Trends in mathematical crystallisation

May 2016

Organiser: Stefan Adams, Markus Heydenreich, Frank den Hollander, Sabine Jansen

Description and aim: The workshop concentrates on the mathematical theory of crystallisation. More precisely, we focus on five topics that are closely connected with crystallisation, and approach these topics from different mathematical angles. These five topics are:

(1) Spatial symmetry breaking at positive temperature
(2) Crystallisation and surface effects at zero temperature
(3) Continuum particle systems (Gibbs point fields, metastability, and Percolation)
(4) Elasticity (variational analysis & gradient fields and quasi-crystals and liquid crystals
(5) Differential/integral geometry

We expect participants from analysis, statistical physics and probability. Our primary goal is to discuss the different approaches towards crystallisation in these disciplines.

Vision: Crystallisation is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas. Crystallisation is also a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. In chemical engineering crystallisation occurs in a crystalliser. Crystallisation is therefore an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent, as compared to precipitation due to chemical reaction.

Crystallisation poses major challenges for mathematicians - it is one of the challenging open interdisciplinary problems involving analysts, probabilists, applied mathematicians, physicists and material scientists. There are many open questions, among which are the following. Most of these have been discussed at the workshop 'Facets of mathematical crystallization' - Lorentz Center Leiden, September 2014. A key challenge of the workshop is to address and clarify their potential further.

(I) What characterises a crystal? What characterises different forms of spatial order?
(II) What should a system be called for which rotational symmetry is broken but translational symmetry is not? A liquid crystal or a hexatic crystal?
(III) Is translational symmetry typically broken at low temperature in $d \geq 3$? What aspects of the interaction potential are crucial for this? Repulsion at short distances and attraction at large distances?
(IV)
- What do zero-temperature models tell us about positive-temperature models?
- Can hard-sphere (or otherwise geometrically constrained) systems teach us anything about systems with finite interactions?
- What is the role of Pirogov-Sinai theory in this context?

(V) Are (small numbers of) defects essential to stabilise a crystal at small positive temperatures? Are crystals typically metastable (because they are obtained after a temperature quench)?
(VI) What can be learned from liquid crystals? What are the order parameters for positive temperature?
(VII) What can be learned from continuum percolation systems in $\mathbb{R}^2$?

(VIII) Does discretisation introduce spurious ground states? In other words, does coarse-graining introduce extra ground states that are not present without the coarse-graining?

(IX) What can the Cauchy-Born rule explain for crystal structures and elasticity?

(X) Is translational symmetry typically broken at low temperature in $d \geq 3$? What aspects of the interaction potential are crucial for this? Repulsion at short distances and attraction at large distances?

(XI) What needs to be measured about a crystal in order to identify its structure?

(XII) How does the theory of finite crystals (Wulff shapes, gradient mod- els, sharp versus rounded edges, etc.) relate to the theory of infinite crystals?

(XIII) What is the role of quantum mechanics for crystallisation?

(XIV) Does the theory of granular media have any bearing on the theory of crystallisation, and vice versa?

(V) Should physicists not have the ambition to build physical systems that can exhibit any thinkable form of crystallisation?

Titles and abstracts

Michael Baake (Bielefeld): *What should we consider as a crystal ?*

Different scientific communities have equally different views on what should be considered as a crystal – and this controversy is likely to persist. The plan of this talk it to review some of the approaches, with some focus on spectral aspects. In particular, we will look at ordered structures from the diffraction theory point of view, and explain how the diffraction spectrum is related to the corresponding dynamical spectrum.

Laurent Bétermin (Heidelberg): *Theta functions and minimization of interaction energies*

The goal of the talk is to explain how to minimize a finite lattice energy of the type $E_f[L] = \sum_{p\in L\setminus\{0\}} f(|p|^2)$, among Bravais lattices $L \subset \mathbb{R}^2$. Indeed, the understanding of this energy per particle is fundamental, when f is a long-range potential, to find the best competitor for the associated crystallization problem with a finite number of points. Our method uses a two-dimensional theta function associated with L. We will show the optimality of the triangular lattice: 1) at any fixed density, if the potential f is completely monotonic; 2) at fixed high density, for a large class of potentials; 3) among all Bravais lattices, without density constraint, for potentials f with a well. Moreover, we will give some results of non-optimality of the triangular lattice, at some fixed densities, and some numerical results in the classical Lennard-Jones potential case. This talk is partially based on a joint work with Peng Zhang (Shanghai Jiao Tong University).

