Melting in two dimensional passive & active matter

Leticia F. Cugliandolo

Sorbonne Université

Institut Universitaire de France

`leticia@lpthe.jussieu.fr`
`www.lpthe.jussieu.fr/˜leticia`

Work in collaboration with

G. Gonnella, **P. Digregorio & I. Petrelli** (Bari, Italia)

A. Suma (Trieste, Italia & Philadelphia, USA)

D. Levis & I. Pagonabarraga (Barcelona, España & Lausanne, Suisse)

La Habana, Cuba, 2024

Aim

Better understanding of melting in two dimensions

Why $2d$?

Experimental realisations but in reality,

because it is interesting from a

fundamental viewpoint

a talk about a classical problem and a

timely active extension

Plan

1. Equilibrium phases: solidification/melting

   Special in two-dimensions

   Solid, hexatic & liquid phases

   Phase transitions

   Topological defects

2. Active matter

   Self-propelled Brownian disks in $2d$

   Phase diagram

   Solid, hexatic & liquid phases ; motility induced phase separation

Plan

1. **Equilibrium phases : solidification/melting**

   Special in two-dimensions

   Solid, hexatic & liquid phases

   Phase transitions

   Topological defects

2. Active matter

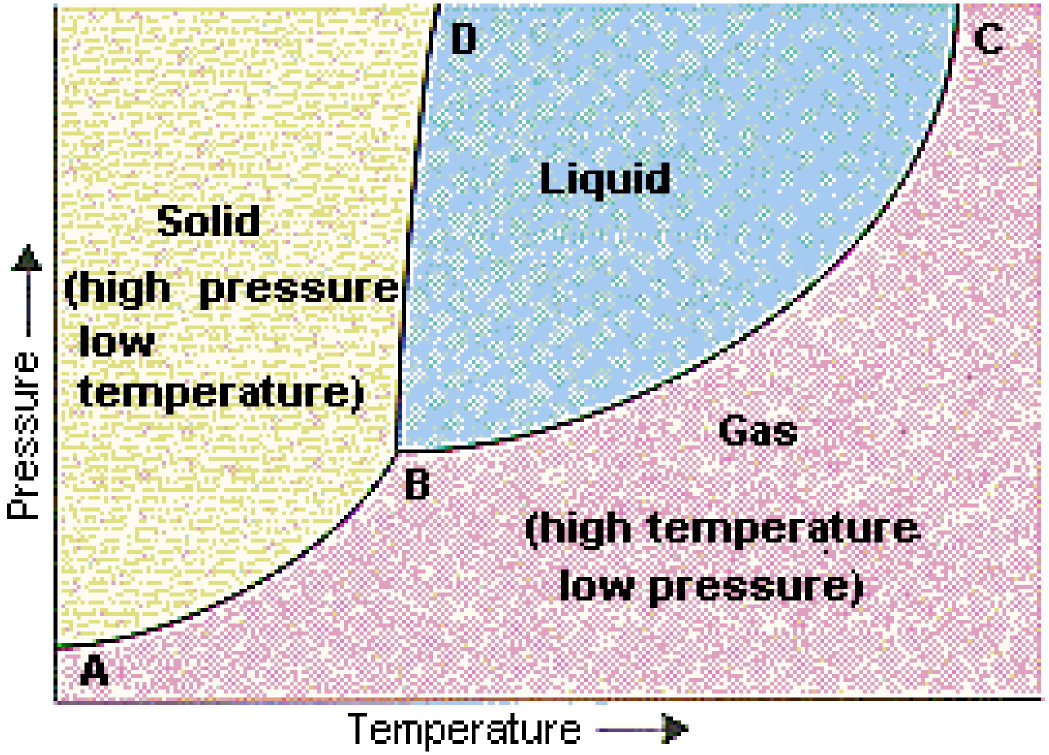
   Self-propelled Brownian disks in $2d$

   Phase diagram

   Solid, hexatic & liquid phases ; motility induced phase separation

Phases of matter

Solid, liquid and gas equilibrium phases



Typical & simple (P, T) phase diagram

Equilibrium phases

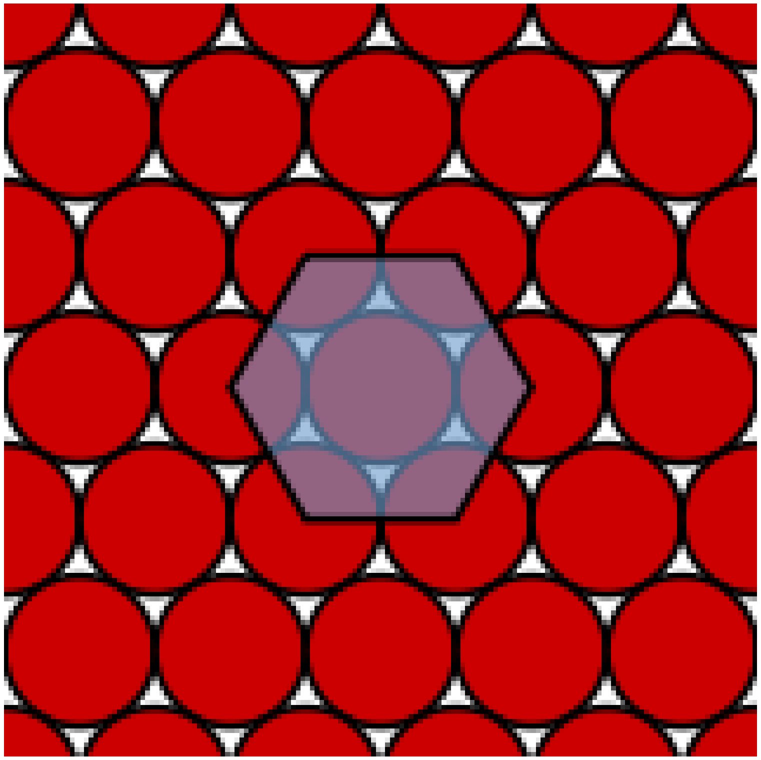
Macroscopic properties

- A gas is an an air-like fluid substance which expands freely to fill any space available, irrespective of its quantity.
- A liquid is a substance that flows freely but is of constant volume, having a consistency like that of water or oil. It takes the shape of its container
- A solid is a material with non-vanishing shear modulus.
- A crystal is a system with long-range positional order.

  It has a periodic structure and its ‘particles’ are located close to the nodes of a lattice.

Hard disks in $2d$

Zero temperature crystal : triangular lattice w/6 nearest neigh.

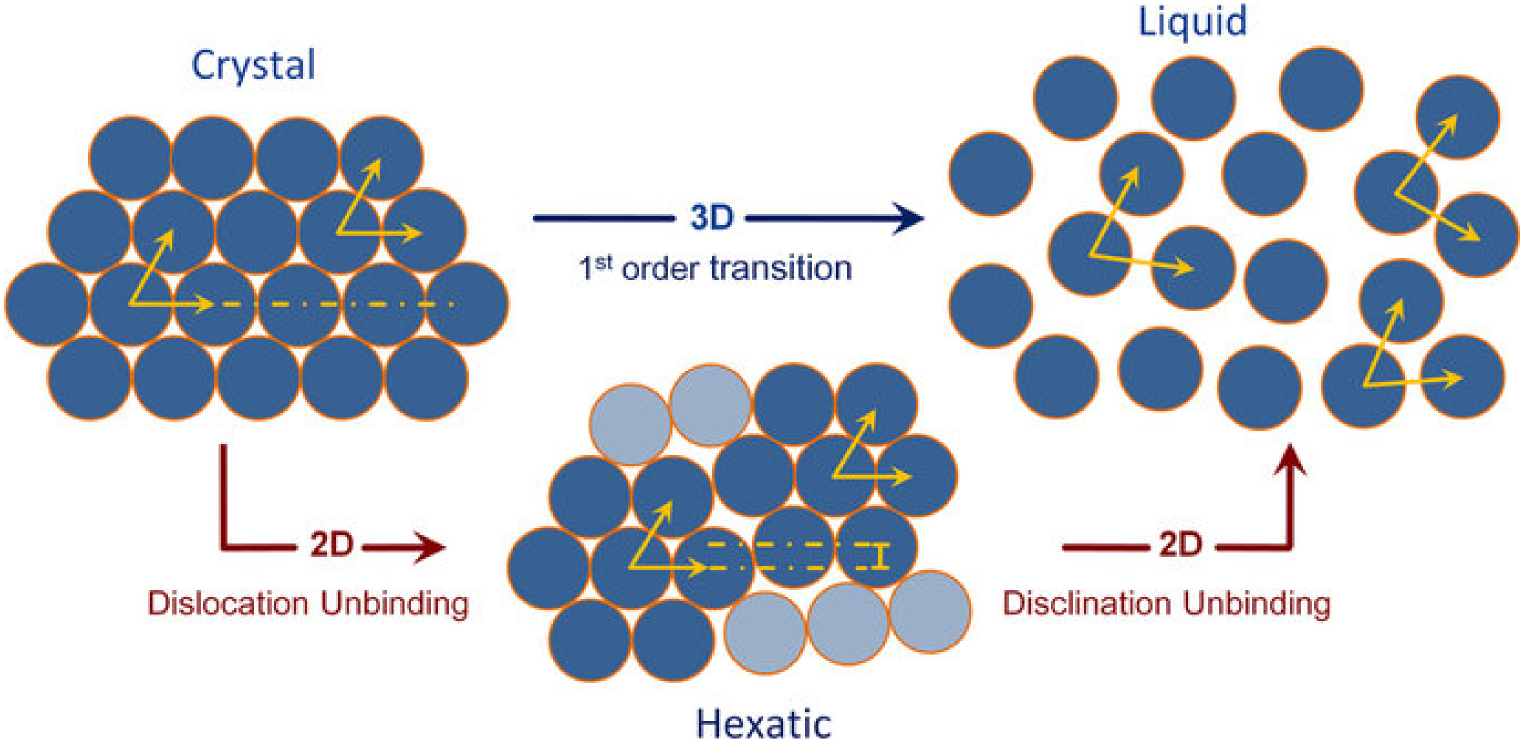


$d = 2$ packing fraction $\phi = S_{\mathrm{occupied}}/S$ at close packing $\phi_{\mathrm{cp}} \approx 0.91$

Freezing/Melting

Different routes in $3d$ and $2d$: mechanisms ?

$T = 0$ Position & orientation order lost



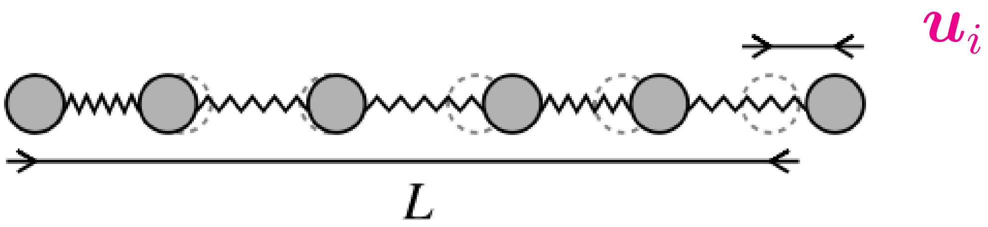
Orientation order preserved also lost

Image from **Pal, Kamal & Raghunathan, Sc. Rep. 6, 32313 (2016)**

Harmonic solids

Peierls 30s: no finite T translational long-range order in $2d$

Consider a crystal made of atoms connected to their nearest-neighbours by Hooke springs. At finite T the atomic positions, ϕ_i, fluctuate, $\phi_i = \boldsymbol{R}_i + \boldsymbol{u}_i$, with $\boldsymbol{u}_i$ the local displacement from a regular lattice site at $\boldsymbol{R}_i$



Open dashed: perfect lattice positions $\boldsymbol{R}_i$ Filled gray: actual positions ϕ_i

Does the long-range positional order (crystal) survive at finite T?

not in $d = 2$ since the mean-square displacement grows with distance

$$\boxed{\Delta^2(\boldsymbol{r}) \equiv \langle (\boldsymbol{u}(\boldsymbol{r}) - \boldsymbol{u}(\boldsymbol{0}))^2 \rangle \simeq k_B T \, \ln r}$$

Positional order

Local density properties

The (fluctuating) local particle number density

$$\rho(\boldsymbol{r}_0) = \sum_{i=1}^{N} \delta(\boldsymbol{r}_0 - \boldsymbol{r}_i)$$

with normalisation $\int d^d\boldsymbol{r}_0\, \rho(\boldsymbol{r}_0) = N$. In a homogeneous system, the *coarse-grained* (averaged over a volume v) local density is constant $[[\rho(\boldsymbol{r}_0)]] = N/V$

Fluctuations

The density-density correlation function $C(\boldsymbol{r} + \boldsymbol{r}_0, \boldsymbol{r}_0) = \langle \rho(\boldsymbol{r} + \boldsymbol{r}_0)\rho(\boldsymbol{r}_0) \rangle$

The average $\langle \ldots \rangle$ is over configurations in a steady state

For homogeneous (independence of $\boldsymbol{r}_0$) and isotropic ($\boldsymbol{r} \mapsto |\boldsymbol{r}| = r$) cases, is simply $C(\boldsymbol{r} + \boldsymbol{r}_0, \boldsymbol{r}_0) = C(r)$

The double sum in $C(\boldsymbol{r} + \boldsymbol{r}_0, \boldsymbol{r}_0) = \langle \sum_{ij} \delta(\boldsymbol{r} + \boldsymbol{r}_0 - \boldsymbol{r}_i)\delta(\boldsymbol{r}_0 - \boldsymbol{r}_j) \rangle$ has contributions from $i = j$ and $i \neq j$: $C_{\text{self}} + C_{\text{diff}}$

Positional order

Local density properties

The density-density correlation function

$$C(\boldsymbol{r}+\boldsymbol{r}_0,\boldsymbol{r}_0) = \langle\rho(\boldsymbol{r}+\boldsymbol{r}_0)\rho(\boldsymbol{r}_0)\rangle = \textstyle\sum_{ij}\langle\delta(\boldsymbol{r}+\boldsymbol{r}_0-\boldsymbol{r}_i)\delta(\boldsymbol{r}_0-\boldsymbol{r}_i)\rangle$$

is linked to the structure factor

$$S(\boldsymbol{q}) \equiv N^{-1}\langle\tilde{\rho}(\boldsymbol{q})\tilde{\rho}(-\boldsymbol{q})\rangle = \frac{1}{N}\langle\sum_{i=1}^{N}\sum_{j=1}^{N} e^{-\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\rangle$$

with $\tilde{\rho}(\boldsymbol{q})$ the Fourier transform of $\rho(\boldsymbol{r})$ by

$$N\,S(\boldsymbol{q}) \;=\; \int d^d\boldsymbol{r}_1\int d^d\boldsymbol{r}_2\, C(\boldsymbol{r}_1,\boldsymbol{r}_2)\, e^{-\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}$$

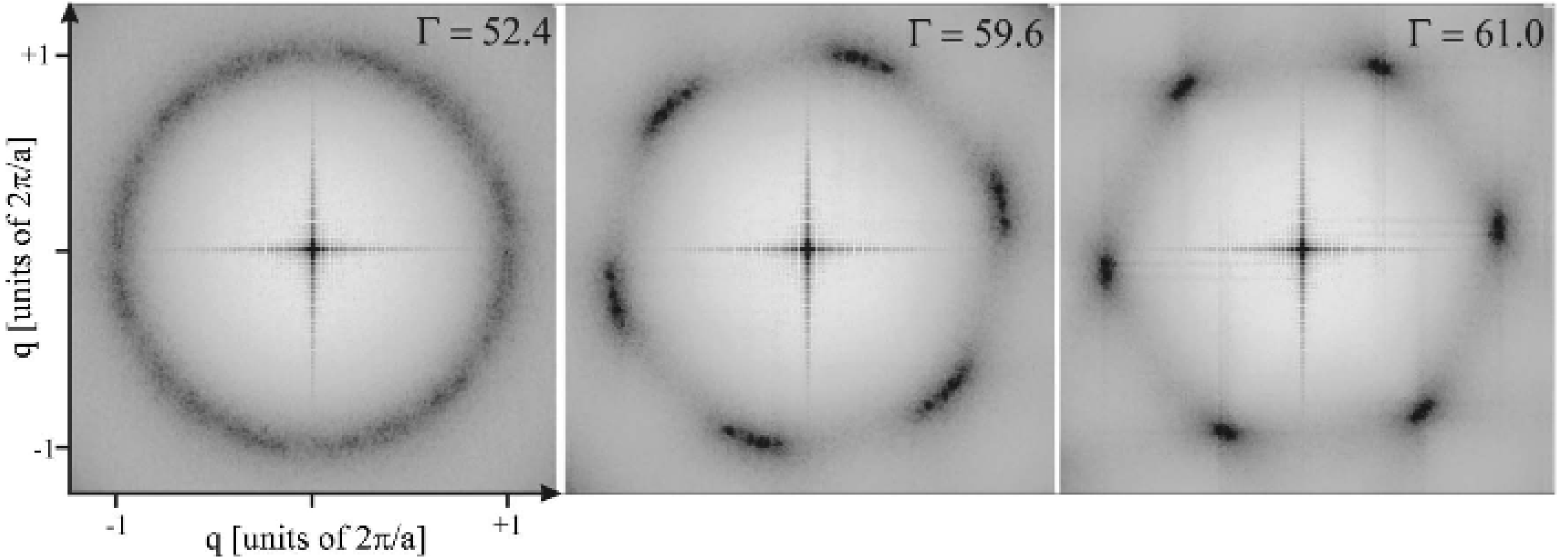
Exercise : prove it

Colloidal suspensions

Structure factor: from fuzzy peaks to a disk as T increases

$$S(\boldsymbol{q}) \equiv N^{-1}\langle\tilde{\rho}(\boldsymbol{q})\tilde{\rho}(-\boldsymbol{q})\rangle = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle e^{-\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)}\rangle$$

High T Low T



Liquid (later) Solid

Figure from **Keim, Maret and von Grünberg, PRE 75, 031402 (2007)**

Crystals vs. Solids

$3d$ vs. $2d$

- A solid is a material with non-vanishing shear modulus.
- A crystal is a system with long-range positional order.

