Polymorphism in Wigner bilayer crystals

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IHP / June 27 2016

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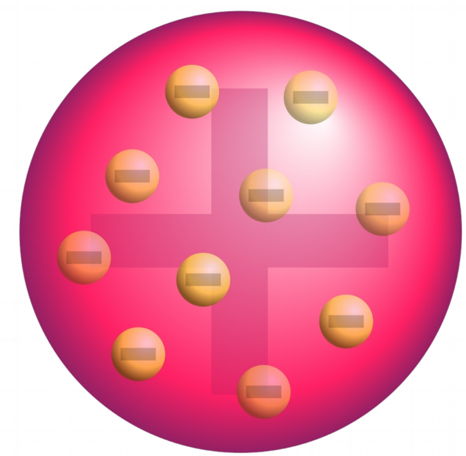
Thomson problem → plum pudding



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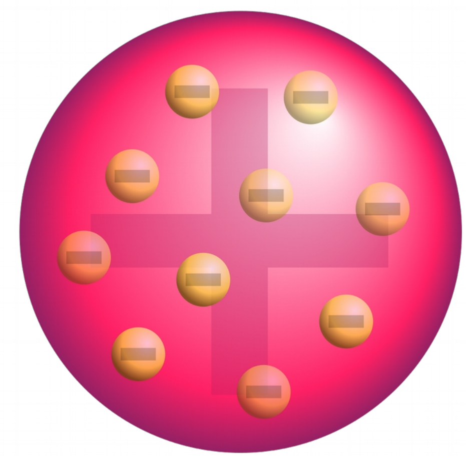

Question :
Thomson pancake ?

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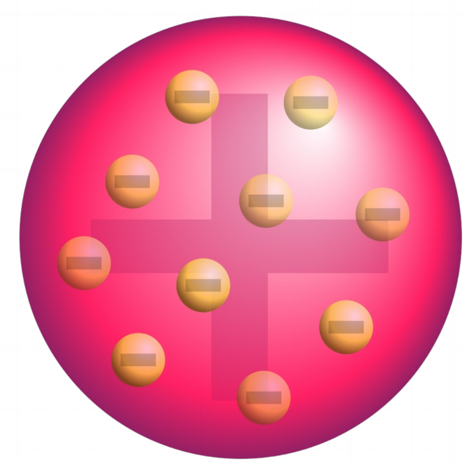
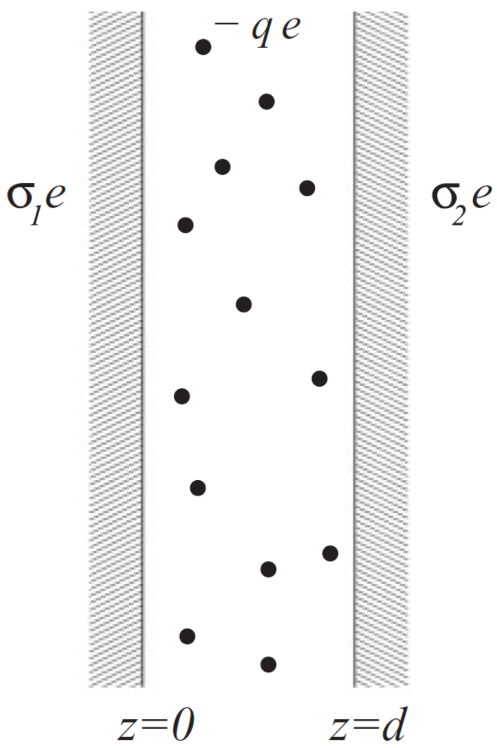


Question :
Thomson sandwich / pancake ?

→ Thomson *asymmetric double* pancake problem



The system

Equivalent point charges confined in a slit

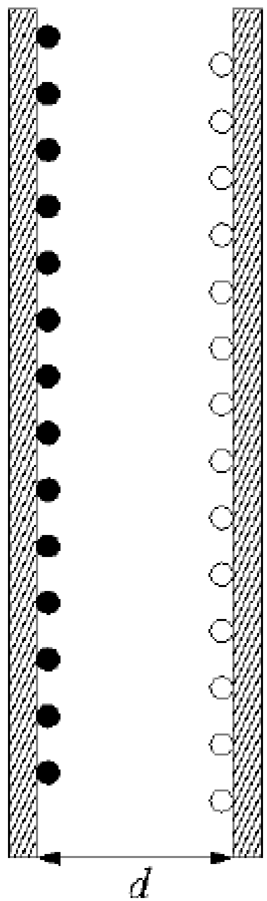
Two planar charged boundaries $z=0$ and $z=d$

Coulomb interactions + global charge neutrality

Optimal (energy min) ground state configuration ?

Asymmetric since $\sigma_1 \neq \sigma_2$

Why a *double pancake* ?



Side view

Earnshaw theorem (1842)

harmonic functions

$$\nabla^2 \varphi = 0$$

NB: does not apply to plum pudding...

… pancake specific

So, why do charges go to border ?

Question:

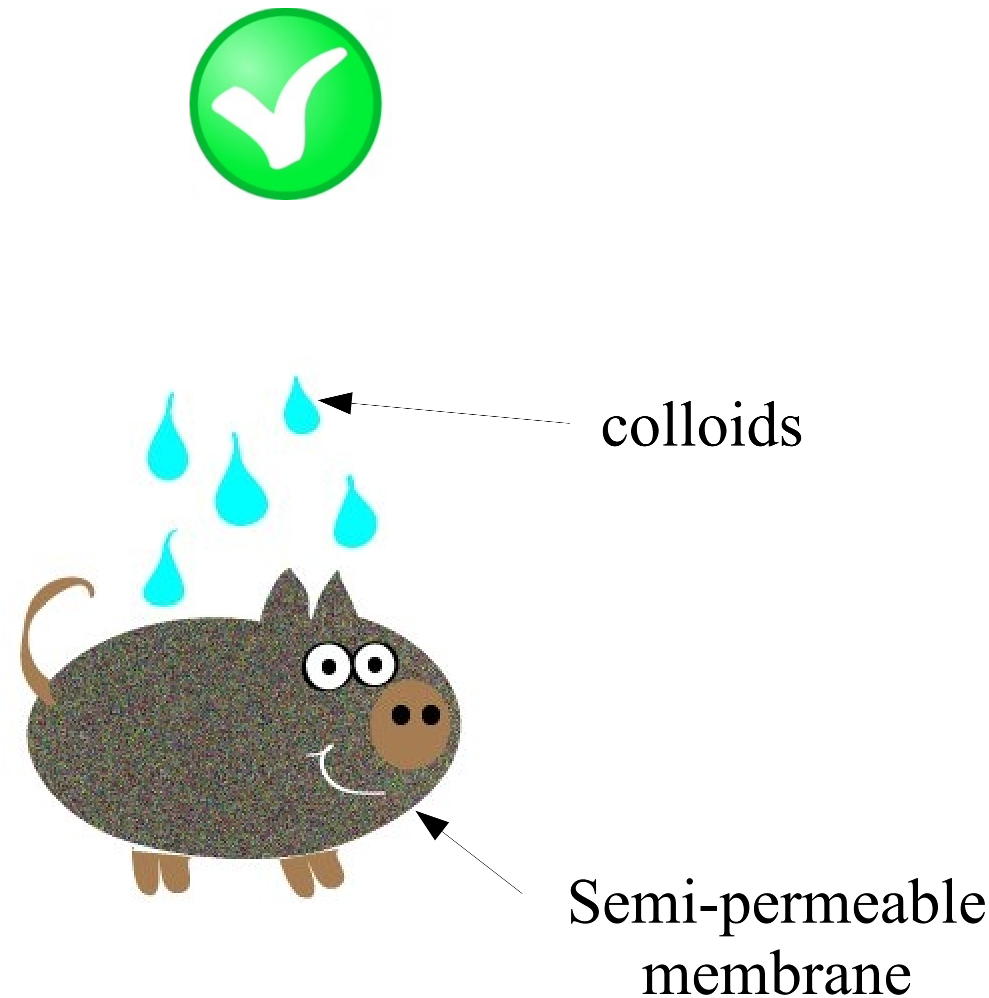
Which arrangement of charges on each plate ?

