Density Functional Theory for Systems with Competing Interactions

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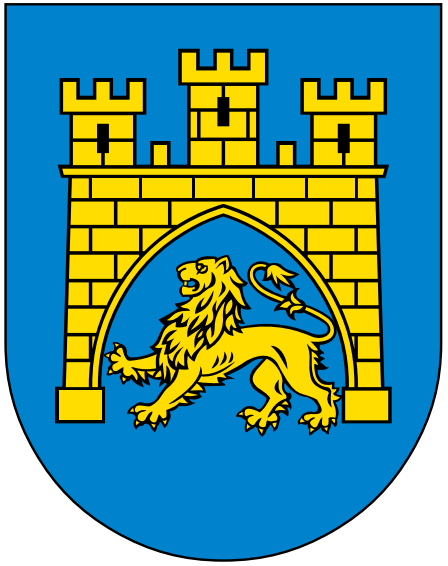


Lviv

Warsaw.

Lviv, 2019

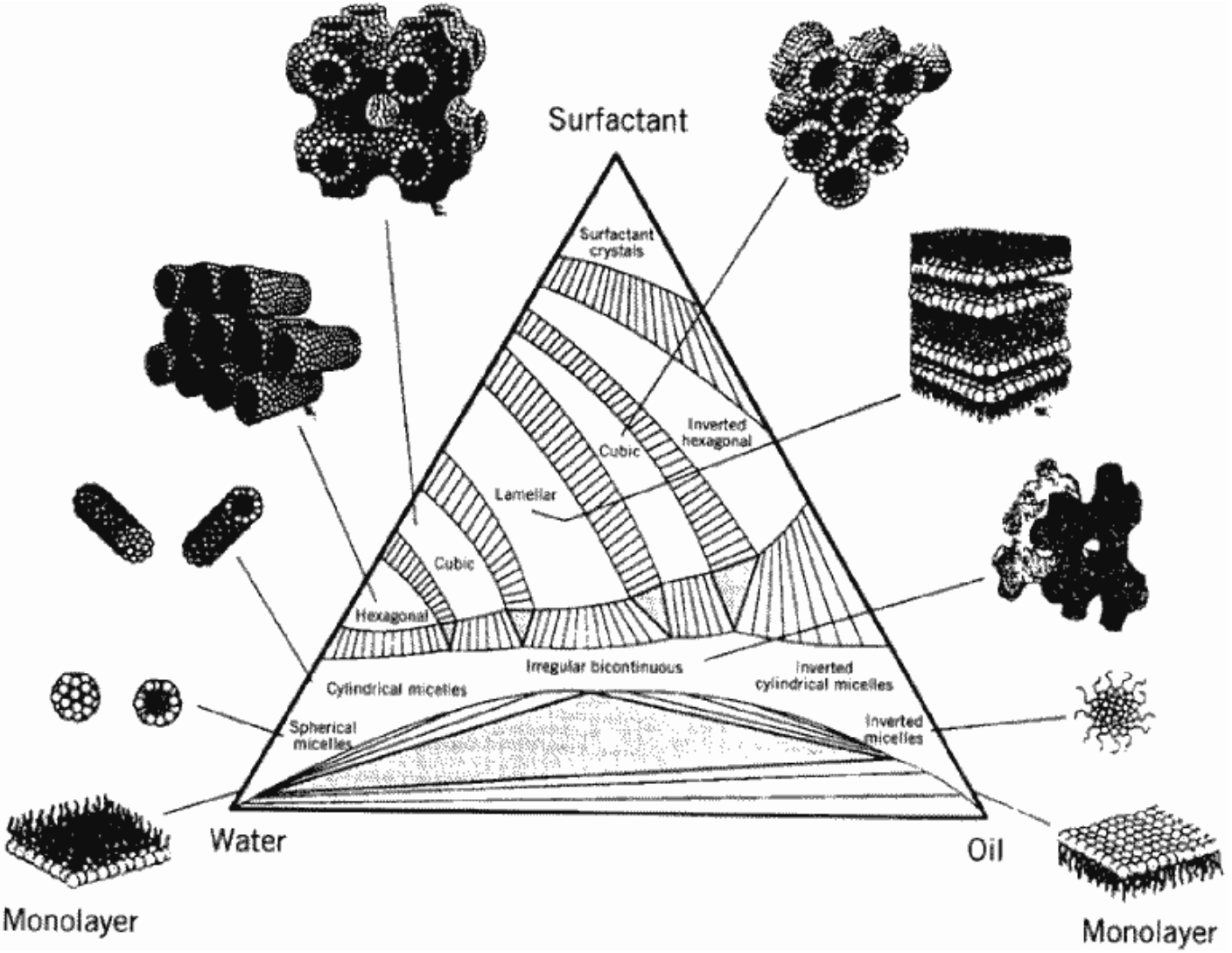
Outline

- Examples of experimental systems with spontaneous inhomogeneities
- Generic shape of competing interactions between spherical particles leading to self-assembly (the mermaid potential)
- Self-assembled structures from simulation studies for the mermaid potential
- Origin of similarity between amphiphilic and colloidal self-assembly
- Effects of fluctuations – illustrations, simple examples and discussion
- Development of the DFT with the fluctuation contribution obtained by the FT methods
- Comparison with simulations

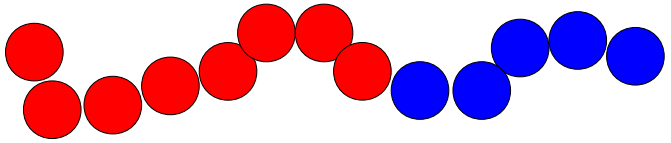
Examples of systems with spontaneous inhomogeneities

1. **Amphiphilic self-assembly**

Schematic phase diagram of oil-water-surfactant mixture

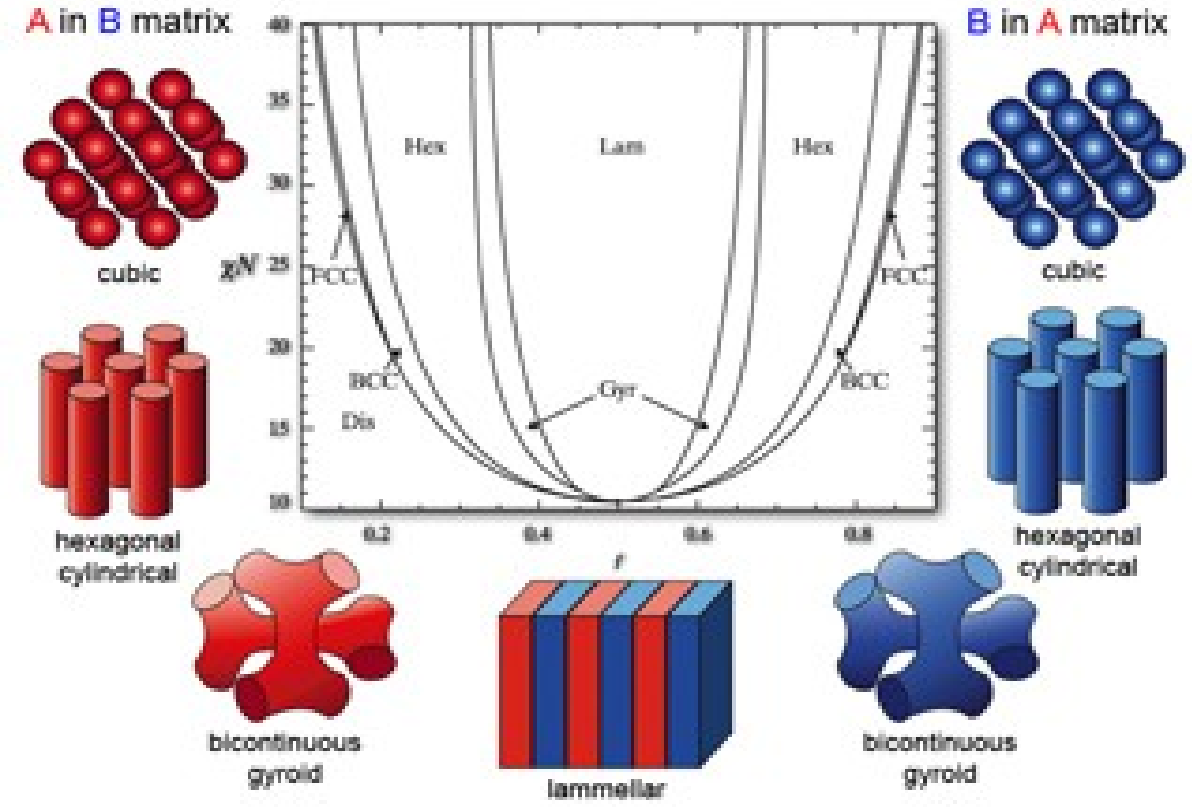


Generic phase diagram and structure of block copolymers



f=[A]/([A]+[B])

● does not mix with ●



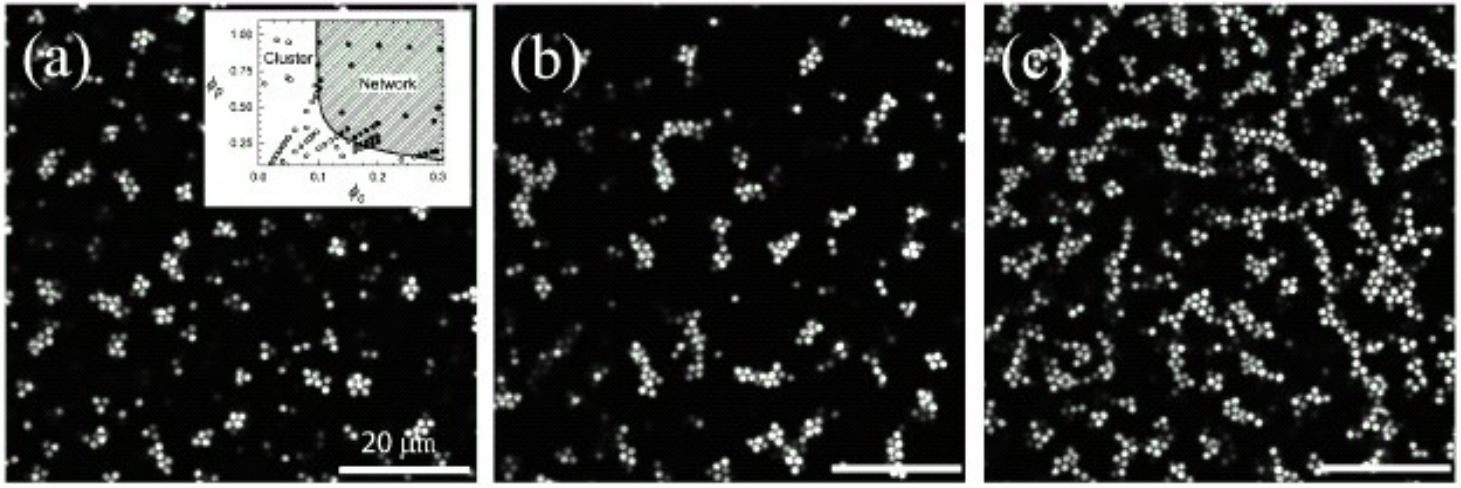
M. W. Matsen and M. Schick

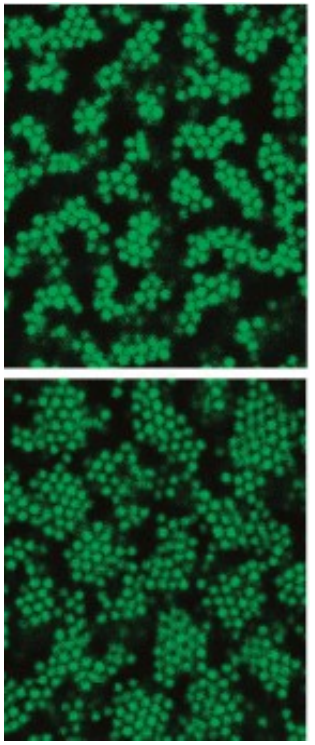
2. Colloidal self-assembly

First experimental observation: A. Stradner et. al., Nature **432**, 492 (2004).

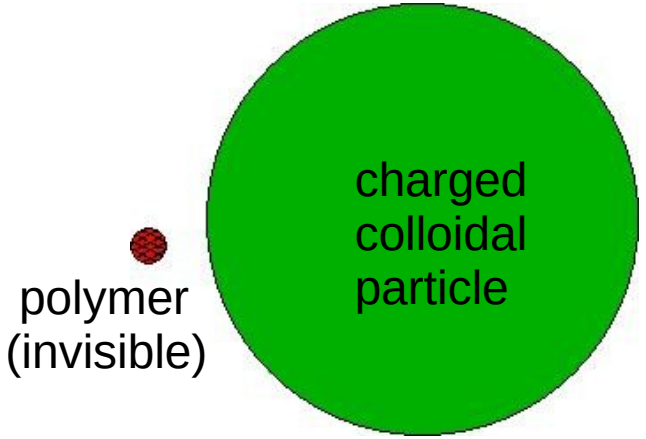
Cluster formation in colloid-polymer mixtures, confocal microscopy.
Interactions: depletion attraction + electrostatic repulsion

A. I. Campbell et. al., Phys. Rev. Lett. **94,** 208301 (2005)



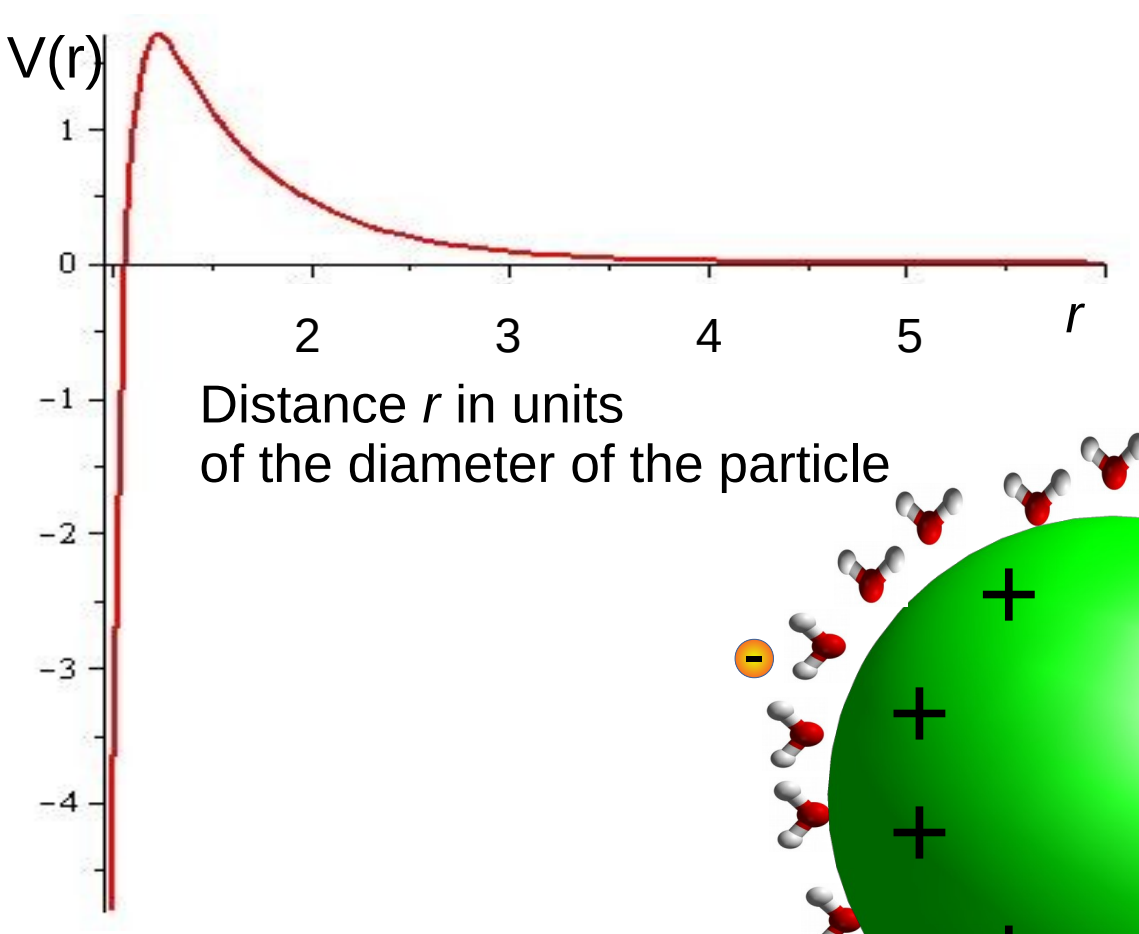


colloid volume fraction ζ_1 < ζ_2 < ζ_3

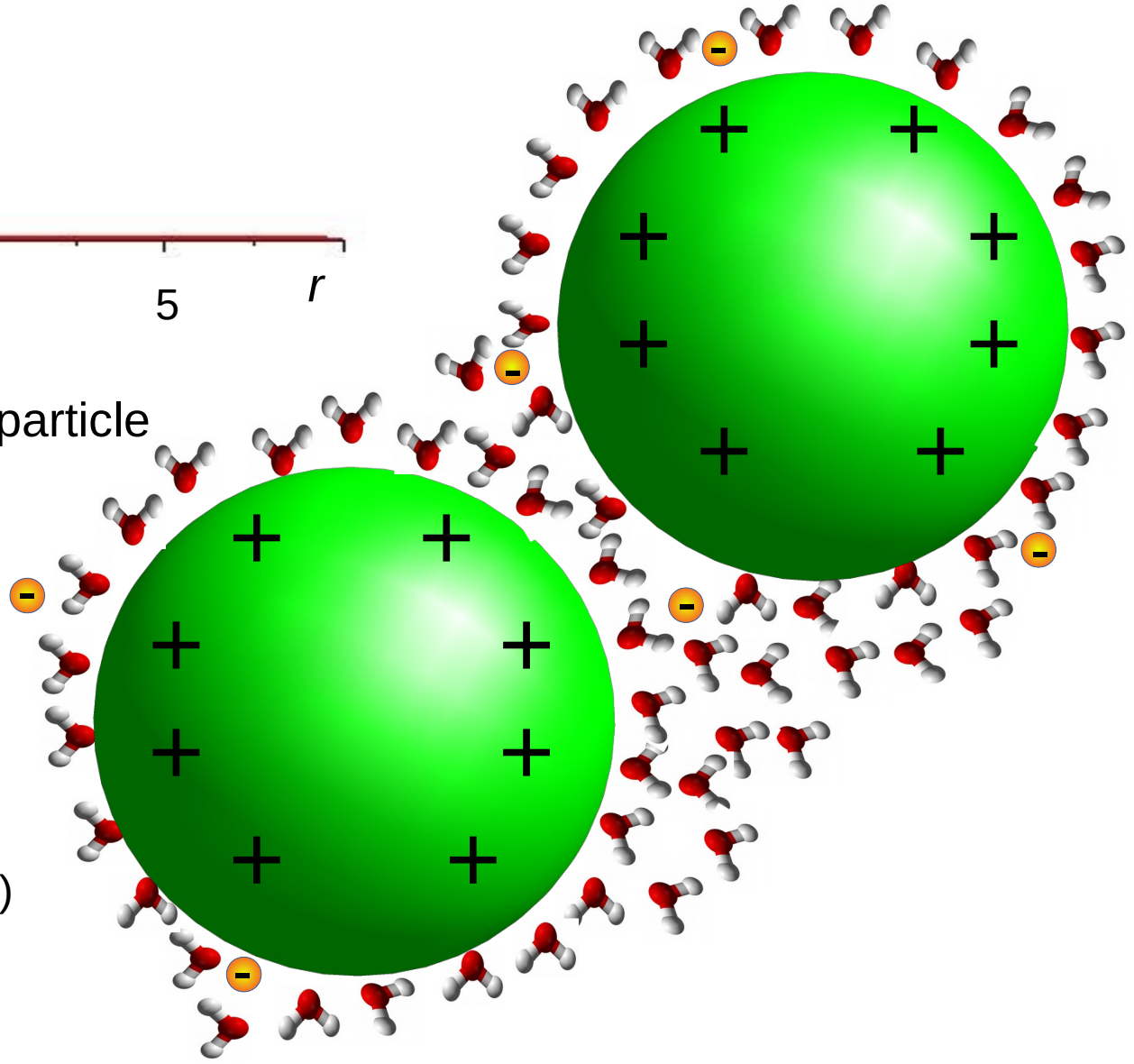


T. H. Zhang et.al.
Phys. Chem. Chem. Phys., **11**, 10827 (2009)

Effective interaction potential between two lysozyme particles in water, determined within the MSA approximation from scattering experiments at room temperature. Solvophobic attraction and screened electrostatic repulsion

