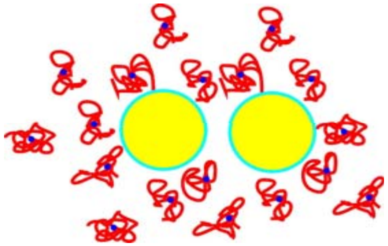
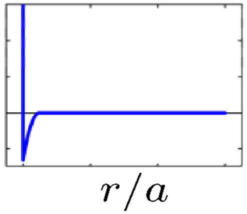
The Program

- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- Lecture 3: Hard spheres
- Lecture 4: Hard spheres + attraction





- Lecture 5: Rods
- Lecture 6: Platelets

Konzentrierung von Kautschukmilchsäften.

Von Prof. Dr. **J. Traube**, Technische Hochschule, Charlottenburg.
(Gummi Zeitung 39, 434 (1925))

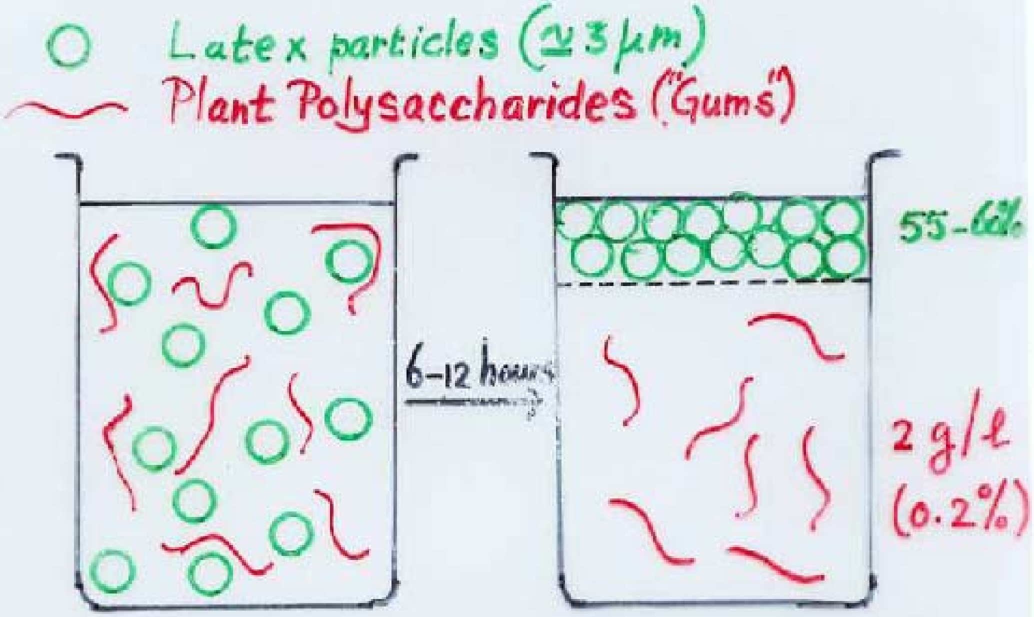
Mein in verschiedenen Ländern zum Patent angemeldetes Verfahren ist sehr einfach. Es erfordert nicht die Anschaffung kostspieliger Apparate und ist in kleinerem wie im größten Maßstabe bequem ausführbar.

Das Verfahren beruht darauf, daß beim Vermischen von Latex mit wässrigen Lösungen bestimmter Pflanzenextrakte beim Einhalten gewisser Bedingungen der Konzentration und Temperatur zwei scharf getrennte Flussigkeitsschichten entstehen, deren obere Schicht fast die gesamte Menge des Kautschuks enthält, während die untere Schicht einen großen Teil der Verunreinigungen des Kautschuks aufnimmt und einen Kautschukgehalt hat, welcher im Maximum 5-6 Prozent beträgt.

Konzentrierung von Kautschukmilchsäften.

Von Prof. Dr. J. Traube, Technische Hochschule, Charlottenburg.

Gummi Zeitung 39, 434 (1925)



es läßt sich sogar noch eine nichtkoagulierte Sahneschicht abschöpfen, in der die Konzentration 70—80 Prozent erreicht.

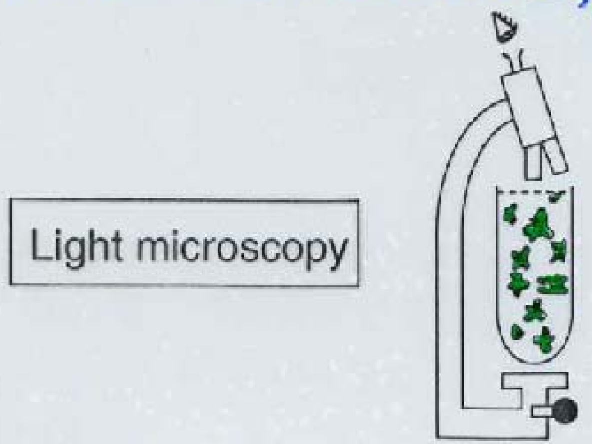
Gießt man derartige Konzentrate in Schalen, in denen Gele aus Gelatine usw. ausgegossen sind, so kann man wasserfreie Kautschukplatten in beliebiger Stärke erhalten

At a meeting of the London Section of the Institution of the Rubber Industry, held at the Royal Empire Society, on 12th April, 1937, Mr. T. R. Dawson presiding, Mr. Baker read the following paper.

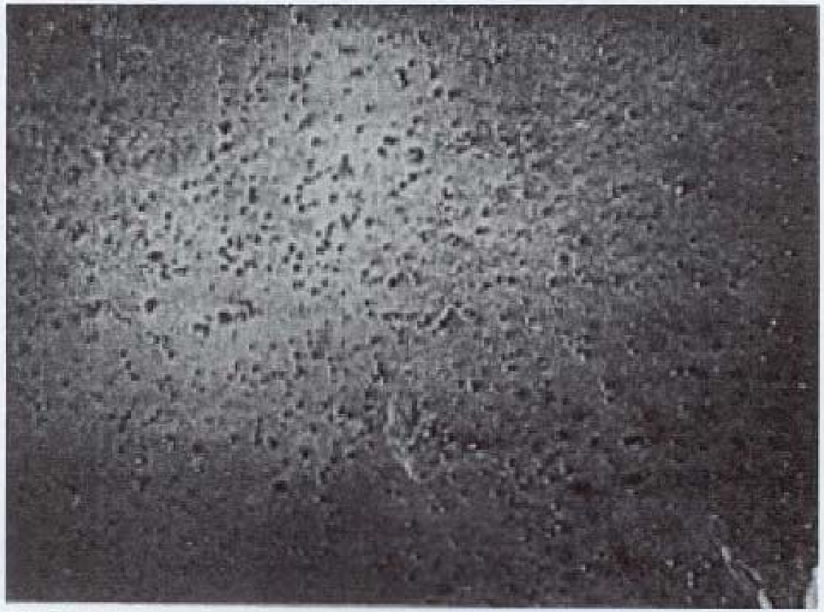
The Concentration of Latex by Creaming

By H. C. BAKER, M.Sc., A.I.C., A.I.R.I. (Sc.).

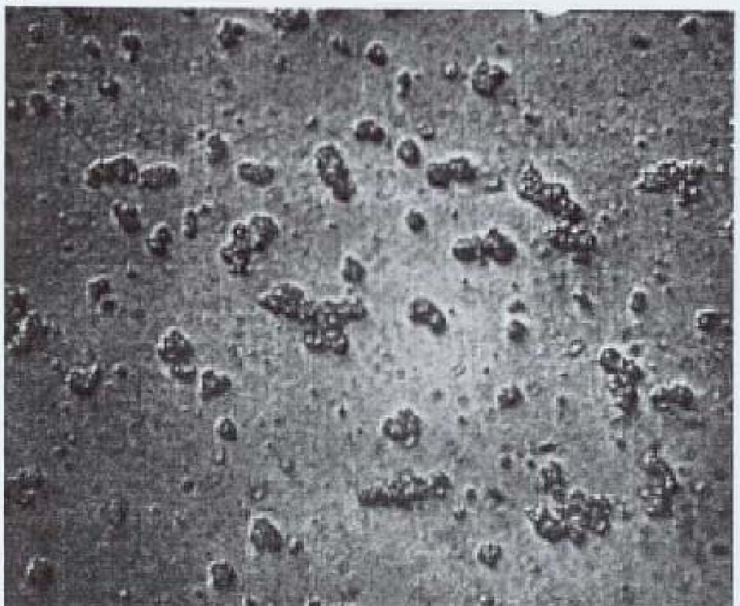
(TRANSACTIONS I.R.I. 13, 70 (1937))



When latex of 2per cent. concentration was mixed with equal volumes of 0·6 per cent. tragon seed gum, thereby bringing the concentration of creaming agent to that used in practice (0·3 per cent.), Brownian movement was slowed down at once with aggregation of the single globules into clusters, and eventually Brownian movement ceased. The size of the clusters two minutes after mixing is shown in Fig. 3, and ten minutes later in Fig. 4. The slide was kept under observation for about an hour, but no further aggregation was observed.

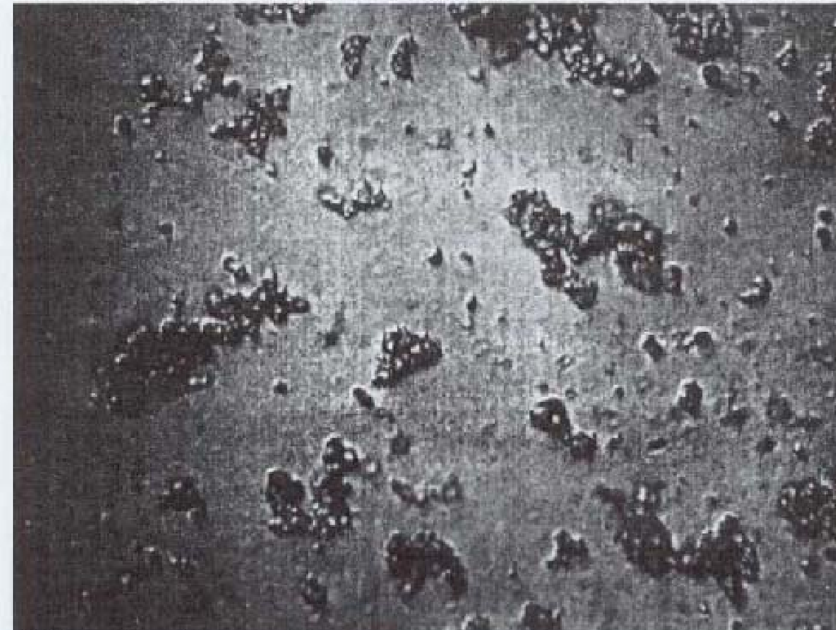


t=0

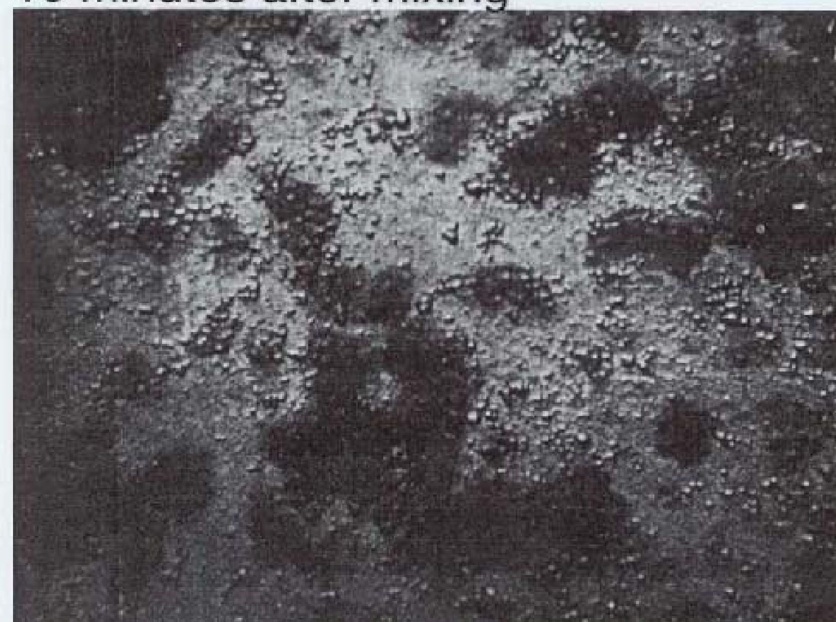


2 minutes after mixing

10 µm



10 minutes after mixing



12 hours after mixing (CREAM) 10 µm

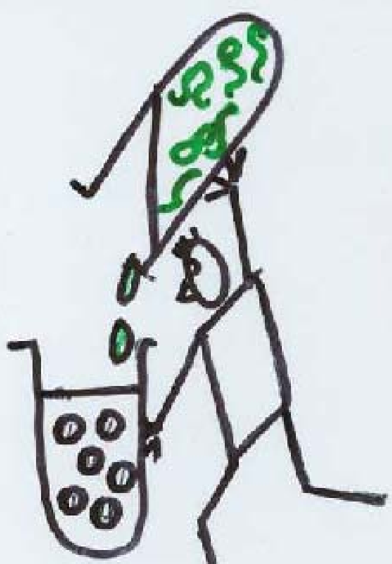
DEPLETION INTERACTION

TUNEABLE ATTRACTION (RANGE AND DEPTH)