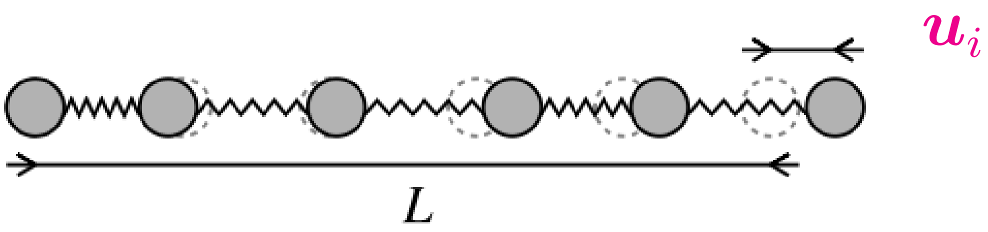
  It has a periodic structure and its 'particles' are located close to the nodes of a lattice.

  The position fluctuations are bounded $\Delta^2 = \langle (\boldsymbol{r}_i - \boldsymbol{r}_i^{\rm latt}) \rangle < \infty$
- $2d$ solids exist but have a weaker ordering than $3d$ ones.
  - They are oriented crystals with no positional order.
  - Critical phase with algebraic relaxation of position correlations.
  - Phase transition *à la* Kosterlitz-Thouless (Nobel Prize).

Harmonic solids

Peierls 30s: but finite T orientational long-range order possible

Consider a crystal made of atoms connected to their nearest-neighbours by Hooke springs. At finite T the atomic positions, ϕ_i, fluctuate, $\phi_i = \boldsymbol{R}_i + \boldsymbol{u}_i$, with $\boldsymbol{u}_i$ the local displacement from a regular lattice site at $\boldsymbol{R}_i$



Dashed: perfect lattice positions $\boldsymbol{R}_i$ Gray: actual positions ϕ_i

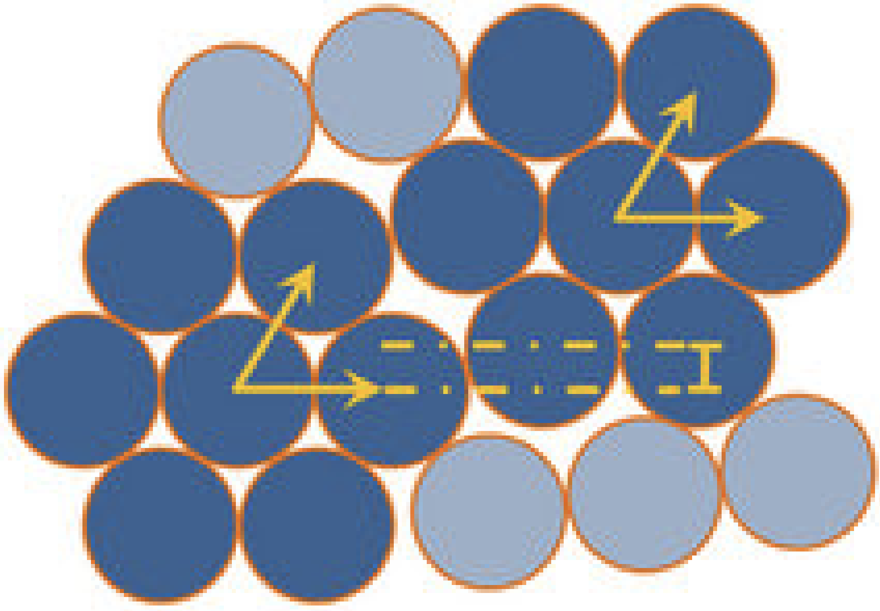
Does the long-range orientational order (solid) survive at finite T?

yes, even in $d = 2$ since the correlation

$$\boxed{C_{\rm orient}(\boldsymbol{r}) \equiv \langle \boldsymbol{u}(\boldsymbol{r}) \cdot \boldsymbol{u}(\boldsymbol{0}) \rangle \to \text{cst}}$$

Harmonic solids

No long-range translational but long-range orientational order



Angles preserved while no periodic order of the disks’ centres.

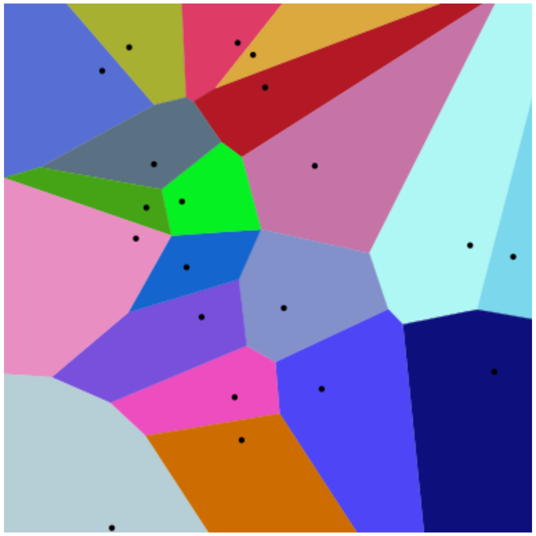
How can one quantify orientational order in general ?

Neighbourhood

Voronoi tessellation to identify nearest-neighbours

A Voronoi diagram is induced by a set of points, called sites, that in our case are the centres of the disks.

The plane is subdivided into faces that correspond to the regions where one site is closest.



Focus on the central light-green face

All points within this region are closer to the dot within it than to any other dot on the plane

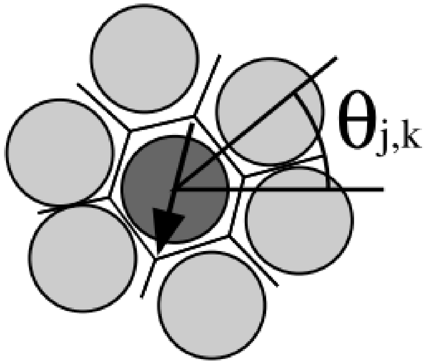
The region has five neighbouring cells from which it is separated by an edge

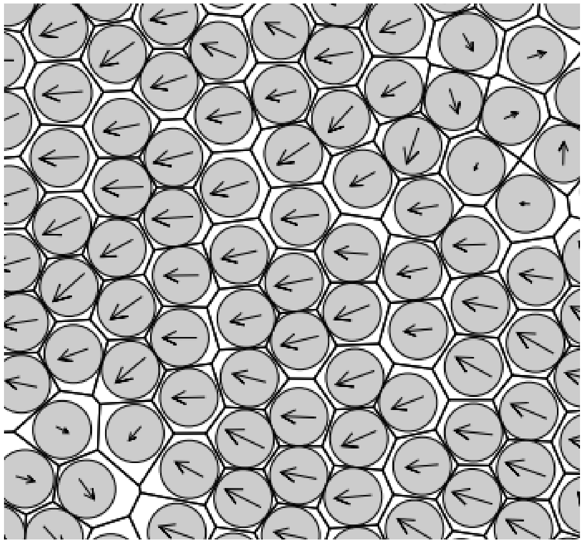
The grey zone has six neighbouring cells

Orientational order

Hexatic order parameter

The local (six) order parameter $\psi_{6j} = \frac{1}{N_{\rm nn}^j} \sum_{k=1}^{N_{\rm nn}^j} e^{6{\rm i}\theta_{jk}}$ (vector)





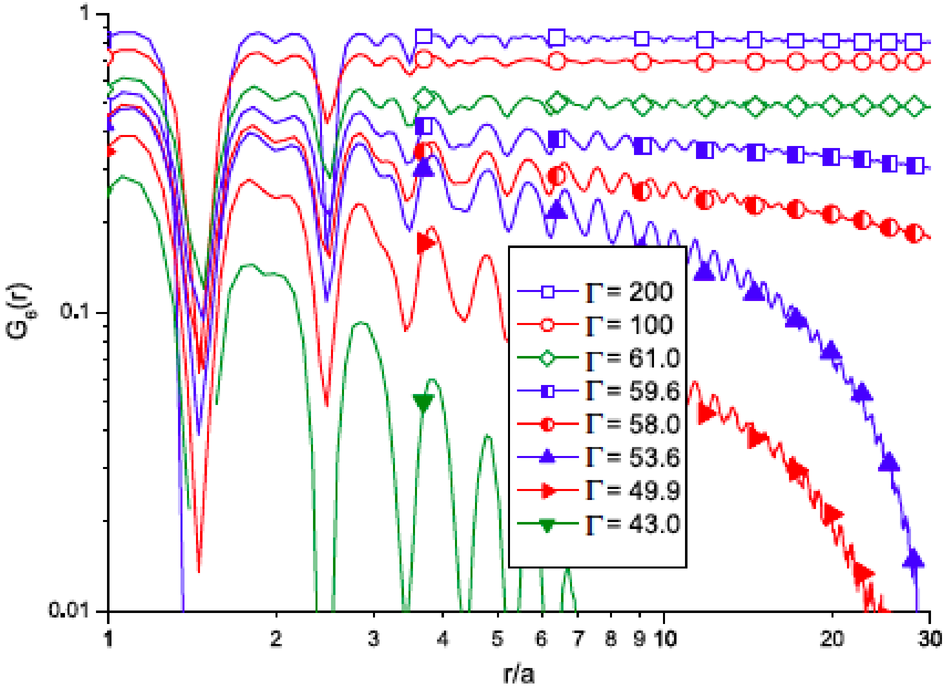
(For beads placed on the vertices of a triangular lattice, each bead j has six nearest-neighbours, $k = 1, \ldots, N_{\rm nn}^j = 6$, the angles verify $\Delta\theta_{jk} = \frac{2\pi}{6}$ and $\psi_{6j} = 1$)

associates arrows (directions) to disks

and measures **orientational order**

$2d$ colloidal suspensions

Hexatic correlation functions



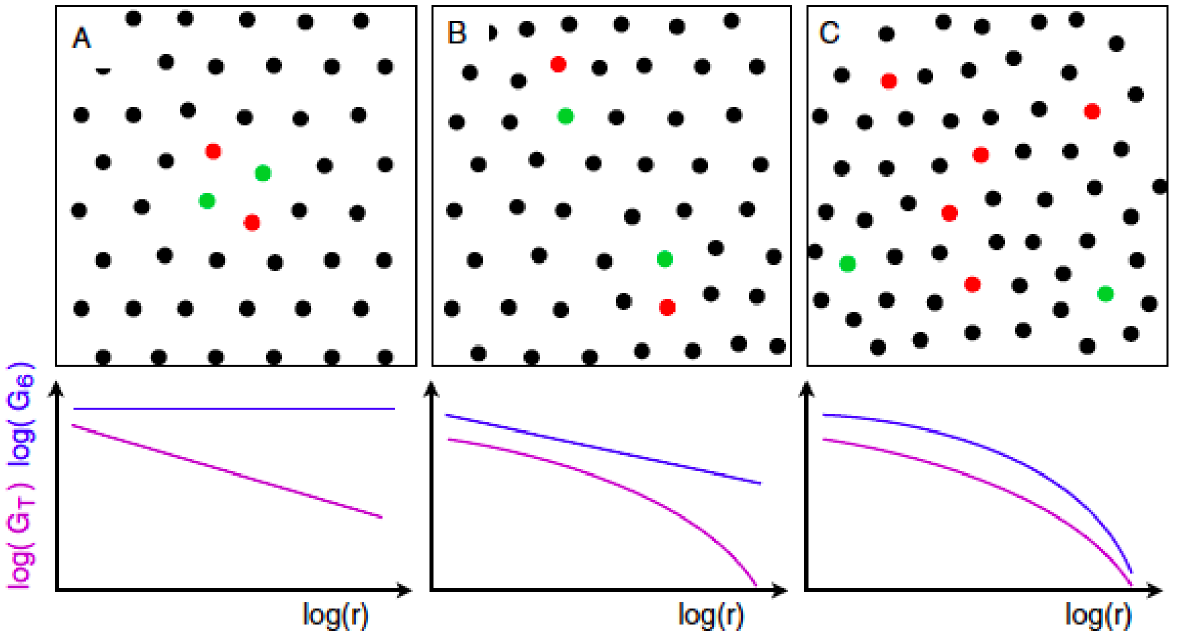
Γ is the control parameter playing the role of inverse temperature

Figure from **Keim, Maret & von Grünberg, PRE 75, 031402 (2007)**

Correlations & defects

Hexatic **Positional** ● **7 neighb** ● **5 neighb**

Solid **Hexatic** **Liquid**



$$\text{long } r: \quad G(r) = \left\{ \begin{array}{llll} \text{ct} & r^{-\eta} & \textbf{Solid} & \text{long range order} \\ r^{-\eta_6} & e^{-r/\xi} & \textbf{Hexatic} & \text{quasi long range order} \\ e^{-r/\xi_6} & e^{-r/\xi} & \textbf{Liquid} & \text{disorder} \end{array} \right.$$

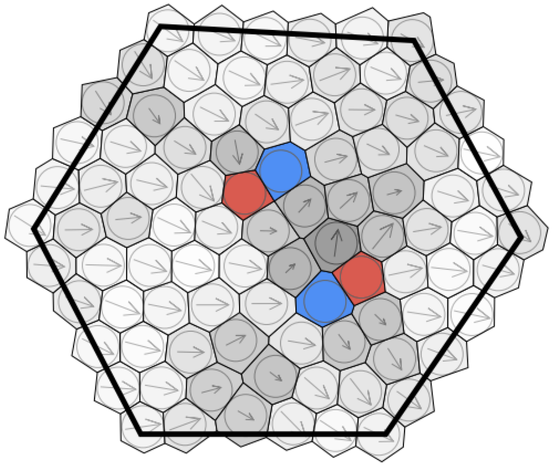
Sketches from **Gasser 10**

What drives the phase transitions ?

Why did we highlight the particles with **5** & **7** neighbours ?

Defects

Unbinding of dislocations: from the solid to the hexatic



A bound pair of dislocations

A free dislocation

In the crystal the centres of the disks form a triangular lattice

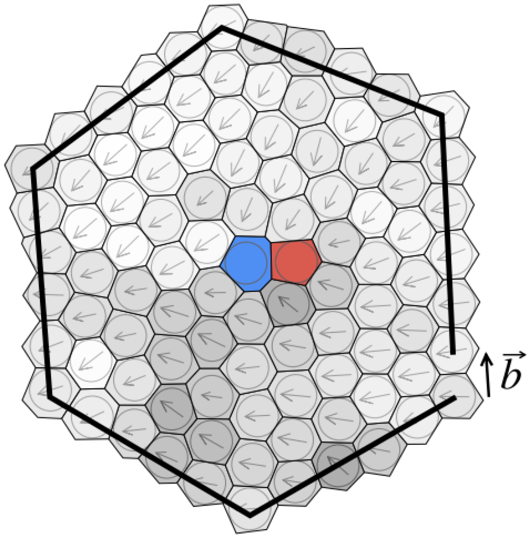
The **blue** disks have seven neighbours and the **red** ones have five.

On the left image: the external path closes and forms a perfect hexagon.

The effects of the defects are confined. This is the **solid** phase.

Defects

Unbinding of dislocations : from the solid to the hexatic



A bound pair of dislocations

A free dislocation

In the crystal the centres of the disks form a triangular lattice

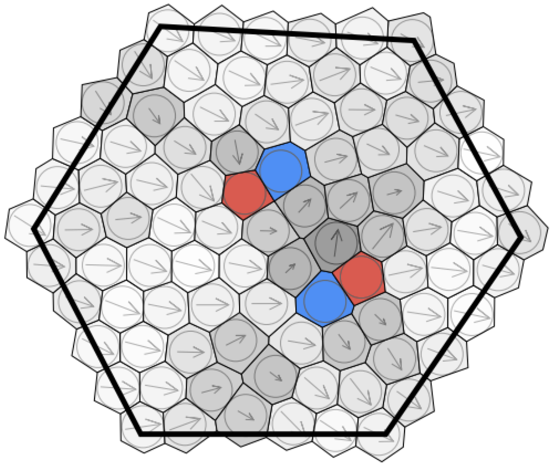
The **blue** disks have seven neighbours and the **red** ones have five.

On the right image : the external path fails to close, no perfect hexagon.

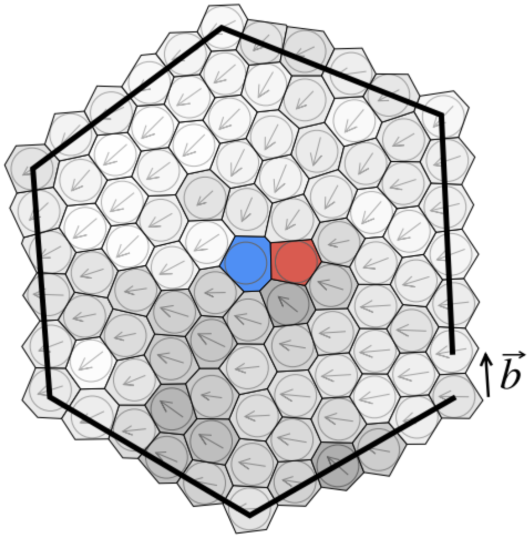
The effect of the defects spreads & kills translation order : **hexatic** phase.

