I. Hard rods on discrete lattices

Density functional theory (DFT)

$$F = F[\rho_i(\boldsymbol{s})]$$

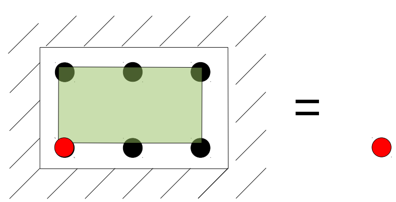
(Free energy is a unique functional of the density distribution over the lattice sites: $\rho_i(\boldsymbol{s}) = n_i(\boldsymbol{s})/\text{site}$, i.e. the functional does not depend on the external potential $V_i(\boldsymbol{s})$)

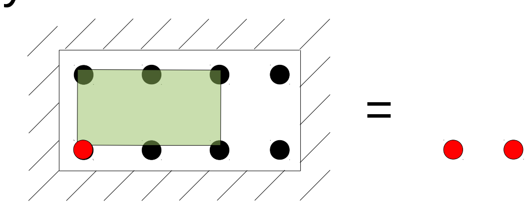
$$F = F^{\text{id}} + F^{\text{ex}} = \underbrace{\beta^{-1}\sum_{\boldsymbol{s}}\sum_i \rho_i(\boldsymbol{s})\left(\log\rho_i(\boldsymbol{s})-1\right)}_{\text{ideal gas contribution}} + F^{\text{ex}}$$

There is a constructive procedure to obtain good approximations for $F^{\text{ex}}[\rho]$

Dimensional crossover:

- imagine cavities which can hold exactly one rod



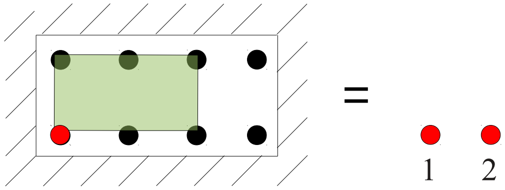


Excess free energy of such a cavity is known exactly: $\beta F^{\text{ex,0D}} = \Phi^{\text{0D}}$

- $F^{\text{ex}}[\rho]$ must deliver Φ^{0D} if density distributions are restricted to such a cavity !

I. Hard rods on discrete lattices: 0D excess free energy

- packing fraction $\eta \leq 1$ = filling probability of cavity



Here, $\eta = \rho_1 + \rho_2 \leq 1$

- excess chemical potential = excess free energy needed to put one rod into cavity

$$\mu^{ex} = -\beta^{-1} \log \langle e^{-\beta H_{1p}} \rangle \quad *$$

H_{1p} : energy (Hamiltonian) for placing particle into cavity
∞ if cavity is filled
0 if cavity is empty

$$\mu^{ex} = -\beta^{-1} \log (1-\eta)$$

* is called „potential distribution theorem“
It looks like the free energy from the partition function for 1 rod in a statistical environment.

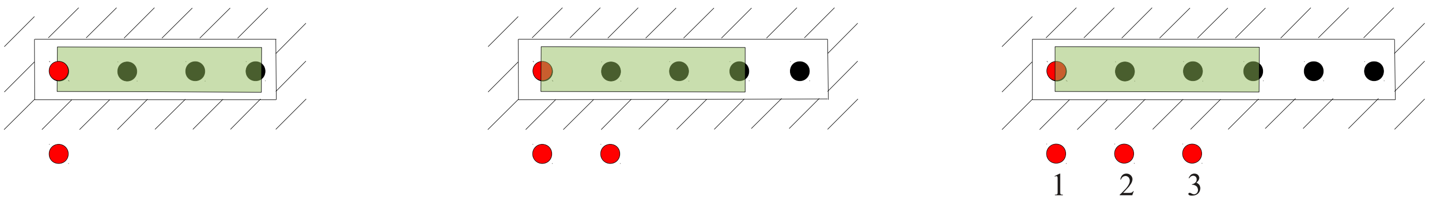
- thermodynamic relation:

$$\beta \mu^{ex} = \frac{d\Phi^{0D}}{d\eta} \quad \rightarrow \quad \Phi^{0D} = \eta + (1-\eta)\log(1-\eta)$$

I. Hard rods on discrete lattices: LC functional - 1D

We will show that for hard rods (1D) this will generate the exact free energy functional!

