Phase transitions in systems of particles with only hard-core interactions

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BSSP - 2019, ICTS, Bengaluru, June 24-28, 2019

Outline

Lecture   I: Introduction
Hard Spheres and long needles ($k \times 1$ rectangles)

Lecture   II: Phase transition in $k \times 2$ rectangles
Approximate calculation of surface tension between
two columnar ordered states

Lecture III: Full packing of a square lattice by long needles:
Structure of the random fully packed state
Entropy per site of full packing for large k

Preliminaries 1: Phases and phase transitions

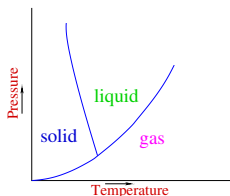Familiar example of solid, liquid and gas as phases of matter.


Figure: The Pressure-Temperature plane: There is a unique equilibrium state for each value of (P, T), except at phase boundaries.

Phases are defined by answers to yes/no questions.

As we vary a parameter (e.g. temprature), if the answer changes, that defines a phase transition.
More generally, a non-analytic response to a small perturbation is sometimes used as a characteristic signal of a phase transition.

Preliminaries 2: general theory of phase transitions
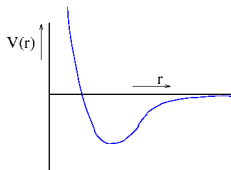
- ▶ To a good approximation, molecules interact by pair-wise additive, Lennard-Jones-type interaction
- ▶ If you put a large number of molecules in a box, at long times there is a unique equilibrium state.
- ▶ In the equilibrium state,
  $\text{Prob}(\{\vec{R}_i, \vec{P}_i\}) = \text{Const. } \exp[-\beta H(\{\vec{R}_i, \vec{P}_i\})]$
- ▶ This prescription gives different phases and sharp phase transitions, for the same H, just by varying T and P, for large number of particles. [R. B. Peierls (1936); Lee and Yang (1952)]

Preliminaries 3: Need for simpler models

- Exact theoretical calculation using Lenard-Jones interactions is not possible.

- But one can check by computer simulations using $\mathcal{O}(10^3)$ particles.

- To understand better, study simpler models, with easier-to-handle interactions, that show similar behavior.

- The singular behavior of physical quantities near phase transitions is characterized by critical exponents.
  According to the Universality Hypothesis, different systems in the same universality class show exactly the same exponents.

Critical exponents are not all there is to know. But, for detailed study, one should select a tractable representative of the phenomena under investigation.

The hard sphere model

One of the oldest models studied: Molecules approximated as hard spheres
Boltzmann, Maxwell (1870's), Adler and Wainwright (1957).

Interestingly, it shows the melting transition, from a crystalline phase to a gas-like phase.

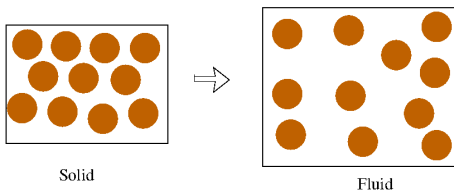A purely geometric phase transition.

Solid   Fluid

Figure: A schematic representation of loss of crystalline order on expansion of a hard-sphere solid.
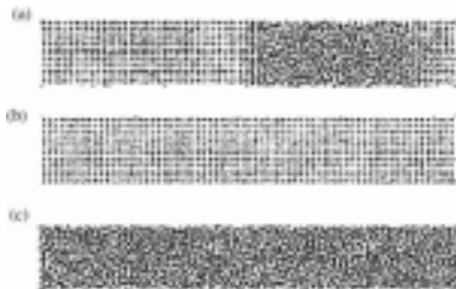
Fluid-solid transition in hard sphere systems