Defects

Unbinding of dislocations : from the solid to the hexatic



A bound pair of dislocations



A free dislocation

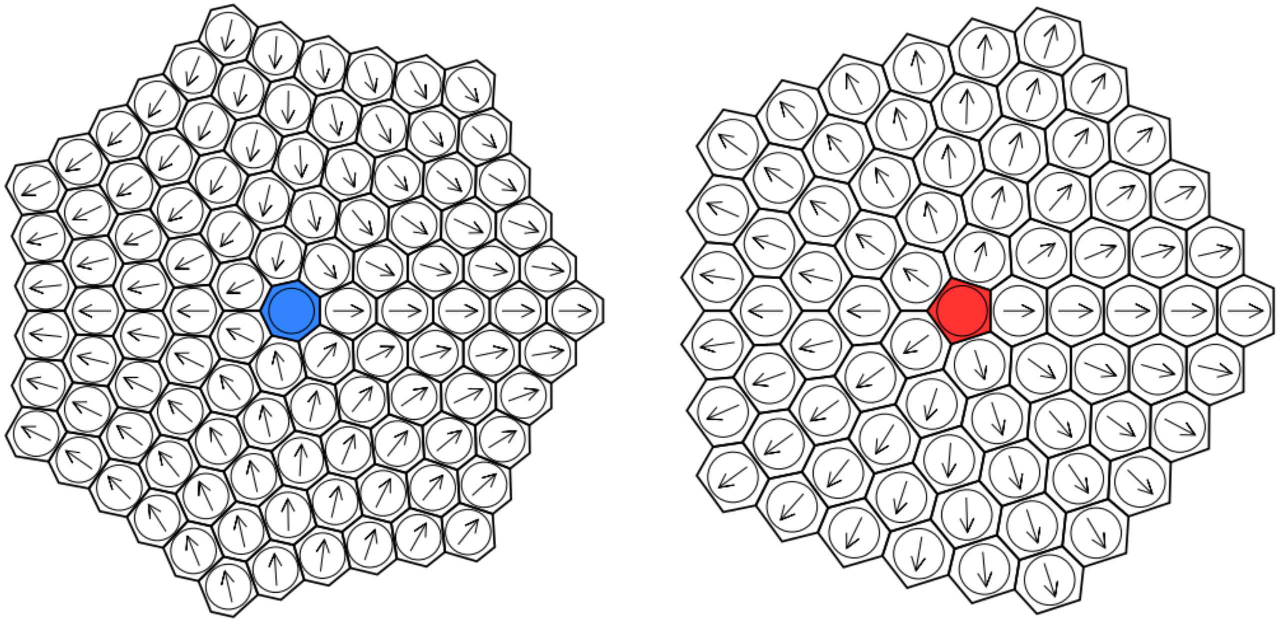
In the crystal the centres of the disks form a triangular lattice

The **blue** disks have seven neighbours and the **red** ones have five.

The underlying arrows are roughly aligned in both images. The hexatic phase keeps quasi long-range orientational order.

Defects

Unbinding of disclinations: from the hexatic to the liquid



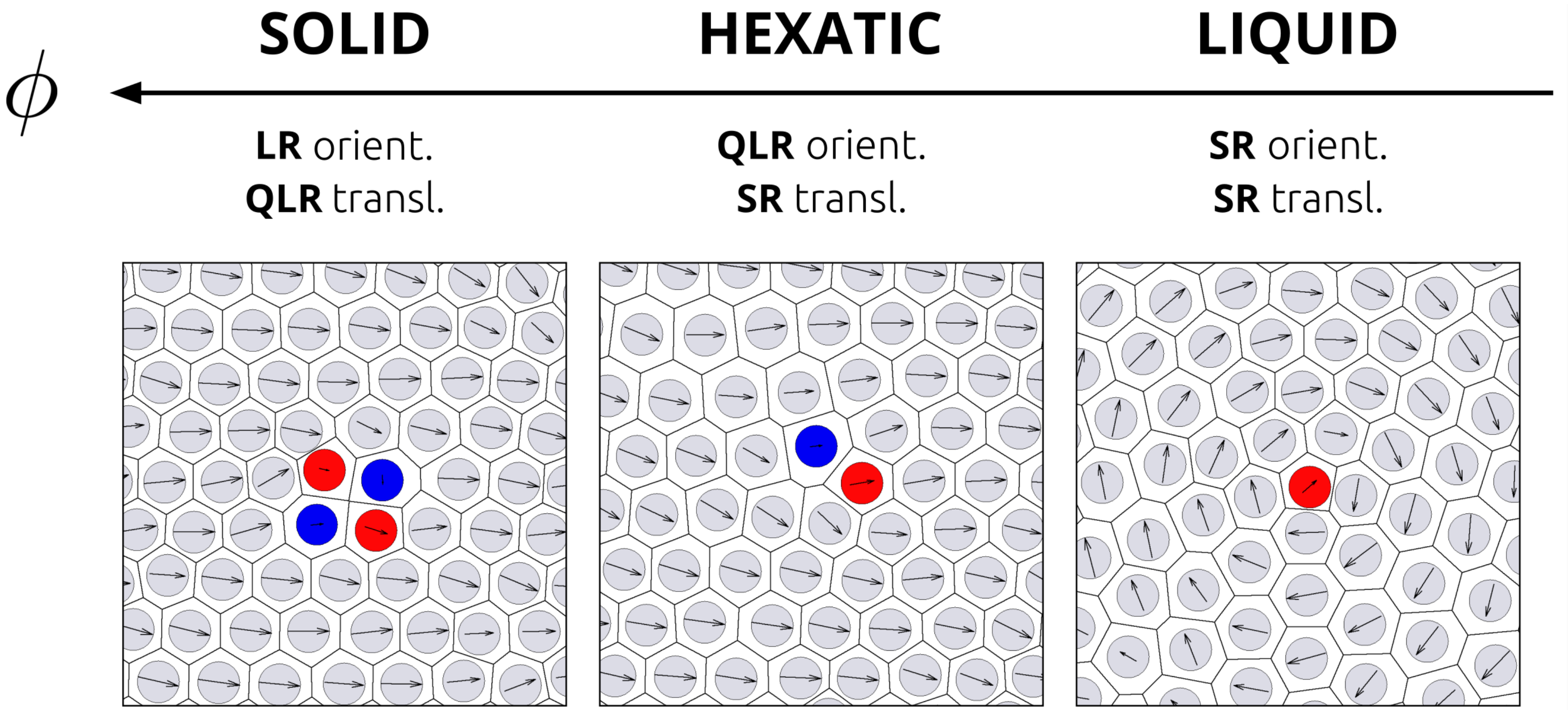
The orientation winds by $\pm 2\pi$ around the **blue** (seven) and **red** (five) defects.

Very similar to the vortices in the $2d$ XY magnetic model.

Halperin, Nelson & Young scenario: the unbinding of disclinations drives a second BKT-like transition to the **liquid**.

Freezing/Melting

Mechanisms in $2d$



Arrows oriented (LR) less oriented (QLR) order lost

● five neighbours ● seven neighbours

Voronoi tesselation

Phases & transitions

Berezinskii, Kosterlitz, Thouless, Halperin, Nelson & Young 70s

	BKT-HNY
Solid	QLR positional & LR orientational
transition	BKT (unbinding of dislocations)
Hexatic phase	SR positional & QLR orientational
transition	BKT (unbinding of disclinations)
Liquid	SR positional & orientational

Two infinite order, $\xi \propto e^{\delta^{-\nu}}$ with $\delta \to 0$,

Berenzinskii, Kosterlitz & Thouless

transitions

Berezinskii-Kosterlitz-Thouless

The $2d$ XY model $-J\sum_{\langle ij\rangle}\vec{s}_i\cdot\vec{s}_j = -J\sum_{\langle ij\rangle}\cos\Delta\theta_{ij}$

At very high temperature one expects disorder and

$$C(r) \equiv \langle \vec{s}_i \cdot \vec{s}_j \rangle_{\rm eq} \sim e^{-r/\xi_{\rm eq}(T/J)} \text{ with } |\vec{r}_i - \vec{r}_j| = r$$

At very low temperature the harmonic approximation is exact and there is quasi long-range order

$$C(r) \sim r^{-\eta} e^{-r/\xi_{\rm eq}(T/J)} \text{ with } \xi_{\rm eq}(T/J) \to \infty \text{ so that } C(r) \sim r^{-\eta}$$

There must be a transition in between.

Assumption: the transition is continuous and it is determined by the unbinding of vortices (topological defects).

Proved with RG, assuming a continuous phase transition.

The correlation length diverges exponentially $\xi_{\rm eq} \simeq e^{a/|T-T_{\rm BKT}|^{-\nu}}$ as $T \to T_{\rm BKT}^{+}$ and it remains infinite in the phase with quasi long-range order.

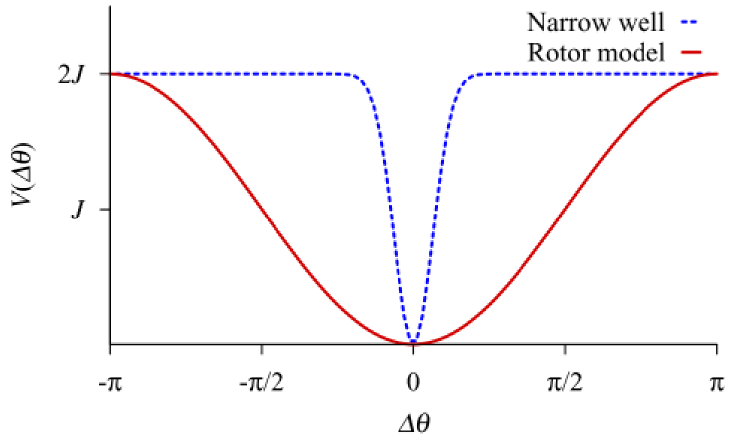
Berezinskii-Kosterlitz-Thouless

Lack of universality of the transition in XY models

The RG proof yields, actually, an upper limit for the stability of the quasi long-range ordered phase.

A first order phase transition at a lower T can preempt the BKT one.

It does for sufficiently steep potentials:



"First order phase transition in an XY model with nn interactions"

Domany, Schick & Swendsen, Phys. Rev. Lett. 52, 1535 (1984)

Berezinskii-Kosterlitz-Thouless

Lack of universality of the transition in XY models

The ^{2}RG proof yields, actually, an upper limit for the stability of the quasi long-range ordered phase.

A first order phase transition at a lower T can preempt the BKT one.

It does for sufficiently steep potentials:

La Habana, 2005

Phases & transitions

BKT-HNY *vs.* a new scenario by Bernard & Krauth 2011

	BKT-HNY	BK
Solid	QLR pos & LR orient	QLR pos & LR orient
transition	BKT (unbinding of dislocations)	BKT
Hexatic phase	SR pos & QLR orient	SR pos & QLR orient
transition	BKT (unbinding of disclinations)	**1st order**
Liquid	SR pos & orient	SR pos & orient

Basically, the phases are the same, but the **hexatic**-**liquid** transition is different, allowing for **coexistence of the two phases** for **hard enough particles**

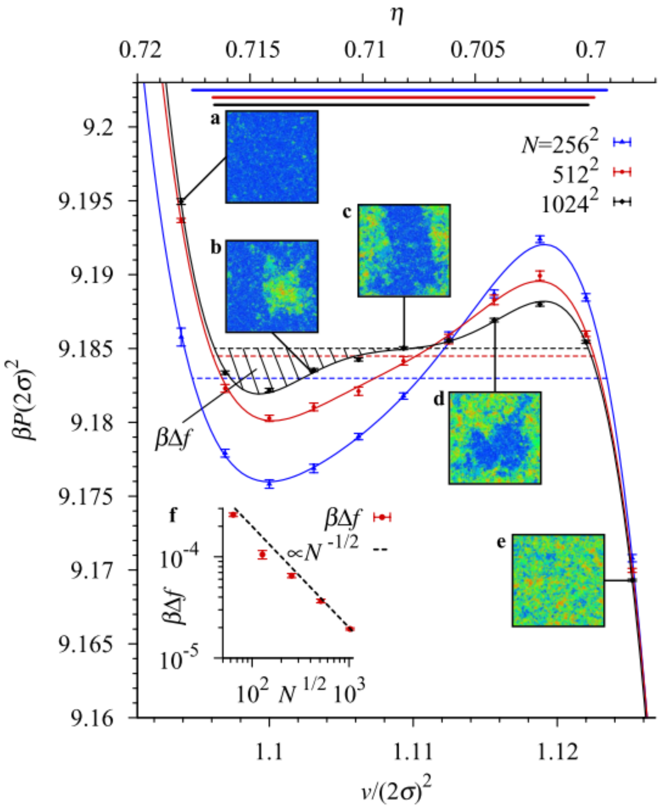
Event driven MC simulations. Sketches from **Bernard's** thesis.

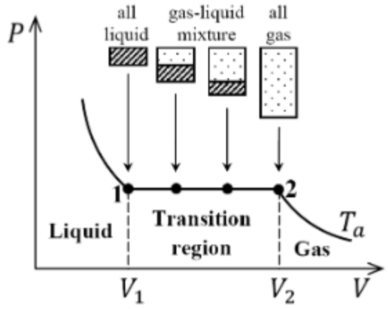
Hard disks

Pressure loop and finite N dependence: evidence for 1st order

Hexatic

Liquid





Similar to Van der Waals model for 1st order phase transitions

P cannot increase with V (stability): phase separation *via* Maxwell construction

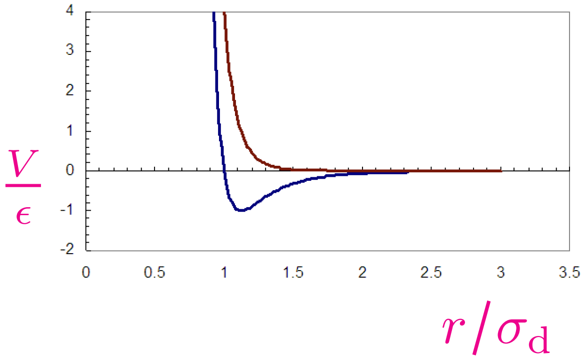
Rather hard disks

Molecular dynamics of overdamped Brownian particles

$$\boxed{\gamma \dot{\mathbf{r}}_i = -\nabla_i \sum_{j(\neq i)} U_{\text{Mie}}(r_{ij}) + \boldsymbol{\xi}_i \ ,}$$

$\mathbf{r}_i$ position of the centre of the ith particle

$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ inter-part distance,



very short-ranged, purely repulsive, Mie potential (truncated Lennard-Jones)

$\boldsymbol{\xi}$ zero-mean Gaussian noise with $\langle \xi_i^a(t)\, \xi_j^b(t') \rangle = 2\gamma k_B T \delta_{ij}^{ab} \delta(t-t')$

packing fraction $\phi = \pi\sigma_d^2 N/(4S)$

parameters $\gamma = 10$ and $k_BT = 0.05$

Digregorio et al. PRL (2018)

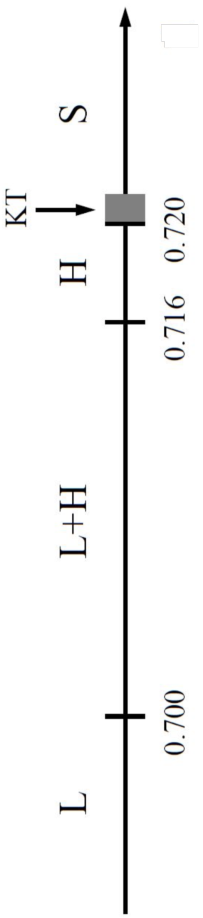
Passive hard disks

Phase diagram

$\phi_{\rm CP}$ ↑

ϕ

$\phi_{\rm RCP}$ ↑



solid

hexatic

co-existence ; 1st order

liquid

$n = 32, T = 0.05, \gamma = 10, m = 1, \sigma_d = 1, \tau_p = 60, N \sim 10^6$

MareNostrum (Barcelona, España) & Galileo (Cineca, Italia) computer facilities

Rather hard disks

Two local observables

Space-point dependent normalized density

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{k=1}^{N} \delta(\mathbf{r} - \mathbf{r}_k)$$

averaged over a volume ℓ^d around the point $\mathbf{r}$ or the position of a particle i

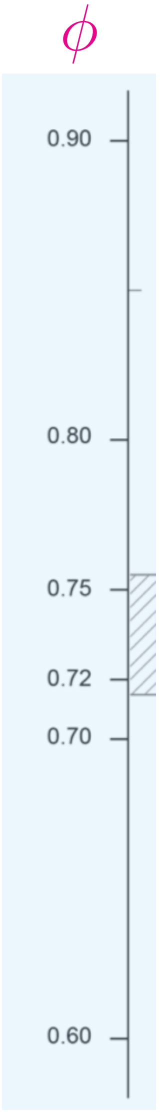
Particle dependent hexatic order parameter – a vector –

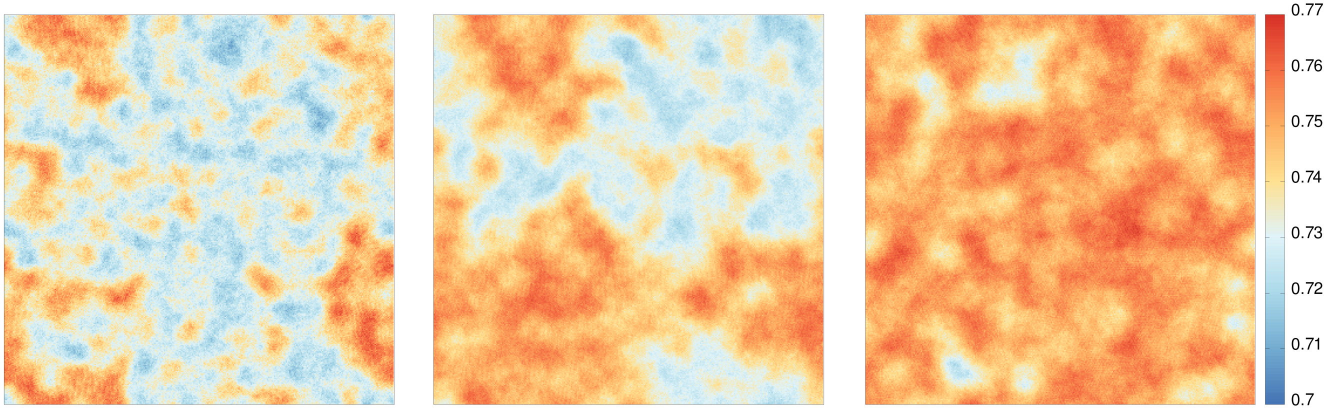
$$\psi_{6j} = \frac{1}{N_{\rm nn}^{j}} \sum_{k=1}^{N_{\rm nn}^{i}} e^{6{\rm i}\theta_{jk}}$$

projected on a preferred direction – the averaged one or a reference axis – and averaged over a volume ℓ^d around a point $\mathbf{r}$ or the position of a particle i