Example: One component, $L = 3$
There are 3 cavities:



Only the largest (maximal) cavity is relevant, others are contained in it.

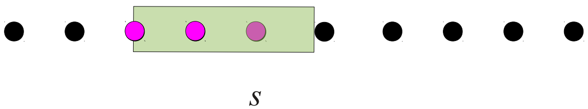
Packing fraction $\eta = \rho_1 + \rho_2 + \rho_3$

Free Energy $\Phi^{0D} = \eta + (1-\eta)\log(1-\eta)$

Note that such a cavity could be anywhere in the system (not just at the points *s* = 1,2,3) .

Trial functional: $\beta F^{ex}[\rho] = \sum_{s=-\infty}^{\infty} \Phi^{0D}\left(n^{(1)}(s)\right)$

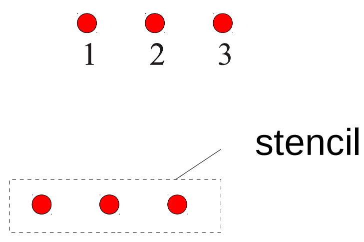
$n^{(1)}(s) = \sum_{s'=s-L+1}^{s} \rho_{s'}$



That is a weighted density which sums over all densities at points *s'* since associated rods at *s'* cover the point *s*!

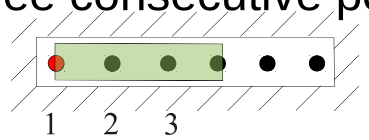
I. Hard rods on discrete lattices: LC functional - 1D

$$\beta F^{\rm ex}[\rho] = \sum_{s=-\infty}^{\infty} \Phi^{\rm 0D}\left(n^{(1)}(s)\right)$$



$$n^{(1)}(s) = \sum_{s'=s-L+1}^{s} \rho_{s'}$$

Not yet OK. The sum over *s* means that you go over the 1D lattice with a stencil that cuts out three consecutive points. When you apply this to the maximal cavity:



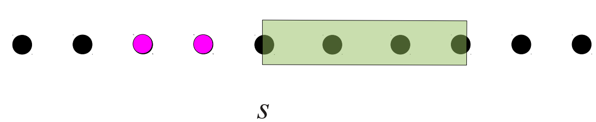
$$\beta F^{\rm ex}[\rho_{\rm cav}] = \Phi^{\rm 0D}(\underset{1}{\bullet}) + \Phi^{\rm 0D}(\underset{1}{\bullet}\ \underset{2}{\bullet}) + \Phi^{\rm 0D}(\underset{1}{\bullet}\ \underset{2}{\bullet}\ \underset{3}{\bullet}) + \Phi^{\rm 0D}(\underset{2}{\bullet}\ \underset{3}{\bullet}) + \Phi^{\rm 0D}(\underset{3}{\bullet})$$

need to be ... ...eliminated

Elimination can be done with:

$$\beta F^{\rm ex}[\rho] = \sum_{s=-\infty}^{\infty} \Phi^{\rm 0D}\left(n^{(1)}(s)\right) - \sum_{s=-\infty}^{\infty} \Phi^{\rm 0D}\left(n^{(0)}(s)\right)$$

$$n^{(0)}(s) = \sum_{s'=s-L+1}^{s-1} \rho_{s'}$$



I. Hard rods on discrete lattices: LC functional - 1D

That's it! The functional

$$\beta F^{\mathrm{ex}}[\rho] = \sum_{s=-\infty}^{\infty} \Phi^{0\mathrm{D}}\left(n^{(1)}(s)\right) - \sum_{s=-\infty}^{\infty} \Phi^{0\mathrm{D}}\left(n^{(0)}(s)\right)$$

is not only correct for all 0D cavities, but for all density distributions!
(Percus 1976, 1989 using way more difficult arguments)