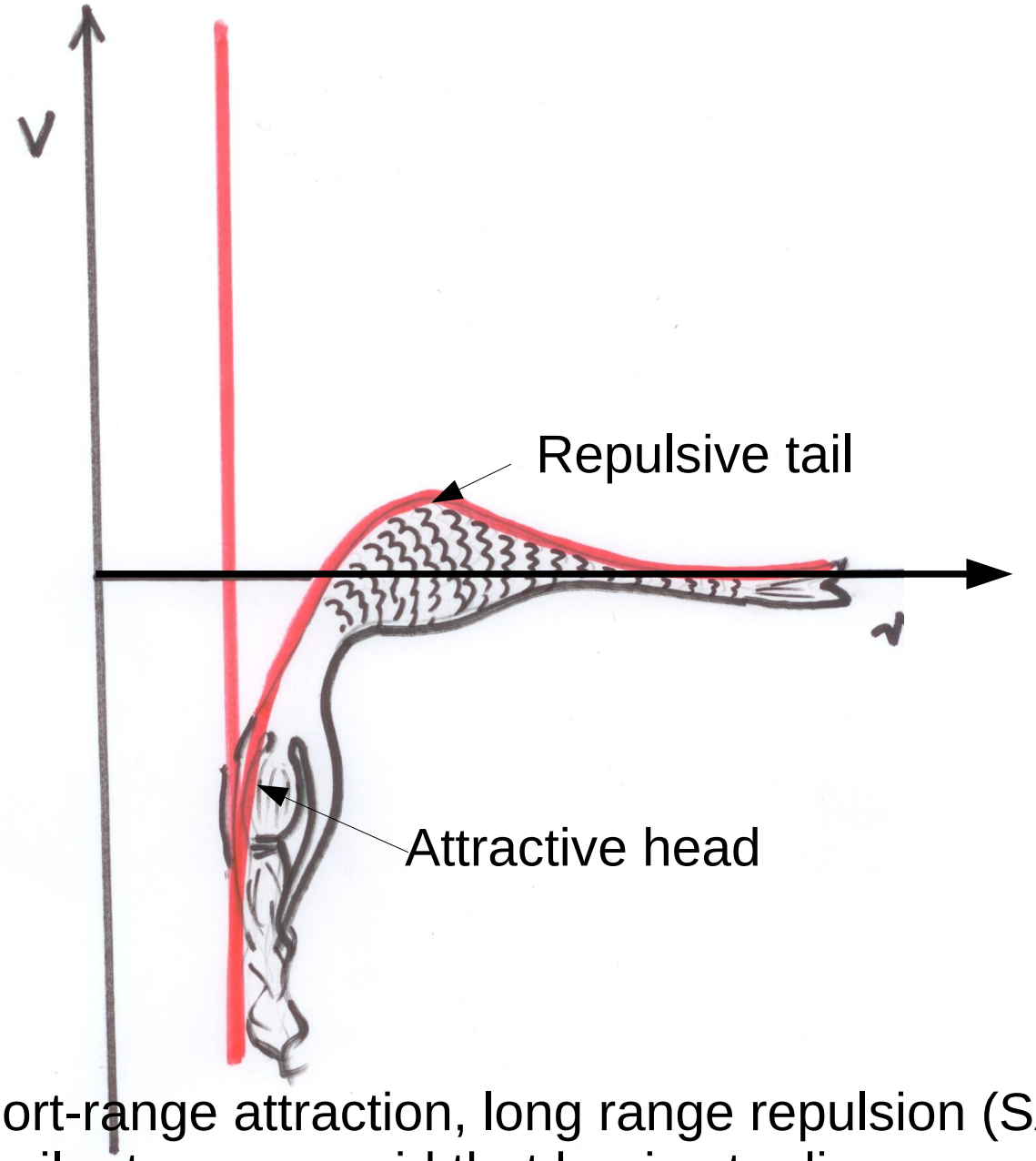


Distance *r* in units
of the diameter of the particle



Shukla et al, PNAS **105** 5075 (2008)

Generic shape of effective interactions in the colloidal self-assembly



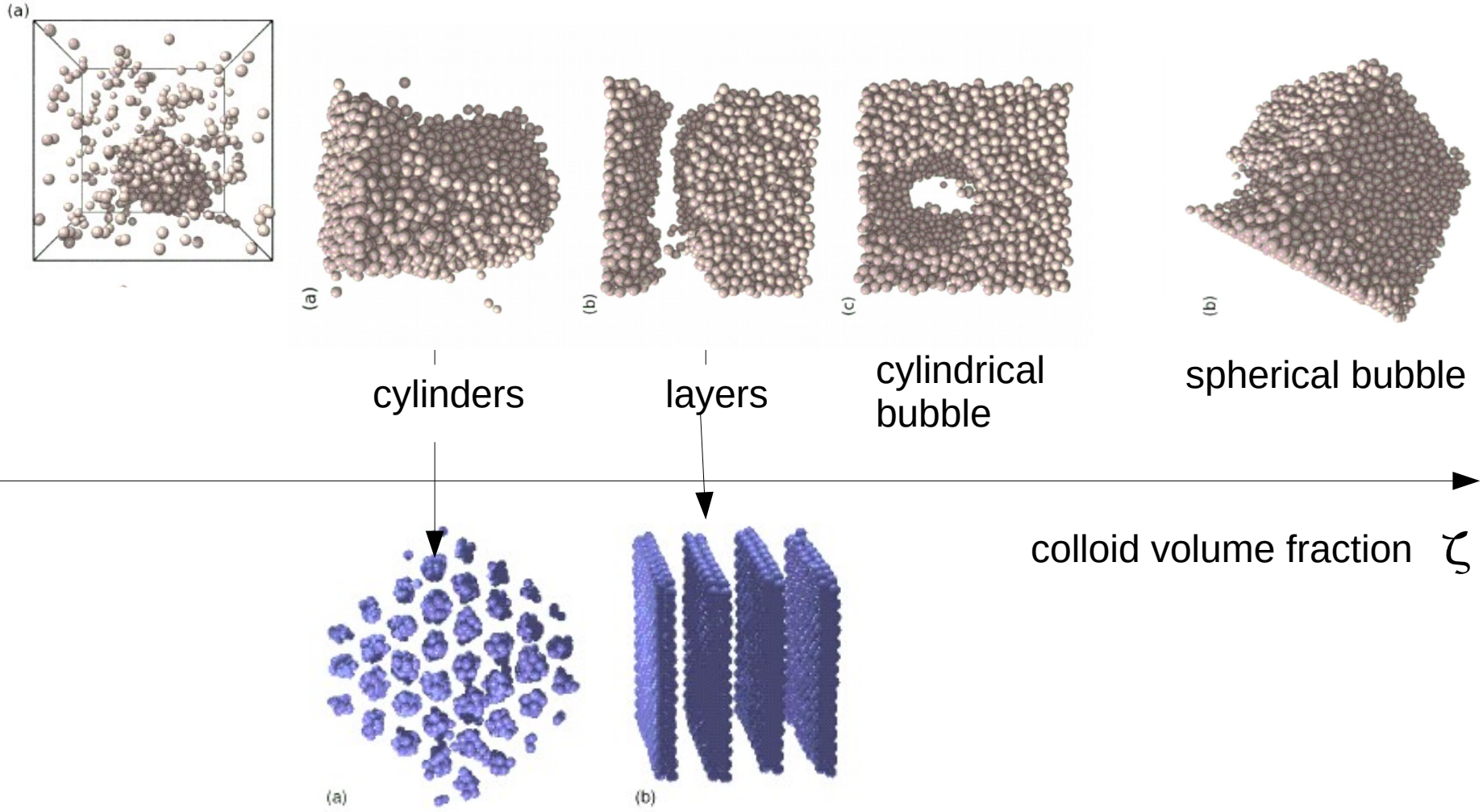
Mermaid potential: short-range attraction, long range repulsion (SALR).
A shape similar to a mermaid that begins to dive.
Politically incorrect name, but a female Warsaw citizen is excused

C. Patrick Royall, “Hunting mermaids in real space: known knowns, known unknowns and unknown unknowns”, Soft Matter, **14**, 4020 (2018)

SALR is very difficult to pronounce, I’ll use “mermaid potential”

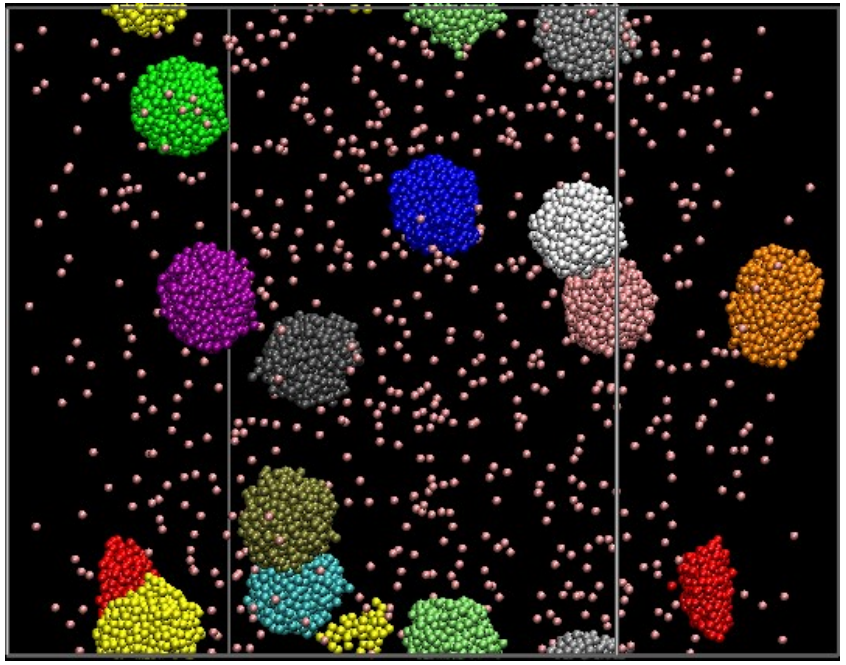
Structures from simulation results for the mermaid potential

Case I: large clusters, A. Archer and N. Wilding PRE **76**, 031501 (2007)

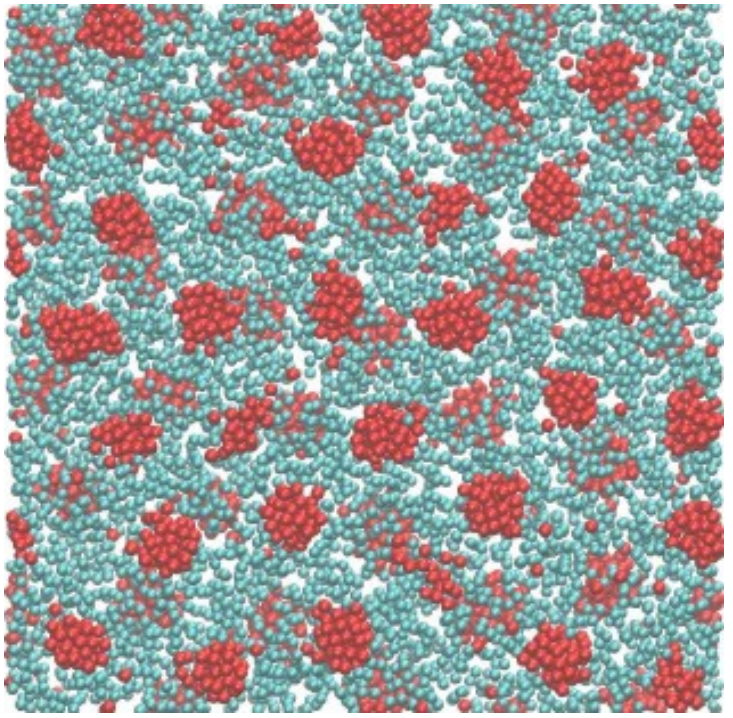


Case II: small clusters, A. de Candia et.al. PRE **74**, 010403 R (2006)

Case III: giant clusters,
M. Sweatman



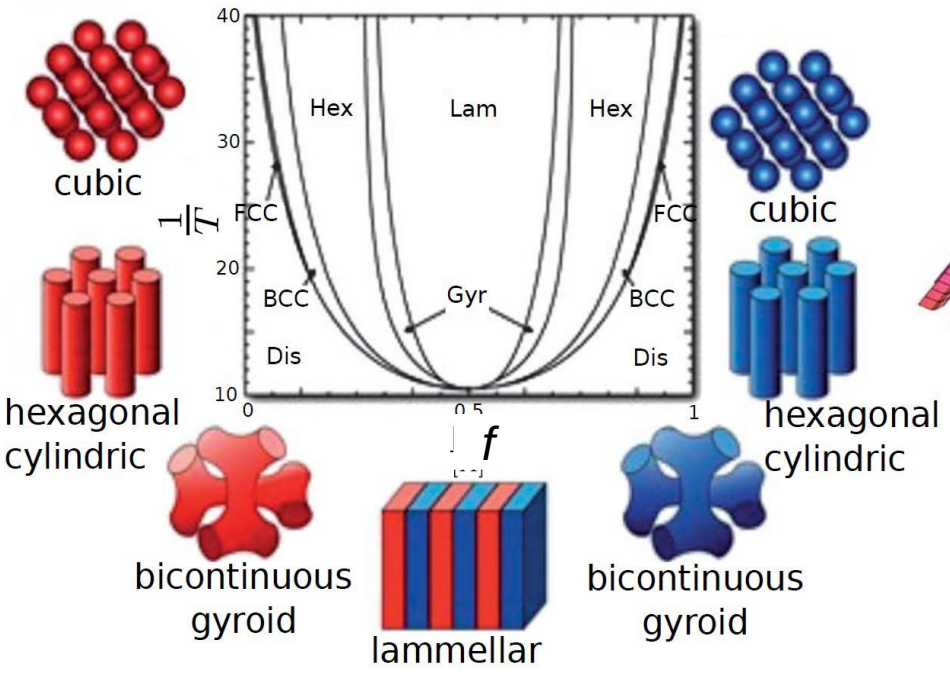
Case IV: clusters in a mixture,
G. Zarragoicoechea, A. Meyra



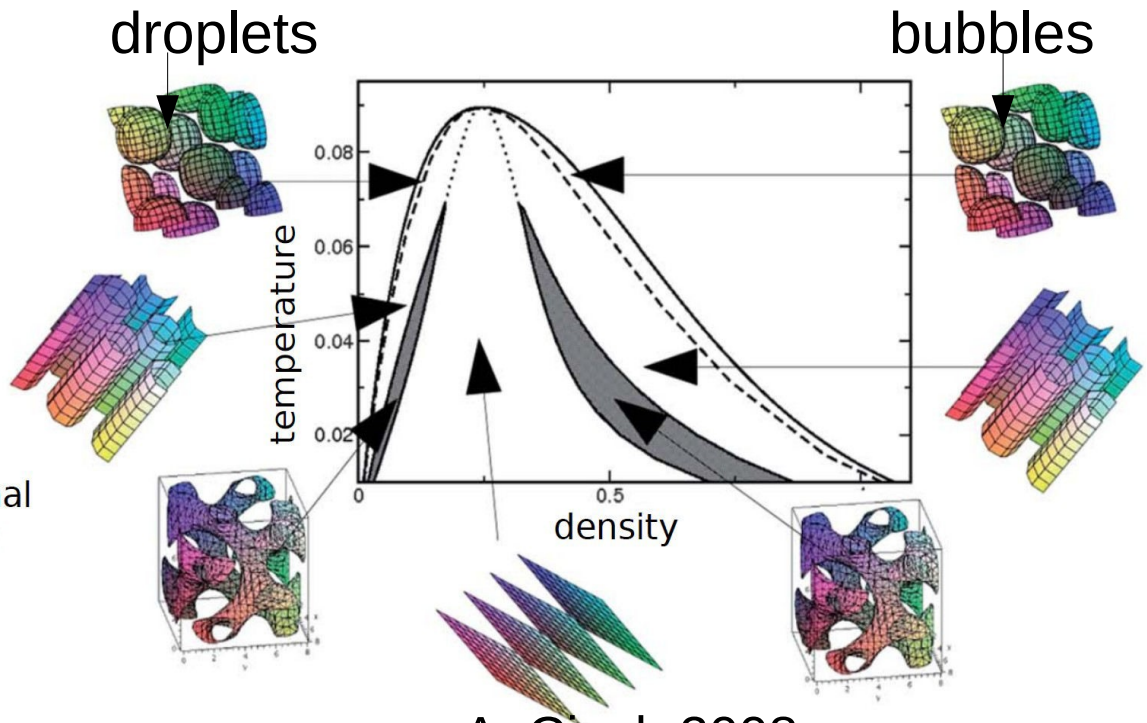
Note the analogy between the clusters in the mermaid systems and micelles in the amphiphilic systems.
Note also that the local density inside the clusters is much larger than between them.

