Simple lattice models of complex systems
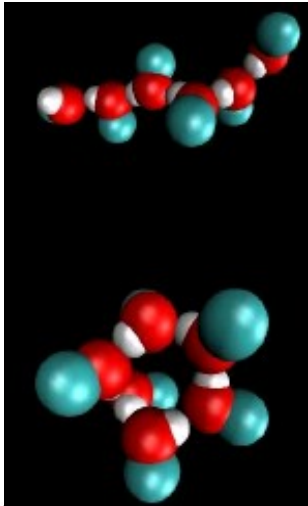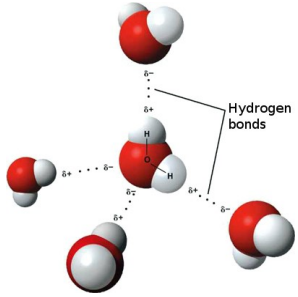
- What kind of complex systems?
- What kind of lattice models?
- Models and results for:

Water
Particles at interfaces
"protein rafts"
Alcohol (methanol)

LIPID RAFT
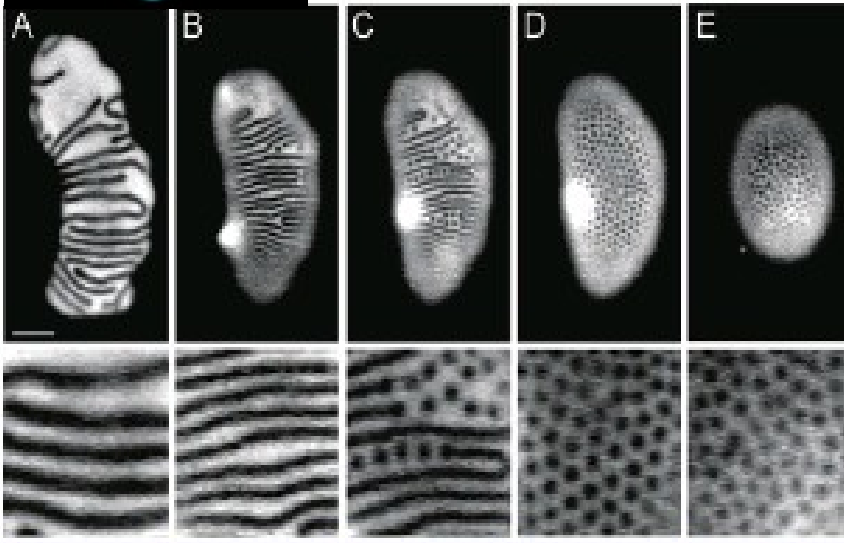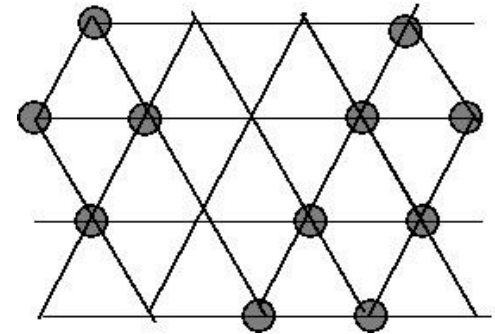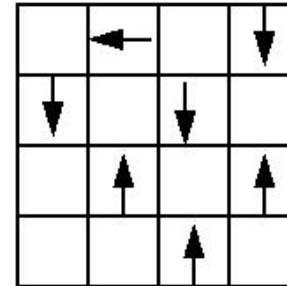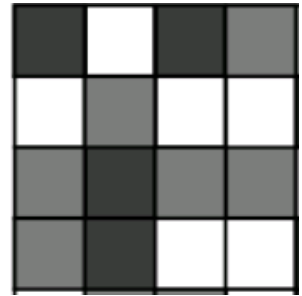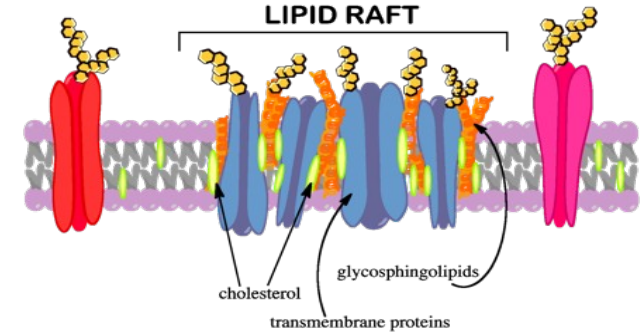
glycosphingolipids

cholesterol

transmembrane proteins
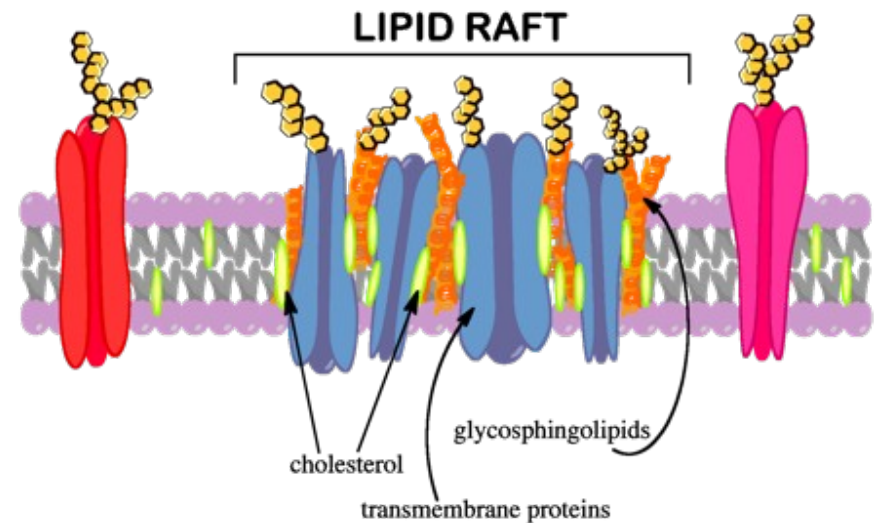
Complex fluids posses

- strongly nonspherical shapes of molecules,
  and/or
- interactions strongly depending on orientations
  and/or
- many components with significantly different sizes and/or interactions

As a result

- distribution of particles is inhomogeneous on a microscopic or a mesoscopic length scale

- local positional or orientational ordering leads to aggregates, clusters, micelles etc.

- ordering of such objects may lead to lyotropic liquid-crystalline phases or soft colloidal crystals

Examples of complex systems

I. Water:
Well known anomalies
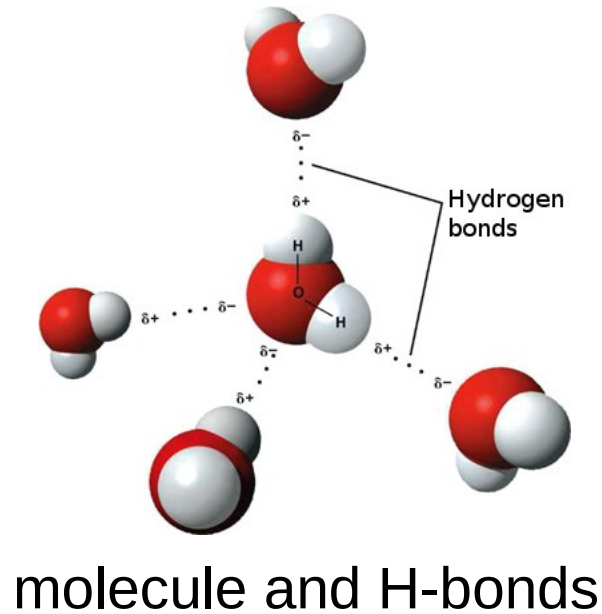
molecule and H-bonds

Phase diagram
for p<2000 bar, dp/dT<0
at the solid-liquid coexistence
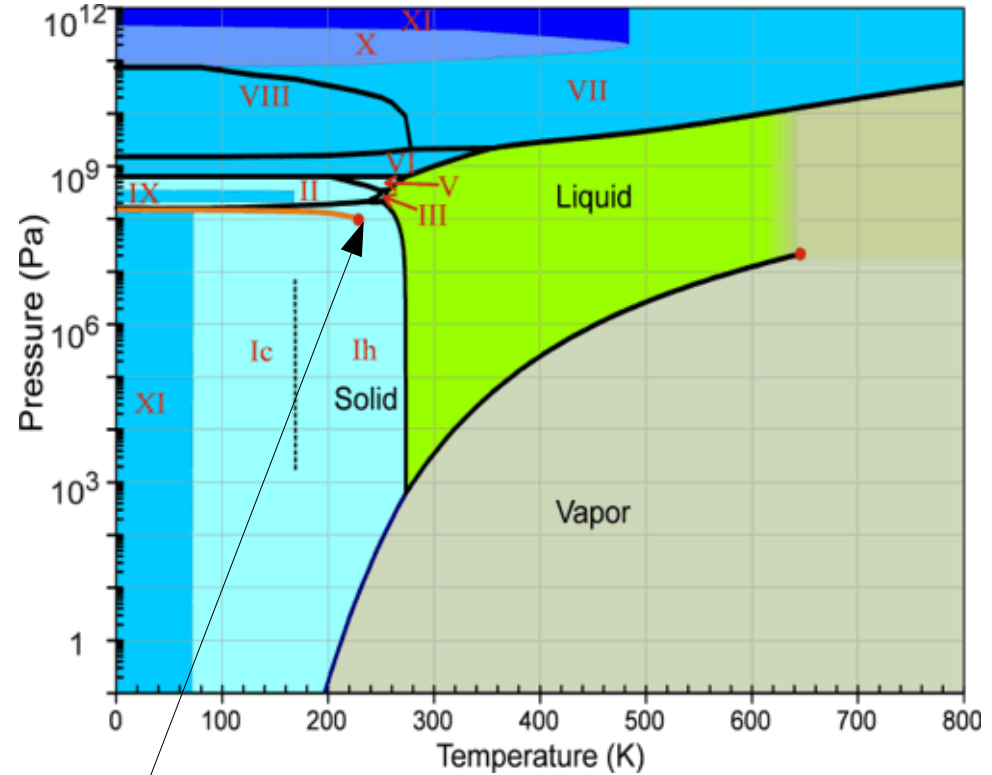
Metastable liquid-liquid transition with a critical point

II. particles at solid or liquid interfaces, or in membranes

Atomic force microscopy reveals sphingomyelin rafts (orange) protruding from a dioleoylphosphatidylcholine background (black) in a mica-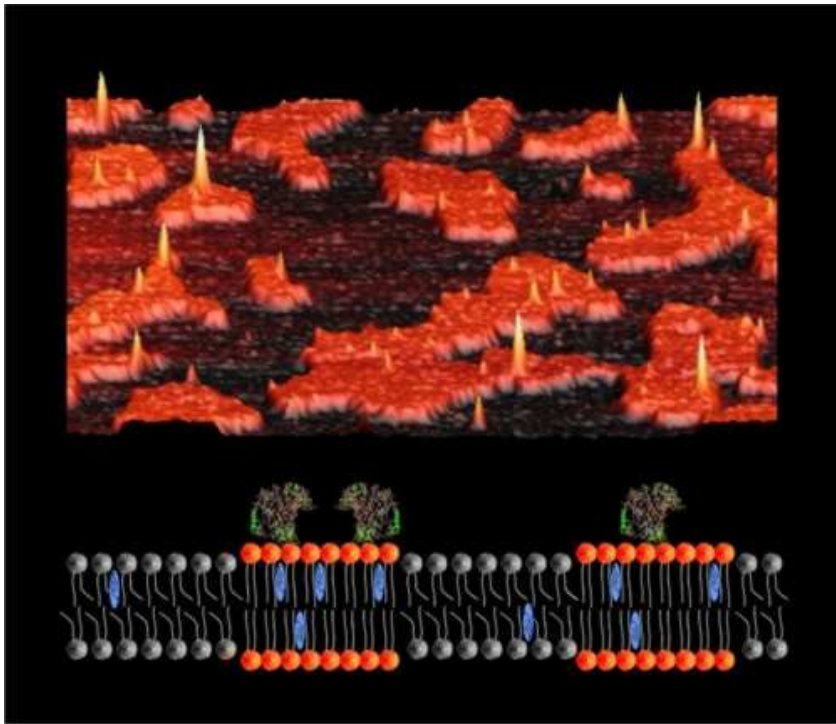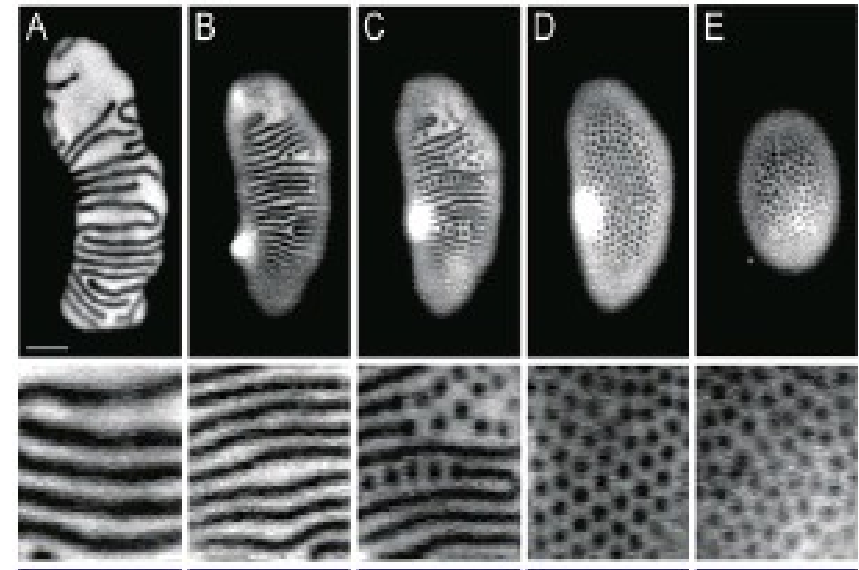supported lipid bilayer. Placental alkaline phosphatase (PLAP; yellow peaks) protein, is shown to be almost exclusively raft-associated. A diagrammatic representation is shown at the bottom. Saslowsky at. al.
J. Biol. Chem.277, 26966-26970(2002)

Epifluorescence microscopy images of lateral phase separation in a vesicle adhering to a supported lipid bilayer. An aligned stripe pattern is transformed into a hexagonal array of circular domains. Rozovsky at. al.
JACS **127**, 36 (2004)