Consequences: For a homogenous fluid we obtain

$$\beta\mu = \log\rho - L\log(1-L\rho) + (L-1)\log\left(1-(L-1)\rho\right)$$

$$\beta p = \log\frac{1-(L-1)\rho}{1-L\rho}$$

Clearly, chemical potential and pressure are diverging when $\rho \to \frac{1}{L}$
(close-packing limit)

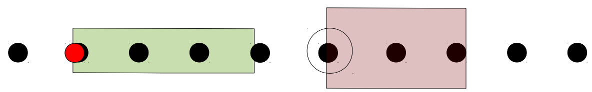
(Lafuente and Cuesta, JPCM 2002, PRL 2004)

I. Hard rods on discrete lattices: LC functional - 1D

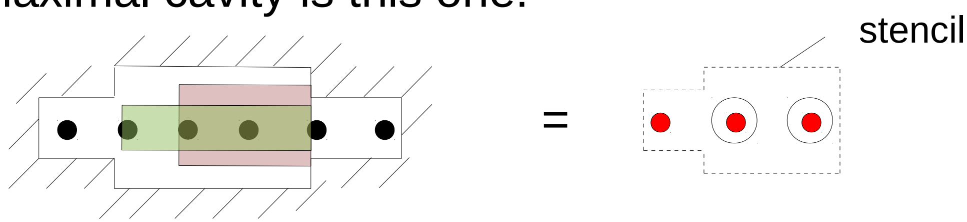
One dimension and many components

Example: M=2 components with L_1=3 and L_2=2

It helps to imagine that species 2 is slightly thicker:



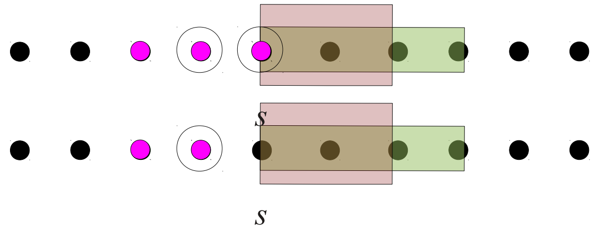
The maximal cavity is this one:



Therefore, we can generalize the weighted densities

$$n^{(1)}(s) = \sum_{s'=s-L_1+1}^{s} \rho_{1,s'} + \sum_{s'=s-L_2+1}^{s} \rho_{2,s'}$$

$$n^{(0)}(s) = \sum_{s'=s-L_1+1}^{s-1} \rho_{1,s'} + \sum_{s'=s-L_2+1}^{s-1} \rho_{2,s'}$$



and our functional still does the job! (Try yourself graphically with the stencil!)

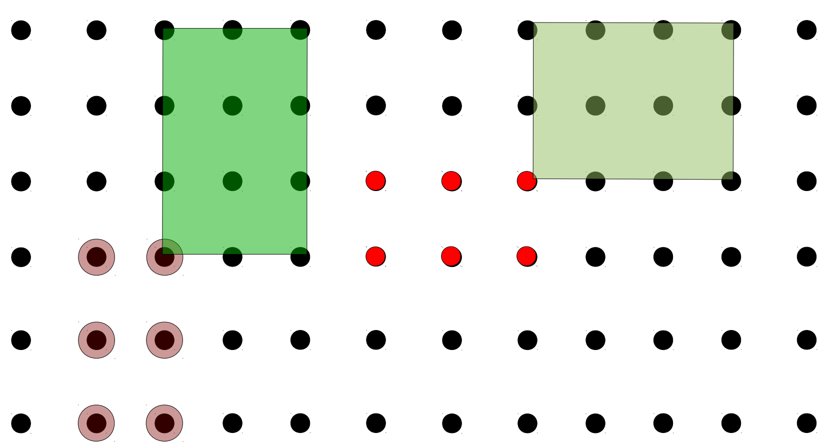
$$F^{\mathrm{ex}}[\rho] = \sum_{s=-\infty}^{\infty} \Phi^{0\mathrm{D}}\left(n^{(1)}(s)\right) - \sum_{s=-\infty}^{\infty} \Phi^{0\mathrm{D}}\left(n^{(0)}(s)\right)$$