COLLOIDAL PARTICLES

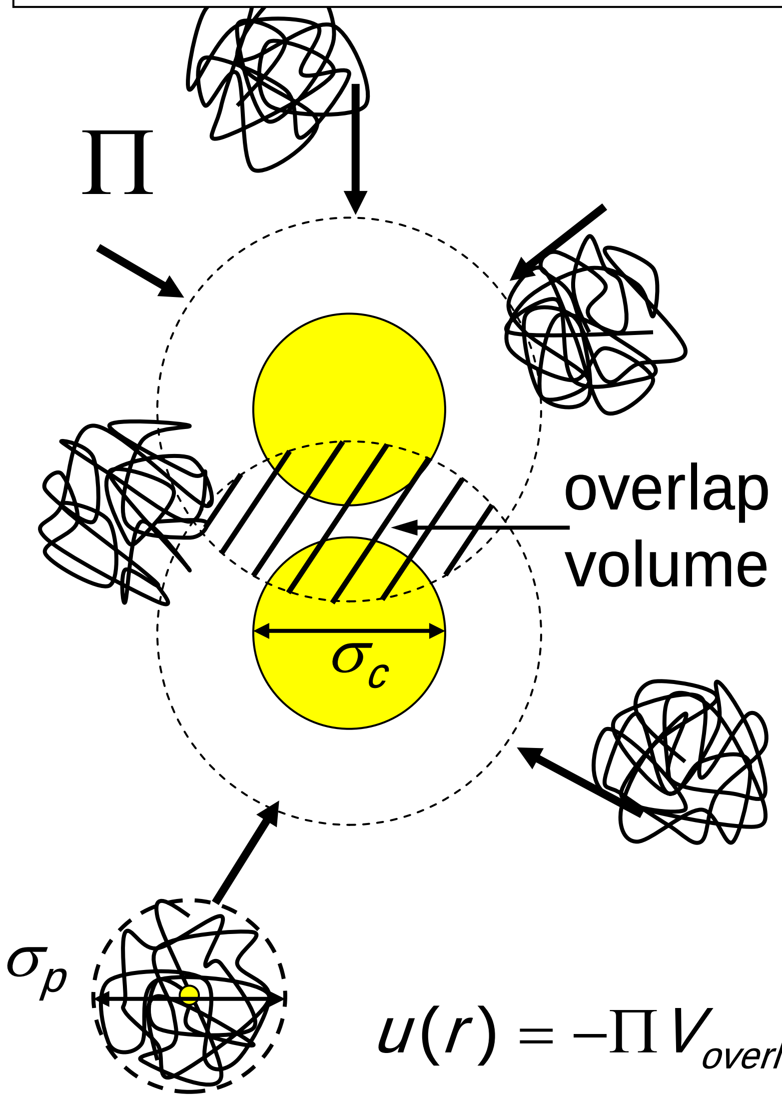
+

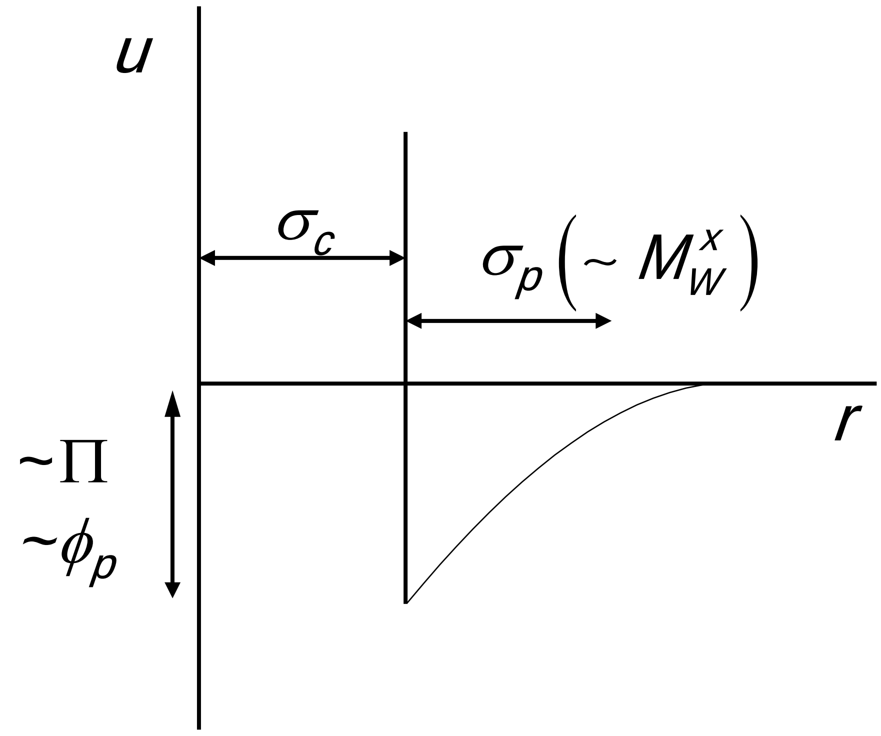
NON-ADSORBING POLYMER MOLECULES



"ADDING A PERTURBATION PHYSICALLY"

Depletion interaction

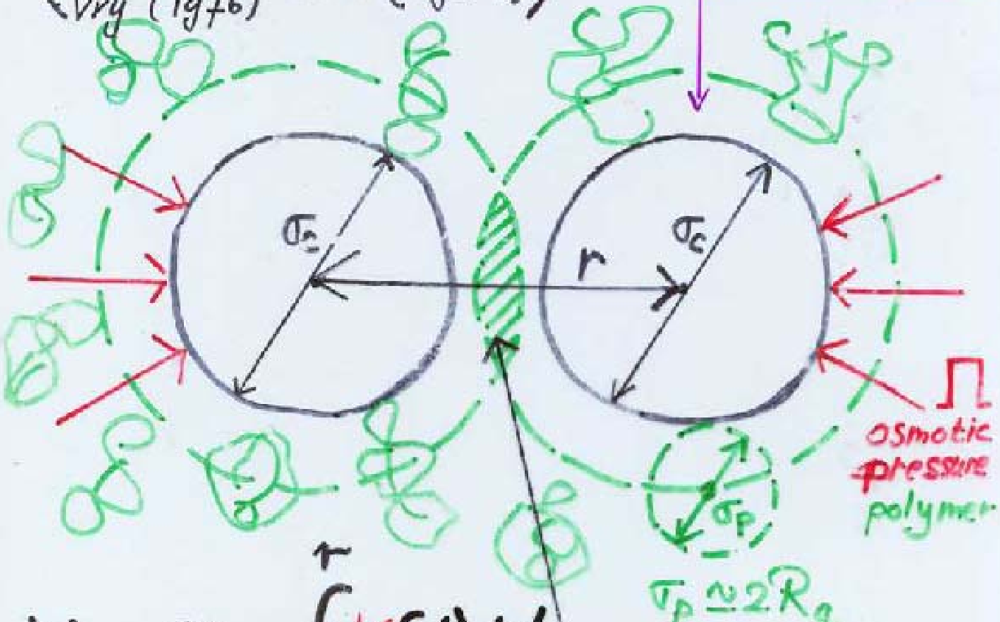




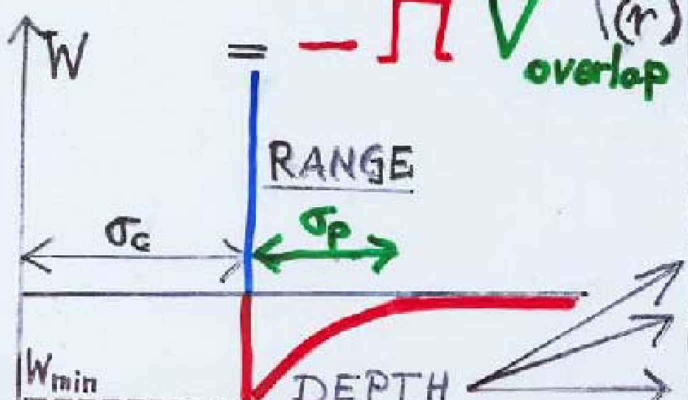
$$u(r) = -\Pi V_{overlap}$$

EFFECT OF FREE POLYMER ON A COLLOIDAL DISPERSION ⟹ DEPLETION INTERACTION

(Asakura + Oosawa (1954) Vrij (1976))



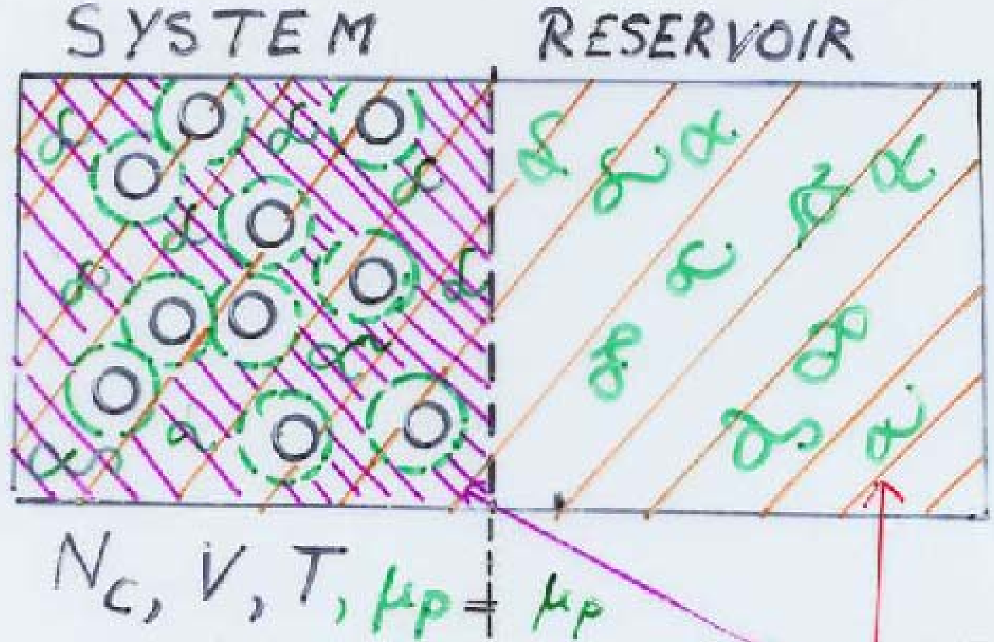
$$W_{depletion}(r) = -\int_{\infty}^{r} K(r')\,dr' = -\Pi\, V_{overlap}(r)$$



$\frac{\lvert W_{min}\rvert}{kT} \simeq \frac{3}{2}\phi_p\left(\frac{\sigma_c}{\sigma_p}\right)$	c_p (g/l)
−1kT	2.5 g/l
−2kT	5 g/l
−4kT	10 g/l

Osmotic Equilibrium Treatment of Phase Separation in Colloid+ Polymer Mixtures

HNWL, Colloids and Surfaces 51 (1990) 419.
HNWL, W.C.K. Poon, P.N. Pusey, A. Stroobants and P.B. Warren, Europhys. Lett. 20 (1992) 559.



$\Omega_p(V_{free})$

$$\Omega(N_c, V, T, \mu_p) = F_0(N_c, V, T) - \Pi(\mu_p) V_{free}$$

Osmotic Equilibrium Treatment of Phase Separation in Colloid – Polymer Mixtures

$$\Omega(N_c, V, T, \mu_p) = F_0(N_c, V, T) + \int_{-\infty}^{\mu_p} \left(\frac{\partial \Omega}{\partial \mu_p'}\right)_{N_c, V, T} d\mu_p'$$

$$= F_0(N_c, V, T) - \int_{-\infty}^{\mu_p} N_p(\mu_p')\, d\mu_p'$$

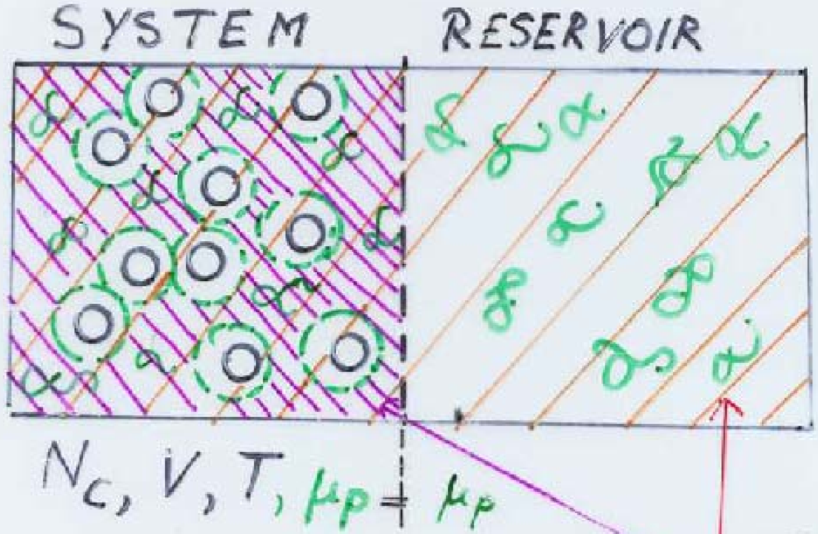
⚠

$$\simeq F_0(N_c, V, T) - \int_{-\infty}^{\mu_p} \langle V_{free} \rangle_0 \underbrace{\rho_p^R\, d\mu_p'}_{d\Pi}$$

$$\boxed{= F_0(N_c, V, T) - \langle V_{free} \rangle_0\, \Pi(\mu_p)}$$

Osmotic Equilibrium Treatment of Phase Separation in Colloid + Polymer Mixtures

HNWL, Colloids and Surfaces 51 (1990) 419.
HNWL, W.C.K. Poon, P.N. Pusey, A. Stroobants and P.B. Warren, Europhys. Lett. 20 (1992) 559.