Figure: (a) Starting configuration used in the series of direct simulations in the constant pressure ensemble. (b) and (c) are the final configurations at $p = 11.70$ (above the melting point) and $p = 11.45$ (below the melting point), respectively. From Noya et al, J. Chem. Phys. **128** (2008) 154507.
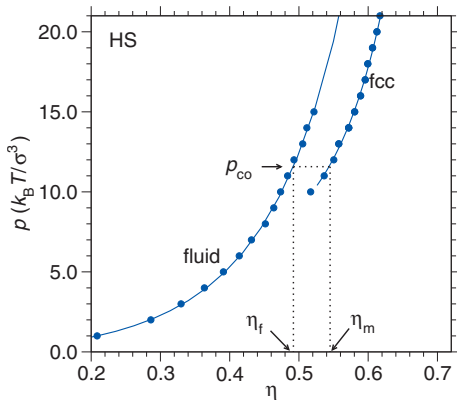
Figure: Phase diagram of the hard-sphere system in the pressure-density plane from Monte Carlo simulations. The solid lines correspond to approximate analytical equation of state, as proposed by Carnahan and Starling (fluid branch) and by Hall (solid branch). The Co-existence is for pressure 11.576, and in the density interval [.492, .545]. From Zykova-Timan et al, J. Chem. Phys. **133** (2010) 014705.

Entropy of Melting: A back-of-the envelop calculation

Consider N molecules in a volume V.

In a gas-like phase, total phase space volume $= \Gamma_g \sim V^N/N!$

If each atom is localized to its own volume V/N,
Total volume of phase space $= \Gamma_s \sim \left[\frac{V}{N}\right]^N$

Then change in entropy per particle on melting
$\Delta S = (k_B/N)\log(\Gamma_g/\Gamma_s) \approx k_B$

This seems approximately satisfied for most simple solids.
Entropy of melting measured in experiments has other contributions from increase of volume on melting, and change in internal energy.

Melting entropy of some selected materials

Material	Entropy in k_B / Molecule
Aluminum	1.45
Copper	1.17
Gold	1.17
Platinum	1.27
Silicon	0.32
Water	2.65

Data taken from internet

The melting transition in hard spheres model

- For the hard-spheres case, all configurations of non-overlapping spheres are equally likely.

- The equation of state simplifies to $P = k_B T\, f(\rho)$.

- There is no liquid-gas transition, but there is a solid-fluid transition as density is decreased.

- The solid phase has periodic density pattern in space. Hence sharp Bragg spots in x-ray diffraction.

- In 3 dimensions, there is a density discontinuity as a function of pressure.
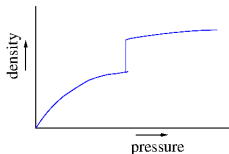
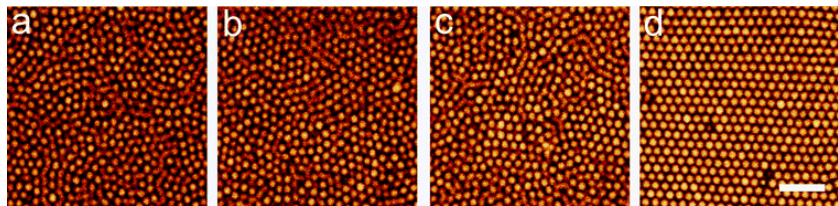Exact equation of state is not known still.

Figure: Confocal microscopy pictures of a system of colloidal particles undergoing crystallization. Here density is 0.54 of close packing density. Panels (a-d) are for time $=$ 600 s, 4500 s, 7200 s, 81900 s. the bar is $10\mu m$. From Tafts et al, Soft Matter 2013, 9, 297.

Other shapes

One can study assemblies of hard objects of other shapes: triangles, squares, hexagons, octahedra, cubes, long rods, rectangles

The strucure of dense-packed state depends on the shape, and so does the nature of transition.

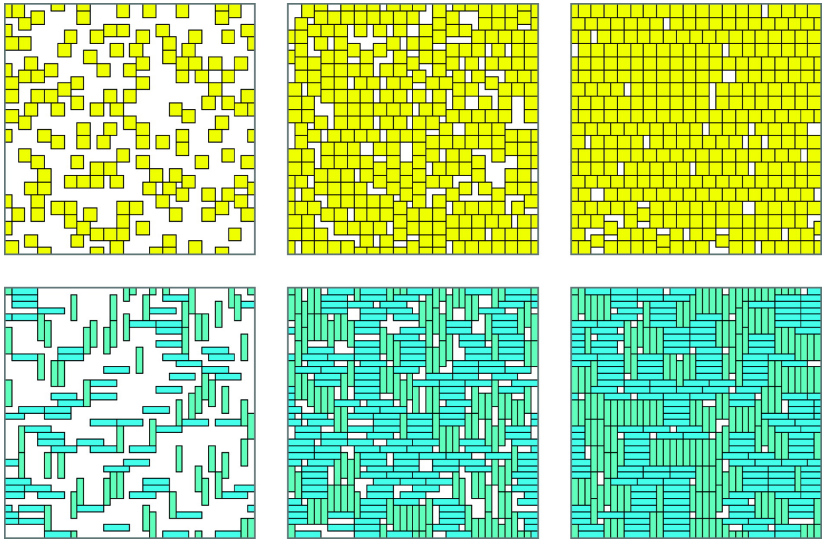Consider centers of molecules can only lie on a grid : lattice models.

