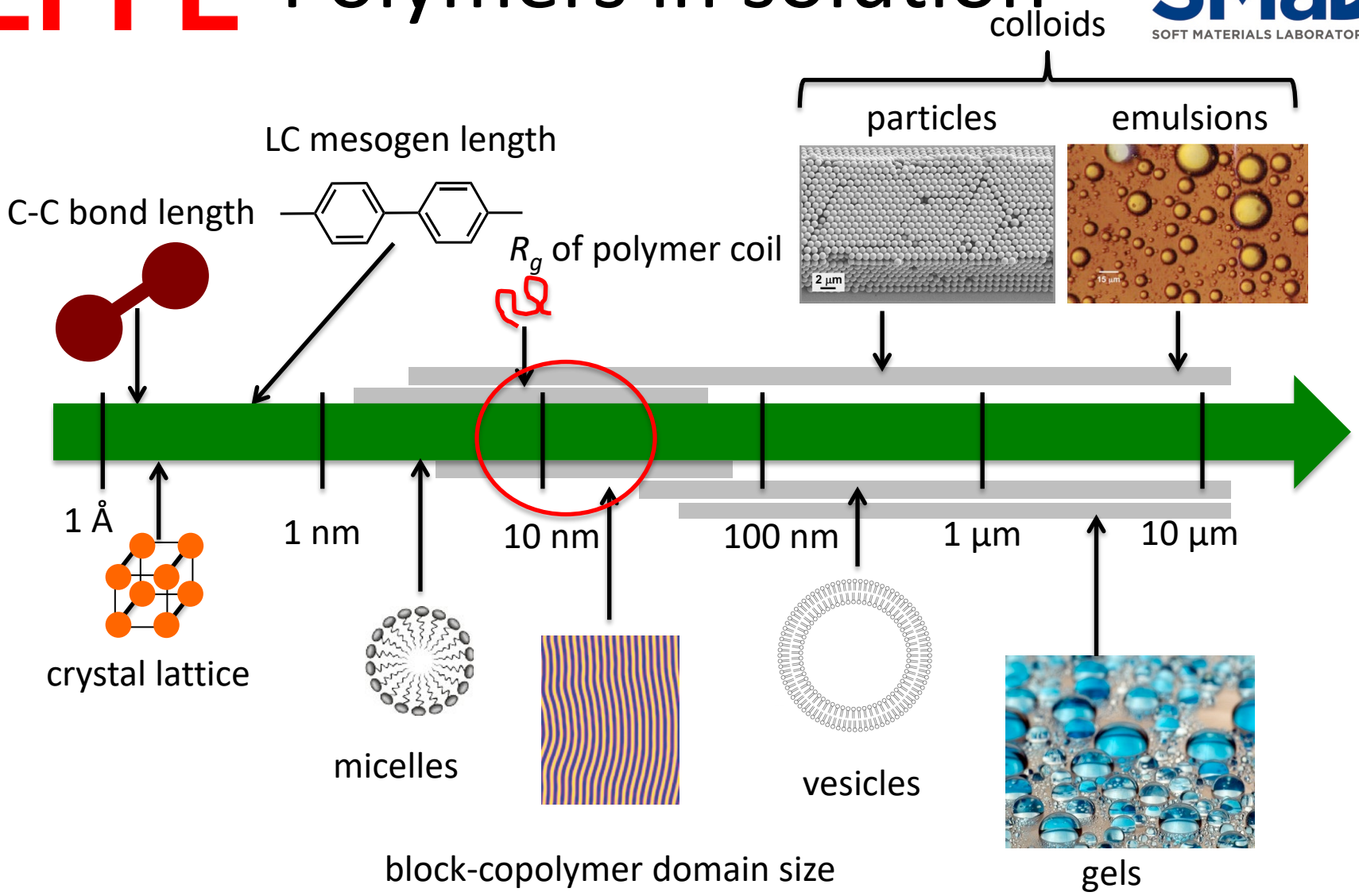
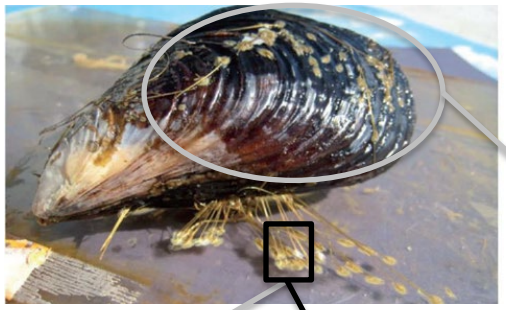
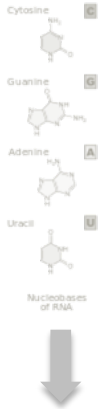
Polymers in solution