$\Omega_p(V_{free})$

$$\Omega(N_c, V, T, \mu_p) = F_0(N_c, V, T) - \Pi(\mu_p) V_{free}$$

$$\mu_c = +\frac{\partial \Omega}{\partial N_c} \qquad P = -\frac{\partial \Omega}{\partial V}$$

COEXISTENCE CONDITIONS →

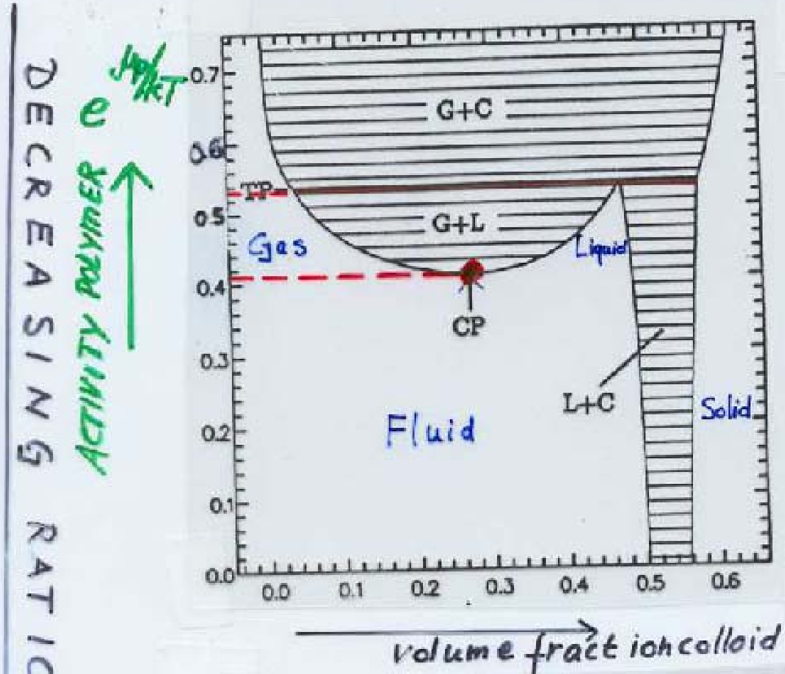
$$\mu_c' = \mu_c'' \qquad P' = P''$$

→ PHASE DIAGRAMS

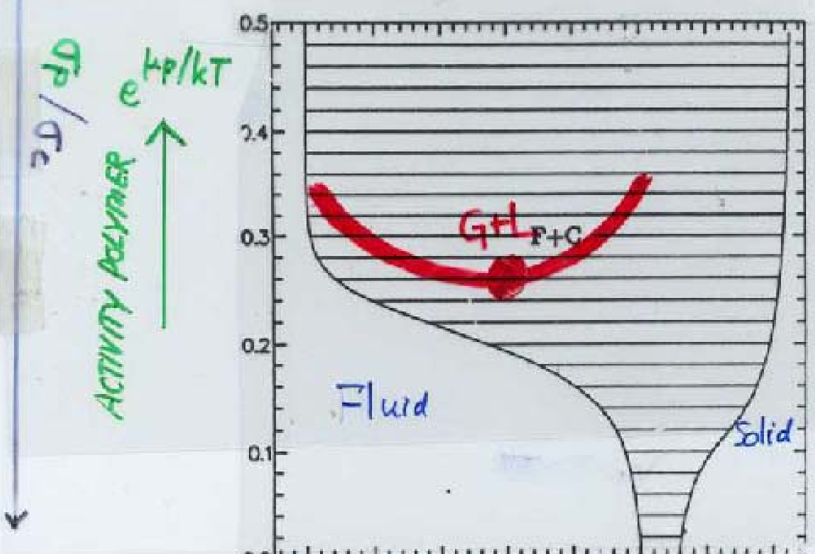
COLLOID- POLYMER MIXTURES

THEORETICAL PHASE DIAGRAMS

FIELD-DENSITY REPRESENTATION



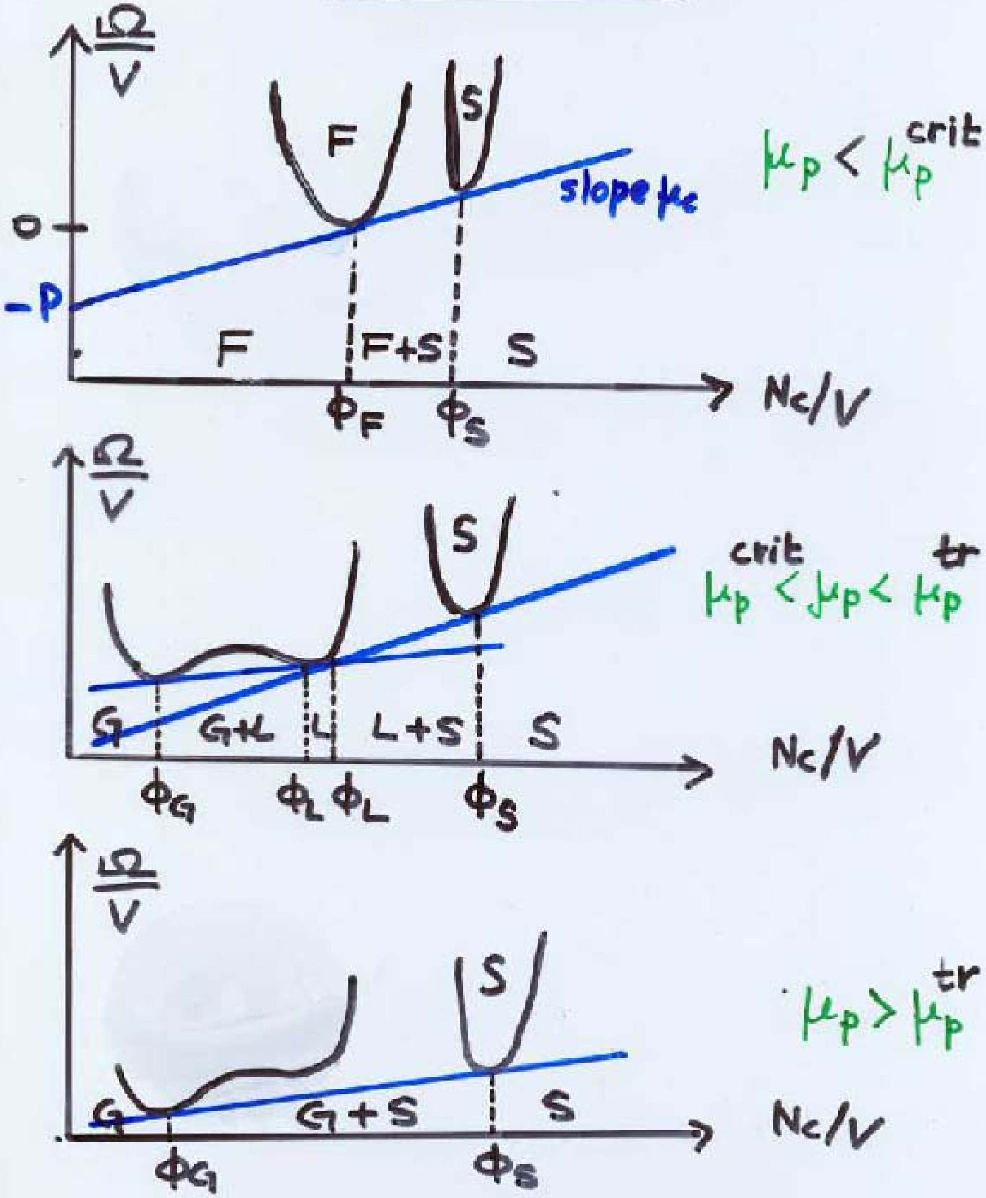
$\frac{\sigma_P}{\sigma_C} = 0.4$



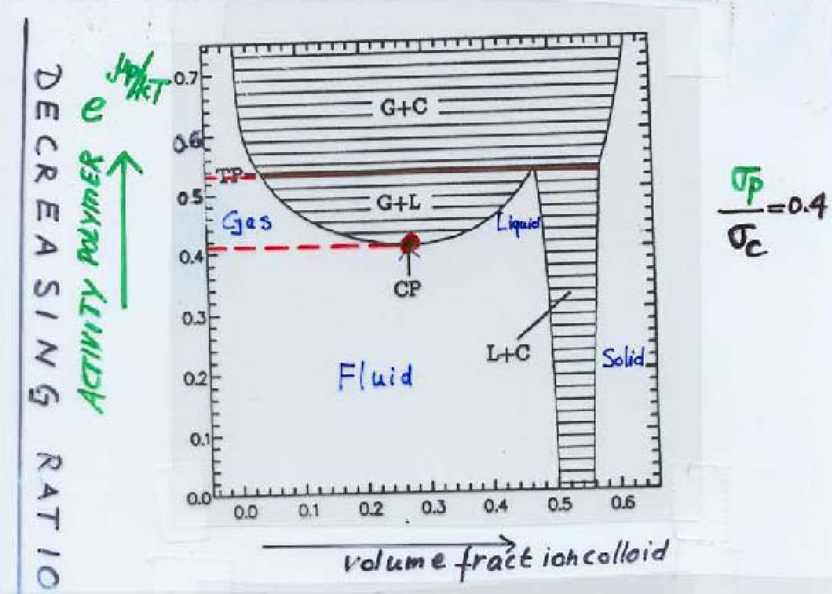
$\frac{\sigma_P}{\sigma_C} = 0.1$

COLLOID - POLYMER MIXTURES
PHASE DIAGRAMS - GRAPHICAL ANALYSIS

$$\left(\frac{\sigma_p}{\sigma_c}\right) \gtrsim 0.3$$



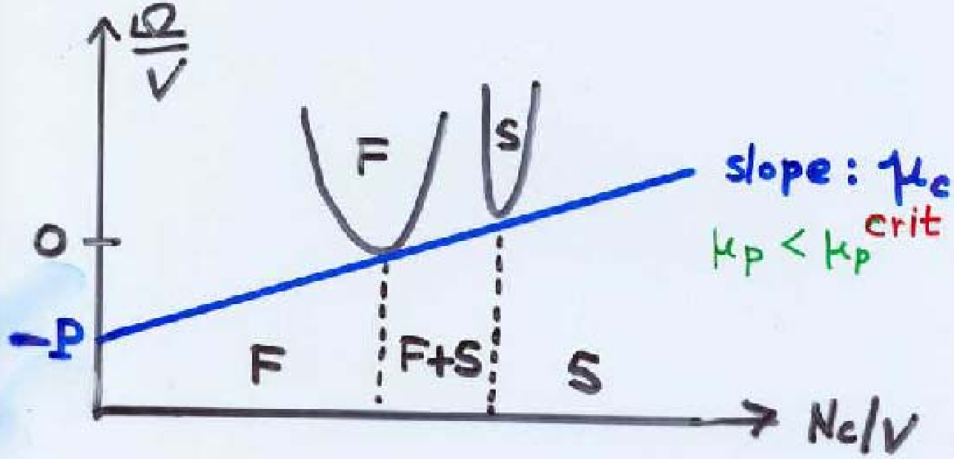
COLLOID - POLYMER MIXTURES — FIELD-DENSITY REPRESENTATION
THEORETICAL PHASE DIAGRAMS

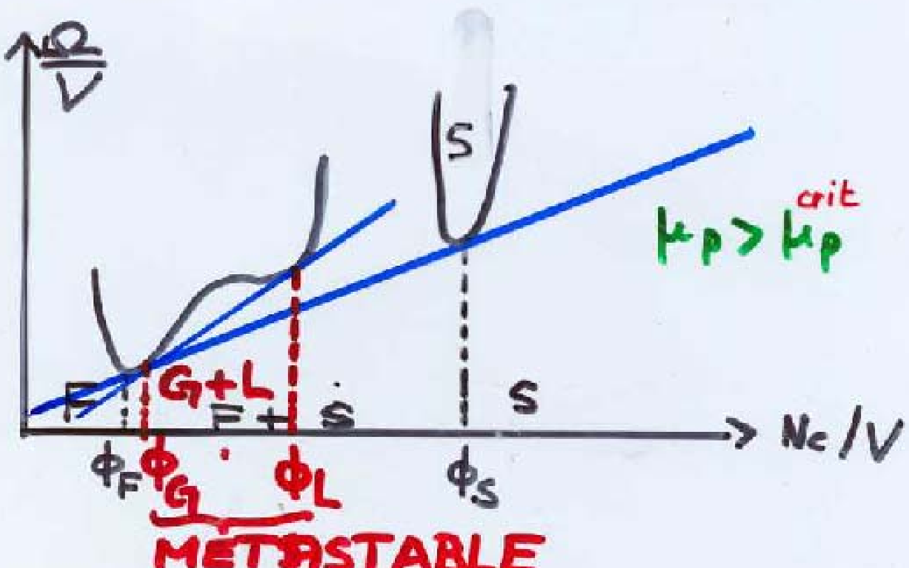


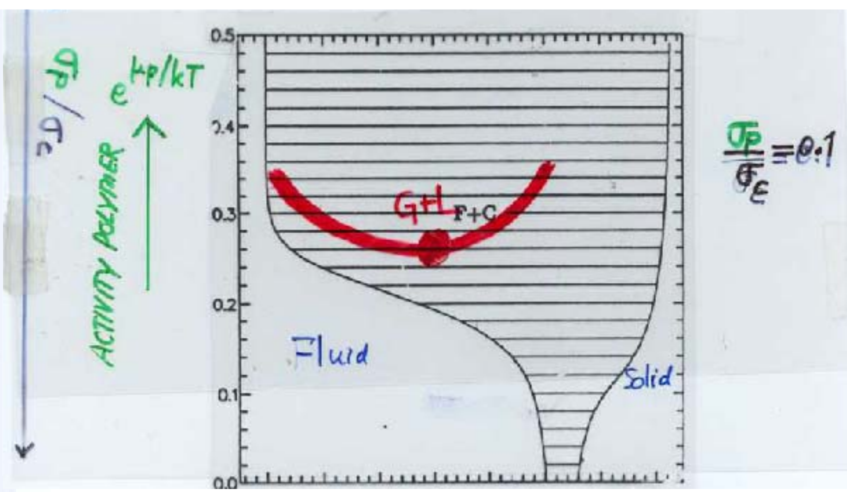
COLLOID-POLYMER MIXTURES

PHASE DIAGRAMS- GRAPHICAL ANALYSIS

$$\left(\frac{\sigma_p}{\sigma_c}\right) \lesssim 0.3$$







How good is free volume theory?