Motivation ?

- Generalization of Wigner monolayer problem
  → realized with e^- at *He* interface
- Bilayers appear in
  - semiconductors,
  - trapped plasmas,
  - colloidal systems

Aside : what are colloids ?

© Surfgoopy

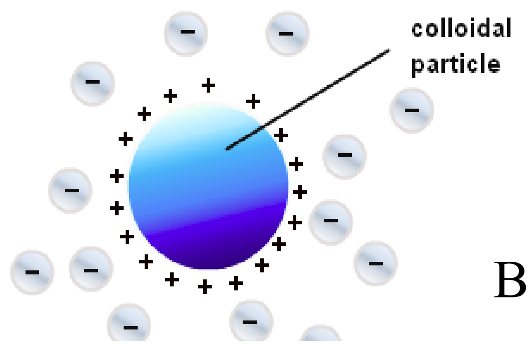


Thus : a colloid is anything, bigger than one nanometer…
(membrane porosity)

Bilayers in colloidal systems ?

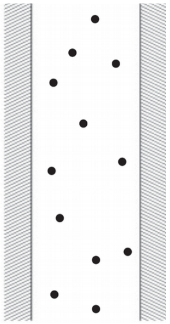
Colloids (macromolecules) often in solvents like water
large dielectric permittivity → charged groups dissociate

Most surfaces become (highly) **charged**



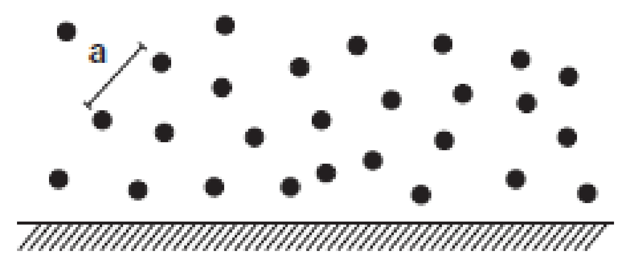
Big 'atoms' + small ions

At small distances → consider plates (curvature neglected)



Equilibrium statistical description at temperature *T*

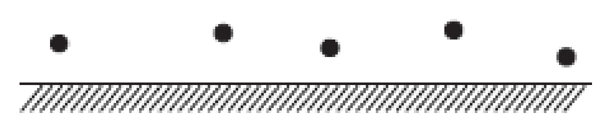
- At 'large *T*', behaviour well understood:
  Poisson-Boltzmann (mean-field) theory

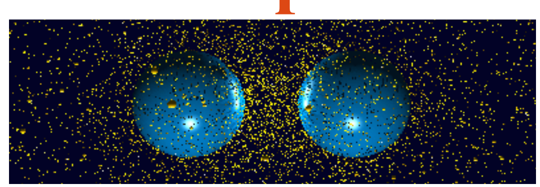


$$\nabla^2 \psi(\boldsymbol{r}) = \kappa^2 \sinh[\psi(\boldsymbol{r})]$$

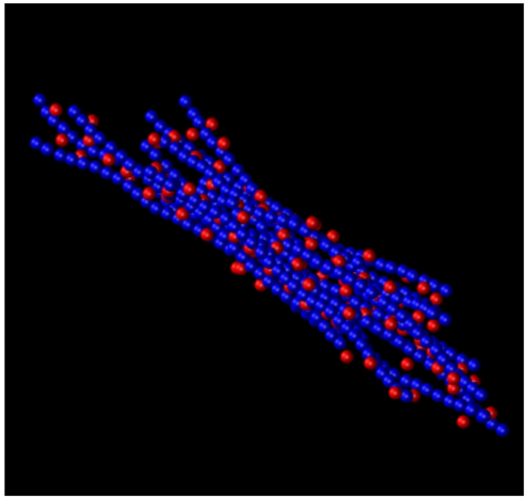
→ like-charged colloids always repel
→ useful connection with *Painlevé III equations*

- At 'small *T*': new phenomena
  rich and counter-intuitive
  → **like charge attraction possible**