Phase diagrams in MF approximation

Amphiphilic systems (block copolymers)



Mermaid (SALR) systems



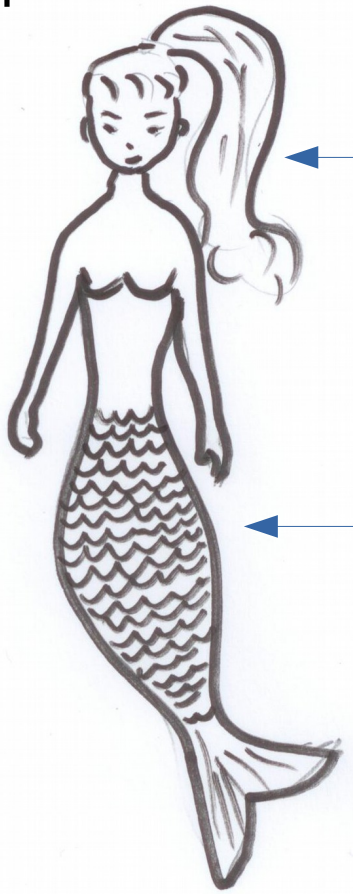
A. Ciach 2008
A. Ciach & W.T. Godz 2010

Despite quite different forms of the interaction potentials, phase behavior in the two types of systems is very similar. Why?

Don’t be misled by the apparent analogy!

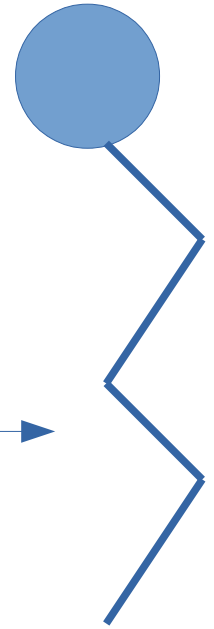
Men point of view

water point of view



Attractive head

Repulsive tail



Amphiphilic molecule

Amphiphilic self-assembly

Phenomenological functional of the local concentration difference between the polar and organic components ϕ

$$F_L[\phi] = \int d\boldsymbol{r} \left[f(\phi(\boldsymbol{r})) - \frac{\zeta_2}{2} (\nabla \phi(\boldsymbol{r}))^2 + \frac{\zeta_4}{4!} (\nabla^2 \phi(\boldsymbol{r}))^2 \right]$$

Periodic structure is stable for $\zeta_2 > 0$

The functional first postulated by **Brazovskii** in 1975,
by L. Leibler in 1980 to describe block copolymers
and by Teubner & Strey in 1987 and Gompper & Schick in 1990
to reproduce structure factor of microemulsions.

Can a similar functional describe the mermaid-potential systems,
and if so, what is the relation of the phenomenological parameters
with the mermaid potential?

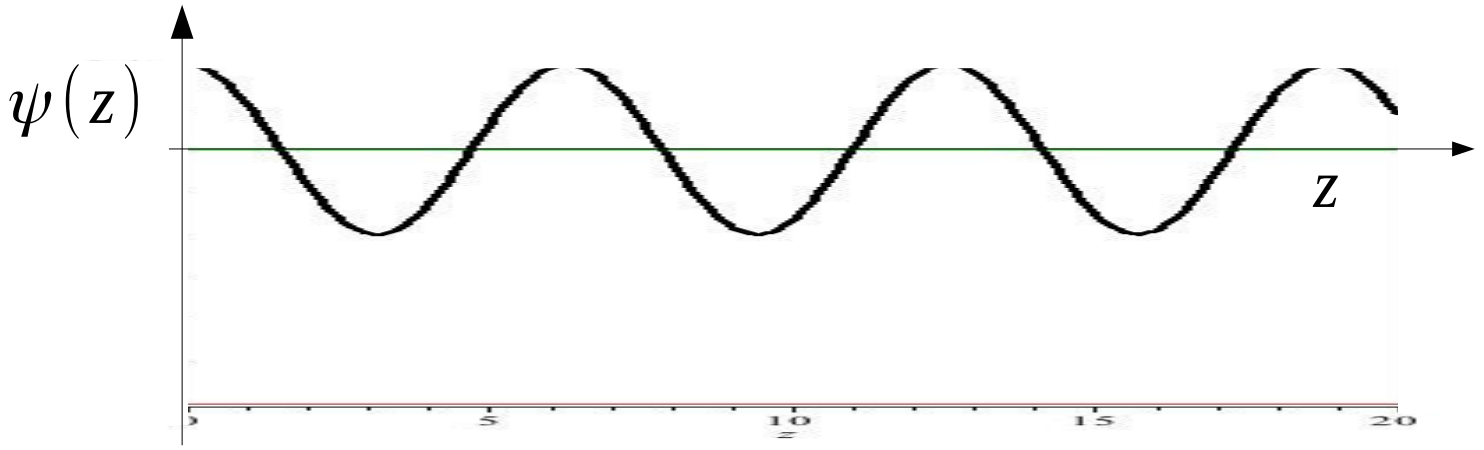
We consider local deviations from the overall volume fraction ζ_0,

$$\psi(\boldsymbol{r}) = \zeta(\boldsymbol{r}) - \zeta_0$$

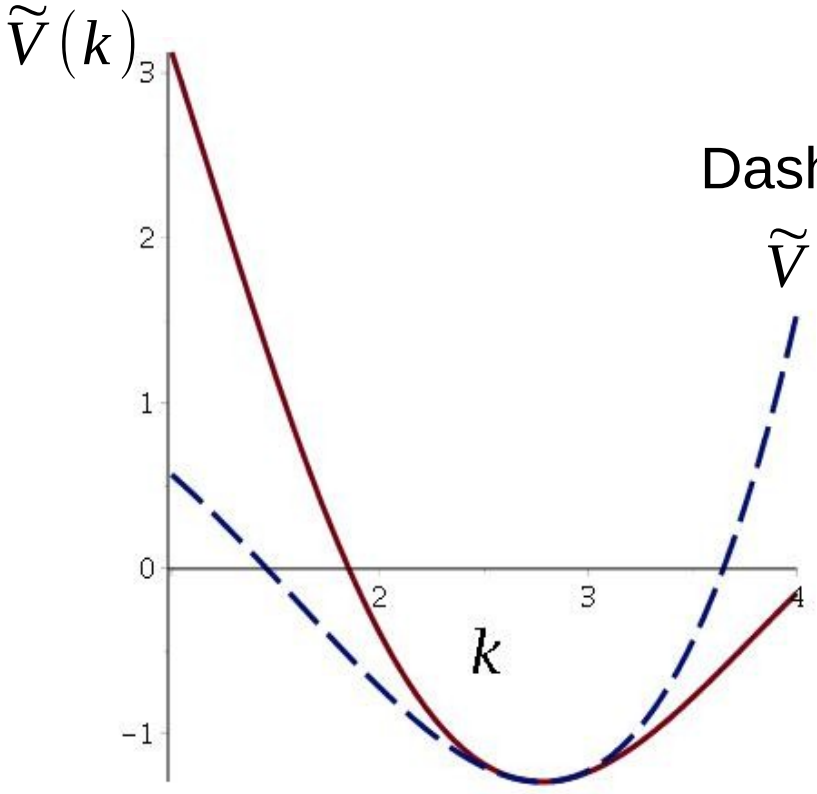
The excess internal energy associated with the inhomogeneities in Fourier representation has the form

$$\beta \Delta U[\zeta, \psi] \approx \frac{\beta}{2} \int d\boldsymbol{k}\, \tilde{\psi}(\boldsymbol{k}) \tilde{V}(k) \tilde{\psi}(-\boldsymbol{k})$$

$\tilde{\psi}(\boldsymbol{k})$ is the amplitude of the plane wave of density with the wave vector $\boldsymbol{k}$



Typical mermaid potential in Fourier representation (solid line) has a minimum at $k_0 > 0$



Dashed line: the approximation

$$\widetilde{V}(k) \approx \widetilde{V}(k_0) + v\left(k^2 - k_0^2\right)^2$$

k_0 is the wavenumber of the density wave leading to the largest energy gain compared to the constant density. The waves with the largest energy gain are the most probable ones.

For attractive potentials, $k_0 = 0$

If only the most probable waves are taken into account, we can use the approximation

$$\widetilde{V}(k) \approx \widetilde{V}(k_0) + v\left(k^2 - k_0^2\right)^2$$

In the Fourier representation $k^2 \rightarrow -\nabla^2$ in the real-space representation

By Fourier transforming back to the real space we obtain for the above approximation for the interaction potential the excess internal energy

$$\Delta U \approx \frac{1}{2}\int d\boldsymbol{r}\left[V_0\,\psi(\boldsymbol{r})^2 - V_2(\nabla\,\psi(\boldsymbol{r}))^2 + V_4(\nabla^2\,\psi(\boldsymbol{r}))^2 \ldots\right]$$

Where $V_0 = \widetilde{V}(k_0) + vk_0^4$ $\qquad V_2 = 2k_0^2 v > 0,$ $\qquad V_4 = v$

and the oscillations of ζ are energetically favorable

We introduce the functional

$$F_L[\psi]=\beta\left(\Omega[\zeta_0+\psi]-\Omega[\zeta_0]\right)$$

Where $\Omega[\zeta]=U[\zeta]-TS[\zeta]-\mu N$ is the grand potential.

From the above approximations for the excess internal energy $\beta\,\Delta U$ and using the local density approximation for the entropy *S* we obtain

$$F_L[\psi]=\int d\boldsymbol{r}\left[f\left(\psi(\boldsymbol{r})\right)-\frac{\beta V_2}{2}\left(\nabla\psi(\boldsymbol{r})\right)^2+\frac{\beta V_4}{2}\left(\nabla^2\psi(\boldsymbol{r})\right)^2\right]$$

which is the same as the functional for the amphiphilic systems!

Whether a phase separation or a formation of inhomogeneous distribution of particles may occur depends on the sign of the second moment of the interactions.

Minimum of this functional gives most probable structures.

The case of weak order in mean-field

In ordered phases the clusters or layers are periodically distributed in space.

Weak order means that in the periodic phases, $\psi(\boldsymbol{r})$ is a superposition of plane density waves in different directions, each with the wavenumber $k = k_0$,

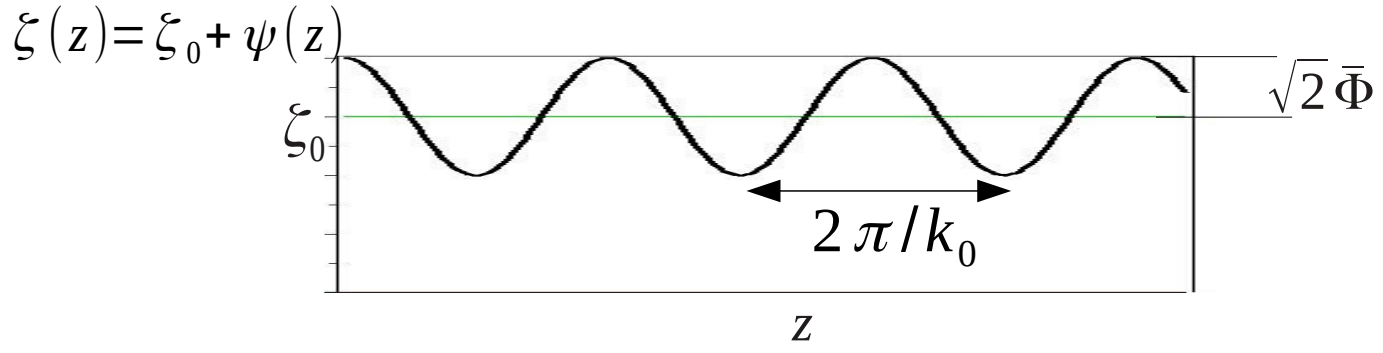
and $\zeta(\boldsymbol{r})$ is characterized by:

the space-averaged value ζ_0,

the amplitude of the oscillations Φ

and the symmetry (geometric factors κ_n), $\kappa_n \Phi^n = \frac{1}{V_u} \int_{V_u} d\boldsymbol{r}\, \psi(\boldsymbol{r})^n$ $\kappa_2 = 1$

in the lamellar phase



The case of weak order in mean-field

Weak order is expected at relatively high T,
where thermal motion has a disordering effect.

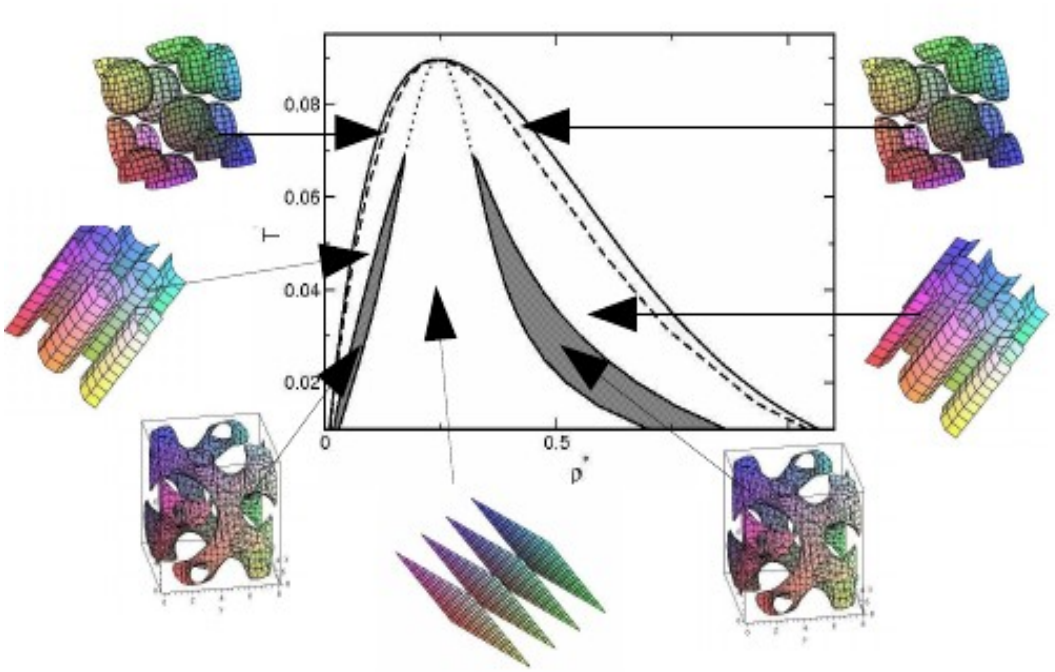
The functional becomes a function of Φ, ζ_0 and κ_n ,

$$\frac{F_L(\zeta_0,\Phi)}{V}=\frac{F_L(\zeta_0)}{V}+\beta\,\tilde{V}(k_0)\frac{\Phi^2}{2}+\sum_{n\geq 2}\frac{a_n(\zeta_0)}{n!}\kappa_n\Phi^n$$

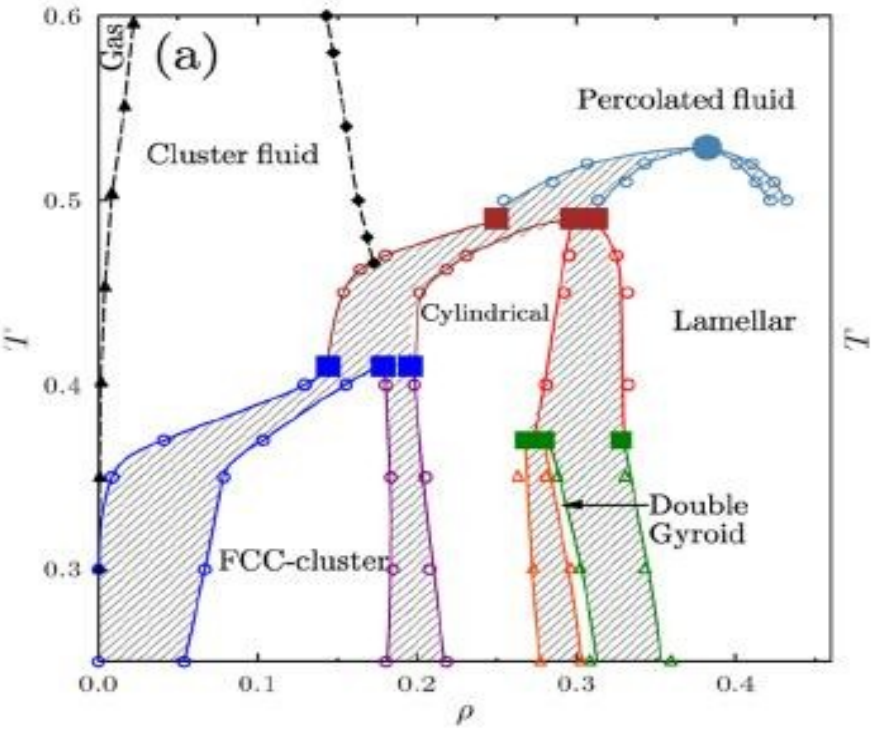
and in MF it takes the lowest value at the equilibrium state.

In fact for the G phase we need two shells to get two networks.

