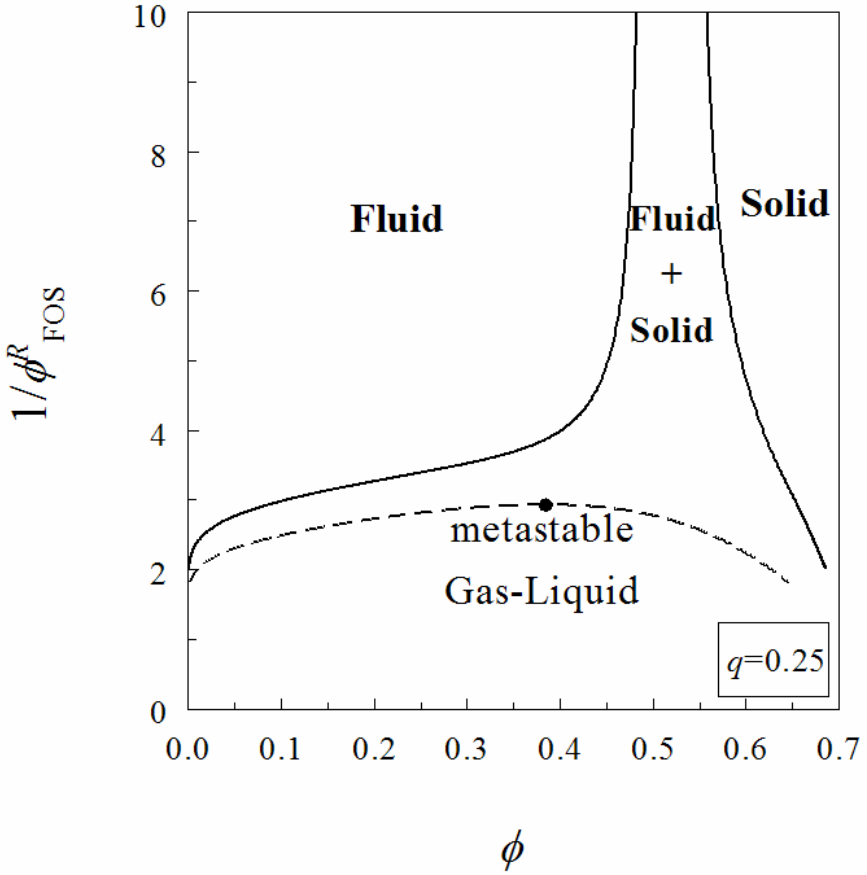
polymer concentration
≈ inversed temperature!

Compare to atomic/molecular fluids with Lennard-Jones interaction:

Lennard-Jones fluid n=12:



colloid-polymer mixture:



Is $dV \cdot \bar{\rho} \rangle\rangle 1$ true?

$$\Pi = \frac{cT}{(V - V_{red})} - \alpha (N/V)^2$$