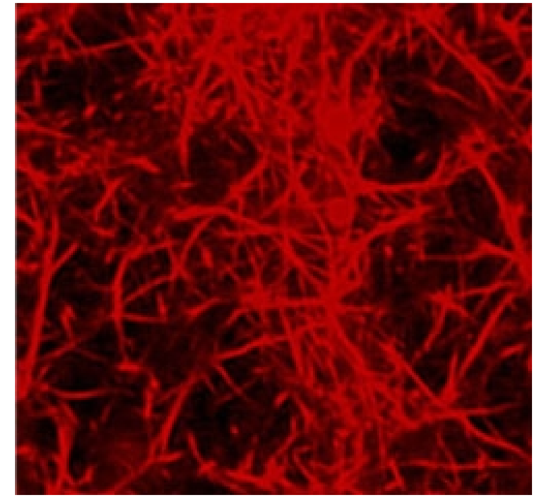




Illustrations



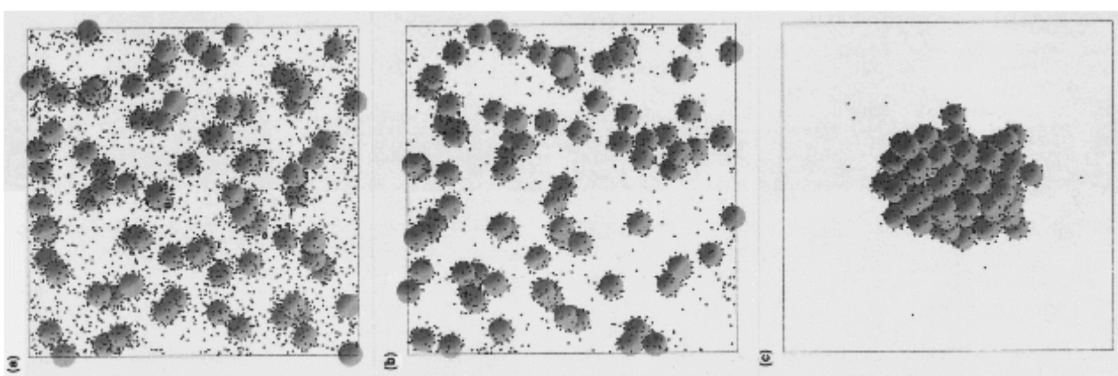
Holm / Sayar



J. Shin et al

DNA bundles

clumping of strands of actin proteins



colloidal aggregates

Lobaskin and Linse

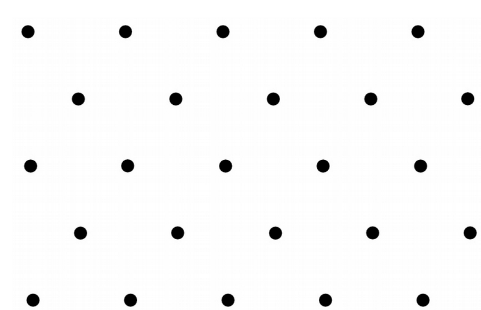
$\downarrow T$

But also : *cohesion of cement*, etc

Necessary to understand $T = 0$ limit
→ ground state properties

Minimize Coulombic energy

Single plate problem well known: triangular Wigner crystal




32 Ft
WIGNER JENŐ 1902-1995
MAGYARORSZÁG

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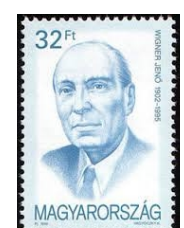
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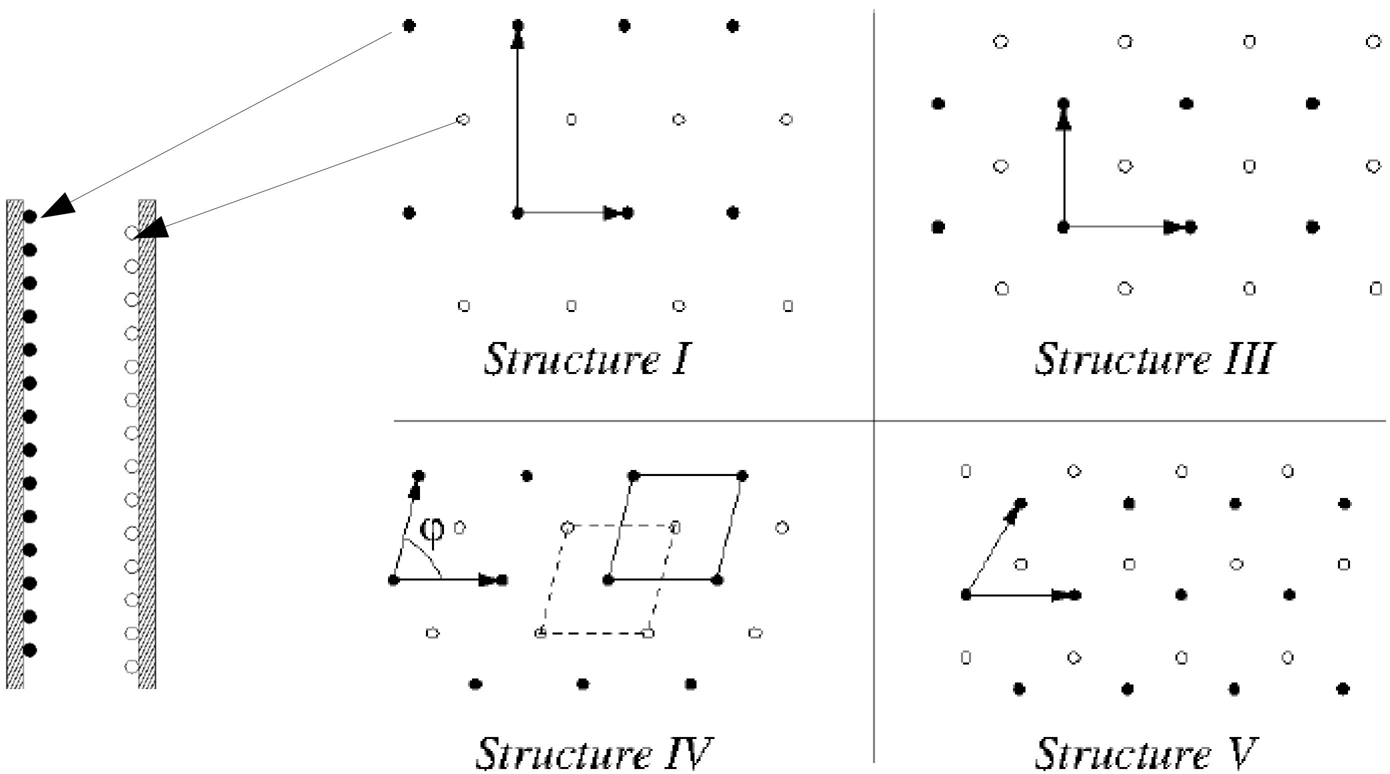
MAGYARORSZÁG

Symmetric two plate phenomenology as distance η increases



At each plate : rectangle, square, rhombus, hexagons

Symmetric case ($\sigma_1=\sigma_2$) still some open questions

- What critical behaviour ?
  How do geometrical features depend on distance η ?
- Precise location of transition points ?
  Stability window for each phase ?
- Does phase I exist for η non zero ?

$\rightarrow$ bane of previous approaches : difficult to compute precisely the Coulombic energy to be minimized (even numerically)

Asymmetric case completely open

Our approach

- Numerical, 2-fold
  - Genetic / evolutionary algorithm
  - Monte Carlo (small temperature)
- Analytical :
  - compute exactly Coulomb energy for prescribed (not too complex) structures
  - find the best
  - bag of candidate structures: given by numerics

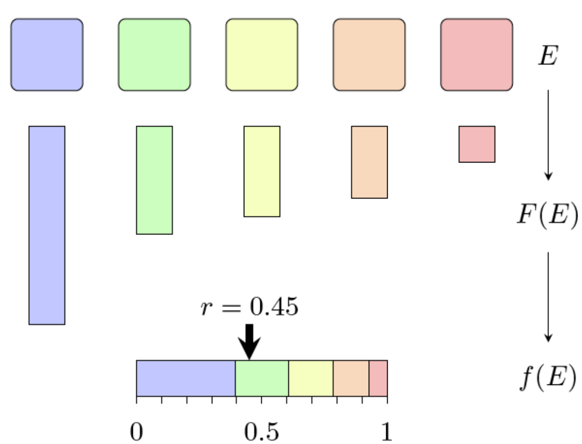
Genetic algorithm

- Search heuristic mimicking natural selection
- Adaptation of population (of structures) to environment
  - *Mutation* (introduction random new traits)
  - *Crossover* (combination good traits)
- Degree of adaptation is fitness → related Coulomb energy