Phase diagram obtained
in the above approximation

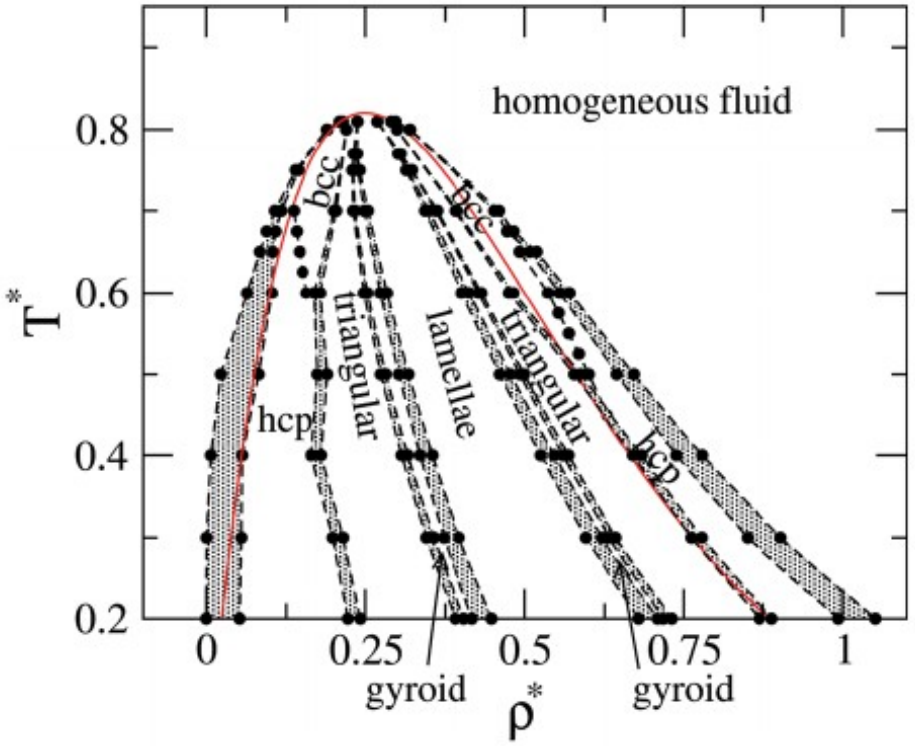


Simulation results
Y. Zhuang and P. Charbonneau (2016)

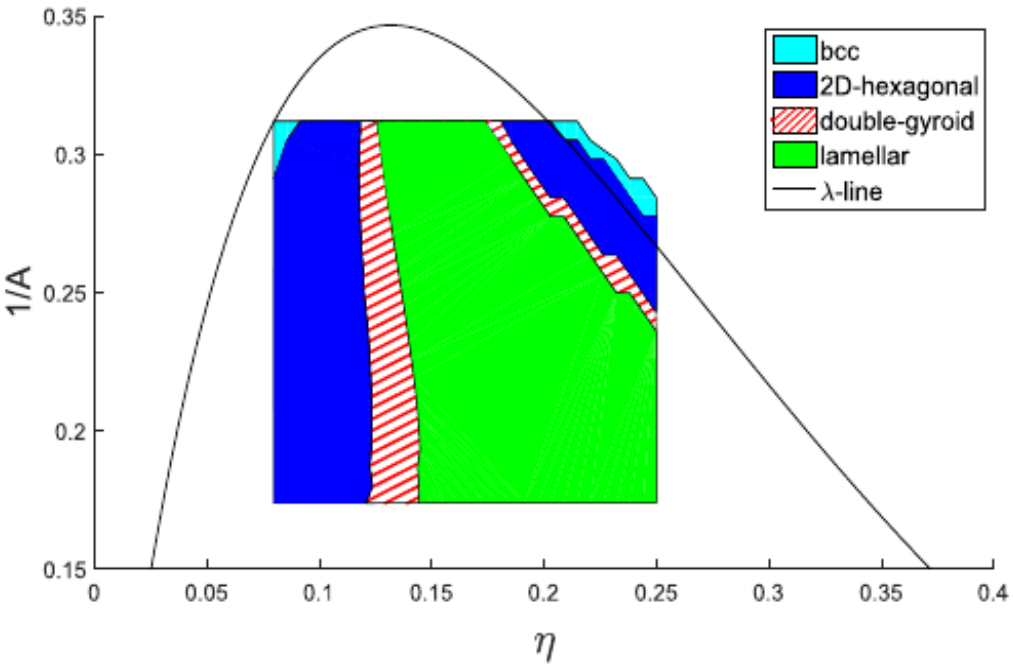


Note the same sequence of the ordered phases at low T,
and the discrepancy at high T.
In simulations the ordered phases loose stability upon heating one by one,
but in the mesoscopic theory
all the phases are stable up to the same temperature.
What is the reason?

Density Functional Theory results



D. Pini, A. Parola (2017),
local density approximation



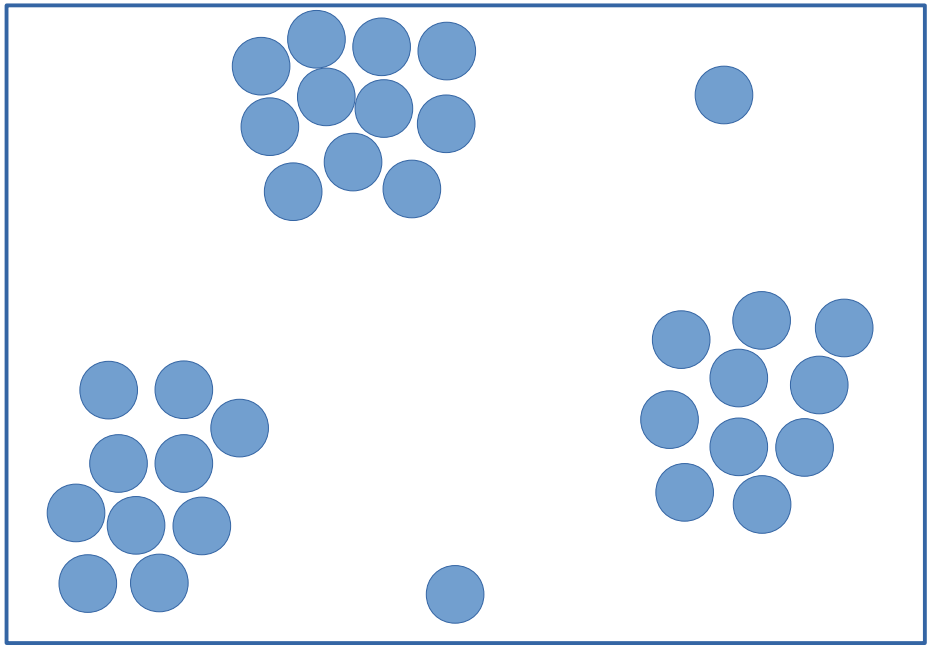
M. Edelmann and R. Roth (2016), White bear
version of the fundamental measure theory

In the MF mesoscopic field theory and in the DFT, the topology of the phase diagram is the same, but in simulations it is different. Why the high-T parts of the phase diagrams in simulations and in the MF-type theories are qualitatively different?

Physical (heuristic) arguments.

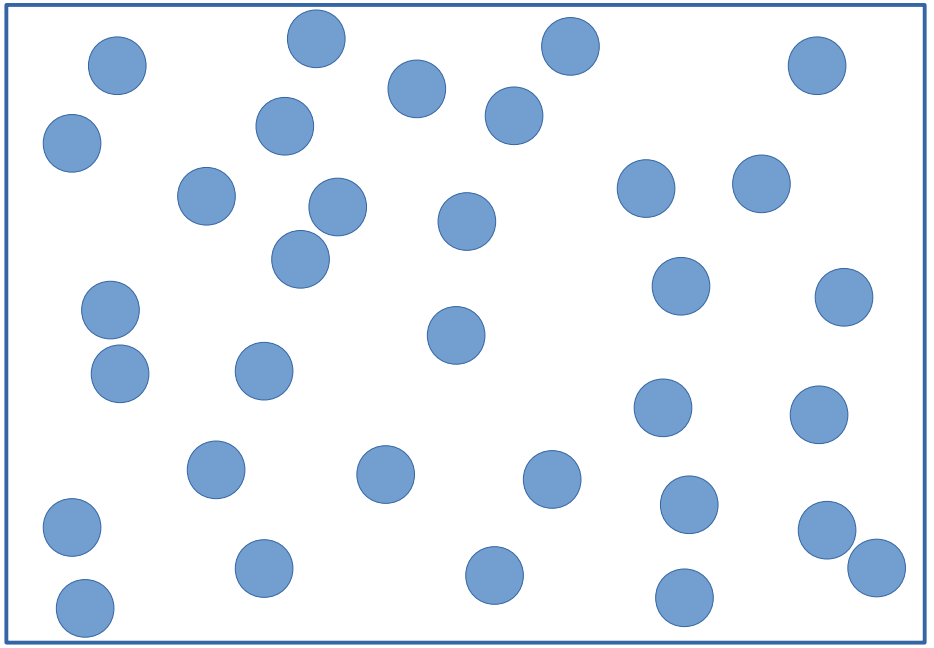
Typical states (snapshots):

Disordered inhomogeneous phase.



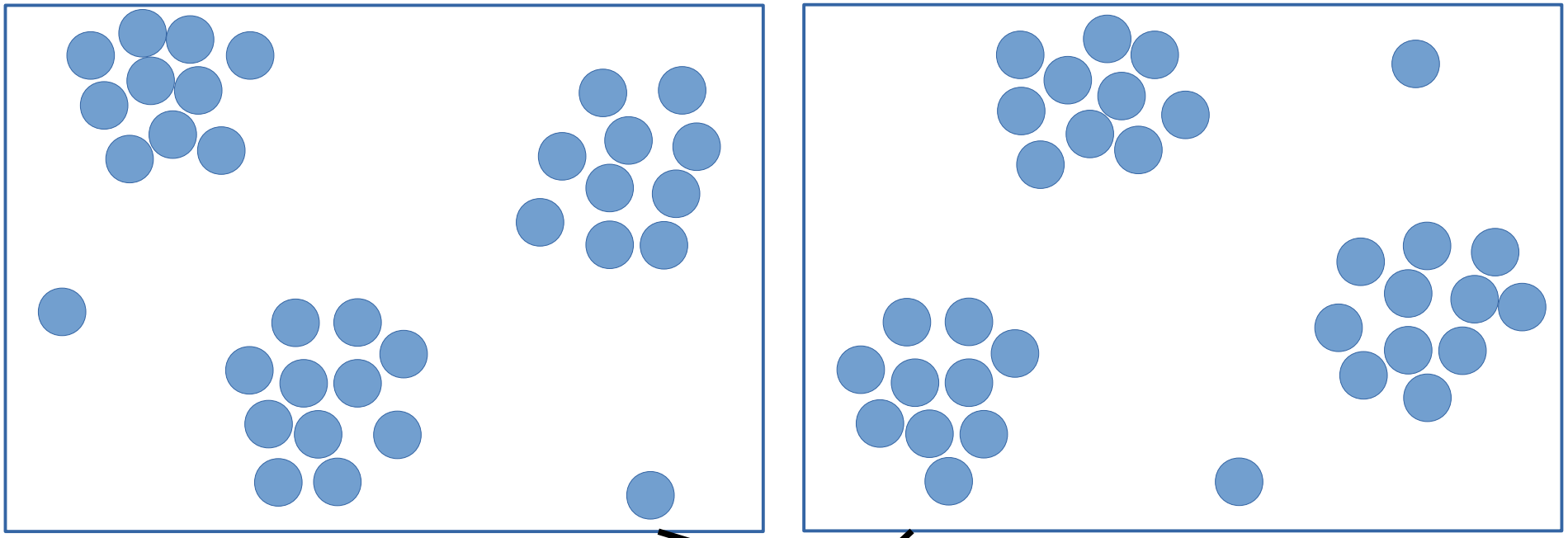
Many pairs of attracting particles, few pairs of repulsing particles

Disordered homogeneous phase



Much fewer pairs of attracting particles and much more pairs of repulsing particles.

Many pairs of attracting particles, few pairs of repulsing particles in each state,



but different positions of the clusters in different states, lead to a constant density after ensemble averaging.

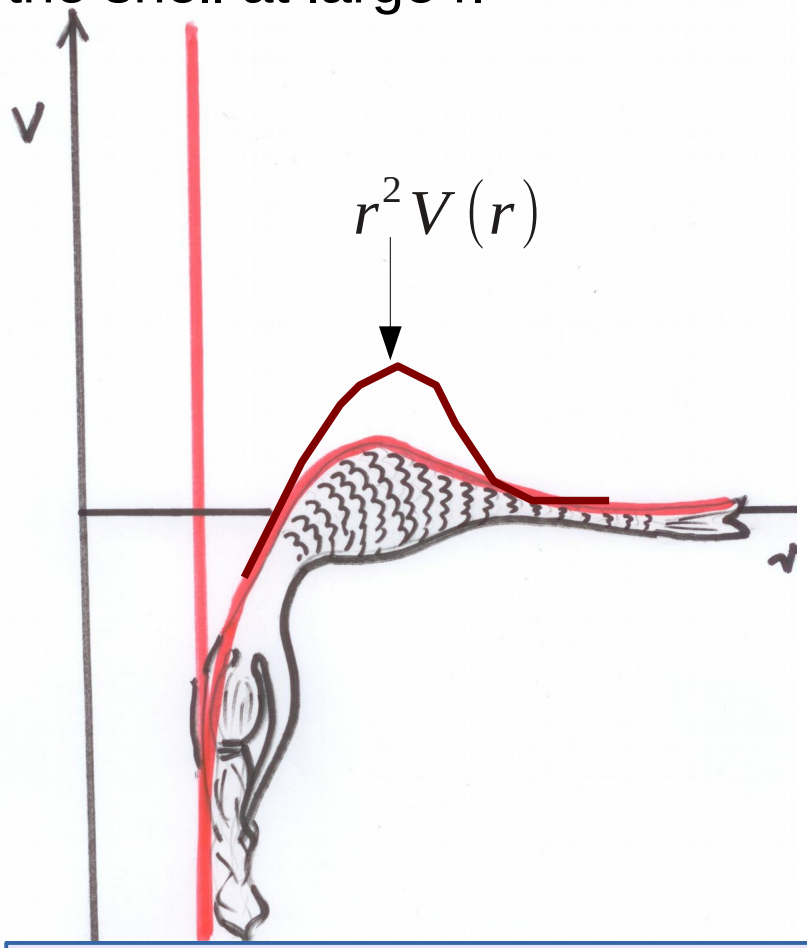
For a constant density, the contribution from the attractive part of the interactions is much smaller, and the contribution from the repulsive part of the interactions is much larger than in the majority of the individual states.

$$U[\zeta]/V = \frac{\zeta^2}{2}\int d\,\Delta \boldsymbol{r}\, V\left(|\Delta \boldsymbol{r}|\right)$$

In the MF theories

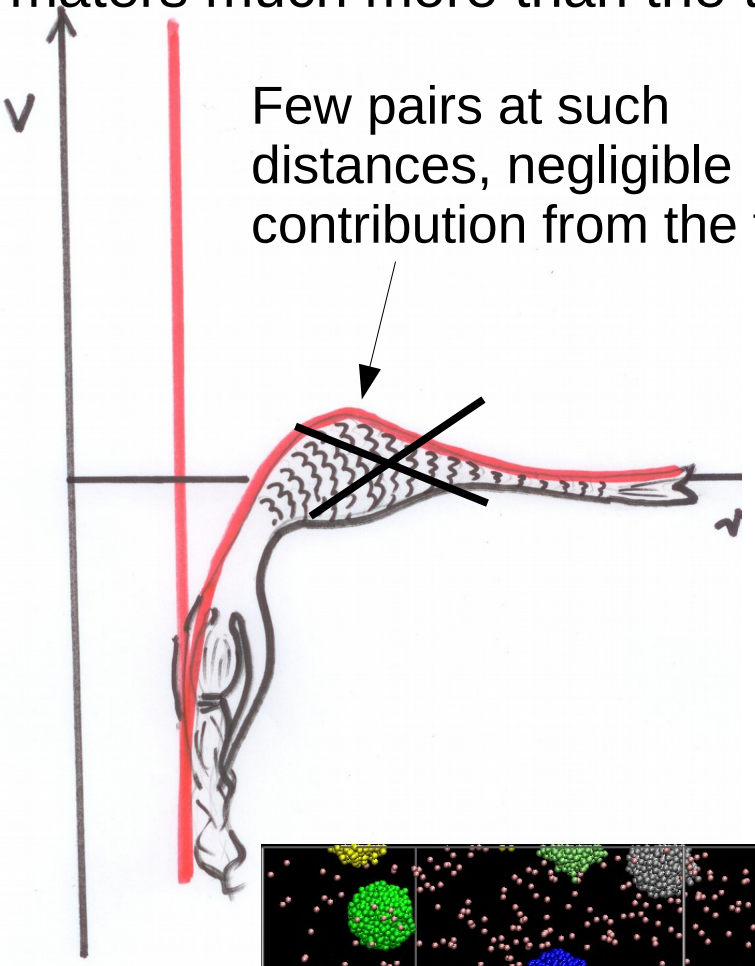
Internal energy in the disordered phase (no periodic order)

In MF, the tail matters much more than the head due to a large area of the shell at large r.

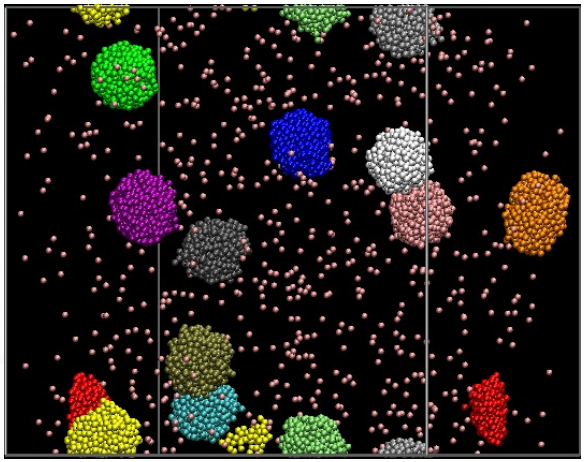


$$U[\zeta]/V = 2\pi\zeta^2 \int_1^\infty dr\, r^2 V(r)$$

In majority of states, the head maters much more than the tail



Few pairs at such distances, negligible contribution from the tail



The MF-type DFT is based on the average density.

The average value is not sufficient to describe a system with large fluctuations.

The simplest and commonly used quantity that measures the deviations of instantaneous states from the average value is the variance.