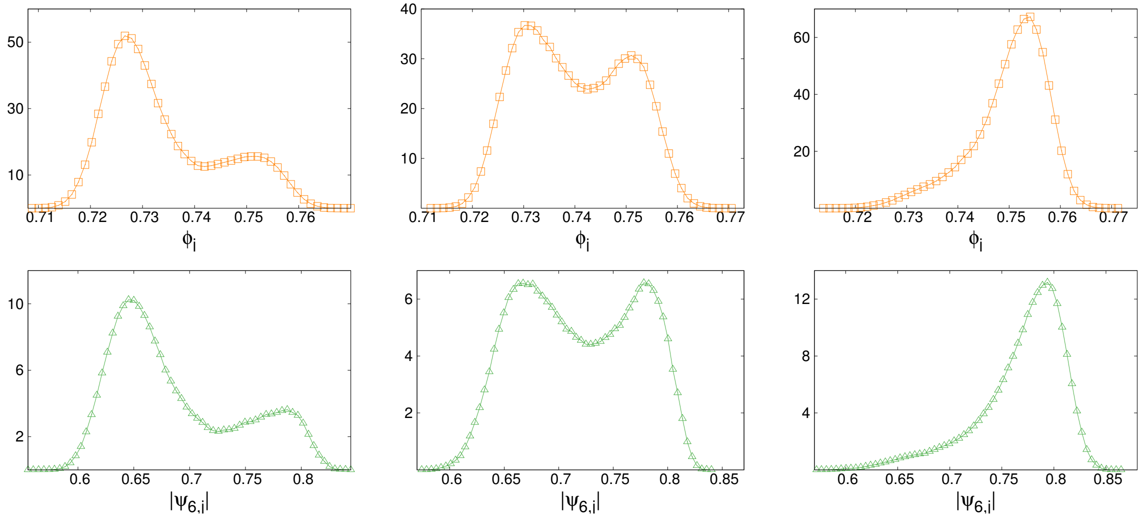
Rather hard disks

Local density & local hexatic parameter





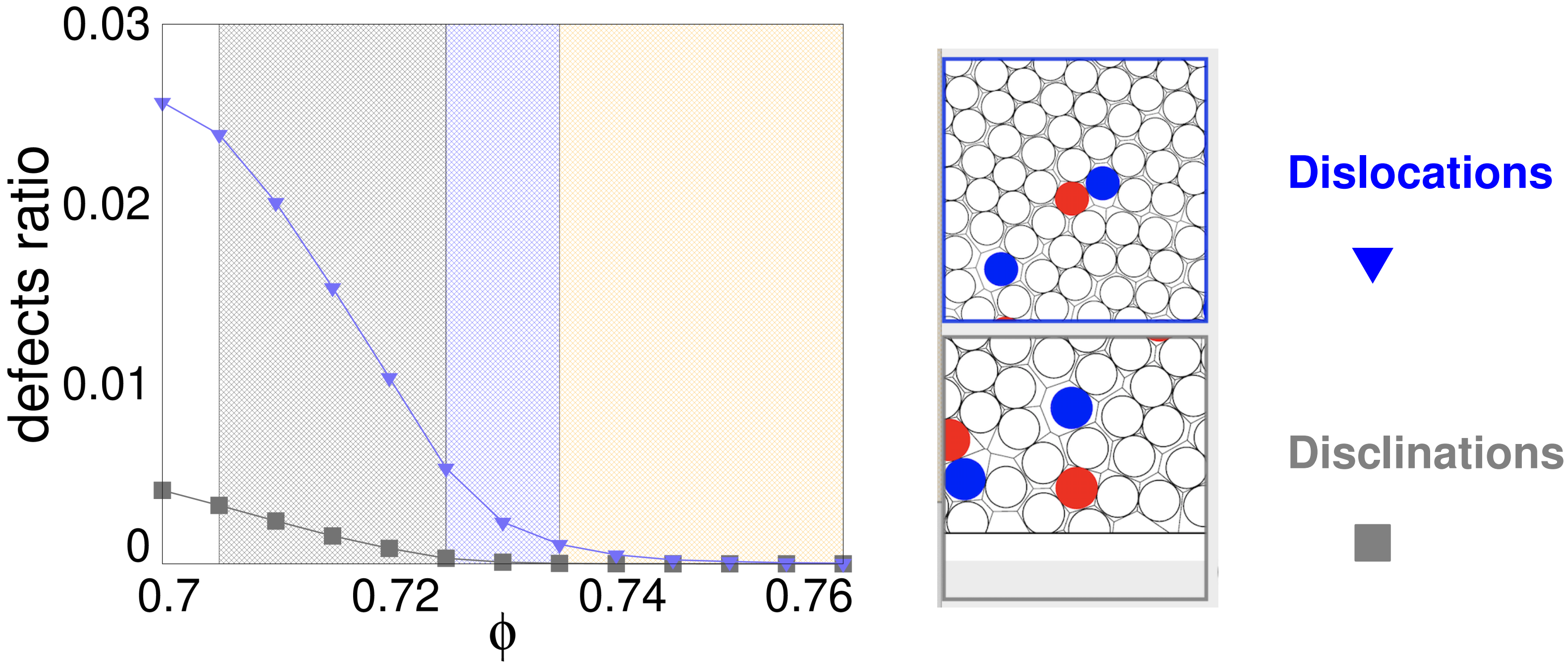
(co-existence) (co-existence) (upper limit of co-existence)



What happens with the defects ?

Unbinding of defects

Solid-hexatic transition & the emergence of the liquid at Pe = 0



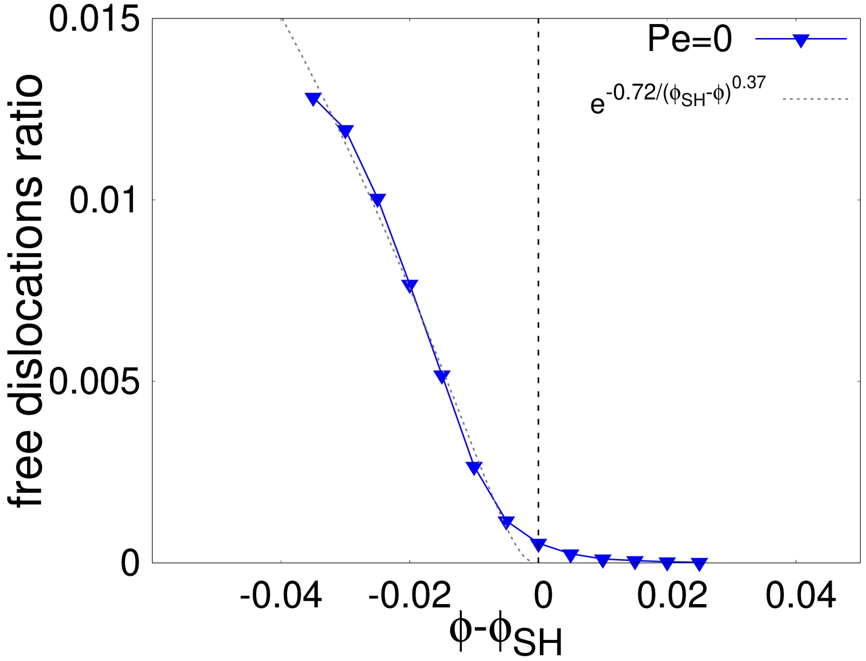
Dislocations ▼ unbind at the solid - **hexatic** transition as in BKT-HNY

Disclinations ■ unbind when the **liquid** appears in the co-existence region

Digregorio, Levis, LFC, Gonnella & Pagonabarraga, Soft Matter 18, 566 (2022)

Unbinding of defects

Free dislocations at the solid-hexatic transition at Pe = 0

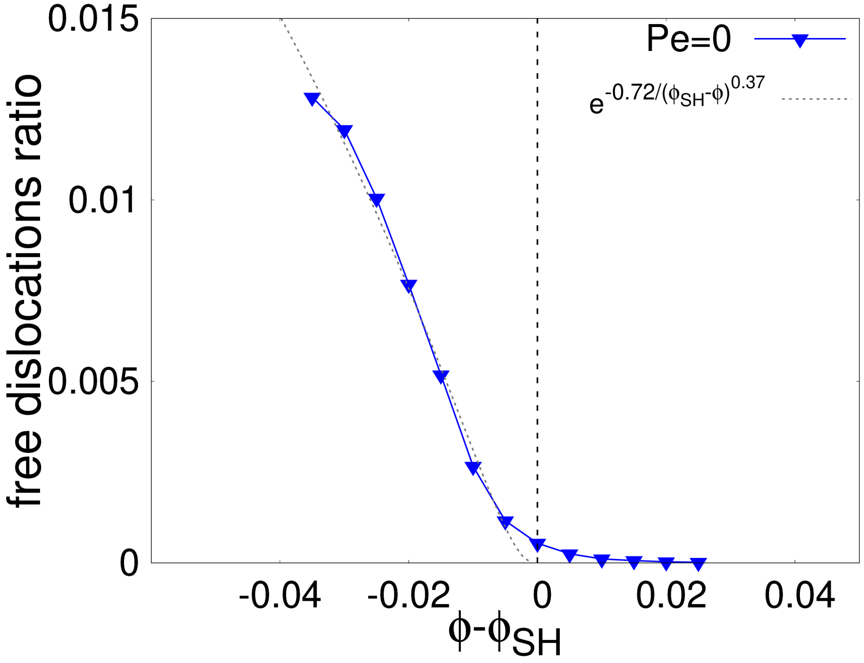


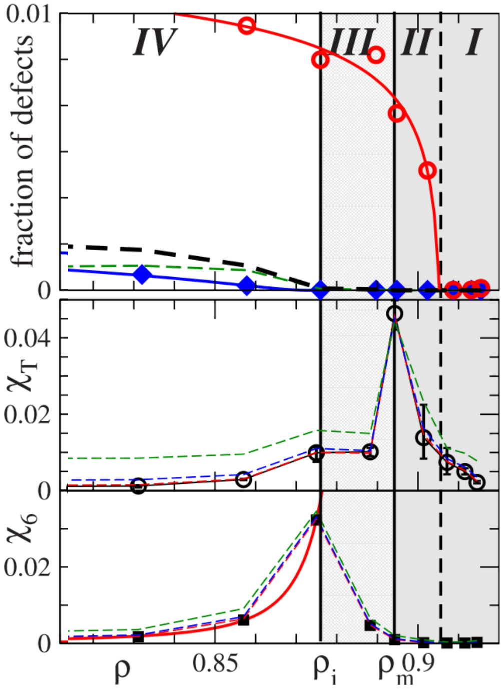
Dislocations ▼ unbind at the **solid** - **hexatic** transition, ϕ_{SH} from the measurement of correlation functions and other observables, with $\nu_{\mathrm{SH}} \approx 0.37$

Digregorio, Levis, LFC, Gonnella & Pagonabarraga, Soft Matter 18, 566 (2022)

Unbinding of defects

Free dislocations at the solid-hexatic transition at Pe = 0





Do **Dislocations** ▼ unbind at the **solid** - **hexatic** transition $\phi_{\rm SH}$? ? ?

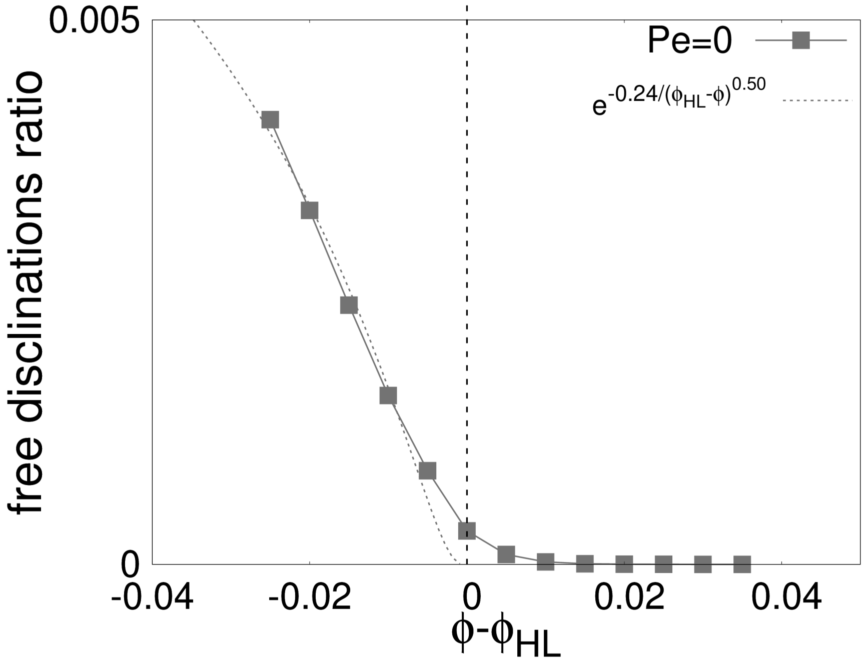
not so clear experimentally though still $\nu_{\rm SH} \approx 0.37$

Digregorio, Levis, LFC, Gonnella & Pagonabarraga, Soft Matter 18, 566 (2022)

Han, Ha, Alsayed, & Yodh, PRE 77, 041406 (2008) Short-range & repulsive microgel

Unbinding of defects

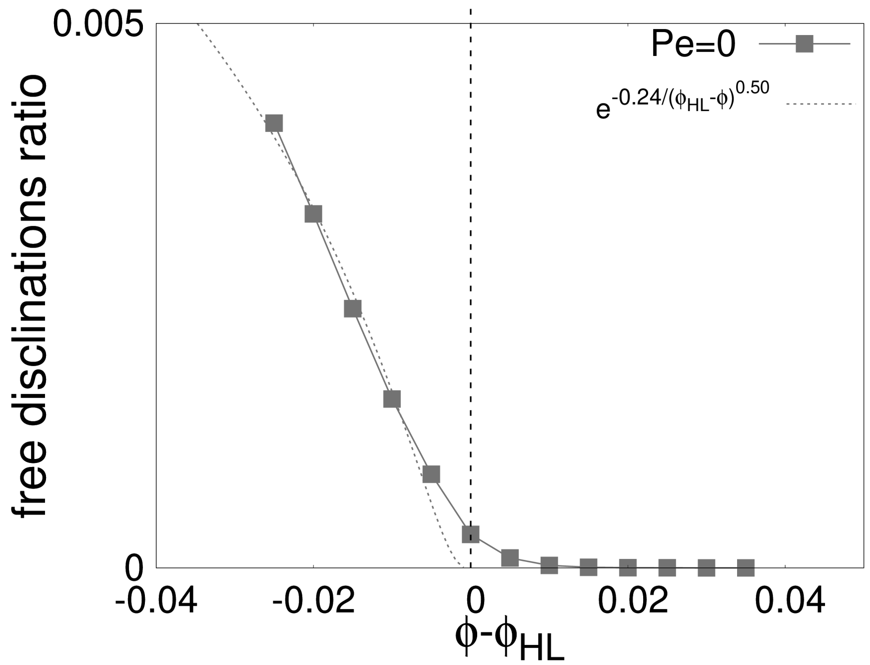
Free disclinations close to the hexatic-liquid transition at Pe = 0

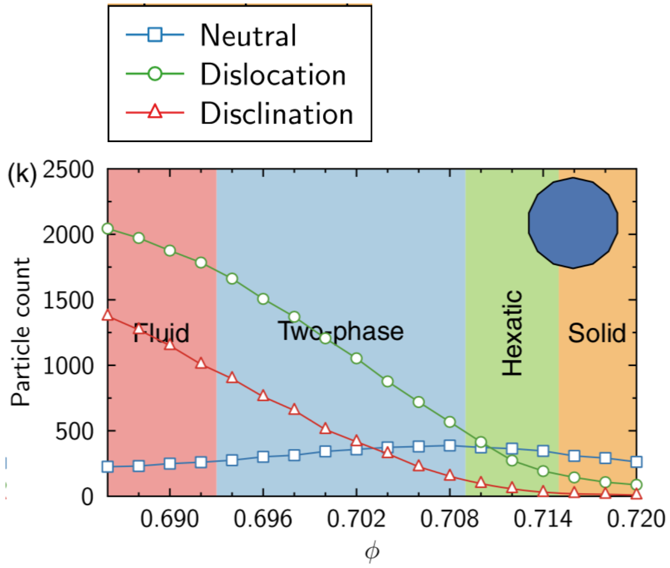


Disclinations ■ unbind when the **liquid** appears in co-existence at $\phi_{\mathrm{H,H+L}}$ and $\nu_{\mathrm{HL}} = 0.5$