$$F(E) = \exp\left[-s\frac{(E-E_{min})}{(E_{max}-E_{min})}\right]$$

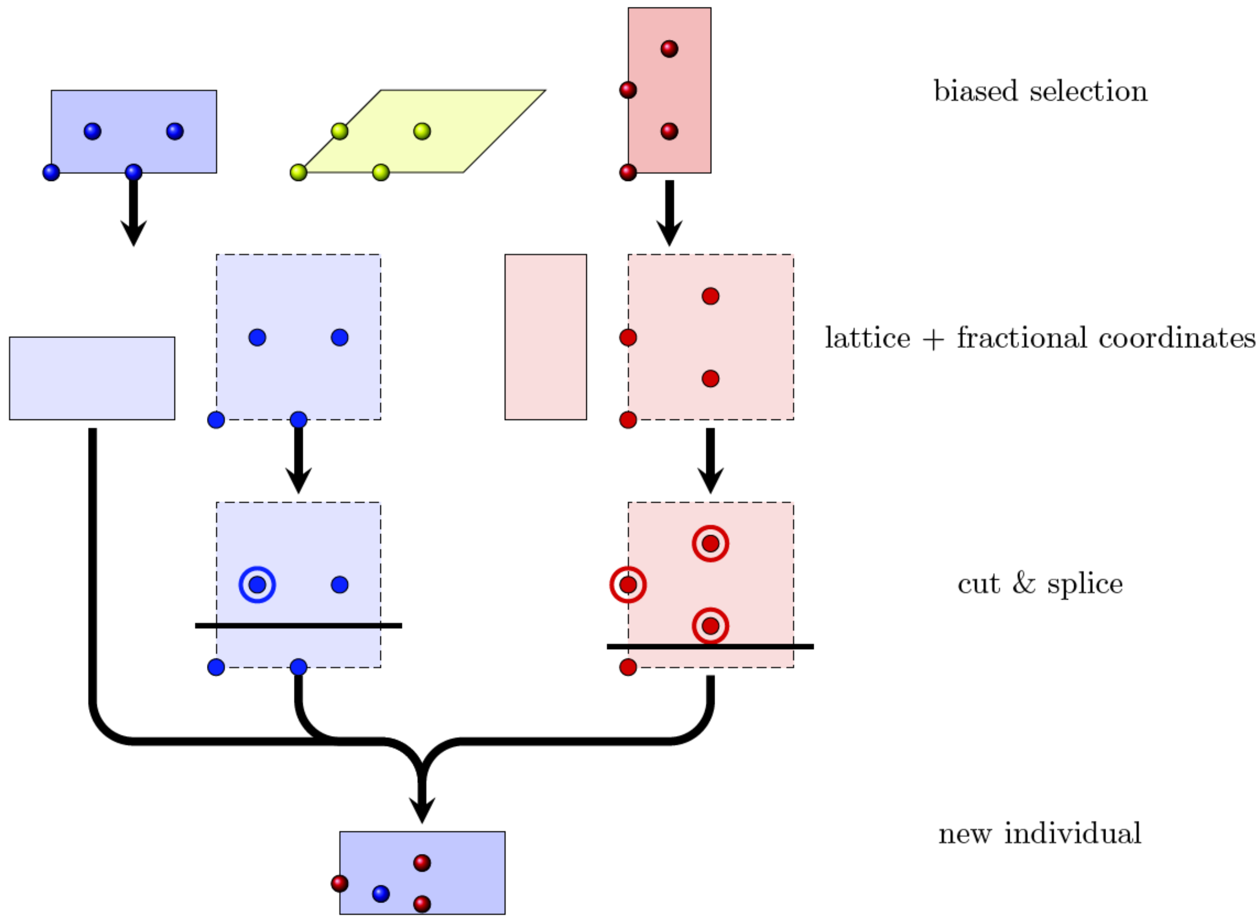
$$\exp(-s) \leqslant F(E) \leqslant 1$$

large s exclude weak candidates from reproduction (s=3)



- Energy calculation : requires care (Ewald summation)

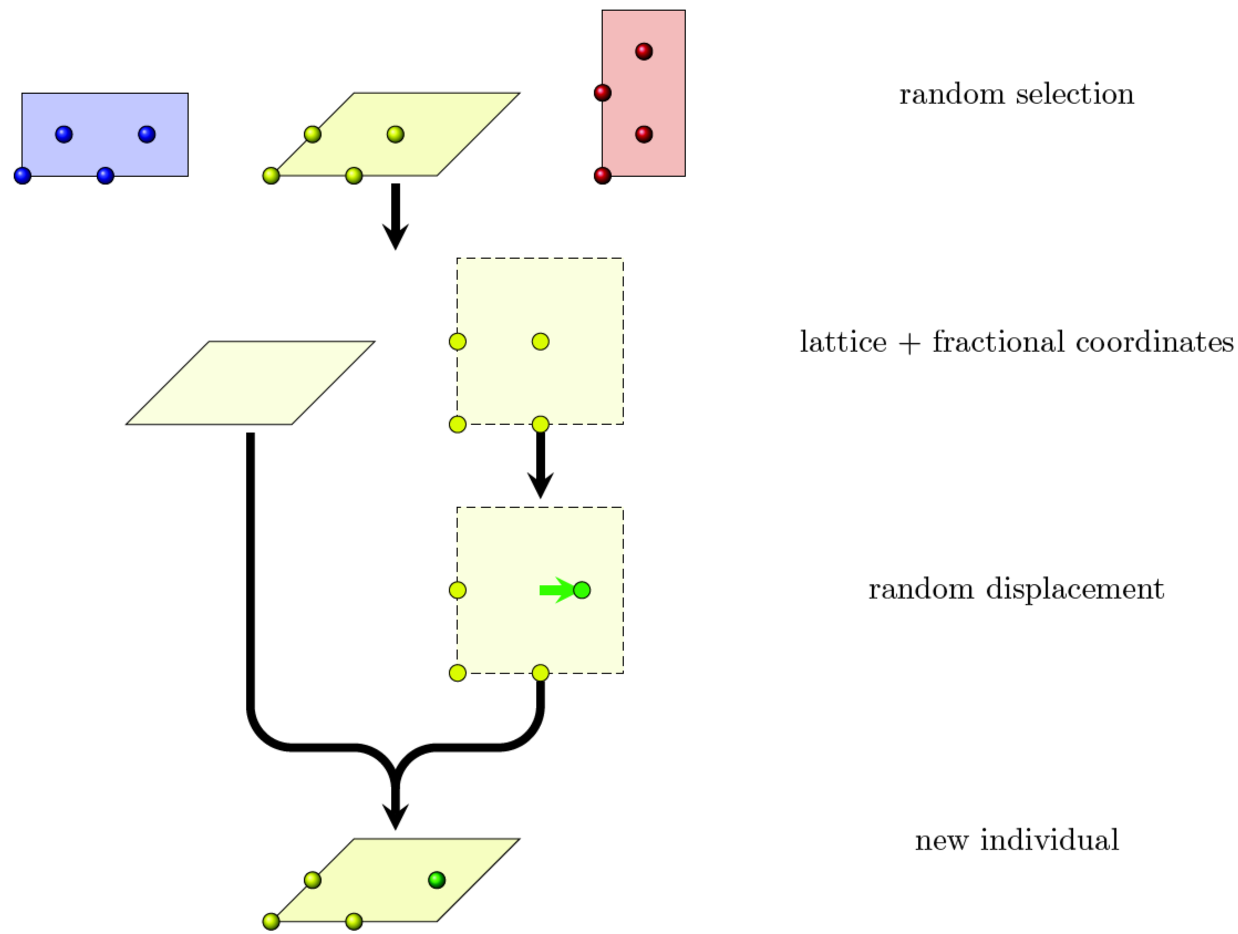
Genetic algorithm (2)
the crossover



Crossover operation, from 2 parents with $N=4$

One parent passes on lattice vectors ; positions and orientations passed on in a more complex way