Figure: Configurations of hard rods and hard squares: Figure from B C Barnes et al, Langmuir (2009) 25, p 6702.
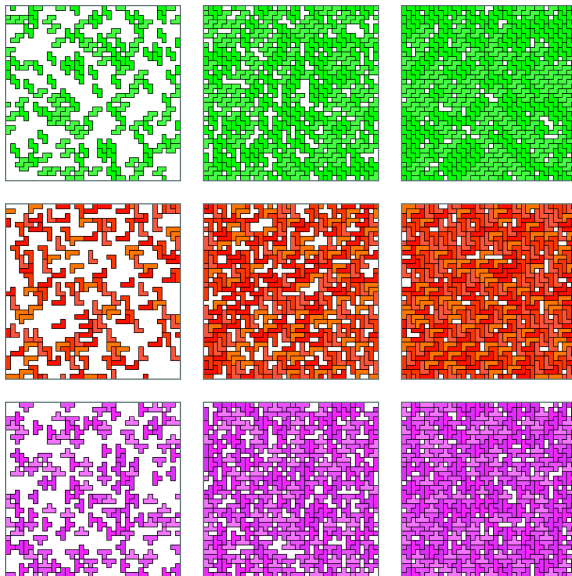
Figure: Tetramino fluids: Molecules with Z,L and T shapes. Simulations Barnes et al, op. cit.

Phase transitions in a system of long rods

Long history

Onsager (1949) used second order virial coefficient calculation to argue that a system of long needle-shaped molecules in solution, will become orientationally ordered if concentration is large enough.

Actually realized with Tobacco-mozaic virus particles in water.

Molecules are orientaionally ordered, but not positionally.

Now called Nematic liquids.

First of many meso-phases: between solids and liquids. Liquid crystals.

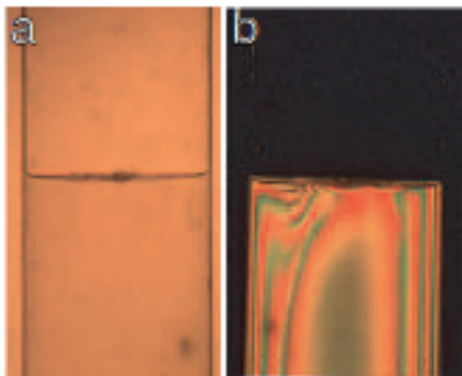Nematic order in Tobacco-Mozaic virus suspension

Figure: Bulk phase separation seen between isotropic and nematic phases of TMV suspension. The right panel is seen in cross polarized light. Figure taken from Z. Dogic and S. Fraden, in ' Soft matter: complex colloidal suspensions', Eds. Gompper and Schick, Wiley (2005).

Lattice model of long rods
Long straight rods of length *k*
$k = 2, 3, \ldots 12$
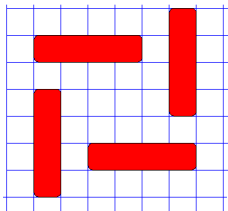
Only hard-core interaction
Ordering transition as a function of density?
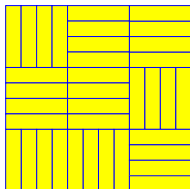
In Lattice models
No phase transition for $k = 2$ Heilmann, Lieb (1972)
$k = 3, 4$ [Ghosh, DD, Jacobsen (2007)]

" It is not quite certain that such a lattice model, even for large p, will lead to a transition"
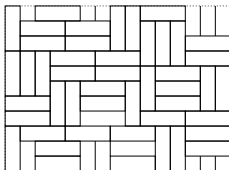in *The Physics of Liquid Crystals*, De Gennes and Prost (1995)

No ordering possible at close packing density

No. of configurations $\geq 2^{N/k^2}$.
More complicated tilings possible.