Xavier Blanc (Paris): *A review on some mathematical results about crystallization*

In this talk, I will review some results on the crystallization conjecture, that is, the mathematical proof of the fact that, under appropriate conditions, interacting particles place themselves into periodic configurations. I will first review classical models at zero temperature, in which few results have been proved. Apart from the question of the emergence of periodicity, determination of the optimal lattice, in link with special functions, will be addressed. Then, some problems regarding the quantum case, in which the notion of crystalline order needs to be defined in a different way. Similarities with positive temperature classical models will be outlined.

David Brydgeds (UBC Vancouver): *The lace expansion for ϕ^4*

The lace expansion provides a formula for the two point function which has been useful for critical percolation, self-avoiding walk and related problems in high dimensions. Recently Akira Sakai has shown that the Ising model and the one component ϕ^4 model admit similar formulas. I will review the basic features of the lace expansion and describe recent work with Mark Holmes and Tyler Helmuth which extends the lace expansion to $O(2)$ symmetric ϕ^4.

Diana Conache (TU Munich): *Lattice approximations of Gibbs point processes*

We consider a classical system of particles in continuum interacting via a pair potential and we approximate it by a sequence of lattice systems indexed by the size of the grid. The spins correspond to the number of particles in a cube of side length equal to the grid size. We prove existence of the Gibbs measures for these lattice systems. Uniqueness also holds in the high temperature regime. Moreover, we establish uniform bounds on the uniqueness parameters.

Luca De Luca (TU Munich): *Discrete differential geometry and 2D crystallization: simplified version of the Heitmann-Radin argument*

We present a simple proof of Heitmann-Radin crystallization using the following decomposition of the energy: For any fixed $N \in \mathbb{N}$ and for any configuration X having N points, the Heitmann-Radin energy $\mathcal{E}_{\mathrm{HR}}(X)$ decomposes as

$$\mathcal{E}_{\mathrm{HR}}(X) = -3\,N + \mathcal{P}(X) + \mu(X) + 3\,\chi(X),$$

where the surface term $\mathcal{P}(X)$ is the *perimeter* of the bond graph generated by X, $\mu(X)$ is the *defect* term measuring how much this graph differs from a subset of the triangular lattice and $\chi(X)$ is the *Euler characteristic* of the bond graph.
Exploiting the discrete differential geometry framework, we provide a simple argument that shows that any minimizer of $\mathcal{P} + \mu + 3\,\chi$ (ad hence of $\mathcal{E}_{\mathrm{HR}}$) is a connected subset of the triangular lattice having simply closed polygonal boundary.
This is a joint work with Gero Friesecke (TU München).

David Dereudre (Lille): *Infinite volume continuum random cluster model*

The continuum random cluster model is defined as a Gibbs modification of the stationary Boolean model in Rd with intensity $z > 0$and the law of radii Q. The formal unnormalized density is given by q^{Ncc} where $q > 0$ is a fixed parameter and Ncc the number of connected components in the random germ-grain structure. In this paper we prove the existence of the model in the infinite volume regime for a large class of parameters including the case $q < 1$ or distributions Q without compact support. In the extreme setting of non integrable radii (i.e. $\int R^d Q(dR) = \infty$) and q is an integer larger than 1, we prove that for z small enough the continuum random cluster model is not unique; two different probability measures solve the DLR equations. We conjecture that the uniqueness is recovered for z large enough which would provide a phase transition result. Our main tools are the compactness of level sets of the specific entropy, a fine study of the quasi locality of the Gibbs kernels and a Fortuin-Kasteleyn representation via Widom-Rowlinson models with random radii.

Gero Friesecke (TU Munich): *Discrete differential geometry and 2D crystallization: energy decomposition via Gauss-Bonnet*

In this talk I argue that it is fruitful for crystallization problems to endow the bond graph of a general particle configuration with a suitable notion of discrete curvature. This idea will be worked out in detail in two dimensions. A suitable recent discrete Gauss-Bonnet theorem by Knill (which I will of course explain) allows to relate the sum/integral of the curvature to topological invariants. This leads to an exact geometric decomposition of pair potential energies, including the Lennard-Jones energy, into (i) a bulk term, (ii) a combinatorial perimeter, (iii) a multiple of the Euler characteristic, (iv) a topological energy contribution due to defects, (v) elastic energy and (vi) energy due to non-bonded interactions. The last two terms vanish in the special case of the Heitmann-Radin energy, and this decomposition then allows a novel understanding of the Heitmann-Radin crystallization theorem as explained in the companion talk by Lucia De Luca, with whom this is joint work.