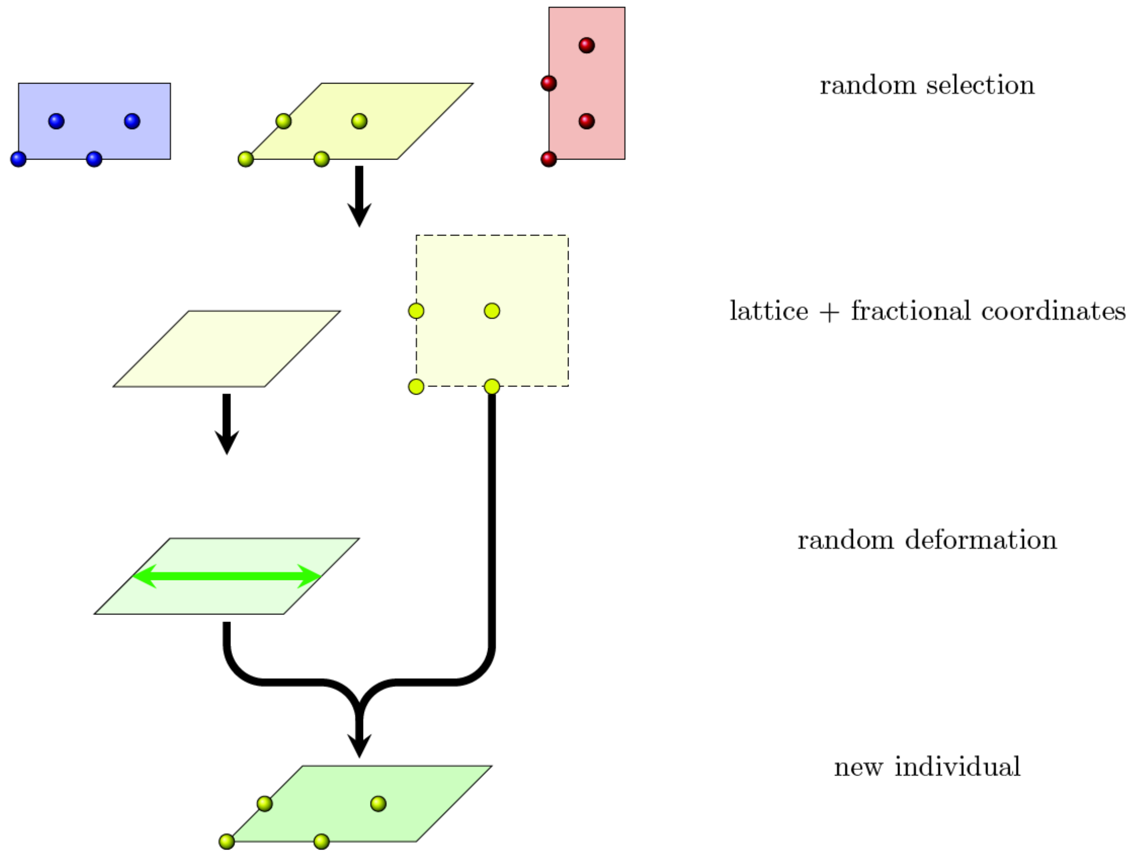
Genetic algorithm (3) mutation / move



Mutation operation (move type)

One candidate picked at random and a particle randomly displaced

Genetic algorithm (4) mutation / strain



Mutation operation (strain type)

One candidate picked at random and lattice vectors randomly deformed

- Genetic algorithm : great tool, but limited $N=40$
- Complementary method : Monte Carlo
  → larger systems ($N=5000$)
  → test stability…
- … yield ~ 10 families of crystals
  each depending continuously on some structural parameters
- Analytical approach

Looking for new series representation of energies of all (tractable) phases

Compute energy : start by “intra”-layer term , embed within a disc

$$\frac{e^2}{2a} \sum_{\substack{j,k \\ (j,k)\neq(0,0)}} \frac{1}{\sqrt{j^2+k^2\Delta^2}}, \qquad j^2+k^2\Delta^2 \leq \left(\frac{R}{a}\right)^2$$

Subtract background, diverging disc radius making use of gamma identity

$$\frac{1}{\sqrt{z}} = \frac{1}{\Gamma(1/2)} \int_0^\infty \frac{dt}{\sqrt{t}} e^{-zt}, \qquad z>0$$

Heavy use of Poisson summation formula

$$\sum_{j=-\infty}^{\infty} e^{-(j+\phi)^2 t} = \sqrt{\frac{\pi}{t}} \sum_{j=-\infty}^{\infty} e^{2\pi i j\phi} e^{-(\pi j)^2/t}$$

related to Ewald summation

Illustration

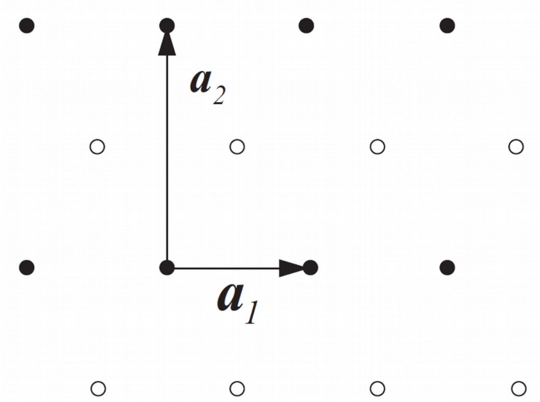
$$S \equiv \sum_{(n,m)\neq(0,0)} \frac{1}{\sqrt{n^2+m^2}} - \mathsf{backgr}$$

$$S = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{\mathrm{d}t}{\sqrt{t}} \left[\theta_3^2(\mathrm{e}^{-t}) - \underbrace{1}_{n=m=0} - \underbrace{\frac{\pi}{t}}_{\text{backgr}} \right]$$

$\theta_3(q) = \sum_{n=-\infty}^{\infty} q^{n^2}$ (Jacobi function)

$$\theta_3(\mathrm{e}^{-t}) \underset{t\to 0}{\sim} \sqrt{\frac{\pi}{t}}$$

For structure II



$$\frac{E(\Delta,\eta)}{e^2\sqrt{n}} = \frac{1}{2^{3/2}\sqrt{\pi}} \int_0^\infty \frac{dt}{\sqrt{t}} \Big\{ \Big[\theta_3(e^{-t\Delta})\theta_3(e^{-t/\Delta}) - 1 - \frac{\pi}{t} \Big] + e^{-\boxed{\eta^2}t} \Big[\theta_2(e^{-t\Delta})\theta_2(e^{-t/\Delta}) - \frac{\pi}{t} \Big] \Big\}$$

$$\theta_2(q) = \sum_j q^{(j-\frac{1}{2})^2}$$

But 2 dangerous limits (large and small t)

→ reexpress as integral over [0,π]

→ introduce series representation

The resulting series : $$z_\nu(x,y) = \int_0^{1/\pi} \frac{dt}{t^\nu} e^{-xt} e^{-y/t} \qquad \text{for } y > 0$$

$$\frac{E(\Delta,\eta)}{e^2\sqrt{n}} = \frac{1}{2^{3/2}\sqrt{\pi}} \Bigg\{ 4\sum_{j=1}^{\infty} \left[z_{3/2}(0, j^2/\Delta) + z_{3/2}(0, j^2\Delta) \right] + 8 \sum_{j,k=1}^{\infty} z_{3/2}(0, j^2/\Delta + k^2\Delta)$$
$$+2\sum_{j=1}^{\infty}(-1)^j \left[z_{3/2}((\pi\eta)^2, j^2/\Delta) + z_{3/2}((\pi\eta)^2, j^2\Delta) \right] + 4 \sum_{j,k=1}^{\infty} (-1)^j(-1)^k z_{3/2}((\pi\eta)^2, j^2/\Delta + k^2\Delta)$$
$$+4 \sum_{j,k=1}^{\infty} z_{3/2}(0, \eta^2 + (j-1/2)^2/\Delta + (k-1/2)^2\Delta) - 4\sqrt{\pi} - \pi z_{1/2}(0,\eta^2) \Bigg\}.$$

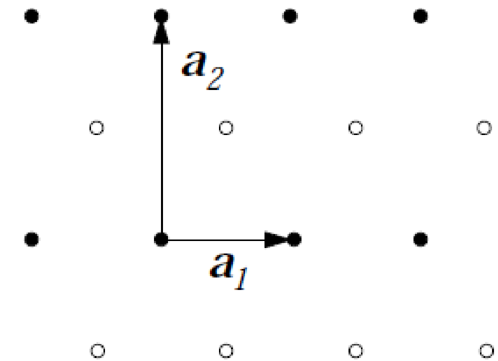
Interest : 3-pronged

Discuss analytically critical behaviour

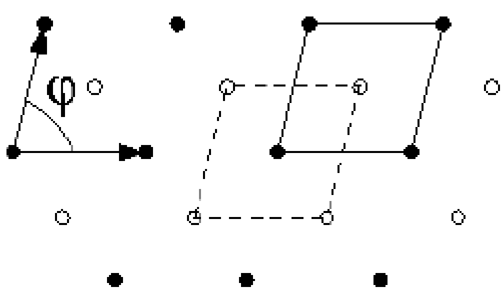
Compute analytically all stability windows / phase diagram

Exceptional convergence properties (4 terms $\leftrightarrow$ 15 digits !)