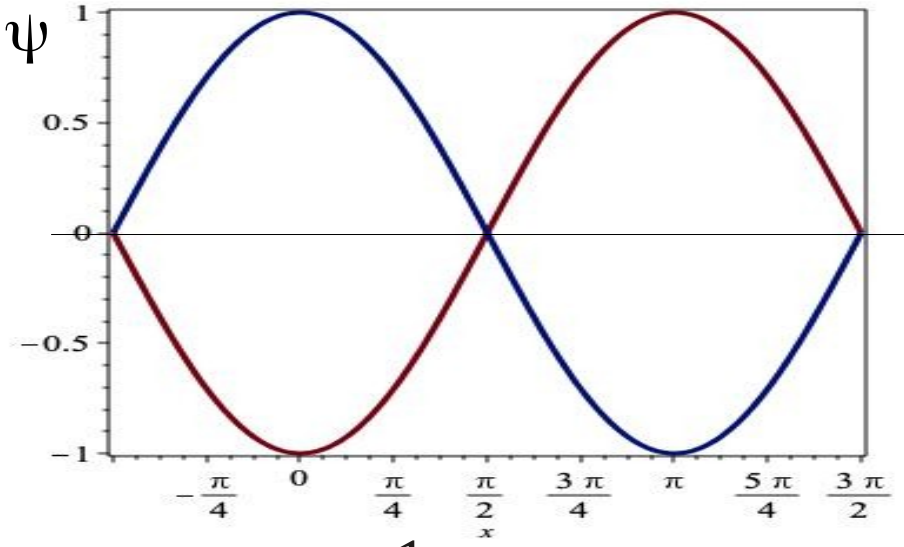
We need a theory for the inhomogeneous system in terms of both, the average density and its variance that allows to:

Calculate the variance $\langle \psi^2 \rangle$ for different (stable/metastable) phases

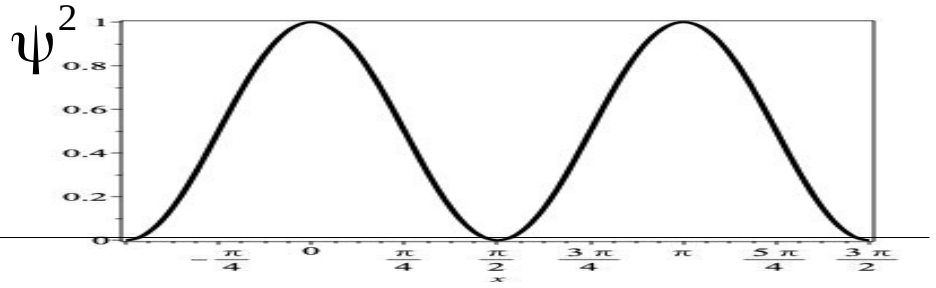
Calculate the contribution to the grand potential associated with $\langle \psi^2 \rangle$

For an illustration, consider a highly simplified case of two states with a single cluster in a different position in each state.

$$\psi(z)=\zeta(z)-\zeta_0$$



$$\langle\psi\rangle=\frac{1}{2}(\psi+\psi)=0$$



$$\langle\psi^2\rangle=\frac{1}{2}(\psi^2+\psi^2)=\psi^2>0$$

A measure of inhomogeneity

If $\psi=0$ in each state (homogeneous system) we have $\langle\psi\rangle=0=\langle\psi^2\rangle$.

What distinguishes the disordered homogeneous and inhomogeneous states is $\langle\psi^2\rangle$

Field-theory results for block-copolymers (Hartree approximation)
Podneks and Hamley, (1997)

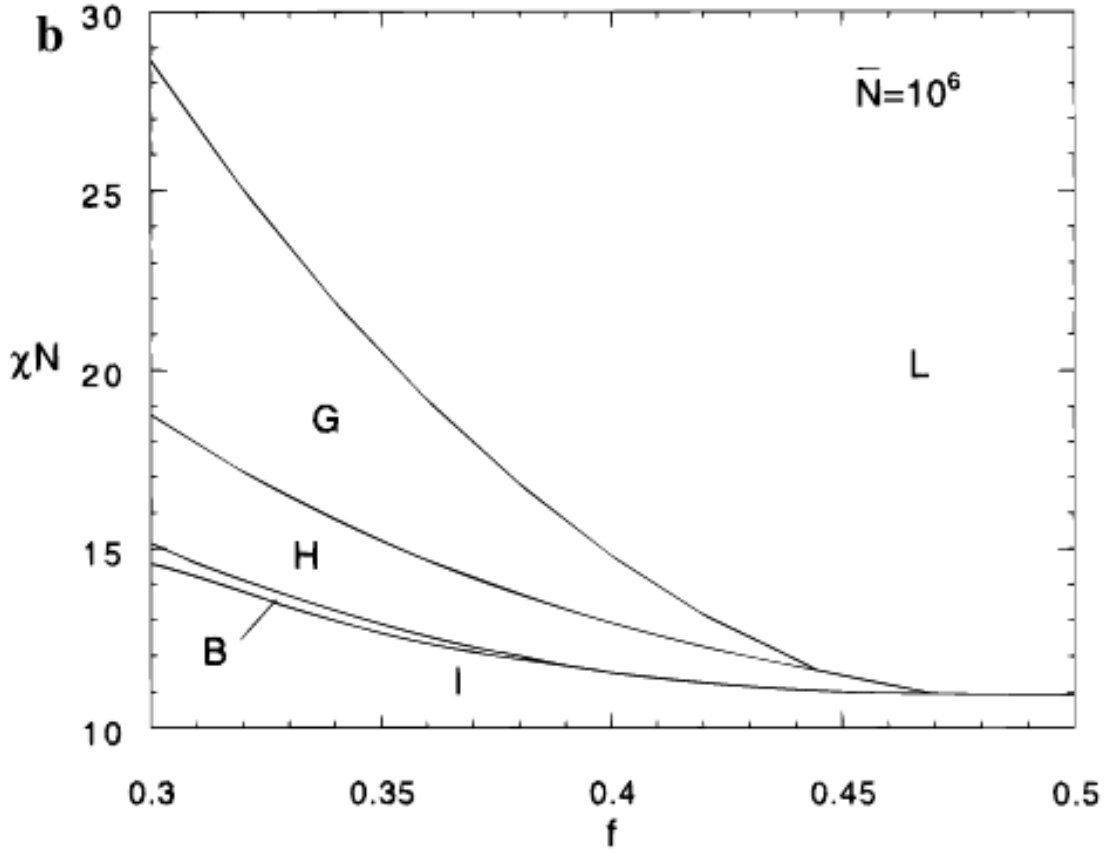


Figure 1. Phase diagrams calculated using the Landau–Brazovskii approximation for diblock copolymers with (a) $\bar{N} = 5 \times 10^3$ and (b) $\bar{N} = 5 \times 10^6$. Key: L, lamellar phase; H, hexagonal phase; G, $Ia\bar{3}d$ (gyroid) phase; I, isotropic (disordered) phase.

Isotropic phase coexists with L, H and B phases as in experiment.
Two-phase regions?

We combine the density functional theory with the Brazovskii field theory.

The former allows to include the microscopic contributions to Ω with frozen fluctuations on the mesoscale.

The latter allows to include the contribution from the fluctuations associated with inhomogeneities on the mesoscopic length scale (formation and/or displacements of the clusters).

Construction of the theory

The grand potential

$$\beta\Omega[\zeta]=\beta\Omega_{co}[\zeta]-\log\int D\,\phi\,\exp\left(-\beta H_f[\zeta,\phi]\right)$$

Standard (MF) DFT
(frozen fluctuations)

mesoscopic fluctuations around $\zeta(\boldsymbol{r})$
(formation/displacements of the clusters)

$$\beta\Omega_{co}[\zeta]=\frac{\beta}{2}\int d\,\boldsymbol{r}_1\int d\,\boldsymbol{r}_2\,\zeta(\boldsymbol{r}_1)V(r)\,\zeta(\boldsymbol{r}_2)+\int d\,\boldsymbol{r}\,\beta f_h(\zeta(\boldsymbol{r}))-\beta\mu\int d\,\boldsymbol{r}\,\zeta(\boldsymbol{r})$$

where $f_h(\zeta(\boldsymbol{r}))$ is the reference-system free-energy density.

$$\beta H_f=\beta\Omega_{co}[\zeta+\phi]-\beta\Omega_{co}[\zeta]$$

In equilibrium, $\langle\phi\rangle=0$ and the extremum condition has the extra term

$$\frac{\delta\beta\Omega[\zeta]}{\delta\zeta}=\frac{\delta\beta\Omega_{co}[\zeta]}{\delta\zeta}+\left\langle\frac{\delta H_f}{\delta\zeta}\right\rangle=0$$

We assume that the periodic structure is destroyed by long-wavelength fluctuations, and make the approximation

$$\beta H_f[\zeta,\phi] \approx \frac{\beta}{2}\int d\boldsymbol{k}\,\tilde{\phi}(\boldsymbol{k})\tilde{V}(k)\tilde{\phi}(-\boldsymbol{k}) + \int d\boldsymbol{r}\sum_{n>1}\frac{A_n[\zeta]}{n!}\phi(\boldsymbol{r})^n - \beta\bar{\mu}[\zeta]\int d\boldsymbol{r}\,\phi(\boldsymbol{r})$$

where

$$\tilde{V}(k) \approx \tilde{V}(k_0) + v\left(k^2 - k_0^2\right)^2$$

$$A_n[\zeta] = \frac{1}{V_u}\int_{V_u} d\boldsymbol{r}\,a_n(\zeta(\boldsymbol{r})) \qquad a_n(\zeta(\boldsymbol{r})) = \frac{d^n \beta f_h(\zeta(\boldsymbol{r}))}{d\zeta(\boldsymbol{r})^n}$$

and V_u denotes the unit-cell volume of the periodic structure $\zeta(\boldsymbol{r})$.

In the Brazovskii field theory, $\Omega[\zeta]$ can be approximated by

$$\beta\Omega[\zeta]=\beta\Omega_{co}[\zeta]-\log\int D\phi\exp\left(-\beta H_G[\zeta,\phi]\right)+\langle\Delta H\rangle$$

where $\beta H_G[\zeta,\phi]=\frac{1}{2}\int d\boldsymbol{k}\,\tilde{\phi}(\boldsymbol{k})\tilde{C}(k)\tilde{\phi}(-\boldsymbol{k})$, $\Delta H=H_f-H_G$

and $\tilde{C}(k)^{-1}=\langle\tilde{\phi}(\boldsymbol{k})\tilde{\phi}(-\boldsymbol{k})\rangle$, provided that $\Delta H\ll H_G$

In the self-consistent one-loop Hartree approximation for the ϕ^6 theory,

$$\tilde{C}(k)\approx\beta\tilde{V}(k)+A_2[\zeta]+\frac{A_4[\zeta]}{2}\langle\phi^2\rangle+\frac{A_6[\zeta]}{8}\langle\phi^2\rangle^2$$

for the mermaid potential $\langle\phi^2\rangle\approx\frac{\alpha}{\sqrt{\tilde{C}(k_0)}}$ $\alpha=\frac{k_0}{4\pi}\sqrt{\frac{k_BT}{\nu}}$

In this approximation, $\Omega[\zeta]$ is a functional of $\zeta(\boldsymbol{r})$

$$\frac{\beta\Omega[\zeta]}{V}=\frac{\beta\Omega_{co}[\zeta]}{V}+\beta\tilde{V}(k_0)\langle\phi^2\rangle+A_2[\zeta]\langle\phi^2\rangle+\frac{3A_4[\zeta]}{8}\langle\phi^2\rangle^2+\frac{A_6[\zeta]}{12}\langle\phi^2\rangle^3$$

where

$$\alpha^2\approx[\beta\tilde{V}(k_0)+A_2[\zeta]+\frac{A_4[\zeta]}{2}\langle\phi^2\rangle+\frac{A_6[\zeta]}{8}\langle\phi^2\rangle^2]\langle\phi^2\rangle^2$$

In equilibrium, $\Omega[\zeta]$ takes the global minimum.

In the disordered phase $\zeta(\boldsymbol{r})=\zeta_0$, and:

$\beta\Omega_{co}[\zeta_0]/V$ is the grand potential of the homogeneous system with the constant volume fraction ζ_0.

The first correction term comes from the decrease of the internal energy in the presence of the density wave with the wavenumber $k=k_0$ and the amplitude $\sqrt{\langle\phi^2\rangle}$.

The remaining terms come from the decrease of the entropy associated with clustering.

We compare $\Omega[\zeta]$ in the disordered phase in the presence of fluctuations, with the MF approximation for the weakly ordered phase.

Weakly ordered in MF with the amplitude Φ (standing density wave)

$$\frac{\beta\Omega_{co}(\zeta_0,\Phi)}{V}=\frac{\beta\Omega_{co}(\zeta_0)}{V}+\beta\tilde{V}_{co}(k_0)\frac{\Phi^2}{2}+\sum_{n\geq 2}\frac{a_n(\zeta_0)}{n!}\kappa_n\Phi^n$$

$$\frac{\beta\Omega(\zeta)}{V}=\frac{\beta\Omega_{co}(\zeta_0)}{V}+\beta\tilde{V}_{co}(k_0)\langle\phi^2\rangle+a_2(\zeta_0)\langle\phi^2\rangle+\frac{3a_4(\zeta_0)}{8}\langle\phi^2\rangle^2+\frac{a_6(\zeta_0)}{12}\langle\phi^2\rangle^3$$

Disordered, with fluctuations $\langle\phi^2\rangle$

The aggregation of particles influences the internal energy in a similar way when the aggregates are localized or not, with $\Phi^2/2$ and $\langle\phi^2\rangle$ playing analogous roles.

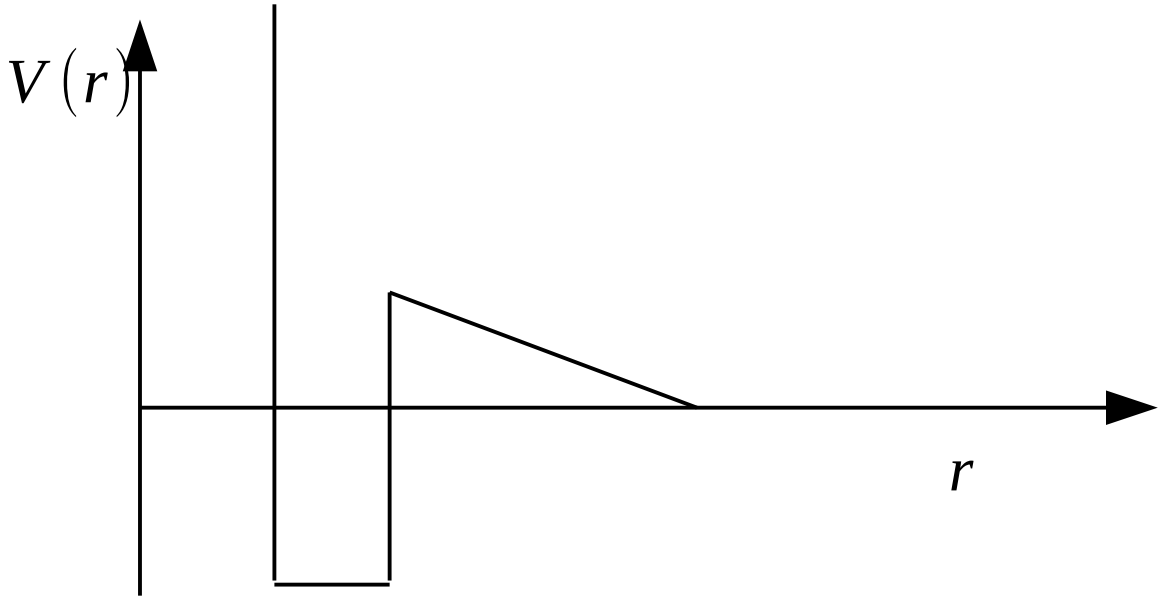
In the same way the fluctuation contribution can be included for the periodic structures. In the case of weak order (high T) the phase diagram can be found easily

In the case of weak order, the equilibrium condition reduces to 2 equations for each set of the geometric factors

$$\frac{\partial \beta \Omega_{co}(\zeta_0, \Phi)}{\partial \zeta_0} + \left\langle \frac{\partial H_f(\zeta_0, \Phi)}{\partial \zeta_0} \right\rangle = 0 \qquad \frac{\partial \beta \Omega_{co}(\zeta_0, \Phi)}{\partial \Phi} + \left\langle \frac{\partial H_f(\zeta_0, \Phi)}{\partial \Phi} \right\rangle = 0$$

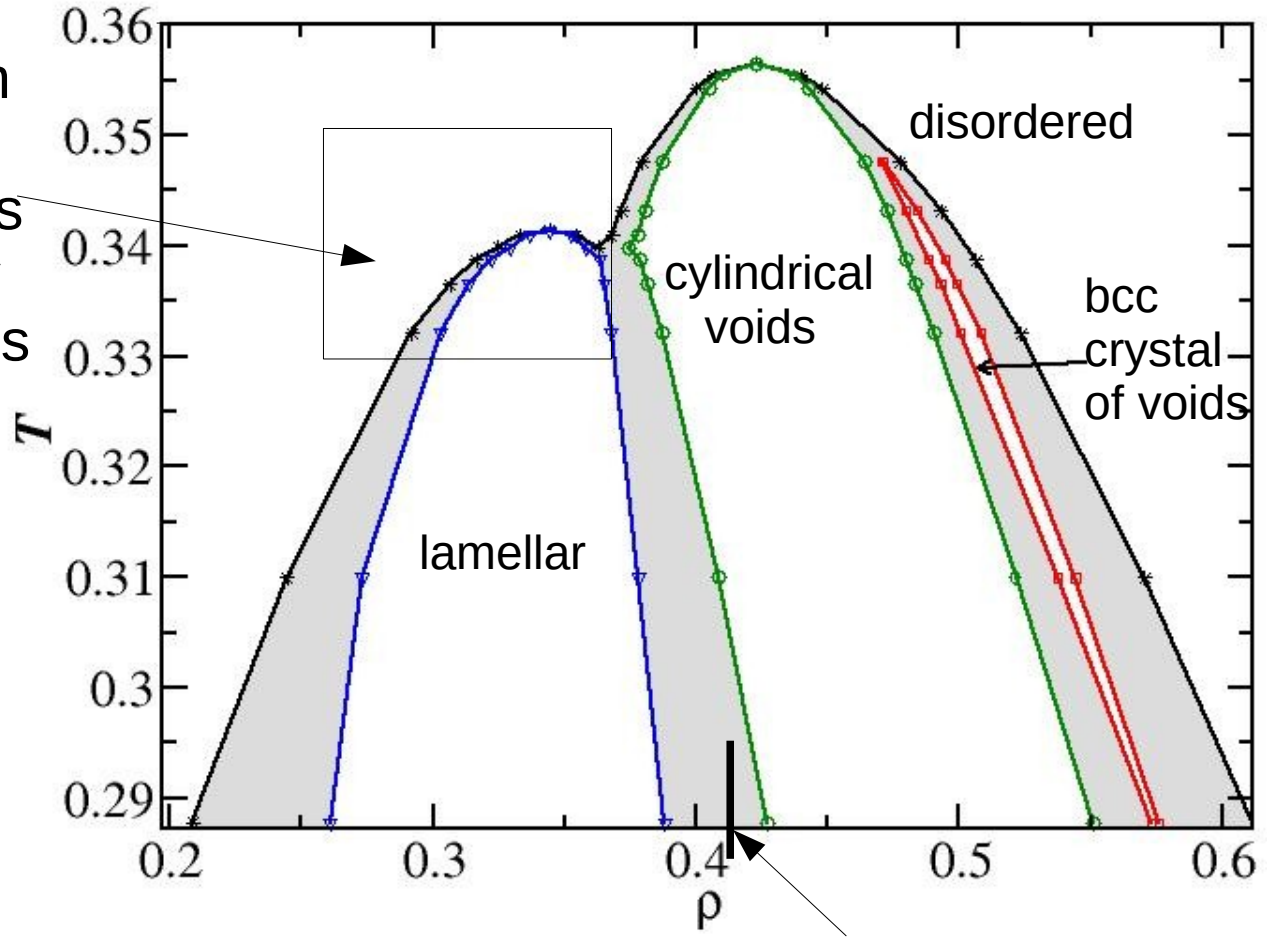
we obtain $\Phi(\zeta_0)$, $\mu(\zeta_0)$, and pressure $p(\zeta_0)$, and by eliminating ζ_0 , we obtain $p(\mu)$ for each periodic structure. From these curves we finally get the high- T part of the phase diagram and the EOS.