LIPID RAFT

cholesterol

glycosphingolipids

transmembrane proteins

WIKIBOOKS
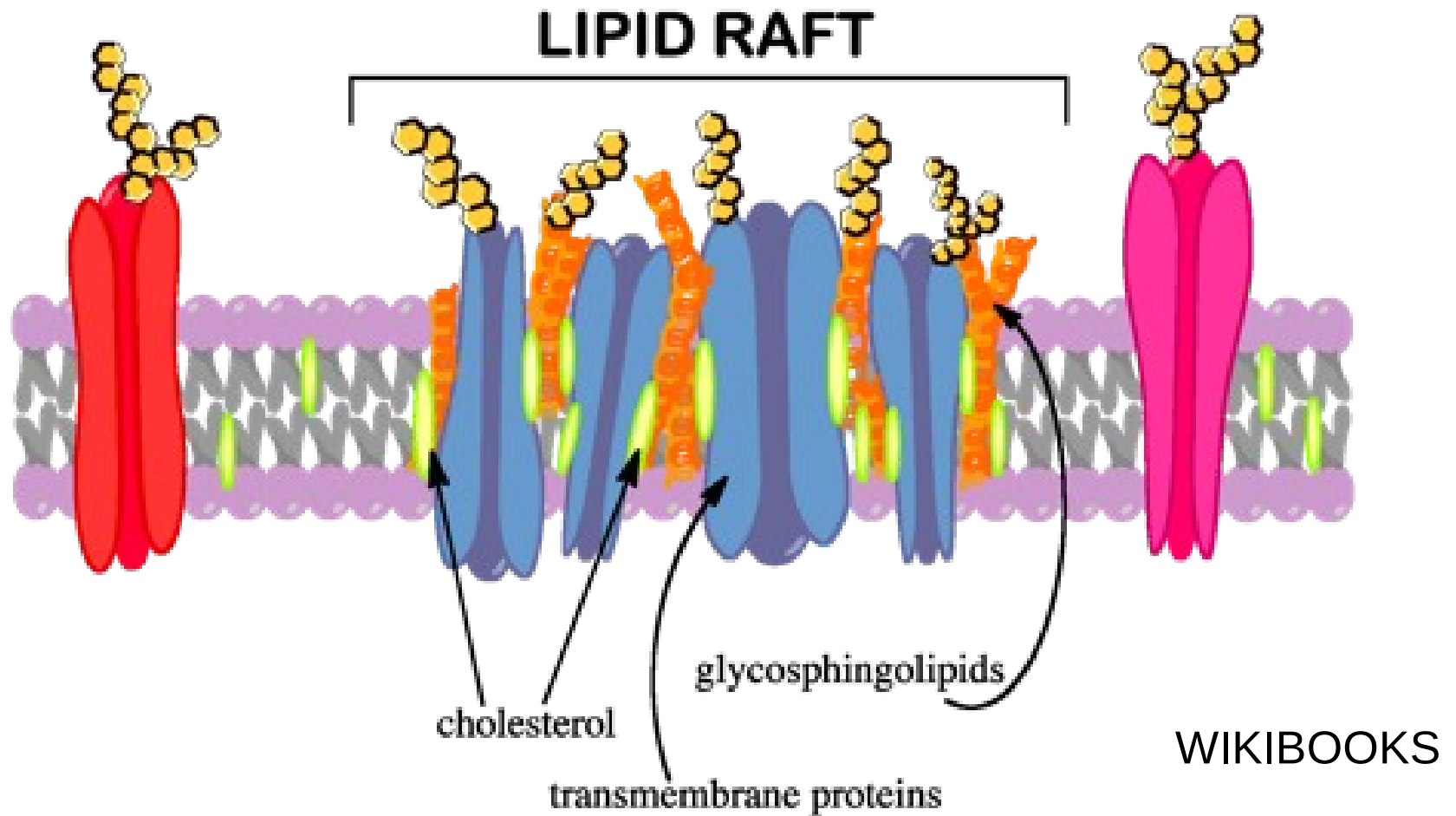
Lipid rafts are small microdomains ranging from 10–200 nm in size, present in cellular membranes. They are enriched in cholesterol and sphingolipids and do not remain intact for very long. Many scientists think they serve as communication hubs by recruiting proteins that need to come together in order to transmit a signal.

III. H-bond forming polar molecules (alcohols)
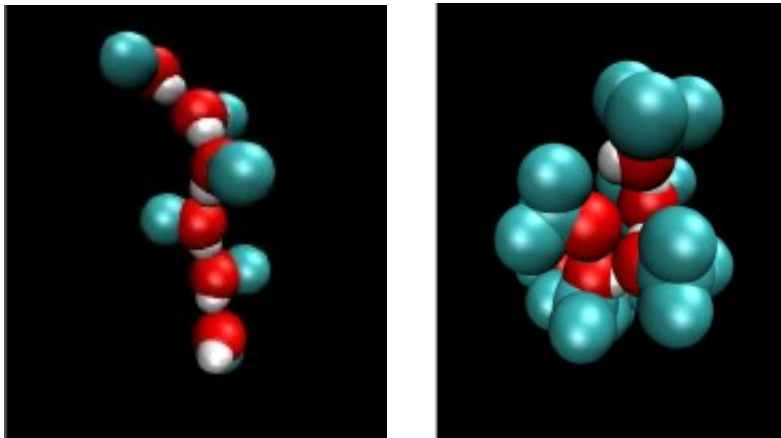
Local orientational ordering in liquid
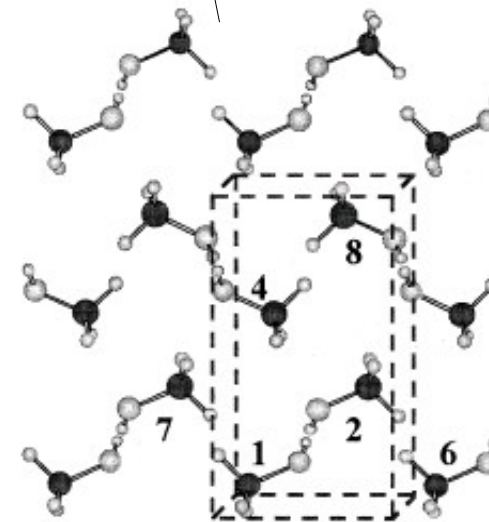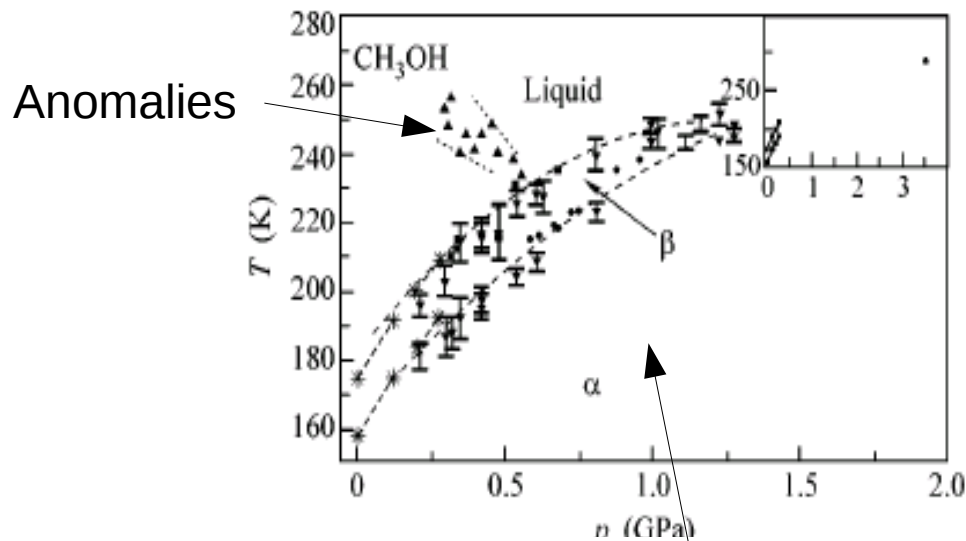
Phase diagram for methanol

Clusters of methanol (left) and thert-butanol (right).
Simulation snapshots
(A. Perera et. al.
PRE **75**, 060502 (2007))

Anomalies

structure of the crystal

Lattice models

- Space is divided into cells labeled by integer numbers,

- Cells can be in one from a small number of states
  associated with microscopic degrees of freedom
  or mesoscopic (coarse-grained) structure

- Probability of a particular distribution of states in all cells
  is given by the Boltzmann factor

Advantages:

- Reduction of degrees of freedom compared to full microscopic modeling

- Ground state gives information about possible ordered structures

- Analytical calculations possible within mean-field (MF) approximation
- And beyond

- Generic models reveal the key factors responsible for particular properties

Statistical-mechanics of lattice models.

For i=1,...,n labeling states the microscopic occupancy operators are defined as

$\hat{o}_i(\boldsymbol{x})=1,$ if the cell x is in the state i

and $\hat{o}_i(\boldsymbol{x})=0,$ if the cell x is not in the state i.

Each cell is in one state, $\sum_{i=1}^{n} \hat{o}_i(\boldsymbol{x})=1$

The "Hamiltonian" takes the form

$$H[\{\hat{o}_i\}]=\frac{1}{2}\sum_{\boldsymbol{x}}\sum_{\boldsymbol{x}'}\hat{o}_i(\boldsymbol{x})V_{ij}(\boldsymbol{x}-\boldsymbol{x}')\hat{o}_j(\boldsymbol{x}')-\sum_{\boldsymbol{x}}(\mu_i+h(\boldsymbol{x}))\hat{o}_i(\boldsymbol{x})$$

Where μ_i and $h_i(\boldsymbol{x})$ are the chemical potential and the external field resp.

Minimum of the Hamiltonian for given form of interactions determines the structure at the ground state as a function of μ_i and $h_i(\boldsymbol{x})$. Easy!

In the mean-field (MF) approximation equilibrium states

$$\{o_i\} = o_1(x), \dots, o_n(x) \quad \text{where } o_i(x) = \langle \hat{o}_i(x) \rangle_{MF}$$

are determined by the minimum of the grand potential

$$\Omega^{MF}[\{o_i\}] = H[\{o_i\}] - TS[\{o_i\}]$$

Entropy on the lattice usually has a form of ideal-mixing entropy. Sometimes Bethe approximation is assumed. Boundary of stability of the homogeneous state is determined by

$$\det C_{ij}(k) = 0 \qquad \frac{\partial \det C_{ij}(k)}{\partial k} = 0$$

where

$$C_{ij}(k) = \frac{\delta^2 \Omega^{MF}[\{o_i\}]}{\delta \tilde{o}_i(k) \delta \tilde{o}_j(k)} \qquad \tilde{o}_i(k) = \sum_x o_i(x) e^{ik \cdot x}$$

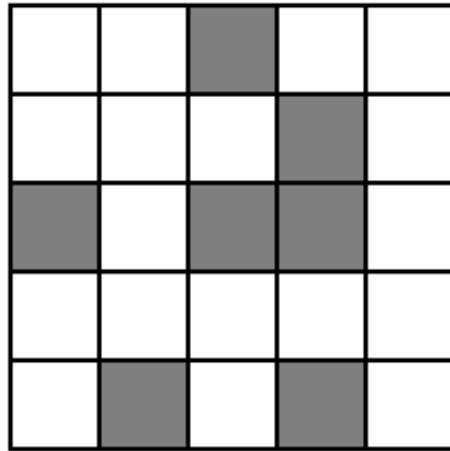Easy! Important information about ordering can be easily obtained analytically.

Lattice gas model for simple fluids

Typical configuration for T>T$_c$
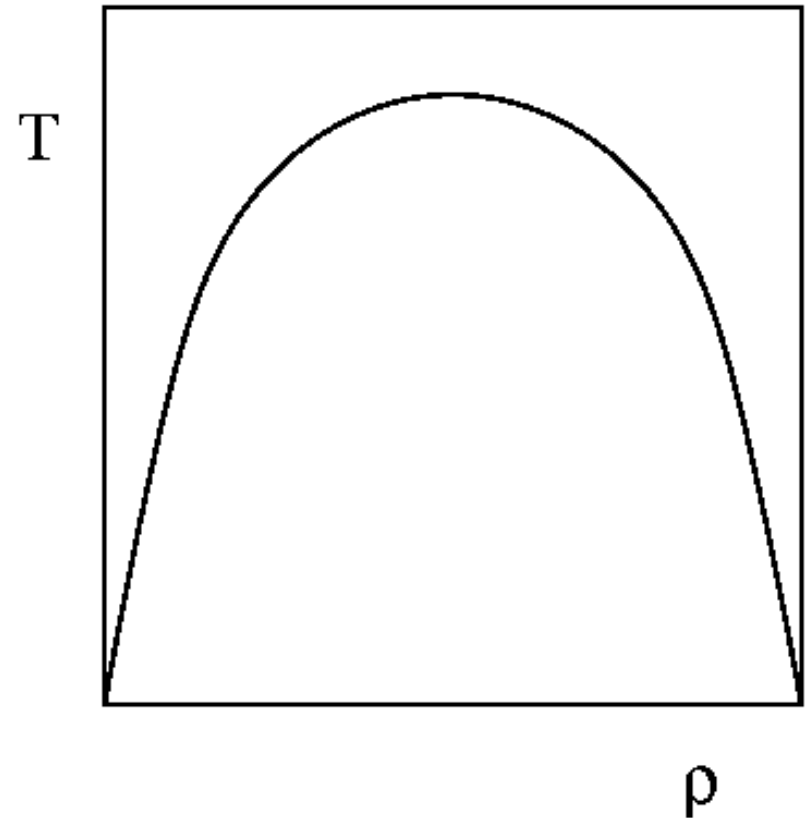
States:

Empty cell ➤

Occupied cell ➤

Nearest-neighbor interaction

$-a$

Probability of a configuration $\quad p = \dfrac{e^{-\beta(E-\mu N)}}{\Xi}$
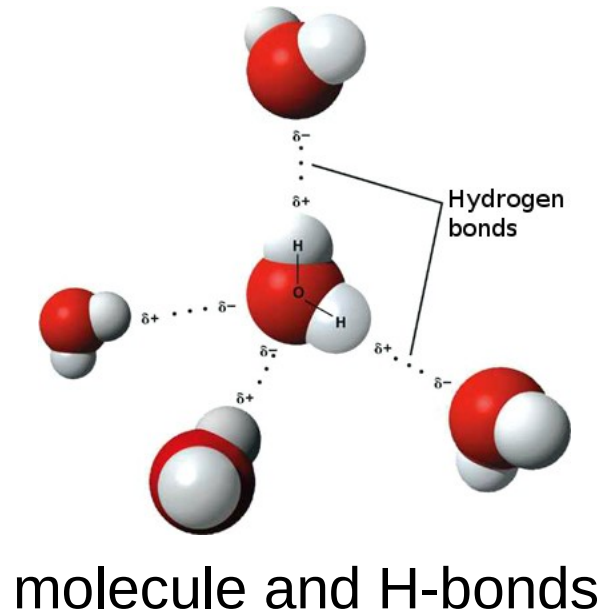
Phase diagram