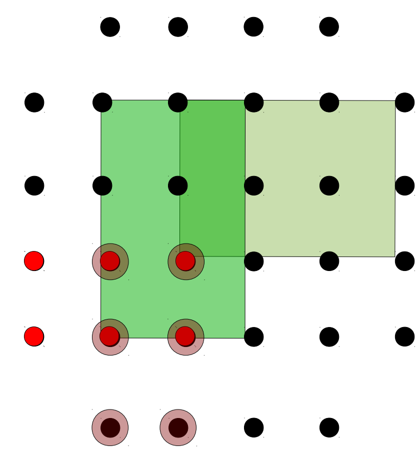
I. Hard rods on discrete lattices: LC functional - D>1

Two dimensions (and more ...)

It is still true that the set of points with nonzero density in a maximal cavity corresponds to the set of points „covered by a rod“

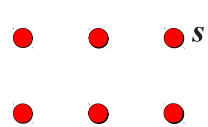
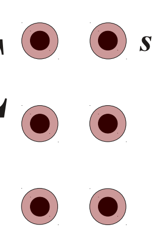
Example: Rods with size 2 x 3





maximal cavity

Thus we generalize the weighted density $n^{(1)}$:

$n^{(1,1)}(s) = \sum$  $+ \sum$ 

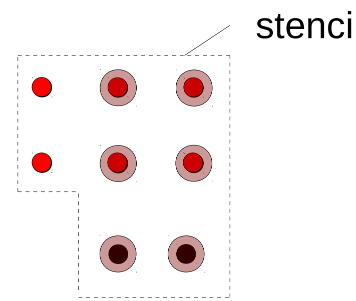
(sum over densities at the points depicted)

I. Hard rods on discrete lattices: LC functional - D>1

Two dimensions (and more ...)

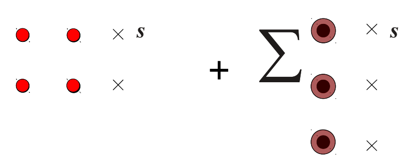
The trial functional would then be

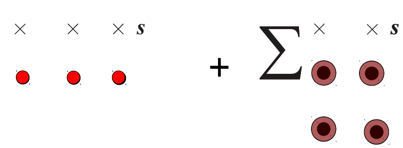
$$\beta F^{\mathrm{ex}}[\rho] = \sum_{\boldsymbol{s}=(s_x,s_y)} \Phi^{0\mathrm{D}}\left(n^{(1,1)}(\boldsymbol{s})\right)$$

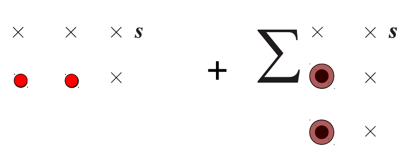


Apply this to the maximal cavity (move the stencil over the cavity density distribution).
The thus generated extra terms can all be eliminated by extending the functional to:

$$\beta F^{\mathrm{ex}}[\rho] = \sum_{\boldsymbol{s}=(s_x,s_y)} \Phi^{0\mathrm{D}}\left(n^{(1,1)}(\boldsymbol{s})\right) - \sum_{\boldsymbol{s}=(s_x,s_y)} \Phi^{0\mathrm{D}}\left(n^{(0,1)}(\boldsymbol{s})\right) - \sum_{\boldsymbol{s}=(s_x,s_y)} \Phi^{0\mathrm{D}}\left(n^{(1,0)}(\boldsymbol{s})\right) + \sum_{\boldsymbol{s}=(s_x,s_y)} \Phi^{0\mathrm{D}}\left(n^{(0,0)}(\boldsymbol{s})\right)$$