To compare with simulations, we assumed the interaction potential of the shape:



This theory in the one-shell approximation

This region can be compared with simulations performed only for low densities

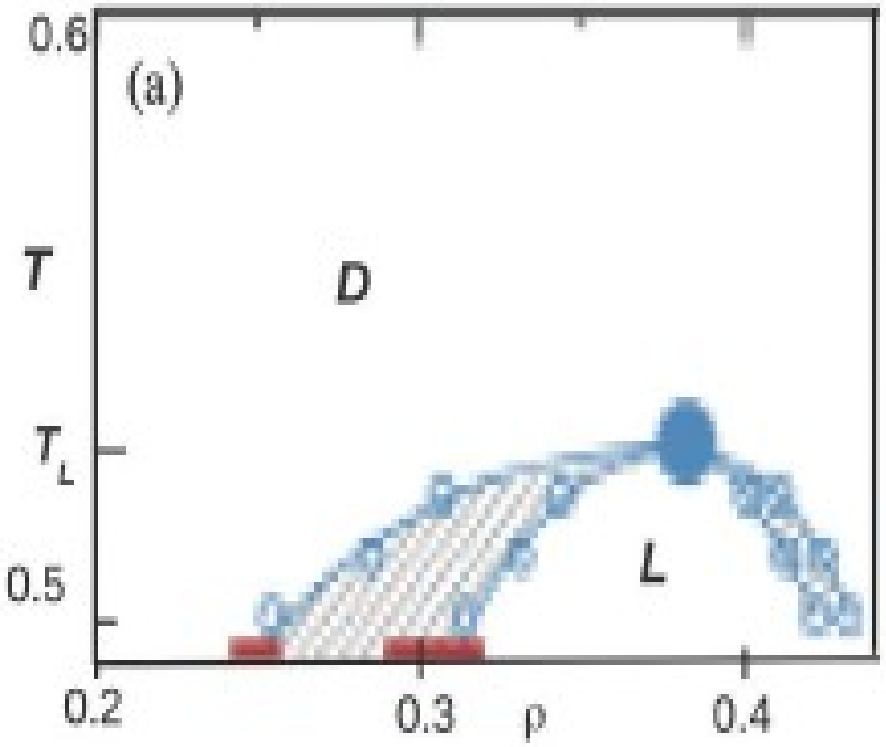


Densities not studied in the simulations

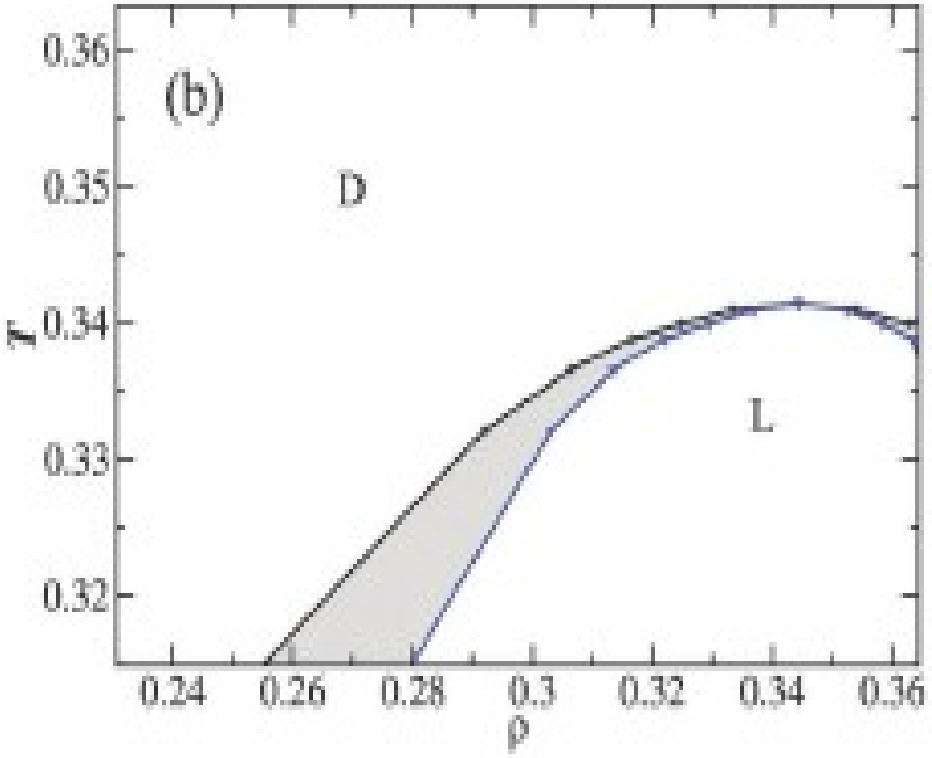
The one-shell approximation for the lamellar phase is valid only at high *T,* where the hexagonal and cubic phases are not stable. At lower T, strong deviations from the sinusoidal shape were observed in DFT (Pini & Parola). The metastable hexagonal and cubic phases appear with decreasing *T i*n the same order as in simulations.

The high-T part of the phase diagram for the same interactions and the same density range as in the simulation studies.

simulation

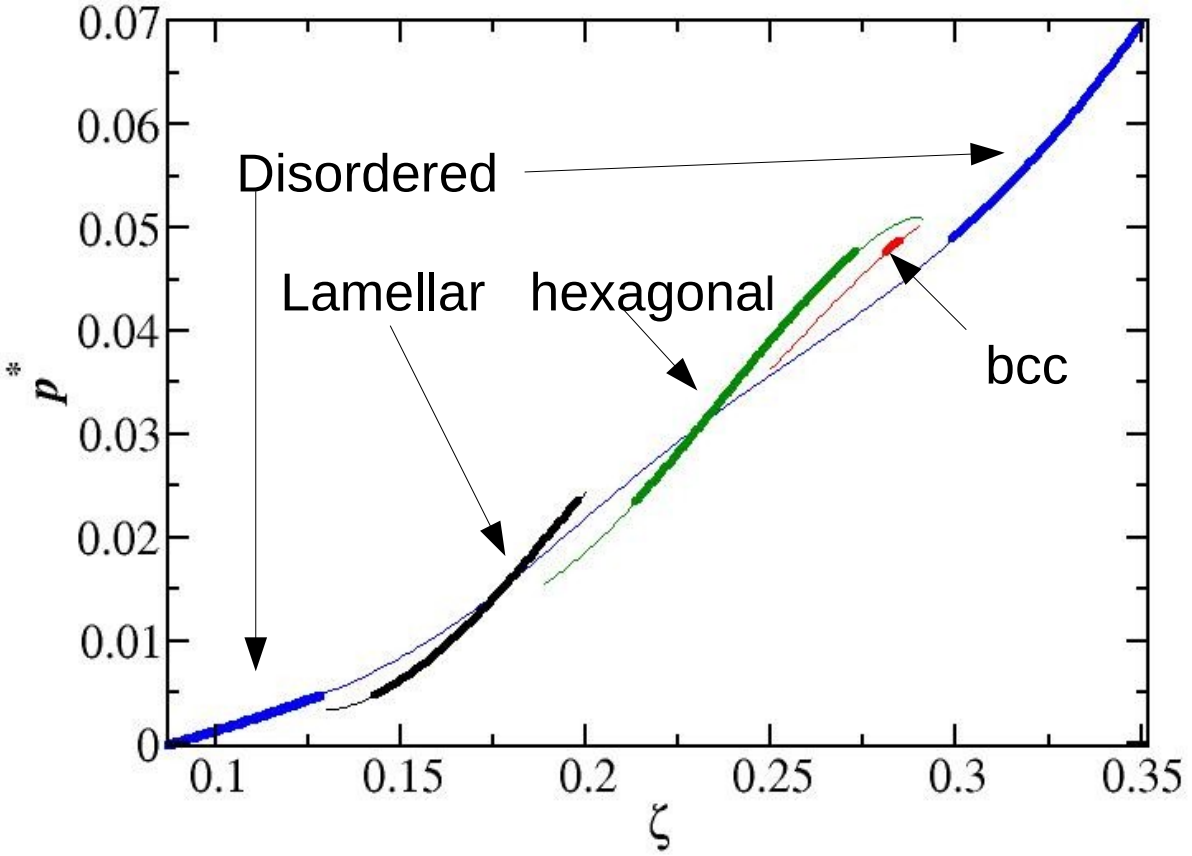


theory



The ordered phases are present at higher density than in MF in both cases. In the theory, the ordered phases appear at lower temperature. It might be associated with the finite-size effect in simulations, where the long-wavelength fluctuations are suppressed by the size of the simulation box. The question of the stability of the hexagonal and cubic phases beyond the one-shell approximation remains open.

EOS



Thin lines concern the corresponding phase in the region of its metastability.
Note the small compressibility of the ordered phases
even in the case of small density.

Summary

The universality of the sequence of ordered phases in self-assembling systems follows from the fact that they can be described by the Landau-Brazovskii functional. This is analogous to universal features of phase transitions in uniform systems described by the Landau functional.

The average value of the energy differs significantly from the energy calculated for the average density. Fluctuations around the average density have to be taken into account to find stability regions of different phases, and to predict properties of the inhomogeneous phase with no translational order. The relevant fluctuations in the disordered phase concern cluster formation, i.e. occur on the mesoscopic length scale.

When the fluctuation contribution is included, a better approximation for the internal energy and the entropy is obtained.
When weakly ordered phases are predicted by MF, we may expect a disordered phase with inhomogeneous distribution of particles.

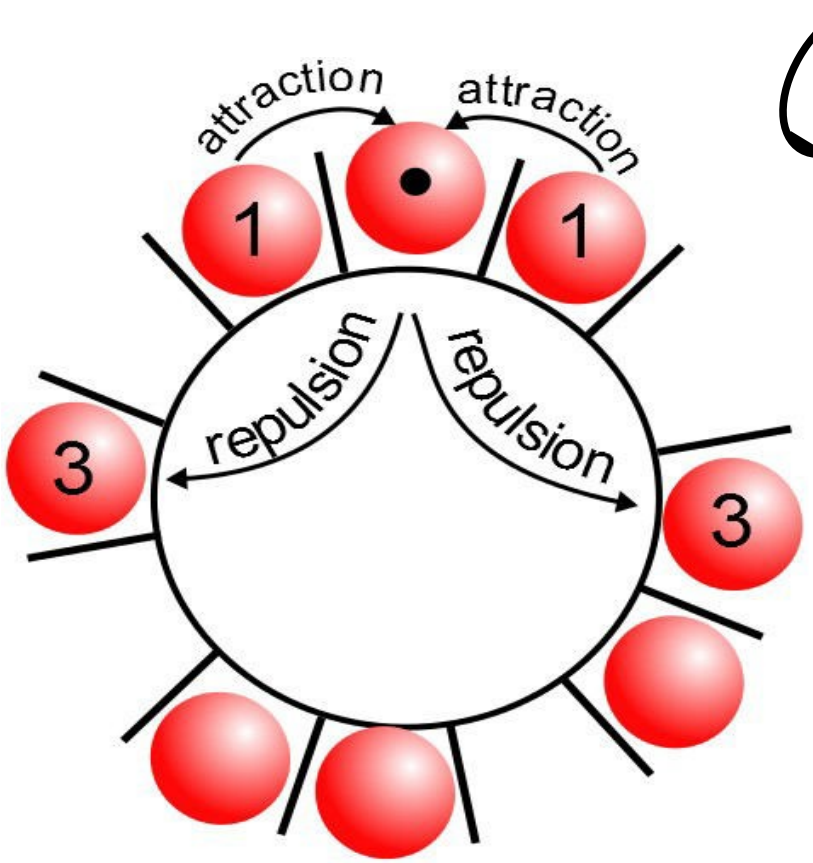
Part II

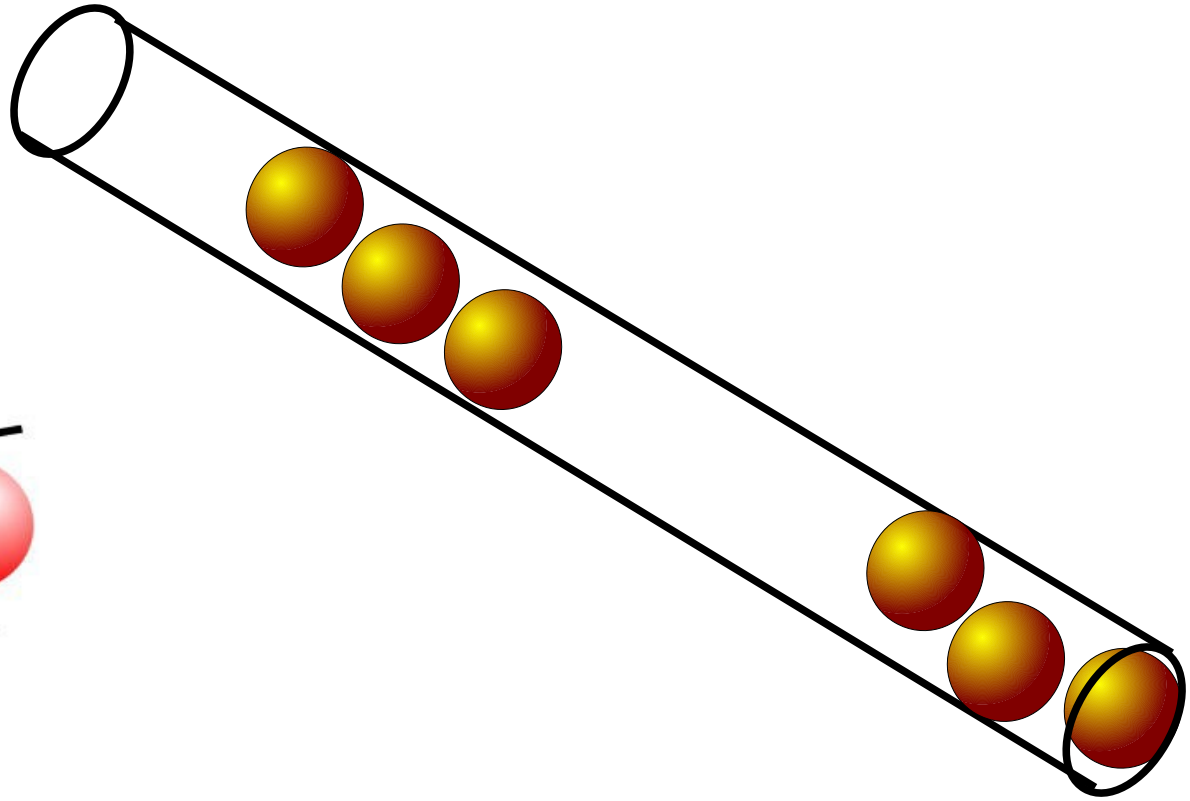
Simple SALR models in 1D and 2D systems

- Ground states in 1D and 2D
- Equation of state in 1D
- Phase diagram in 2D
- Effects of confinement:
anomalies and structural reorganizations

Simple generic lattice model of SALR systems in 1D.