T

ρ

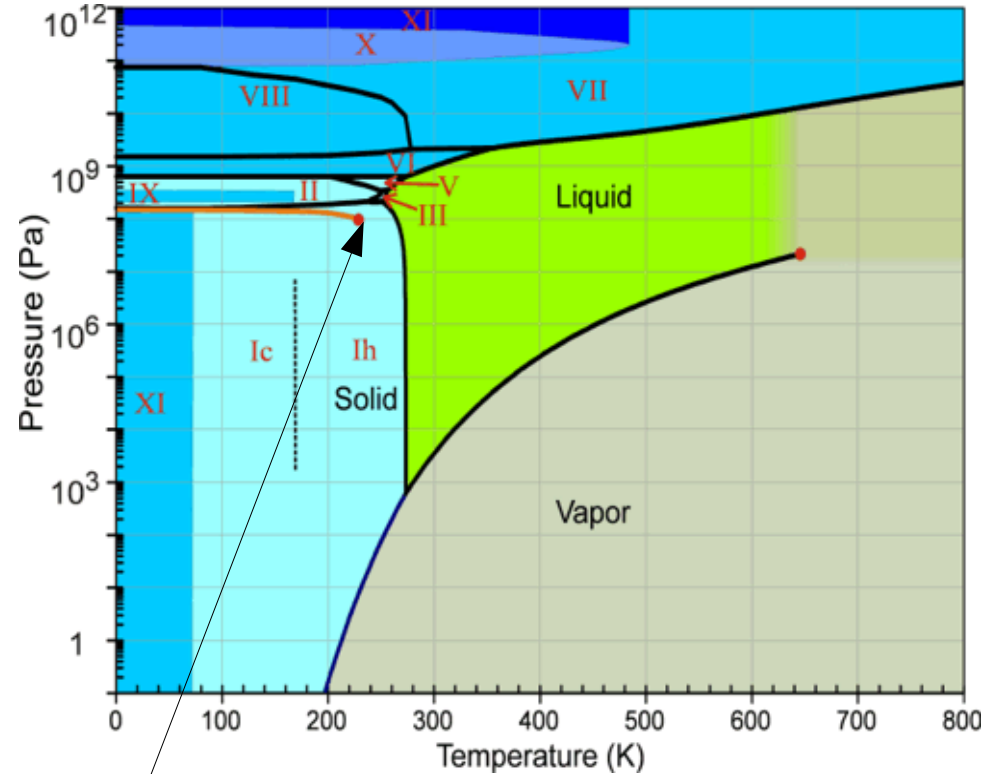Grand potential $\quad \Omega = -kT ln \,\Xi$

I. Water:
Lattice gas model is oversimplified for description of the well known anomalies.
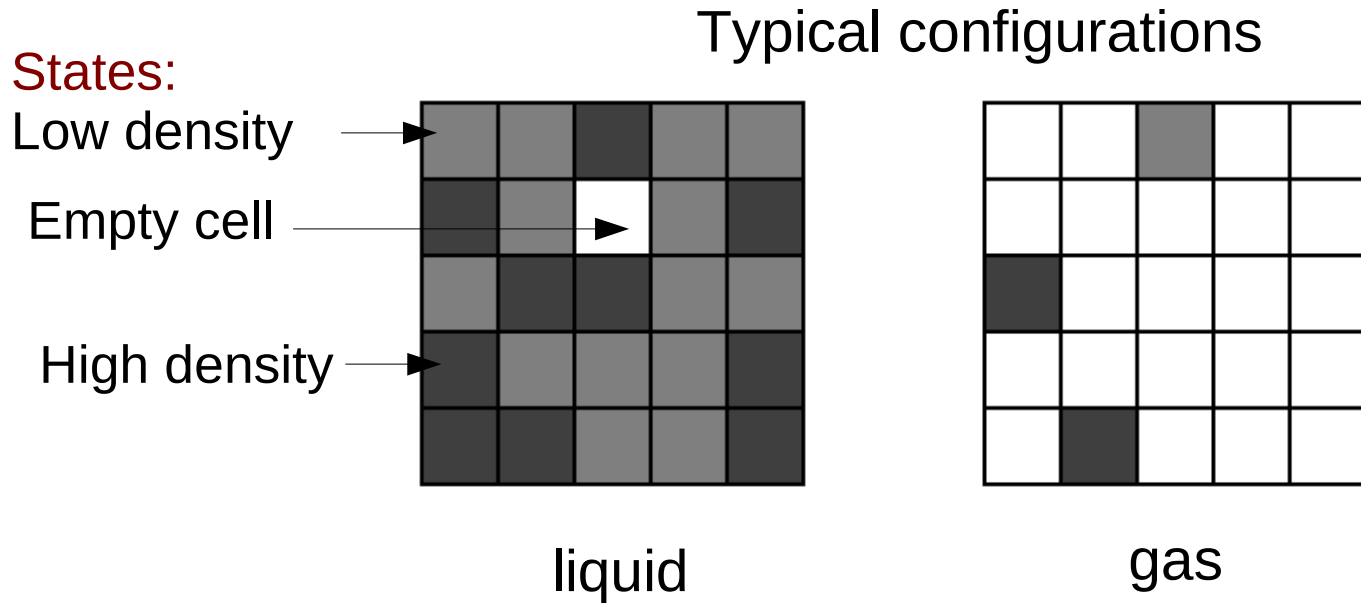## What is the necessary and sufficient modification of it to model water?

molecule and H-bonds

Phase diagram
for p<2000 bar, dp/dT<0
at the solid-liquid coexistence

Metastable liquid-liquid transition with a critical point

I. Lattice gas model for water
A.Ciach, W.T. Gozdz and A. Perera, PRE **78** 021203 (2008)

Typical configurations

States:

Low density ⟶

Empty cell ⟶

High density ⟶

a - van der Waals

h - H-bond

2δ – relative density difference

volume of the lattice cell v = volume per molecule in ice

liquid

gas

Interaction energies

$-a-h$

$-a(1+2\delta)$
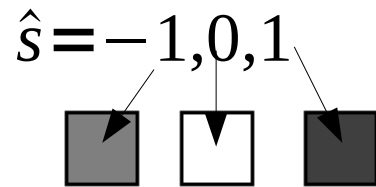
$-a(1+2\delta)^2$

Probability of a configuration

$$p = \frac{e^{-\beta(E-\mu(N_L+N_H(1+2\delta)))}}{\Xi}$$

Density in a configuration

$$\rho = \rho_L \frac{(N_L + (1+2\delta)N_H)}{V}$$

Hamiltonian – Blume-Emery-Griffith model for a binary mixture

$$H[\{\hat{s}\}]=\frac{-1}{2}\sum_{nn}[(J_{ll}\hat{s}(\boldsymbol{x})\hat{s}(\boldsymbol{x}')+4J_{gl}\hat{s}^2(\boldsymbol{x})\hat{s}^2(\boldsymbol{x}'))+2Q\,\hat{s}(\boldsymbol{x})\hat{s}^2(\boldsymbol{x}')]$$

$$-\mu\sum_{x}[\delta\,\hat{s}(\boldsymbol{x})+(1+\delta)\hat{s}^2(\boldsymbol{x})]$$

$$\hat{s}=-1,0,1$$

$\hat{s}$ - concentration

$\hat{s}^2$ - cell occupancy

$\hat{\rho}=\delta\,\hat{s}+(1+\delta)\hat{s}^2$ - density

Probability of the configuration $\{\hat{s}\}$:

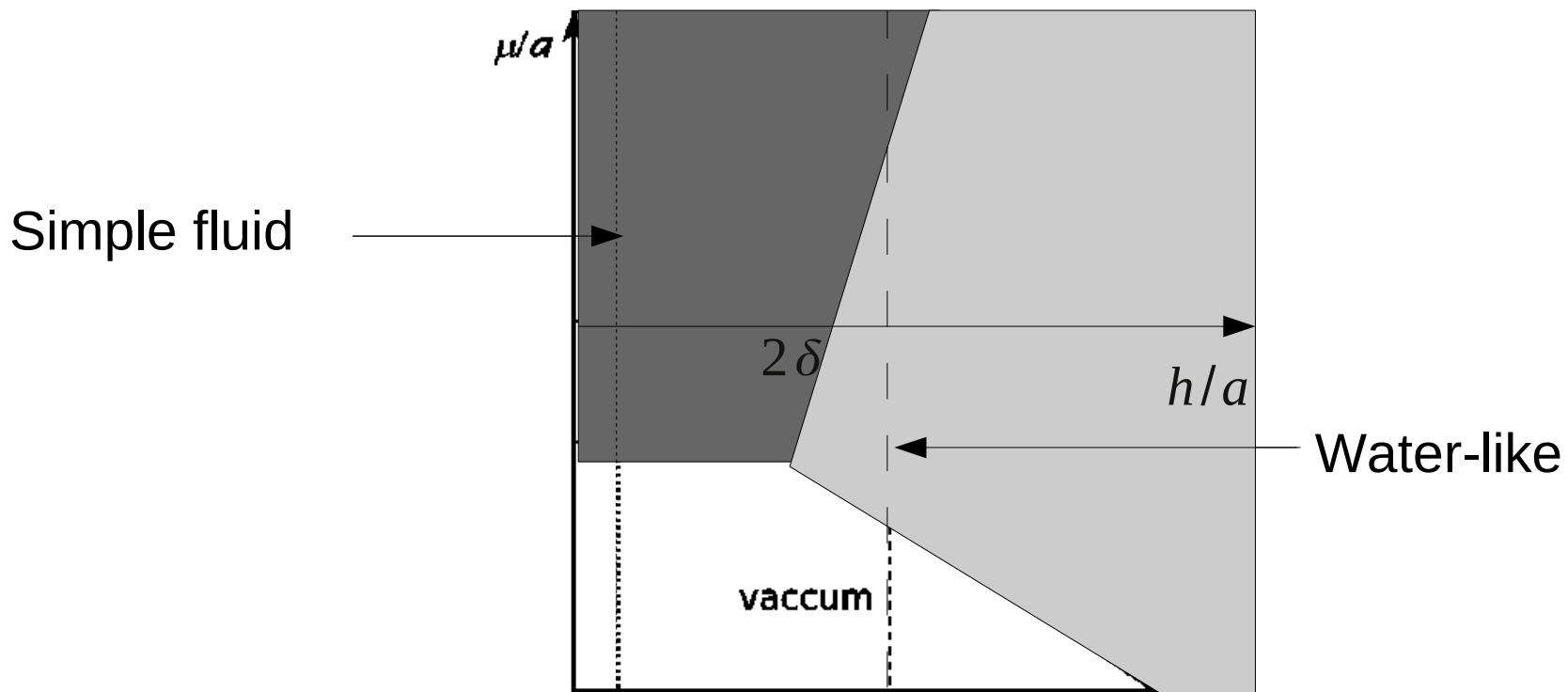$$p[\{\hat{s}\}]=\frac{e^{-\beta H[\{\hat{s}\}]}}{\Xi}\qquad \Xi=\sum_{\{\hat{s}\}}e^{-\beta H[\{\hat{s}\}]}$$

grand potential $\quad \Omega=-pvV=-kT\ln\Xi$

$$J_{ll}=a\,\delta^2+\frac{h}{4}$$

$$J_{gl}=a(1+\delta)^2+\frac{h}{4}$$

$$Q=a\,\delta(1+\delta)+\frac{h}{4}$$

Ground state (T=0K) dependence on the model parameters

Simple fluid

Water-like

μ/a

2δ

h/a

vaccum

By assuming the coexistence between the high-density and
the low-density phases at p=2000 bar we obtain a
relation between the model parameters a,h,v,δ.
Further relations follow from the values of critical temperatures
in the model and experiment

The model parameters:
v=35 A^3
a=3.6 *kJ/mol*
h=1.1 kJ/*mol*
δ=0.12

In water:
v~33 A^3
a~5.5 *kJ/mol*
$$h = \frac{2}{3*4\pi} * E_H = 0.05 * 23\,kJ/mol = 1.2\text{kJ}/mol$$
δ~0.1

Mean-field (MF) approximation:
each molecule is in the external field resulting from interactions with
the remaining molecules in their equilibrium positions.
Average values are approximated by the most probable values.