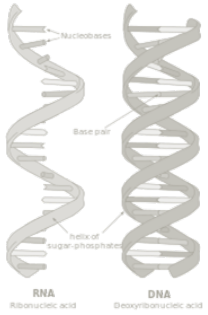


Course outline



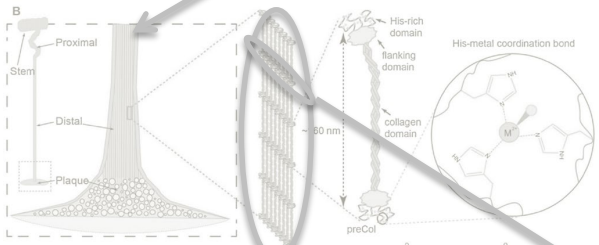
Introduction





Ordered materials

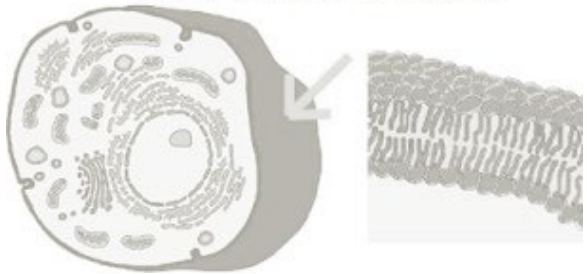
Thermotropic liquid crystals



E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

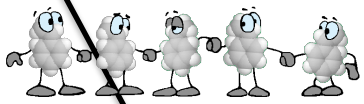
Lyotropic liquid crystals

Cell Membrane

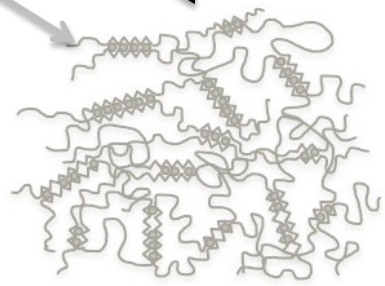


Disordered materials

Polymers

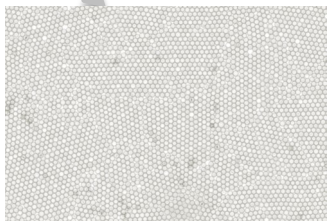


Gels



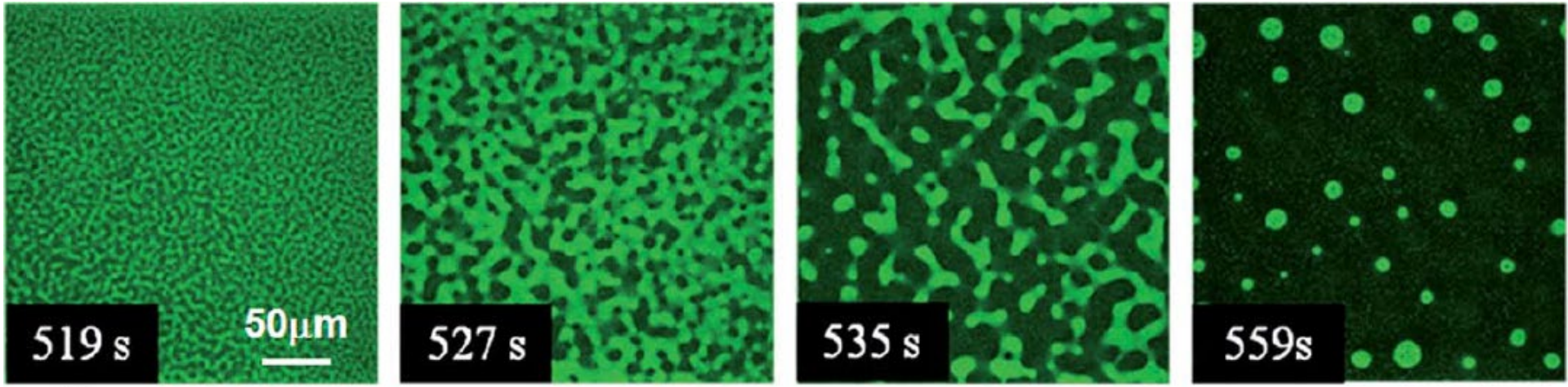
Colloids

Nanoparticles



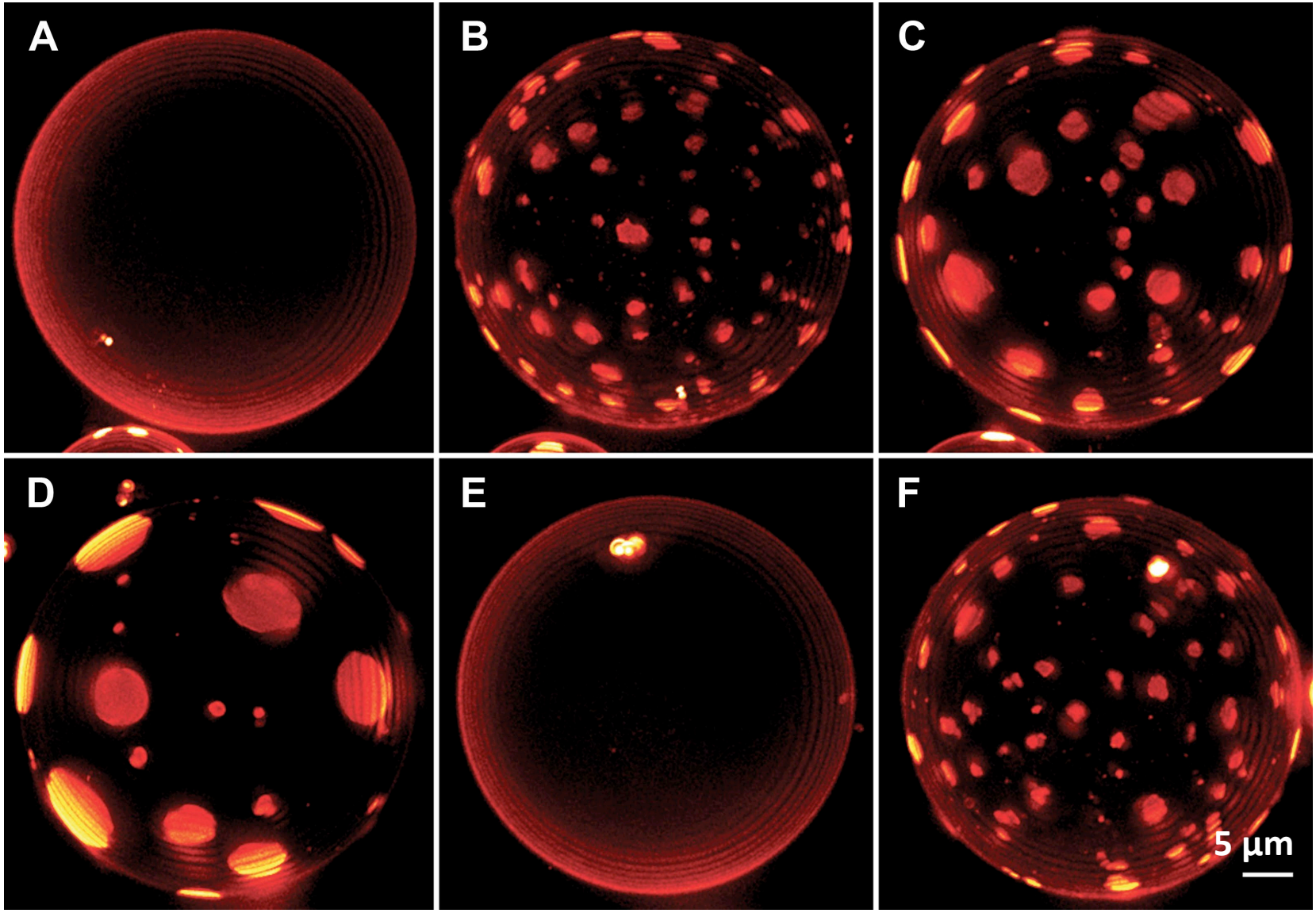
Emulsions

Phase separations of polymers



N. Kimura, K. Kawazoe, H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata, *Soft Matter*, 2013, **9**, 8428-8437

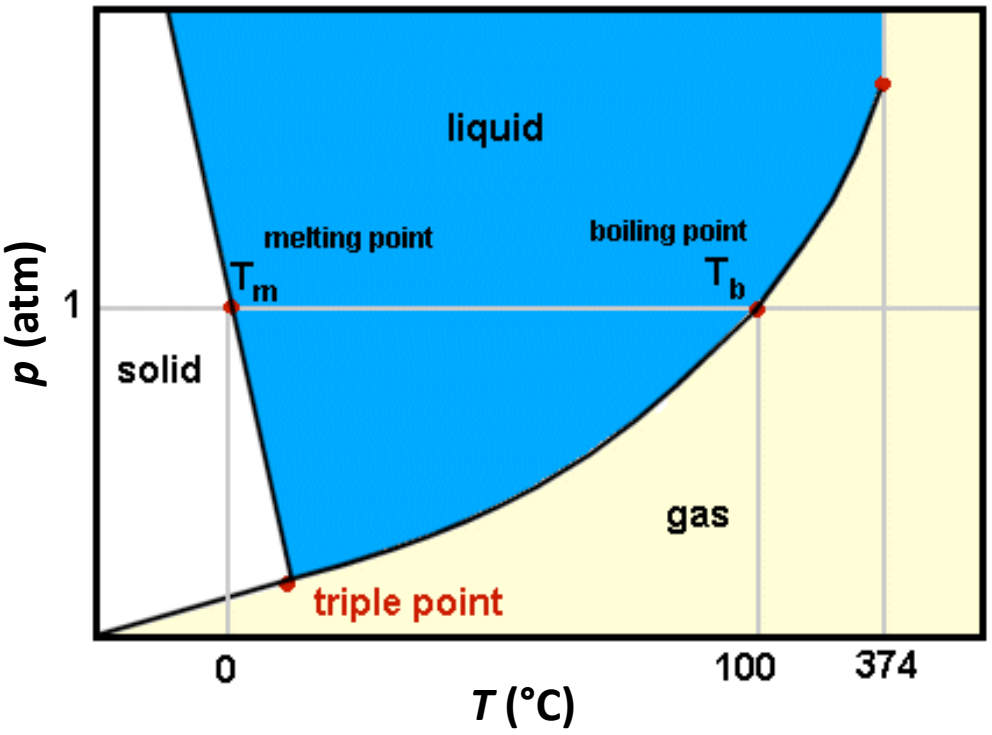
Phase separations in nature



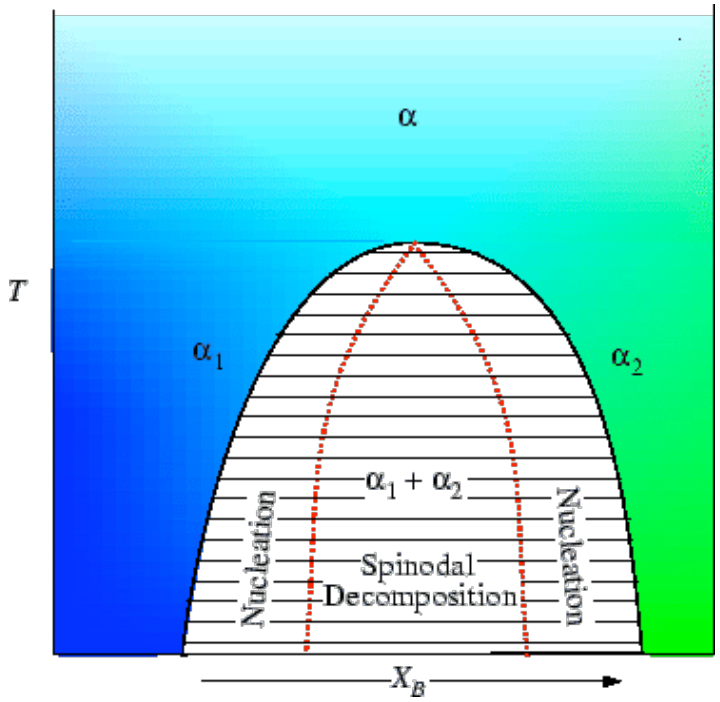
K. Oglęcka, P. Rangamani, B. Liedberg, R. S. Kraut and A. N. Parikh, *eLife*, 2014, **3**, e03695

Phase diagrams

one phase

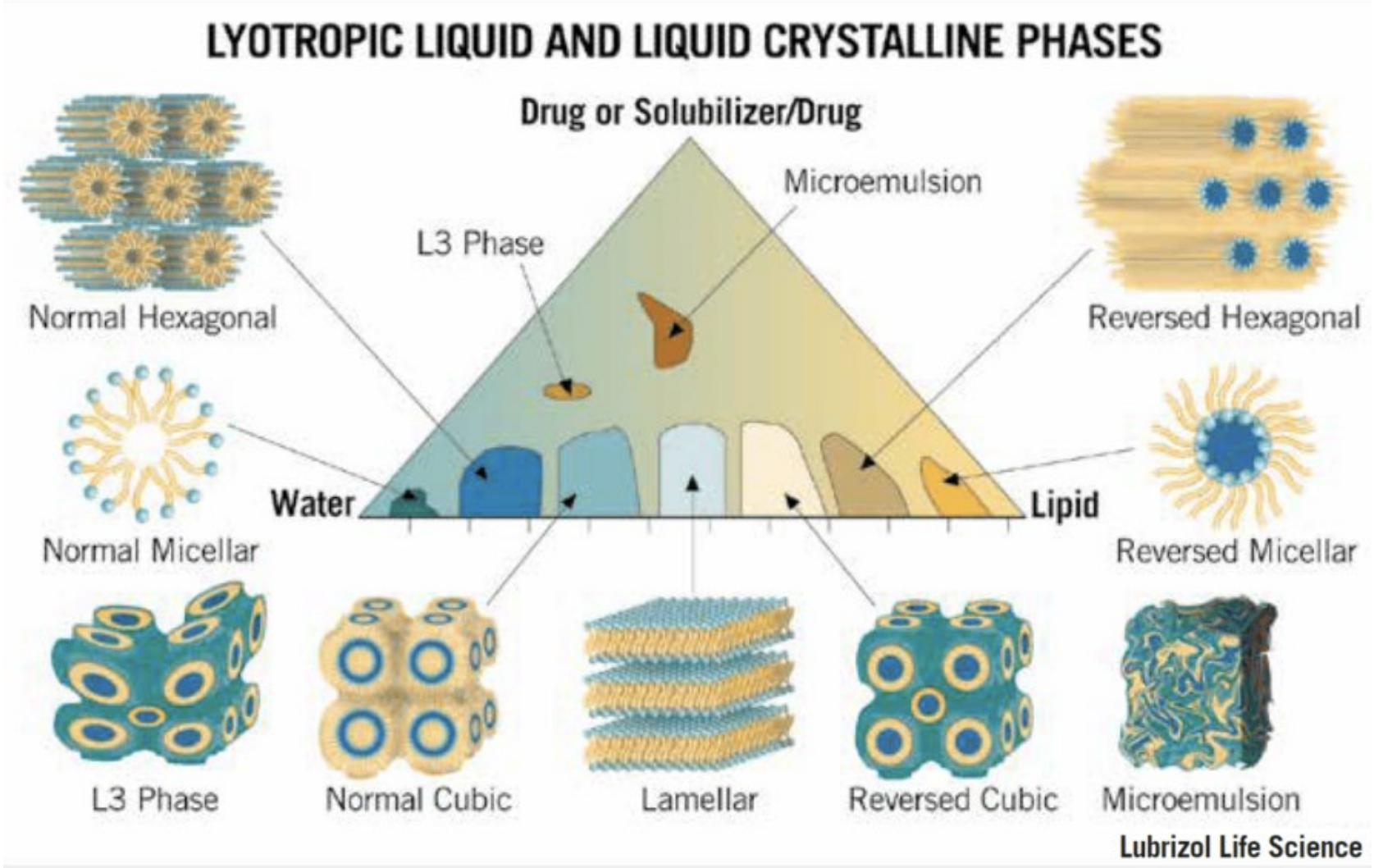


multiple phases



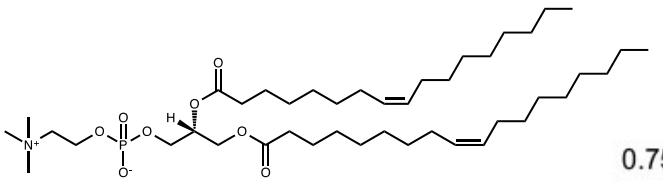
For more details: See “Polymer physical chemistry and materials properties”, taught by Eva Klok.

Phase separation in soft matter

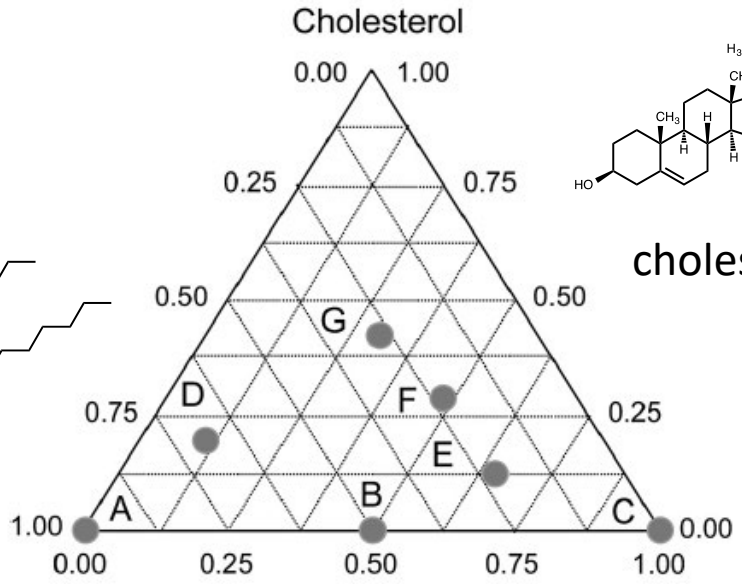


https://agnopharma.com/technical-briefs/cubic-phase-particles/

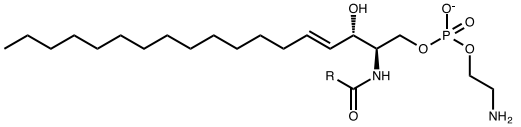
What drives phase separation?