Unbinding of defects

Free disclinations close to the hexatic-liquid transition at Pe = 0





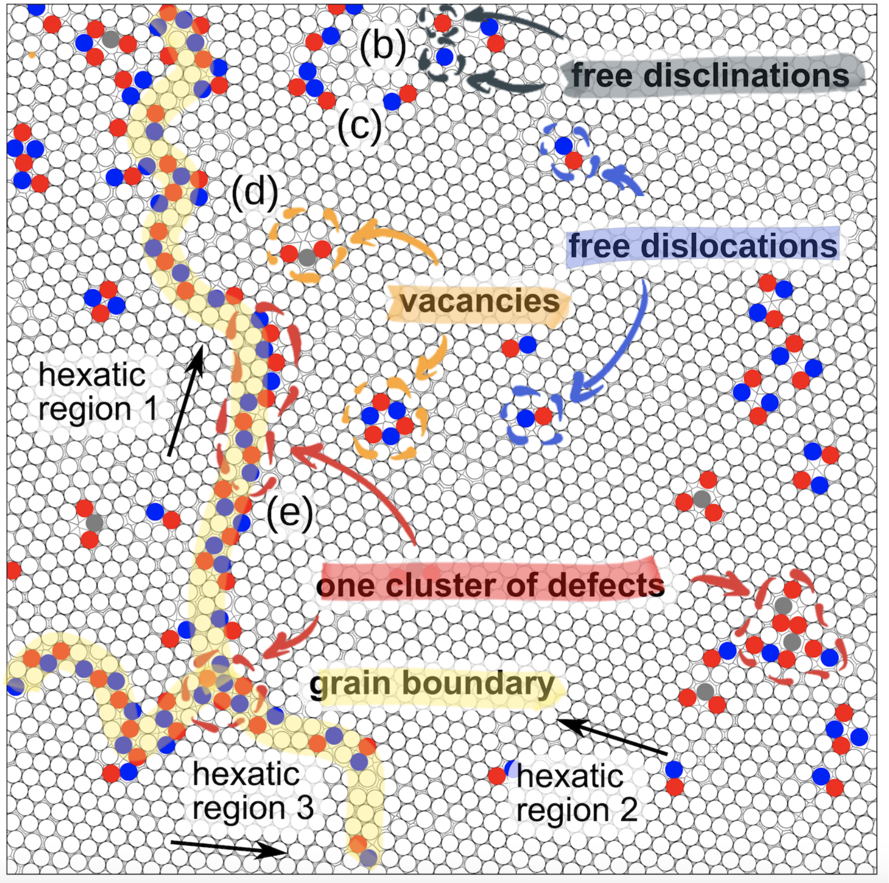
Disclinations ■ unbind when the **liquid** appears in co-existence at $\phi_{\rm H,H+L}$ and $\nu_{\rm HL} = 0.5$

Digregorio, Levis, LFC, Gonnella & Pagonabarraga, Soft Matter 18, 566 (2022)

Anderson, Antonaglia, Millan, Engel & Glotzer, PRX 7, 021001 (2017) MC hard

Grain boundaries & clusters

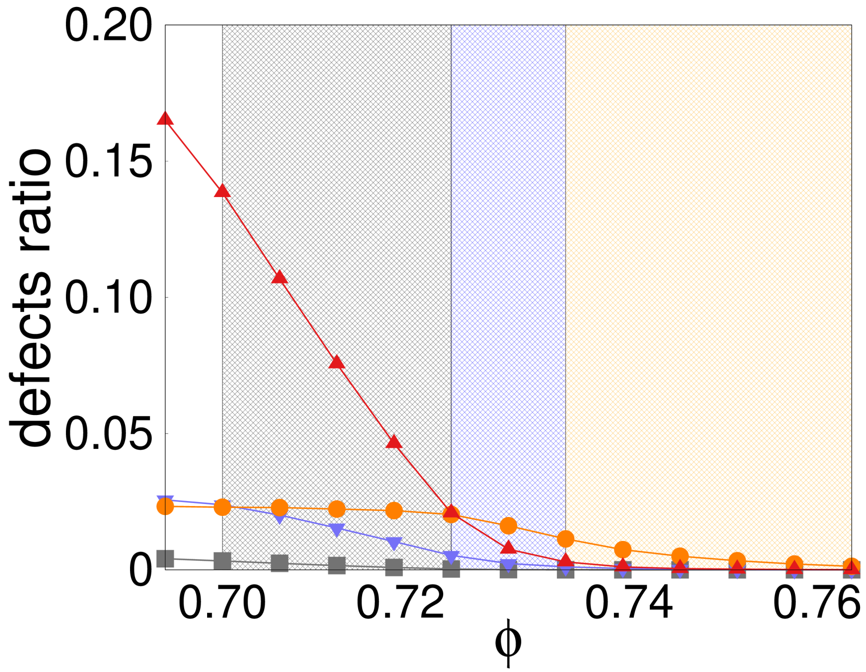
Classification



The classification in **Pertsinidis & Ling**, PRL 87, 098303 (2001)

Proliferation of clusters

Within the co-existence region at Pe = 0

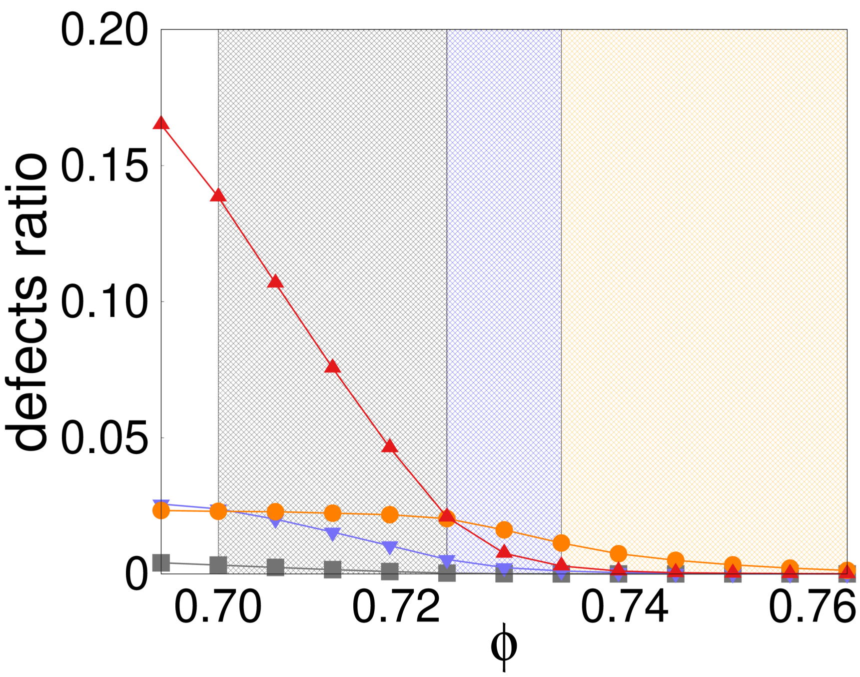


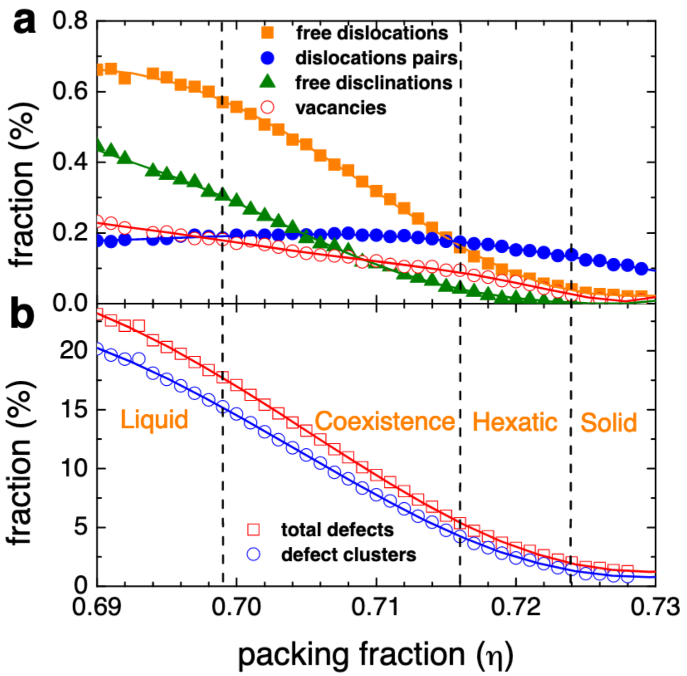
Clusters ▲ proliferate within the co-existence region

Vacancies ● remain approximately constant within the co-existence region

Proliferation of clusters

Within the co-existence region at Pe = 0





Clusters ▲ proliferate within the co-existence region

Vacancies ● remain approximately constant within the co-existence region

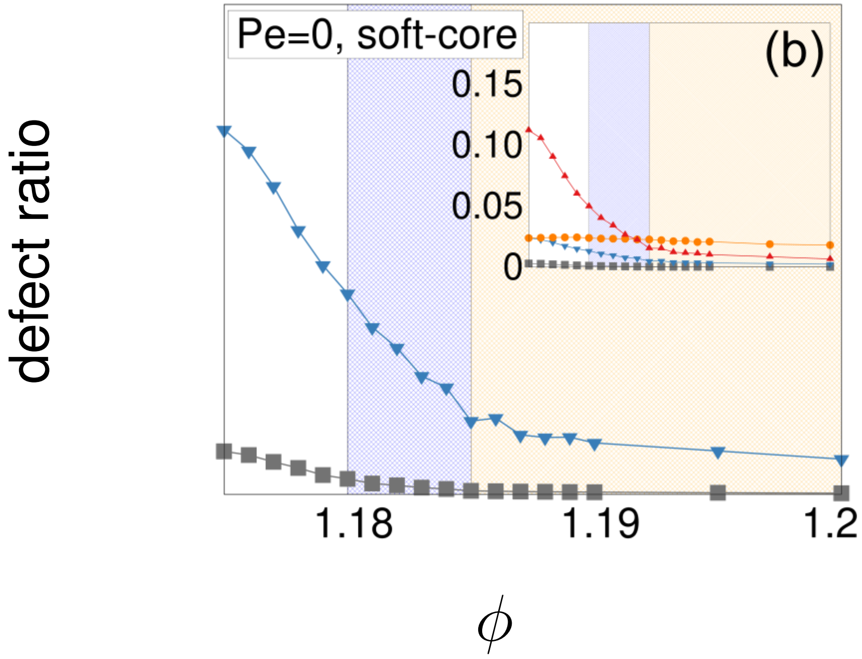
Digregorio, Levis, LFC, Gonnella & Pagonabarraga, Soft Matter 18, 566 (2022)

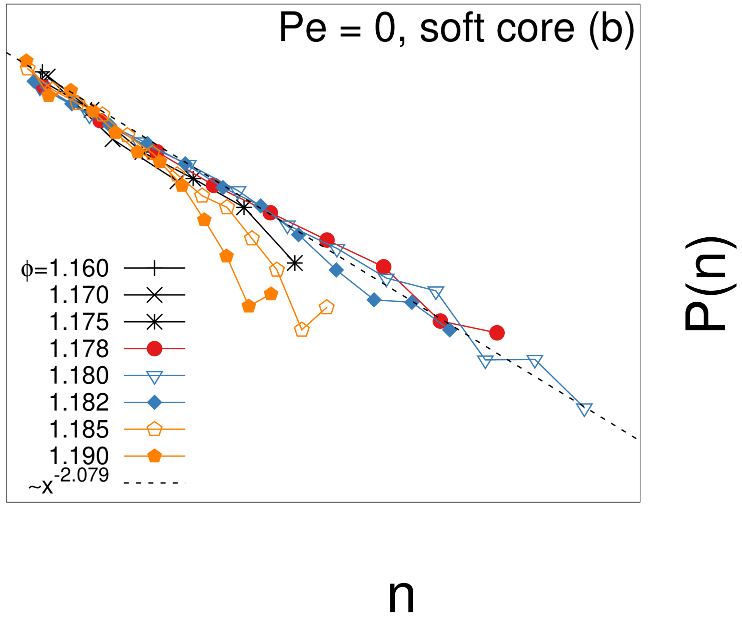
Qi, Gantapara & Dijkstra, Soft Matter 10, 5419 (2014) Event drive MD hard disks

Is this really related to the 1st order nature of the transition ?

Soft disks

Defect ratio & size distribution





For soft disks the **hexatic**-**liquid** transition is **continuous**, no signature of co-existence. Still, similar picture ; proliferation of clusters with aspects of percolation at the hexatic-liquid transition.

Not clear. Open issue.

Plan

1. Equilibrium phases : solidification/melting

   Special in two-dimensions

   Solid, hexatic & liquid phases

   Phase transitions

   Topological defects

2. **Active matter**

   Self-propelled Brownian disks in $2d$

   Phase diagram

   Solid, hexatic & liquid phases ; motility induced phase separation

Active matter

Definition

Active matter is composed of large numbers of active "agents", each of which consumes energy in order to move or to exert mechanical forces.

Due to the energy consumption, these systems are intrinsically out of thermal equilibrium.

Uniform energy injection within the samples (and not from the borders).

Coupling to the environment (bath) allows for the dissipation of the injected energy.

Active matter

Realisations & modelling

- Wide range of scales: macroscopic to microscopic

  Natural examples are birds, fish, cells, bacteria.

- Also artificial realisations: Janus particles, granular, etc.

- $3d$, $2d$ and $1d$.

- Modelling: very detailed to coarse-grained or schematic.

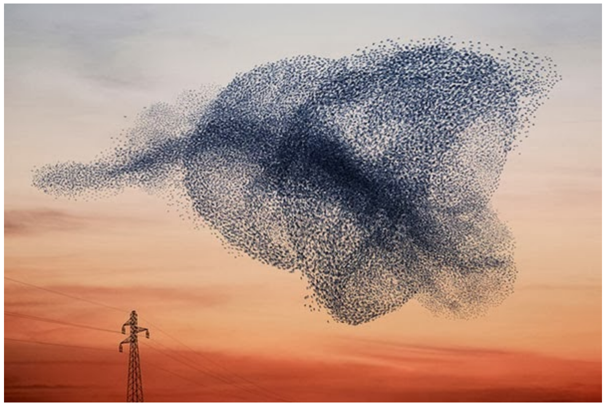
  - microscopic or *ab initio* with focus on active mechanism,

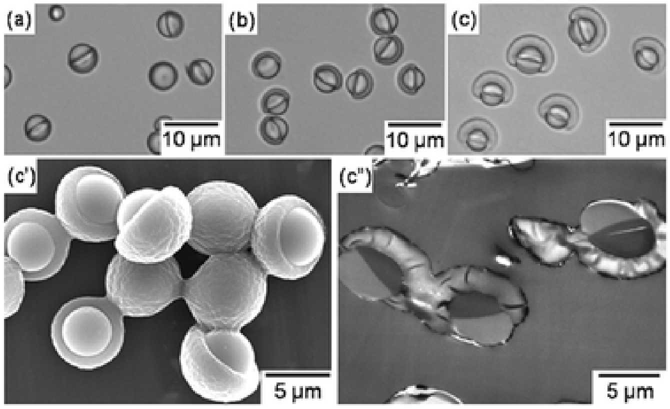
  - *mesoscopic*, just forces that do not derive from a potential,

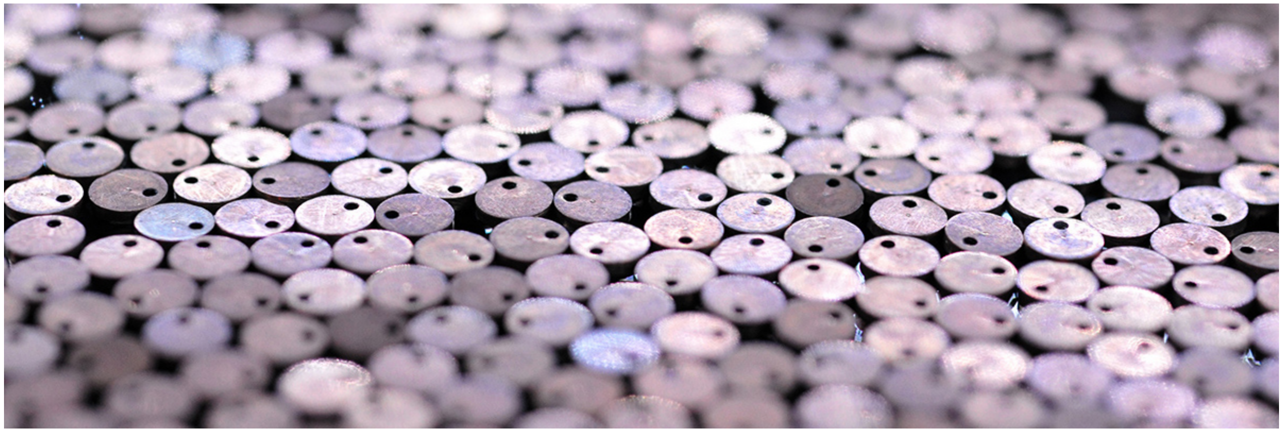
  - *Cellular automata* like in the Vicsek model.

Active matter

Natural & artificial systems







Experiments & observations **Bartolo et al.** Lyon, **Bocquet et al.** Paris, **Cavagna, et al.** Roma, **di Leonardo et al.** Roma, **Dauchot et al.** Paris, just to mention some Europeans

Active disks

Overdamped Brownian particles (the standard model)

Active force $\mathbf{F}_{\rm act}$ along $\mathbf{n}_i = (\cos\theta_i(t), \sin\theta_i(t))$

$$\gamma \dot{\mathbf{r}}_i = F_{\rm act}\mathbf{n}_i - \nabla_i \sum_{j(\neq i)} U_{\rm Mie}(r_{ij}) + \boldsymbol{\xi}_i \; , \qquad \dot{\theta}_i = \eta_i \; ,$$

$\mathbf{r}_i$ position of the centre of ith part & $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ inter-part distance,

short-ranged repulsive Mie potential,

$\boldsymbol{\xi}$ and η zero-mean Gaussian noises with
$\langle \xi_i^a(t)\, \xi_j^b(t')\rangle = 2\gamma k_B T \delta_{ij}^{ab}\delta(t-t')$ and $\langle \eta_i(t)\, \eta_j(t')\rangle = 2D_\theta \delta_{ij}\delta(t-t')$.