In MF the critical point temperature T_c is overestimated.
Exact result for T_c in the Ising model is $T_c \sim 4.5/6 T_c^{MF} = 0.75\ T_c^{MF}$

Mean-Field (MF) approximation: Functional of two fields,

$$\Omega^{MF}[s(\boldsymbol{x}),\eta(\boldsymbol{x})]=H[s(\boldsymbol{x}),\eta(\boldsymbol{x})]-TS[s(\boldsymbol{x}),\eta(\boldsymbol{x})]$$

On the lattice the entropy S has the ideal-mixing entropy form

The fields $\quad s=\langle\hat{s}\rangle_{MF},\eta=\langle\hat{s}^2\rangle_{MF}$

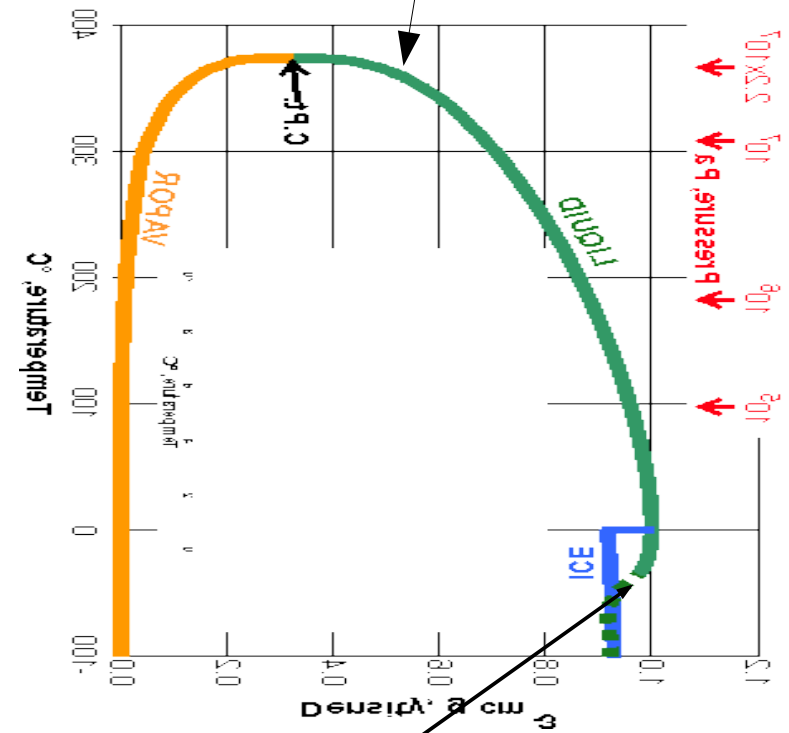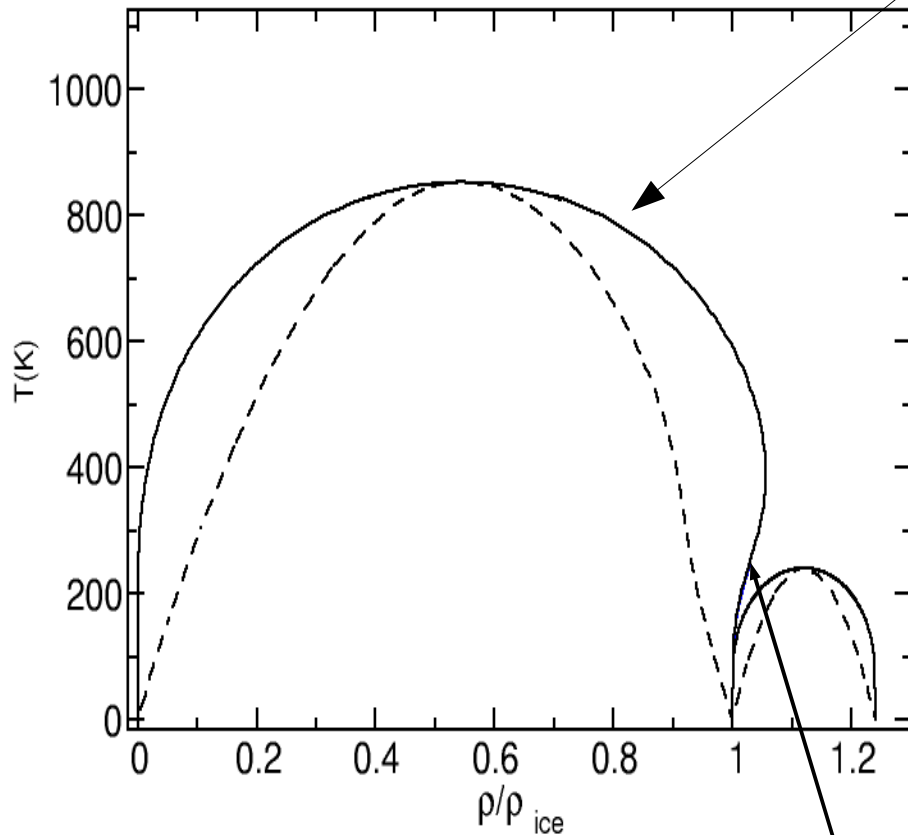satisfy the minimum condition $\quad\dfrac{\partial\Omega^{MF}}{\partial s}=0=\dfrac{\partial\Omega^{MF}}{\partial\eta}$

Spinodal surface: $det[\partial^2\Omega^{MF}]=0$
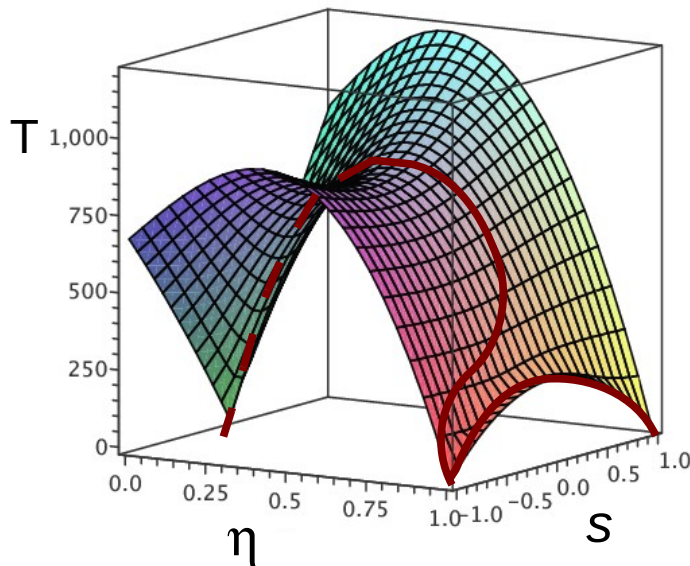
The density: $\quad\rho=[(1+\delta)\eta+\delta s]\rho_{ice}$

Spinodal (dashed) and binodal lines in MF

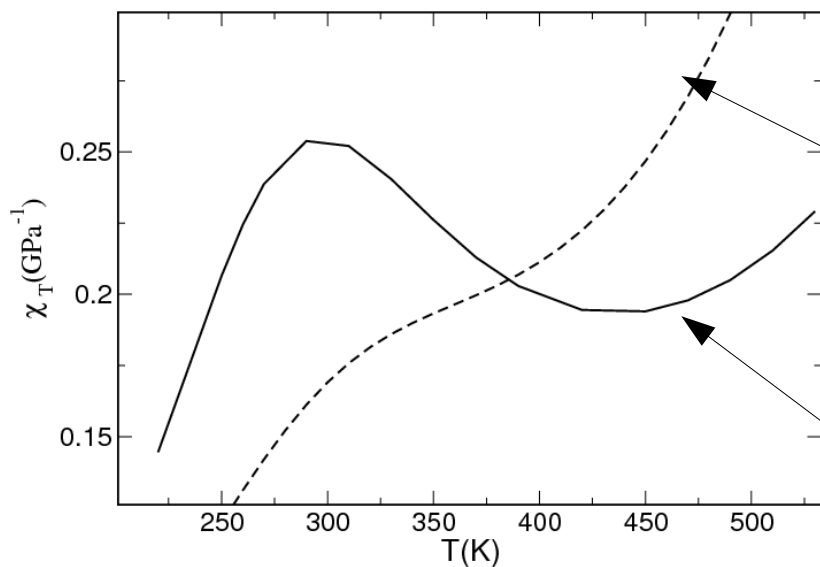## Gas-liquid coexistence in the model and in experiment
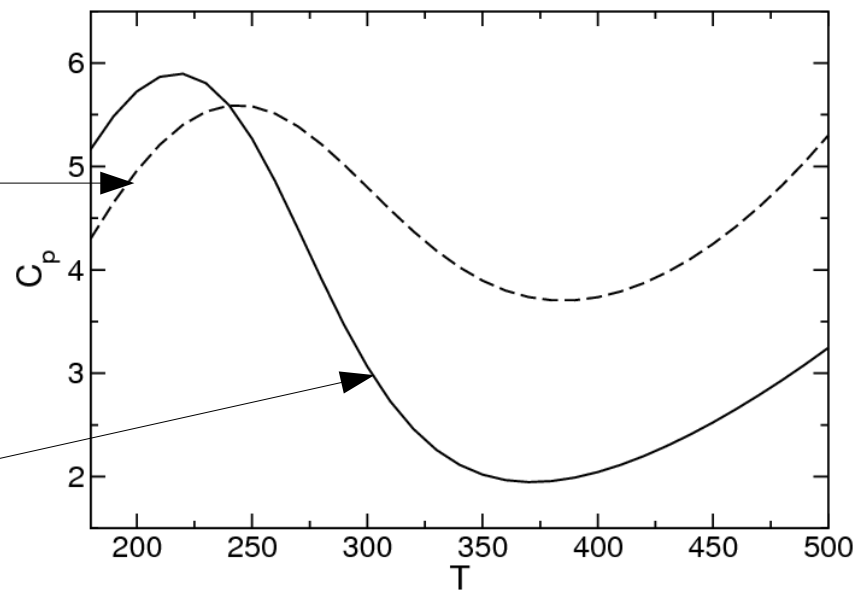

Anomalous density increase

EOS isobars
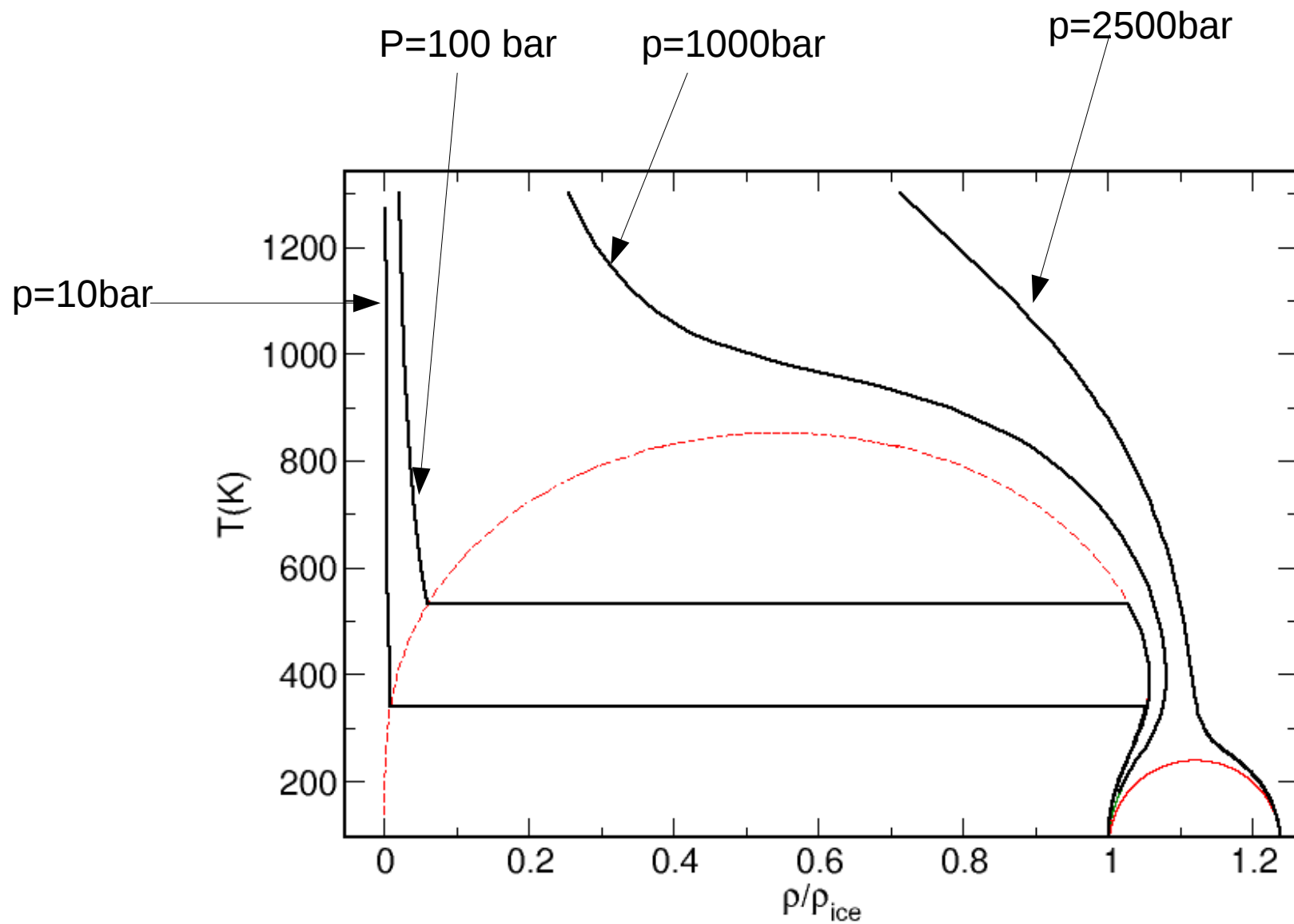
Critical pressure in the model is p=653 bar
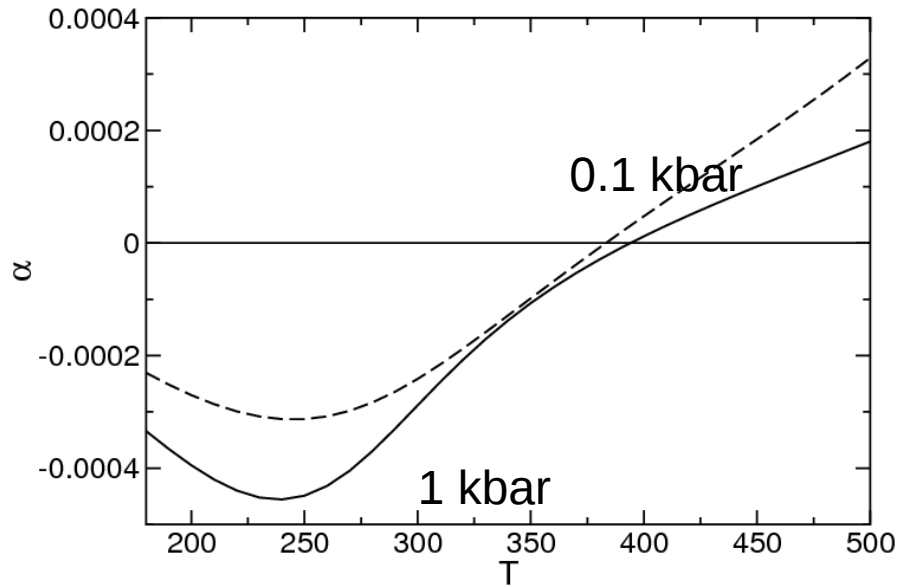
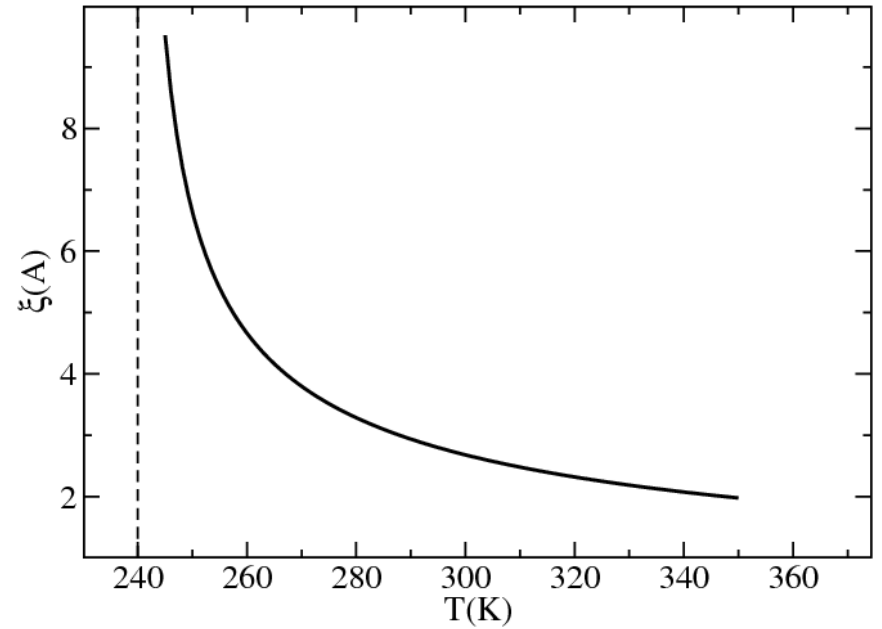Isothermal compressibility