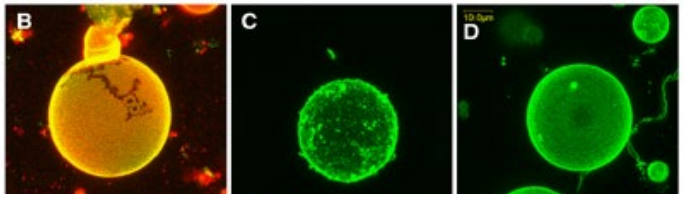
1,2 dioleoyl-sn-glycero-3-phosphocholine (DOPC)



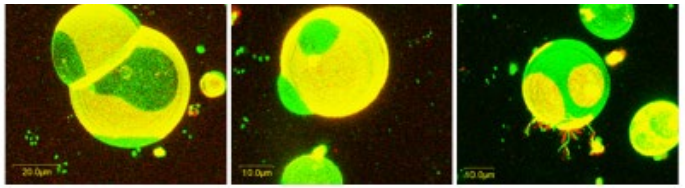
cholesterol



sphingomyelin (SM)



Gradients in the chemical potential, $\Delta\mu$



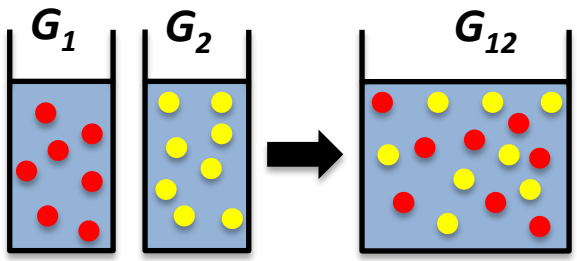
Ariola, F. S.; Li, Z.; Cornejo, C.; Bittman, R.; Heikal, A. A. *Biophysical Journal* **2009**, *96*, 2696

Miscibility of polymers

$$G = pV + \sum_{i=1}^{H_n} \mu_i N_i - TS$$

ΔG_m: molar Gibbs energy [J]
ΔH_m: molar enthalpy of mixing [J]
ΔS_m: molar entropy of mixing [J/K]

Mixing occurs if $\Delta G_m = G_{1,2} - (G_1 + G_2) \leq 0$



$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Ideal solution:

$$\Delta H_m = 0$$

Some small molecules show an ideal behavior where ΔH_m can be approximated to be zero.

Polymers do not display an ideal behavior.

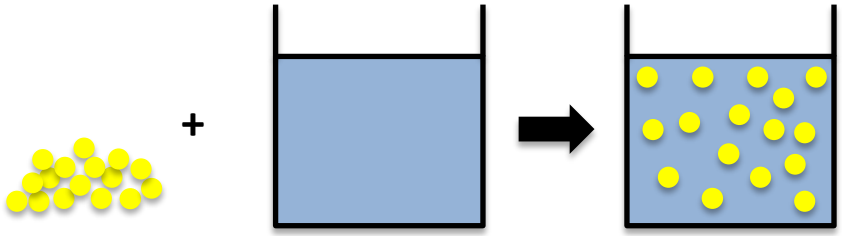
Change in Entropy

S: entropy [J/K]
p: probability that a certain state is taken [-]
Φ: volume fraction [-]

The configurational entropy:

$$S = -k_B \sum_i p_i \ln p_i$$

$$\Delta S_m = -k_B(\Phi_A \ln \Phi_A + \Phi_B \ln \Phi_B)$$



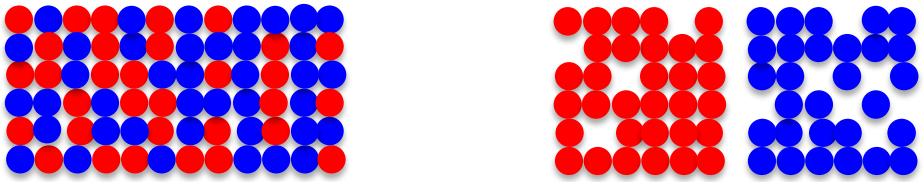
Assumption: The probability for the nearest neighbor of A to be A is equal to that of the nearest neighbor of A to be B.

Change in enthalpy

Assuming the mixing does not involve changes in the volume, we can write:

E_{xy}: bond energy between atom x and y [J]
Φ: fraction of sites occupied [-]
z: coordination number of the lattice [-]

$$\Delta H_m = \frac{z}{2}\overbrace{\left(\Phi_A^2 E_{AA} + \Phi_B^2 E_{BB} + 2\Phi_A\Phi_B E_{AB}\right)}^{H_{AB}} - \frac{z}{2}\overbrace{\left(\Phi_A E_{AA}\right)}^{H_A} + \overbrace{\left(\Phi_B E_{BB}\right)}^{H_B}$$



Change in enthalpy if two solutions are mixed

Assuming the mixing does not involve changes in the volume, we can write:

E_{xy}: contact energy (negative value) [J]
Φ: fraction of sites occupied [-]
z: coordination number of the lattice [-]
χ: Flory-Huggins interaction parameter [-]

$$\Delta H_m = \frac{z}{2}\left(\Phi_A^2 E_{AA} + \Phi_B^2 E_{BB} + 2\Phi_A\Phi_B E_{AB}\right) - \frac{z}{2}\left(\Phi_A E_{AA} + \Phi_B E_{BB}\right)$$

$$\Delta H_m = \frac{z}{2}\left((\Phi_A^2 - \Phi_A) E_{AA} + (\Phi_B^2 - \Phi_B) E_{BB} + 2\Phi_A\Phi_B E_{AB}\right)$$

assuming $\Phi_A + \Phi_B = 1$

$$\Delta H_m = \chi \Phi_A \Phi_B k_B T \quad \rightarrow \quad \chi = \frac{z}{2k_B T}\left(2E_{AB} - E_{AA} - E_{BB}\right)$$

$$\frac{\Delta G_{mix}}{k_B T} = \Phi_A \ln \Phi_A + \Phi_B \ln \Phi_B + \chi \Phi_A \Phi_B$$

But:

$$G = \overbrace{pV + \sum_{i=1}^{n} \mu_i N_i}^{H} - TS$$

➔ This equation is only valid if
$\Delta p = 0$
$\Delta V = 0$

Flory Huggins theory

$$\Delta G_m = k_B T\left(\overbrace{N_1 \ln \Phi_1 + N_2 \ln \Phi_2}^{\text{entropy}} + \overbrace{\chi N_1 \Phi_2}^{\text{enthalpy}}\right)$$

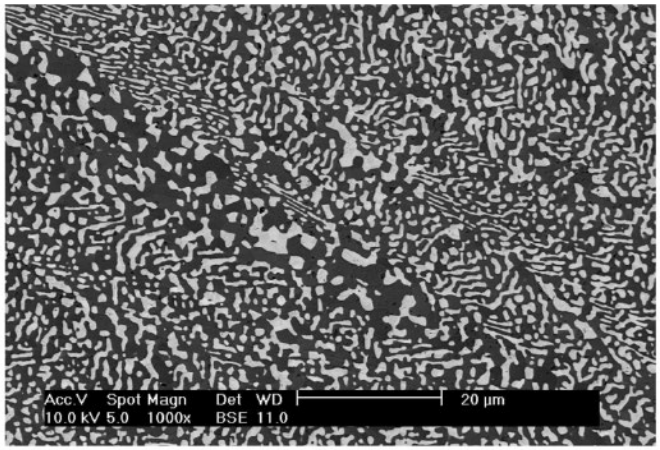
N: number of moles [-]
Φ: mole fraction [-]

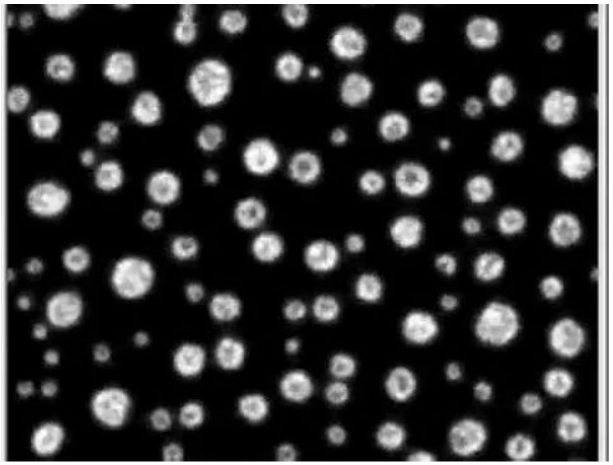
But this theory makes assumptions:

- The volume does not change upon mixing.
- The chain flexibility and specific solvent-polymer interactions have no contribution to the entropy. However, for solvent-polymer interactions to be random ΔE_{AB} must be zero such that χ must also be zero. Thus, theory is inconsistent.
- χ can also have an entropic contribution which is neglected here.

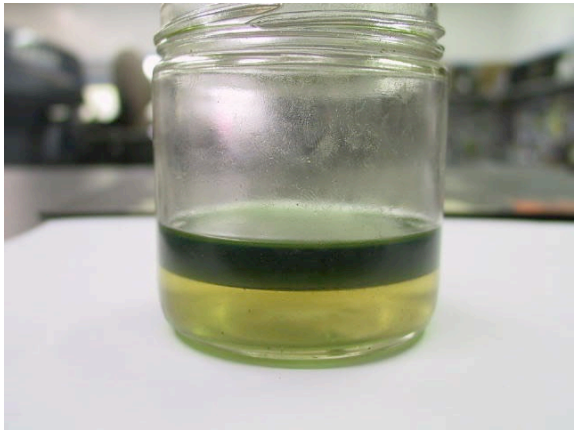
However, it is a good first approximation of the thermodynamics of many polymer mixtures.

Phase separation



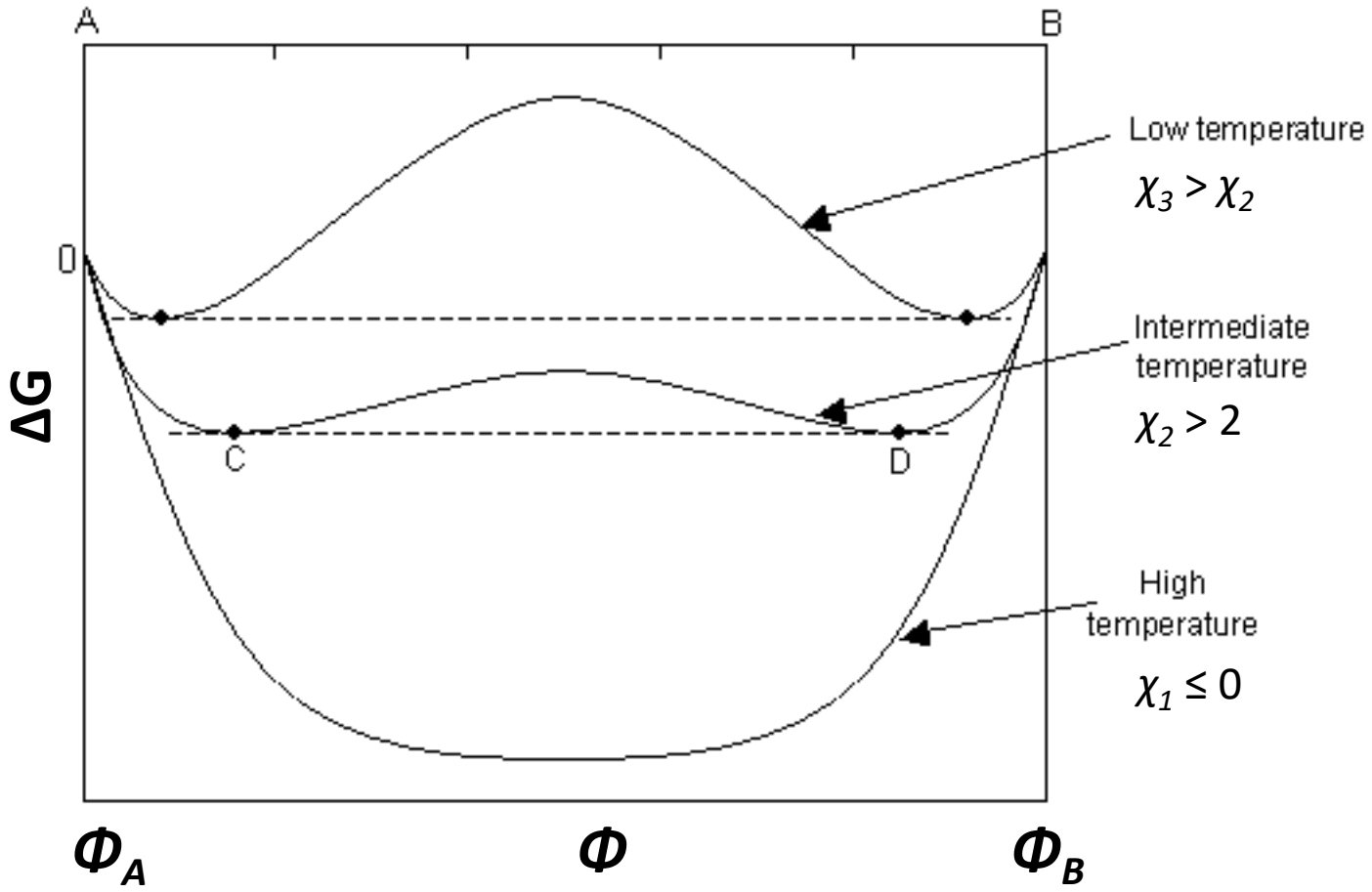


M. Sadiq, et al., *Journal of Electronic Materials* **42**, 492 (2013).



Phase diagram

$$\frac{\Delta G_{mix}}{k_B T} = \Phi_A \ln \Phi_A + \Phi_B \ln \Phi_B + \chi \Phi_A \Phi_B$$



http://www.doitpoms.ac.uk/tlplib/solid-solutions/printall.php

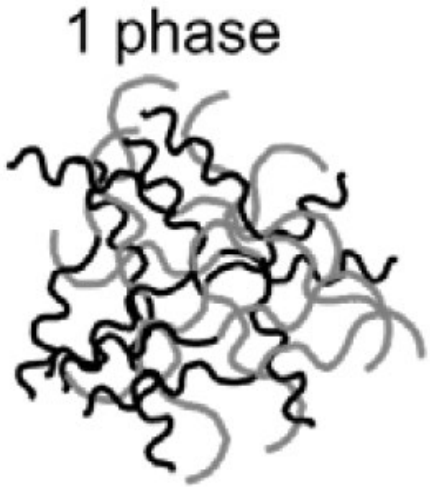
How does a phase diagram for polymer solutions look like?