Earlier work

There are two phase transitions, at critical densities ρ_{c1} and ρ_{c2}. [Ghosh and Dhar, 2007]
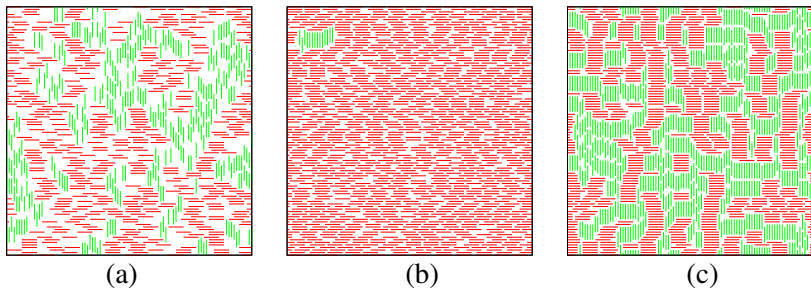

Figure: Typical configurations of the system in equilibrium at densities (a) $\rho \approx 0.66$ (b) $\rho \approx 0.89$, and (c) $\rho \approx 0.96$ on a square lattice. Here, $k = 7$ and $L = 98$.
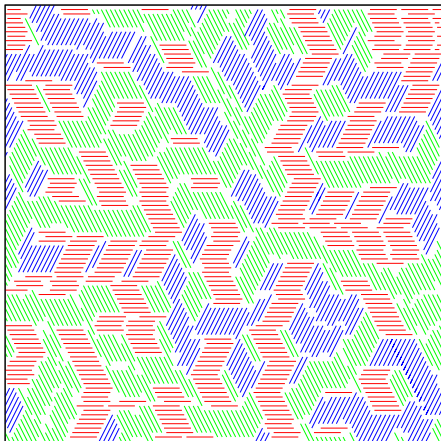
Figure: A typical configuration of the system in equilibrium at density $\rho \approx 0.96$ ($\mu = 7.60$) on a triangular lattice. Here, $k = 7$ and $L = 98$.

Phase transitions: hard rods in 2-d

First transition at ρ_{c1} from isotropic to nematic phase is studied well by simulations by Matos Fernandez et al (2008), Fischer and Vink(2009).
Ising Universality class on the square lattice.
$q = 3$ Potts model universality class on the triangular lattice.

Second transition is hard to study because standard Monte Carlo dynamics involving diffusion and evaporation/ deposition becomes very slow due to jamming.

We shall call the three phases isotropic, nematic, and high-density disordered (HDD) phase.

Monte Carlo Algorithm

- Begin with any configuration of rods.
- Choose a row or column at random
- Remove all the rods lying on this row/ column.
- Reoccupy empty intervals on this row/column, with correct 1-d line grand-canonical weights.
- Repeat

This is a non-local algorithm, satisfies detailed balance.

It can be parallelized. Empty all horizontal rows together. These can be occupied independently.
Then do the same with vertical columns.
We were able to simulate lattices of linear size ~ 2500, and densities up to 0.995
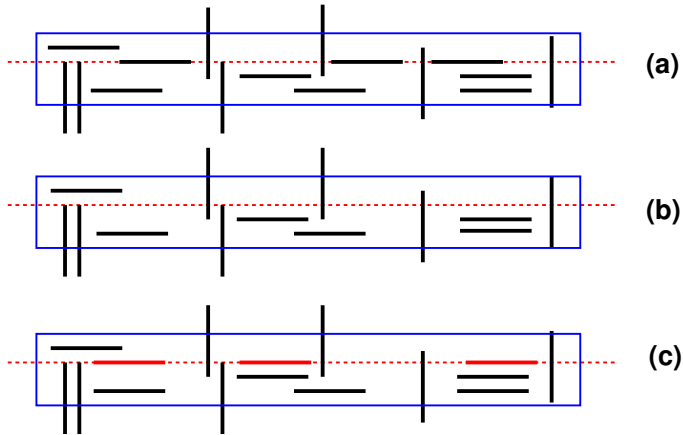
Figure: The Monte Carlo algorithm. The three panels show the configuration at differents stages of the evolution. (a) initial configuration (b) evaporation (c) deposition.