Constant-pressure specific heat

We observe minimum of the compressibility, but only for high pressures
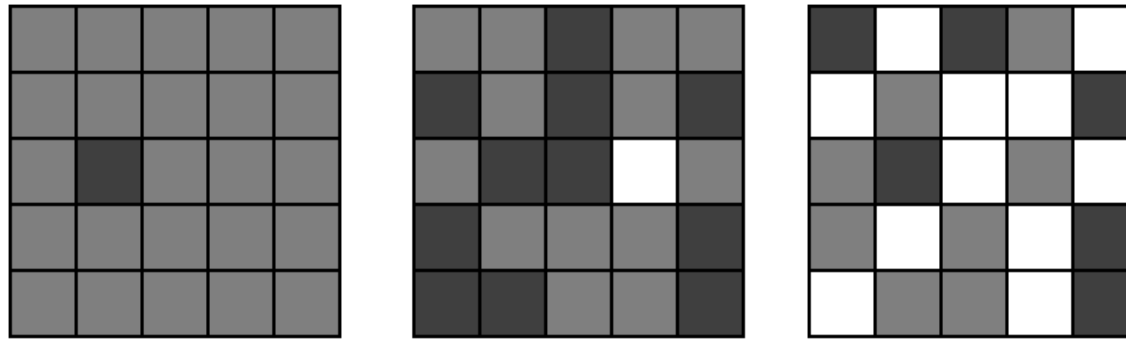
Thermal expansivity

## Correlation length at the critical density of the mestastable liquid-liquid critical point

For p<2000 bar low density at low T. T increases –
mixing of the two forms of water – density increases.
Further increase of T – mixing of the occupied and empty cells -density decreases.

T

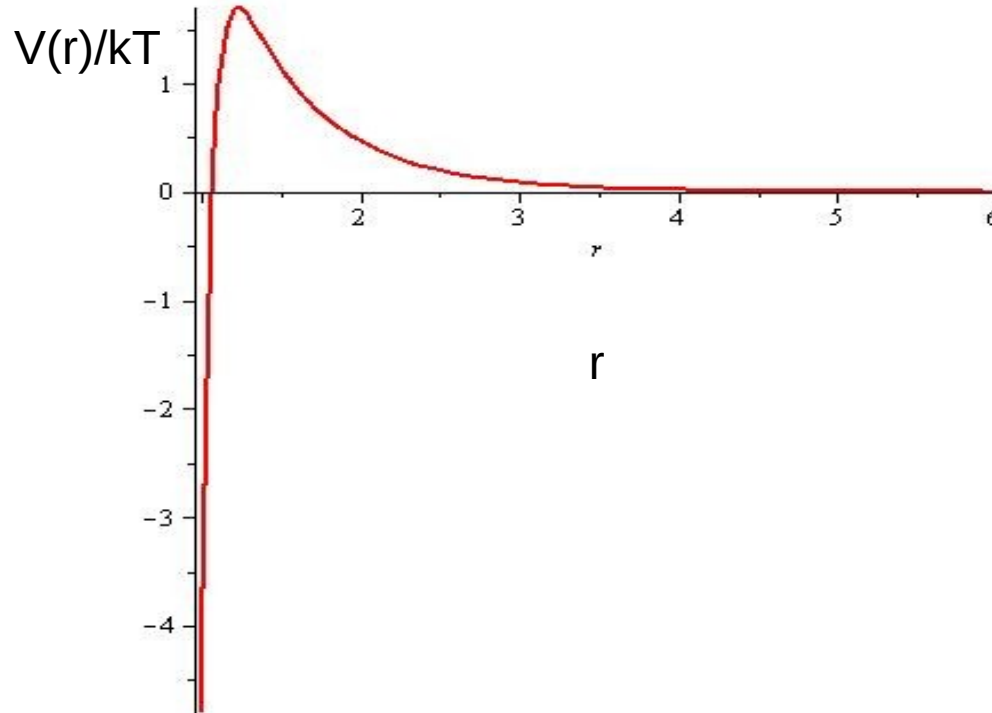For p>2000bar compact structure at low T. T increases
-mixing of the two forms of water – density decreases.
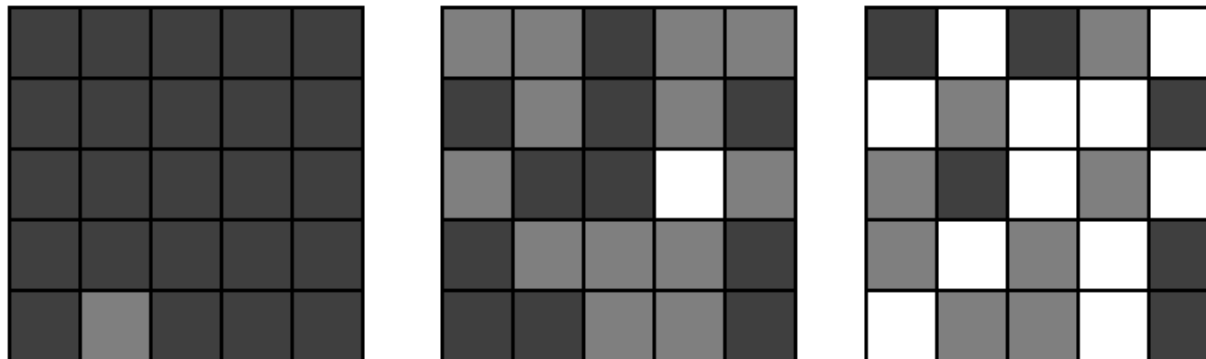
T

II. Particles at interfaces or membranes

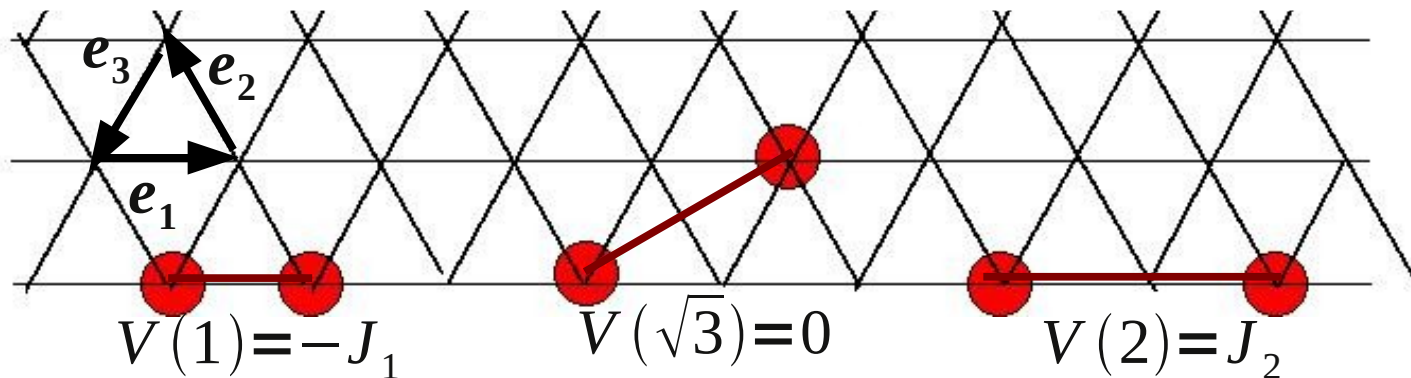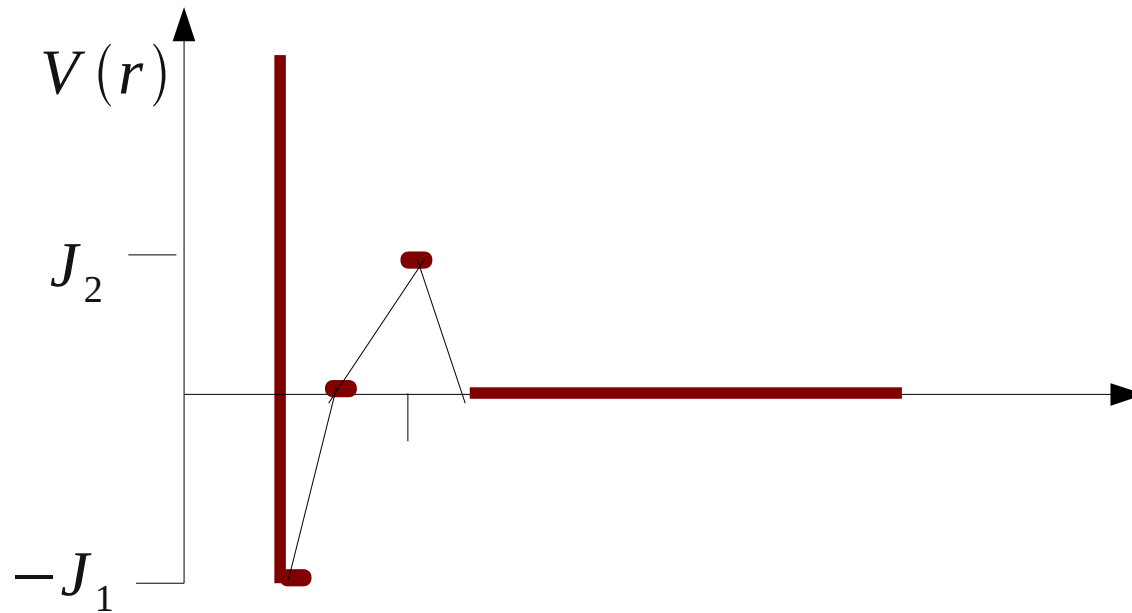Short range attraction long range repulsion (SALR) potential

Example: experimentally determined effective potential for lysozyme in water
Shukla et.al. PNAS **105**, 5075 (2008)

Short-range strong attraction often results from van der Waals,
hydrophobic or depletion interactions

Long-range repulsion often results from the presence of charges.
It may also result from deformations of the membrane
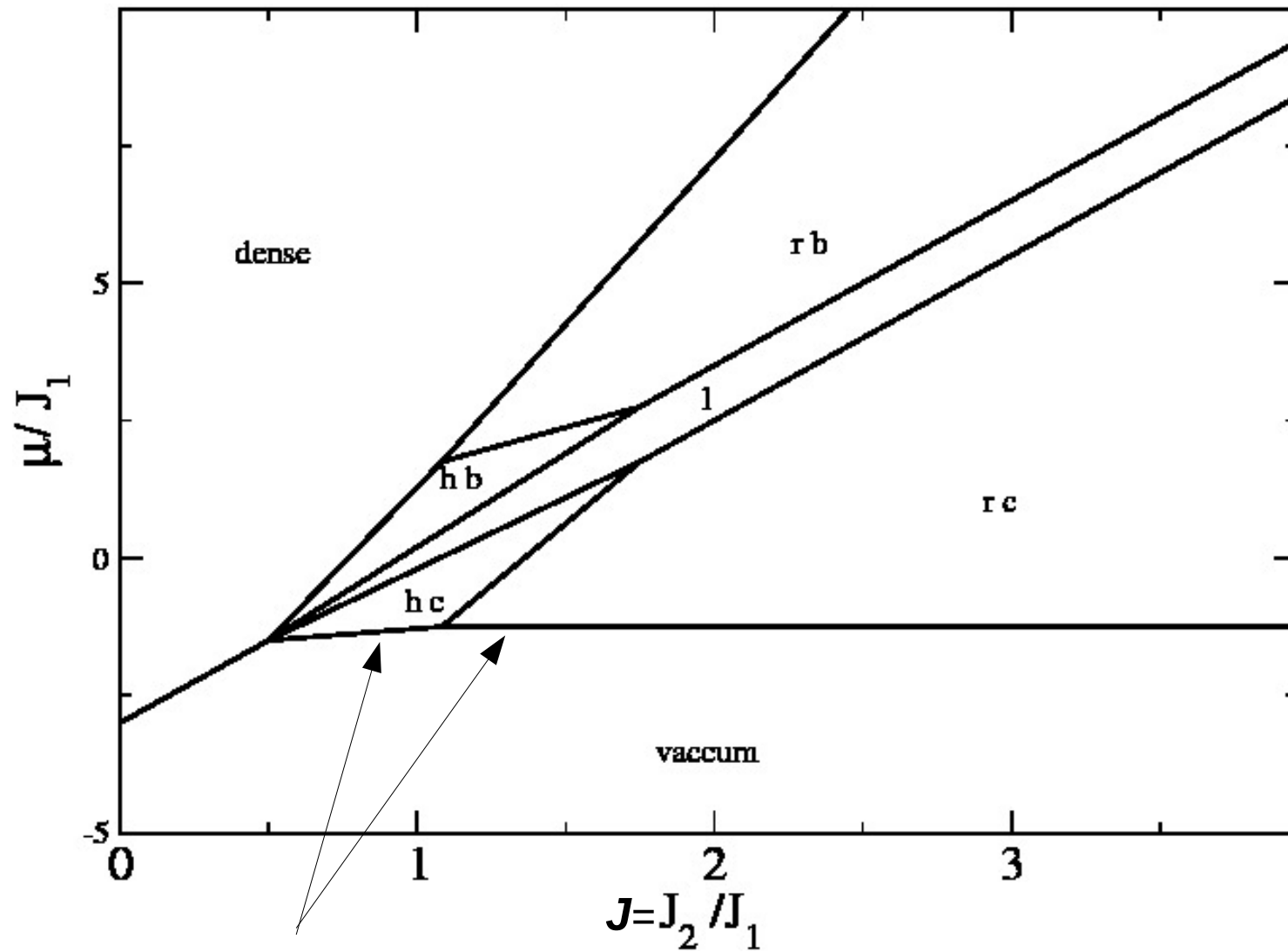due to the presence of particles