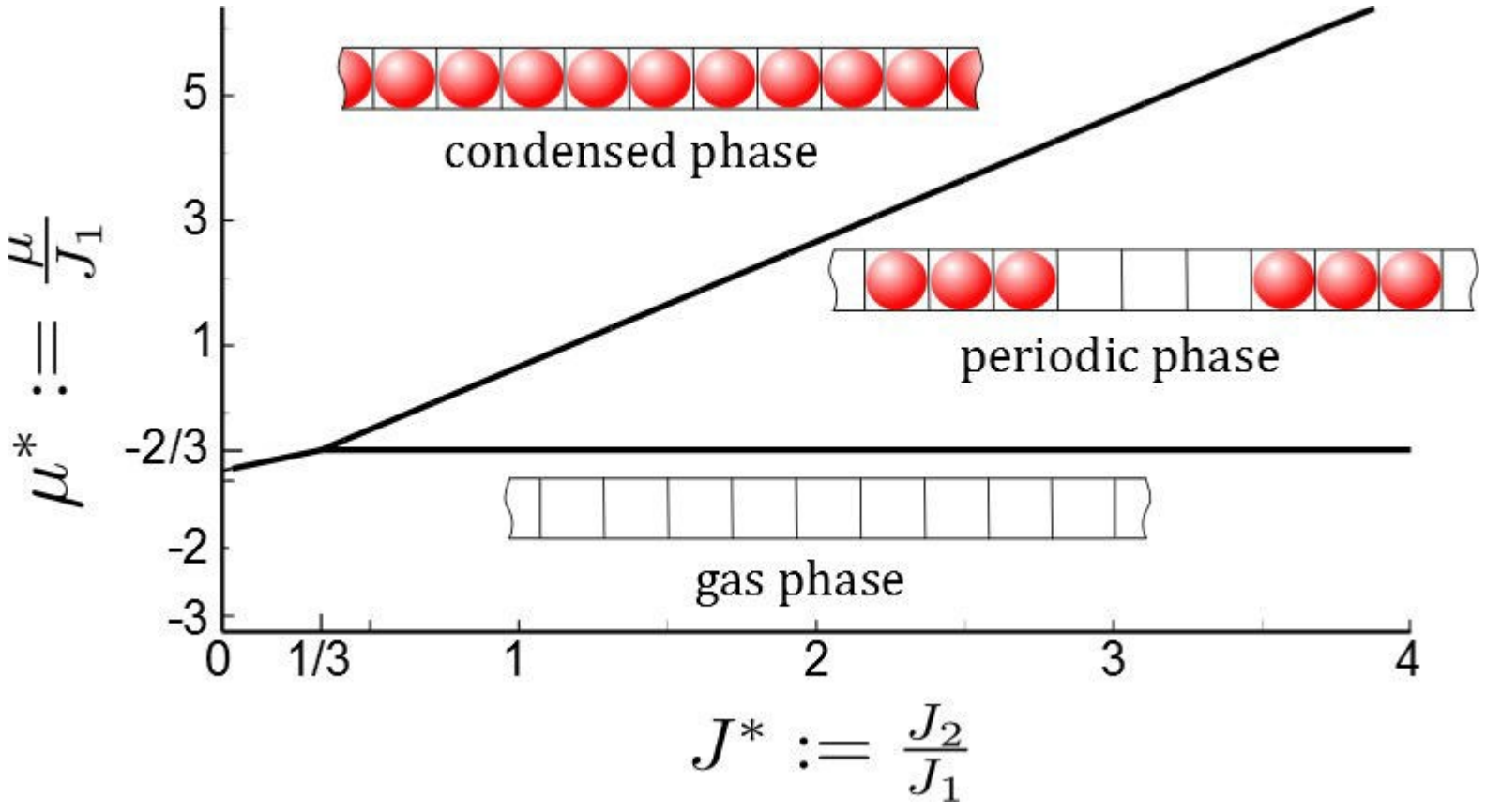
Attraction J_1 between the first and repulsion J_2 between the third neighbors, excluded multiple occupancy of lattice cells.
It can describe charged particles in long tubes, or adsorbed at tubules.





Ground state (T=0) in 1D

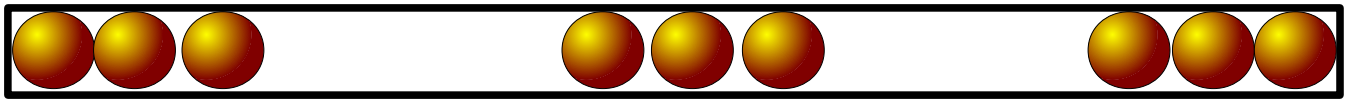
in the reduced chemical potential and the repulsion-to-attraction ratio variables



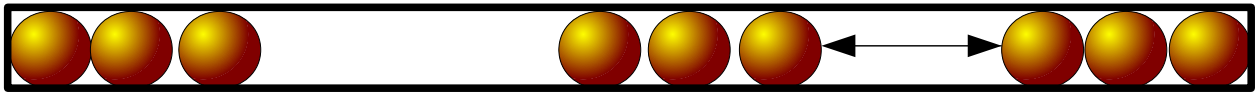
The energetically favored structure in the absence of thermal motion

Effect of the self-assembly into clusters on pressure

Structure at low T and density 1/2



Structure at low T and density >1/2



repulsion between some clusters appears when the distance between them is smaller than the range of repulsion.

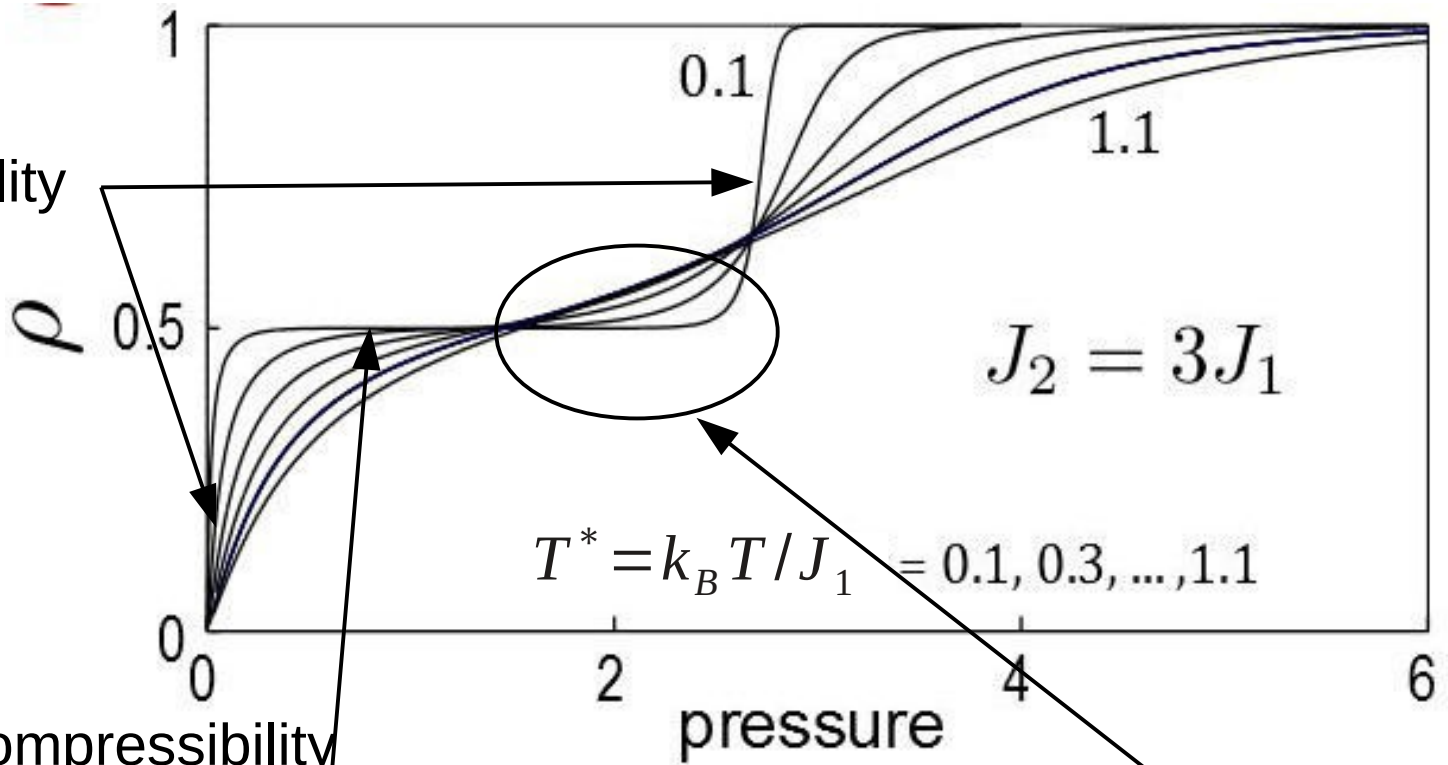
Pressure must overcome the repulsion between the clusters to induce decrease of volume (increase of density). Large increase of pressure is necessary to increase the density at low T.

At high T the particles are more randomly distributed and the pressure changes more gradually with density

Equation of state in the 1D model.

Exact results by the transfer matrix method

Very large compressibility

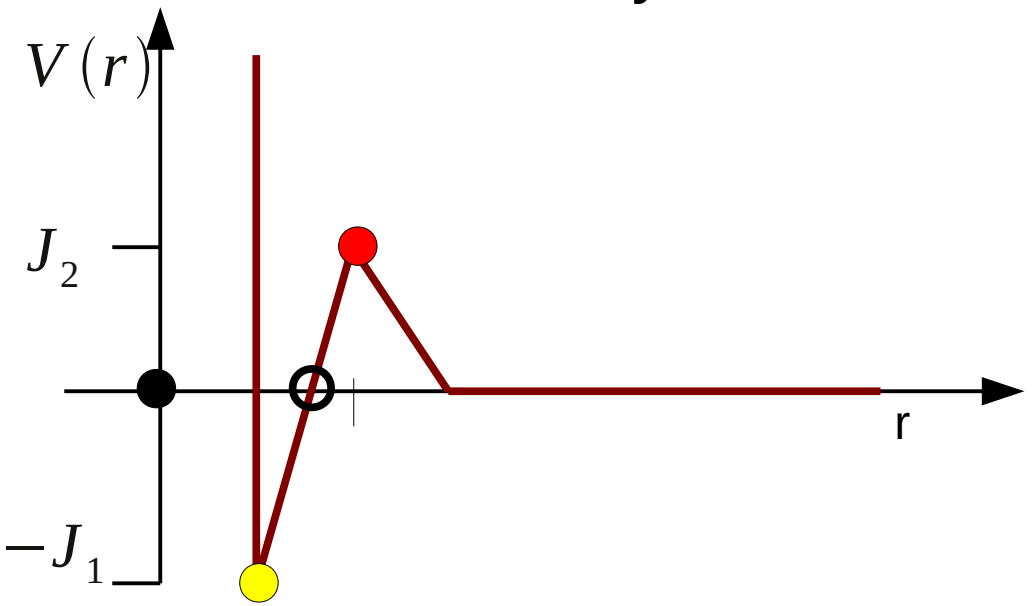


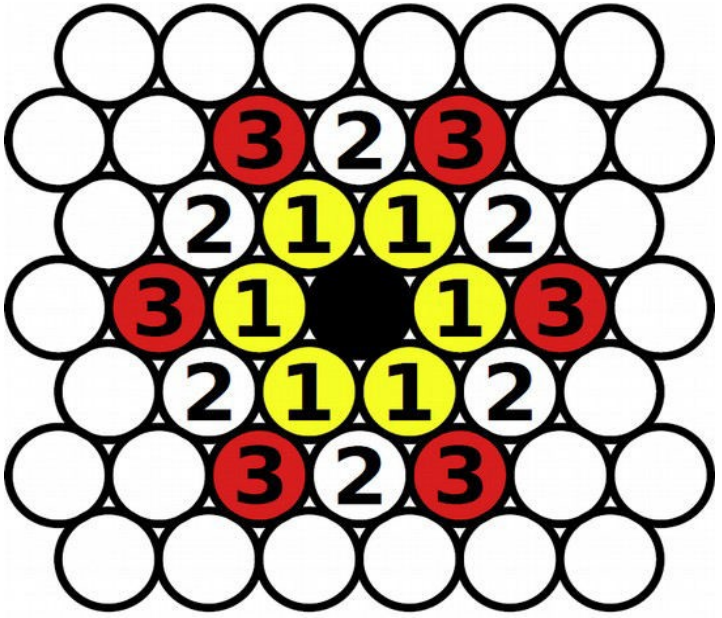
Very small compressibility at the density corresponding to the periodically ordered clusters (no repulsion).
For $\rho > 0.5$ pressure must overcome the repulsion.

Anomalous ***increase*** of pressure for ***decreasing*** T at fixed density ~0.6

J. Pękalski, A. Ciach, N. G. Almarza J. Chem. Phys. **138,** 114903 (2013)

Simple generic model of the SALR systems in 2D



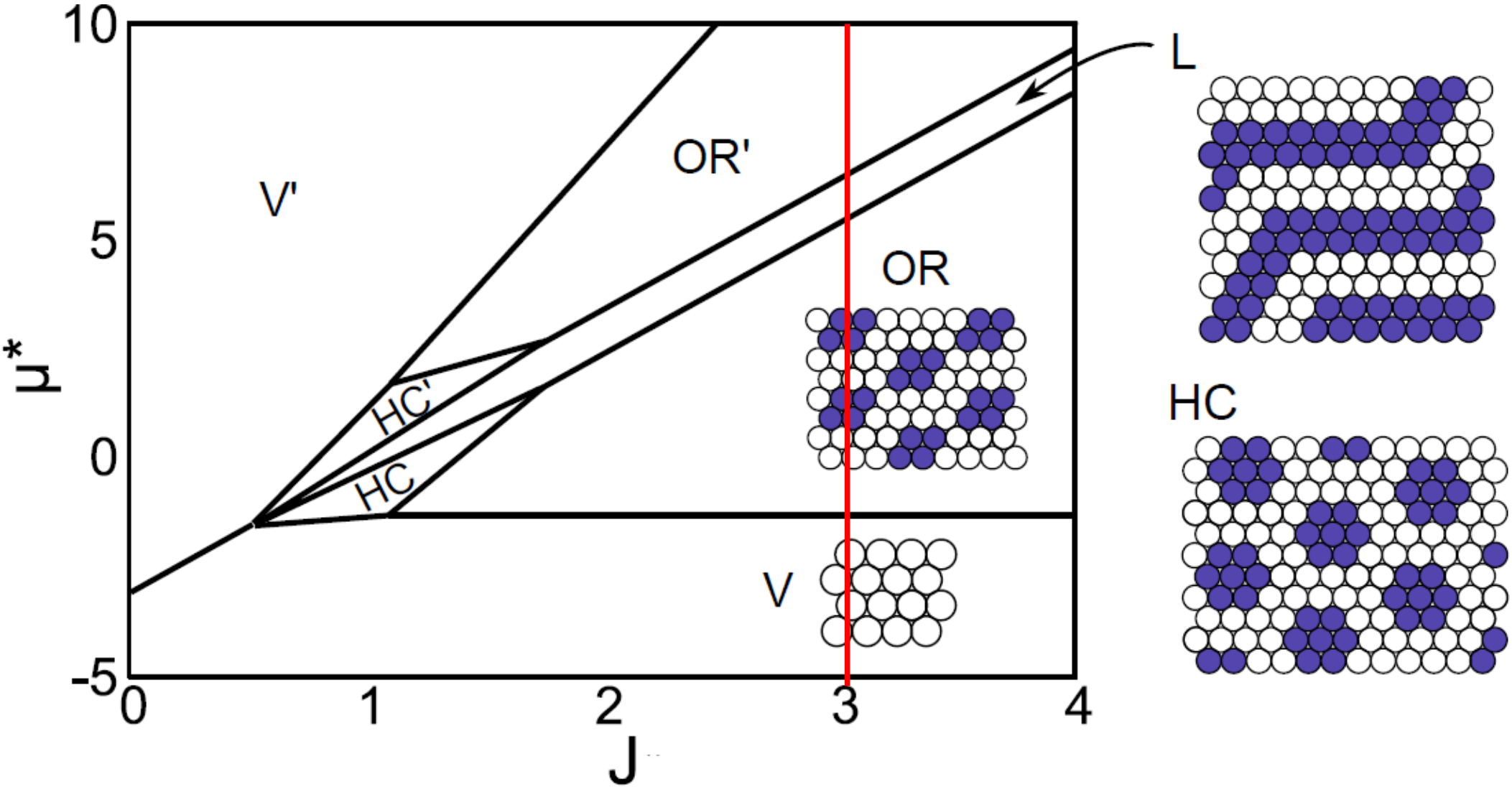


Repulsion to attraction ratio: $J=J_2/J_1$

attracts (first neighbor) and repels (third neighbor)

Ground state (T=0) in 2D

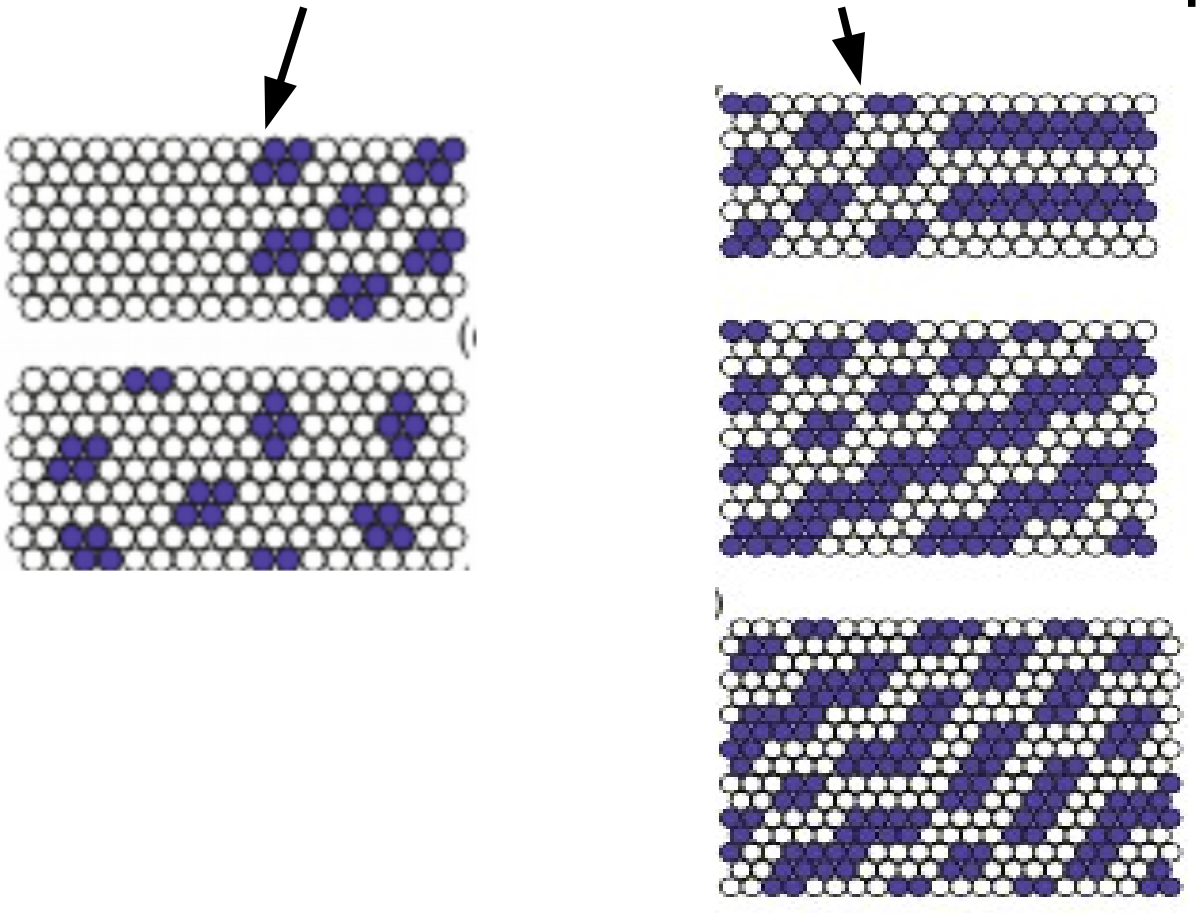
in the reduced chemical potential and the repulsion-to-attraction ratio variables