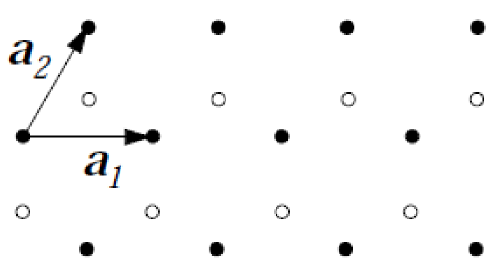
First, clarify symmetric case ($\sigma_1=\sigma_2$)



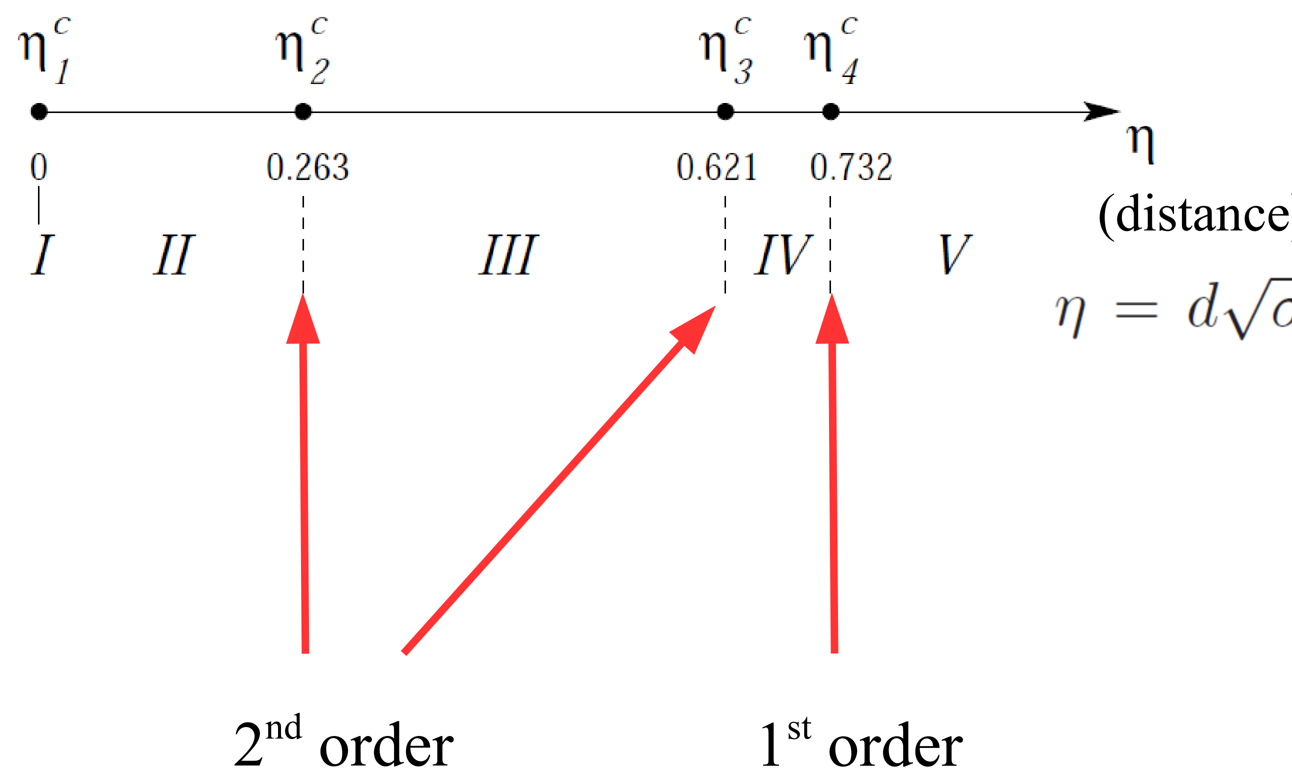
Structures I, II, III



Structure IV



Structure V



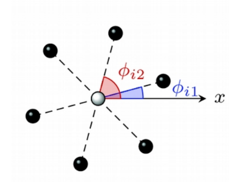
$\mathrm{II} \to \mathrm{III}:$ $\quad$ aspect ratio $- 1 \propto \sqrt{\eta^c - \eta}$

$\mathrm{III} \to \mathrm{IV}:$ $\quad \dfrac{\pi}{2} -$ angle $\propto \sqrt{\eta - \eta^c}$

General case: how to quantify order ?

- Introduce bond orientational order parameters

$$\langle e^{n\ i\ \ angle} \rangle$$



$$\Psi_n^{(L)} = \frac{1}{N_L} \left| \sum_{i \in L} \frac{1}{\sum_{j \in \mathcal{N}_i} l_{ij}} \sum_{j \in \mathcal{N}_i} l_{ij} \exp(\imath\, n\, \theta_{ij})] \right|$$

Sum over nearest neighbors j of particle i in Voronoi construction
Weighted by length l_{ij} of corresponding side of Voronoi cell
$n = 4, 5, 6, 7, 8, 10, 12, 18, 24$

4 types indexed L (plate 1, plate 2, 1+2, 2 with neighbors in 1)

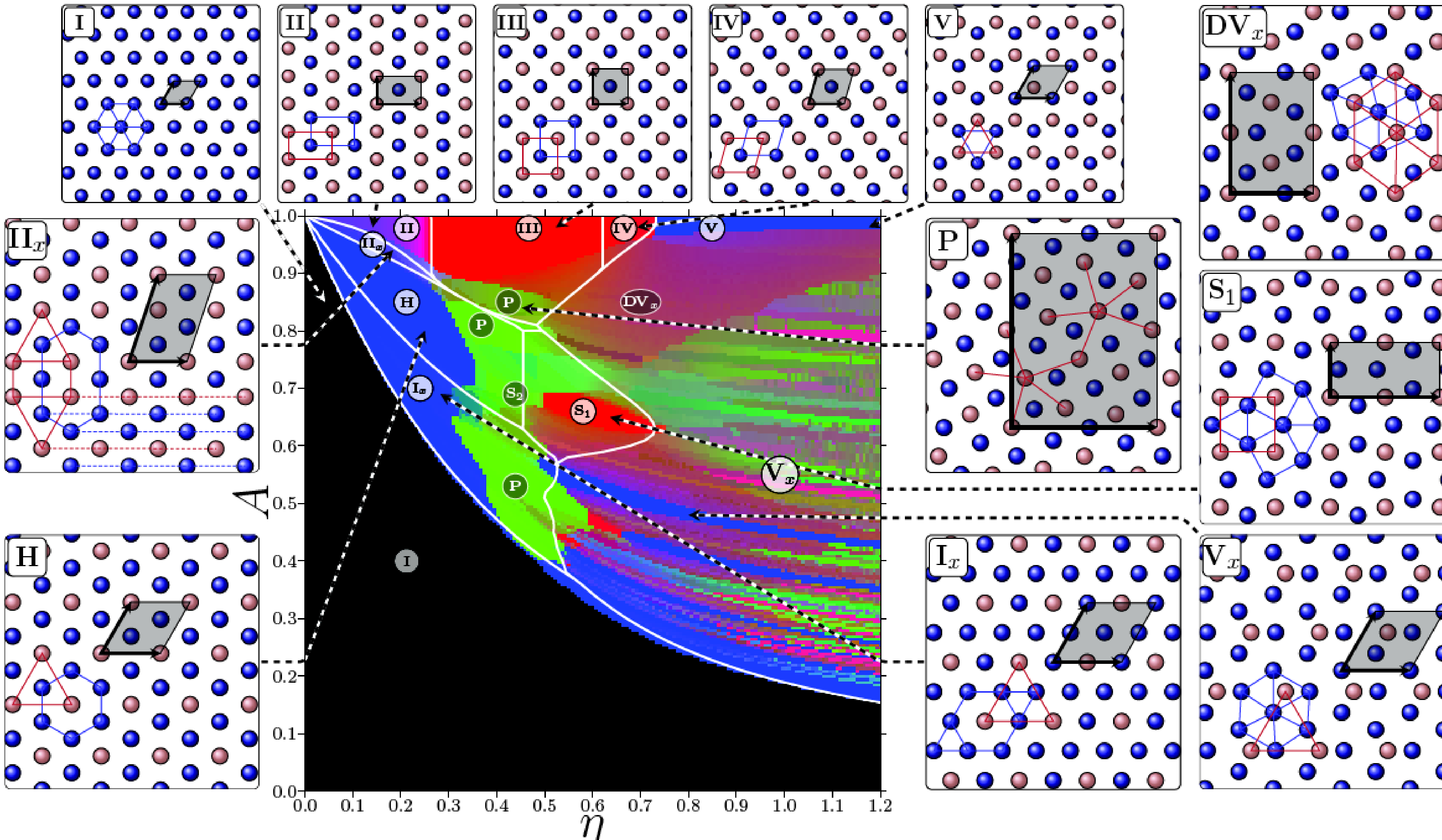
- Another important parameter is occupation index $x = N_2 / N_{tot}$