Triangular lattice with the interaction potential

$$V(\Delta x) = -J_1 \sum_{i=1}^{3} \left(\delta^{Kr}(\Delta x + e_i) + \delta^{Kr}(\Delta x - e_i) \right)$$

$$+ J_2 \sum_{i=1}^{3} \left(\delta^{Kr}(\Delta x + 2e_i) + \delta^{Kr}(\Delta x - 2e_i) \right)$$

$V(r)$

J_2

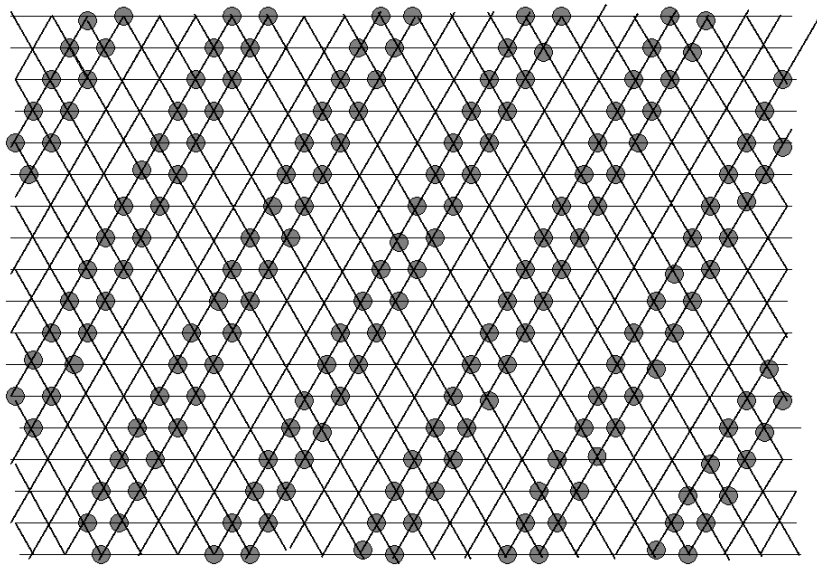$-J_1$

e_3 e_2

e_1

$V(1) = -J_1$

$V(\sqrt{3}) = 0$

$V(2) = J_2$

Ground state of the model
A.C., N. Almarza, unpublished

dense
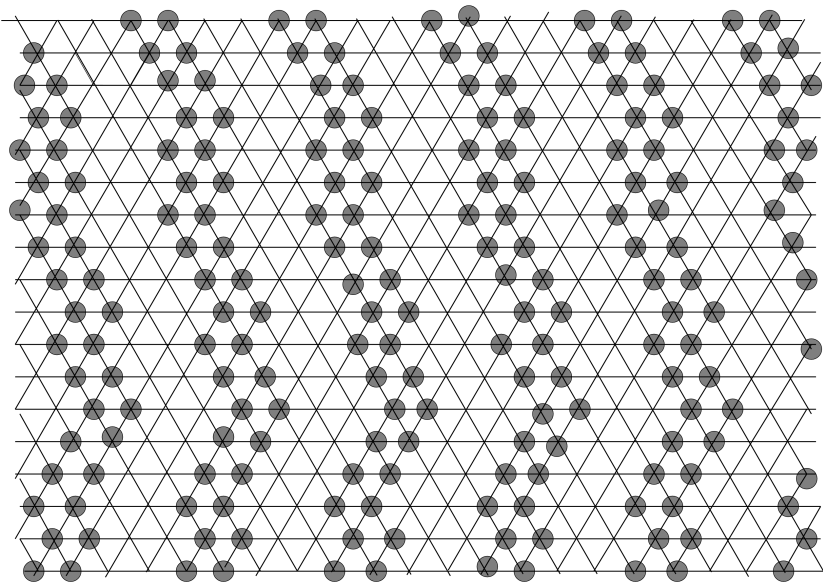
r b

μ/ J₁

h b

r c

1

h c

vaccum

J=J₂ /J₁

Three-phase lines

Rhombus clasters (rc)

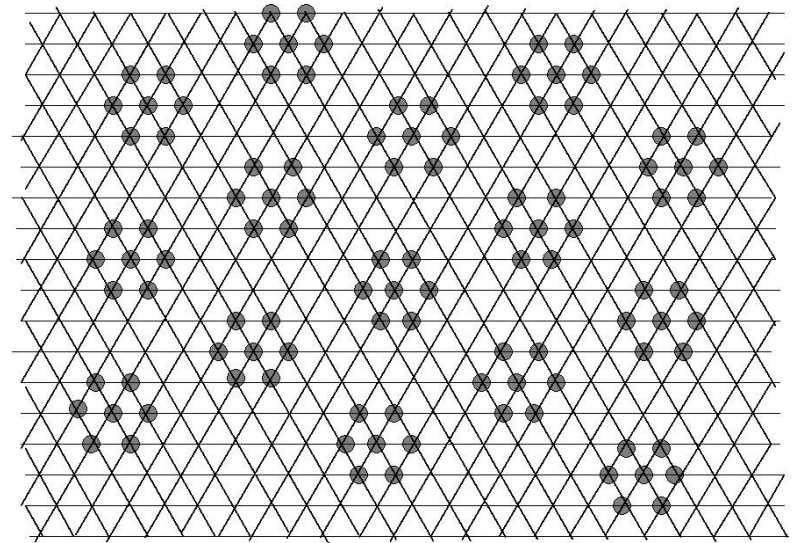Lamellar (l)
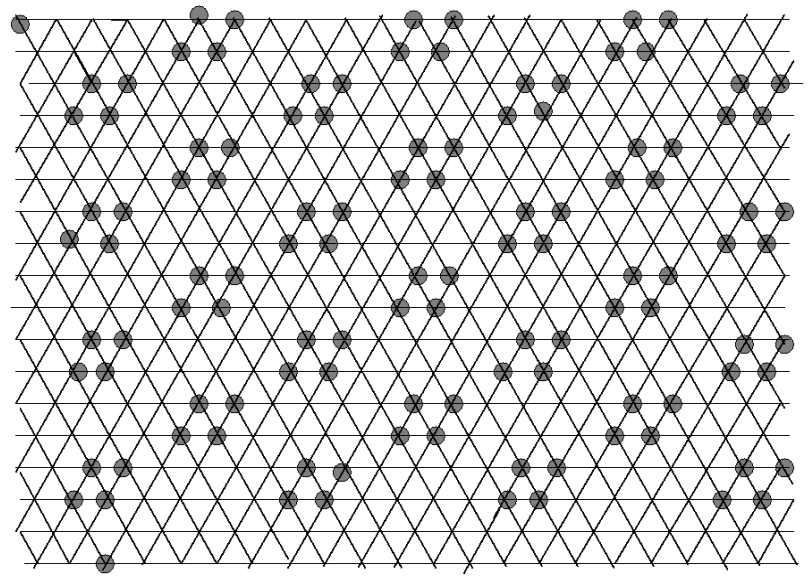
Hexagonal clasters (hc)

rb and *hb* are "negatives" of the *rc* and *hc* phases respectively. At the three-phase lines fluids consisting of clusters with any separations larger than in a respective crystal are stable.

At low T the above patterns can represent thermodynamically stable phases in various systems, with ordering on different length scales, if there is a competition between attractive and repulsive interactions. At curved vesicles more complex effects may play a role.
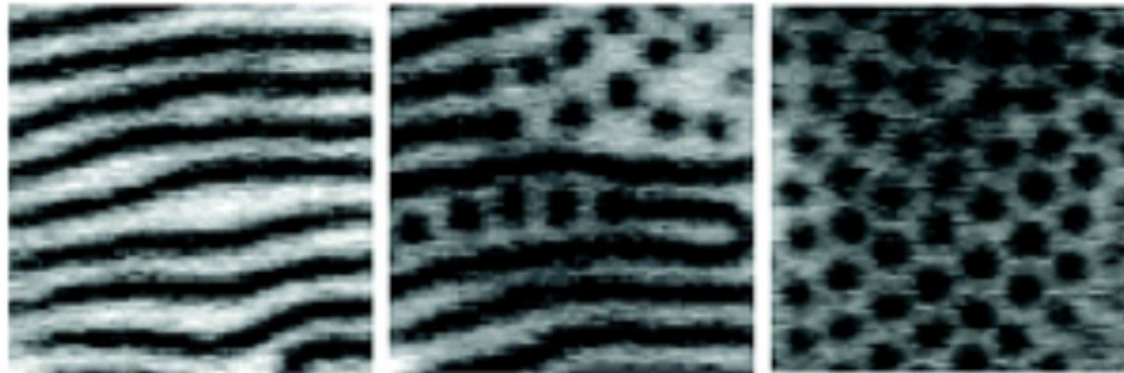
Boundary of stability of the disordered phase
For high T

Gas-liquid separation for weak repulsion $J < 1/4$

$$\frac{k_B T}{J_1} = 6(1-J)\rho(1-\rho) \qquad \cos k_b = 1$$

Spinodal line

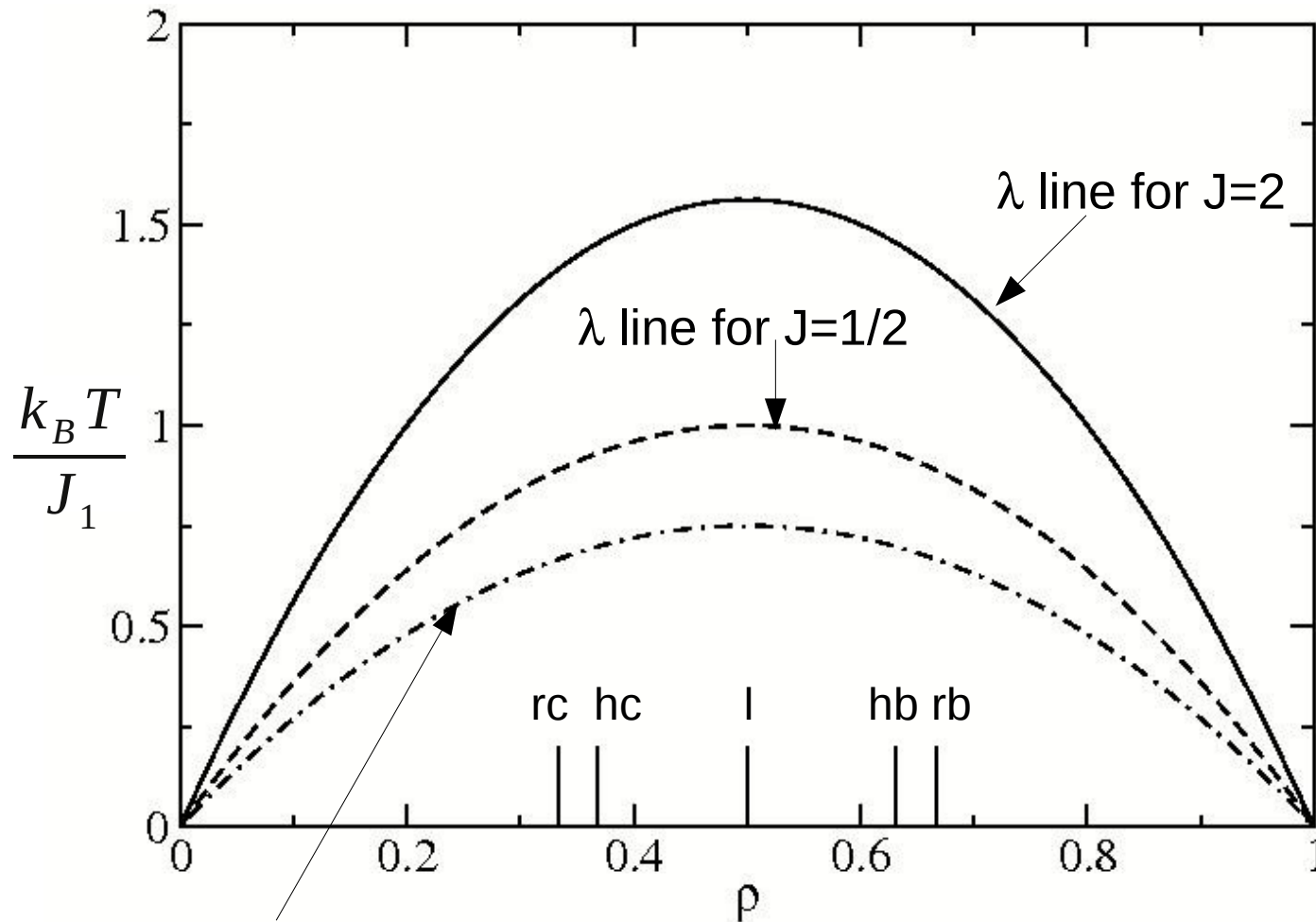Periodic ordering of clusters or stripes for strong repulsion $J > 1/4$

$$\frac{k_B T}{J_1} = \frac{(1+2J)^2}{2J}\rho(1-\rho) \qquad \cos k_b = \frac{1}{4J}$$

λ line

Period of density modulations in the inhomogeneous phase $\quad \lambda = \dfrac{2\pi}{k_b}$

Instabilities of the disordered phase with respect to periodic ordering (microseparation) and with respect to gas-liquid separation
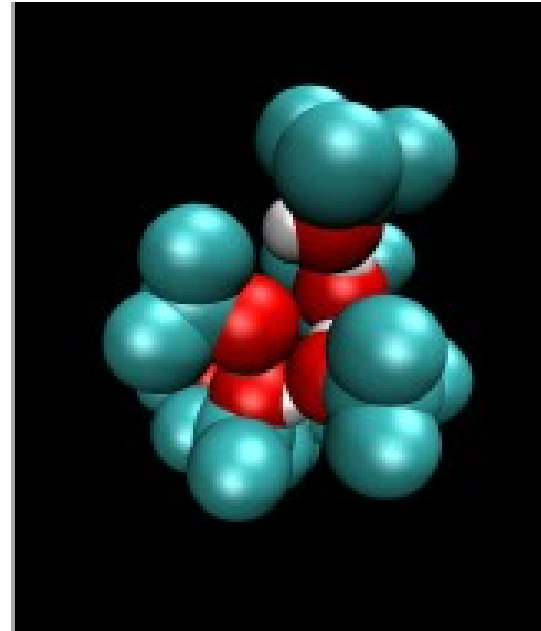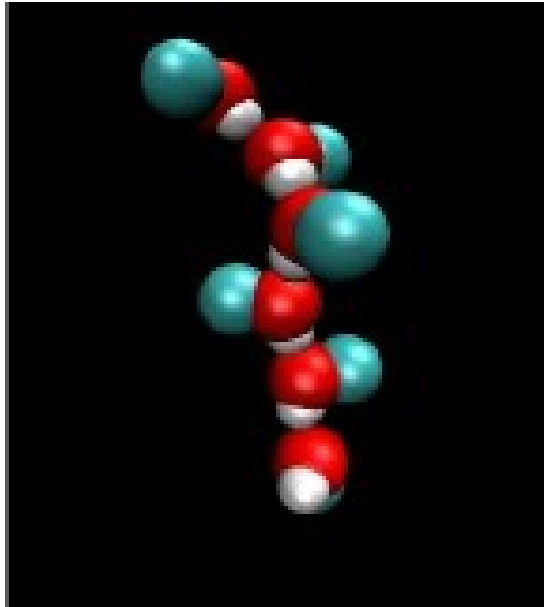