Fortini, Dijkstra, Schmidt, Wessels PHYSICAL REVIEW E 71, 051403 (2005)

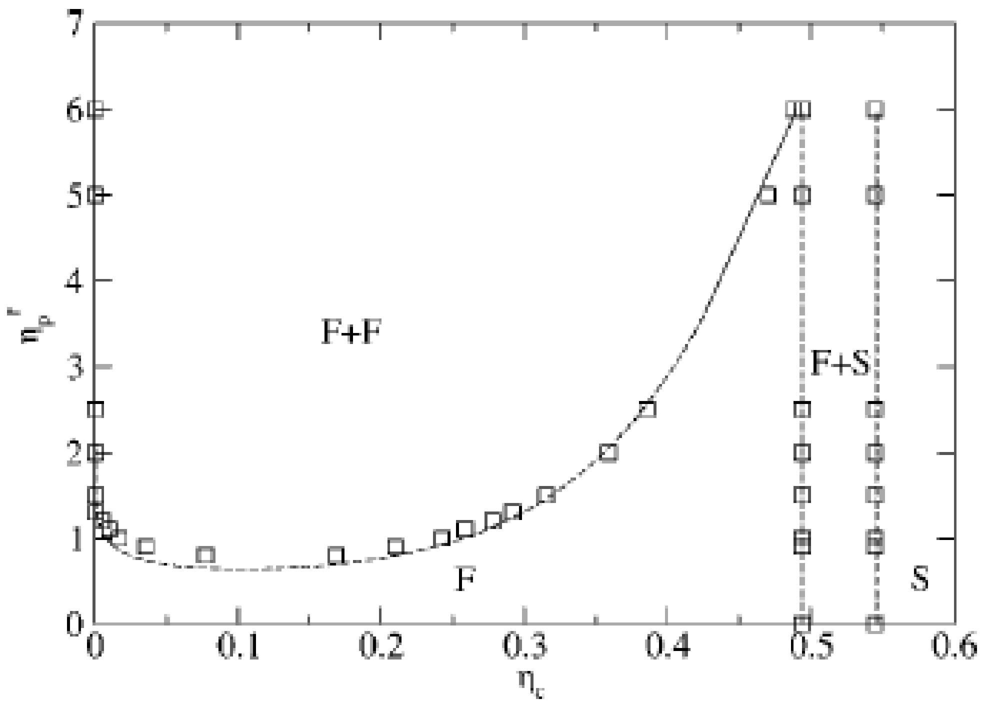
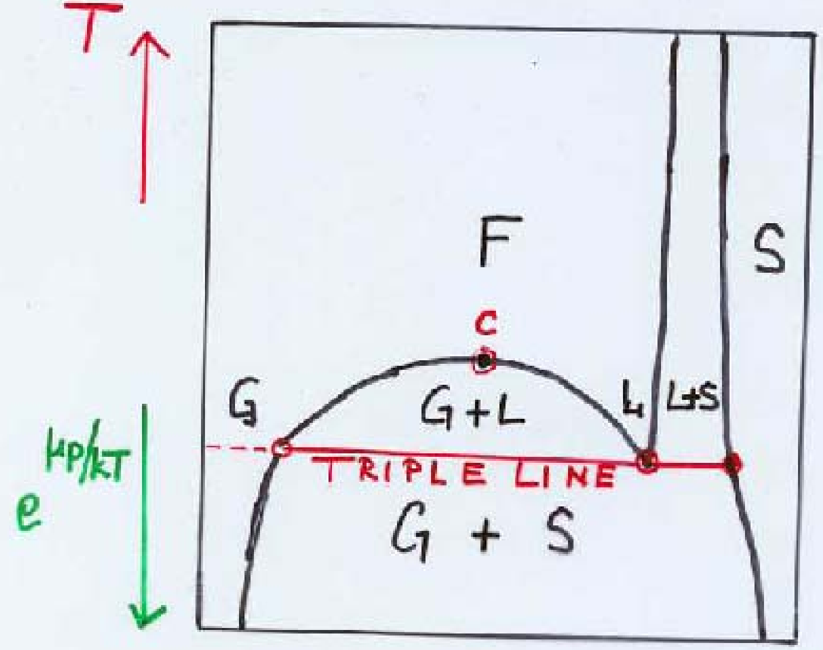
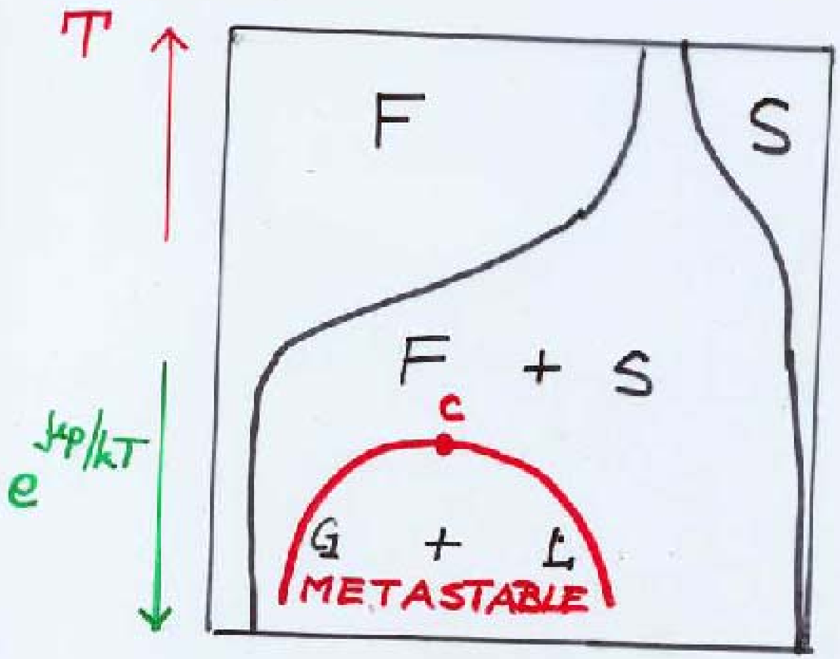


FIG. 3. Phase diagram of the AOV model for size ratio $q=1$ as obtained from simulations, taken from Refs. [17] (symbols), and free volume theory [11] (dashed line) as a function of the colloid packing fraction η_c and the polymer reservoir packing fraction η_p^r. F and S denote the stable fluid and solid (fcc) phase. F+S and F+F denote, respectively, the stable fluid-fluid, and fluid-solid coexistence region.


T
$e^{\mu p/kT}$
F
S
c
G
G+L
L
L+S
TRIPLE LINE
G + S


T
$e^{\mu p/kT}$
F
S
F + S
c
G + L
METASTABLE

Phase diagram

Polymer Concentration –

Colloid Concentration

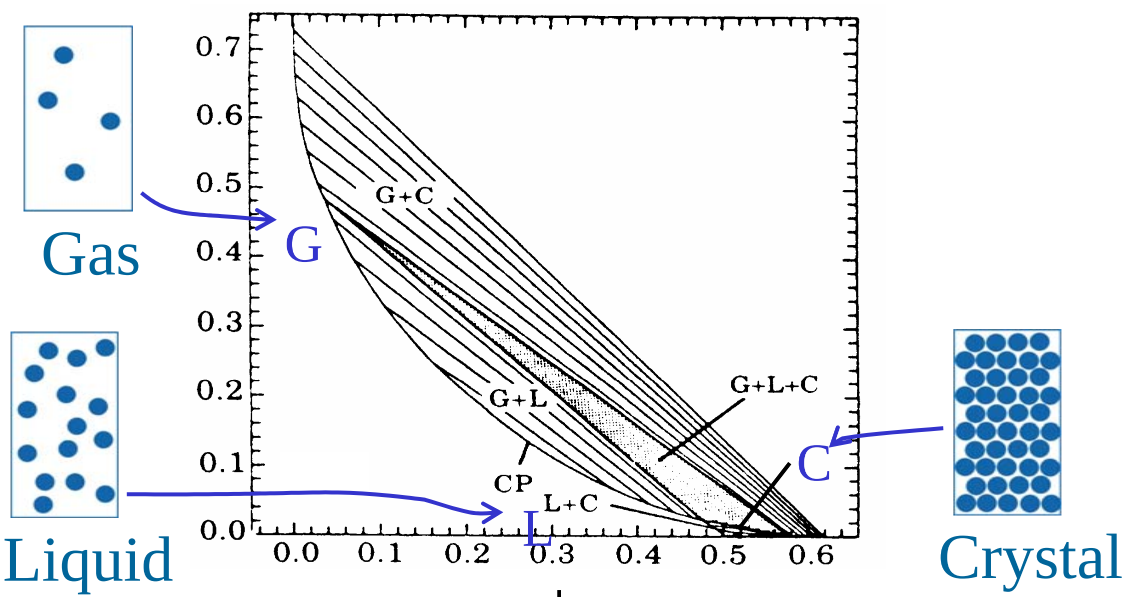
Representation

$$\frac{\partial \Omega}{\partial \mu_p} = - N_p = - \langle V_{free} \rangle_0 \, \rho_p^R$$

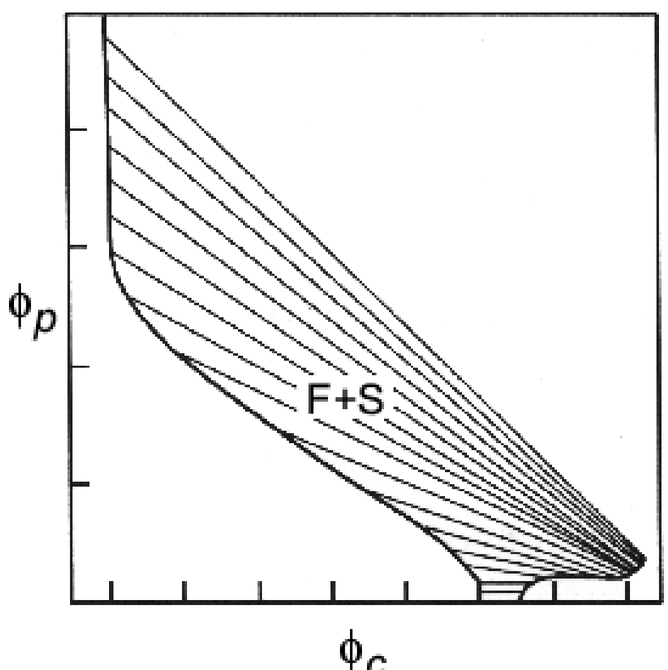
$$\Rightarrow \rho_p^S = \rho_p^R \, \frac{\langle V_{free} \rangle_0}{V}$$

$$\boxed{\rho_p^S \neq e^{\mu_p/kT} \, \frac{\langle V_{free} \rangle}{V}}$$

Phase diagram: polymer – colloid concentration representation



$\sigma_p / \sigma_c > 0.3$

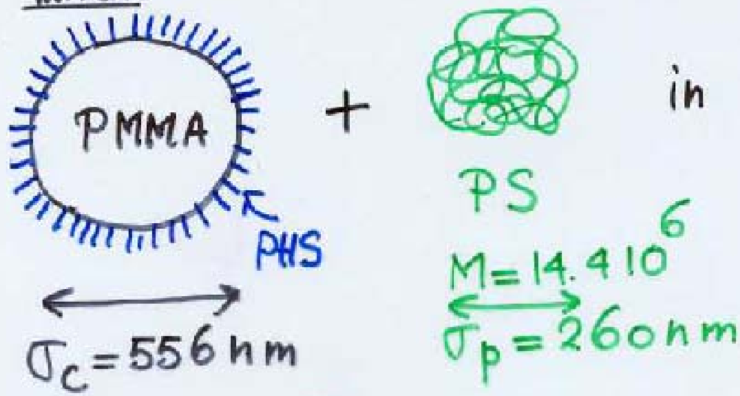


$\sigma_p / \sigma_c < 0.3$

Illet, Orrock, Poon, Pusey

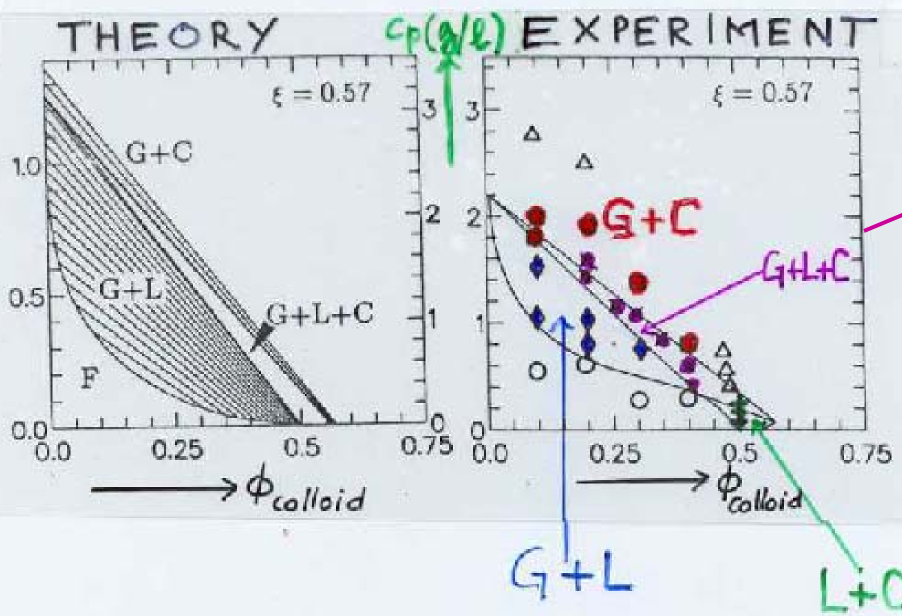
Phys. Rev E 51, 1344 (1995)