Properties of the HDD phase:

Consider high density phase, with a few rods removed.

Each rod removed creates k vacant sites.

If we allow the nearby rods to slide into vacancies, these vacancies undergo a diffusive motion.

There are k vacancies per rod removed. Each has a different colour. It keeps it colour when it diffuses.

Figure: Break-up into k sublattices. Here $k = 4$

Consider removing only one rod. Then, we allow the k-mers to diffuse.
The k different-colored vacancies may form a bound molecule, or be in an unbound state.

Then, at small densities, a system will be in a molecular state, and on increasing density go to a 'plasma state'.
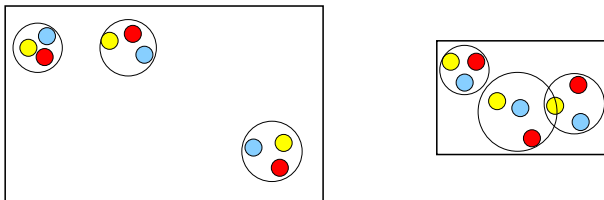

Figure: The binding-unbinding transition of colored vacancies on increasing density

Aside, an exercise for students:

Hydrogen gas at low densities, becomes more ionized as you decrease the density, as explained by Meghnad Saha. But in Quark-Gluon Plasma, it is the opposite. Why?

Let $Prob(r_1, r_2, ..r_k)$ be the probability that the vacancies are found at $r_1, r_2, ...$

This is like the "wavefunction" of the bound state.

By symmetry, we would expect $Prob(r_1, r_2, ..r_k) \sim \prod_{i \neq j} \frac{1}{(r_{ij})^x}$

The value of x depends on k. Only known exact value for $k = 2$.
Numerical estimates for $k = 3, 4$.

Perhaps the bound state exists only for $k \geq 7$, and this explains why HDD phase exists only for $k > 7$.

Let d_{ij} = average distance of vacancy of color i from nearest neighbor of color j

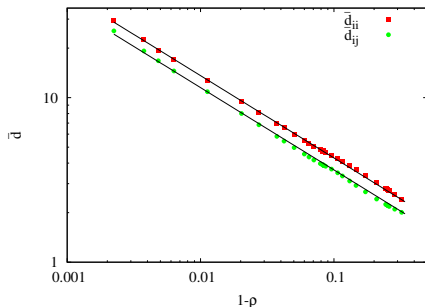If bound state of defects, $d_{samecolour} \gg d_{differentcolour}$.

Figure: The average distances d_{ii} and d_{ij}, on the square lattice, between a vacancy on sublattice i and the nearest vacancy on sublattice j as a function of density ρ. The $i \neq j$ data are averaged over all $j \neq i$. The solid lines show the functions $K(1 - \rho)^{-1/2}$, for $K = 1.36$ and 1.12. Data is for $k = 7$ and $L = 168$.

Properties of the HDD phase...

- Finite orientational order-parameter susceptibility, hence not too-slow decay of orientational correlations
- stacks have an exponential distribution of sizes
- Ordered phase can not be considered as bound state of vacancies
  The analogy discussed earlier, is interesting, suggestive, but incorrect in detail

Critical exponents of the second transition have been estimated from simulations: $\nu \approx o.90$; $\alpha/\nu \approx 0.22$, $\beta/\nu \approx 0.22$
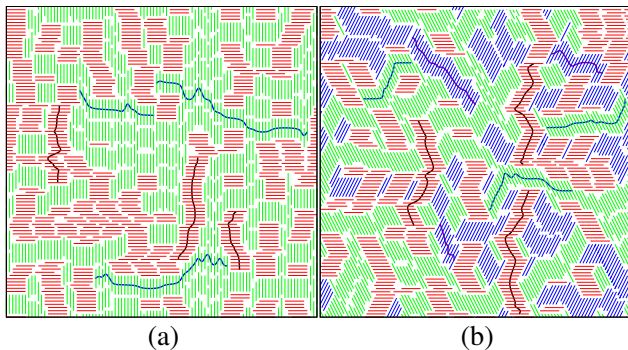
Properties of the HDD phase: Stacks