$n^{(0,1)}(\boldsymbol{s}) = \sum$ 

$n^{(1,0)}(\boldsymbol{s}) = \sum$ 

$n^{(0,0)}(\boldsymbol{s}) = \sum$ 

I. Hard rods on discrete lattices: LC functional - D>1

Two dimensions (and more ...): summary

So, the general form of the Lafuente-Cuesta functional on hypercubic lattices is given by

$$\beta F^{\mathrm{ex}} = \sum_{\boldsymbol{s}} D_{\alpha_1} \ldots D_{\alpha_d} \Phi^{0\mathrm{D}}\left(n^{(\alpha_1,\ldots,\alpha_d)}(\boldsymbol{s})\right)$$

where

d	number of dimensions
$D_\alpha f(\ldots,\alpha,\ldots) = f(\ldots,1,\ldots) - f(\ldots,0,\ldots)$	difference operator
$n^{(\alpha_1,\ldots,\alpha_d)}(\boldsymbol{s})$	weighted densities $(\alpha_i = 0,1)$

$$n^{(\alpha_1,\ldots,\alpha_d)}(\boldsymbol{s}) = \sum_{p=1}^{M} \left(\sum_{s'_1 = s_1 - L_1^p}^{s_1 - 1 + \alpha_1} \ldots \sum_{s'_d = s_d - L_d^p}^{s_d - 1 + \alpha_d} \right) \rho_{p,s'} =: \sum_{p=1}^{M} w_p^{\alpha} * \rho_p(\boldsymbol{s})$$

discrete convolution

M	number of parallelepiped species
$\boldsymbol{L}^p = \{L_{1,\ldots}^p, L_d^p\}$	vector of parallelepiped side lengths of species p
$\boldsymbol{s} = \{s_{1,\ldots}, s_d\}$	lattice position vector
$w_p^{\alpha}(\boldsymbol{s})$	weight function for species p
$\boldsymbol{\alpha} = \{\alpha_{1,\ldots}, \alpha_d\}$	weight function index

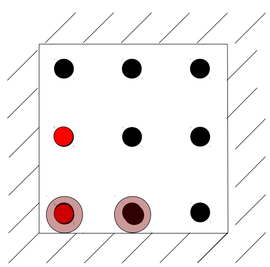
I. Hard rods on discrete lattices: LC functional - D>1

Two dimensions (and more ...)

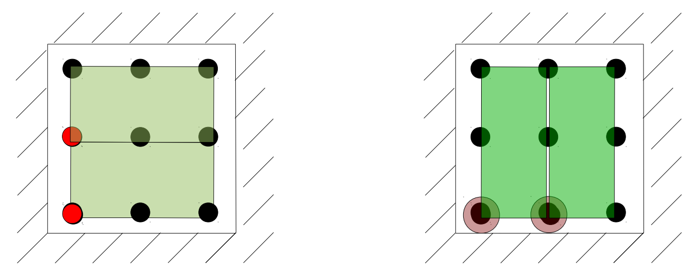
Unfortunately, these functionals in 2D and 3D are not exact anymore...

Reasons? „Correlations“ in 2-particle cavities

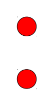
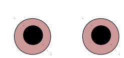
Example: Correlated 2-particle cavity for rods with length 2 x 1



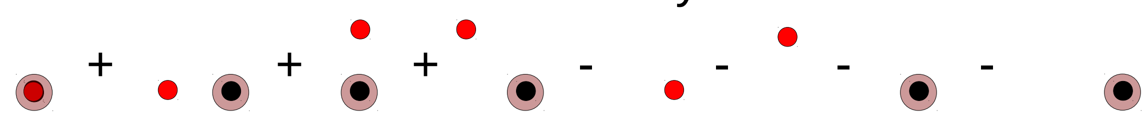
holds



Consequently terms in the free energy should depend on

 and  separately

But the 0D-functional delivers only



...but they might offer a good picture of the model to start with!