Reference: L.De Luca, G.F., Crystallization in two dimensions and a discrete Gauss-Bonnet theorem, arXiv 2016

Tyler Helmuth (Berkeley): *Dimensional Reduction for Generalized Continuum Polymers*

A striking example of dimensional reduction established by Brydges and Imbrie is an exact relation between the continuum hard sphere gas in d dimensions and continuum branched polymers in $d+2$ dimensions. I will discuss a new proof of dimensional reduction that also applies to more general models of continuum polymers. The proof is essentially combinatorial, in contrast to the original proof which uses supersymmetry.

Sebastian Kapfer (Erlangen): *Melting of Soft Particles in Two Dimensions and the Hexatic Phase via Monte Carlo*

The melting transition of two-dimensional solids has been the subject of continued debate for more than fifty years, mainly due to the KTHNY theory of defect unbinding predicting an intermediate hexatic phase with short-range positional order and quasi-long-ranged orientational order. For hard disks, the KTHNY scenario has been essentially confirmed by Monte Carlo simulation, even though the liquid-hexatic step is of first order [1]. A key problem in these simulations are the large correlation lengths, which we tackle using a new rejection-free global-balance Monte Carlo algorithm [2]. We show that the hard disk result transfers to soft interactions with inverse power-law or Yukawa potentials [3]. The order of the liquid-hexatic step can be tuned from first-order to continuous by softening the potential. We show that there is always a hexatic phase separating the liquid and solid phases, and identify two regimes of the hexatic with vastly different correlation lengths. The density of defects can be related to the correlation length, even though defects turn out to be strongly interacting.
[1] E. P. Bernard, W. Krauth, Phys. Rev. Lett. 107, 155704 (2011). [2] M. Michel et al., J. Chem. Phys. 140, 054116 (2014). [3] S. C. Kapfer, W. Krauth, Phys. Rev. Lett. 114, 035702 (2015).

Wilfrid Kendall (Warwick): *Ising models and multiresolution quad-trees*

Quite a while ago, I found myself working on the application of Ising models in multiresolution image analysis (Kendall and Wilson, 2003). I shall review this work, which produced a phase transition diagram that made sense of results from numerical experiments in multiresolution image analysis. I shall then take the opportunity to discuss a question which still remains open, concerning interfaces, in the hope that this may provoke people to provide an answer!

Reference

Kendall, W. S., & Wilson, R. G. (2003). Ising models and multiresolution quad-trees. Advances in Applied Probability, 35(1), 96–122.

Günter Last (Karlsruhe): *Volume maximizing hard-core thinnings*

It is not easy to come up with tractable mathematical models for stationary random collections of non-overlapping particles. In the first part of this talk we shall provide a short review of some known thinning models. In the second part of the talk (based on joint work with Christian Hirsch) we shall introduce and discuss a volume maximizing thinning model based on an arbitrary stationary process of possibly overlapping particles.

Mathieu Lewin (Paris): *Jellium, the Uniform Electron Gas and Crystallization*

This talk is dedicated to the discussion of open mathematical questions for two important systems that play a central role in today's quantum physics and chemistry.

The "Uniform Electron Gas" (UEG) is by definition an infinite gas of charged particles, placed in a way that the density is constant everywhere in space. This system is always confused with "Jellium", where the particles are submitted to an external uniform background without any constraint on their density. In 1934, Wigner has conjectured that Jellium crystallizes, a fact that is only known in dimension 1 at present. The Jellium energy is related to the Epstein Zeta function.

In this talk I will review the existing mathematical results on the subject and present a new work with E.H. Lieb where we discovered that Jellium and the UEG are probably different systems. Our argument relies on the knowledge that Jellium crystallizes, which is therefore only rigorously known in 1D.

Franz Merkl (LMU Munich): *Spontaneous breaking of rotational symmetry*

As was shown by Fröhlich/Pfister, Richthammer and others in the tradition of the famous Mermin-Wagner theorem, translational symmetry cannot be spontaneously broken in two dimensional particle systems at positive temperature under rather weak condition. The situation is quite different for rotational symmetry. For (over?-)simplified models of 2D crystals at positive temperature without defects or only with simple kinds of defects, I will explain why rotational symmetry can be spontaneously broken. However, for more realistic models of defects,there are more questions than answers. I will ask some of them.