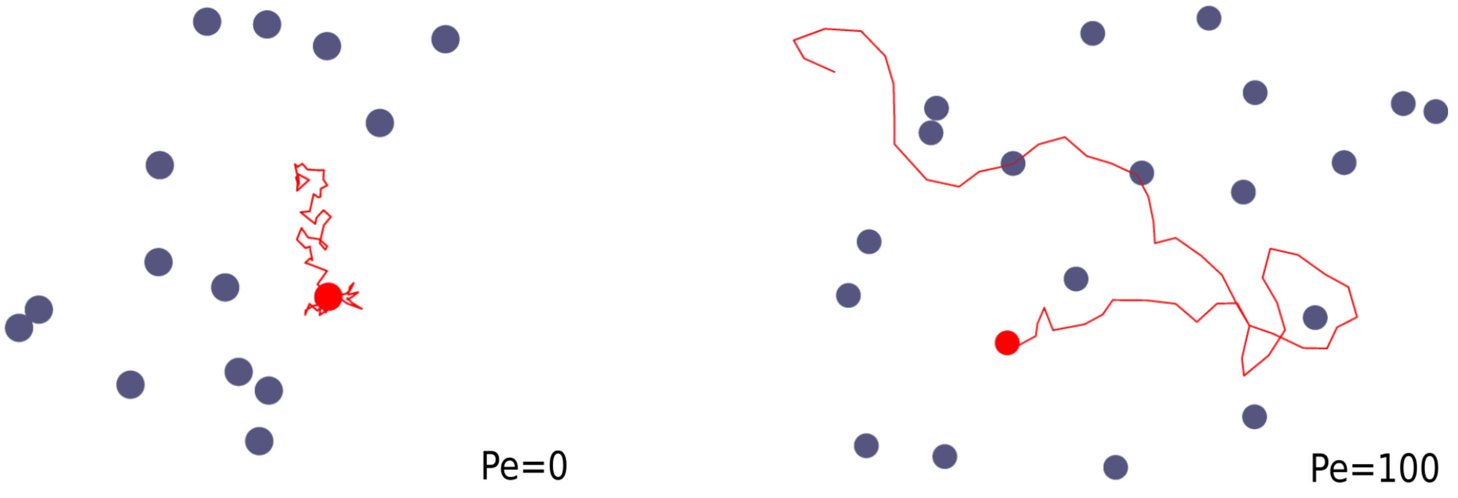
The units of length, time and energy are given by $\sigma_{\rm d}$, $\tau = D_\theta^{-1}$ and ε

$D_\theta = 3k_BT/(\gamma\sigma_d^2)$, $\phi = \pi\sigma_d^2 N/(4S)$, $\gamma = 10$ and $k_BT = 0.05$

Péclet number Pe = $F_{\rm act}\sigma_{\rm d}/(k_BT)$ measures activity

Active Brownian disks

The typical motion of particles in interaction



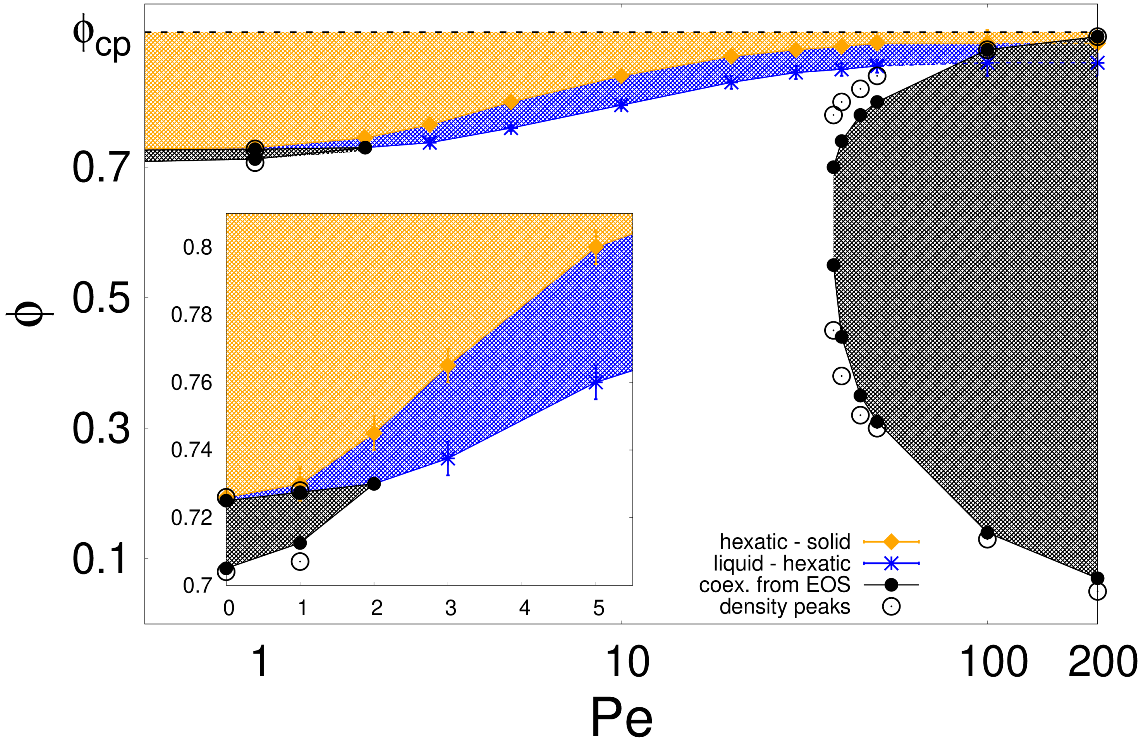
The active force induces a persistent random motion due to

$$\langle \mathbf{F}_{\rm act}(t) \cdot \mathbf{F}_{\rm act}(t') \rangle \propto F_{\rm act}^2 \, e^{-(t-t')/\tau_p}$$

with $\tau_p = D_\theta^{-1}$

Active disks

Phase diagram with solid, hexatic, co-existence, MIPS & liquid



Motility

induced

phase

separation

gas & bubble

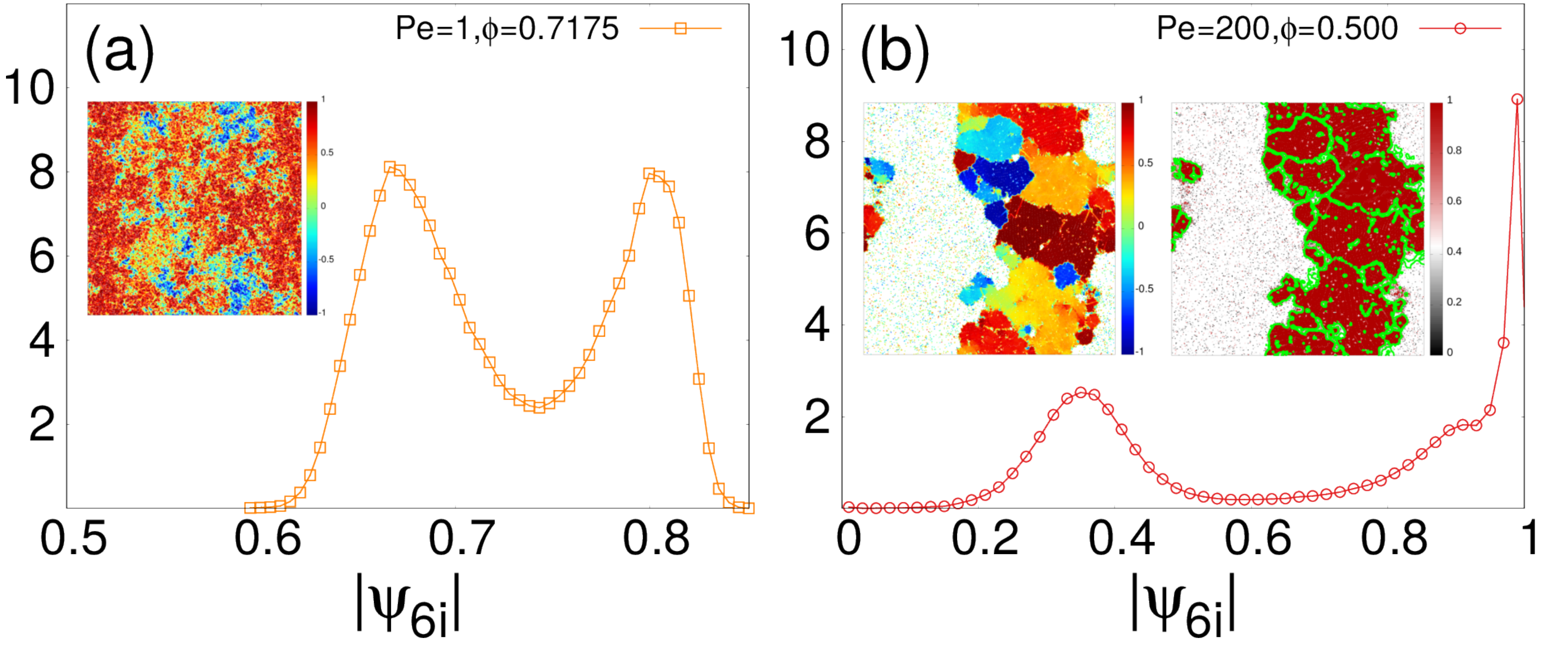
From pressure $P(\phi)$, correlations G_T & G_6, distributions of ϕ_i & ψ_{6i} at $k_BT = 0.05$

Digregorio, Levis, Suma, LFC, Gonnella & Pagonabarraga, PRL 121, 098003 (2018)

Active disks

Modulus of the local hexatic order parameter

Pe = 1 Pe = 200



Co-existence in passive limit and in MIPS

Active disks

Solid, hexatic, liquid & MIPS

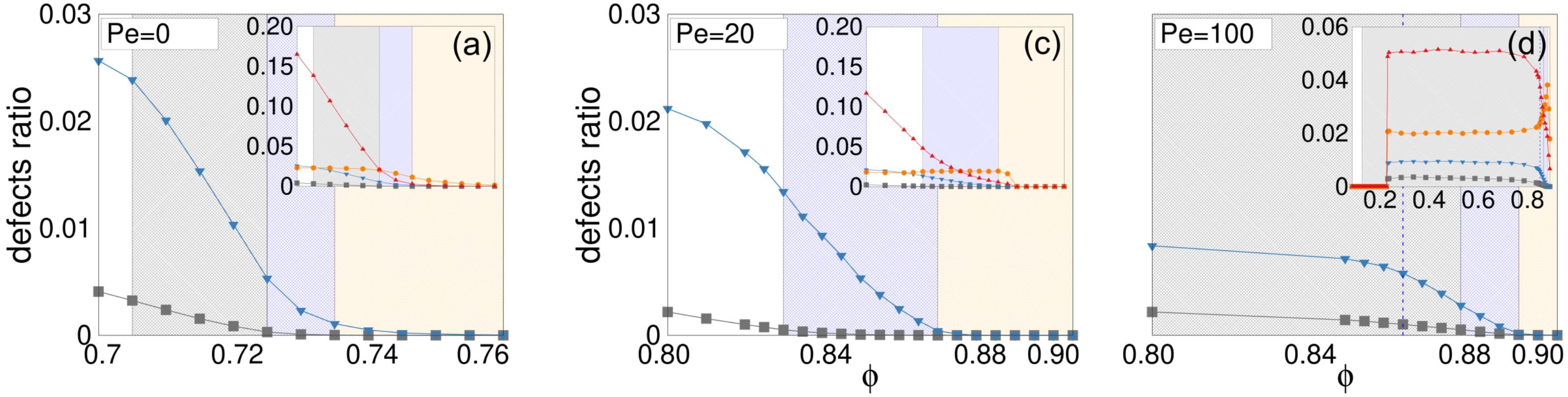
1st order
w/co-existence

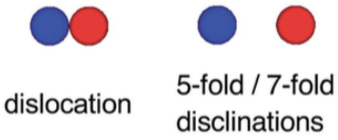
à la KTHNY

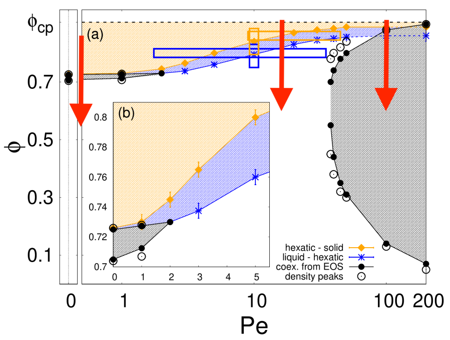
free dislocations at solid-hex

free disclinations in the liquid

in MIPS



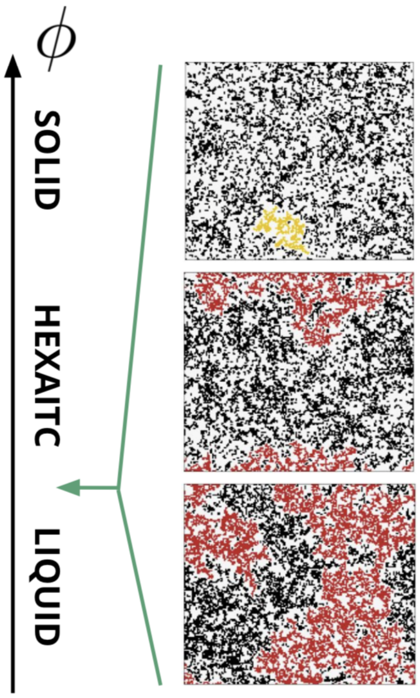


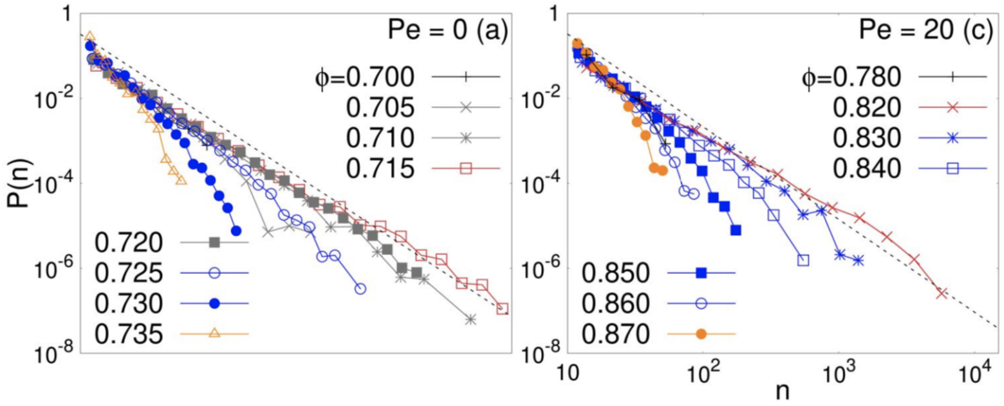


Digregorio, Levis, LFC, Gonnella & Pagonabarraga, arXiv:1911.06366

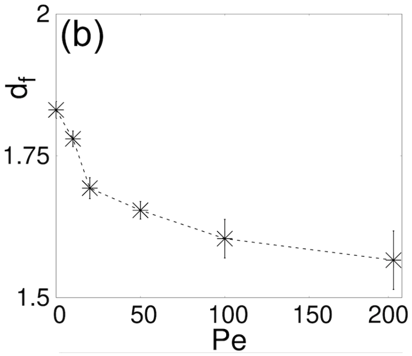
Defect clusters

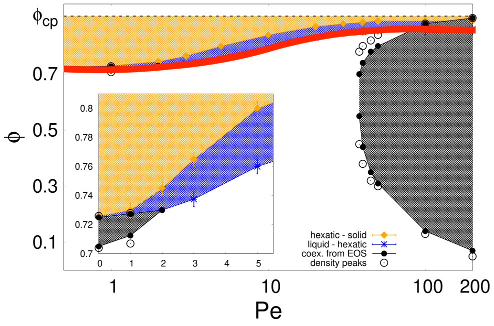
Percolation features $P(n) \sim n^{-\tau}$





$\tau \approx d/d_f + 1$

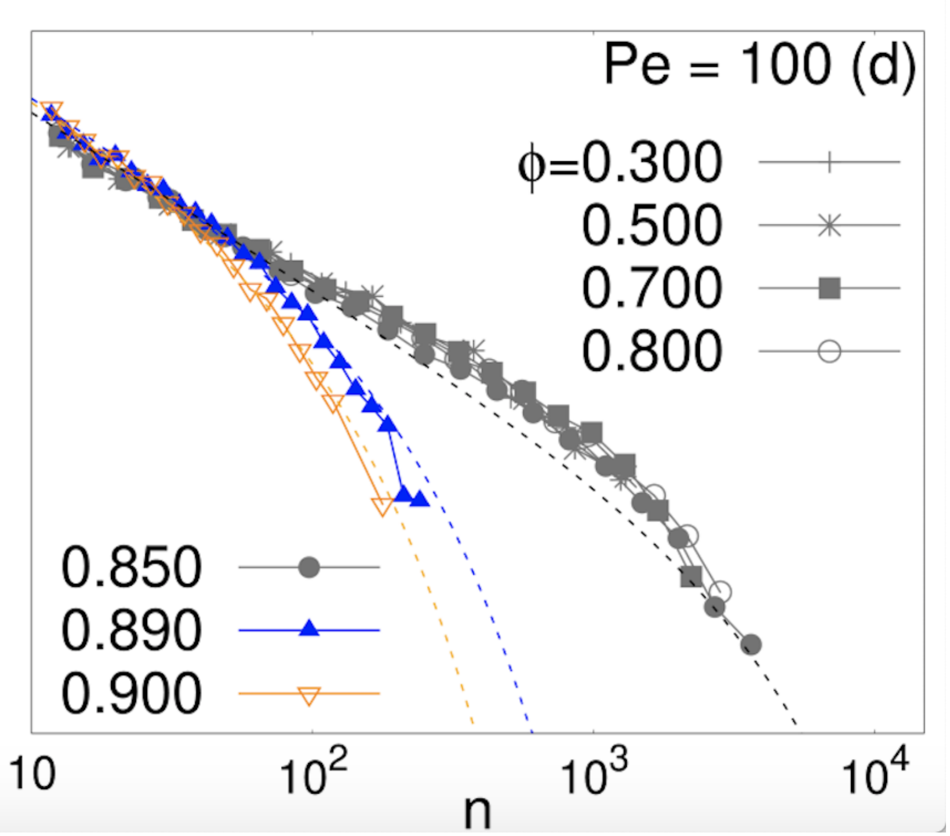




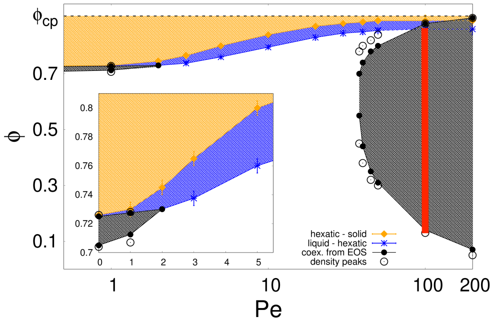
d_f from the radius of gyration of the clusters

Defect clusters

Within MIPS: the grain boundaries



$$P(n) \simeq n^{-\tau} e^{-n/n^*}$$



Independence of ϕ at fixed Pe within MIPS

Melting

Mechanisms

– Unbinding of dislocations at **solid** - **hexatic** $\forall$ Pe

$\nu_{\rm SH} \approx 0.37$ (KTHNY) at all Pe **Universality**

– Unbinding of disclinations when the **liquid** appears $\forall$ Pe

$\nu_{\rm HL} \approx 0.5$ (KTHNY) but hard to tell

However, very hard to be sure about the “free-ness” of these defect.