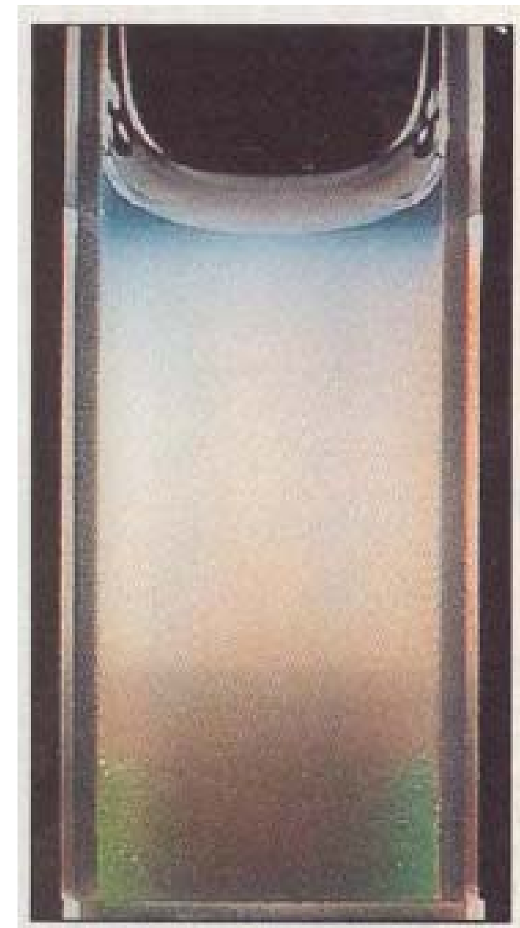
Phase Behavio(u)r of a model colloid-polymer mixture



in cis-decalin

size ratio: $\xi = \frac{\sigma_p}{\sigma_c} = 0.57$





G

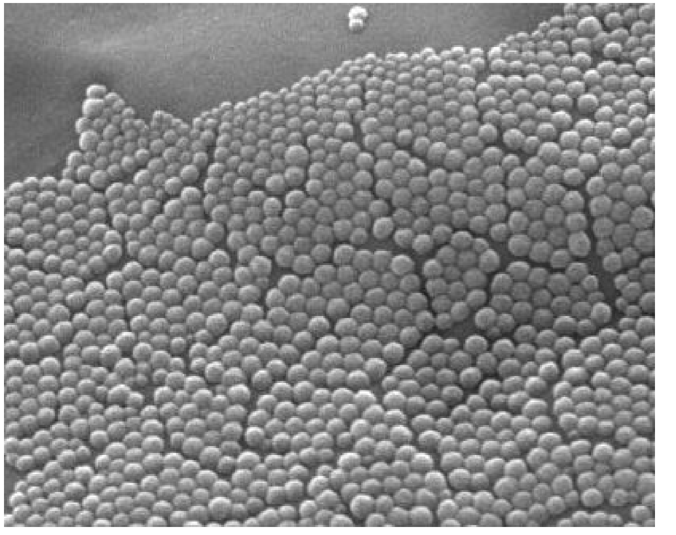
L

C

D.G.A.L. Aarts, R.P.A. Dullens and H.N.W. Lekkerkerker

Interfacial dynamics in demixing systems with ultralow interfacial tension

New Journal of Physics 7 (2005) 40



Fluorescent PMMA spheres

σ_c ~ 50 nm

polydispersity < 10%

+

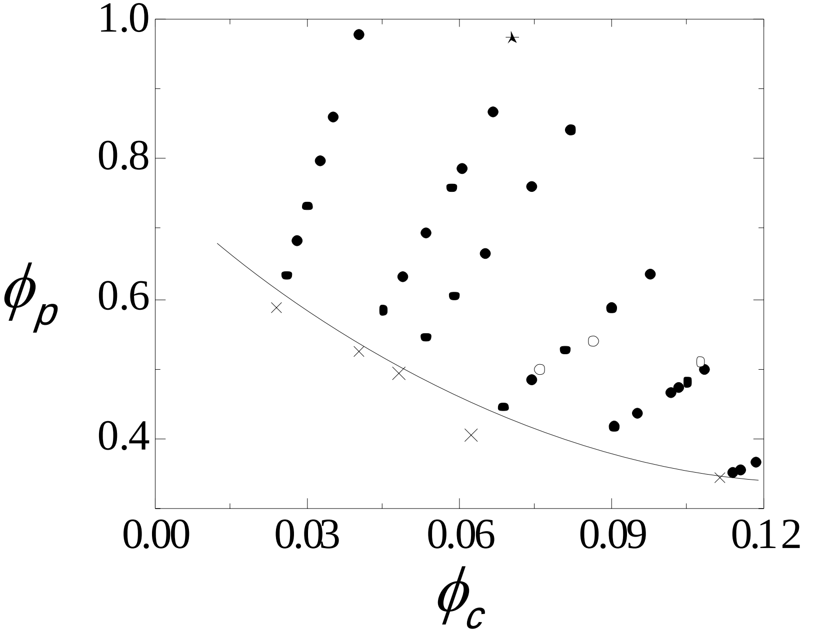
polystyrene polymer

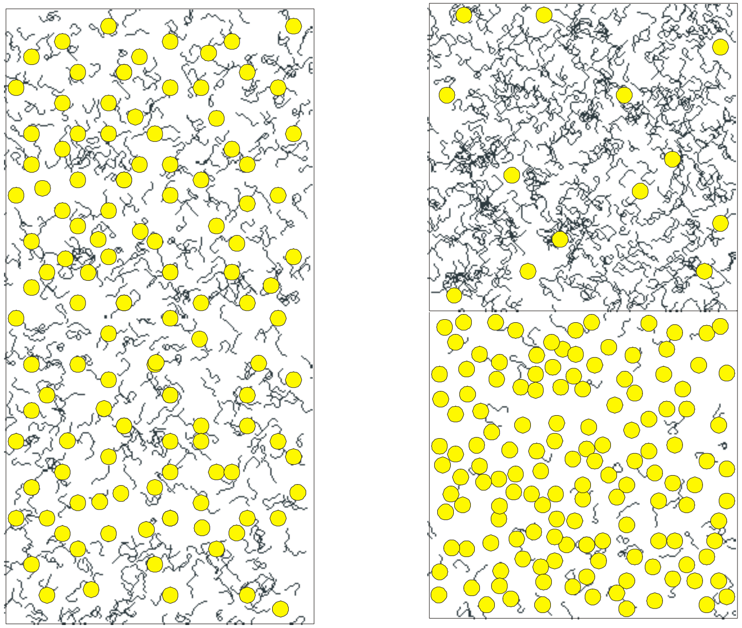
M_w ~233 kg/mol and

σ_p ~ 30 nm

in decaline

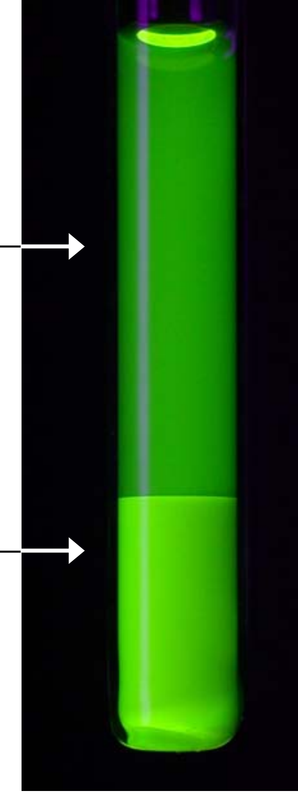
size ratio $q = \frac{\sigma_p}{\sigma_c}$ ~ 0.6



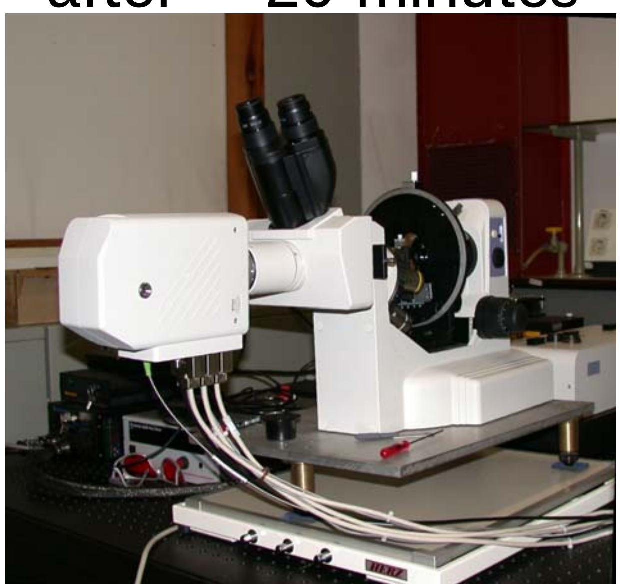


colloid poor:
GAS

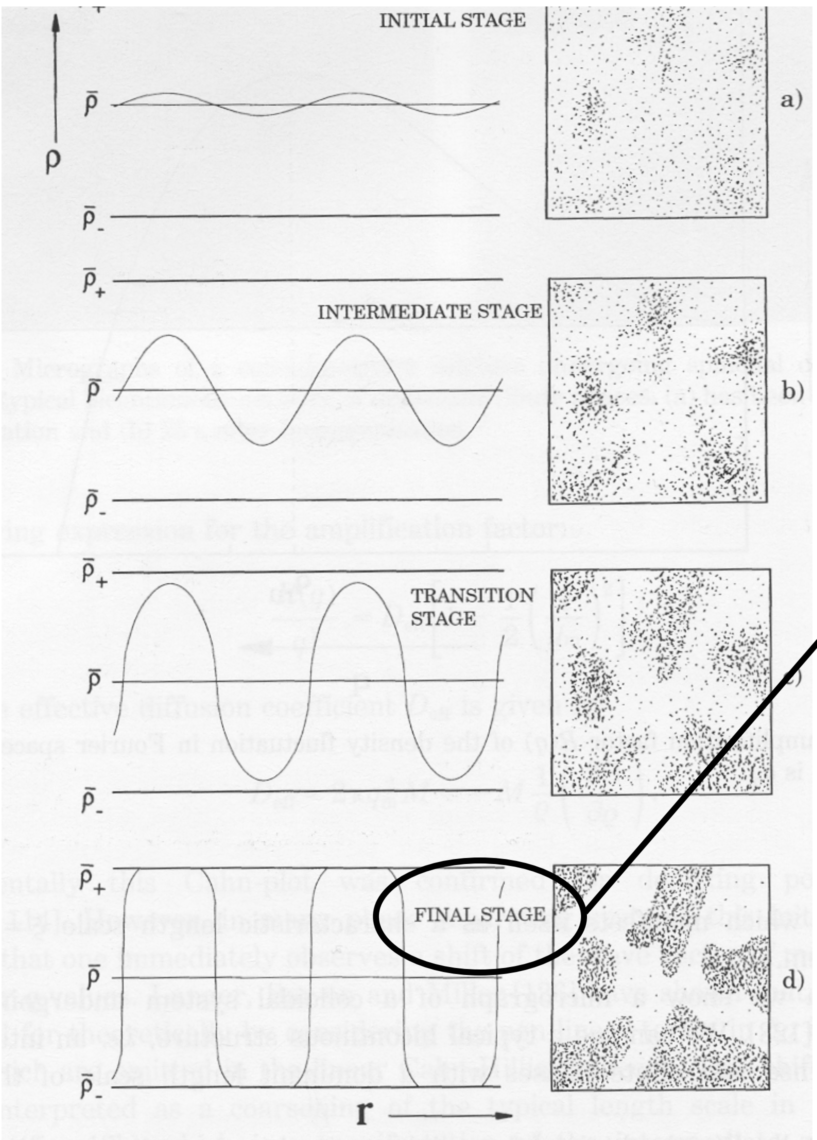
colloid rich:
LIQUID



after ~ 20 minutes



Stage 1: Spinodal decomposition



That’s where it all starts in our experiment!!!

Stage 2 Capillary flow

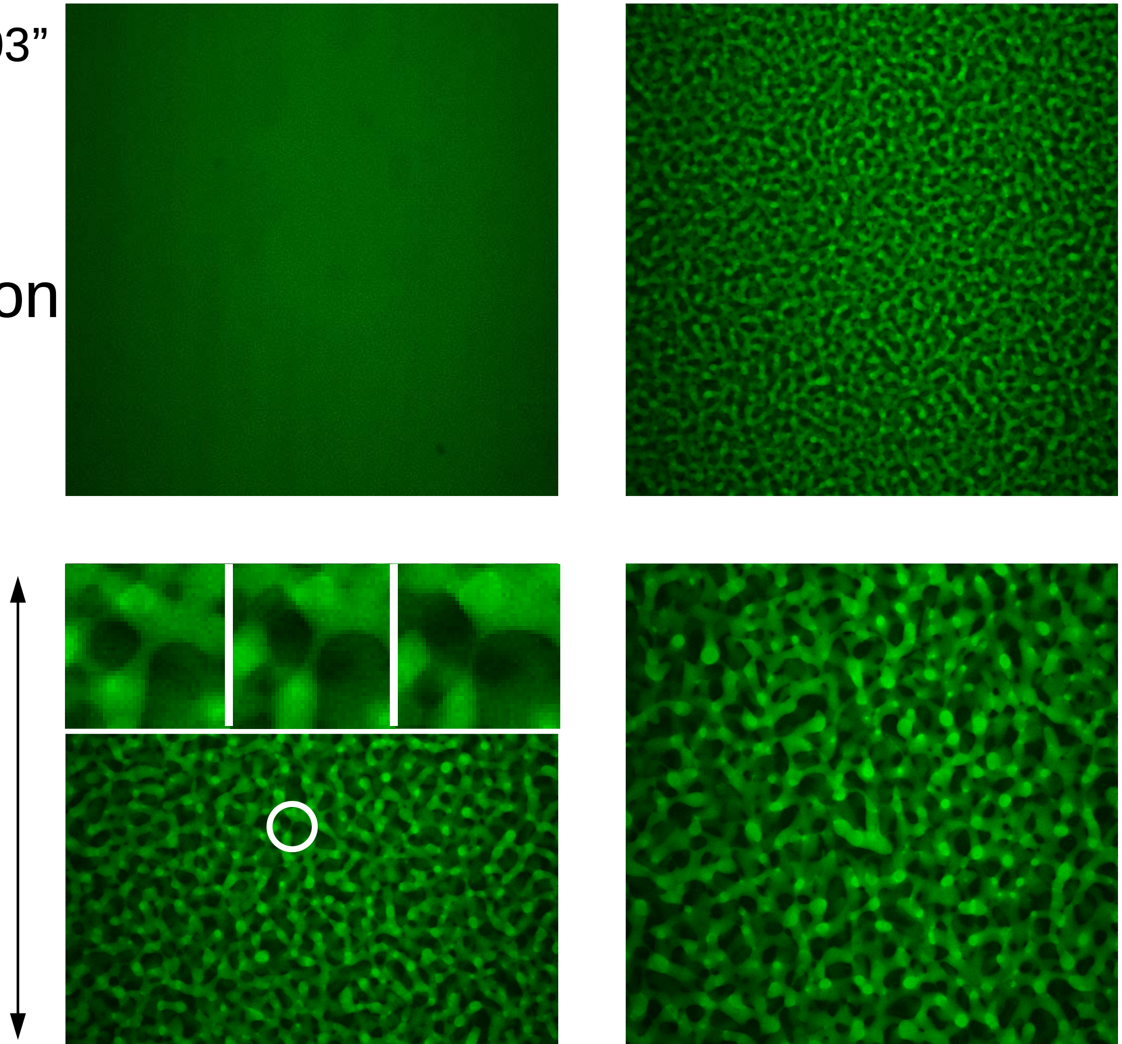
t = 0' 03"