A. Identical to the phase diagram for two fluids
B. Phase diagrams for polymer solutions do not exist
C. The spinodal and binodal lines can be asymmetric
D. It only contains a binodal and no spinodal line.

When does phase separation occur?

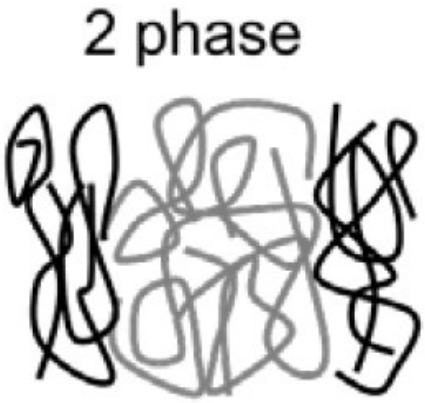
For polymers:

$\chi < \chi_c$



homogeneous mixture

$\chi > \chi_c$

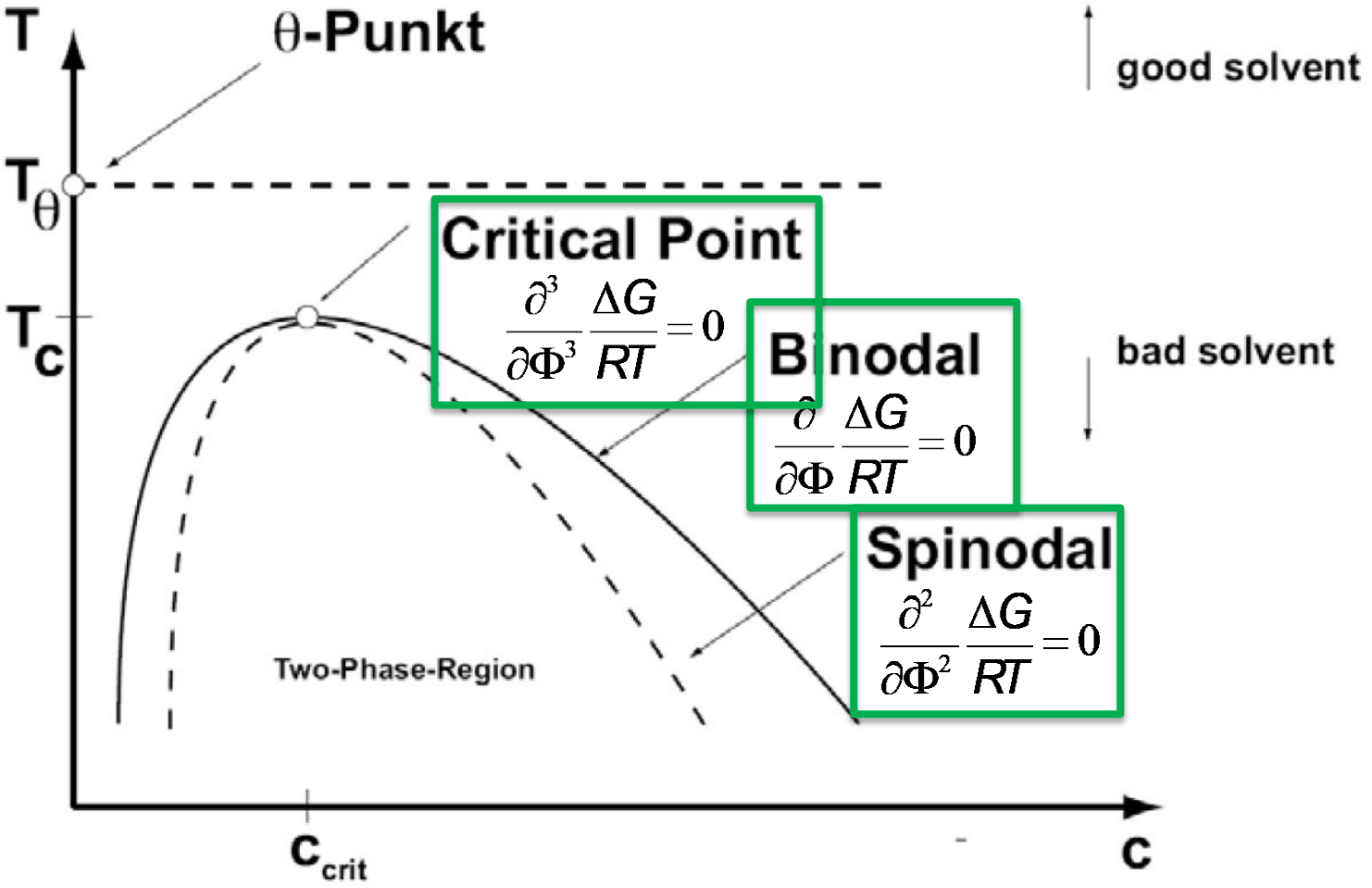


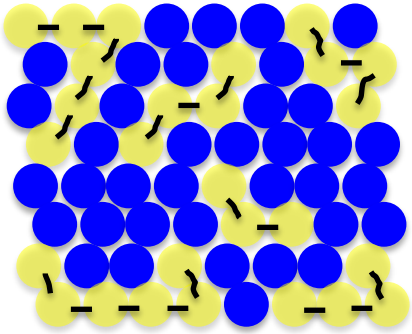
phase separation

What is χ_c?

Lee, W. H.; Park, Y. D. *Polymers* **2014,** *6* (4), 1057-1073.

Phase diagram of a binary mixture containing at least one polymer





Polymer solutions

$$\frac{\Delta G}{RT} = (1-\Phi)\ln(1-\Phi) + \frac{\Phi}{N}\ln\Phi + \chi\Phi(1-\Phi)$$

with $R = k_B N_A$

$$\frac{\partial}{\partial\Phi}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial}{\partial\Phi}\frac{\Delta G}{RT} = -\ln(1-\Phi) - 1 + \frac{\ln\Phi}{N} + \frac{1}{N} + \chi - 2\chi\Phi = 0$$

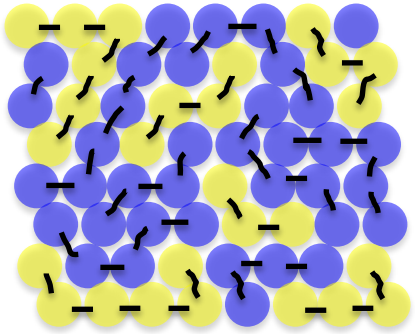
$$\frac{\partial^2}{\partial\Phi^2}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial^2}{\partial\Phi^2}\frac{\Delta G}{RT} = \frac{1}{1-\Phi} + \frac{1}{N\Phi} - 2\chi = 0$$

$$\frac{\partial^3}{\partial\Phi^3}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial^3}{\partial\Phi^3}\frac{\Delta G}{RT} = \frac{1}{(1-\Phi)^2} - \frac{1}{N\Phi^2} = 0$$

➔ $\Phi_c = \frac{1}{1+\sqrt{N}}$ for large N: $\Phi_c \approx \frac{1}{\sqrt{N}}$

➔ $\chi_c \approx \frac{1}{2} + \frac{1}{2\sqrt{N}}$

R: gas constant [J mol^{-1} K^{-1}]
k_B: Boltzmann constant [J molecule^{-1} K^{-1}]
N_A: Avogadro constant [molecules/mol]
N: degree of polymerization [-]



Polymer blends

$$\frac{\Delta G}{RT} = \frac{(1-\Phi)}{N_1}\ln(1-\Phi) + \frac{\Phi}{N_2}\ln\Phi + \chi\Phi(1-\Phi)$$

$$\frac{\partial}{\partial\Phi}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial}{\partial\Phi}\frac{\Delta G}{RT} = -\frac{\ln(1-\Phi)}{N_1} - \frac{1}{N_1} + \frac{\ln\Phi}{N_2} + \frac{1}{N_2} + \chi - 2\chi\Phi = 0$$

$$\frac{\partial^2}{\partial\Phi^2}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial^2}{\partial\Phi^2}\frac{\Delta G}{RT} = \frac{1}{(1-\Phi)N_1} + \frac{1}{N_2\Phi} - 2\chi = 0$$

$$\frac{\partial^3}{\partial\Phi^3}\frac{\Delta G}{RT} = 0 \qquad \frac{\partial^3}{\partial\Phi^3}\frac{\Delta G}{RT} = \frac{1}{(1-\Phi)^2 N_1} - \frac{1}{N_2\Phi^2} = 0$$

➔ $$\Phi_c = \frac{1}{1+\sqrt{\frac{N_2}{N_1}}}$$

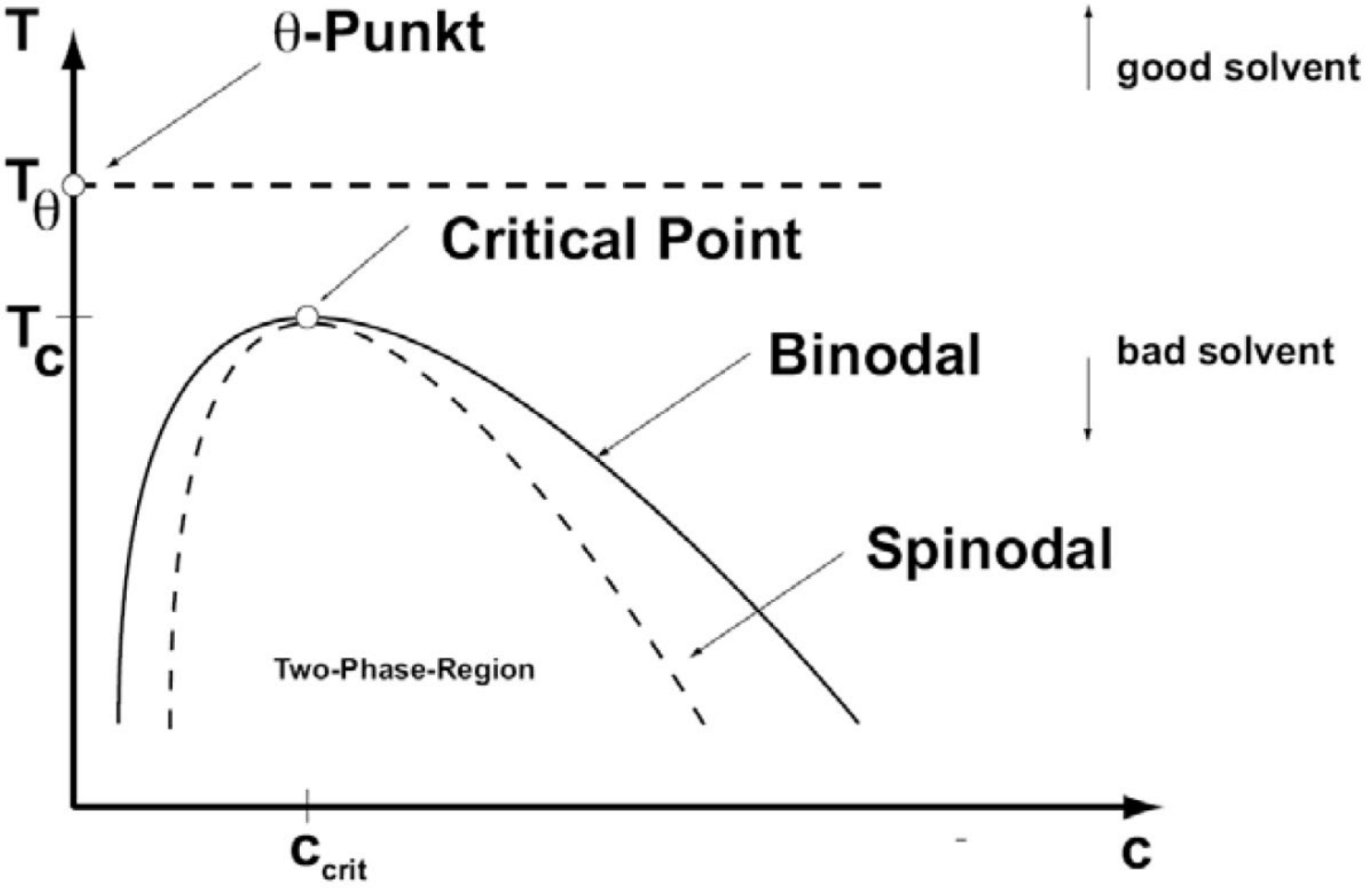
➔ $$\chi_c = \frac{1}{2N_2}\left(1+\sqrt{\frac{N_2}{N_1}}\right)^2$$