λ line for J=2

λ line for J=1/2

$\dfrac{k_B T}{J_1}$

rc hc   l   hb rb

ρ

Gas-liquid spinodal for J=1/2

For J=1/4 the spinodal and λ lines merge together, and $\lambda = \dfrac{2\pi}{k_b} = \infty$

For J>1 no gas-liquid spinodal (even metastable)

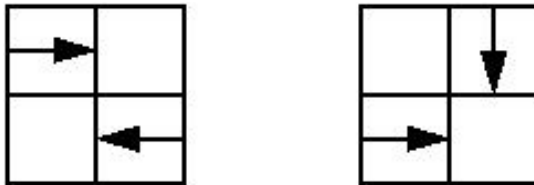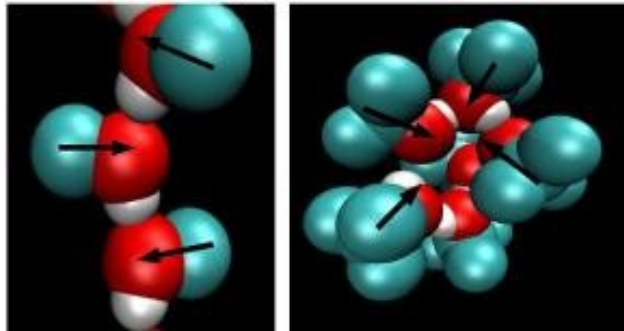# III. H-bond forming polar molecules (alcohols)

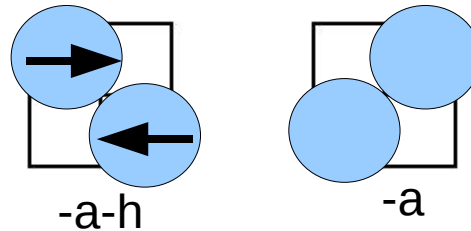## Local orientational ordering in liquid

Clusters of methanol (left) and thert-butanol (right).
Simulation snapshots (A. Perera et. al. PRE **75**, 060502 (2007))
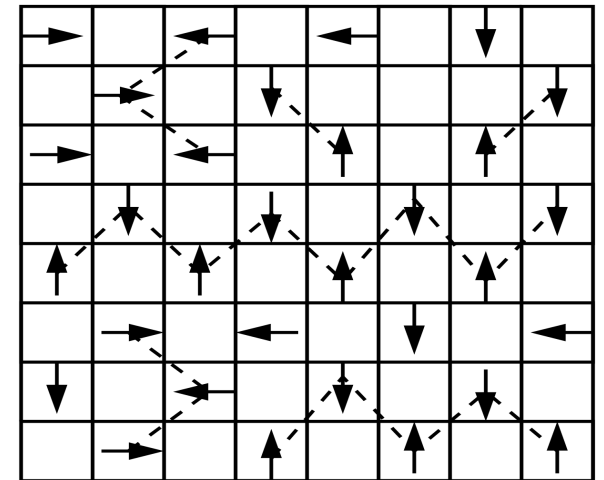
Lattice gas model for methanol
A.C. and A. Perera JCP **131** 044505 (2009)

Configurations for which
H-bonds are formed

Interaction energies
for methanol

−a−h   −a

Typical microstate with
arrows representing
orientations of
molecules and H-bonds
Indicated by dashed lines.

- The cell can be empty or occupied.
- In the occupied cell the vector connecting the tail with the head of the molecule can have 2d orientations in d dimensions. 2d+1 states
- Nearest-neighbor occupancy excluded (bulky tails).
- Van der Waals interactions -*a* assumed between next-nearest neighbors.
- H-bonds -*h* for the configurations shown above for methanol (left) and thert-butanol (right) in addition to vdW interactions.

Ground state

y ↑

x →
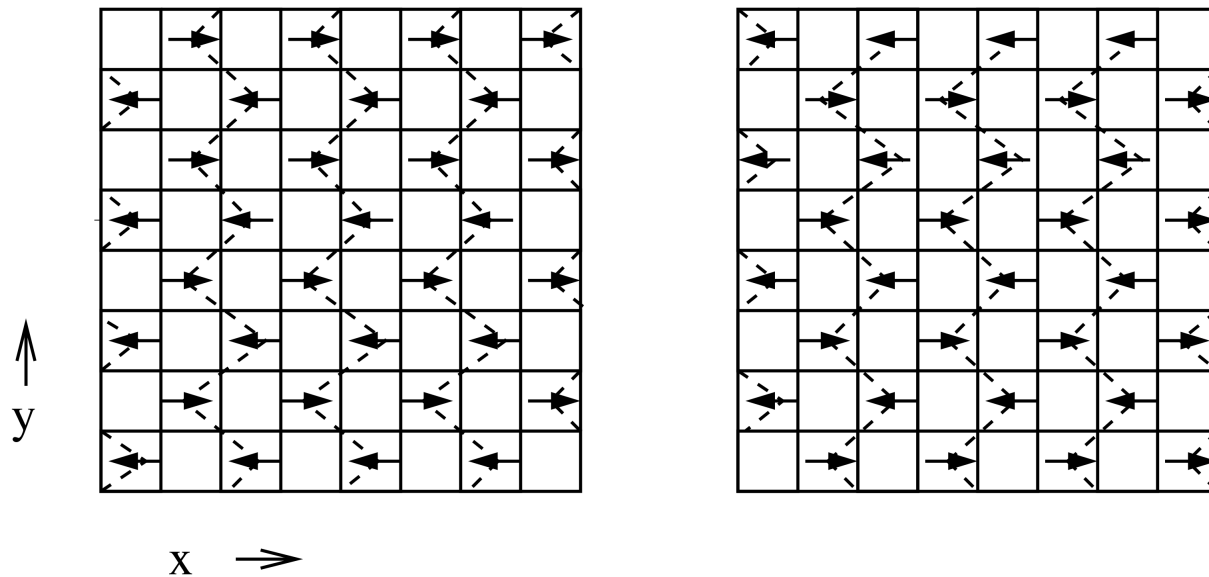
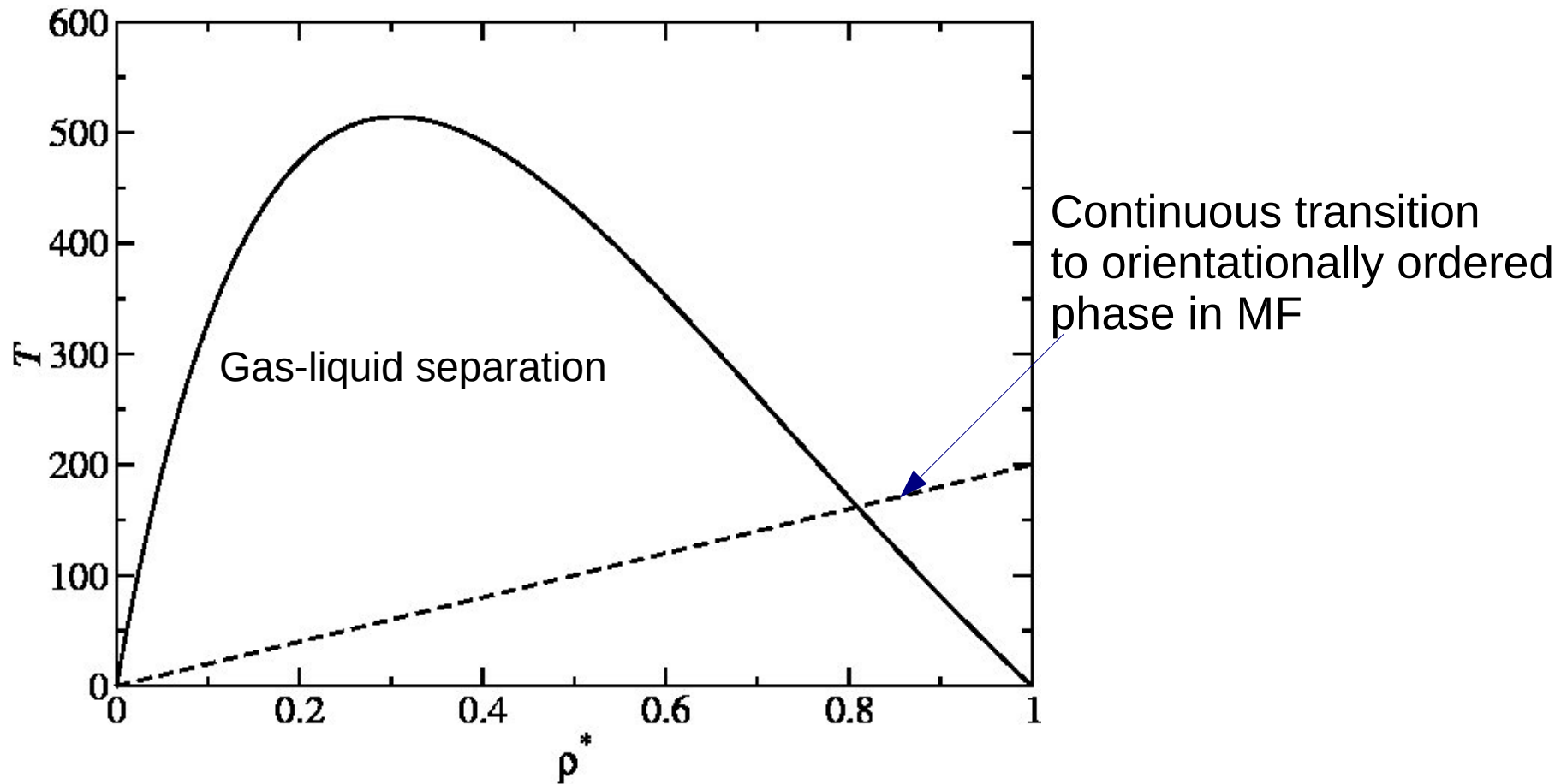z=n   z=n+1
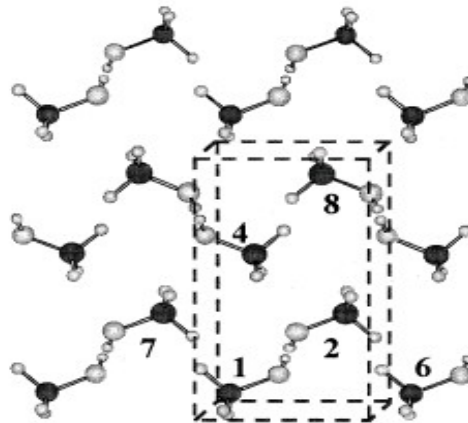
structure of the crystal at low T

Mean-field (MF) phase diagram for optimized interaction parameters with the Bethe approximation for the entropy.

Gas-liquid separation

Continuous transition to orientationally ordered phase in MF

Phase diagram for methanol

Anomalies
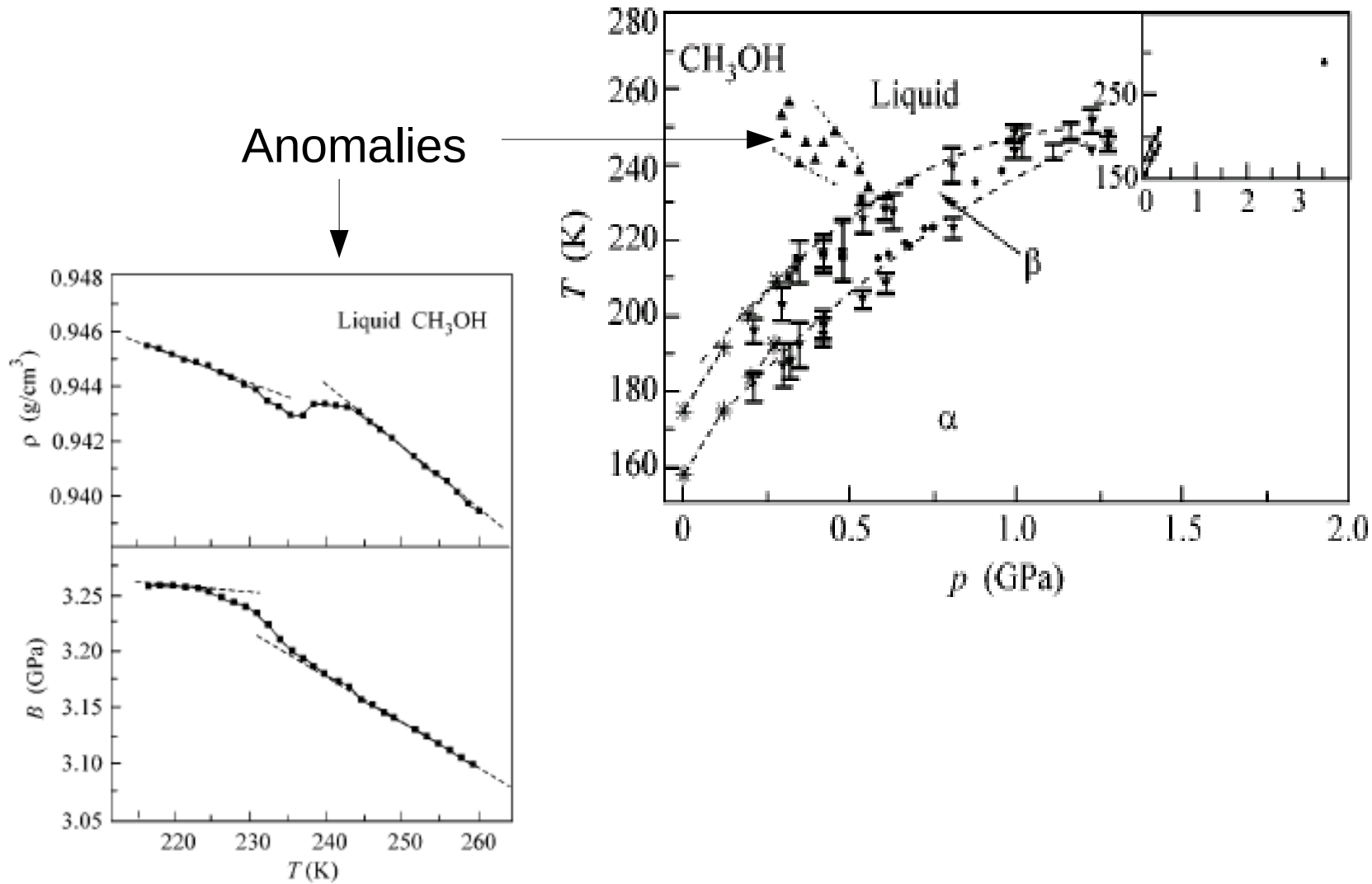
Gromnitskaya, et. al. JETP Letters, **80**, 597(2004)
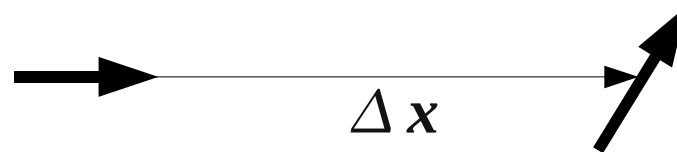
Description of orientational ordering