$$\textit{Indeed}\,,\quad x \neq x_{neutr}\,,\quad \textit{always}$$

How to present results ?

- Introduce bond orientational order parameters ψ_n
- Focus on 4- 5- and 6- fold symmetries (ψ_4, ψ_5, ψ_6)
- Then : RGB coloring scheme, for each pixel of phase diagram
  - **ψ_4 : red**
  - **ψ_5 : green**
  - **ψ_6 : blue**
- Encodes type of symmetry in graphic way
  projects 5-dim space onto plane

Full asymmetric problem



$$A = \sigma_2/\sigma_1$$

ψ_4 : red, ψ_5 : green, ψ_6 : blue

34000 state points

Analytical : I, I_x, II, II_x, III, IV, V, V_x, S

Particles on plate 2 with neighbors in plate 1

A number of unexpected features

competition between commensurability and neutralization

- Appearance of macroscopic charges
- Exotic phases (snub, pentagonal, distorted…)
- Non conventional phase transitions
  distinct critical indices (β=2/3 or 1/2)

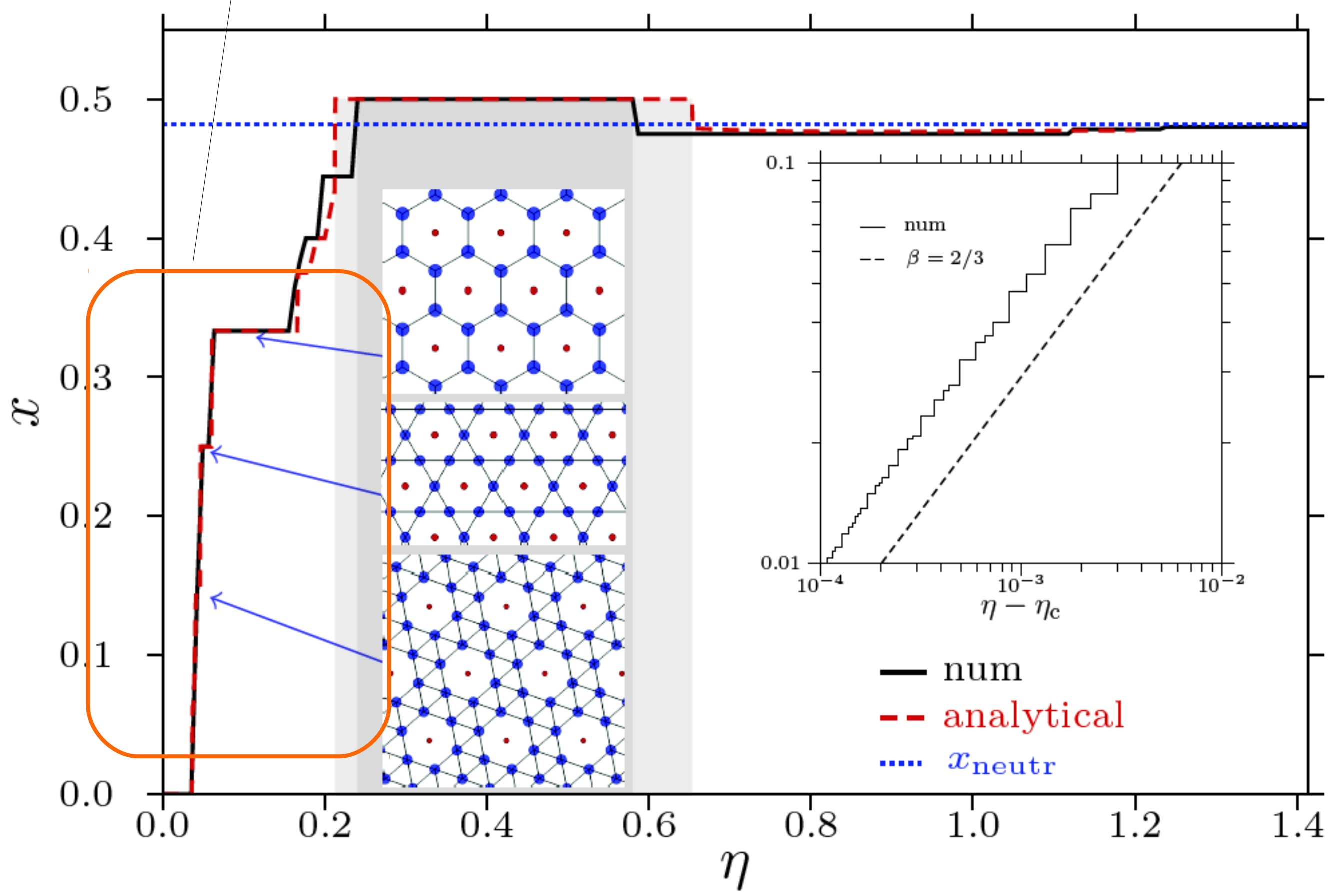
$$\frac{E_{\mathrm{I}_x}(x,\eta) - E_{\mathrm{I}}(\eta)}{e^2 N\sqrt{\sigma_1+\sigma_2}} = f(\eta)x + \frac{2^{3/2}\pi}{\lambda}\eta^2 x^{5/2} + O(x^{7/2})$$

$$x \propto (\eta - \eta_c)^\beta \text{ with } \beta = 2/3$$

- Long range attraction
  Symmetric → exponential force [exp(-η)]
  Asymmetric → always algebraic ($1/\eta^2$)
- Overcharging possible (plate 2), but atypical

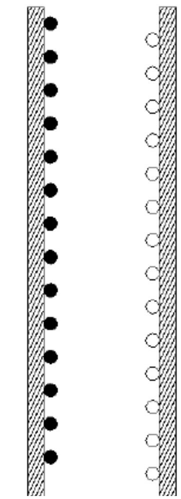
Cascade of I_x structures

$x = 1/(j^2 + jk + k^2) \rightarrow 1/3, 1/4, 1/7, 1/9...$



$x = N_2 / N_{tot}, \ A = 0.93$

Conclusion



- Point charges confined in a slab
  Thomson sandwich → two pancakes
- Combined analytical/numerical techniques
- Surprising variety of structures, all periodic
- Due to asymmetry
  - Plate-plate pressure becomes long range
  - Macroscopic charges emerge
  - New phase transitions appear (not Landau type)