special case:

If the degree of polymerization is the same for both polymers: $N_1 = N_2 = N$

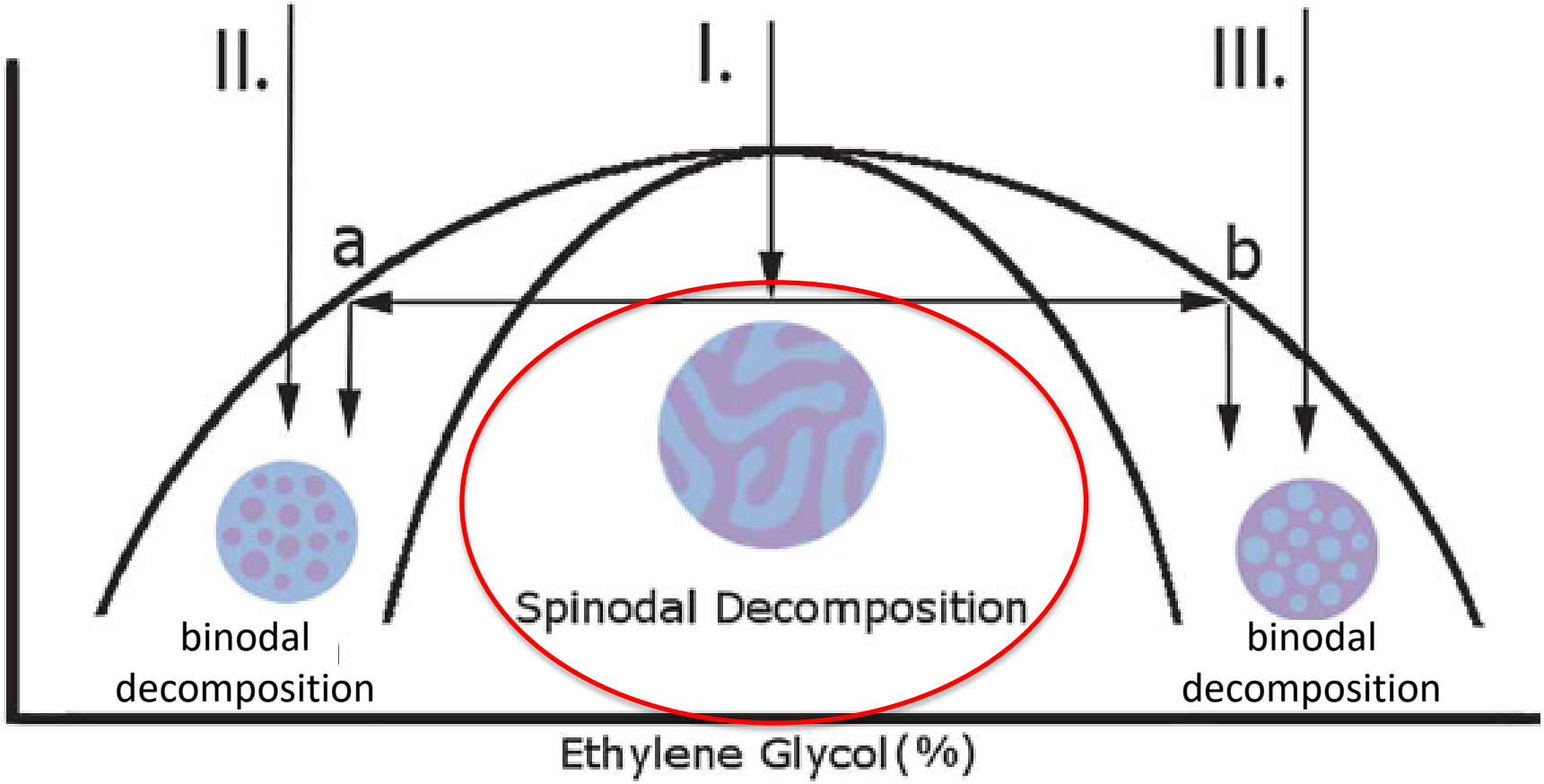
$$\chi_c = \frac{2}{N}$$

Phase diagram of a binary mixture containing at least one polymer



Phase separation

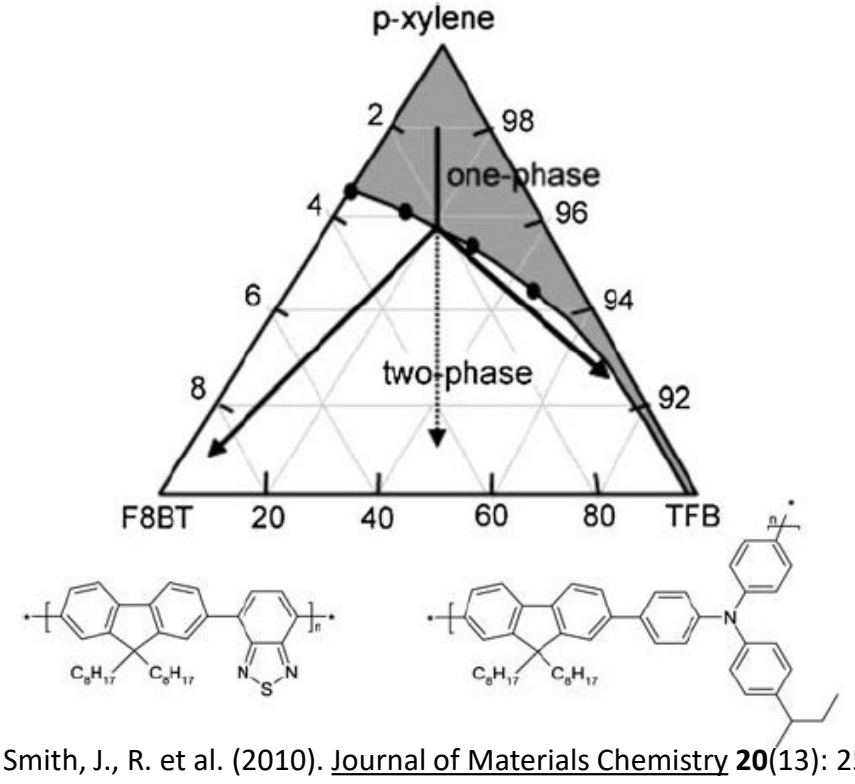
Example: mixture of nitromethane and ethylene glycol

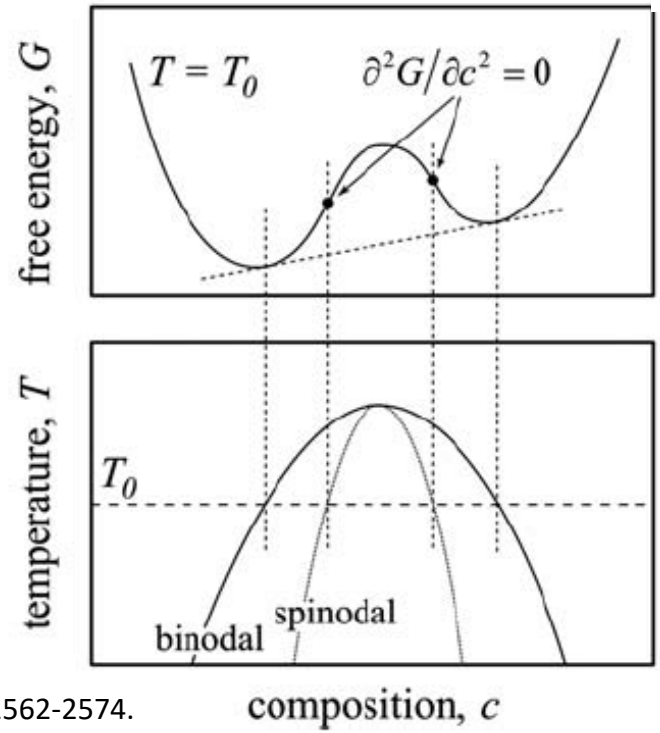


Witt, J. A.; Mumm, D. R.; Mohraz, A. *Soft Matter* **2013**, *9*, 6773.

Spinodal decomposition

spinodal decomposition





Smith, J., R. et al. (2010). Journal of Materials Chemistry **20**(13): 2562-2574.

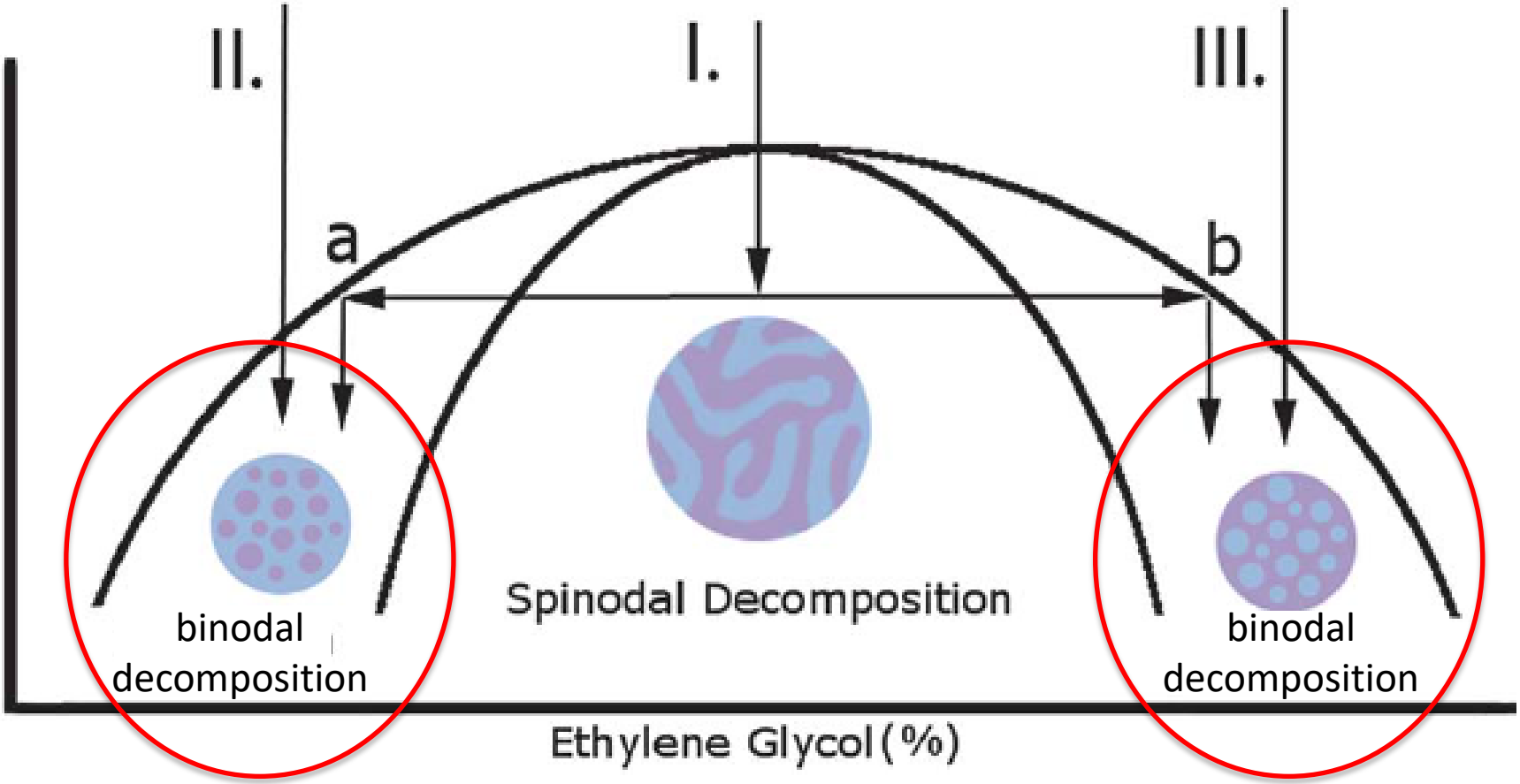
Small fluctuations in temperature or concentrations lead to a spontaneous phase separation.