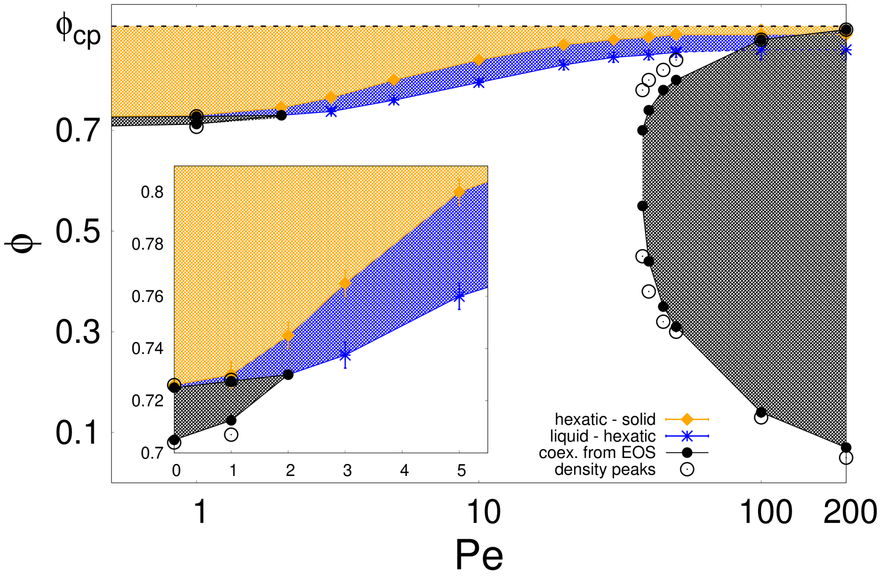
– Clusters overwhelmingly abundant at ≈ the **hexatic** - **liquid** transition

Percolation features $\forall$ Pe, no qualitative difference between 1st order and continuous. $d_f \searrow$ for Pe $\nearrow$

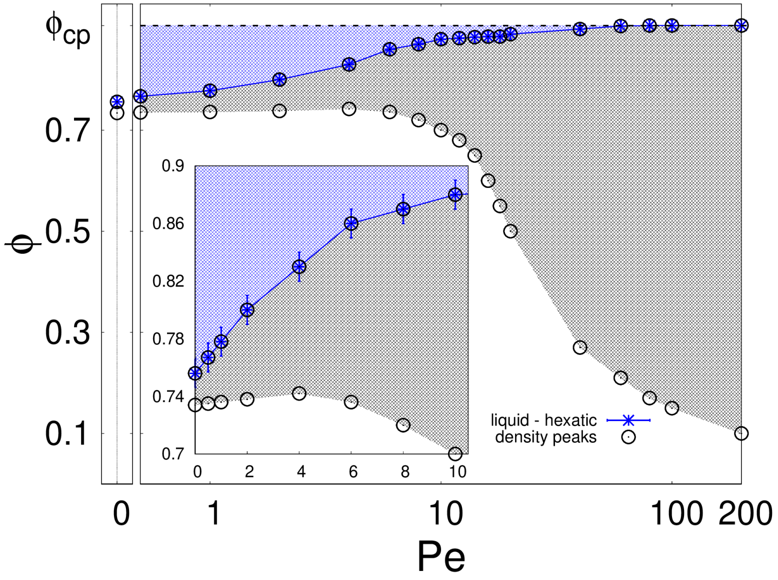
Is the liquid invading and melting the hexatic through the interfaces between micro-domains ? Can one distinguish 1st order from continuous ?

Active Brownian systems

Phase diagrams & plenty of interesting facts



Disks



Dumbbells

Summary & conclusions

There is still a lot to be understood in the very "classic" problem of melting of passive systems in two dimensions.

New picture with a first order phase transition towards the liquid.

The standard lore on topological effects is only partially verified.

Effects of activity?

We have established the phase diagram of active Brownian particles and we have studied the statistics of topological defects.

This is a problem in which numerical simulations have been of great help.

P. Digregorio's PhD Thesis, Università di Bari, Italia 2020.

Fluctuation-dissipation

Linear relation between χ and Δ^2 in equilibrium

$$\boxed{P(\zeta, t_w) \to P_{\text{eq}}(\zeta)}$$

- The dynamics are stationary

$$\Delta^2_{AB}(t, t_w) = \langle [A(t) - B(t_w)]^2 \rangle = [C_{AA}(0) + C_{BB}(0) - 2C_{AB}(t - t_w)]$$

$$\to \Delta^2_{AB}(t - t_w)$$

- The fluctuation-dissipation theorem between spontaneous (Δ^2_{AB}) and induced (R_{AB}) fluctuations

$$R_{AB}(t - t_w) = \frac{1}{2k_BT} \frac{\partial \Delta^2_{AB}(t - t_w)}{\partial t} \theta(t - t_w)$$

holds and implies

$$\boxed{\chi_{AB}(t - t_w) \equiv \int_{t_w}^{t} dt' \, R_{AB}(t, t') = \frac{1}{2k_BT}[\Delta^2_{AB}(t - t_w) - \Delta^2_{AB}(0)]}$$

Fluctuation-dissipation

Linear relation between χ and Δ^2 out of equilibrium ?

$$\boxed{P(\zeta, t_w) \neq P_{\text{eq}}(\zeta)}$$

- The dynamics are stationary

$$\Delta^2_{AB}(t, t_w) = \langle [A(t) - B(t_w)]^2 \rangle = [C_{AA}(0) + C_{BB}(0) - 2C_{AB}(t - t_w)]$$

$$\to \Delta^2_{AB}(t - t_w)$$

- The fluctuation-dissipation theorem between spontaneous (Δ^2_{AB}) and induced (R_{AB}) fluctuations

$$R_{AB}(t - t_w) \neq \frac{1}{2k_B T} \frac{\partial \Delta^2_{AB}(t - t_w)}{\partial t} \, \theta(t - t_w)$$

does not hold but one can propose

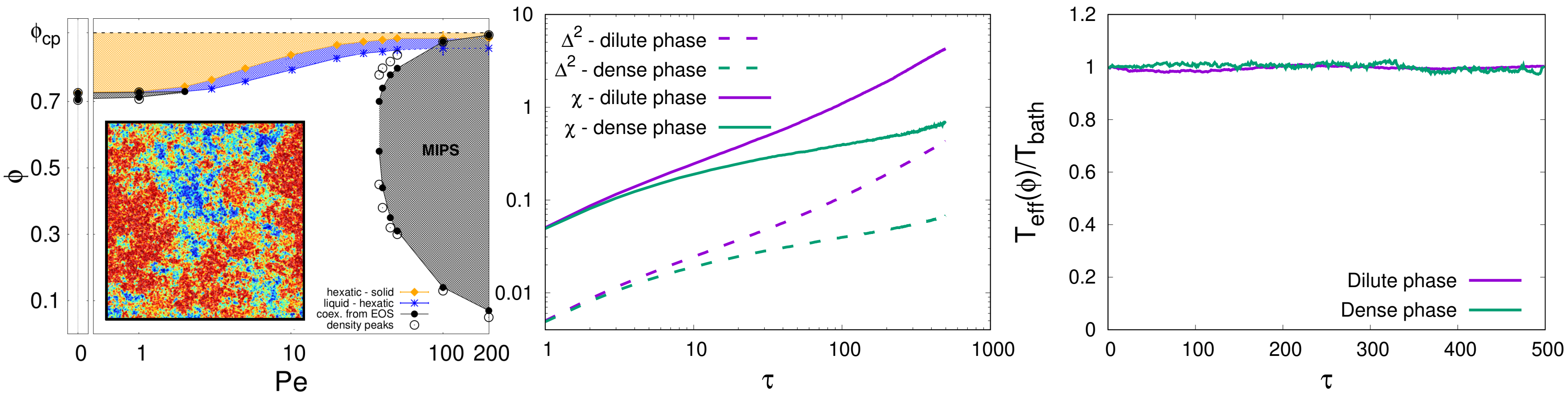
$$\boxed{\chi_{AB}(t - t_w) \equiv \int_{t_w}^{t} dt' \, R_{AB}(t, t') = \frac{[\Delta^2_{AB}(t - t_w) - \Delta^2_{AB}(0)]}{2k_B T_{\text{eff}}(t - t_w)}}$$

Teff = T

Co-existence in equilibrium

Pe = 0 $\phi = 0.710$

Integrated linear response & mean-square displacement: their ratio (FDT) $\tau = t - t_w$



Method: linear response computed with Malliavin weights (no perturbation applied) as proposed by **G. Szamel** for active matter systems.

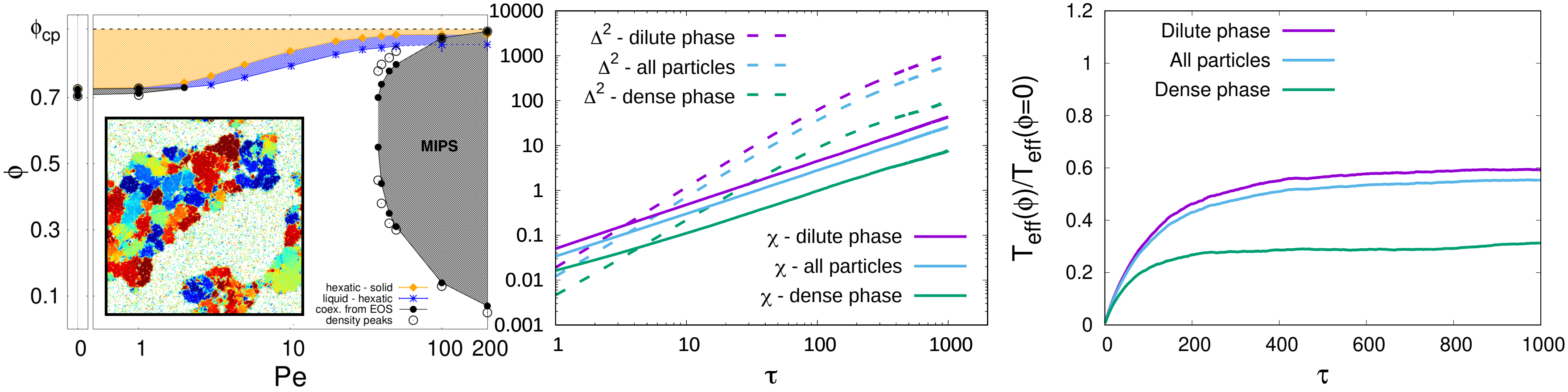
Petrelli, LFC, Gonnella & Suma, in preparation

Teff ≠ T

Co-existence in MIPS

Pe = 50 $\phi = 0.5$

Integrated linear response & mean-square displacement: their ratio (FDR) $\tau = t - t_w$



Method: linear response computed with Malliavin weights (no perturbation applied) as proposed by **G. Szamel** for active matter systems.

Petrelli, LFC, Gonnella & Suma, in preparation

$2d$ colloidal suspensions

Hexatic correlation functions

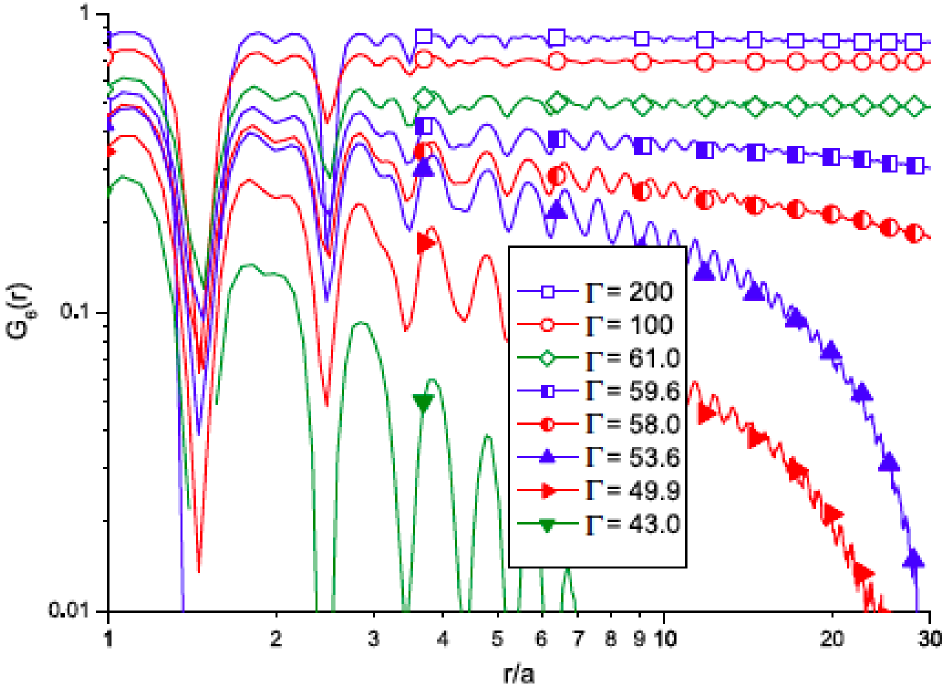
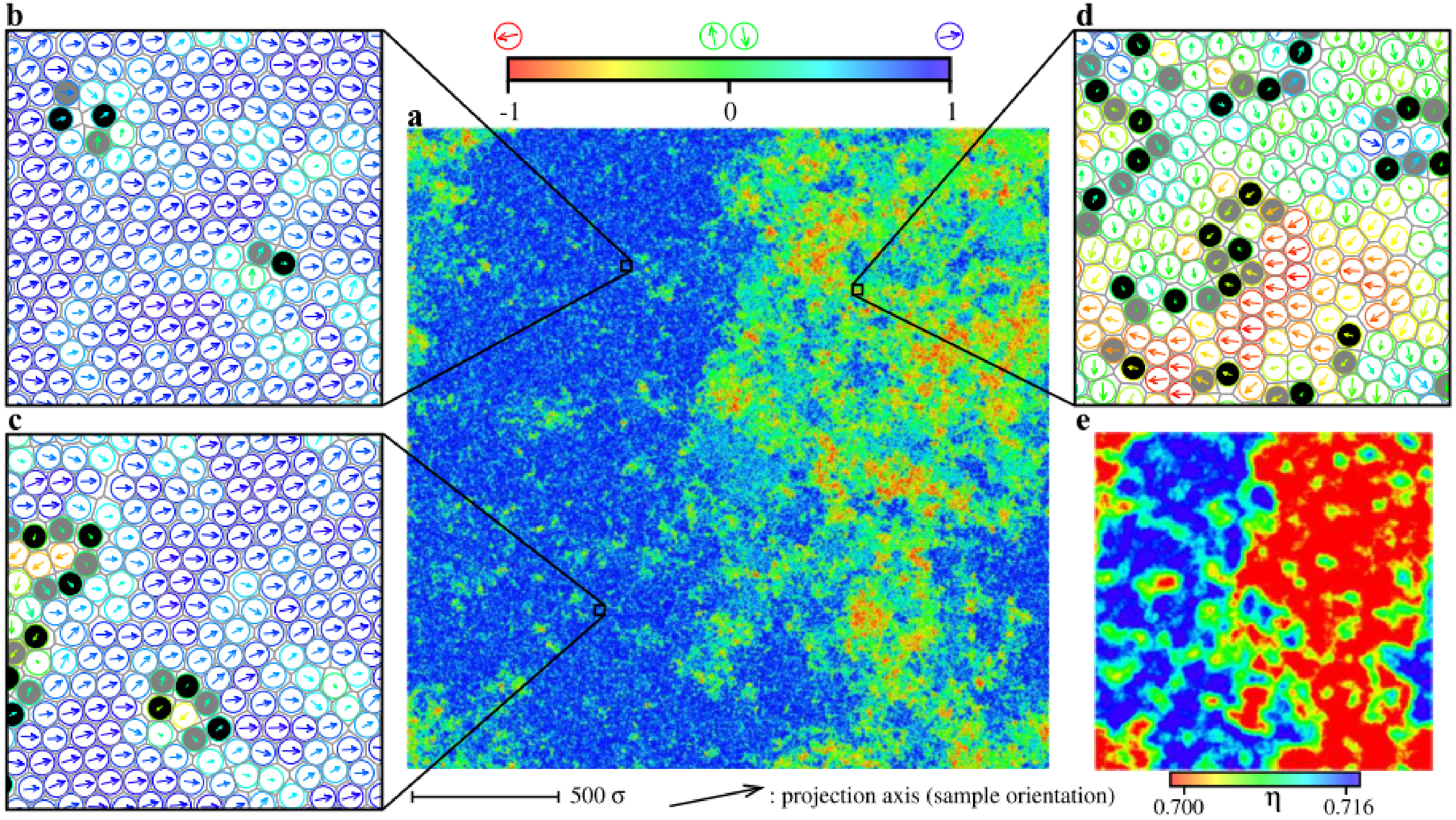