Thank you

In collaboration with

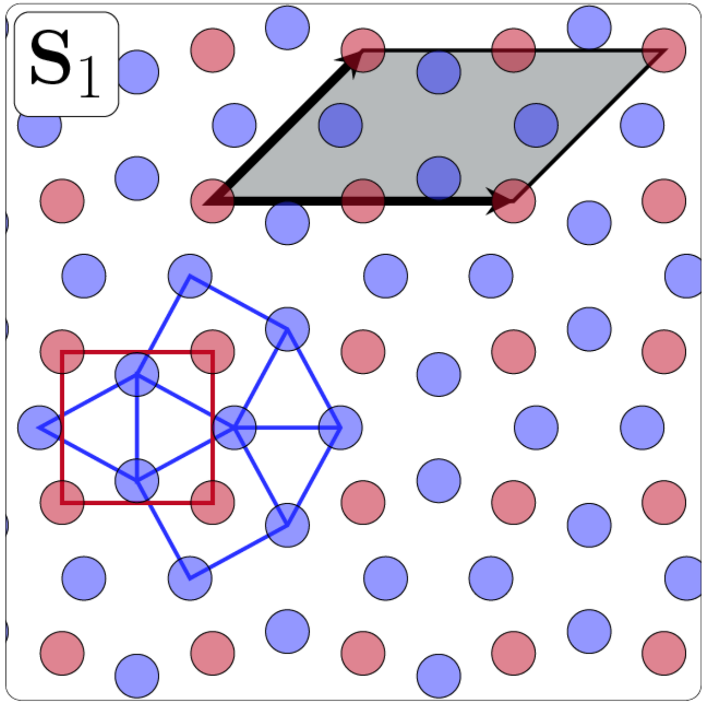
Moritz Antlanger (Vienna)

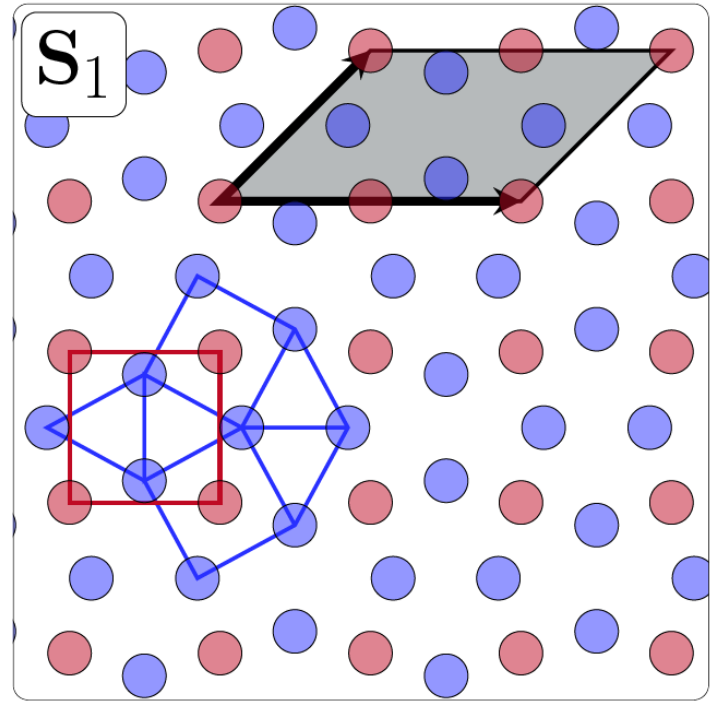
Gerhard Kahl (Vienna)

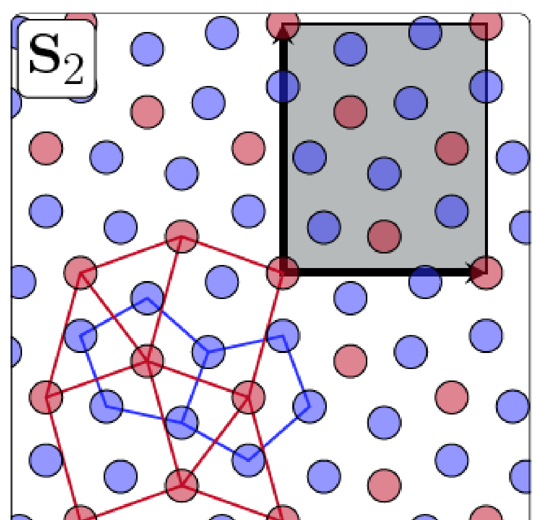
Martial Mazars (Orsay)

Ladislav Samaj (Bratislava)

Snub phase







Nomenclature

I	$x = 0$		hexagonal monolayer
II	$x = 1/2$	$\Psi_4^{(1,2)} = 1,\ 0 < \Psi_6^{(1,2)} < 1$	rectangular bilayer
III	$x = 1/2$	$\Psi_4^{(1,2)} = 1,\ \Psi_6^{(1,2)} = 0$	square bilayer
IV	$x = 1/2$	$0 < \Psi_4^{(1,2)} < 1,\ 0 < \Psi_6^{(1,2)} < 1$	rhombic bilayer
V	$x = 1/2$	$\Psi_4^{(1,2)} = 0,\ \Psi_6^{(1,2)} = 1$	hexagonal bilayer
I_x	$0 < x < 1/3$	$\Psi_6^{(3)} > 0.9$	
H	$x = 1/3$	$\Psi_6^{(3)} > 0.9$	honeycomb (layer 2)
II_x	$1/3 < x < 1/2$	$\Psi_6^{(3)} > 0.9$	
V_x	$0 < x < x_{\mathrm{neutr}}$	$(1-x)\Psi_6^{(1)} + x\Psi_6^{(2)} > 0.9$	hexagonal bilayer
DV_x	$2/5 \leq x < 1/2$	$0.5 \leq \Psi_6^{(1,2)},\ \Psi_4^{(1)} \sim 0.4,\ \Psi_5^{(2)} \sim 0.3$	Distorted hexagons
S_1	$x = 1/3$	$\Psi_5^{(1)} > 0.9,\ \Psi_4^{(2)} > 0.9$	snub square (layer 1)
Pentagonal structures			
S_2	$x = 1/3$	$\Psi_5^{(2)} > 0.45$	snub square (layer 2)
P-type	$1/3 < x < 1/2$	$\Psi_5^{(2)} > 0.45$	pentagonal in layer 2
	or $0 < x < 1/3$	or $\Psi_5^{(4)} > 0.9$	pentagonal holes

Aside : Painlevé classification

non-linear differential equations of second order

$$A(y)\frac{d^2y}{dx^2}+B(y)\frac{dy}{dx}+C(y)\left(\frac{dy}{dx}\right)^2+D(y)=0$$

$$A,B,C,D\ polynomials\ y,\ analytic\ x$$

Critical points (essential singularities, branch points) : mobile ? fixed? Fixed : 50 canonical types (44 elementary + 6 transcendents)

$$(I)\quad \frac{d^2y}{dx^2}=6y^2+\alpha x$$

$$(II)\quad \frac{d^2y}{dx^2}=2y^3+xy+\mu$$

$$(III)\quad xy\frac{d^2y}{dx^2}=x\left(\frac{dy}{dx}\right)^2-y\frac{dy}{dx}+ax+by+cy^3+dxy^4$$

$$(IV)\quad 2y\frac{d^2y}{dx^2}=\left(\frac{dy}{dx}\right)^2-a^2+2(x^2-b)y^2+8xy^3+3y^4$$

$$(V)\quad x^2(y-y^2)\frac{d^2y}{dx^2}=x^2(1-3y)\left(\frac{dy}{dx}\right)^2-xy(1-y)\frac{dy}{dx}+ay^2(1-y)^3+b(1-y)^3+cxy(1-y)+dx^2y^2(1+y)$$

$$(VI)\quad y(1-y)(x-y)\frac{d^2y}{dx^2}=\left[x-2(x+1)y+3y^2\right]\left(\frac{dy}{dx}\right)^2+\ldots$$

Ewald summation