coarsening

spinodal decomposition

pinch-off

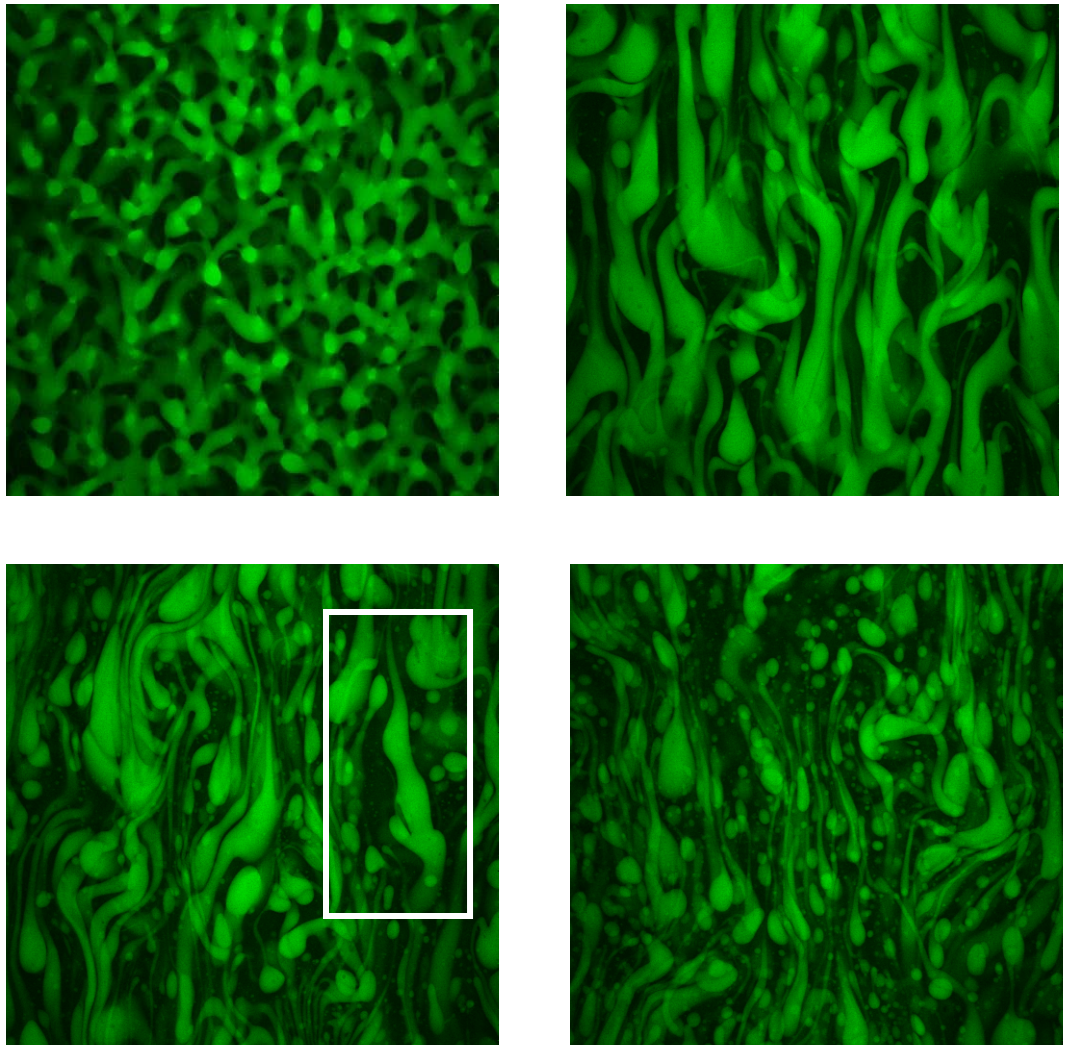
1.4 mm



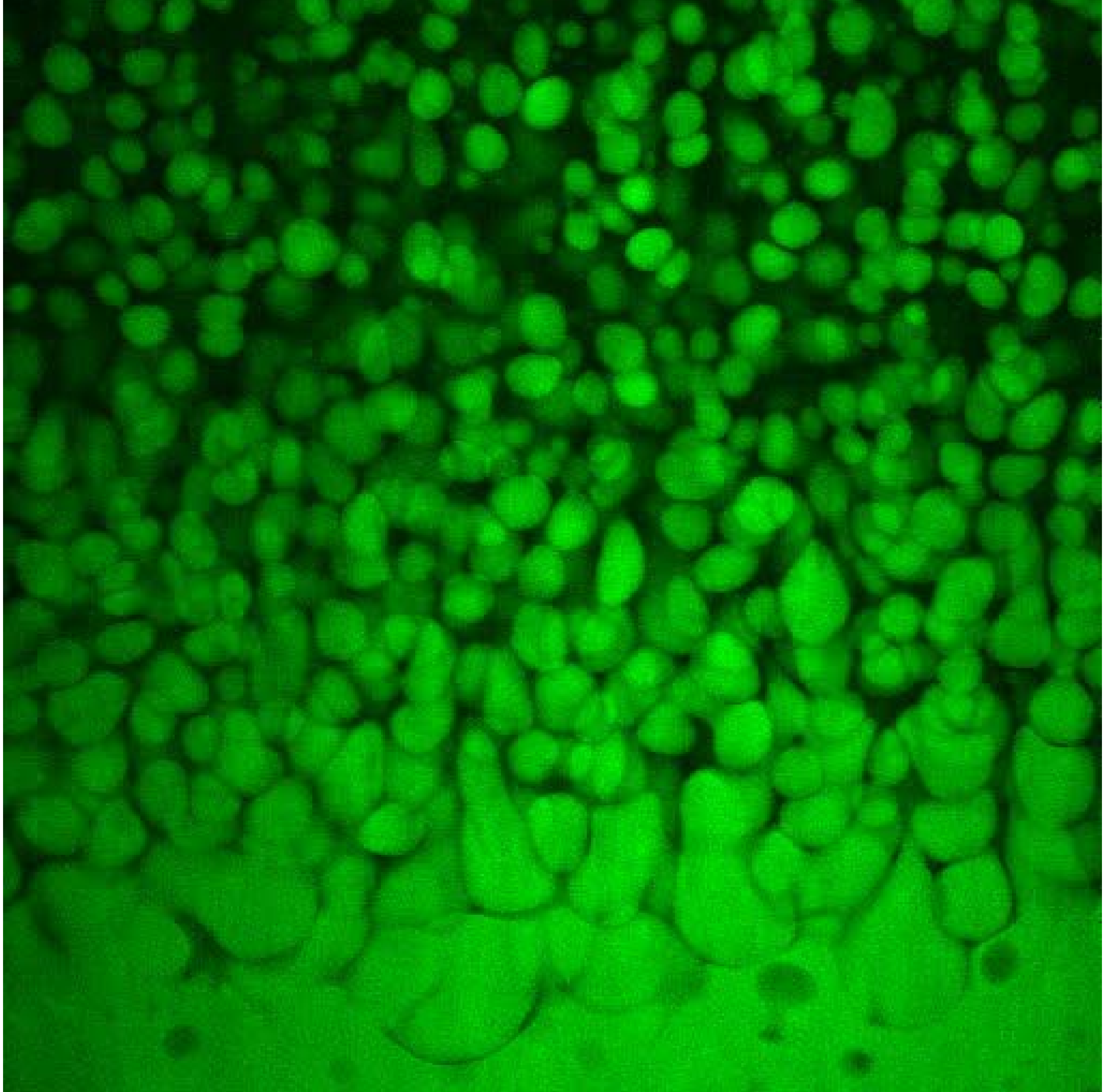
t = 0' 45"

Stage 3 Gravity driven flow

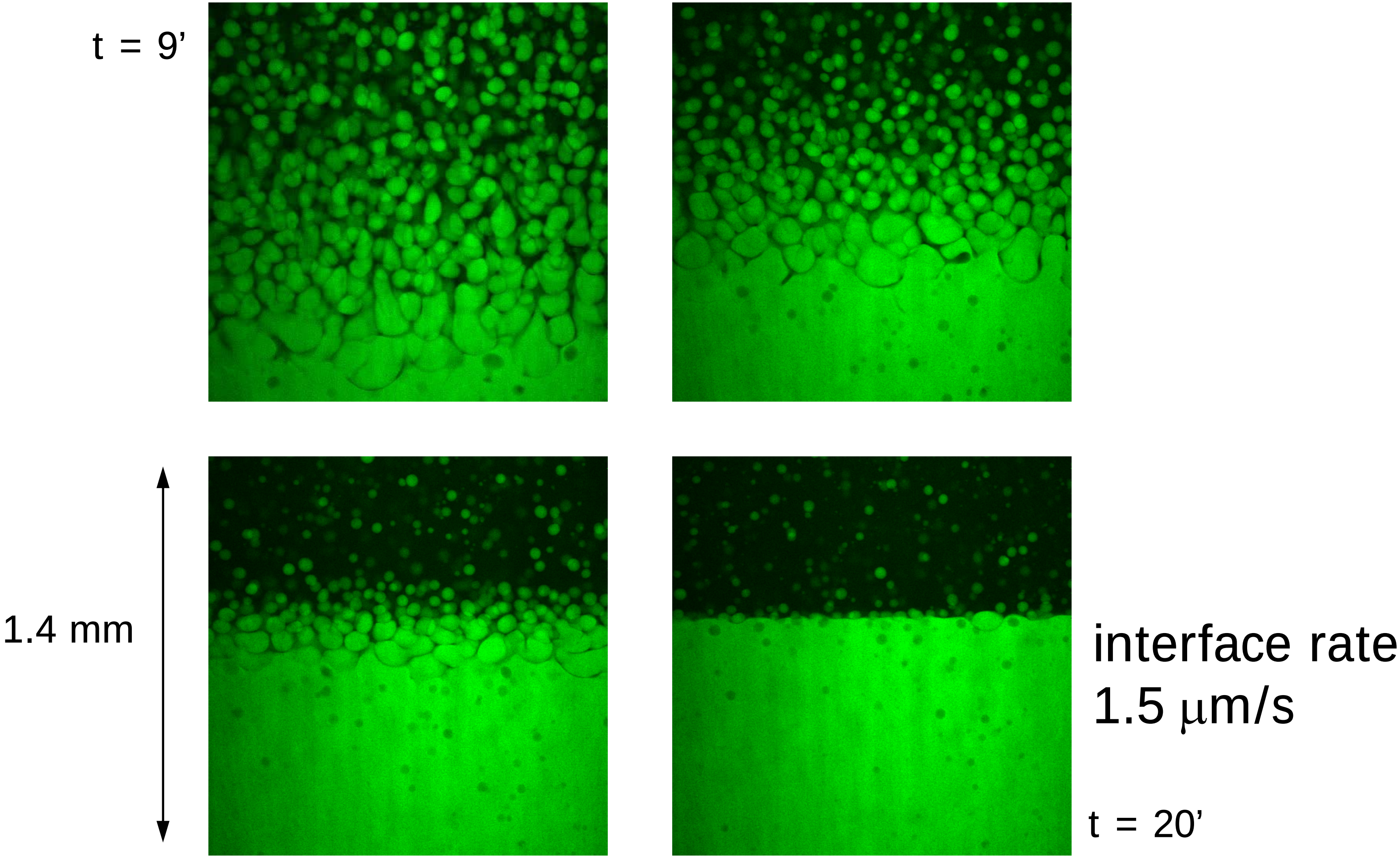
t = 0’ 56”



t = 2’ 57”



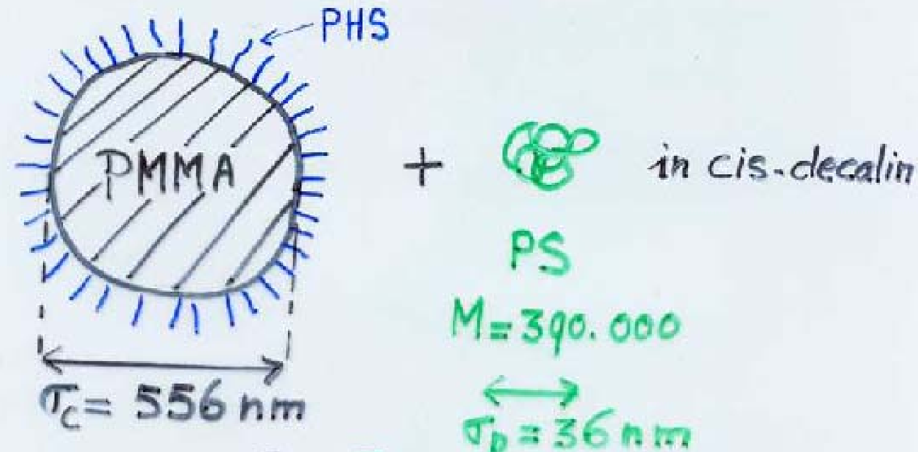
Stage 4 Interface formation



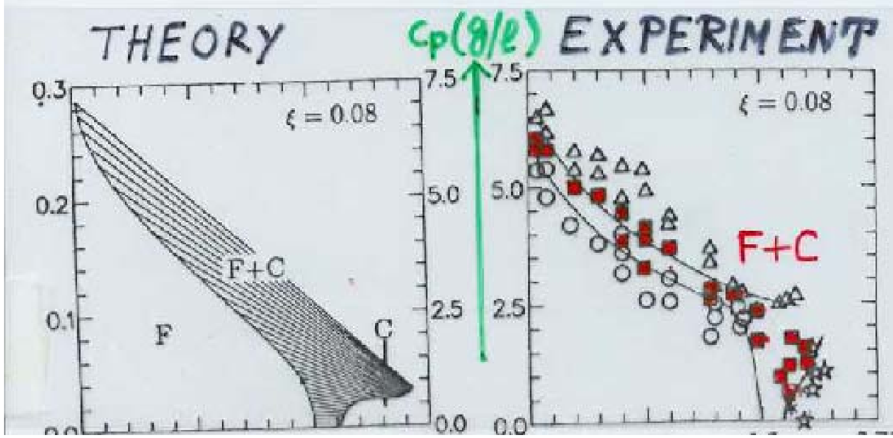
Illet, Orrock, Poon, Pusey

Phys. Rev. E 51, 1344 (1995)