Figure from **Keim, Maret & von Grünberg, PRE 75, 031402 (2007)**

Hard disks in two dimensions

Coexistence



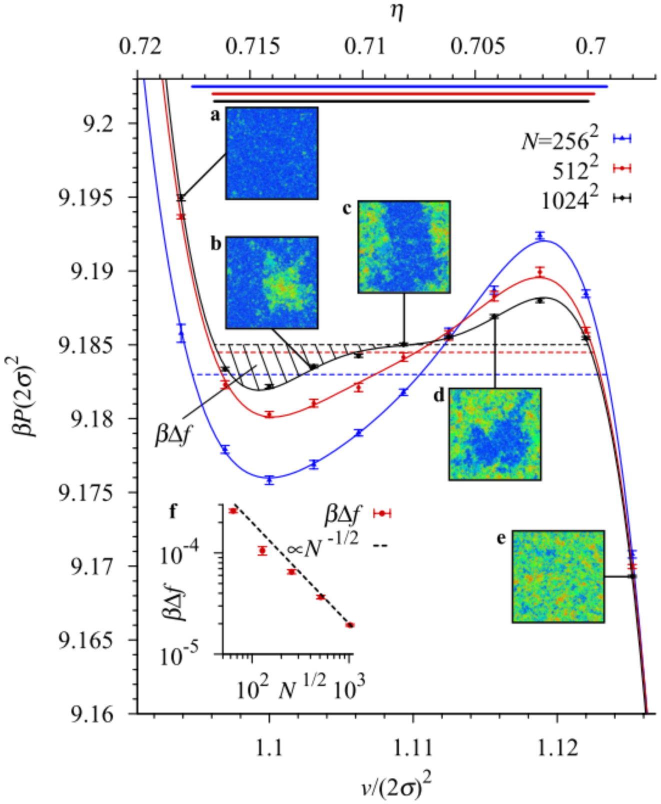
“Two-step melting in two dimensions : first-order liquid-hexatic transition”

Bernard & Krauth, PRL 107, 155704 (2011)

Hard disks in two dimensions

Pressure loop and finite N dependence

Hexatic Liquid

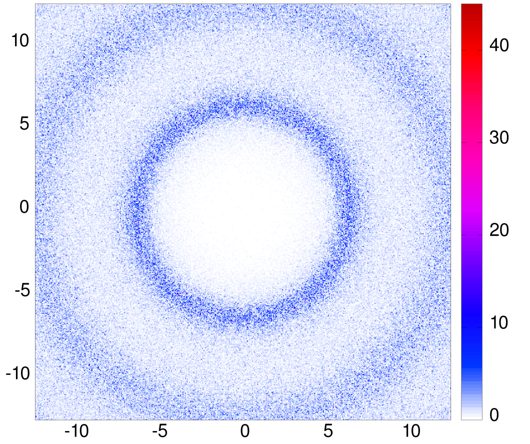


A system with PBCs has a ~ flat interface with surface energy scaling as $S \simeq L^{d-1} = \sqrt{N}$ and $f \simeq N^{-1/2}$. Verified in the inset for $\phi \simeq 0.708$

Passive system

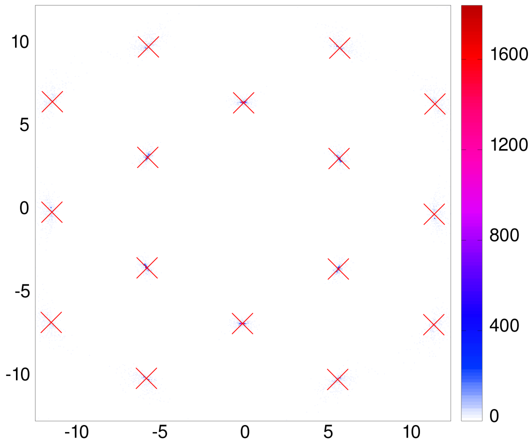
Structure factor - very low and very high density

$\phi = 0.66$



Liquid

$\phi = 0.76$



Solid

Bragg peaks

Primitive vectors

$$\boldsymbol{q}_1 = \frac{4\pi}{a\sqrt{3}}\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$$

$$\boldsymbol{q}_2 = \frac{4\pi}{a\sqrt{3}}(0, 1)$$

Unit of length

$$a = \left(\frac{\pi}{2\sqrt{3}\phi}\right)^{1/2} \sigma_{\rm d}$$

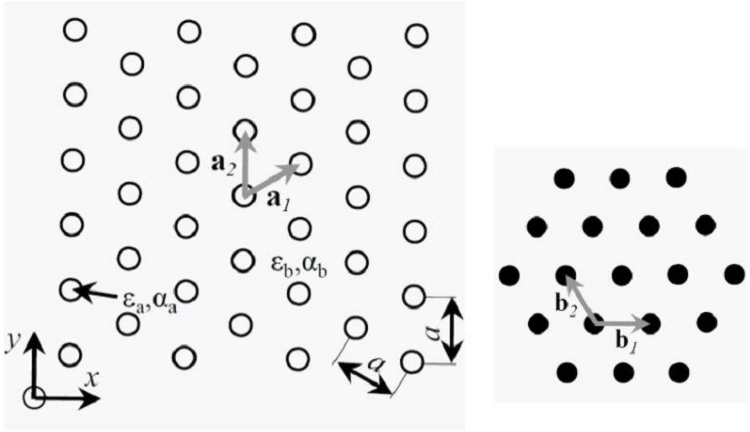
Observables

Structure factor in $2d$: test of positional order

$\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ are the positions of the disks i and j and $\boldsymbol{q}$ is a wave-vector :

$$S(\boldsymbol{q}) = \frac{1}{N} \sum_{ij} e^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_i - \boldsymbol{r}_j)}$$

Visualisation : two dimensional representation in the (q_x, q_y) plane.



(a)

(b)

Triangular lattice in real space

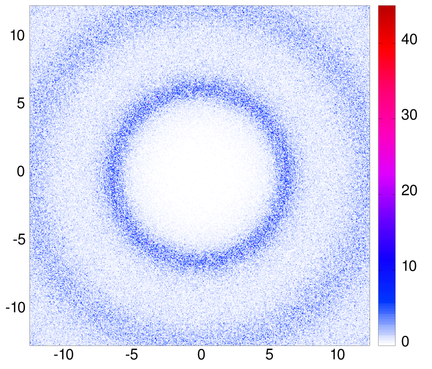
Hexagonal lattice in reciprocal space

Passive system

Structure factor - progressive increase in density

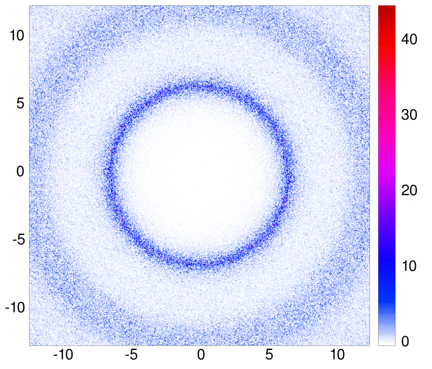
$\phi = 0.66$

(liquid)



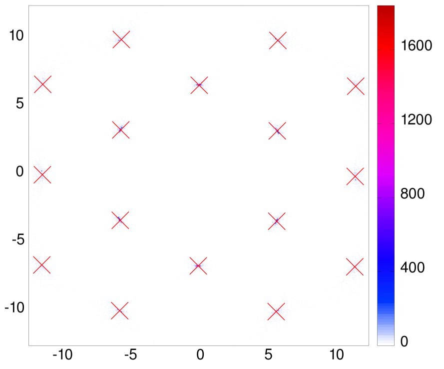
$\phi = 0.72$

(liquid)



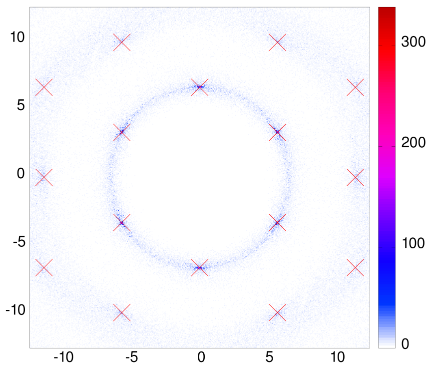
$\phi = 0.76$

(solid)



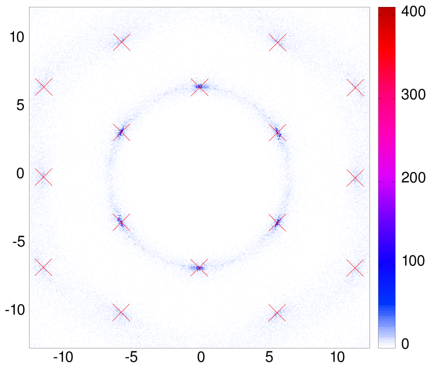
$\phi = 0.734$

(co-existence)



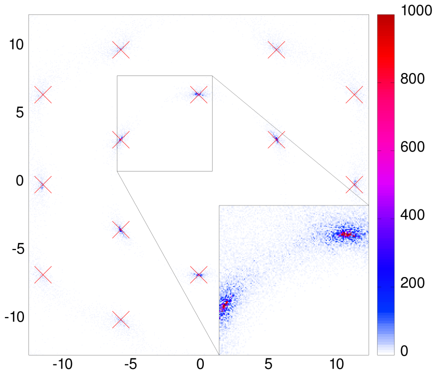
$\phi = 0.74$

(co-existence)



$\phi = 0.75$

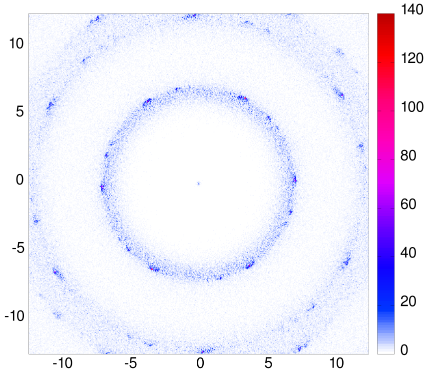
(co-existence)



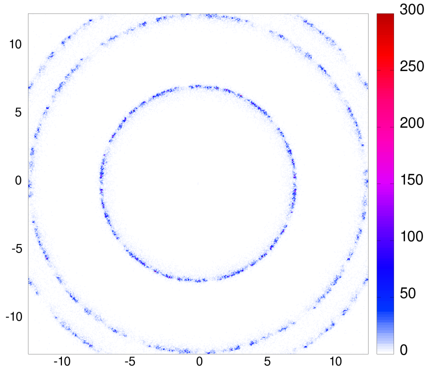
Active system

Structure factor Pe = 10 & Pe = 40

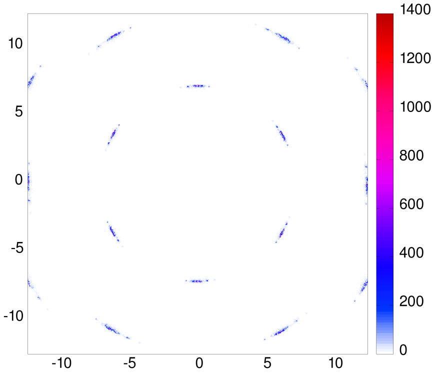
$\phi = 0.734$



$\phi = 0.84$



$\phi = 0.88$

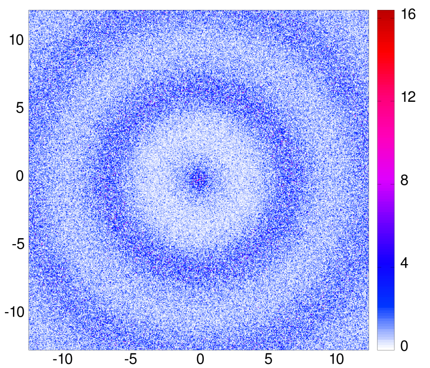


Pe = 10

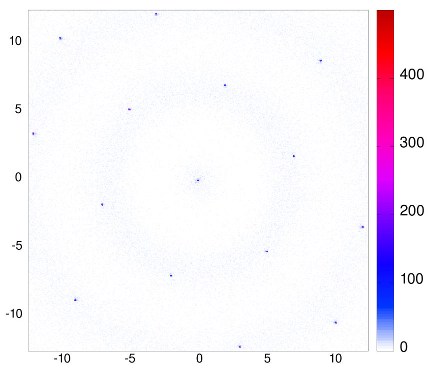
(liquid)

(upper limit of co-existence)

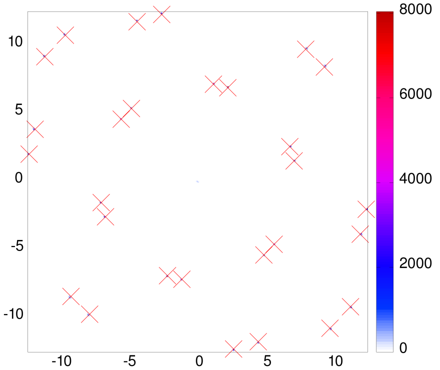
$\phi = 0.26$



$\phi = 0.28$



$\phi = 0.34$



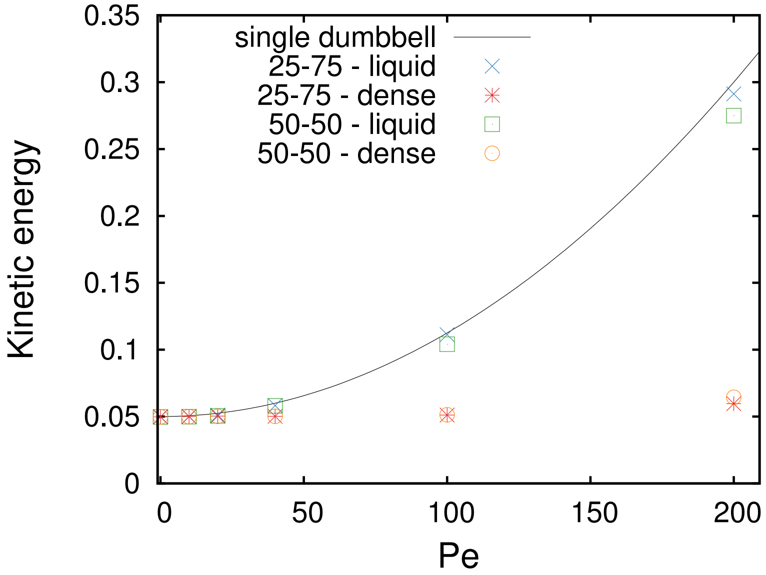
Pe = 40

(liquid)

(lower limit of co-existence)

Kinetic energy

Two populations in co-existence region



→ Liquid/disordered

→ Dense/hexatic

The averaged hexatic modulus is computed for each particle on a radius of 10 σ_{d} around the particle itself, and a particle is considered to be inside a cluster only if this value is greater than 0.75. Those particles contribute to the "dense" branch.

Petrelli, Digregorio, LFC, Gonnella, Suma, Eur. Phys. J. E 41, 128 (2018)

Active dumbbell

Control parameters

Number of dumbbells N and box volume S in two dimensions:

packing fraction $\boxed{\phi = \dfrac{\pi\sigma_{\rm d}^2 N}{2S}}$

Energy scales:

Active work $2\sigma_{\rm d}\, F_{\rm act}$

thermal energy k_BT

Péclet number $\boxed{\text{Pe} = \dfrac{2F_{\rm act}\sigma_{\rm d}}{k_BT}}$

Active force $Lv \mapsto \sigma_{\rm d}\, F_{\rm act}/\gamma$

viscous force $\nu \mapsto \gamma\sigma_{\rm d}^2/m_{\rm d}$

Reynolds number $\boxed{\text{Re} = \dfrac{m_{\rm d}F_{\rm act}}{\sigma_{\rm d}\gamma^2}}$

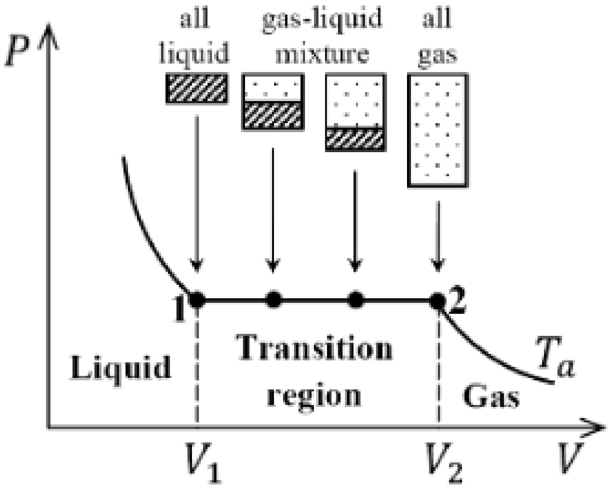
$\text{Pe} \in [0, 200]$ $\text{Re} < 10^{-2}$ $\boxed{N = 512^2 \simeq 2.6 \times 10^5}$

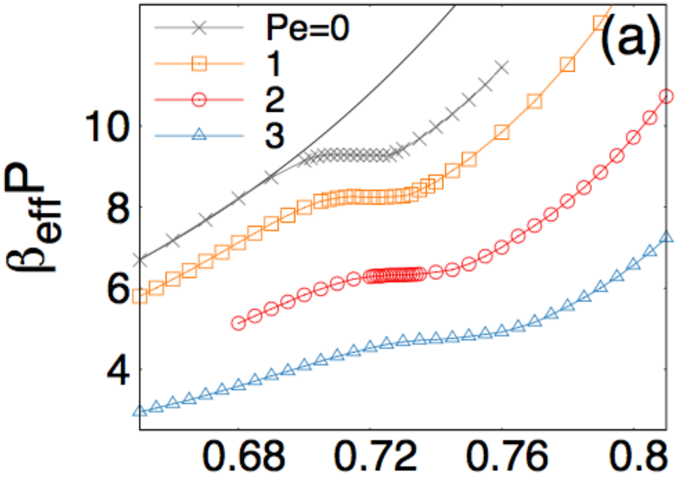
Stiff molecule limit: vibrations frozen.

Interest in the ϕ, $F_{\rm act}$ and k_BT dependencies, $k_BT = 0.05$ fixed.

Active disks

Equation of state (eos) : pressure





$$\Delta P = P - P_{\rm gas} = \frac{F_{\rm act}}{2V}\sum_i\langle \mathbf{n}_i\cdot\mathbf{r}_i\rangle - \frac{1}{4V}\sum_{i,j}\langle\nabla_i U(r_{ij})\cdot(\mathbf{r}_i-\mathbf{r}_j)\rangle$$