Solutes diffuse from low solute concentrations to regions with higher solute concentrations. Hence, they diffuse against the concentration gradient.

https://www.youtube.com/watch?v=RlKCladAxlo

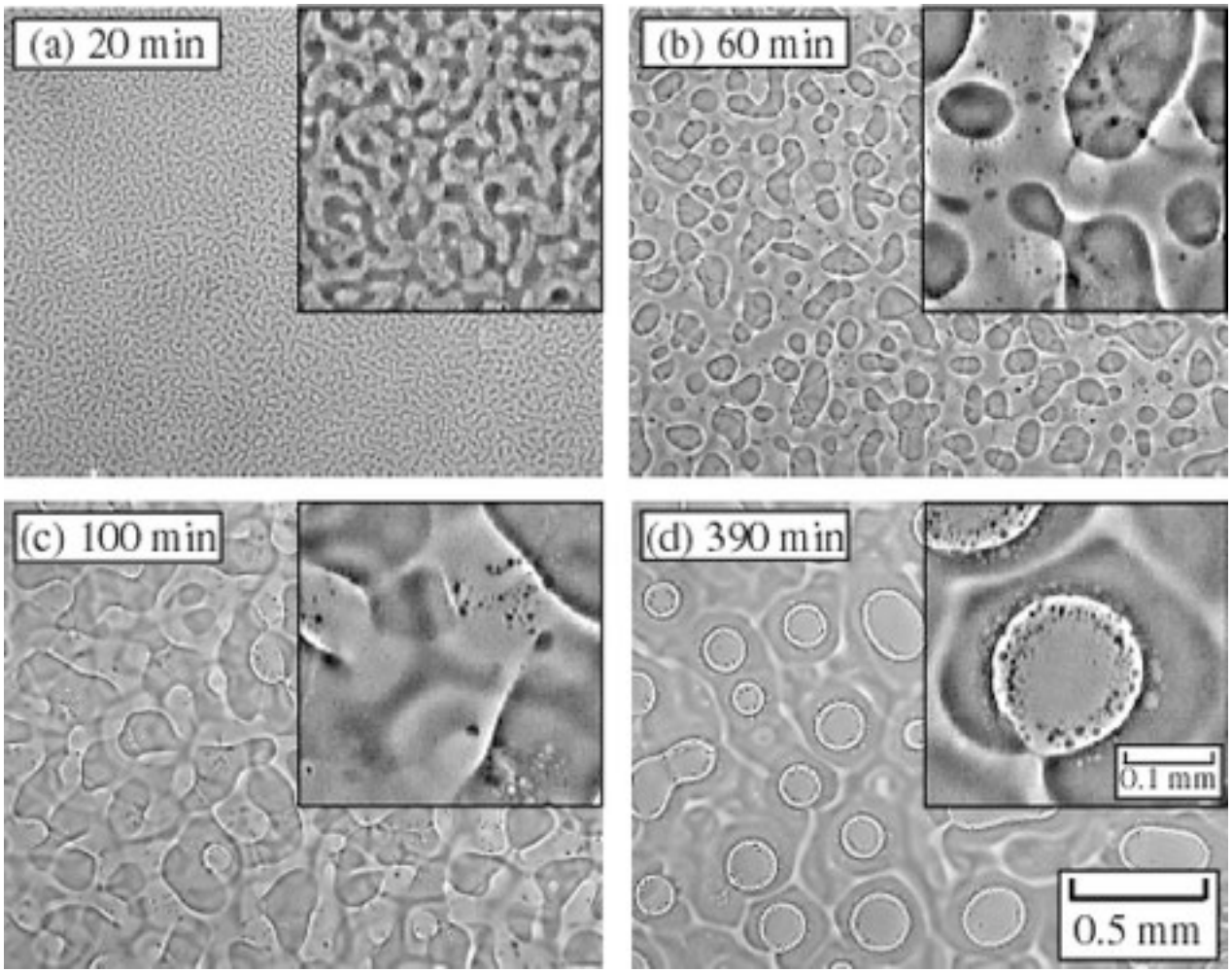
Phase separation

Example: a mixture of nitromethane and ethylene glycol



Witt, J. A.; Mumm, D. R.; Mohraz, A. *Soft Matter* **2013**, *9*, 6773.

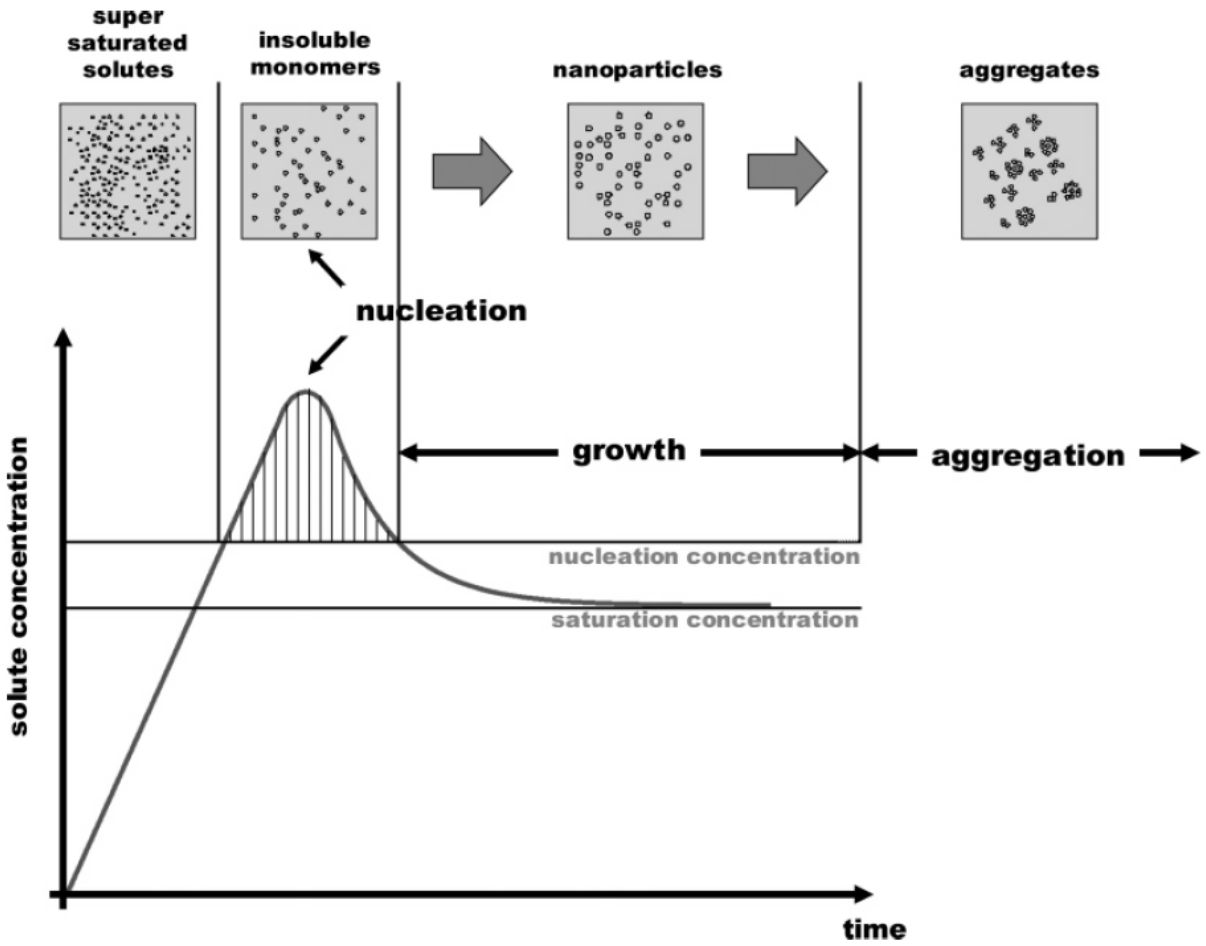
Phase separated polymers



T. Nambu, Y. Yamauchi, T. Kushiro, S. Sakurai, *Faraday Discussions* **128**, 285 (2005)

Binodal decomposition

The system is in a metastable state: It phase separates if the energy barrier is overcome. In this case, phase separation occurs through nucleation and growth.



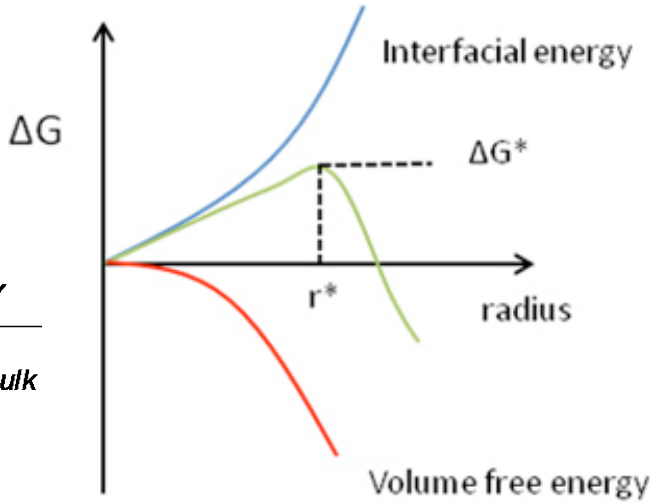
deMello, A. J. *Lab on a Chip* **2004**, *4*, 11N.