I. Hard rods on discrete lattices: LC functional

Results: 3D - rods with length 1x1x*L*

order parameter: $Q = \frac{\rho_1 - (\rho_2 + \rho_3)/2}{\rho}$

$Q > 0$: 1 is majority species

$Q < 0$: 1 is minority species

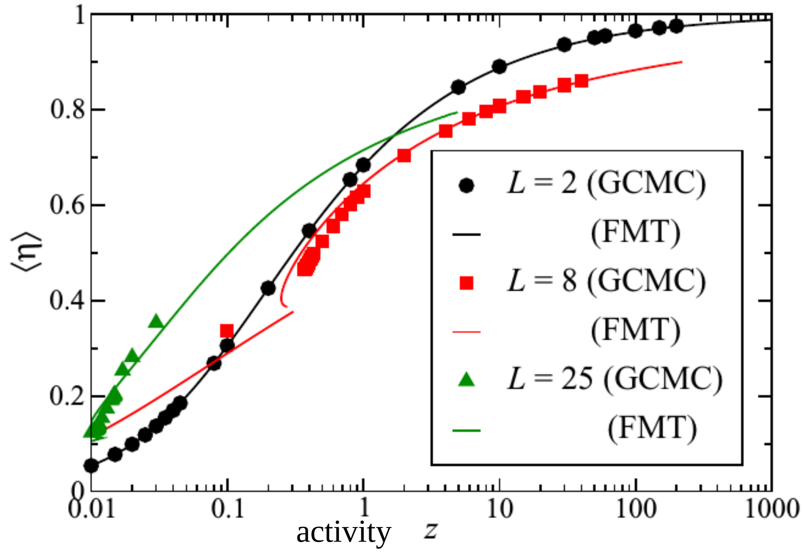
FMT

- nematic transition always with one majority species for $L \geq 4$
- strong first order transition (similar to continuum hard rods)

SIM

- nematic transition for $(L \geq 7)$: one minority species $L \geq 5$ one majority species $(L = 5,6)$
- very weak first order transition (unlike continuum hard rods): strong fluctuations

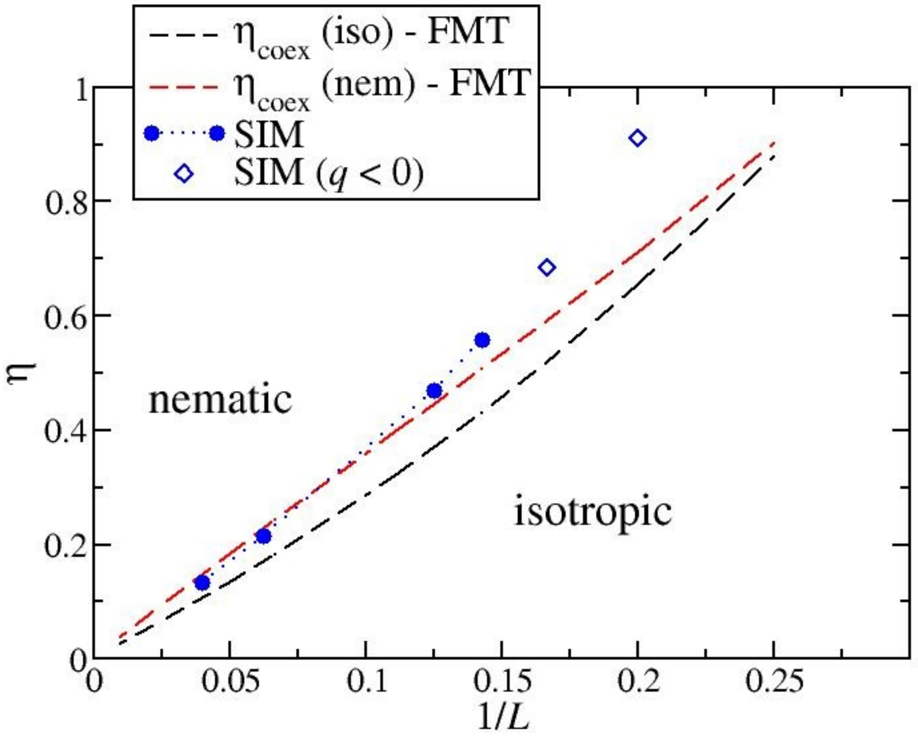
“packing” is well described



I. Hard rods on discrete lattices: LC functional

Results: 3D - rods with length 1x1x*L*

Phase diagram



in simulations:
no density gap detectable!