Figure: A picture of stacks in the HDD phase, shown here as wiggly lines, for (a) square lattice and (b) triangular lattice. The snapshots are for $\mu = 7.60$. Rods of different orientations are shown in different colors.
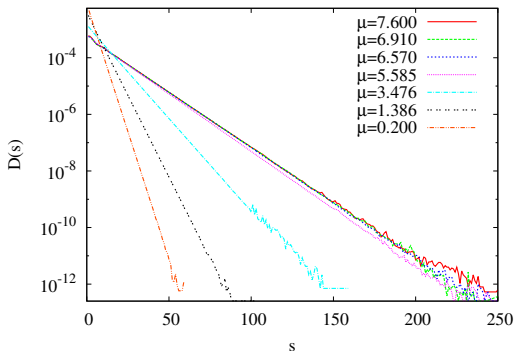
Distribution of stack sizes

Figure: Stack distribution in the LDD phase ($\mu = 0.200$), intermediate density nematic phase ($\mu = 3.476$), HDD phase ($\mu = 7.600$), and at two critical points ($\mu = 1.3863, 5.570$) are shown. Data are for $L = 280$, $k = 7$, and the square lattice.
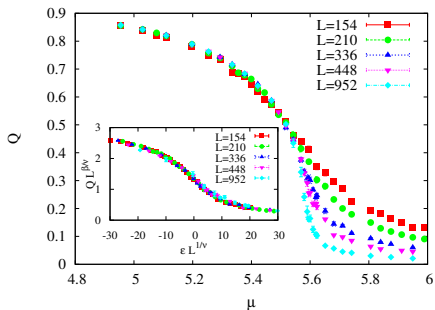
Critical exponents at the second transition:

Figure: The variation of the order parameter Q with chemical potential μ for different systems sizes of a square lattice. Inset: Data collapse for square lattices when scaled Q is plotted against $\epsilon L^{1/\nu}$ with $\nu = 0.90$, $\beta/\nu = 0.22$ and $\epsilon = (\mu - \mu_c)/\mu_c$.
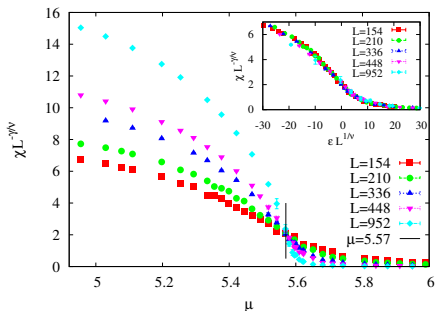
Critical exponents at the second transition:

Figure: The variation of χ, the mean of the square of the order parameter, with chemical potential μ for different system sizes of a square lattice. The curves cross at μ_c when χ is scaled by $L^{-\gamma/\nu}$, with $\gamma/\nu = 1.56$. Inset: Data collapse for square lattices when $\chi L^{-\gamma/\nu}$ is plotted against $\epsilon L^{1/\nu}$ with $\nu = 0.90$, and $\epsilon = (\mu - \mu_c)/\mu_c$.
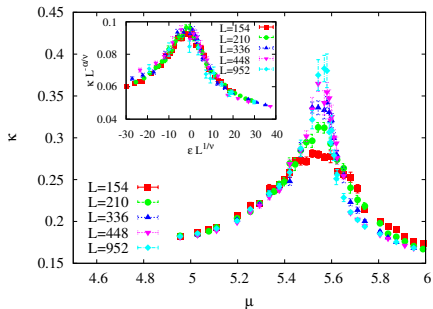
Critical exponents at the second transition:

Figure: The variation of compressibility κ with chemical potential μ for different system sizes of a square lattice. Inset: Data collapse for square lattices when the scaled κ is plotted against $\epsilon L^{1/\nu}$ with $\nu = 0.90$, $\alpha/\nu = 0.22$, and $\epsilon = (\mu - \mu_c)/\mu_c$.

Summary and concluding remarks

- ▶ models with purely hard core interactions are interesting
- ▶ Hard spheres gives a simple model of melting.
- ▶ More complicated shapes can describe other mesophases.
- ▶ In particular, long rods on a lattice undergo two phase transitions.
- ▶ Nature of the high-density disordered phase, and phase transition not fully understood.

Thank You