Nucleation and growth

Nucleation:

$$\Delta G = \frac{4}{3}\Pi r^3 \Delta G_{bulk} + 4\Pi r^2 \gamma$$

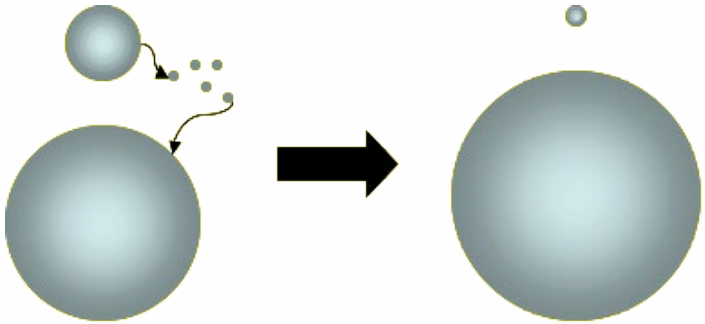
Nucleation occurs if $\Delta G \leq 0$ ➔ $r_{crit} = \frac{2\gamma}{\Delta G_{bulk}}$



http://2011.igem.org/Team:KULeuven/Thermodynamics

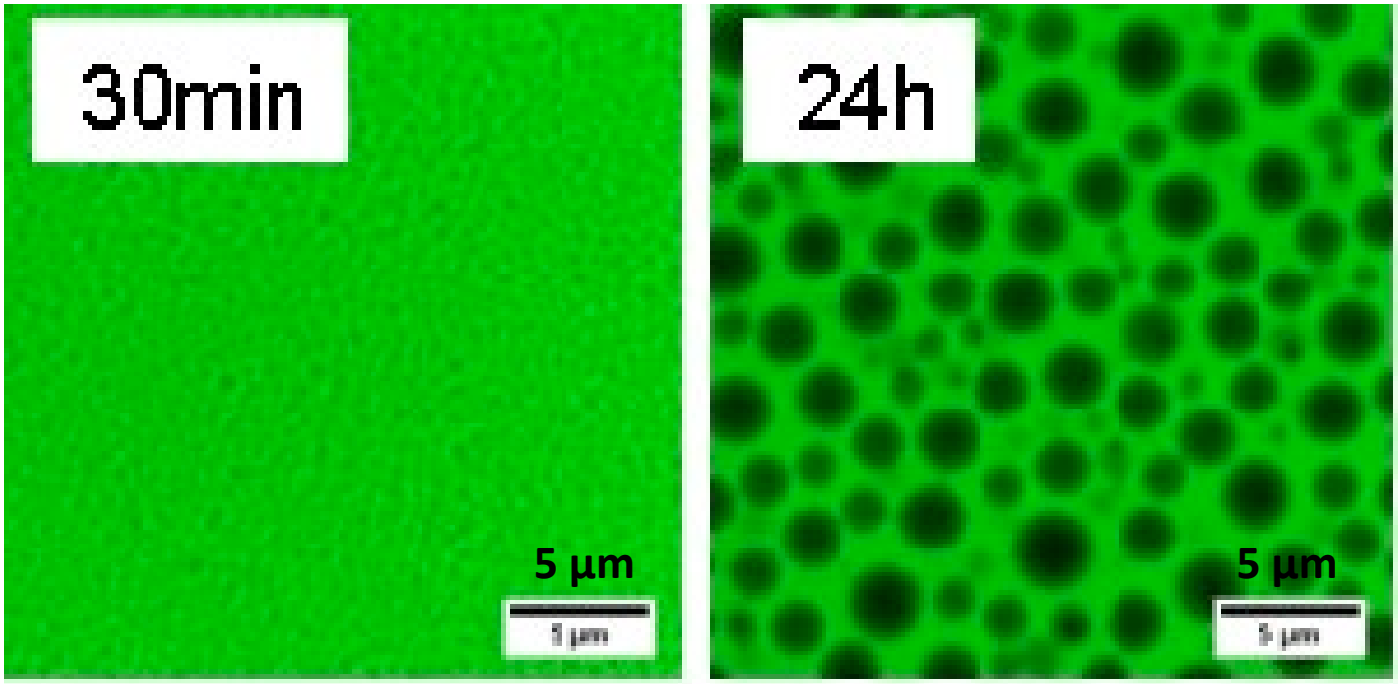
Growth:

One frequently occurring mechanism for growth is Ostwald ripening: The larger particles grow on the expense of the smaller ones.



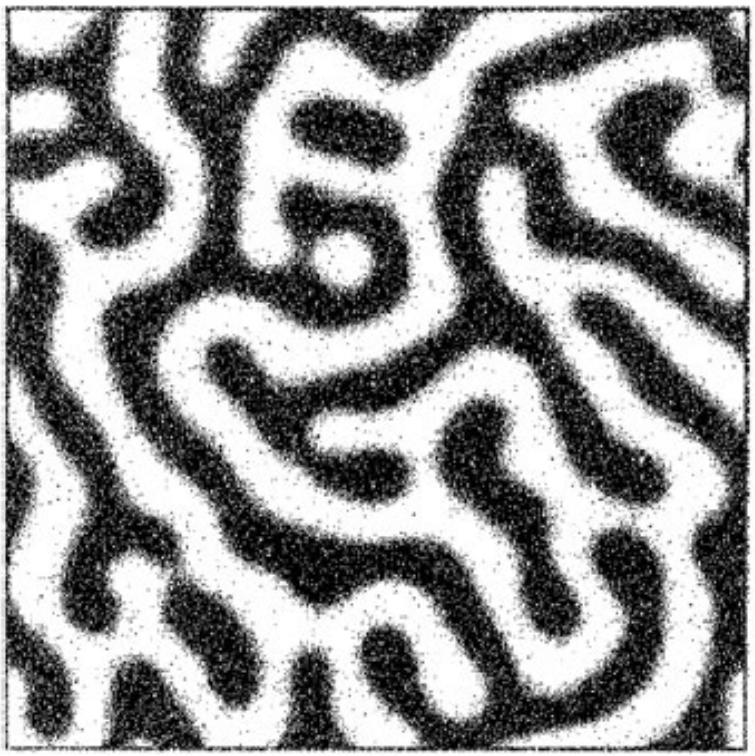
https://www.youtube.com/watch?v=IWJreldRjfs

Phase separation

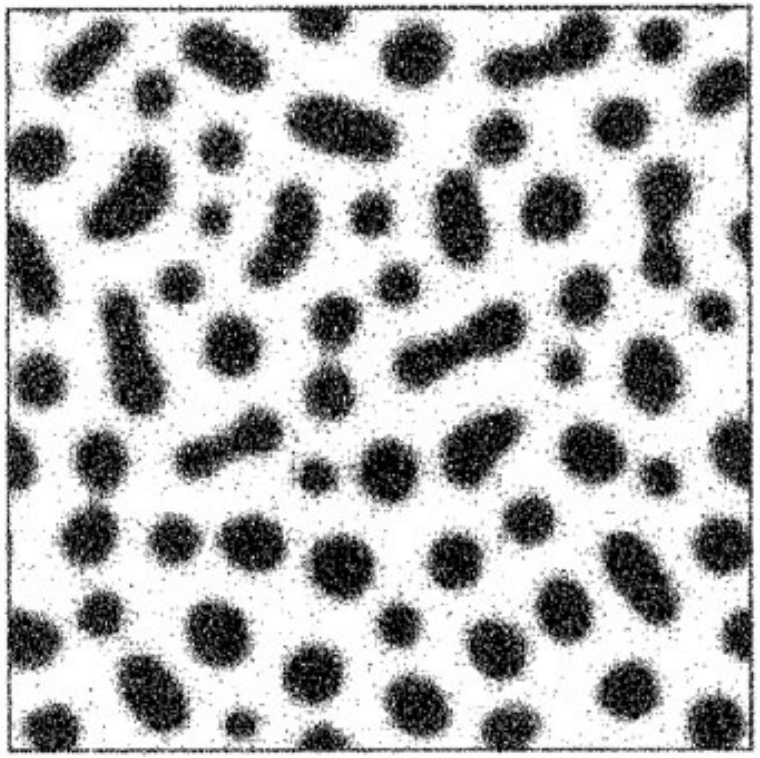


http://www2.mpip-mainz.mpg.de/~koynov/koynov/methods/clsm.html

Why do we care?



spinodal decomposition

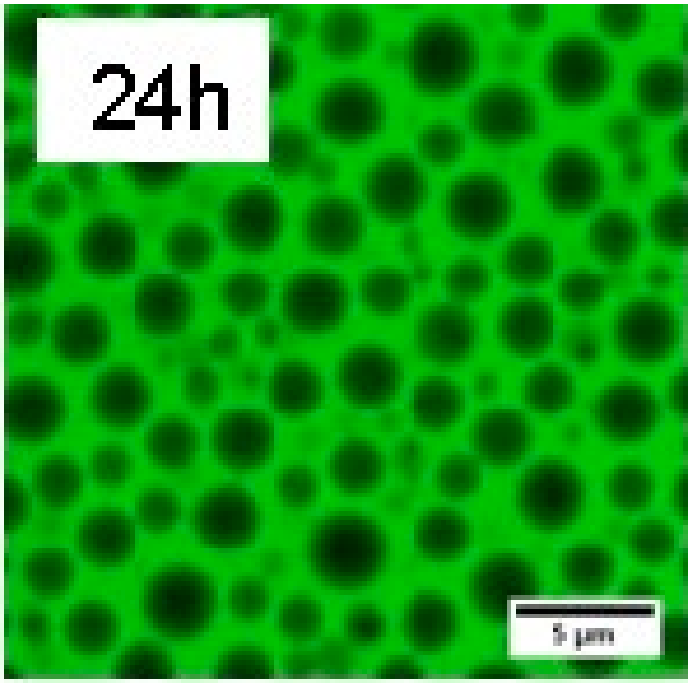


binodal decomposition

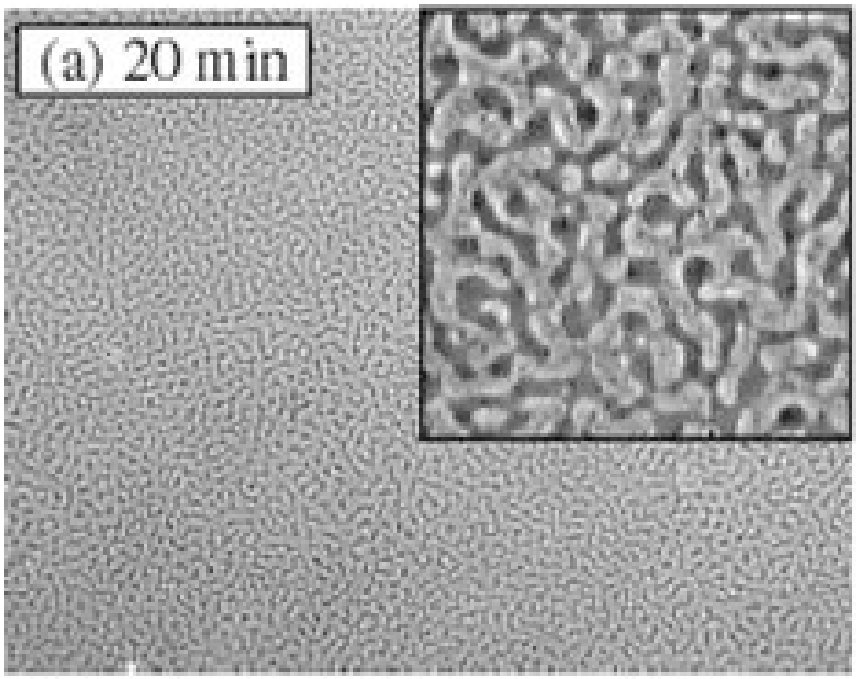
The resulting structures are very different.