PHASE BEHAVIO(U)R OF A MODEL COLLOID-POLYMER MIXTURE



size ratio $\xi = \frac{\sigma_p}{\sigma_c} = 0.08$



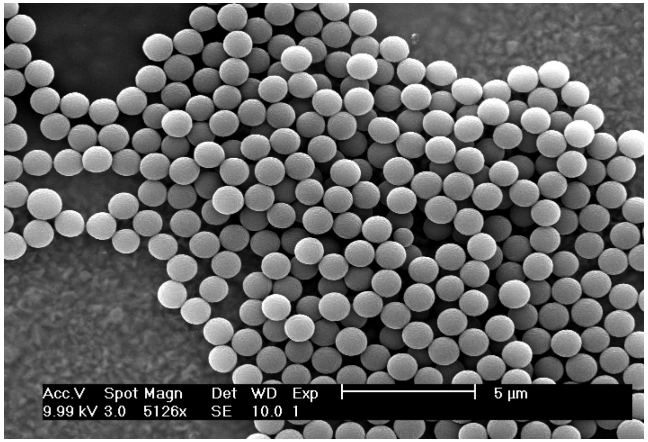
E.H.A. de Hoog, W.K. Kegel, A. van Blaaderen and HNWL

Direct observation of crystallization and aggregation in a phase-separating colloid-polymer suspension

Phys. Rev. E, 64 (2001) 021407-1

Colloid:

PMMA-latex
fluorescently labeled
sterically stabilised
R: 600 nm
polydispersity: 3%



Polymer:

poly(styrene)
R_g: 46 nm
M_w: 2000 kg/mol
M_w/M_n: 1.11
overlap conc.:
8.15 mg/ml

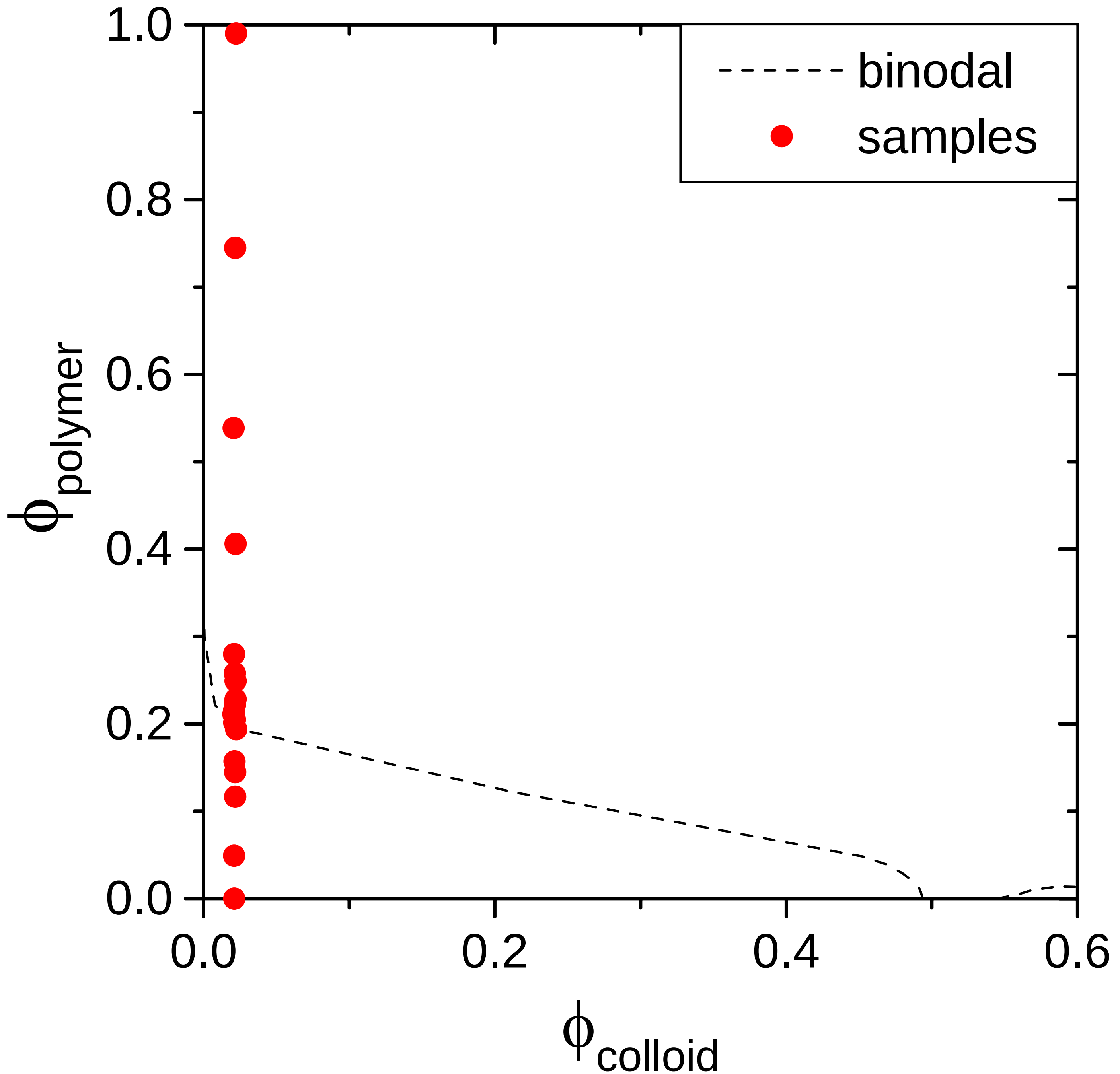
Solvent:

mixture of:

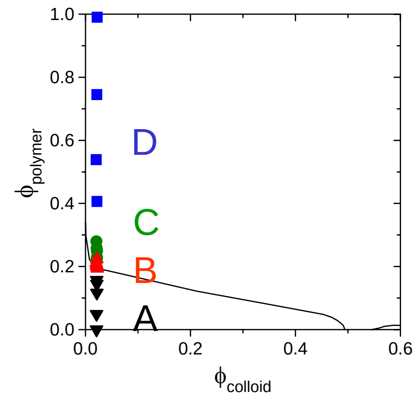
- tetralin
- cis-decalin
- carbon tetrachloride

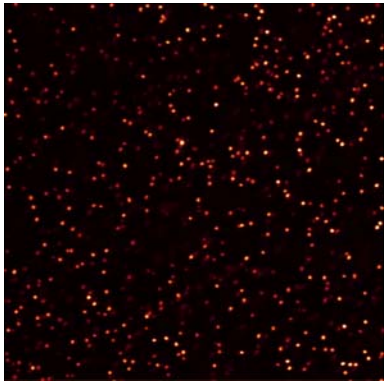
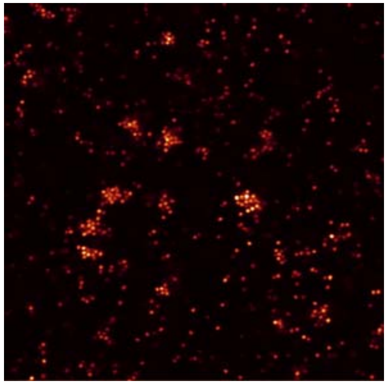
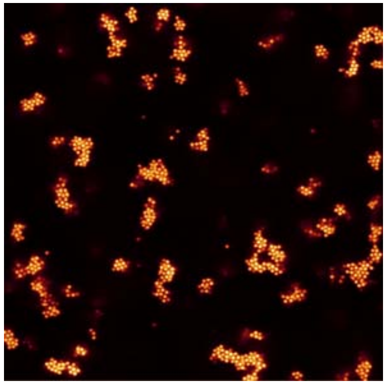
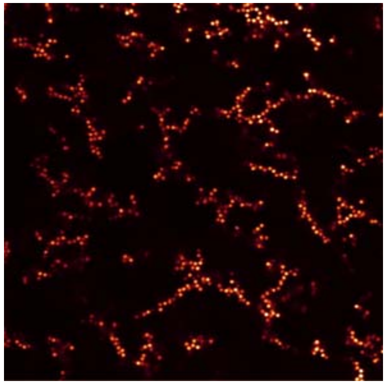
matches almost:

- density
- index of refraction

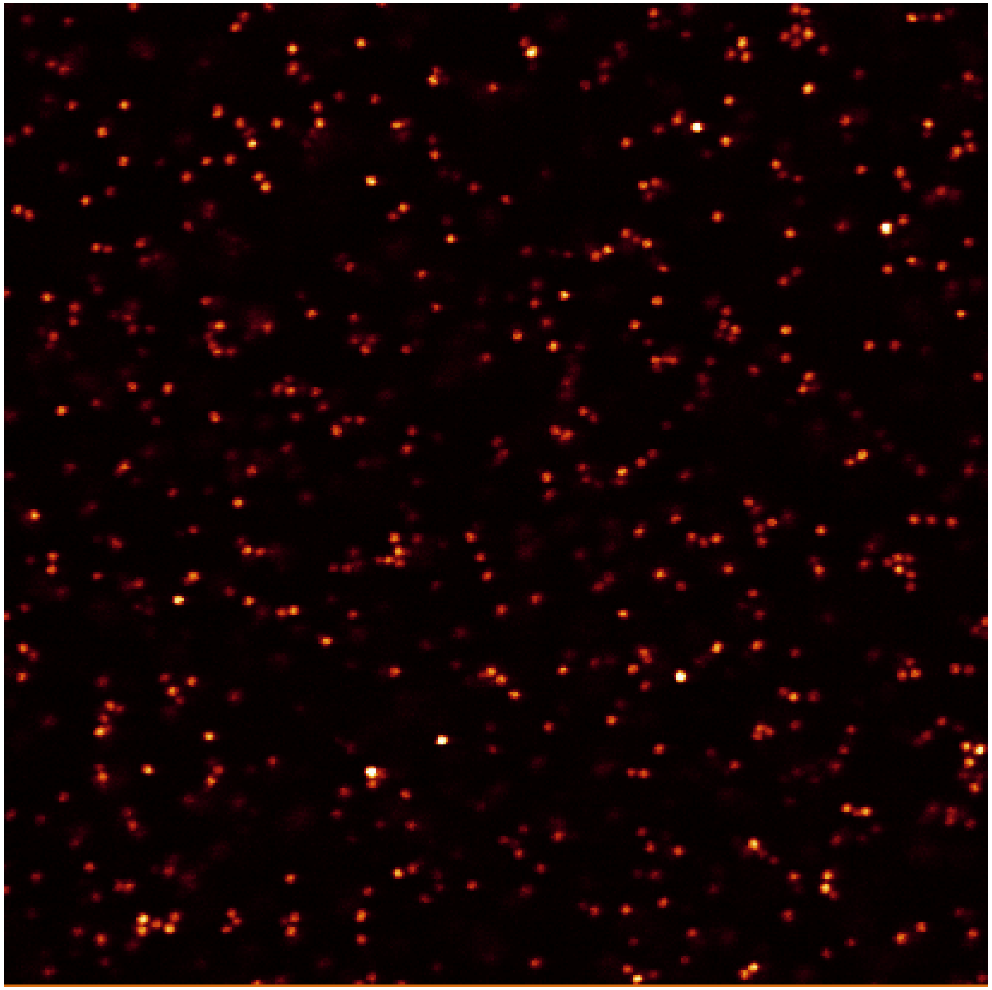


1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
binodal
samples
$\phi_{polymer}$
$\phi_{colloid}$



Regime A	Regime B	Regime C	Regime D
			
0 - 1.28 mg/ml	1.58 - 1.72 mg/ml	1.75 - 2.28 mg/ml	3.31 -9.04 mg/ml
• no phase separation • slow sedimentation	• nucleation-like mechanism • small degree of crystallinity	• aggregation leading to compact clusters • dense sediment	• aggregation leading to elongated clusters • dilute sediment