V', HC' and OR' are “negatives” of V, HC and OP respectively

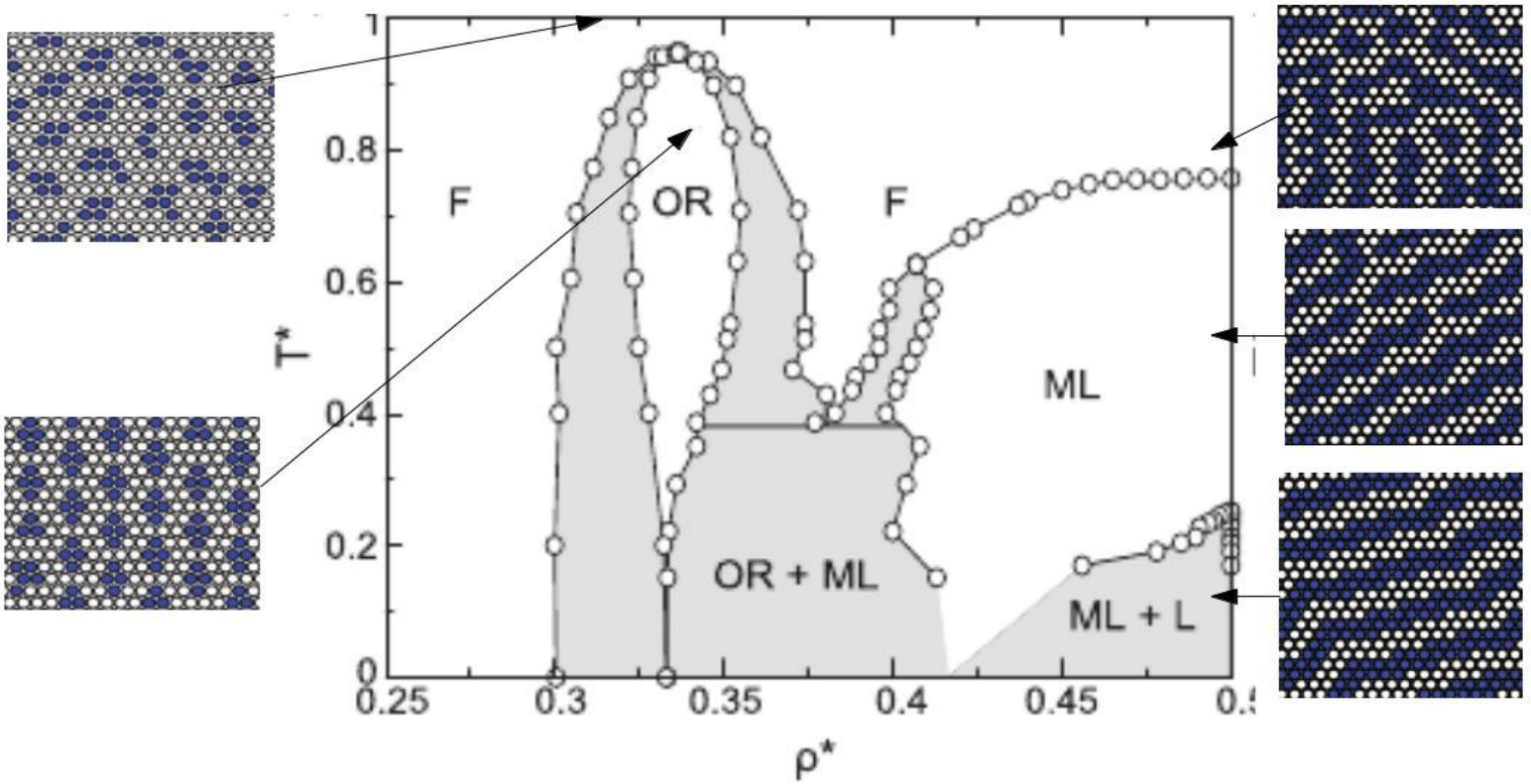
. J. Pękalski, A. Ciach, N. G. Almarza J. Chem. Phys. 140 114701 (2014)

Degeneracy of the GS at the coexistence between the vacuum – OR and OR - lamellar phases



The entropy per lattice site does not vanish, and the surface tension between the two ordered phases vanishes at the phase coexistence. We interpret this state as a disordered inhomogeneous phase coexisting with the two ordered phases. This disorder is not induced by thermal motion!

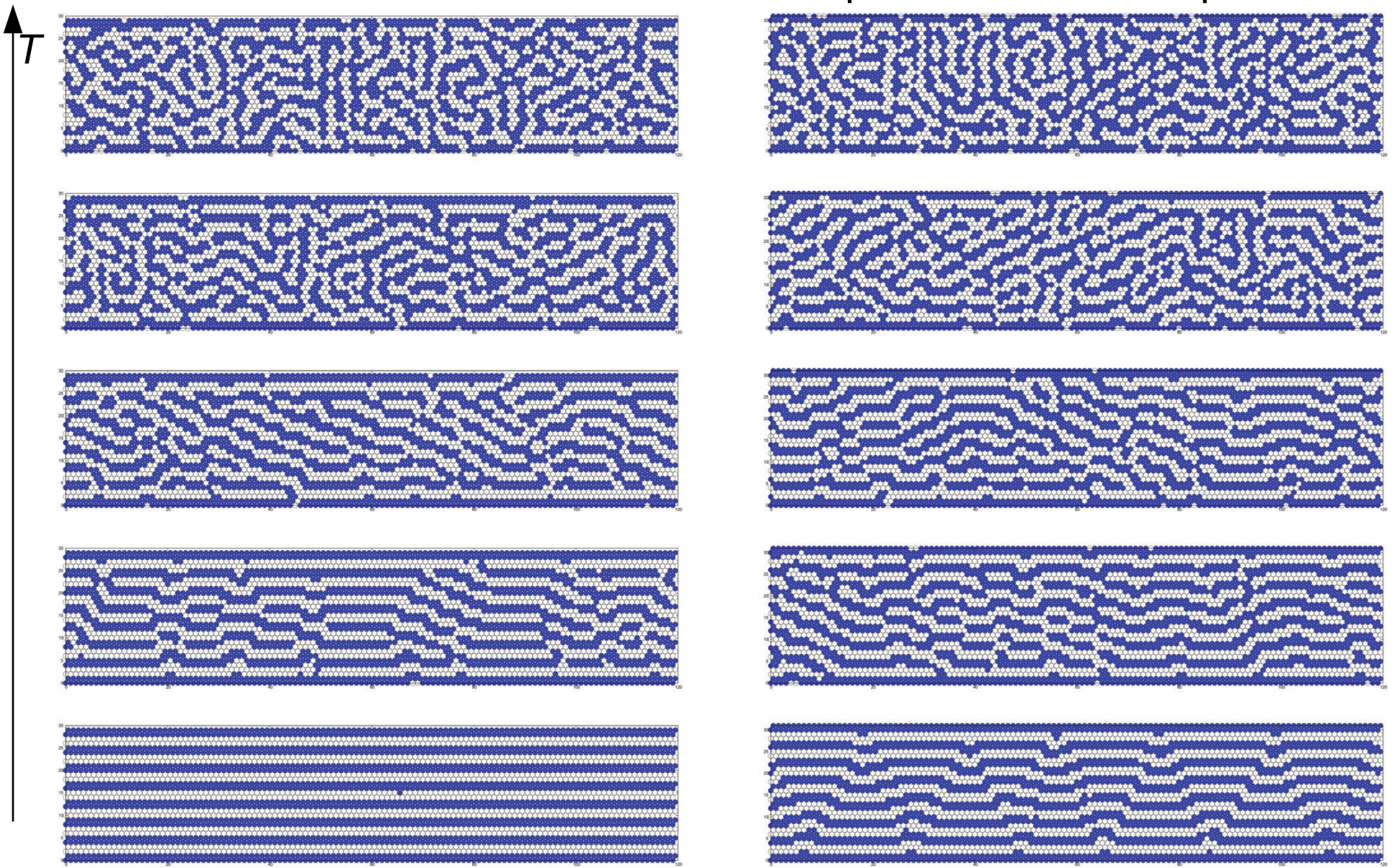
Phase diagram in the 2D model obtained by MC simulations



F is an isotropic fluid with no translational order
ML is the molten lamella phase with orientational and without translational order
L is the lamellar phase with both orientational and translational order
OR is the cluster phase with hexagonally ordered rhombuses

N. G. Almarza, J. Pękalski, A. Ciach J. Chem. Phys. **140** 164708 (2014)

Slit with attractive walls, the chemical potential favors stripes

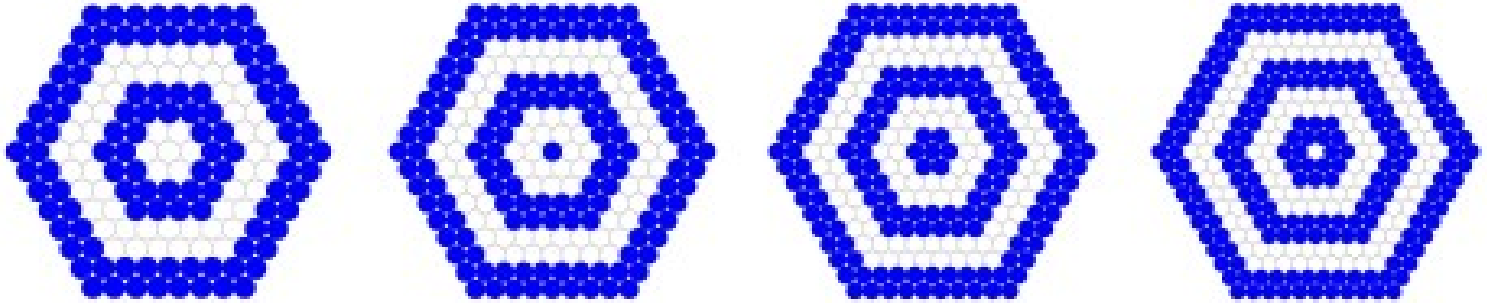


Width commensurate with the period

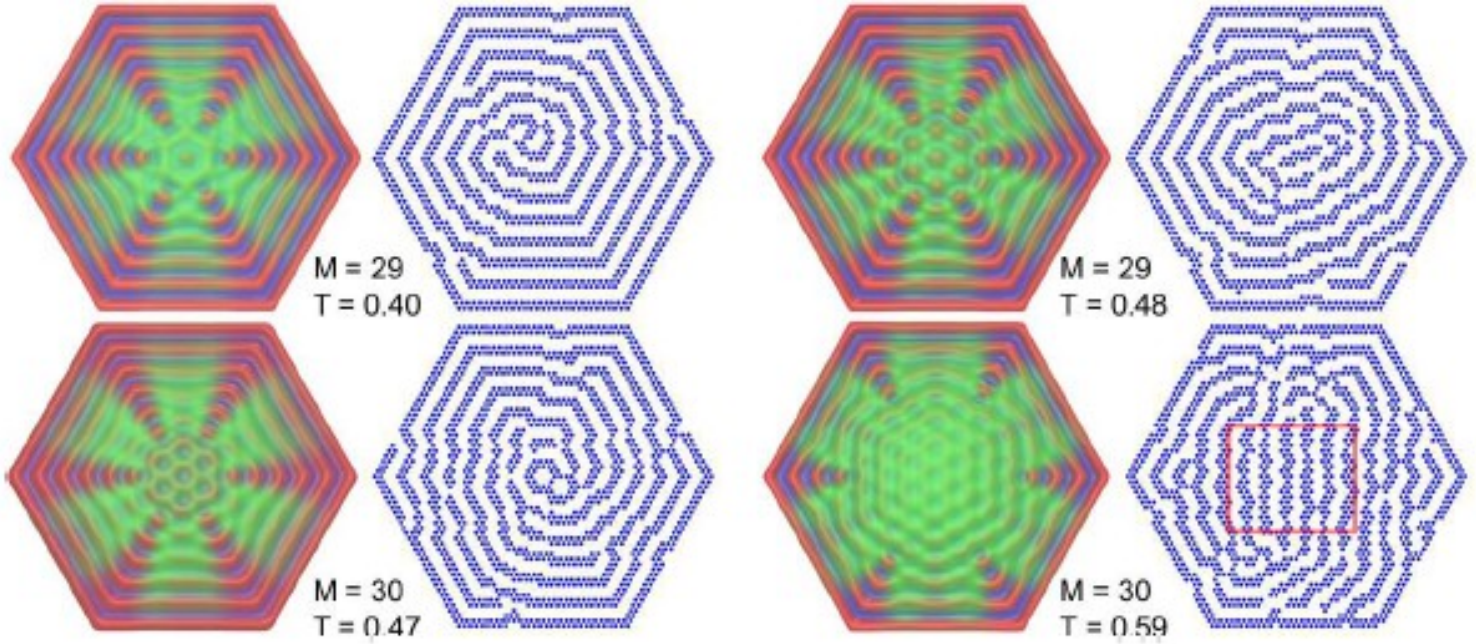
Width incommensurate with the period

N. G. Almarza, J. Pękalski and A. Ciach, Soft Matter, **12,** 7551 (2016)

Hexagonal confinement, attractive walls



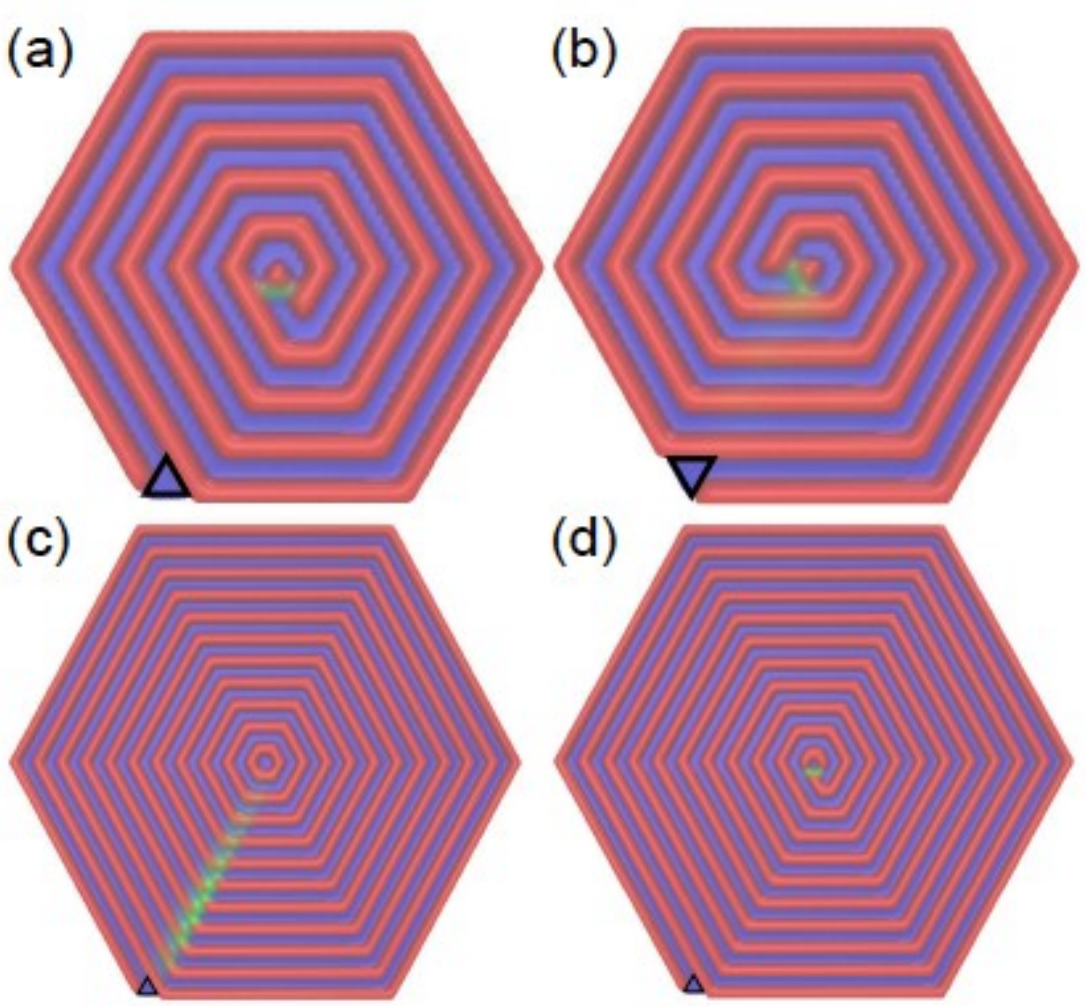
Ground states for different sizes



Maps of average density (left columns)
and typical snapshots (right columns, in blue)

Average densities in a presence of a triangular wedge.

Spirals with a chirality depending on the orientation of the wedge are formed, except from the hexagons with no central defect (with appropriate edge lengths).



J. Pękalski, E. Bildanau, A. Ciach, to be published

Summary of part II

•Self-assembly leads to various anomalies, such as:
-vanishing surface tension between ordered phases at T=0
-increase of pressure for decreasing T or increasing volume

•Confinement can have both disordering and ordering effects

•Ordered patterns absent in the bulk may occur in confinement

•Globally chiral structures with designed chirality can occur spontaneously in closed systems with symmetry of the boundaries broken by a tiny obstacle