Gebauer, D.; Kellermeier, M.; Gale, J. D.; Bergstrom, L.; Coelfen, H. *Chemical Society Reviews* **2014**, *43*, 2348

Why do we care?



http://www2.mpip-mainz.mpg.de/~koynov/koynov/methods/clsm.html

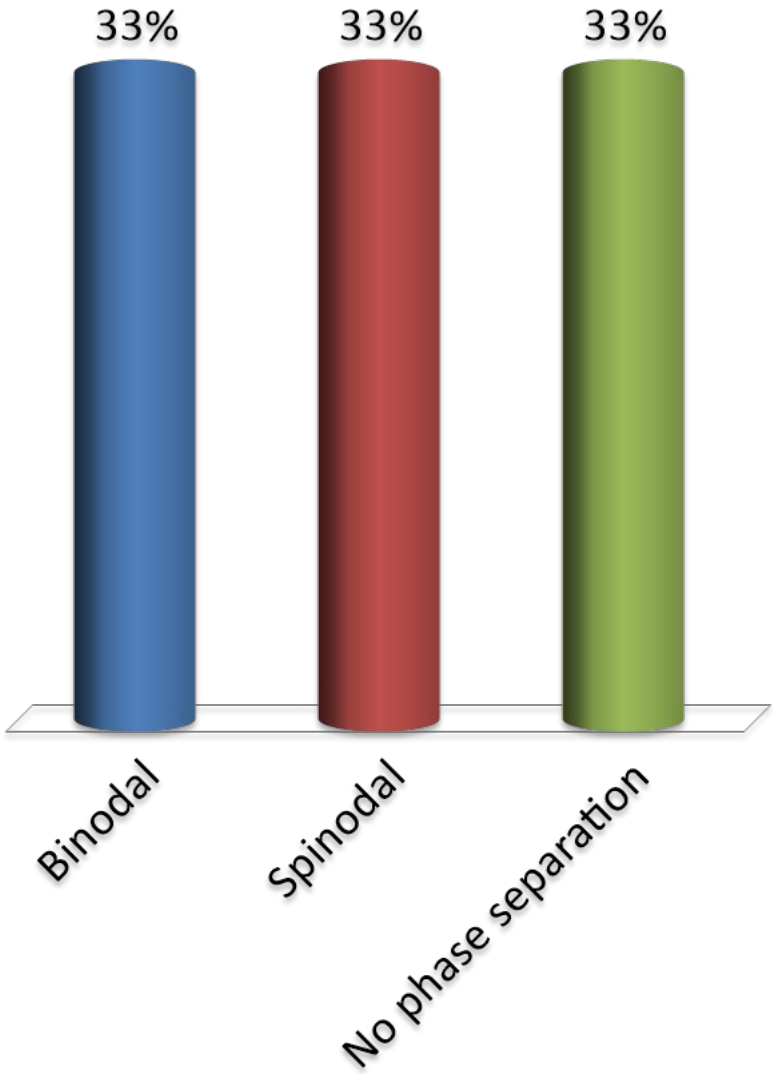


T. Nambu, Y. Yamauchi, T. Kushiro, S. Sakurai, *Faraday Discussions* **128**, 285 (2005)

The resulting structures are very different.

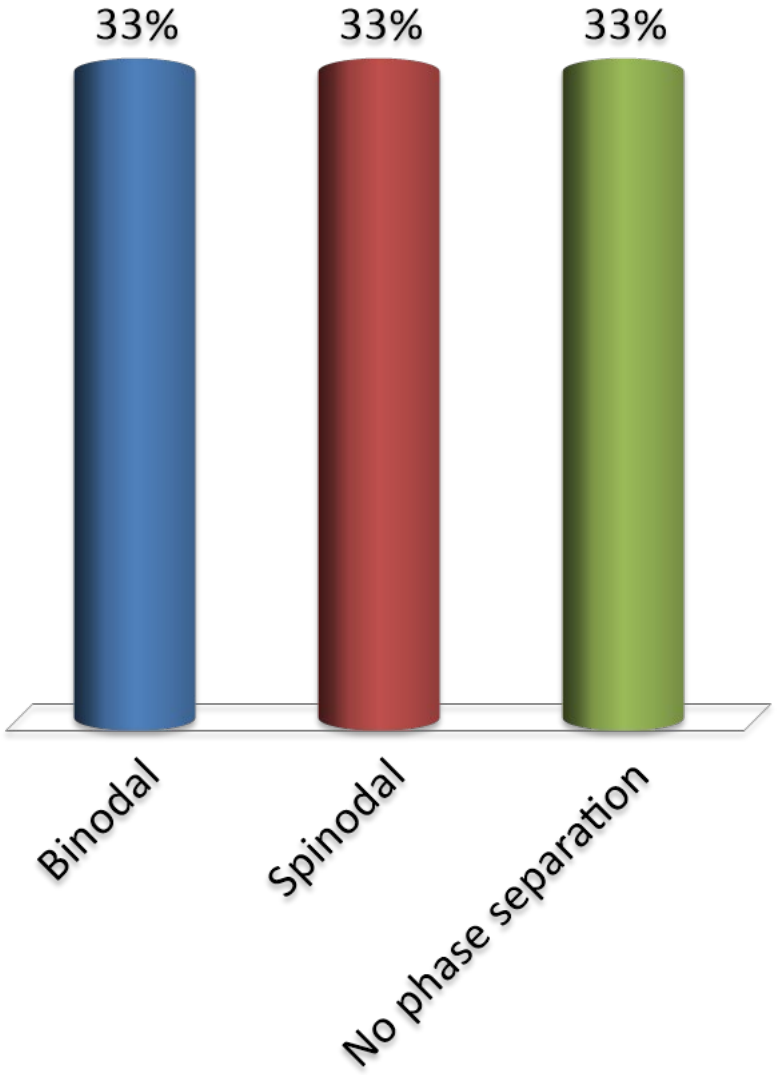
What type of a phase separation do you want if the resulting material should be used as filters?

A. Binodal
B. Spinodal
C. No phase separation



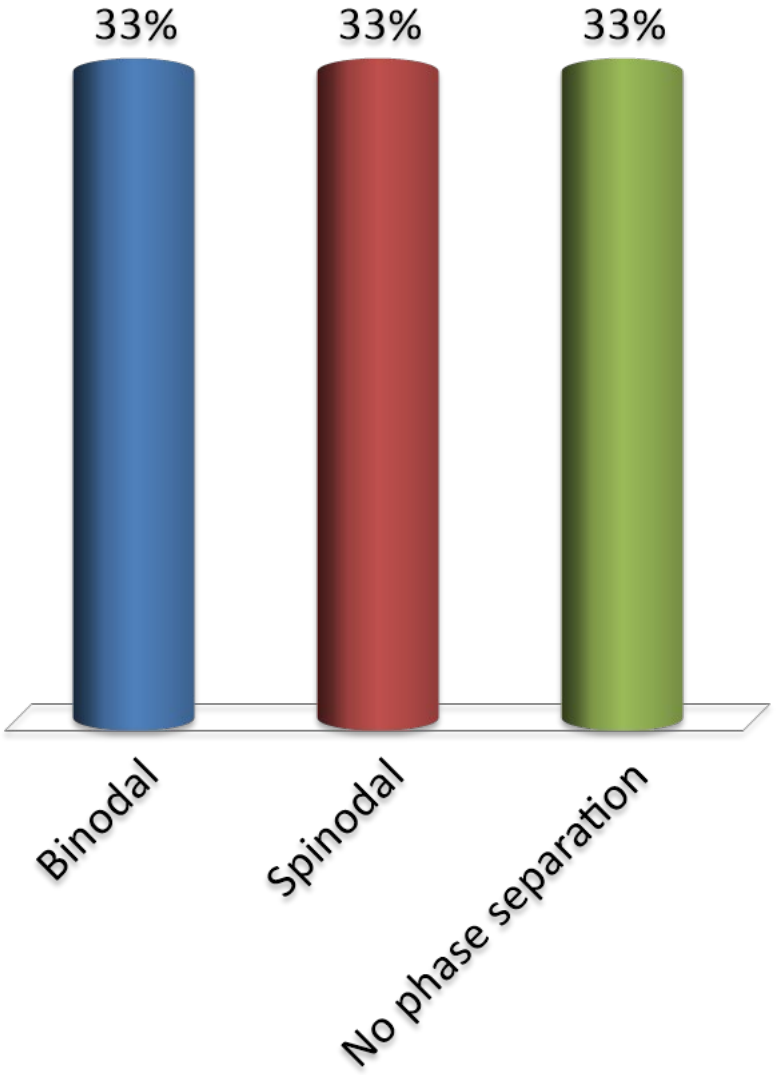
What type of a phase separation do you want if the resulting material should be used as supports for catalysis?

A. Binodal
B. Spinodal
C. No phase separation

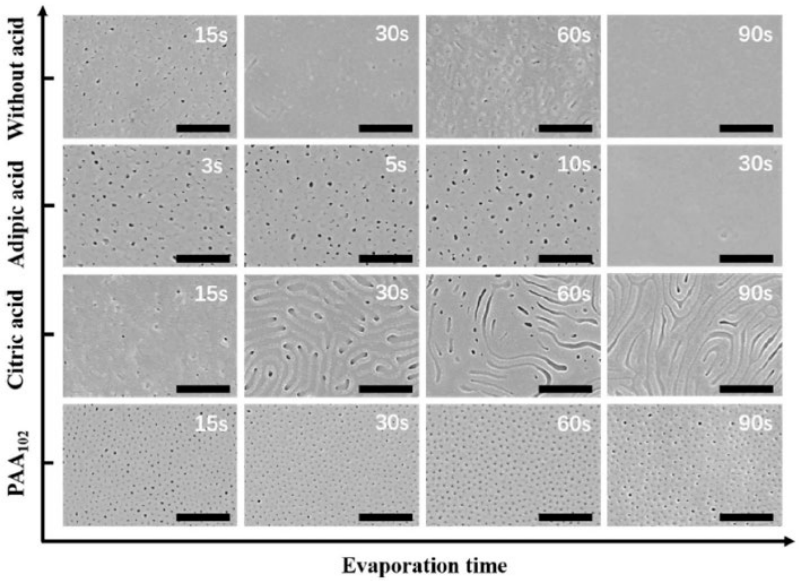


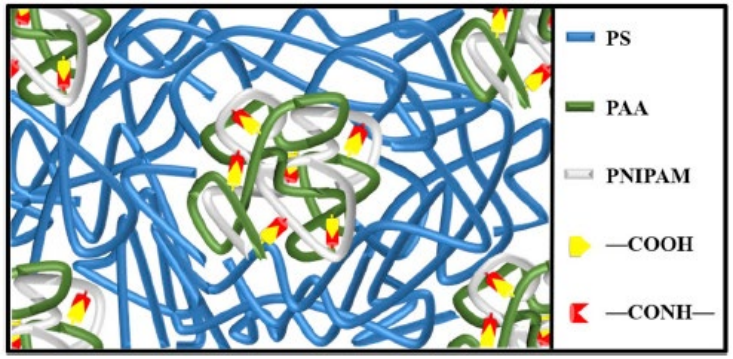
What type of a phase separation do you want if the resulting material should be used as lightweight structural supports?

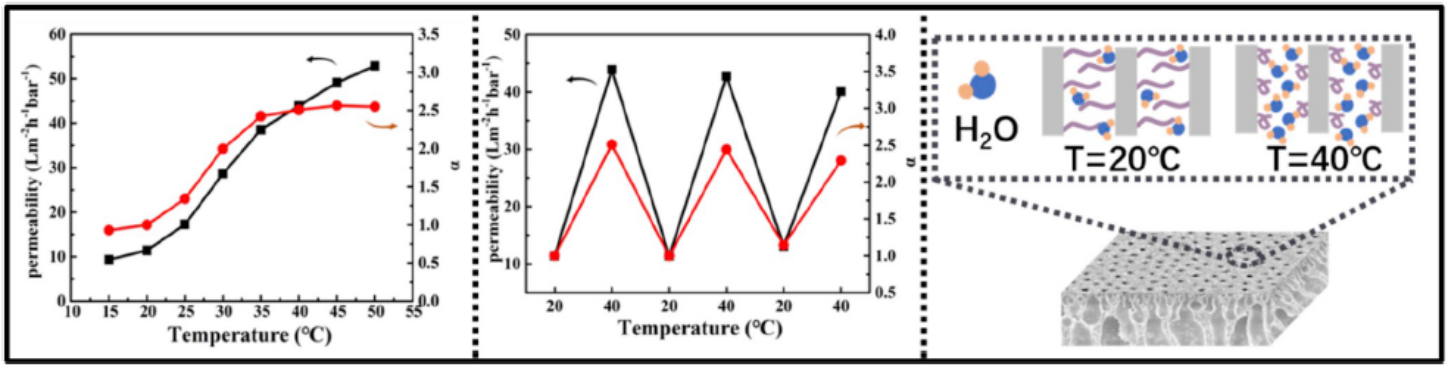
A. Binodal
B. Spinodal
C. No phase separation



Application:
Phase separation of PS-b-PNIPAM block-copolymers







Zhu, G.-D.; et al. *Journal of Membrane Science* **2019**, *589*, 117255