Mathew Penrose (University of Bath): *Random parking and rubber elasticity*

Rényi's random parking process on a domain D in d-space is a point process with hard-core and no-empty-space properties that are desirable for modelling materials such as rubber. It is obtained as follows: particles arrive sequentially at uniform random locations in D, and are rejected if they violate the hard-core constraint, until the accepted particles saturate D. We describe how any real-valued functional on this point process, provided it enjoys certain subadditivity properties, satisfies an averaging property in the thermodynamic limit. Consequently in this limit, one has a convergence of macoroscopically-defined energy functionals for deformations of the point process, to a homogenized limiting energy functional. We may also apply the results to derive laws of large numbers for classical optimization problems such as travelling salesman on the parking point process. This is joint work with Antoine Gloria.

Elena Pulvirenti (Leiden): *Metastability for the Widom-Rowlinson model*

In this paper we study the Widom-Rowlinson model on a finite two-dimensional box subject to a stochastic dynamics in which particles are randomly created and annihilated inside the box according to an infinite reservoir with a given chemical potential. The particles are viewed as points carrying disks and the energy of a particle configuration is equal to minus the volume of the total overlap of the disks. Consequently, the interaction between the particles is attractive. We are interested in the metastable behaviour of the system at low temperature when the chemical potential is supercritical. In particular, we start with the empty box and are interested in the first time when the box is fully covered by disks. In order to achieve the transition from empty to full, the system needs to create a sufficiently large droplet, called critical droplet, which triggers the crossover. We compute the distribution of the crossover time, identify the size and the shape of the critical droplet, and investigate how the system behaves on its way from empty to full. This is a joint work in progress with F. den Hollander, S. Jansen, R. Kotecký.

Thomas Richthammer (Hildesheim): *Rigidity of 2D crystals: the hard disk model*

The hard disk model is a particularly simple two-dimensional Gibbsian point process. The particles can be viewed as disks and the only interaction is that any two disks are not allowed to overlap. It is conjectured that the particles arrange themselves into a triangular lattice provided that the particle density is sufficiently high. We would like to know how rigid this lattice structure is. For increasing size of the system it is believed that the fluctuations of the lattice direction remain small; on the other hand it is known that the fluctuations of particle positions grow unboundedly. We give a lower bound on these fluctuations: If the size of the system is 2n x 2n and the disks are of size 1, then the fluctuations of particle positions are at least c log(n) with positive probability. The result carries over to fairly general interacting particle systems in two dimensions, but in this context hard disks are particularly interesting and difficult.

Bernd Schmidt (Augsburg): *Existence and convergence of solutions of the boundary value problem in atomistic and continuum nonlinear elasticity theory*

We show existence of solutions for the equations of static atomistic nonlinear elasticity theory on a bounded domain with prescribed boundary values. We also show their convergence to the solutions of continuum nonlinear elasticity theory, with energy density given by the Cauchy-Born rule, as the interatomic distances tend to zero. These results hold for small data close to a stable lattice for general finite range interaction potentials. We also discuss the notion of stability in detail.

Siamak Taati (Leiden): *Quasicrystal phases at positive temperature*

I will present a finite-range lattice gas model that has quasicrystal phases at positive temperature. The construction is based on three ingredients from the theory of cellular automata (CA) and tilings: 1) a method of simulating a CA with another CA that is resilient against noise, due to Toom (1980), Gacs and Reif (1988), 2) the existence of aperiodic sets of Wang tiles that are deterministic in one direction (e.g., based on Ammann's golden tiles, 1980), and 3) the observation going back to Domany and Kinzel (1984) that the space-time diagrams of positive-rate probabilistic CA are Gibbs measures.

Florian Theil (Warwick): *Orientational order in two dimensions*

A classic phenomenon in Statistical Mechanics is the emergence of crystalline phases at low temperature. Until recently not much was known about this problem in the case of atomistic systems with unbounded degrees of freedom. I will explain the link between crystal formation and orientational order. Then I will demonstrate that orientational order emerges in many realistic two-dimensional systems.

Dimitris Tsagkarogiannis (Sussex): *Thermodynamics for spatially inhomogeneous magnetization and Young-Gibbs measures*

We derive thermodynamic functionals for spatially inhomogeneous magnetization on a torus in the context of an Ising spin lattice model. We calculate the corresponding free energy and pressure (by applying an appropriate external field using a quadratic Kac potential) and show that they are related via a modified Legendre transform. The local properties of the infinite volume Gibbs measure, related to whether a macroscopic configuration is realized as a homogeneous state or as a mixture of pure states, are also studied by constructing the corresponding Young-Gibbs measures. This is joint work with A. Montino and N. Soprano-Loto.