Regime B



t/τ_B=401

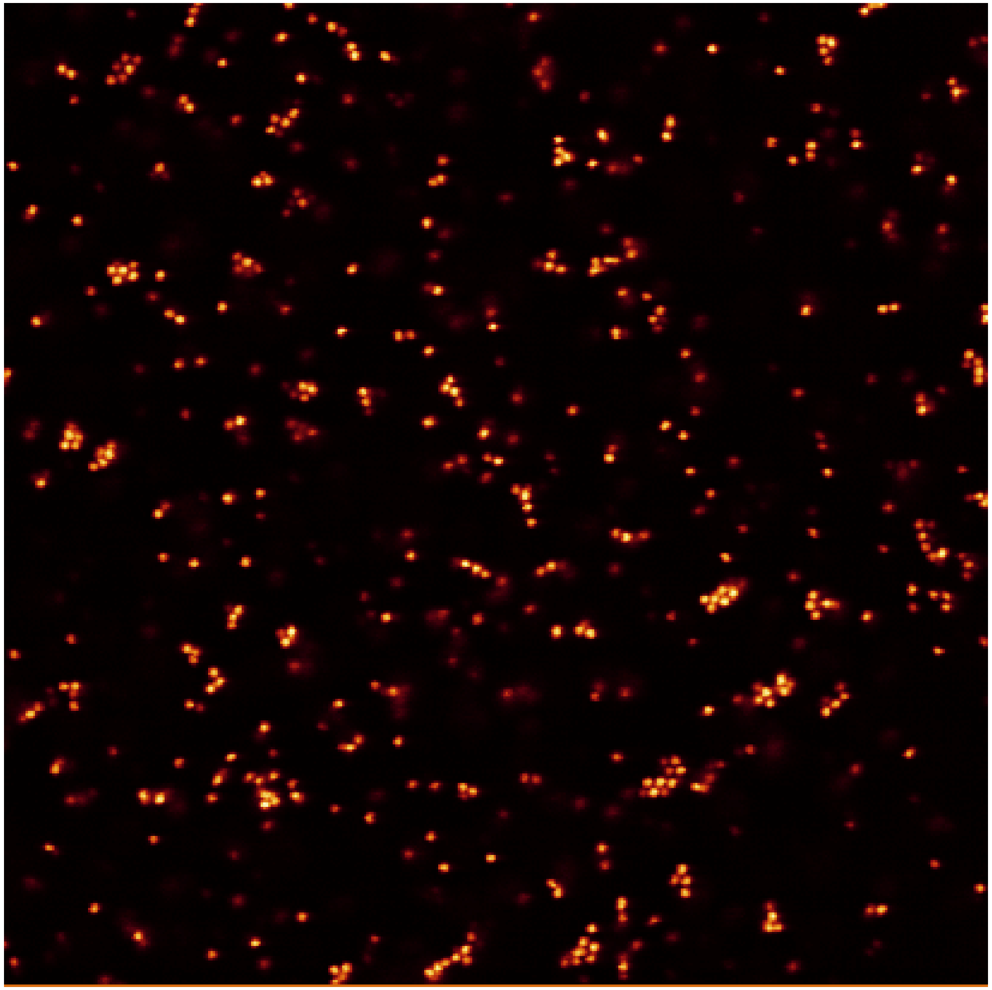
~ 18 min.

low
polymer concentration

↓

small
attraction

Regime C



t/τ_B=400

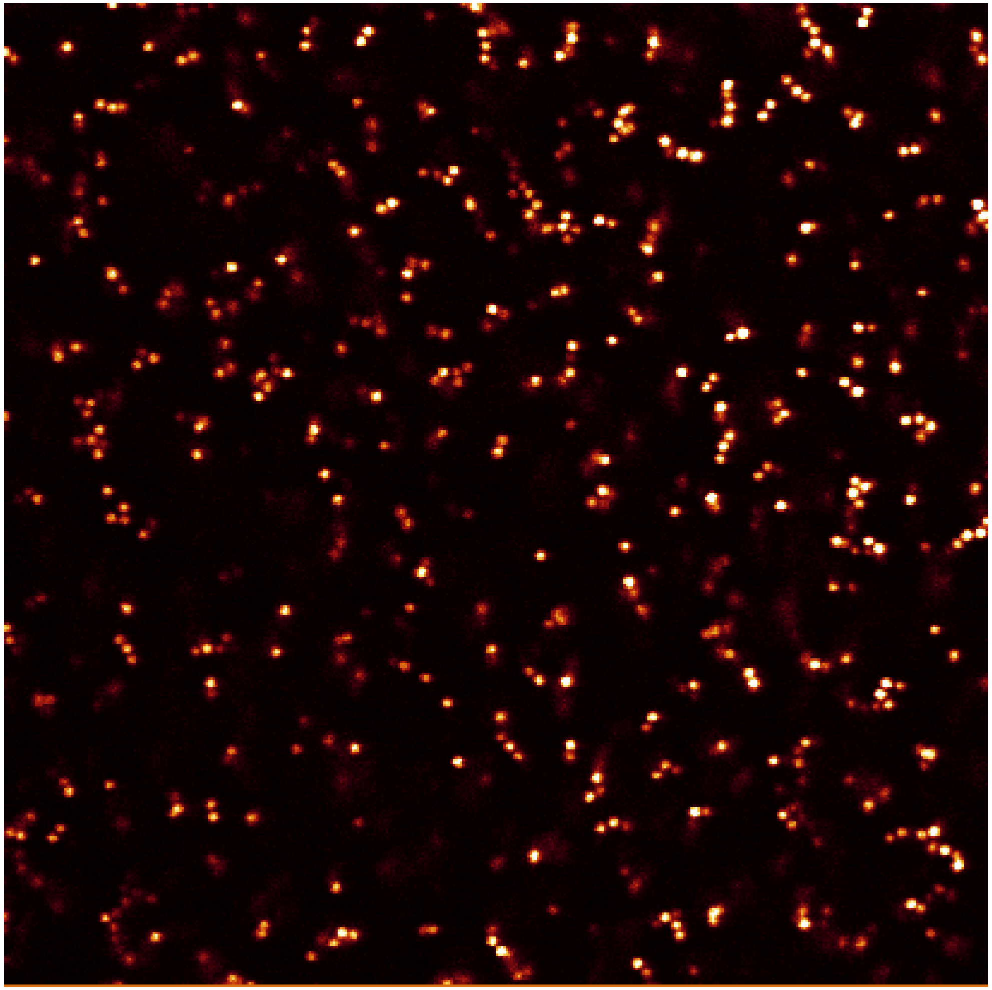
~ 20 min.

intermediate
polymer concentration

⬇

intermediate
attraction

Regime D



t/τ_B=398

~ 35 min.

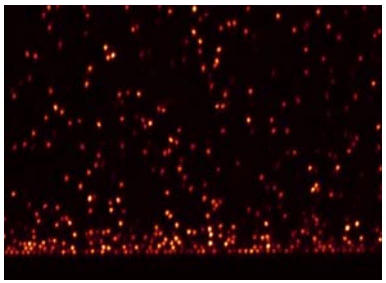
high
polymer concentration

↓

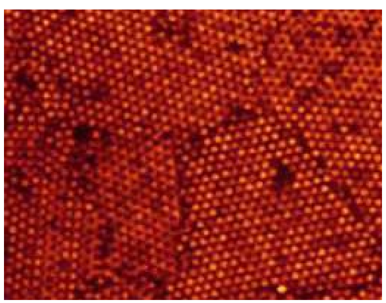
large
attraction

Final structures

Regime A



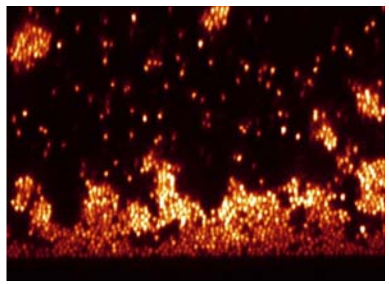
xz-scan; 0:27:45



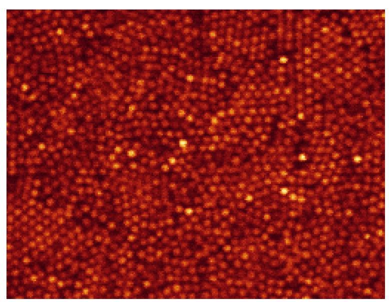
xy-scan; 1 week

- no phase separation
- slow sedimentation

Regime B



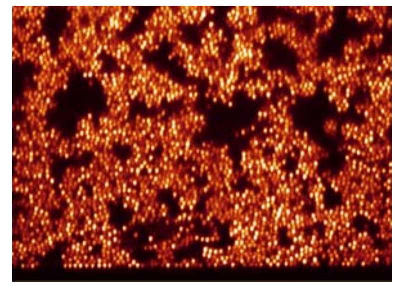
xz-scan; 0:40:51



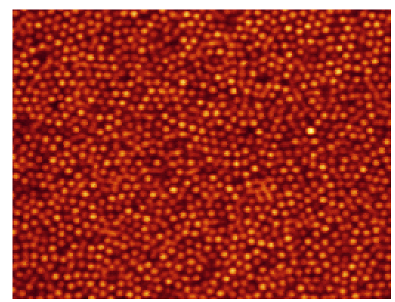
xy-scan; 2 days

- nucleation-like mechanism
- small degree of crystallinity

Regime C



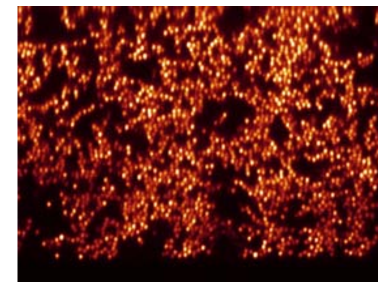
xz-scan; 0:42:25



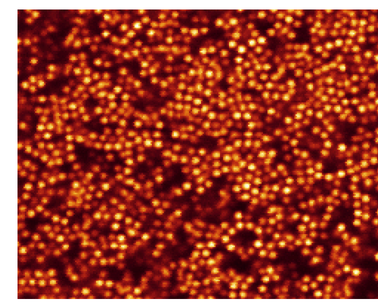
xy-scan; 3 days

- aggregation leading to compact clusters
- dense sediment

Regime D



xz-scan; 1:17:11



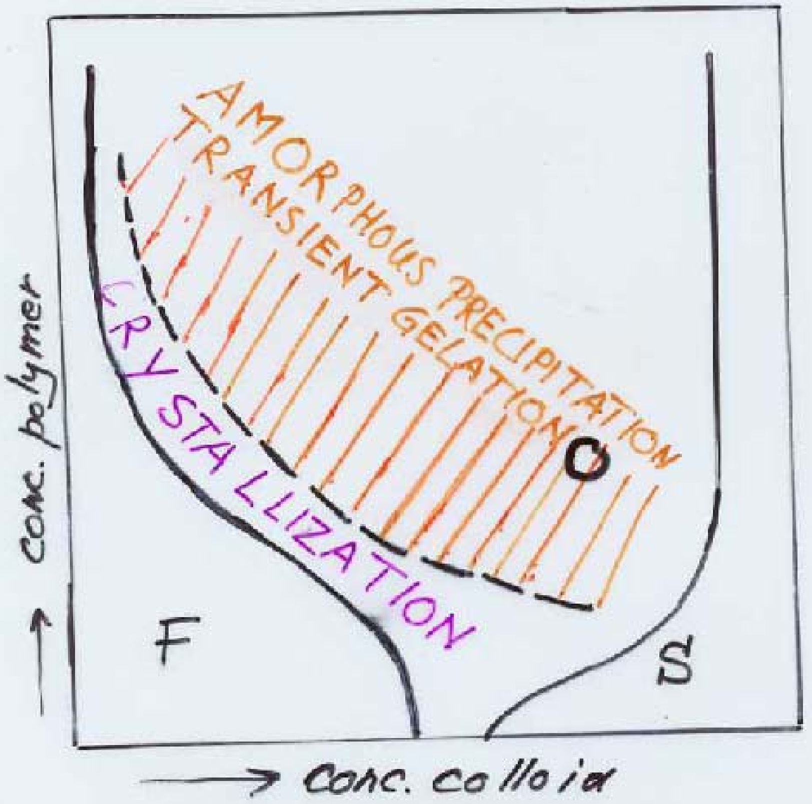
xy-scan; 3 days

- aggregation leading to elongated clusters
- dilute sediment

"MORPHOLOGY"

PHASE DIAGRAM COLLOID + POLYMER MIXTURE

"Small" Polymer : $\sigma_p / \sigma_c < \frac{1}{3}$



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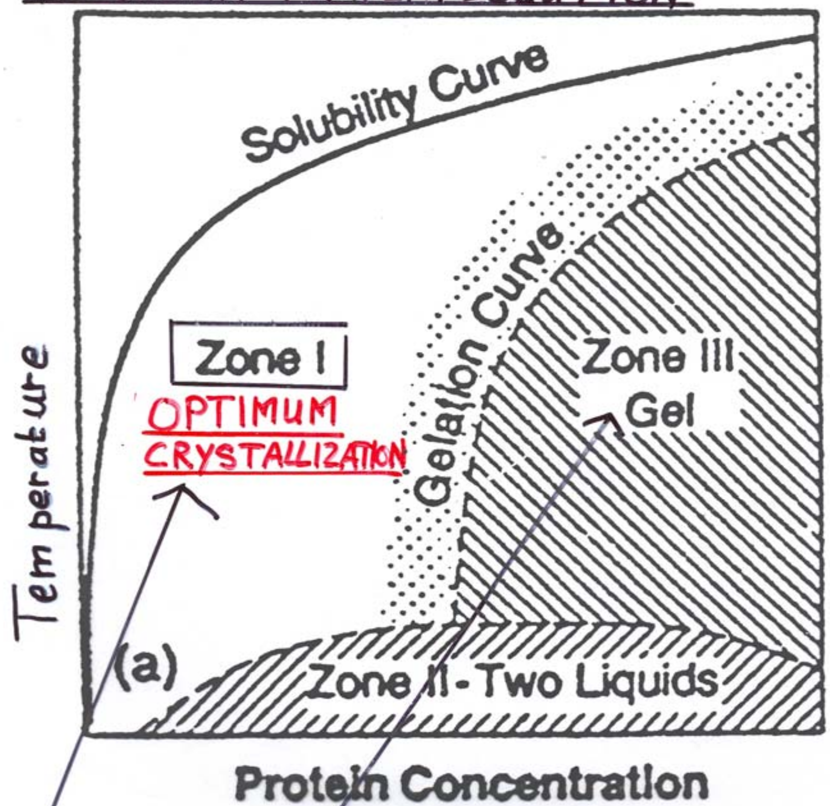
"MORPHOLOGY" PHASE DIAGRAM
GLOBULAR PROTEIN SOLUTION



Zone I Optimum Crystallization

CRAGGS | CRYSTALLIZING AGGREGATES

versus

PRAGGS | PRECIPITATING AGGREGATES

The end of lecture 4