We define functions based on average values of the scalar product of the unit vectors $\hat{\boldsymbol{n}}$ representing orientations of the molecules separated by $\Delta \boldsymbol{x}$

$$G(\Delta \boldsymbol{x})=\langle \hat{\boldsymbol{n}}(\boldsymbol{x})\cdot\hat{\boldsymbol{n}}(\boldsymbol{x}+\Delta \boldsymbol{x})\rangle=\sum\nolimits_{i=1}^{3} G_i(\Delta \boldsymbol{x})$$

$$G_i(\Delta \boldsymbol{x})=\langle \hat{n}_i(\boldsymbol{x})\hat{n}_i(\boldsymbol{x}+\Delta \boldsymbol{x})\rangle \qquad \tilde{G}_i(\boldsymbol{k})=\sum\nolimits_{\Delta \boldsymbol{x}} G_i(\Delta \boldsymbol{x})e^{i\Delta \boldsymbol{x}\cdot\boldsymbol{k}}$$

We should know what is the orientation of the second particle when:

1. $\Delta \boldsymbol{x}\|\hat{\boldsymbol{n}}(\boldsymbol{x})$

$\Delta \boldsymbol{x}$

2. $\Delta \boldsymbol{x}\perp\hat{\boldsymbol{n}}(\boldsymbol{x})$

$\Delta \boldsymbol{x}$
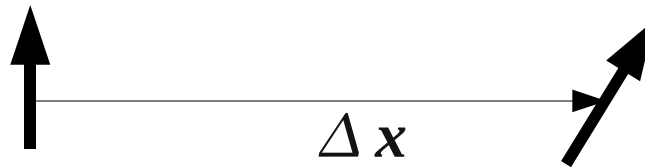
Results in Fourier representation

$\tilde{G}_1(k_1,k_2,k_2)$

k_3

k_2

k_1

$\boldsymbol{n}$

$\tilde{G}_1(k_1,0,0)$

$s_{//}$

$\tilde{G}_1(0,k_2,k_2)$ $\tilde{G}_1(0,k_2,\pi)$

$s_{\perp}$
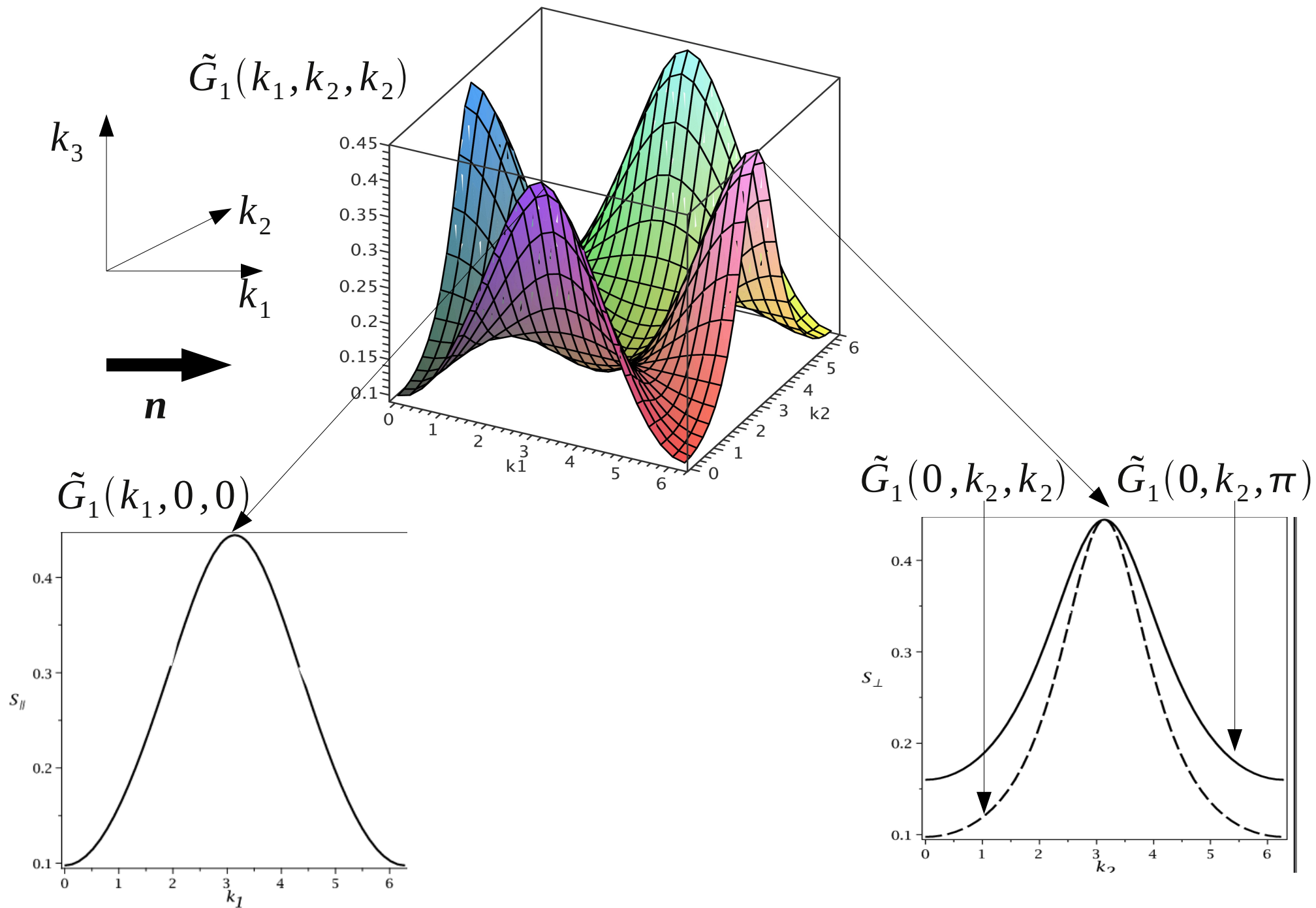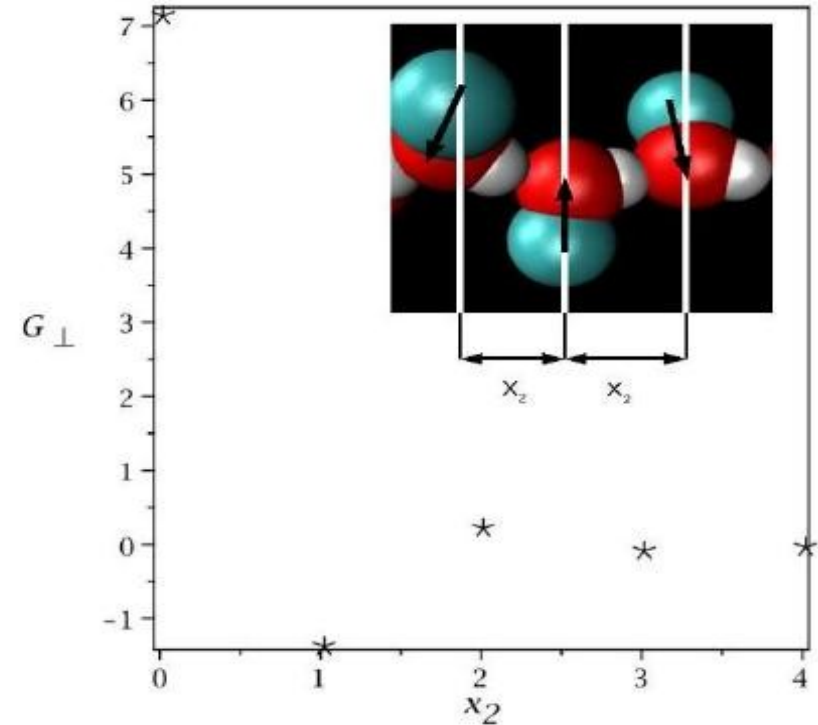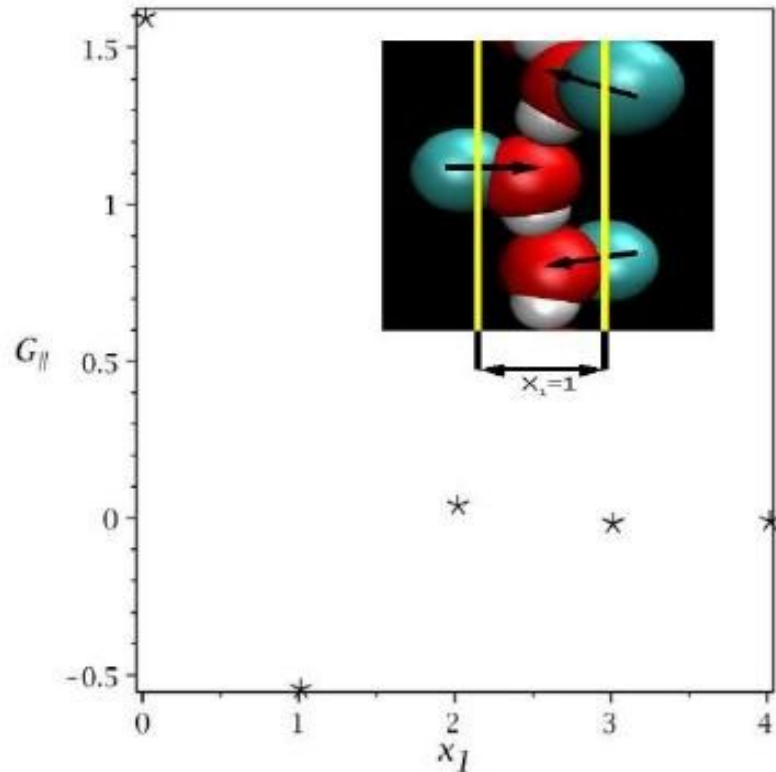
In real-space representation

$$G_1(x_1) = \int_{-\pi/2}^{\pi/2} \frac{dk_1 e^{-ik_1 x_1} \tilde{G}_1(k_1, 0, 0)}{2\pi}$$


Oscillatory orientational ordering in both, parallel and perpendicular directions with respect to the orientation of the first molecule.
The model reproduces the orientational ordering and suggests a new method of investigating orientational order of polar molecules
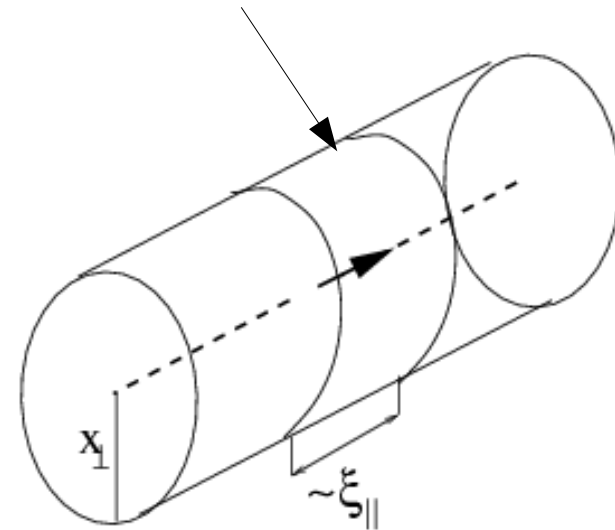
Geomertical interpretation

Our functions represent
the sum of scalar products between a chosen molecule and all molecules

at the surface perpendicular to it
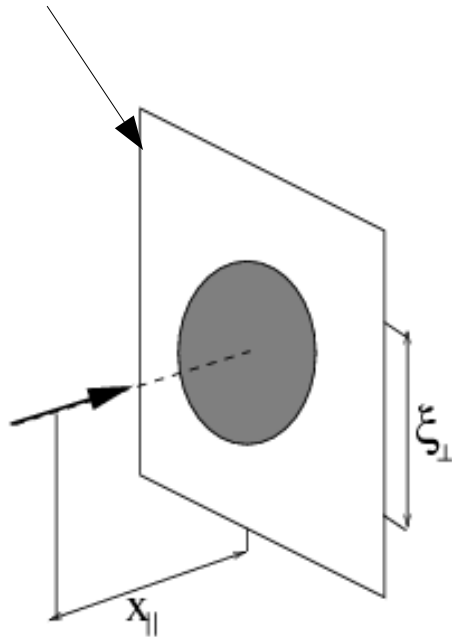
or at a surface of a cylinder
with the axis parallel to it

$$G_{'\parallel'}(x_{'\parallel'}) = \sum_{x_{'\perp'}} G(x_{'\parallel'}, x_{'\perp'})$$

$$= \sum_{x_2} \sum_{x_3} G_1(x_1, x_2, x_3)$$

$$G_{'\perp'}(x_{'\perp'}) = \sum_{x_{'\parallel'}} G(x_{'\parallel'}, x_{'\perp'})$$

$$= \sum_{x_1} G_1(x_1, x_2, x_3)$$

Very simple models
can describe very complex phase behavior and/or structure

Complexity often results from simple interactions
if there are competing tendencies in them

In the lattice models it is easier
to detect the origin of complex behavior

Collaborators

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